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Adaption to scientific and technical progress under Directive 2002/95/EC

Results previous evaluation
Exemption No. 13

"Lead and cadmium in optical and filter glass"

(Excerpt from ERA Report 2004)

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2.6 Lead and cadmium in optical and filter glass

2.6.1 Introduction

Most optical glass and optical filters do not require lead or cadmium. Almost all camera lenses are now made using lead-free lenses. However, there are a small number of specific applications for which there are no lead-free or cadmium free alternatives. In many cases all of these can be achieved with a lead-free formulation but, in a few specific applications, no alternative matches all of the characteristics. Some examples of applications for optical glass which contain lead include:

- There are no alternatives to lead optical glass for projectors (described below)
- Certain types of lenses such as those used in surveying equipment and certain professional camera lenses
- Some types of gradient index lens (e.g. Selfoc).
- Micro-lithography equipment
- Certain types of high quality printers
- Other applications currently outside of the scope of the RoHS Directive, i.e. Medical Devices and Monitoring and control Instruments.

Table 3. Some characteristics of lead glasses

Characteristic	Lead- glass	Lead-free glass
High refractive index (R.I.). Useful for minimising lens size	Easily achieved	Achieved by use of certain oxides but it is not possible to make gradient index lenses without lead.
Abbe number, ideally low	Important characteristic	Possible to match high refractive index, and low Abbe number of lead glass BUT cannot match other optical properties.
"Blue" wavelength light transmission (light appears "orange" if this is low)	Typically 95% transmission at 450nm	Typically 70% transmission at 450 nm (with same glass thickness), even if R.I and Abbe number are matched (for high R.I. glass).
Stress-birefringence (distortion of glass causes poor image quality)	Can be very good with lead glass	Can be achieved but other characteristics such as TCE cannot be matched so cause distortion.

Other important optical glass properties include chromatic aberration, partial dispersion, thermal coefficient of expansion and many others. It is often possible to match one or more of the optical characteristics of a lead glass with a lead-free glass but there are certain applications where it is not possible to match all of critical characteristics that can be achieved with a lead glass.

Cadmium and lead are used in coloured glass filters. It is possible to produce coloured glass or plastic filters without these metals but in some circumstances, a very sharp wavelength cut-off (~100% to

~0% transmission over a small wavelength range) is required and in these cases, cadmium and/or lead are essential.

2.6.2 Characteristics

Blue- wavelengths light transmission

Lead-free optical glass can be produced which transmits a very high percentage of light of all wavelengths unless high refractive index is also required. Lenses for high magnification can be made with less material and so are lighter and smaller if they have a high refractive index. It is possible to produce high refractive index lenses without lead but, in these types of glass, blue light transmission is inferior to the lead-types and causes a yellowing of the image, particularly where thick lenses are required. Figure 9 shows a comparison of optical transmission through a lead-containing glass with an equivalent lead-free glass of the same dimensions.

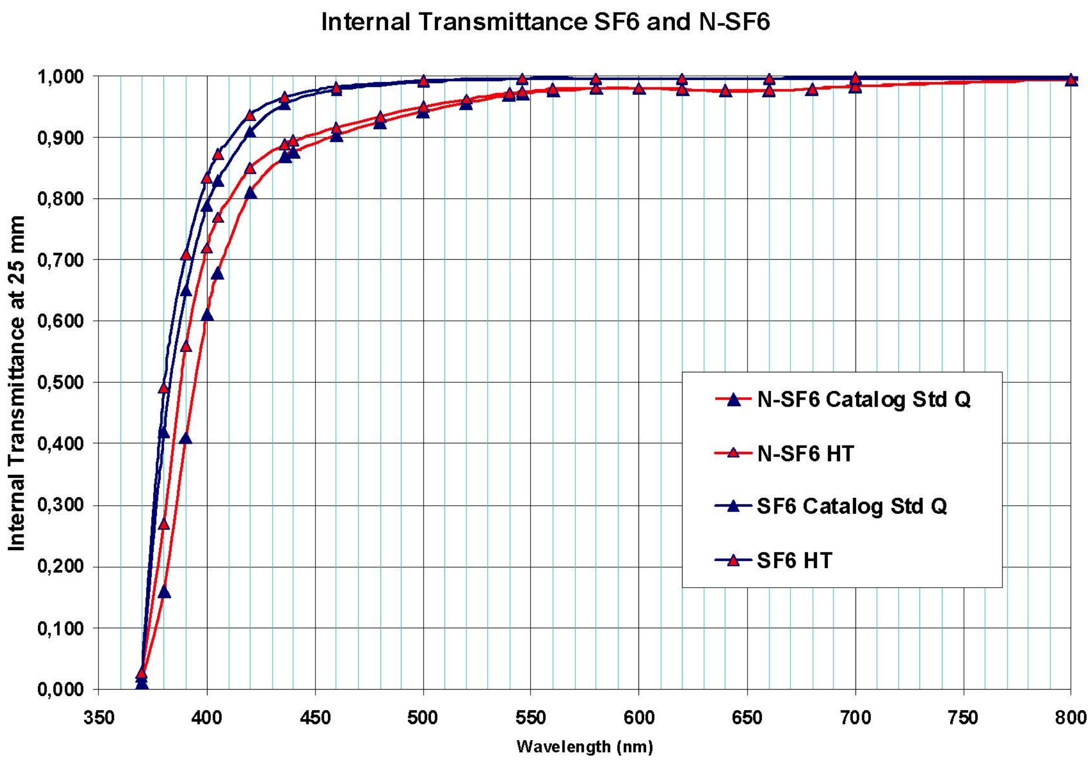


Figure 9. Comparison of light transmission through lead glass (SF6) and equivalent lead-free glass (N-SF6) from Schott Glass.

Stress-birefringence

Optical glass beam splitters are used in projectors and backlit televisions. These products use four beam splitters in total; one each for blue, red and green light and one to recombine these colours to produce the image. The beam splitters are designed to either transmit or reflect light depending on the angle of polarisation, which is switched electronically and scanned to produce the image. The glass used for the beam splitters must have a combination of properties and although each individual property could be met by a lead-free glass, the combination of properties can be achieved only with glass containing lead. The important properties are:

- High light transmission – for high refractive index glass at blue wavelengths high transmission is possible only with lead
- Low TCE – possible with lead free glass unless low stress birefringence also required
- Robustness
- Ease of fabrication – lead glass is easier to fabricate
- High refractive index – possible with lead-free but with limitations
- Low stress birefringence – very few glass types have very low stress optical constants, of these most include lead. The very few without lead have high TCE.

Stress is applied to the beam splitter as a result of heat from the projector lamp but can also result from the way it is mounted. Stress to beam splitters affects the image obtained from the projector as shown in Figure 10 which compares the images obtained in tests with two types of glass. The image is supposed to be a perfect black but the glass with high stress birefringence is distorted giving a coloured image.

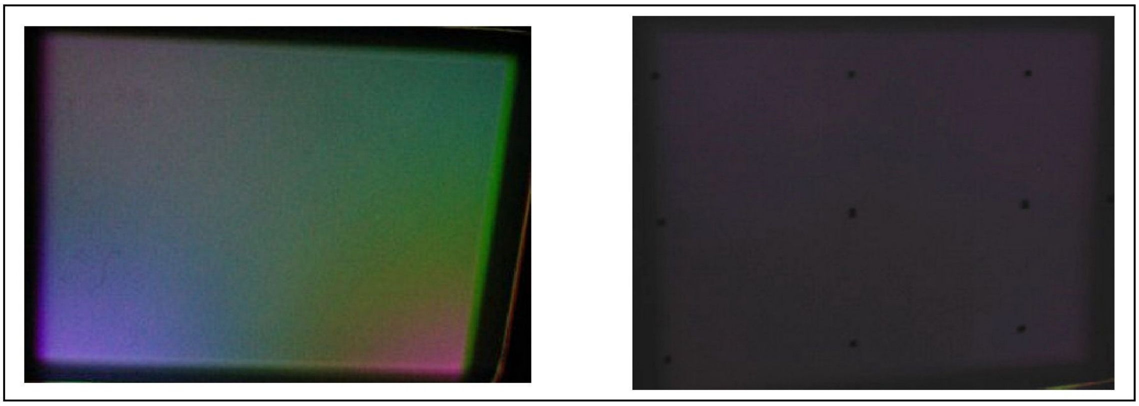


Figure 10. Stress birefringence test images. The left image is lead-free glass (K = 2.77), the right is lead-glass (K = 0.06)

<u>Gradient Index glass</u>

Gradient index (GRIN) lenses are cylindrical glass rods that are used for optical telecommunications and in printers, copiers, scanners and fax machines. They have a gradient of ion concentration from the outer surface to the centre and this gradient is matched by a refractive index gradient. They are produced from glass containing pairs of alkali metals such as caesium, potassium, sodium and lithium. The glass rods are treated with molten salts containing one of the pair so that ions are exchanged for the other (ion exchange). This reduces the concentration of one of the pair at the outer edge and produces a parabolic concentration gradient as shown in Figure 11.

Lead-free glass is used in lenses used for telecommunications but lead is required for applications where a clear image is required. The purpose of lead is mainly to control the ion exchange process so that a smooth concentration gradient is achieved. This gives lenses which produce a clear image whereas without lead, the gradient is less precise resulting in distortion to the image although lead-free glass is suitable for telecommunications applications where an “image” is not required. As with all types of optical glass, lead increases the refractive index and lowers melting point.

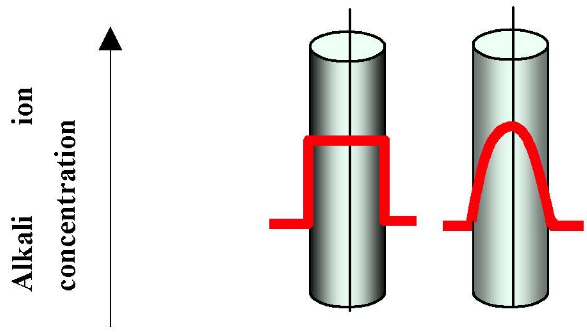


Figure 11. Alkali metal ion concentration gradient (equivalent to the refractive index) before (left) and after (right) ion exchange

<u>**Literature survey on lead-free optical glass**</u>

The scientific and patent literature has been reviewed. There are publications on many types of lead-free glass where lead has been replaced by barium, titanium, bismuth or another material. Where lead is added to obtain a high refractive index, lead-free alternatives are available. For example, US patent application publication US2003/0191006 A1 9th October 2003[12] discloses glass compositions with refractive index of 1.9 to 2.07. The compositions are however slightly yellow as two essential ingredients, bismuth and cerium oxides, are both yellow compounds and so this will reduce blue light transmission. These formulations are useful for certain applications but will not be suitable for all of those where lead glass is currently used.

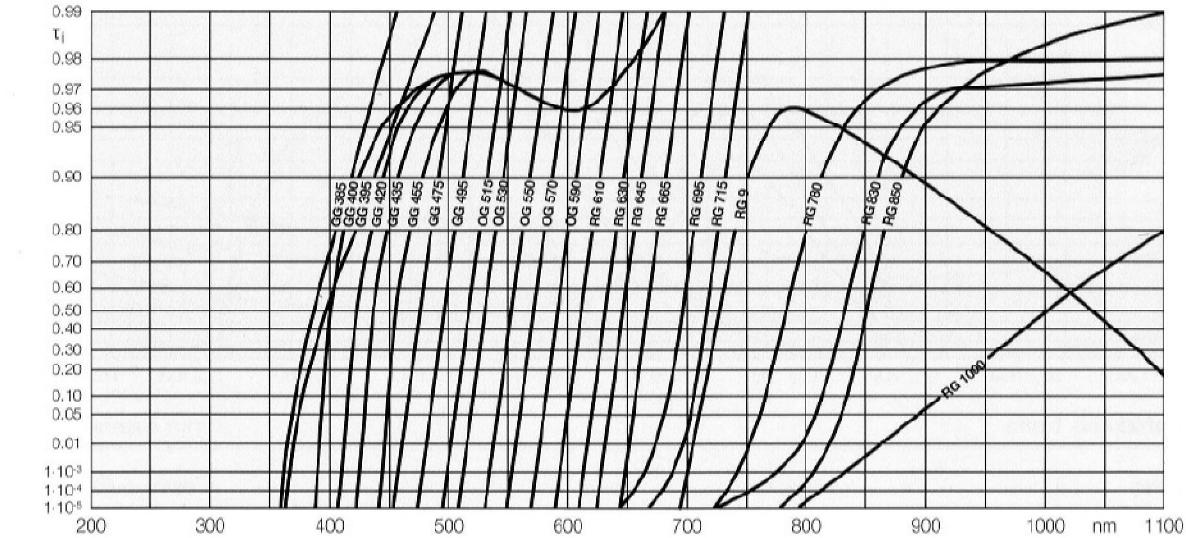
2.6.3 Optical Filters

Glass filters are “coloured” by adding various materials. These materials need to be thermally stable, as they become part of the glass. Both lead and cadmium are used to obtain particular colours. These filters are made in relatively small quantities but have a wide variety of uses although many of these are in medical devices, monitoring and control instruments and military equipment. Examples of applications which would be covered by the RoHS Directive include:

- Runway lighting
- Lighting for infra-red security cameras

- Professional camera filters
- Television cameras
- Bar code reader
- Projectors

One important characteristic of these light filters shown in Figure 12.



Glass thickness 3 mm

Figure 12. Light transmission plotted against wavelength for optical filters

The red/orange/yellow filters contain cadmium and some of the dark blue filters contain lead. Cadmium filters have a sharp “cut off”. For example, many of those shown in figure 12 transmit 0% of light at one wavelength and 100% at a 50 nm higher wavelength. Being able to achieve a sharp cut off over a small wavelength range is important for some applications. A literature search for cadmium free optical filters has identified a small number of possible alternatives but all have disadvantages which make them unsuitable for at least some of the applications where cadmium is currently used.

Alternatives

A search of the scientific literature identified very few alternatives to cadmium based glass filters. The following options have been identified but none are suitable as alternatives for all applications:

1. Red glass coloured by gold. This has been used for centuries for stained glass windows however the cut-off slope is much less steep than can be achieved with the red cadmium filters

2. US Patent Application Publication US 2003/0123167 A1 3rd. July 2003[13]. Describes “steep edge filters” which uses, for example, $CuInS_2$ (copper indium sulphide) as the semiconductor material as a

substitute for cadmium compounds however there are significant differences that limit the applications of this alternative technology:

- $CuInS_2$ and the related compounds added to glass are thermally unstable and a large proportion is lost by evaporation.

- The technique proposed in this patent application is to deposit a thin coating of these materials on a glass surface. Thin films coatings are more easily damaged than solid glass filters.

- The data provided in the patent application for one example shows that transmission at 100% to 0% occurs over a wavelength range of over 100nm which is about double that possible with cadmium.

3. US Patent 4,228,349 14th Oct. 1980[14]. Uses a thin plate of a III-IV semiconductor such as indium/gallium arsenide. These must be very thin, are very fragile and suitable only as filters in optical telecommunications.

4. Plastic filters. Plastics can be coloured with organic pigments that have similar, although not identical, characteristics to cadmium glass filters. However, these are unstable and darken at elevated temperature and bleach under UV and sunlight.

5. Interference filters. These are glass filters which can be used to transmit a narrow wavelength range of light. The wavelength (colour) depends however on the viewing angle and so these are unsuitable for some applications.

2.6.4 Summary of the case for an exemption

The majority of optical glass in current use does not contain lead or cadmium. Most of the individual properties of lead glass can be matched by a lead-free alternative but there are a small number of very diverse applications which require a combination of critical characteristics that cannot be matched by a lead-free glass. There are also certain applications where there are no alternatives to filter glass containing cadmium.

connections to PCBs without soldering but which can be removed and re-inserted without damage to the connector or the PCB.

4.5 Lead as a coating material for the thermal conduction module C-ring

Thermal conduction modules are the central processor units used in the Z-Series main-frame computers produced by IBM. The C-ring is the seal used between the glass-ceramic circuit and the liquid cooled copper plate, which is used to remove heat from the semiconductor chips.

4.6 Lead and cadmium in optical and filter glass

Optical components used in electrical equipment such as glass lenses, optical filters and prisms where no lead-free alternative is suitable. Lead in the glass of electronic components is not included in this exemption as this is covered by item 5 of the Annex of the RoHS Directive.

4.7 Optical transceivers for industrial applications

This exemption request was made to cover optical transceivers and the solder connections made to the PCB to which they are attached. Optical transceivers convert optical signals into electrical signals using glass-fibre connected to a photosensitive semiconductor, convert electrical signals into optical signals using a laser diode or LED attached to an optical fibre or one device may contain both functions.

4.8 Lead in solders consisting of more than two elements for the connection between the pins and the package of microprocessors with a lead content of more than 85% in the proportion to the tin-lead content (exemption until 2010)

A lead-based solder with a melting point higher than standard lead-free solders and eutectic tin/lead but containing <85% lead which is used to attach pins to the carriers of microprocessor packages. This alloy is not covered by the exemption listed as item 7.1 of the Annex of the RoHS Directive which is for solders which contain >85% lead (see section 1.3).

4.9 Lead in high melting temperature type solders (i.e. tin-lead solder alloys containing more than 85% lead) and any lower melting temperature solder required to be used with high melting temperature solder to complete a viable electrical connection

This exemption is intended for internal (Level 1) connections made between the semiconductor die and the carrier in flip-chip packages which have higher power consumption and currently use high melting temperature solder bumps (>85% lead) which are connected to the carrier with eutectic tin/lead (~37% lead). The bump composition will have <85% lead. This exemption would also include situations where high melting point solder balls (e.g. on ball grid array packages) are attached to a PCB with a lead-free solder. It is <u>not</u> intended to permit the use of solders containing lead for