

APPLICABILITY OF EXEMPTIONS 13 B AND 39 IN ANNEX III OF DIRECTIVE 2011/65/EU FOR THE USE OF CADMIUM IN NANOSYS MATERIAL

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1 Background

1.1 The Nanosys Material and Its Functionality

Nanosys developed a material ("Nanosys material") based on cadmium-containing nanocrystals and an organic matrix. The material is fluorescent in that it absorbs incident light and re-emits it at the same and different wave lengths. Depending on its thickness, the Nanosys material absorbs all or just a certain wave length portion of the incident light. Figure 1 gives an impression of the Nanosys material.

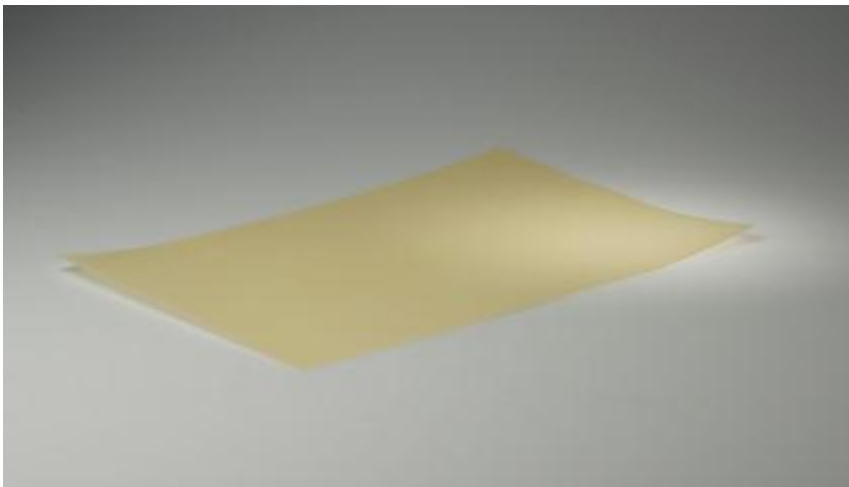


Figure 1: The Nanosys material

Nanosys wants to use its material for fluorescent optical glass and filter technology for down-conversion (i.e., conversion of light from one wave length to another wave length), filtering and optical coating layers for products such as light projectors and displays, e.g., T.V. backlight sources. The material and its processing is described in (Nanosys 2011). Figure 2 presents a schematic view of the Nanosys material.

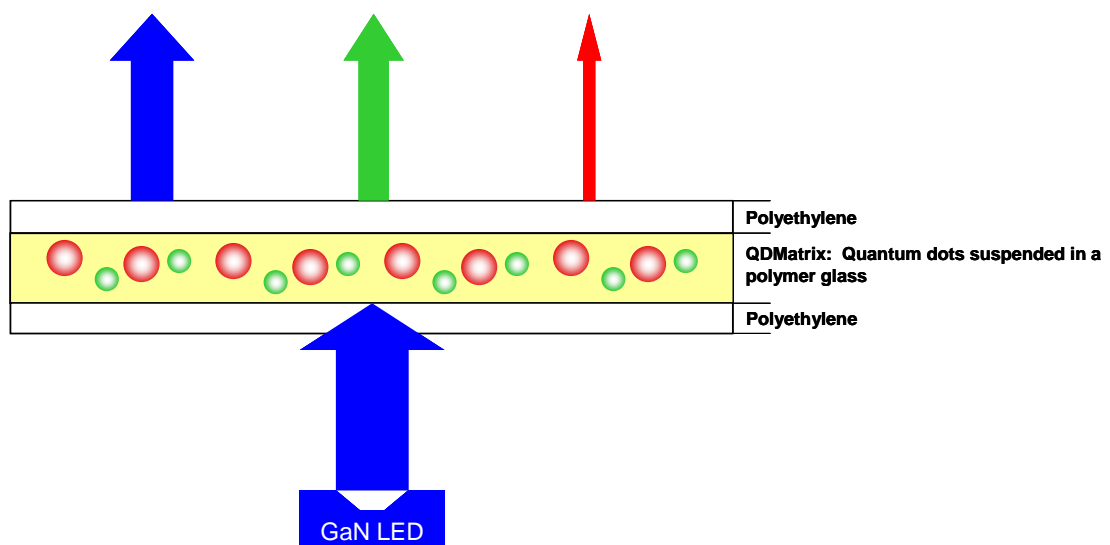


Figure 2: Construction and functionality of the Nanosys material (source: Nanosys)

The material, according to Nanosys, has a glass transition temperature of around 80 °C. Above this temperature, the material will soften but not melt. It is flexible breaking at about 150 % elongation.

1.2 Legislative Background

The European (RoHS Directive 2003) banned the use of the following substances in electrical and electronic equipment from 2006 on:

- lead
- cadmium
- hexavalent chromium
- mercury
- polybrominated diphenyl-ethers (PBDE)
- polybrominated biphenyls (PBB)

The (RoHS Directive 2003) allowed exemptions from these restrictions under certain conditions specified in art. 5 (1)(b) of (RoHS Directive 2003) listed in the Annex of that directive. Since 2008, the RoHS Directive was under review, and the recast (RoHS Directive 2011) was officially published on 1 July 2011. The list of exemptions in the annex of (RoHS Directive 2003) was transferred unchanged to Annex III of the (RoHS Directive 2011).

According to the (RoHS Directive 2003), exemptions had to be reviewed at least every four years. The Commission took the initiative with starting an online stakeholder consultation. The exemptions were extended if stakeholders could justify the continuation with the criteria of the exemption article 5 (1) (b).

As an important change, the (RoHS Directive 2011) extends the list of exemption criteria in its article 5 (1) (a) and restricts the maximum validity of all exemptions in Annex III to five years. After this maximum validity period, the exemptions expire, unless industry and/or its suppliers take the initiative and can justify the continuation of exemptions based on the criteria in article 5 (1)(a). Exemptions with an expiry date prior to the maximum validity period expire at that date, of course.

The Nanosys material contains cadmium. The use of cadmium in electrical and electronic equipment is banned in the European Directive 2011/65/EU (RoHS Directive 2011), if the cadmium concentration is higher than 0.01 % of weight in the homogeneous material. The concentration of cadmium in most applications of the Nanosys material will be higher than 0.01 % assuming that the homogeneous material is the polymer glass containing the "quantum dots" (see Figure 2).

Exemption 13 b and 39 in Annex III of the (RoHS-Directive 2011), however, allow the use of cadmium in filter glass and in II-VI color converting LEDs in concentrations above the 0.01 %:

Exemption 13 b:

- Cadmium and lead in filter glasses and glasses used for reflectance standards
- The exemption expires on 20 July 2016.

Exemption 39:

- Cadmium in colour converting II-VI LEDs ($< 10 \mu\text{g Cd per mm}^2$ of light-emitting area) for use in solid state illumination or display systems
- The exemption expires on 1 July 2014

It shall be evaluated whether and how far the above exemptions cover the use of the Nanosys material in the applications specified in the exemptions. Fraunhofer IZM since 2005 has been involved into the reviews of exemptions from the substance restrictions of the RoHS Directive under contract of the European Commission. Nanosys hence asked Fraunhofer IZM to give its opinion on the above issue.

This report is not a final assessment of the validity of exemptions 13 b and 39 for the use of the Nanosys material in filter glasses and in II-VI color converting LEDs. The RoHS Directive holds the producers of electrical and electronics devices responsible for the RoHS compliance of the products they put on the European Union market. The producers themselves classify whether their product falls under the scope of the RoHS Directive, and whether certain exemptions apply for a specific use of a certain material. The interpretation of legal texts and thus the correctness of a producers' self assessment in the end is the authority of the European Court of Justice. Fraunhofer IZM's statement on the validity of exemptions 13 b and 39 for the Nanosys material and its applications is based on its long experience and expertise with RoHS exemption review processes, but cannot be a final assessment of the case.

2 Use of Nanosys Material in Filter Glass (Exemption 13 b)

Exemption 13 b covers the use of Nanosys materials

- if the Nanosys material is a "glass" despite of the fact that it is based on organic materials
- and
- if the device applying the Nanosys material works as a "filter" despite of the fact that, depending on its thickness, it may not be selective for light of specific properties such as wave length etc., but color converts all incident light into light of different wave lengths.

1.3 Is the Nanosys Material a “Glass”?

Glass generally is understood as inorganic material. The Nanosys material is, however, based on organic material. Material scientific glass definitions were investigated to clarify whether glasses may also be based on organic materials.

1.3.1 Definitions of “Glass”

Several sources were investigated for definitions of “glass”. The investigation shows that there is no generally acknowledged standard definition of “glass”:

1. Glass is an amorphous solid. (Doremus 1994)
2. Glass includes all materials which are structurally similar to a liquid. However, under ambient temperature they react to the impact of force with elastic deformation and therefore have to be considered as solids. (Pfaender 1996)
3. Glass is a “hard, brittle, generally transparent or translucent material typically formed from the rapid cooling of liquefied minerals.” (Educational Resource of the U.S. Environmental Protection Agency and Earth 911.org)
4. Glasses are noncrystalline or amorphous substances. Nevertheless, the term vitreous state is restricted to (i) solids obtained from melts, or (ii) solids produced by other methods and obtained in a compact form or as thin coherent films [...]. Glasses have numerous properties in common with crystalline solids, such as hardness and elasticity of shape [...]. The term 'amorphous solid state' has a more comprehensive meaning broader than that of the 'vitreous state'. All glasses are amorphous, but not all amorphous substances are glasses. (Feltz 1993)
5. A glassy (or synonymously, vitreous) material is an amorphous solid that exhibits a glass transition. (Thus, by definition, all glasses are amorphous, but not all amorphous solids are necessarily glassy.) The glass transition is marked (as a function of temperature) either by a change in slope of extensive thermodynamic quantities (e.g., volume or entropy) or, equivalently, as a discontinuity in derivative quantities (e.g., specific heat or thermal expansivity). (Elliot 1994)
6. As kinetically frozen forms of liquid, glasses are characterized by a complete lack of long-range crystalline order and are the most structurally disordered types of solid known. (Jeanloz et al. 1991)
7. “Organic glass “[is] a fully synthetic plastic material available in a vitreous state. It consists of macromolecular organic compounds which do not follow any principle of periodic arrangement and are hence amorphous.”¹

Several authors define “amorphous” and “solid”:

8. An amorphous (or synonymously, non-crystalline) material can be defined as one which is topologically disordered and which does not exhibit either the long-range translational order (periodicity) characteristic of single crystals, or the long-

¹ Carl Zeiss,
http://www.zeiss.com/de/ophtalmic/comp/home_e.nsf/6f2a76c25f0237fbc12566fe003b25ff/1d18a0f6dd711d634125689500320b97?OpenDocument, last accessed 22 September 2011

range orientational order characteristic of quasicrystals. Within this definition, such materials could be either solid or liquid, and this distinction is essentially simply one of timescale. (Elliott 1994)

9. [...] Amorphous solids are characterized by a topological disorder, so there is no long-range order (or periodicity) in their structure. However, this does not mean that amorphous solids are structurally completely random (i.e., gas-like) at all length scales. In fact, covalent materials, in particular, exhibit a rather high degree of structure organization at length scales corresponding to several atomic separations [...]. On the other hand, materials characterized by non-directional centro-symmetric interatomic interactions, e.g. metals or completely ionic materials, are intrinsically much more disordered even at short length scales. (Elliott 1994)
10. "A material is amorphous when it has no long-range order, that is, when there is no regularity in the arrangement of its molecular constituents on a scale larger than a few times the size of these groups. [...]" (Doremus 1994)
11. Amorphous substances, like crystalline solids, are usually characterized by certain areas of short-range order [...] A long-range order, as in crystals, does not exist in amorphous substances. The designations 'amorphous' and 'noncrystalline' describe the same fact [...]. (Feltz 1993)
12. amorphous solid, any noncrystalline solid in which the atoms and molecules are not organized in a definite lattice pattern. Such solids include glass, plastic, and gel.²
13. "Polymers [...] can be amorphous (totally lacking positional order on the molecular scale) or semicrystalline (containing both crystalline and amorphous regions in the same sample)."³
14. A solid is a rigid material; it does not flow when it is subjected to moderate forces [...]." (Doremus 1994)
15. A material is a solid when there is no observable long-range translational diffusive motion during the duration of the experiment; in other words, dynamic disorder is absent. (Elliott 1994)

1.3.2 Interpretation

No definition could be found limiting glass to non-organic materials. Only definition 3 in the above definitions list mentions the base materials of glass stating that glass is "typically formed from the rapid cooling of liquefied minerals." (Educational Resource of the U.S. Environmental Protection Agency and Earth 911.org). The term "typically" is, however, not exclusive and implies that glass may also consist of other materials than inorganic minerals. Definition 3 also is the only definition describing glass as a "brittle" substance. This property does not apply to the Nanosys material, as it is rather elastic compared to inorganic glass.

² Encyclopedia Britannica online, <http://www.britannica.com/EBchecked/topic/21328/amorphous-solid>; last accessed 25 September 2011

³ University of Rochester, Introduction to Polymer Chemistry: Crystalline and Amorphous Polymers, <http://chem.chem.rochester.edu/~chem421/cryst.htm>, last accessed 25 September 2011

Definition 5 additionally requires a “glass” to be “[...] an amorphous solid that exhibits a glass transition. According to Nanosys, the Nanosys material has a glass transition temperature of around 80 °C.

Even though there is no generally acknowledged standard definition of “glass”, all definitions focus on the inner structure and define glass as an amorphous solid or an amorphous, solidified liquid. According to these definitions, a material can be a glass irrespective of whether it consists of inorganic or organic base materials, as long as the material exhibits an amorphous solid structure.

Despite of the fact that the Nanosys material is based on polymers and thus is an organic material, it can be a glass if it exhibits the structural properties of amorphousness and solidity according to the above definitions.

1.4 Is the Nanosys Material Applied as a Filter in the Meaning of Exemption 13 b?

Depending on its thickness, the Nanosys material absorbs all or just a portion of incident light and re-emits it at a different wave length. Generally, filters are understood as devices, which are transmissible for a certain spectrum of the incident light and absorb other parts of the spectrum. The question arising hence is whether the Nanosys material can actually be addressed as a “filter”. A first investigation on the internet did not yield satisfying results. In a second investigation round, definitions of “filter” could be accessed in German, European and international standards.⁴

1.4.1 Definitions of “Filter”

The (ERA 2004) report about the investigation of exemptions speaks of “optical filters” in the context of nowadays exemption 13 b. (ERA 2004) explicitly mentions “coloured glass filters”. These filters require the use of cadmium to achieve a sharp cut-off at certain wave lengths of incident light to achieve a high light transmission in the desired wave length spectrum and a well-defined attenuation or complete cut-off at other wave lengths. (Ökoinstitut 2009) builds upon (ERA 2004) and only speaks of „filter glass”.

Similar to the definition of “glass”, no universal and generally acknowledged standard definition could be found for “filter” or “optical filter”. In standards and draft standards, several definitions for “filters” could be found.

1. A filter is an optical device selecting and/or influencing wave length, color temperature, direction of oscillation and/or intensity of a radiation, which the device lets pass or reflects⁵

⁴ Deutsches Institut für Normung e. V. (DIN, German Institute for Standardization), <http://www.din.de/cmd;jsessionid=DB2B7C260007329396FAB8336FC056DE.2?level=tpl-home&languageid=en>; last accessed 14 October 2011

⁵ DIN 58629-1:2006, Optik und optische Instrumente - Begriffe für die Mikroskopie - Teil 1: Lichtmikroskopie (Optics and optical instruments - Vocabulary for microscopy – Part 1: Light microscopy); http://www.beuth.de/cn/J-09DDFF339E8878E3F401236145FC6ADA.3/bGV2ZWw9dHBsLUxhbmdhbnplaWdlJnNtb2lkPTgzOTMzMTU1Jmxhbmd1YWdlaWQ9ZW4*.html, last accessed 12 October 2011; in German language only, translated from German

2. A filter (synonym: optical filter) is a directionally transmissible component for changing the radiation performance or light stream, the relative spectral distribution, or both properties of the transmitted radiation ⁶
3. A filter is a device selecting a broad or narrow range of the electromagnetic spectrum (color and neutral grey filter, conversion temperature blue filter (CTB), conversion temperature orange filter (CTO), anti-UV- or anti-IR-filter). Grey filters reduce the transmitted light for a known degree without selecting any wave length.⁷
4. A filter is a viewing glass weakening radiation, normally of a specific wave length.⁸

Besides definitions for “filter”, there are definitions for “conversion filters” and “conversion glass”.

5. A color conversion filter (synonym: conversion filter) is a filter changing the color temperature characteristics of a light source ⁹
6. A conversion glass is a colored glass which, due to its specific transmission characteristics, increases or decreases the color temperature of a radiation source in the visible spectrum.¹⁰

1.4.2 Interpretation

Definitions in a standard are not of a general, universal character but define terms for the use in that particular standard. In the absence of generally acknowledged definitions for “filter”, the definitions in standards may, however, at least be useful to see the range of different filter definitions.

Definition 1 defines a filter, besides being selective, as an optical device influencing wave length or color temperature etc. “Influencing” can be interpreted as any kind of change of the incident light, such as the color conversion of all or just a portion of incident light by the Nanosys material.

⁶ CIE 17.4/IEC 60050:1987 (845-04-105): International Lighting Vocabulary; <http://www.cie.co.at/publ/abst/17-4-89.html>; last accessed 12 October 2011, translated from German

⁷ Draft DIN EN 16163: Conservation of cultural property - Exhibition lighting of cultural property; <http://www.nabau.din.de/cmd?level=tpl-art-detailansicht&committeeid=54738847&artid=134517944&bcrumblevel=2&languageid=en>; last accessed 12 October 2011; translated from German

⁸ CIE 17.4: 845-04-105: DIN EN 165:2006-09, Personal eye protection – Vocabulary; <http://www.beuth.de/langanzeige/DIN-EN-165/en/85118831.html>; last accessed 12 October 2011

⁹ DIN 58629-1:2006: Optik und optische Instrumente - Begriffe für die Mikroskopie - Teil 1: Lichtmikroskopie (Optics and optical instruments - Vocabulary for microscopy – Part 1: Light microscopy); http://www.beuth.de/cn/J-09DDFF339E8878E3F401236145FC6ADA.3/bGV2ZWw9dHBsLUxhbmdhbnplaWdlJnNtb2lkPTgzOTMzMTU1Jmxhbmd1YWdlYWQ9ZW4*.html, last accessed 12 October 2011; in German language only, translated from German

¹⁰ DIN 1259-1:2001-09: Glas - Teil 1: Begriffe für Glasarten und Glasgruppen (Glass - Part 1: Terminology for glass types and groups), <http://www.beuth.de/langanzeige/DIN-1259-1/de/38566720.html>, last accessed 12 October 2011; in German language only, translated from German

Definition 2 focuses on the change of the incident light in terms of radiation performance and/or the spectral distribution. According to these definitions, the Nanosys material could be described as a filter, as it changes the relative spectral distribution of the incident light.

Definition 5 qualifies the Nanosys material as conversion filter. Definition 6 as well covers the non-selective conversion properties of the Nanosys material for incident light, but additionally requires that the glass is colored. Figure 1 shows that the Nanosys material has a slightly yellow color in ambient light. The other filter definitions describe the selective transmission and attenuation as a crucial property of “filters”.

The filter definitions thus are more diverse compared to the glass definitions. Only filter definition 1 and 2 would clearly cover the Nanosys material in applications, where it absorbs all incident light. As the above collection of definitions is not complete, it must be assumed that there may be more diverse definitions, where only some allow describing the Nanosys material as a filter in all its functionalities.

A remaining question is whether the term “filter” in the wording of exemption 13 b is meant as an umbrella term comprising all kinds of filters including “conversion filters”. Filter definitions 1 and 2 include the color converting function as a property of a filter supporting the assumption that “filter” is an umbrella term for all kinds of filters. In the review reports of (ERA 2004) and (Oekoinstitut 2009), conversion filters are not mentioned explicitly in the justification for exemption 13, neither in the reports nor in the stakeholder submissions to the (Review 2008) of exemption 13 in 2008. Other types of filters are mentioned, however, supporting the assumption that “filter” is an umbrella term for several types of different optical devices. The variety of properties mentioned in the list of filter definitions above supports this point of view. Additionally, it can be argued that irrespective of the original intention of an exemption, the wording of the exemption is the main yardstick when deciding whether a material or a technology is covered by a certain exemption.

Compared to the glass definitions, the filter definitions are more inhomogeneous in their scope and criteria. As at least some of the definitions of “filter” cover the functionality of the Nanosys material, it may be justified to classify it as a “filter”.

1.5 Conclusion

Exemption 13 b in Annex III of the (RoHS Directive 2011) allows the use of cadmium and lead in filter glasses. The applicability of exemption 13 b on the use of the cadmium-containing Nanosys material in filter glass depends on

- whether the inorganic Nanosys material can be understood as a glass in the material scientific sense
- and
- whether the functionality of the Nanosys material is actually that of a “filter”.

An investigation of glass definitions shows that there is no universal and generally acknowledged standard definition. Nevertheless, all definitions emphasize the non-crystalline, amorphous structure of a solid substance to qualify it as a glass. No definition

restricts glass to inorganic substances. Provided the Nanosys material exhibits such an amorphous structure in the sense of these definitions, it is justified to call it a glass.

The definitions of “filter” or “optical filter” and “conversion filter” are more inhomogeneous. The fluorescent Nanosys material acts as a color converter absorbing a certain spectrum or all incident light and re-emitting it, partially with the same and at other wave lengths. It is not necessarily selective for incident light, and it does not necessarily attenuate certain wave lengths of incident light selectively. Some of the filter definitions justify calling the function of the Nanosys material a “filter” or “optical filter”. It must, however, be taken into account that the definitions are all related to standards, which define terms specifically for the needs of the respective standard and thus are not necessarily of general nature.

Summing up, exemption 13 b in the author’s opinion covers the use of cadmium in Nanosys material applied as filter glass.

2 Use of the Nanosys Material in Color Converting II-VI LEDs

Nanosys intends using its cadmium-containing material as II-VI color converter material in LEDs as illustrated in Figure 2 on page 4. Exemption 39 covers the use of cadmium in such a converter material:

- Cadmium in colour converting II-VI LEDs ($< 10 \mu\text{g Cd per mm}^2$ of light-emitting area) for use in solid state illumination or display systems
- In order to be covered by exemption 39, the Nanosys material
- must act as a II-VI color converter.
- must contain less than $10 \mu\text{g}$ of Cd per mm^2 of light emitting area
- must be linked to and convert the light of an LED
- must be part of an LED used in solid state illumination or display systems.

Exemption 39 does not set any further conditions or restrictions such as geometrical or constructional properties or concerning the type of material used as II-VI color converter.

The Nanosys color converting material contains cadmium-selenide and hence is a II-VI material used as a II-VI color converter according to exemption 39. Nanosys quantifies the cadmium content of the material with less than $10 \mu\text{g}$ of Cd per square millimeter of light emitting area. Figure 2 on page 4 illustrates the intended application of the Nanosys material. The material is used to convert the light of an LED.

Exemption 39 covers the use of the cadmium-containing Nanosys material in II-VI color-converted LEDs, as long as the LED is used in solid state illumination or in display systems.

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