1. Name and address of applicant

John Van Derlofske, Ph. D. | Senior Research Scientist
3M Optical Systems Division
3M Center, Bldg 235-1E-54 | Maplewood, MN 55144
Office: 651.736.8271
jvanderlofske@mmm.com | www.mmm.com

2. Summary of the application

Quantum dot light control films are a new technology that has been developed to enable liquid crystal displays (LCD) to give a technically superior image with a much higher range of colors than is currently possible from other commercially available LCD technologies. These thin films contain cadmium for which substitution is currently not technically practical. Traditional LCDs display only a fraction of the colors that are visible to the human eye. In fact, they do not even produce the same range of color that cathode ray (CRT) technology did when it was introduced in the 1950's. Quantum dot technology can achieve a significantly larger range of colors (a 60% - 100% improvement) giving the viewer noticeably better color images.

Quantum dot films function by converting light of one color into a different color within a precise wavelength range that can be tailored by control of the quantum dot particles. Alternative LCD technologies give broader ranges of colors which cannot be tailored to optimum wavelengths. Recently OLED displays have been developed and have been used mainly for small-size screens of smart phones, etc., as manufacture of larger size OLEDs have proved to be technically challenging. Recently, some OLED manufacturers have claimed that larger size OLEDs can be constructed and will give the same color gamut as quantum dot films, but the energy consumption of an OLED display is estimated to be significantly higher than quantum dot film LCDs. Calculations show that the cadmium generated in waste from the additional electricity generation required to operate OLEDs far exceeds the amount of cadmium present in an equivalent quantum dot film. Therefore, the primary justification for this exemption is that only quantum dot LCDs are able to achieve 100% color gamut for all screen sizes and a secondary justification is that the potential substitutes have a greater negative environmental impact.

3. Description of materials and equipment for which the exemption is required

Quantum dot light control films are components of liquid crystal displays (LCDs) used to spectrally convert light from one color to another. These are polymeric films doped with small amounts of quantum dots that result in displays with very high color quality (high color gamuts). The ability of a display to present a large range of colors, or the size of its color gamut, is an extremely important factor in determining a display's perceptual quality.(1)(2)(3) The technological pursuit of improved color display quality is of upmost importance, due to specialized needs for enhanced color depth and range, and the amount of time that technical personnel and consumers interface with electronic display devices.

Quantum dot (QD) films provide several advantages to creating high color quality displays. They are the most energy efficient way, compared to all currently available technologies, to achieve wide color gamuts. QD films, therefore, enable higher quality electronic devices that consume less power and as a result will ultimately result in less RoHS controlled substances (such as Pb, Hg and Cd) being emitted in to the atmosphere through the burning of fossil fuels (coal and oil) for electricity. The addition of quantum dot light control films is also the easiest solution to implement into current LCD production and is scalable to any size LCD screen.

3.1 Quantum Dot Light Control Film Function

LCDs are ubiquitous in today's society. In applications ranging in size from 3" smartphones to 108" televisions, they entertain us and connect us to the virtual world. Great strides have been made over the years in LCD visual quality. LCD refresh rates, resolution, and contrast levels have all improved dramatically. However, one area that still lags behind is color performance. This is particularly true for smaller sized displays, such as those in smartphones and tablets, where the range of colors that can be presented is only 50%-70% that of cathode ray tube (CRT) technology when it was first introduced.

Although new display technologies (e.g., organic light emitting diode (OLED) displays, Red/Green/Blue (RGB) LEDs, wide color gamut phosphors) have been recently introduced that improve color performance, no one solution commercially exists for high quality color displays that is energy efficient and easily adoptable for all applications. Quantum dot light control films are currently in development to rectify this situation. Quantum dots are a new class of non-naturally occurring materials that can be tuned to efficiently emit narrow spectral distribution light at the optimum wavelength for LCDs.(4) QD films can provide high efficiency solutions for high quality LCD color performance that is easily scalable to any size display.

A main factor that determines the maximum color performance of an LCD is the spectral interaction between the light emitted from the backlight and the liquid crystal panel color filters. An LCD has two main components, the liquid crystal panel and the back light unit (BLU). The panel consists of millions of individually addressable pixels, each of those made up of red, green and blue sub-pixels. The sub-pixels get their color properties from absorptive color filters (CFs) that overlay them. The BLU contains light sources (typically white yttrium aluminium garnet (YAG) based LEDs at the present) and provides spatially uniform light to the back side of the panel. The spectral distribution of the light sources in the BLU convolved with the spectral transmission of the panel color filters mainly determines the final spectra of the light exiting an LCD. See Figure 1.

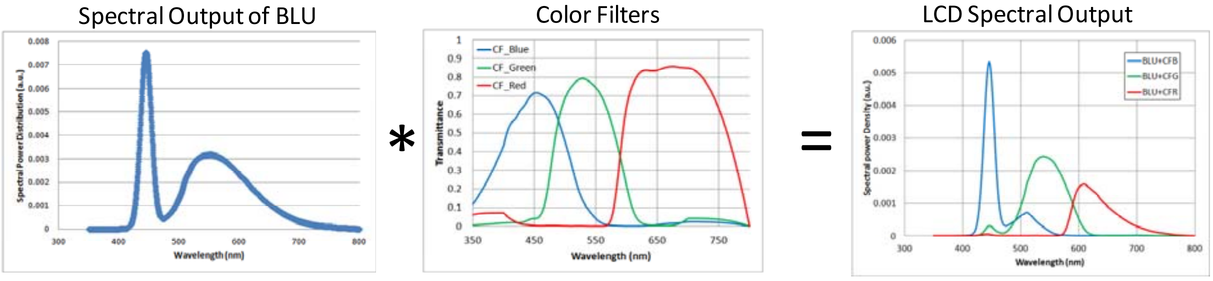


Figure 1. Representative example output spectral distribution of an LCD. The white LED based spectral output of the BLU passes through the three (red, green, and blue) color filters (CF) to produce the final LCD spectral distribution. This distribution then determines the color quality of the display.

To maximize the color performance of an LCD, the output spectral distribution of each sub-pixel should be as narrow as possible. Narrow spectral distributions of the primary red, green, and blue (R,G,B) sub-pixels result in a large color gamut area. Color gamut is a measure of a display's ability to generate a range of colors, and is typically defined by the tristimulus R, G, B area in the CIE 1931 2^{o} Chromaticity space or the CIE 1976 UCS Chromaticity Space.(5) Commission Internationale d'Eclairage (CIE) has developed several color standards including these two. Color gamut is often represented as percentage of area relative to a standardized color gamut space, such as the 1953 NTSC (National Television System Committee) color space. A larger color gamut area (with a higher % NTSC) means that the display can generate a larger range of colors than a display with a lower % NTSC. This is illustrated below in Figure 2. The blue horseshoe shape in Figure 2 represents all of the colors visible to the human eye, and the red and green triangles represent the colors that a standard LED-LCD and a QD film based LCD are capable of displaying.

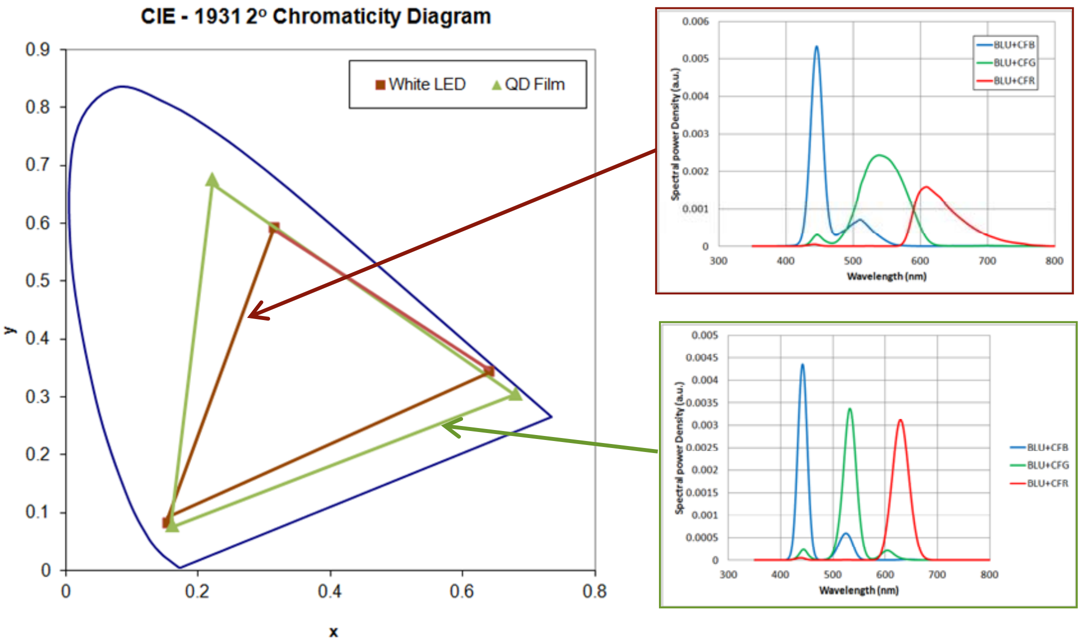


Figure 2. Primary sub-pixel spectra and color gamut size. The narrower spectral distributions (particularly the red and green distributions) of an LCD with QD films produce a larger color gamut (~94% NTSC) than a traditional LCD (~65% NTSC). BLU+CFX denote the spectral light distribution coming from the back light unit (BLU) through the blue, green or red color filter (CFB, CFG, and CFR respectively).

To achieve narrow sub-pixel output spectral distributions in an LCD either the color filters have to be highly absorptive, which is not desirable due to significantly lower efficiency (of colored light output as a % of BLU light output) and higher energy consumption, or the input spectral distribution from the BLU must have narrow spectral ranges and closely matched in peak wavelength to the transmission of the color filters. Currently, the YAG based white LEDs used in most LCDs have broad spectral distributions in the green and red regions and do not match the color filters in peak wavelengths. See Figure 3(4).

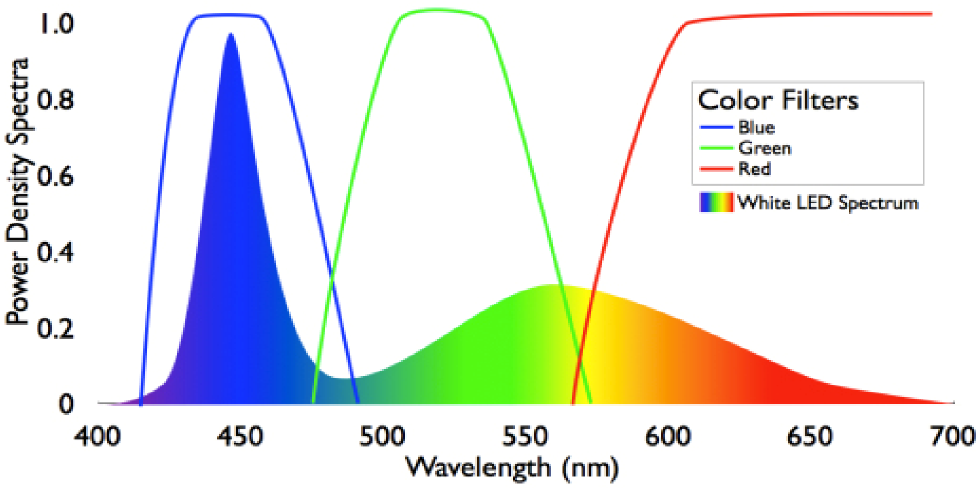


Figure 3. Spectrum of a typical white YAG based LED BLU, compared with an example set of red, green and blue color filters. The spectrum of the light sources does not match well with the color filters (CFs) resulting in a limited color gamut size.

Quantum dots are uniquely suited to enable narrow sub-pixel output spectral distributions in an LCD. They produce narrow output spectral distributions that are easily tuneable in peak wavelength to match any set of LCD color filters. Furthermore, QDs are capable of doing this with high efficiency and this reduces energy consumption.

3.2. Quantum Dot Technology

Quantum dots are semiconductor nanocrystals, on the order of 3-7nm in size, in which excitons (an electron and hole excited pair) are confined on all three spatial dimensions. The wavelength of the light output from a semiconducting material is dependent on the band gap between normal and excited electron energy states. The spatial confinement of the electrons and holes of the quantum dot materials leads to higher band gaps compared to the band gap of same material in bulk. As a result, the band gaps of the quantum dots can be changed continuously by changing their physical size. Quantum dots are typically synthesized via solution chemistry (carefully controlled precipitation processes). By controlling different synthesis conditions, e.g., precursor and ligand concentrations, temperature and time of the reaction, quantum dots of different sizes can be obtained.

By using a core/shell nanocrystal structure, where the core of the quantum dot is one material and the shell is a different material, high photo luminescent quantum efficiency (i.e., high energy photon to low energy photon conversion efficiency) can be obtained. The shell material has higher band gaps than the core material and serves to shield the photo-generated electrons and holes from the outer nanocrystal surface where surface defects exist which can lead to nonradiative electron-hole recombination. The shell also greatly extends the lifetime of the quantum dots by making them less susceptible to the chemical changes surrounding the quantum dots.

Quantum dots used in light control films are cadmium selenide (CdSe)/Zinc sulphide (ZnS) core/shell nanocrystals.(6) These CdSe/ZnS quantum dots have been optimized to deliver high quantum efficiency as well as to meet the lifetime requirements in display applications. The high quantum efficiency, typically >88%, is necessary for QD film based backlights to deliver higher power efficiency (12% - 45% more energy efficient than traditional LED-LCDs for color gamut sizes from 70% NTSC to 100% NTSC).

Quantum dots can be pumped with a blue source, such as the GaN LED, to emit at any wavelength beyond the pump source wavelength. The emission spectra of quantum dots have narrow line-widths and are free of satellite peaks, thus making them ideal candidates for display backlights to achieve high color purity and increased system energy efficiency. QDs convert light with very high efficiency (>88% quantum efficiency) and with very narrow output spectral distribution of only 30 – 40nm full width at half maximum (FWHM). Quantum dot emission can be tuned across most of the visual spectrum by controlling the size of the quantum dot as it is fabricated; larger quantum dots emit light of longer peak wavelengths, see Figure 4. Due to their tuneability, narrow spectral output distributions, and high quantum efficiencies, quantum dots are ideal for creating BLU light sources to increase color gamut size and maximize LCD color performance.

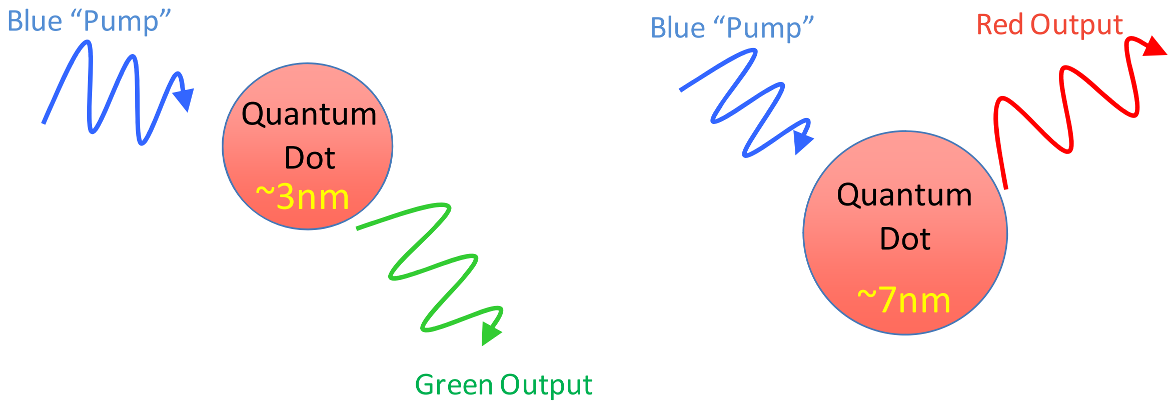


Figure 4. Effects of quantum dots size on spectral output. Smaller QDs emit shorter wavelength light when exposed to a blue source.

3.3. Quantum Dot Light Control Film Construction

Quantum dots can be included into an LCD by incorporating a small amount of quantum dots (typically 3-5ug/cm^2) into a polymeric film that is inserted into the BLU. This quantum dot light control film can have the sole purpose of tailoring the output spectral light distribution for high color performance or it can have additional optical functionality (i.e., polarization, reflection, refraction, scattering). When using QD film the only other change to the LCD system that is necessary is to substitute the white LEDs with blue LEDs (nominally by using the same GaN LEDs but without the YAG phosphor). See Figure 5 for a representative example of QD film in an LCD system.

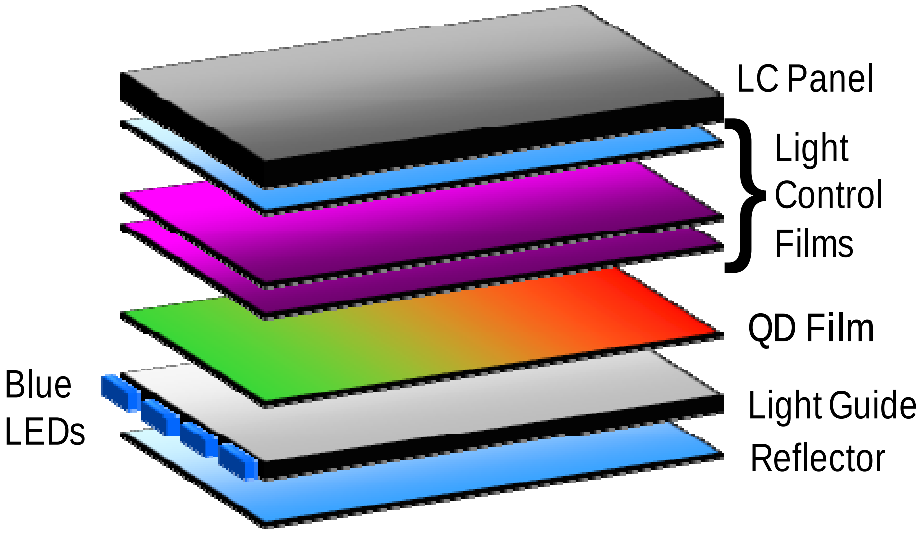


Figure 5. Schematic of QD film in an example LCD system.

As shown in Figure 5, the QD film construction is as follows. Two different sized quantum dots, nominally green and red emitting, are incorporated into a polymer film. The smaller (~3nm in size) green dot would have a peak wavelength of approximately 540nm and a FWHM of approximately 30nm. The larger (~7nm in size) red dot would have a peak wavelength of approximately 615nn and a FWHM of approximately 40nm. The QD film would convert some of the blue "pump" light to green and red and allow some of the blue light to leak through unaffected. The spectral output of the blue LED has a FWHM of approximately 15nm and peak wavelength that ranges from 440nm to 460nm. In this way, narrow red, green and blue spectra of the appropriate peak wavelengths can be generated and high color gamuts can be achieved. No other LCD high color gamut technology currently available, or near commercialization, can achieve this performance.

The total amount of quantum dots needed, as well as the ratio of green to red dots, depends on a number of factors. These include: the desired color specifications of the display, the amount of light recycling (number and efficiency of light reflections) in the BLU, and the properties of the color filters in the panel. The concentration of quantum dots, and therefore, the concentration of cadmium in QD film depend on these factors and the total thickness of the film. However, no more than 20 µg of cadmium/cm^2 of screen area should be used for any application. Typically, only 3 – 5 µg of cadmium/cm^2 of screen area would be used.

It is important to note that while the QD film in an LCD application contains at most 20 µg of Cadmium per cm^2 of screen area, it is contained within a physical device. The Cadmium is bound to selenium in a core structure, encased within a shell, surrounded by ligands, held in a matrix material within an LCD assembly. An LCD with QD film could easily be disposed of properly, ensuring that the contained Cadmium does not contaminate the environment.

The diagram below shows the construction of the quantum dot film material.

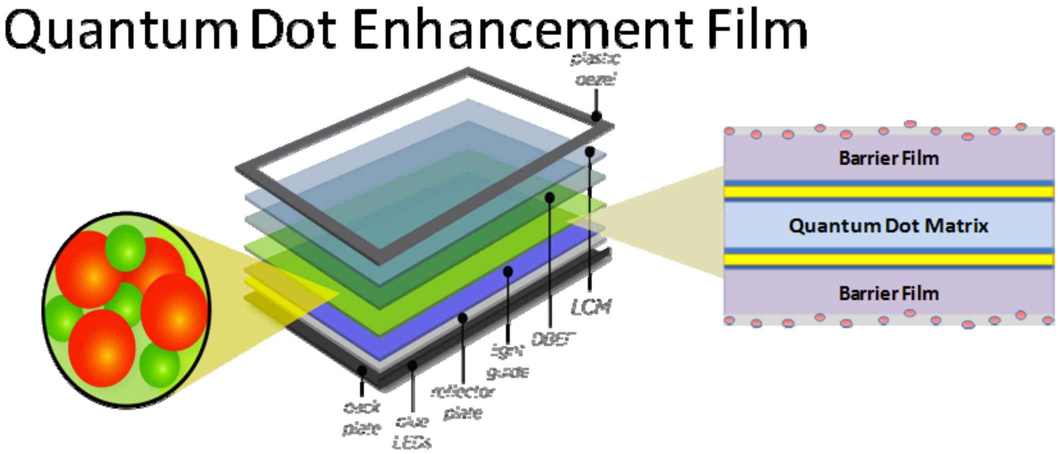


Figure 6: Quantum Dot Film in and LCD showing a blow out of the Quantum Dot Film

Quantum dots are typically synthesized via solution chemistry (carefully controlled precipitation processes). By controlling different synthesis conditions, e.g., precursor and ligand concentrations, temperature and time of the reaction, quantum dots of different sizes can be obtained.

By using a core/shell crystal structure, where the core of the quantum dot is one material and the shell is a different material, high photo luminescent quantum efficiency (i.e., high energy photon to low energy photon conversion efficiency) can be obtained (**see Figure 7**) The shell material has higher band gaps than the core material and serves to shield the photo-generated electrons and holes from the outer crystal surface where surface defects exist which can lead to nonradiative electron-hole recombination. The shell also greatly extends the lifetime of the quantum dots by making them less susceptible to chemical changes that can occur.

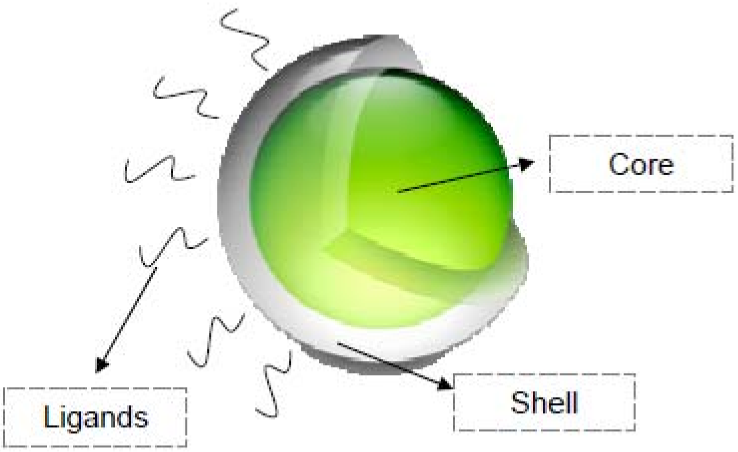


Figure 7: Core / Shell / Ligand Structure of the Quantum Dots

Quantum dots used in light control films are typically CdSe/ZnS core/shell crystals. These CdSe/ZnS quantum dots have been optimized to deliver high quantum efficiency as well as to meet the lifetime requirements in display applications. Cadmium containing crystals are placed into a supporting organic matrix for use in an LCD display, as shown in the example below.

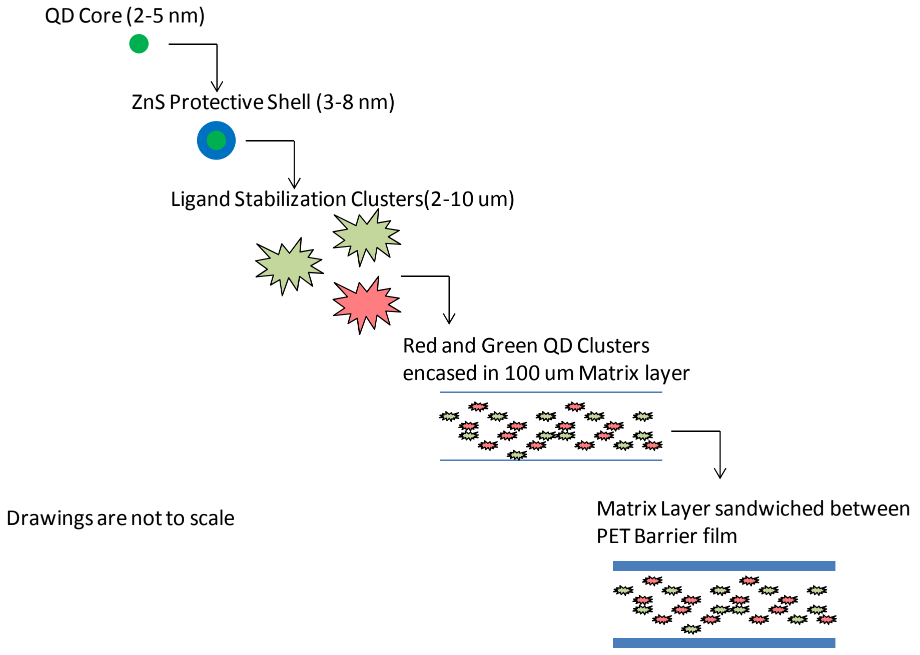


Figure 8: Quantum Dot film product description

Typically, two different sized quantum dots, nominally green and red emitting, would be incorporated into the polymer film. The Cadmium atoms are bound to selenium atoms in a core structure, and these are encased within, for example, a ZnS shell. These core/shell crystals are surrounded by ligand material, which are held within a matrix material, and this is finally is encased between PET films (**see Figure 8**). This QDEF film is then combined with other polymeric material layers within an LCD assembly.

In order to protect and isolate the quantum dots, they must be complexed into a ligand material and various amino silicones are used. The amine functionality on the silicone complexes (bonds) to the surface of the quantum dots forming a psuedo-crosslinked network of polymeric amino-silicone – QD material. This network helps to separate the quantum dots from each other and confine them in a dispersed form within the matrix polymer. The amino silicone-QD material is dispersed into a barrier matrix polymer material, however all the quantum dot particles remain complexed in the amino silicone phase (see Figure 9). The matrix material used can be a variety of polymer materials. The main function of the matrix polymer is to confine the quantum dots between the two protective PET barrier layers.

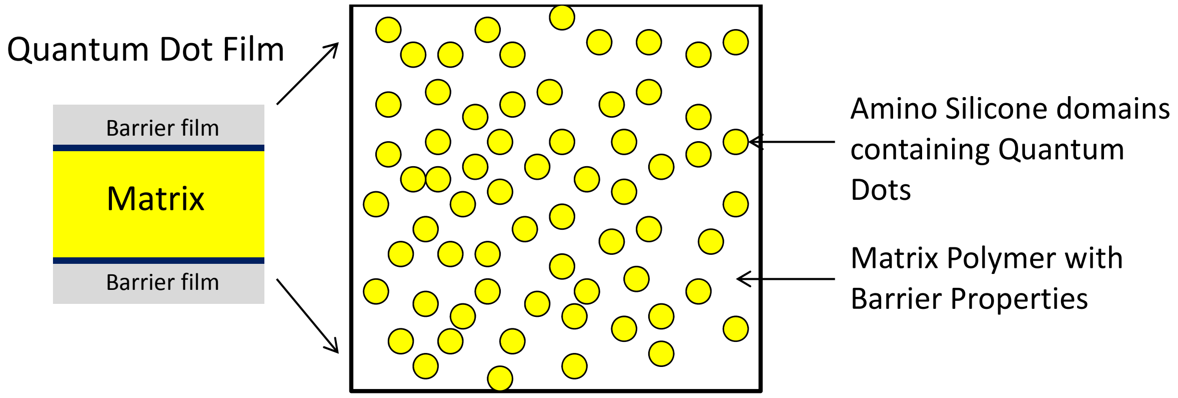


Figure 9: Amino Silicone domains in the Quantum Dot polymer film

The cadmium is present only in the QD film which according to the RoHS directive's definition is a homogeneous material as it cannot be mechanically disjointed into separate materials. The REACH Regulation 1907/2006 Annex XVII gives a concentration limit for "cadmium in plastic materials", which is a different definition to RoHS. As shown in figure 5, the light guide, the QD film and the three filters are tightly combined in the product to form a "plastic material" in which the overall cadmium content is <0.01%, i.e. below the REACH concentration limit.

Additionally, the cadmium is dispersed in types of polymer (which contains silicones) that are not listed in entry 23 of REACH Annex XVII. The matrix material is a sequence of dimethylsiloxane combined with dimethylsiloxane repeat units that have been functionalized with amine side chains. The side chains can have signal or bifunctional amino groups and can range from 3 to 10 carbons in length. The monomer units are a minimum of 12 repeat units covalently bound together to form the polymer chain. The weight average molecular weight for these polymers is ~8000-14,000 g/mol with a polydispersity of ~2 -2.5.

3.4. Quantum Dot Light Control Film Efficiency

Quantum dot light control films are the most energy efficient way to achieve high color gamuts in LCD systems. A case study of 55" LCD TVs has concluded that QD films result in an average power savings of 46% over existing LCD technologies.(7) 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). The EU televisions eco-design study found that televisions in the EU are used on average 4 hours per day so 50,000 hours is equivalent to a lifetime of 34 years and 25,000 hours is equivalent to 17 years. Furthermore, the cadmium in the QD-LCD can be recovered safely by recycling whereas the cadmium and other toxic metal emissions from power generation contaminate the environment, enter the food chain, etc.

The spectral interactions in an LCD system, and the impacts of these interactions on total system efficiency, can be modelled. The general LCD factors that need to be specified for such modelling include: the light source spectral distribution; the amount and efficiency of light recycling in the BLU; and the spectral absorptance functions of the color filters. To include QD films into the modelling one must also specify: the spectral absorptance functions of the quantum dots; the quantum efficiency of the dots (how efficiently do they convert input photons to output photons); the spectral emitance functions of the quantum dots; the total concentration of quantum dots; and the relative proportion of green to red dots.

The above factors were determined and modelling analysis was performed for the currently commercially viable (in production now or in the near future) LCD systems capable of achieving high color gamuts. These include LCD systems employing: standard QD films, cadmium free QD films, hybrid LEDs (LEDs with two dies and a phosphor), highly absorptive color filters, wide color gamut white LEDs (red phosphor doped YAG), and RGB LEDs. All of these technologies are capable of producing high gamuts on their own or in conjunction with modifying the color filters (by making them more absorptive). These technologies will be further described in more detail in Section 5- Analysis of Possible Alternatives.

Figure 10 shows a summary of the relative efficiency modelling results for a target color gamut size of 70% NTSC. This is approximately the same size as the standard sRGB color space, used commonly for monitors, printers, tablets, and the internet.(8) The QD film solution is greater than 12% more efficient than any other wide color gamut LCD technology.

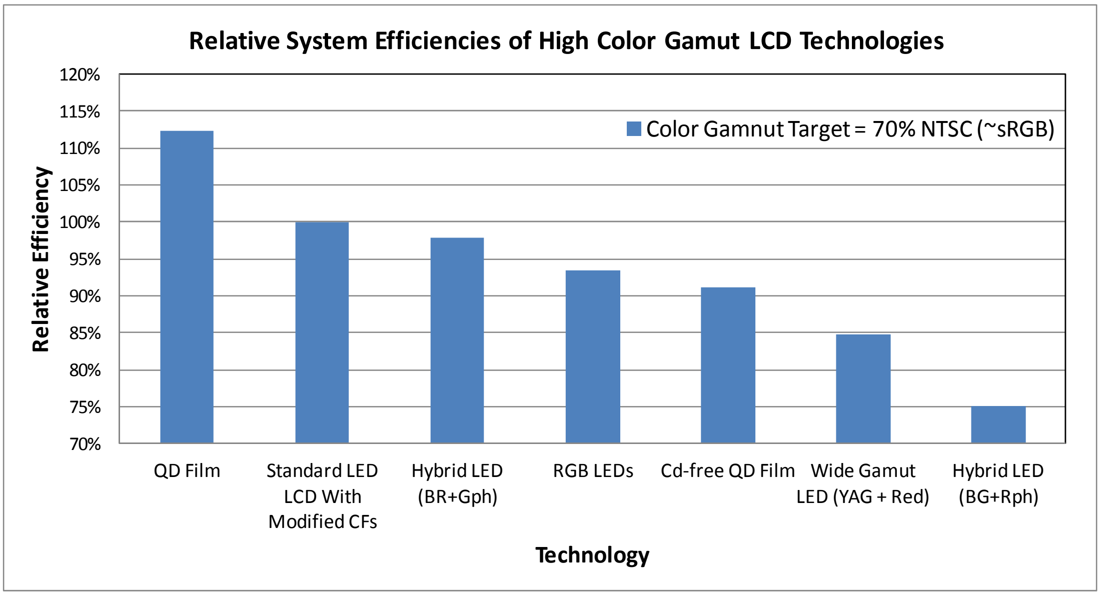


Figure 10. Summary of relative efficiency modelling for a color gamut target of 70% NTSC. Note that the relative efficiencies are normalized as a reference to the standard LED-LCD at 100%.

Figure 11 shows a summary of the relative efficiency modelling results for a target color gamut size of 100% NTSC. This is approximately the same size as the standard Adobe RGB color space, developed to encompass most of the colors achievable by CMYK color printers.(9) The QD film solution is greater than 15% more efficient than any other wide color gamut LCD technology.

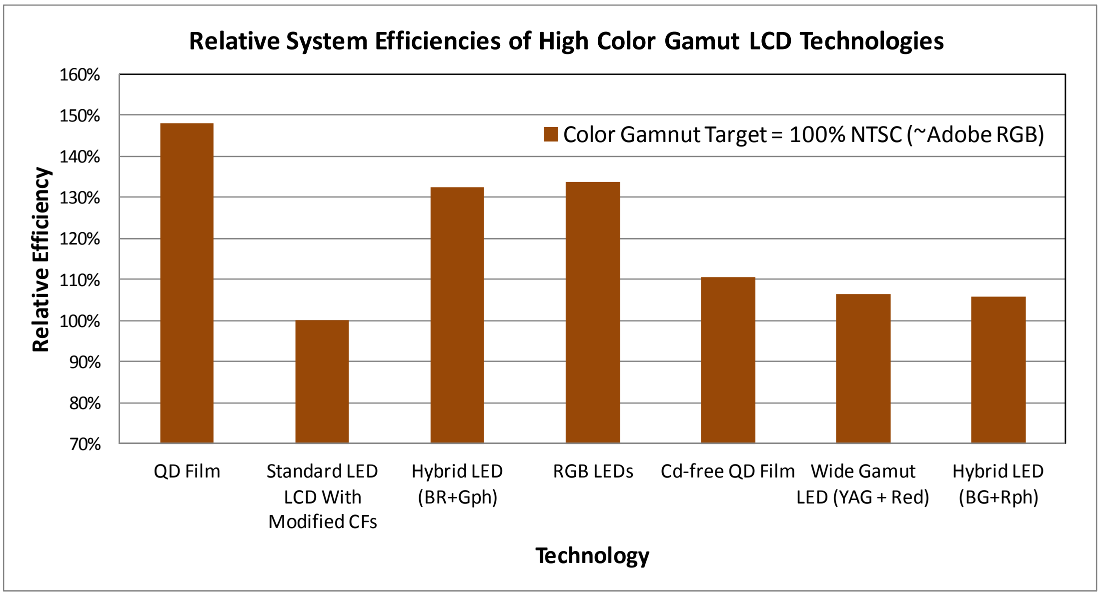


Figure 11. Summary of relative efficiency modelling for a color gamut target of 100% NTSC. Note that the relative efficiencies are normalized as a reference to the standard LED-

LCD at 100%. Also note that this theoretical modelling analysis was performed for illustrative purposes only, currently in practice, only QD film and RGB LED technologies can achieve 100% NTSC color gamut in LCDs.

4. Justification for exemption

This exemption is based primarily on the absence of substitute display types that can provide desired performance characteristics including:

- Equal or better color performance
- Equal or better energy consumption; substitutes would consume greater energy, causing shorter battery life which is not acceptable to users of portable devices such as mobile phones and tablet PCs
- All sizes of displays – one possible substitute OLEDs cannot currently be made in acceptable yields except in small sizes and cannot be made in larger sizes in sufficient quantities to meet a fraction of the current world wide display needs due to limited capacity.

The only two potential substitutes (described in section 5) that may be suitable as replacements will not be available commercially until 2021 at least.

A secondary justification for this exemption is that all of the apparent substitutes described below have higher energy consumption in the use phase and this will have an overall negative environmental impact.

5. Analysis of possible alternatives

5.1 Traditional LED LCDs with More Absorptive Color Filters

One method for achieving higher color gamuts in LCDs that is used in the marketplace today is to increase the absorption of the panel's color filters. However, this method is inefficient due to the lower light transmission through the filters and leads to higher device energy consumption. Furthermore, the inefficiency increases with high color gamut targets. For a color gamut target of approximately 70% NTSC a reduction in system efficiency of greater than 12% is seen, and for a color gamut target of approximately 100% NTSC, a reduction in system efficiency of greater than 45% is seen, when comparing an LCD with highly absorptive color filters to the QD film solution (see Figures 10 and 11). As stated above, for a 55" TV, this energy savings results in 110 mg of net environmental Cadmium avoided.(7)

Additionally, highly absorptive color filters are difficult to manufacture and are not scalable to all LCD applications. In order to make highly absorptive color filters the physical thickness of the filters are increased. To make color filters capable of producing a color gamut size of 100% NTSC it is necessary to increase the physical thickness of the color filters by more than 2.5 times, thus making them unusable for smaller LCD applications (i.e., tablets and smartphones) as this would make the displays too thick for these slim devices.

5.2 RGB LEDs

Another currently used method for achieving higher color gamuts in larger sized LCDs (typically notebooks and larger) is to employ a combination of red, green and blue (RGB) LEDs in the backlight, replacing the white YAG based white LEDs. The RGB solution is less energy efficient than QD films as follows; approximately 19% less efficient for a 70% NTSC color gamut target and by approximately 14% less efficient for a 100% NTSC target (see Figures 10 and 11).

The lower efficiency of the RBG system is due to the low emission efficiency of the green LED. RGB LEDs utilize the InGaN and AlInGaP semiconductor material systems for the blue-green and amber-red portions of the visible spectrum, respectively. However, as can be seen in Figure 12, the power efficiency of conventional LEDs is very low in the green & amber region. Backlights for LCDs that utilize one or more clusters of red, green and blue LEDs currently use 2 green LEDs within each cluster to compensate for the low efficiency of the green LEDs (as shown in Figure 13).

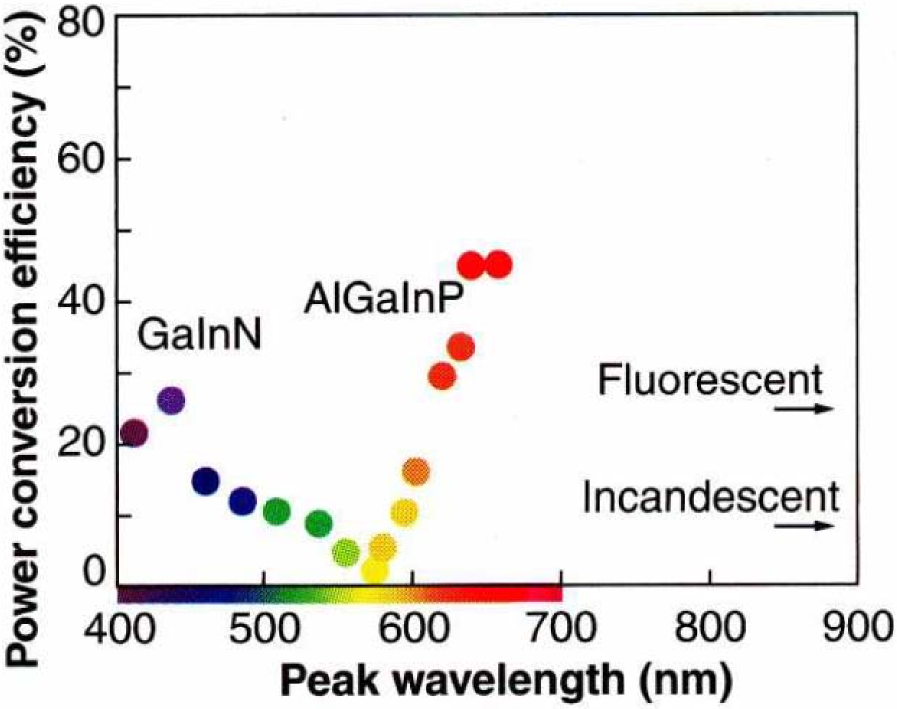


Figure 12. Efficiency of conventional LEDs (from D. Nicol et al. Laser Focus, March 2006).

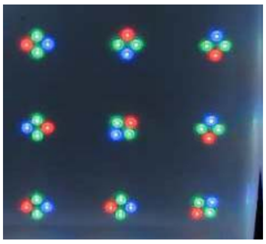


Figure 13. RGGB LED cluster used in a display backlight – note use of two green LEDs with one red and one blue.

Another problem with RGB LEDs is their temperature and age stability (in which the amount of light emitted by an LED die drops significantly as the device temperature increases or as it ages). This is particularly noticeable when multiple single-color LEDs are combined together in a system. It has been found that the different dies change color at different rates as a function of temperature or age and a very noticeable color shift occurs as the operating temperature changes or as the device ages. As a result, the color quality deteriorates.

A descriptive example of this is an LCD TV display that uses RGGB clusters of LEDs (such as displayed in Figure 13 above). When power is first applied to the unit there is usually a reddish tint to the displayed images (as a result of the increased efficiency of the red AlInGaP LEDs at a lower temperature). The output flux of the red LEDs in the system decreases faster than that of the blue and green InGaN LEDs as a result of the warming of the LEDs during operation. The systems are usually designed to have best color balance at normal operating temperature (resulting in noticeably lower performance at other temperatures).

Additionally, RGB LEDs are not scalable to all LCD sizes. Due to the extremely thin cross section of smaller hand held applications (i.e., smartphones and tablets) these do not have the physical space to employ the four dies.

5.3 Hybrid LEDs

Another LCD technology that could potentially be used to achieve higher color gamuts are hybrid or phosphor converted LEDs. Hybrid LEDs are not currently used in LCD backlight applications but some configurations have been introduced for general lighting. These LEDs typically are made of two dies and a phosphor, where the short-wavelength blue die excites the phosphor to emit light of a desired wavelength while the other spectral components come from the two dies directly. It should be noted that although hybrid LEDs do offer some advantages over traditional LED sources, they still fundamentally rely on phosphor technologies, which have a relatively broad emission spectrum. The phosphors which emit light with the narrowest wavelength range have a spectral FWHM of approximately 40 – 55 nm. By comparison, the spectral width of quantum dots can be designed to be significantly narrower (approximately 30-40 nm).(10)

One hybrid LED configuration consists of blue and red dies plus a green phosphor (BR+Gph). The blue die is used to excite the green phosphor, resulting in red, green and blue output light (some blue light leaks through the phosphor). This configuration has the advantage of getting rid of the inefficient green die and producing narrow blue and red spectral emission. However, the green spectral emission from the phosphor is still relatively broad compared to quantum dots, resulting in lower efficiencies (see Figure 14). The BR+Gph hybrid LED solution is less efficient than QD films by approximately 14% for a 70% NTSC color gamut target and by approximately 15% for a 100% NTSC target (see Figures 10 and 11). It is also important to note that the BR+Gph hybrid LED has not yet been commercialized, and development is still underway to address stability and efficiency issues.

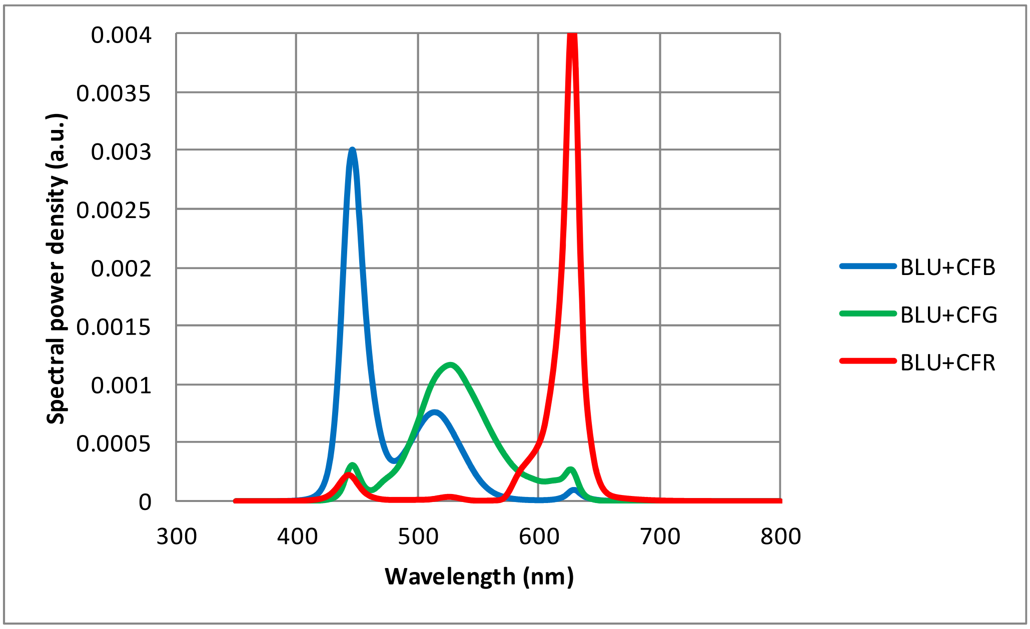


Figure 14. Spectral output distribution of an LCD system with BR+Gph hybrid LEDs, where BLU+CFX denotes the spectral light distribution coming from the back light unit (BLU) through the blue, green or red color filter (CFB, CFG, CFR respectively). Note the relatively broad spectral output width of the green emission peak. This results in lower system efficiencies of approximately 14-15%.

Another design of hybrid LED configuration consists of blue and green dies plus a red phosphor (BG+Rph). The blue die is used to excite the red phosphor, resulting in red, green and blue output light. This configuration has the advantage of producing narrow blue and green spectral emission. However, the lower efficiency green die is still present and the red spectral emission from the phosphor is relatively broad compared to quantum dots, resulting in lower efficiencies (see Figure 15). Because of this the BG+Rph hybrid LED solution is significantly less energy efficient than QD films by approximately 27% for a 70% NTSC color gamut target and by approximately 42% for a 100% NTSC target (see Figures 10 and 11).

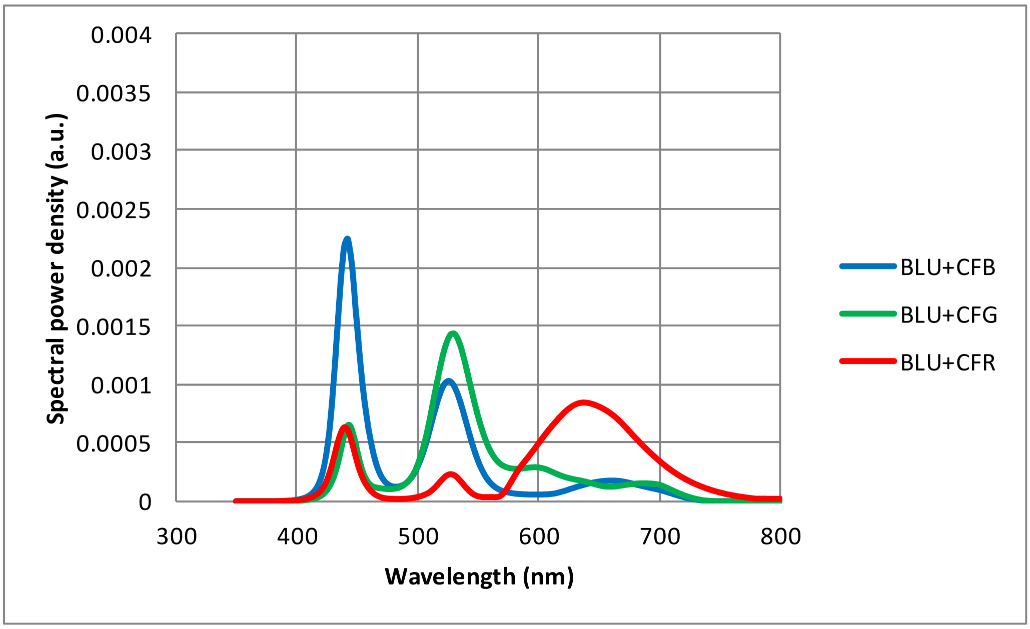


Figure 15. Spectral output distribution of an LCD system BG+Rph hybrid LEDs, where BLU+CFX denotes the spectral light distribution coming from the back light unit (BLU) through the blue, green or red color filter (CFB, CFG, CFR respectively). Note the relatively broad spectral output width of the red emission peak. This, and the lower efficiencies of the green dies, results in lower system efficiencies of approximately 27-42%.

As with the RGB LED solution, hybrid LEDs have issues with temperature and age stability, as well as form factor, that do not make them universally adoptable to all LCD applications. Currently available packages are too large for smaller LCD applications, and due to the stability issues of using red and blue dies with diverging temperature and aging performance, BG+Rph hybrid LEDs would need specialized controllers. As a result of these technical limitations, hybrid LEDs are not yet used for displays and are used only for lighting applications at present.

5.4 Wide Color Gamut White LEDs

Quantum dots film solutions stand out against emerging iterations of YAG phosphor technology such as red phosphor doped YAG (or the wide color gamut white LED), which adds some red-emitting phosphor to the green-yellow emitting YAG to boost color performance. This idea is similar to quantum dot technology in that it attempts to engineer a spectrum of white light by combining two phosphor materials with different emission spectra.

However, these crystalline phosphor materials are still fundamentally limited by their atomic structure and therefore cannot be precisely tuned to match the absorption spectra of the color filters. Additionally, the emission spectra of wide color gamut white LEDs is still relatively broad compared to QDs (see Figure 16). This leaves display manufacturers with a system that result in efficiency losses due to the relatively wide FWHM output of the phosphors and smaller color gamut sizes. The wide color gamut white LED solution is less energy efficient than QD films; approximately 27% less efficient for a 70% NTSC color gamut target and approximately 41% less efficient for a 100% NTSC target (see Figures 10 and 11).

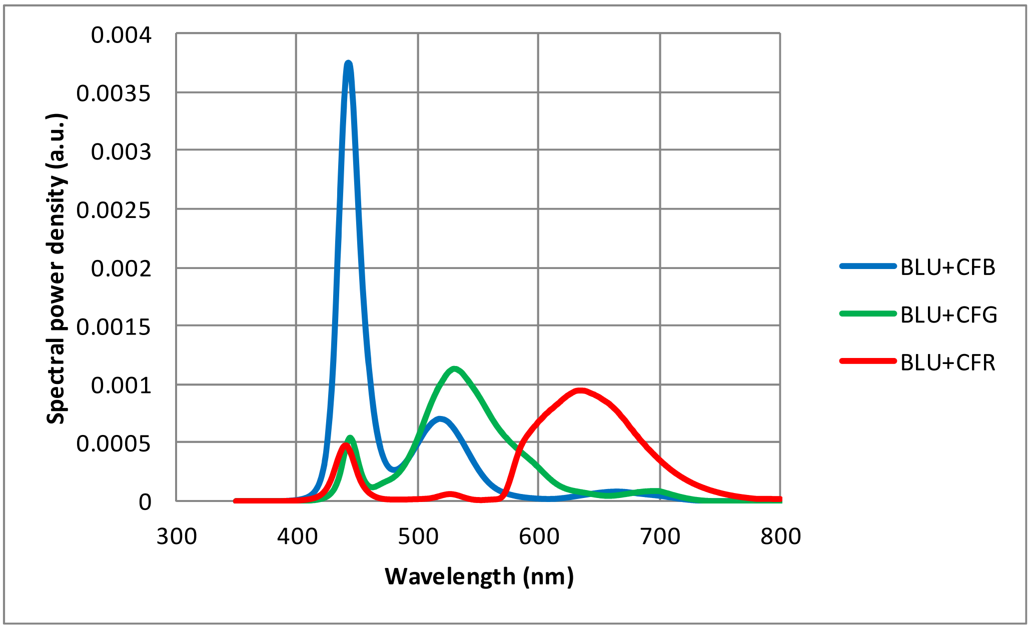
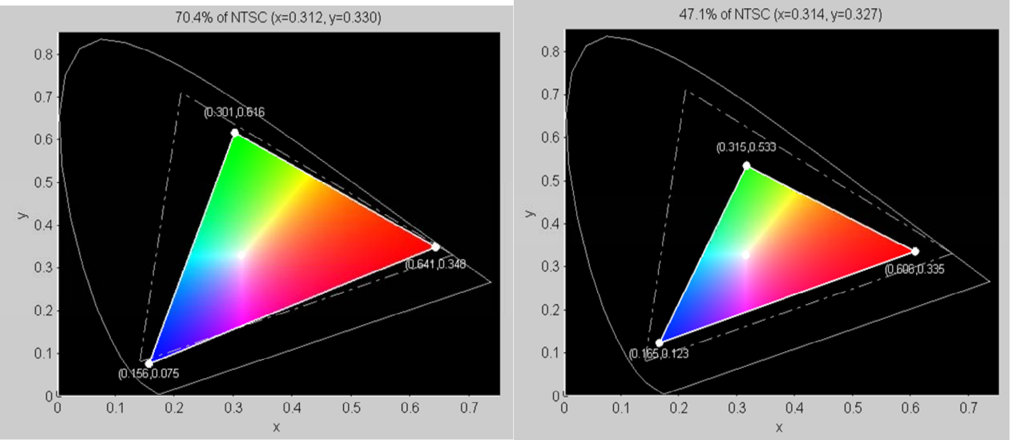


Figure 16. Spectral output distribution of an LCD system with wide color gamut LEDs, where BLU+CFX denotes the spectral light distribution coming from the back light unit (BLU) through the blue, green or red color filter (CFB, CFG, CFR respectively). Note the relatively broad spectral output width of the green and red emission peaks. This results in lower system efficiencies of approximately 27-41%.

5.5 Cadmium Free Quantum Dots

Quantum dots can be made based on other elemental materials. However, Cadmium based quantum dots are the only material choice today that is able to meet both the performance and lifetime requirements for LCD applications. The current technology is the result of over two decades of extensive research and development on CdSe/ZnS quantum dots. Cadmium free (Cd-free) quantum dots, e.g., InP based core/shell nanocrystals, are currently under research and development by numerous research institutions and companies. At present, however, these Cd-free quantum dots still suffer from low quantum efficiencies which results in half the energy efficiency of Cd-based quantum dots in display backlights. Furthermore, Cd-free quantum dots have wider emission spectra than cadmium based dots, resulting in reduced color gamut size in LCD applications. Figure 17 shows the relative LCD color gamut size for Cd and Cd-free films based on the same energy consumption. As available today, Cd-free film solutions are less efficient than QD films by approximately 21% for a 70% NTSC color gamut target and by approximately 37% for a 100% NTSC target (see Figures 10 and 11).



QD Film

Cd-Free QD Film

Figure 17. LCD color gamut size comparison of Cd and Cd-free QD film solutions. Due to the lower efficiencies and broader emission spectra of the Cd-free film, the color gamut of the Cd-free solution is significantly smaller (~70% NTSC for QD film vs. ~47% NTSC for Cd-free QD film), all else being equal.

The Cd-free quantum dot lifetimes are also currently well short of the 20,000 hour (2.3 years) minimum requirements for displays applications. Significant new discoveries in the InP-based core/shell quantum dots (e.g., shell materials, precursors, ligands, and synthesis conditions) and/or other compound semiconductors are necessary to enable Cd-free quantum dots to reach the same level of comparable maturity as CdSe/ZnS quantum dots. It is estimated that this effort could take another 7 years (at minimum) to commercialize.

5.6 Other Types of Displays – OLEDs and Plasma

Other types of display technologies exist that are fundamentally different than LCD technologies, most notably organic light emitting diodes (OLEDs) and plasma technologies. Both of these technologies are capable of producing higher color gamut sizes. However, they both also suffer from severe limitations, primarily around efficiency, scalability, and capacity.

5.6.1 OLED Displays

OLEDs are another technology that can be used for displays. OLEDs are self emitting like traditional LEDs, they directly convert electricity to light. Further, OLEDs can be patterned into red, green and blue addressable sub-pixels and therefore do not need a BLU or color filters. OLEDs displays offer several advantages over traditional white LED based LCD displays, one of which is the ability to produce a high color gamut area. OLED displays can have gamut areas greater than 100% NTSC.

OLED displays however, also suffer from some significant disadvantages. One of which is power consumption. OLED displays consume significantly more power than do LCDs. As an illustrative example a study was performed by DisplayMate that compared two very popular smartphone devices, the iPhone 5 (LCD screen) and the Galaxy S III (OLED based).(11) It was found that after normalizing for maximum brightness and screen size the OLED display consumed almost three times the power than the LCD display (2.2 watts consumed by the OLED display vs. 0.74 watts consumed by the LCD display). This is clearly a severe limitation for battery powered portable devices as well as the environmental implications. The battery life of a smartphone with an OLED display can be as little as one third that of a CdSe QD display.(11)

Other significant disadvantages of OLED displays revolve around the manufacturing process used to make them. Currently, the OLED manufacturing process is expensive and centred around making small display sizes. At present the largest OLED screen commercially available is approximately 5 in (127 mm) in diagonal. Larger prototype TV sized OLED displays have been shown at industry shows and are just becoming commercially available at extremely small scales (1000's of units per year). Proposed mass introduction dates have been pushed back due to technical manufacturing issues, namely very poor yields.(12) Further, due to the complexity of manufacturing OLEDs, the current capacity to make them is relatively small. The world wide capacity for manufacturing LCDs is approximately 230 million m^2 per year.(13) OLED capacity is only a fraction of this, approximately 2 million m^2 per year with a projection of approximately 9 million m^2 per year by 2016.(14)

In contrast to OLED displays, QD film is relatively easy to manufacture in larger quantities. For these reasons, QD films used in LCDs are superior to OLED technology to provide large color gamut displays for all applications. Even if one were willing to accept the lower energy efficiencies of OLED displays, over the next five years or so there will simply not be enough OLED capacity or size choices to provide screens for every application that would like to have high color quality.

5.6.2 Plasma Displays

Plasma is another technology that can be used for displays.(15) A plasma display panel (PDP) uses small addressable cells containing electrically charged ionized gasses. When a voltage is applied across a cell the gas forms plasma and emits UV photons. These photons then excite phosphors on the inside of the cell. Depending on the phosphors used red, green, and blue light can be achieved to form sub-pixels. Since plasma displays fundamentally rely on phosphor technologies, which have relatively broad spectral emission widths, they have gamut areas similar to standard YAG LED based LCD screens. Plasma flat panel displays have color gamuts that range approximately from 70-80% NTSC.

However, plasma displays also suffer from some significant disadvantages. One of which is power consumption. Plasma displays consume significantly more power than do LCD displays for the same luminance, approximately 2-4 times as much power.(15)(16)(17) Additionally, plasma displays are relatively thick and heavy. Due to these physical limitations plasma displays are currently only available in sizes of approximately 40in (102 cm) diagonal and above. For these reasons, QD films used in LCDs is superior to plasma technology to provide large color gamut displays for all applications.

Life cycle comparison of alternative options

This section compares the mining, extraction, manufacture, use and end of life phases for cadmium and possible substitutes. This is useful if it shows that the impact of cadmium is small and the impact of alternatives is similar or worse. To complete this section we first need to determine which possible substances need to be considered.

6. Extraction and refining

Most cadmium extraction is as a by-product from zinc mining and refining. Some zinc ores have higher concentrations of cadmium so the cadmium must be separated to avoid cadmium impurities in products. Although cadmium is a relatively scarce metal, the naturally occurring cadmium concentrations in zinc ore can exceed the RoHS maximum concentration limit of 100ppm. Global consumption of cadmium was ~18,000 tonnes per year in 2000.(6) Consumption of cadmium in the EU is decreasing significantly due to restrictions from the RoHS directive, the Batteries directive and the REACH Regulations and some more limited restrictions are gradually being introduced in other countries. However 12 million tonnes of zinc is produced annually and this is not decreasing and so cadmium supplies are plentiful, whether there is a use for it or not.

7. Use phase

Life cycle cadmium emissions are not only related to the mining, extraction, production and end of life phases for this technology and the alternative types of display, but they are also due to the cadmium is emitted by electricity generation. Electricity consumption is most significant in the use phase. This was demonstrated by the life cycle assessment carried out during the televisions eco-design preparatory study, DG TREN Lot 5 (see http://www.ecotelevision.org/). Cadmium emissions from electricity generation depend on the mix of power sources. Burning coal and oil both emit cadmium but the amounts depend on the sources of these fuels. Coal can contain up to 300 grams per tonne. Emission scrubbers remove a large proportion of toxic metal emissions from flue gases, but they cannot remove all of these. Data published for the UK shows that 4.0 tonnes of cadmium was emitted to air in 1970 but this decreased to 180kg in 2009 due to improved gas scrubbing and increased use of alternatives to coal for electricity generation. (18) Data for the EU is published (http://www.eea.europa.eu/publications/eu-emission-inventory-report-1990-2010) shows that in 2010, ~12 tonnes of cadmium, ~180 tonnes of lead and ~30 tonnes of mercury were emitted from EU energy generation and distribution.

OneSource has calculated that for a 55 inch LCD-LED television using QD film, the emissions of cadmium from electricity generation are reduced by 110mg per year as compared to a similar performing standard LED-LCD television without QD film, but this uses data for electricity generated in the USA. Comparable data on cadmium emissions per kWh electricity generated in USA and in Europe exists but the accuracy is uncertain. Emissions will be different due to the different mix of generation sources and emission scrubber efficiencies.

Electricity generation in the EU27 in 2010 was 3181TWh (Eurostat data [1]) and cadmium emissions from electricity generation in 2010 was 12.2 tonnes (EEA data[2]). Therefore, 3.8µgCd are emitted per kWh in the EU compared to 25.5µgCd per kWh in the USA.

OneSource calculated that operating a 55” LED-LCD television in the USA will result in the emission of 149.38mg Cd. Therefore the same television operating for the same period of time in the EU would emit:

$$(3.8/25.5) \times 149.38 = 22.3\text{mg Cd per year.}$$

This total quantity of cadmium emissions saved over a typical 15 year lifetime by using a QD-LCD is larger (335mg of Cd) than the amount of cadmium that would be present in the QD display of a 55” QD-LCD television that contains 39.7 mg of Cd. Consumption of less electricity will also result in lower emissions of lead, mercury and other toxic metals in the ratio given above.(19) The range of materials used and the construction processes for QD-LCD TVs and standard LED-LCD TVs are very similar except for the substitution of QD-BLU for

---

[1] http://epp.eurostat.ec.europa.eu/statistics_explained/index.php?title=File:Electricity_Statistics,_2011_(in_GWh).png&filetimestamp=20121128151011

[2] http://www.eea.europa.eu/publications/eu-emission-inventory-report-1990-2010

the LED-BLU and so the environmental impacts of both designs over their entire life cycles will be very similar except for the cadmium present in the QD film and the lifetime cadmium emissions for electricity generation in the use phase, where QD-LCDs emit far less cadmium overall. QD displays will also emit less greenhouse gases and less toxic metals due to the lower electricity demand.

The QD Film used in a display device such as an LCD application is contained within the physical device. The cadmium is encapsulated within the film and not accessible. This means that consumers are able to enjoy using the display device without being exposed to cadmium.

8. Re-use and recycling of materials from waste EEE

The QD film in an LCD application contains at most 20 μg/cm^2 of Cadmium; it is contained within a physical device. The Cadmium is bound to selenium in a core structure, which is encased within a non-toxic inorganic shell, surrounded by ligands, held in a glassy matrix/film within an LCD assembly.

It is very likely that display devices that use this technology will be collected and recycled with other consumer electrical equipment as required by the WEEE directive. Recycling processes used in the EU are regulated by EU legislation which closely limits emissions of hazardous substances such as cadmium and there is no published information that EU recyclers do not comply with these restrictions. Most WEEE in the EU is treated thermally which causes cadmium to oxidise and at high temperature this is fairly volatile and so is very efficiently collected with other volatile metals such as zinc and lead. From these, cadmium is separated for safe disposal as a waste by-product.

Some WEEE is exported out of the EU for recycling. This trade is already regulated through the EU's waste shipment regulations that restrict the export of hazardous waste to non-OECD countries. There will also be new obligations from the recast WEEE directive. This legislation should prevent unsafe recycling in developing countries but inevitably relies on effective enforcement.

Inevitably, some WEEE is not separately collected and recycled, especially small devices and so some displays will be sent to landfill for disposal. Leaching studies have been performed, and no detectable level of cadmium leaches out of the QD film (21) and so this cadmium should not pose a risk.

Comparison of life-cycles:

The only technically viable substitutes for Cd based QD-displays that may in the future be able to provide the same color performance and that are suitable as substitutes for most current applications are the Cd-free QD films that are being developed and potentially also OLEDS. The performance of Cd-free QD is not currently suitable, as explained above. OLEDs cannot yet be made into large-size displays and do not have near the capacity to serve the market. A direct comparison of these three types of displays in all life-cycle phases is given below. This compares only the parts within televisions, mobile phones, etc. that are display technology-specific. The housings, power supplies and control electronics are excluded as these will be very similar or identical for all three options:

Life cycle phase	**Cd – based QD display**	**Cd-free QD display**	**OLED display**
Different materials.	Cadmium and selenium	Indium and phosphorous	Various organic and organometallic compounds: triarylamines, polycyclic aromatic and hetero-aromatic compounds, Aluminium quinolates, Iridium cyclometalated complexes, Indium Tin Oxide, metals and their alloys (Al, Ag, Mg).
Other non-standard parts used	BLU, color filters	BLU and colour filters (same as Cd-based)	BLU not needed. Colour filters may be needed in specific applications. Circular polarizer used for contrast. Various designs used, which consist of complex arrays of layers
Extraction / refining	Cadmium is recovered as a by-product from zinc refining	Indium is a very scarce material obtained as a by-product from mining other metals.	Manufacture of OLED chemicals are complex processes consisting of 1 to 5 synthetic steps typically. Materials purification requires several liquid or gas phase purification steps.
Display manufacture	Energy consumption small compared to use phase*	Energy consumption small compared to use phase*	Energy consumption small compared to use phase*
Use	Lower energy consumption than all other technologies	Current prototypes consume more energy than CdSe QD displays (see figures 6 and 7) although research is underway to reduce use-phase energy consumption.	These will consume three times higher power consumption in use phase than CdSe QD.
End of life	Likely to be collected and recycled with other WEEE. Cd is recovered for safe disposal using professional EU smelting processes. In event of landfill disposal, cadmium leaching does not occur.	Likely to be collected and recycled with other WEEE. Indium content of WEEE may be too low in concentration to be worthwhile recovering.	Likely to be collected and recycled with other WEEE. Thermal recycling will destroy OLEDs. Safe high temperature processes should be used but if unsafe burning is used, polycyclic aromatic hydrocarbons are likely to be emitted.

* No published data on these energy consumptions. However, the televisions eco-design study found (for LCD-TVs) that the most significant environmental impact was energy consumption in the use phase.

9. *Other information*

It is estimated that typically 147 kg of cadmium will be placed on the EU market annually by this application. Table 1 outlines the calculations used to develop this estimation. Using the same numbers it is estimated that 565 kg of cadmium will be placed on the world market annually (i.e. the EU has a 26% share of global sales).

Application	Global Annual LCD Area (1) (m^2)	EU Share of LCD Area (2) (m^2)	% Using QD Film(3)	LCD Area Using QD Film in EU (m^2)	Typical Cd Content per LCD Screen Area (g/m^2)	Total EU Cadmium (kg)
TV	157,333,925	26%	2%	818,136	0.05	41
Monitor	29,365,561	26%	3%	190,876	0.05	10
Notebook/Ultrabook	22,819,763	26%	7%	415,320	0.05	21
Tablets	12,174,293	26%	60%	1,899,190	0.03	57
Small displays (phones, etc.)	12,000,660	26%	20%	624,034	0.03	19
					Total	***147***

1. Based on forecasts from iSuppli in the Q4 2011 LCD Market Tracker Database and the Q4 2011 Small & Medium Display Market Tracker Database
2. Estimated based on EU's share of global GDP
3. Estimates for the potential use of QD film for the various segments

Table 1. Summary of values used to estimate total amount of cadmium placed in the EU market annually by quantum dot films in LCD screens.

10. *Proposed plan to develop substitutes and timetable*

Replacement of cadmium – commercial estimated in 7 years (by 2021) (minimum)

The only potential high color quality substitute that does not have significantly higher energy consumption is Cd-free QD films.

Cd-free QD research (based on InP) predicted to reach current color quality and energy consumption performance with only prototypes available by 2019.

Time to full-scale commercialisation expected by July 2021.

11. *Proposed wording for exemption*

Cadmium in light control materials used for display devices

References

1) Choi, S. Y., Luo, M. R., and Pointer, M. R. 2007. The key attributes that influence the image quality of a large display. *AIC 2007 - Color Science for Industry*. pp. 178-180.
2) Sakurai, M., et al. 2008. Effects of display properties on perceived color-gamut volume and preference. *Journal of the SID* 16/12, pp. 1203-1211.
3) Xia, J., Yin, H.C., Heynderickx, I. 2006. Preferred balance between luminance and color gamut in mobile displays. *Journal of the SID* 14/10. pp. 873-881.
4) Hartlove, J. 2011. Quantum dots unleash high-color-gamut performance in LED-backlit displays. LEDs Magazine.
5) Wyszecki, G., and Stiles, W. S. (1982) *Color Science: Concepts and Methods, Quantitative Data and Formulae*, 2nd Edition, New York, NY: John Wiley and Sons.
6) http://en.wikipedia.org/wiki/Cadmium
7) Quantum Dot Enhancement Film Cadmium Emissions Analysis, SourceOne, Inc., http://www.sourceone-energy.com/
8) http://en.wikipedia.org/wiki/SRGB
9) http://en.wikipedia.org/wiki/Adobe_RGB_color_space
10) Exemption 39: Cadmium in colour converting II-VI LEDs (< 10 µg Cd per mm 2 of light-emitting area) for use in solid state illumination or display systems
11) Soneira, R. M. Flagship Smartphone Display Technology Shoot-Out. 2012. http://www.displaymate.com/Smartphone_ShootOut_2.htm
12) http://www.flatpanelshd.com/news.php?subaction=showfull&id=1350628136
13) Based on forecasts from iSuppli in the Q4 2011 LCD Market Tracker Database and the Q4 2011 Small & Medium Display Market
14) Young, B. 2012. Apple, Hon Hai, Sharp and AMOLEDS. OLEDs World Summit Pre-Conference Webinar. San Francisco, CA.
15) http://en.wikipedia.org/wiki/Plasma_display
16) http://www.energystar.gov/index.cfm?fuseaction=find_a_product.showProductGroup&pgw_code=TV
17) http://www.displaymate.com/shootout.html#series1
18) http://naei.defra.gov.uk/emissions/emissions_2009/summary_tables.php?action=unece&page_name=Cd09.html
19) J. M. Pacyna "Atmospheric Emissions of Arsenic, Cadmium, Lead and Mercury from High Temperature Processes in Power Generation and Industry". Leads, Mercury, Cadmium and Arsenic in the Environment, 1987 pub J Wiley and Sons Ltd.

20) V. M. Fthenakis, H. C. Kim and E. Alsema, “Emissions from Photovoltaic Life Cycles”, Environ Sci Technol 2008, (42) 2168.

21) Pace Analytical Services. 2012. QD Film Leaching Study. (see accompanying report)