# THE DEVELOPMENT OF NEW TYPES OF GLASS FRITS WITH SPECIAL OPTICAL PROPERTIES FOR THE INCORPORATION OF LUMINESCENT MATERIALS

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Luminescent materials occur widely in nature as minerals. These are often only recognizable when exposed to ultraviolet (UV) light, whereby the UV radiation only makes up a small part of the light spectrum (see Figure 1). In the course of this the crystals convert the **UV** light (**100-380 nm**), which is invisible to humans, into visible light (400-800 nm).

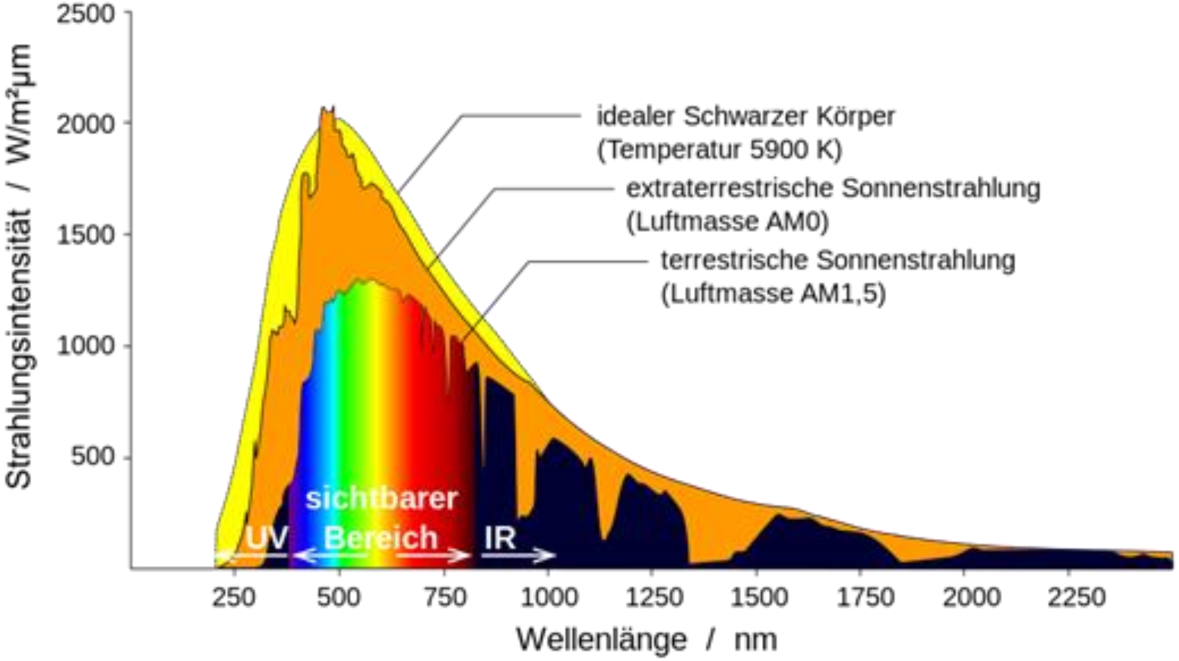

*Figure 1*

*Picture by Degreen [CC-BY-SA-2.0-de (http://creativecommons.org/licenses/by-a/2.0/de/deed.en)]*

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An example of this can be seen in Figure 2 where a mineral is seen in daylight (A) and under UV light (B).
Some types of these crystals are even able to store the energy from UV light or visible light and subsequently, after exposure, to **re-emit this as light with a higher wave length**. This is called luminescence or afterglow.

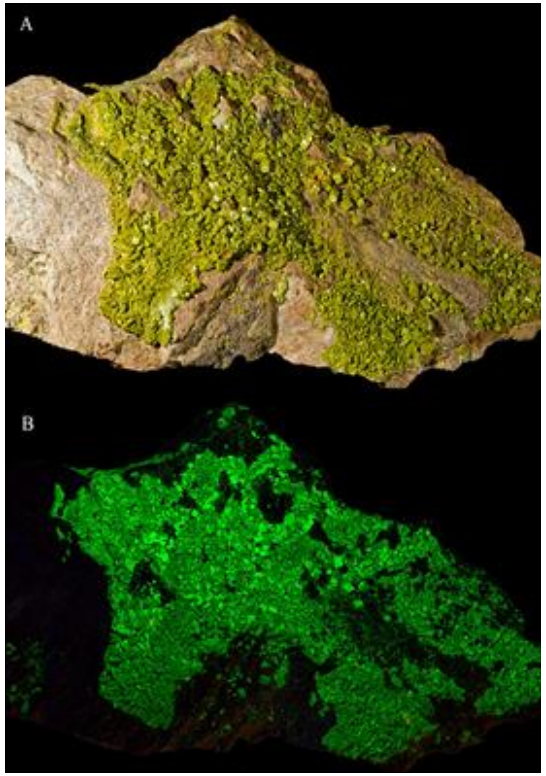

*Figure 2*
*Picture by Didier Descouens [CC-BY-SA-3.0 (http://creativecommons.org/licenses/by-sa/3.0)]*

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In **1602** the Bolognese alchemist Casciorolo succeeded in creating the first artificial, luminescent compound. He was attempting to produce gold and discovered the "**glowing stone of Bologna**". Scientific studies on phosphorescence were carried out by Becquerel at the end of the 19th century. Although the luminescent properties of minerals had been known for a long time it was only in 1950 that the production of doped zinc sulphide ($ZnS:Cu$) was described. Pigments used prior to this contained radioactive compounds.

*Picture by M. M. Pattison Muir [Public Domain]*

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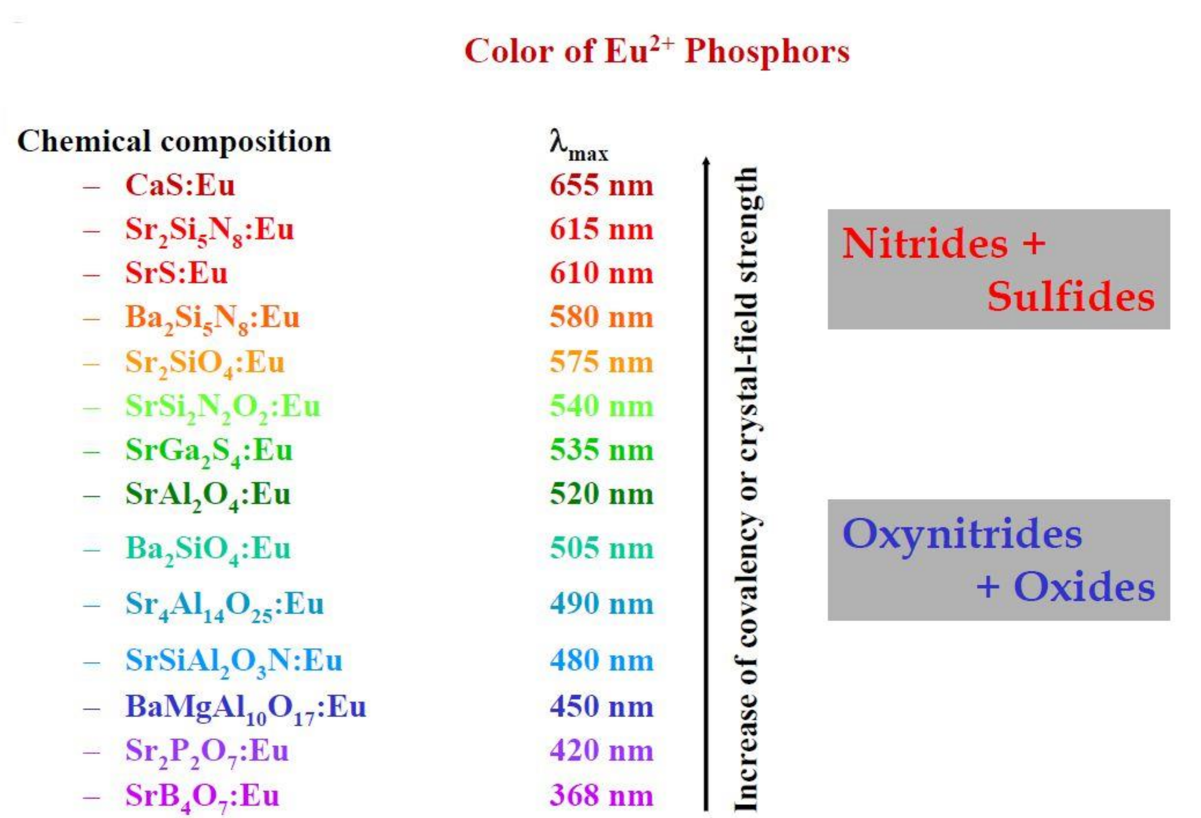
For several years there has been a new group of luminescent pigments on the market. **Alkaline earth aluminates** e.g. strontium aluminate (SrAl2O4:Eu,Dy) are doped with rare earths such as europium and show considerably better luminescent properties than zinc sulphide doped with copper. Furthermore the alkaline earth aluminates are less sensitive to high temperatures. The following investigations were carried out based on this luminescent pigment.



Color of $Eu^{2+}$ Phosphors

| Chemical composition | $\lambda_{max}$ |
|---|---|
| – CaS:Eu | 655 nm |
| – $Sr_2Si_5N_8$:Eu | 615 nm |
| – SrS:Eu | 610 nm |
| – $Ba_2Si_5N_8$:Eu | 580 nm |
| – $Sr_2SiO_4$:Eu | 575 nm |
| – $SrSi_2N_2O_2$:Eu | 540 nm |
| – $SrGa_2S_4$:Eu | 535 nm |
| – $SrAl_2O_4$:Eu | 520 nm |
| – $Ba_2SiO_4$:Eu | 505 nm |
| – $Sr_4Al_{14}O_{25}$:Eu | 490 nm |
| – $SrSiAl_2O_3N$:Eu | 480 nm |
| – $BaMgAl_{10}O_{17}$:Eu | 450 nm |
| – $Sr_2P_2O_7$:Eu | 420 nm |
| – $SrB_4O_7$:Eu | 368 nm |

Increase of covalency or crystal-field strength

Nitrides + Sulfides

Oxynitrides + Oxides

*Picture by T. Jüstel [https://www.fh-muenster.de/fb1/downloads/personal/juestel/juestel/_18356/Anorganische_Leuchtstoffe-Schluesselmaterialien_fuer_hocheffiziente_Lichtquellen__Maerz_2005_.pdf]*

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The requirements of the luminescent enamel with regard to optical properties are very high. <u>**Above all a luminescent enamel must demonstrate the highest possible permeability for UV radiation as well as for visible light**</u>. On the one hand during irradiation as much light of a particular wavelength as possible must reach the luminescent pigment in the enamel, and on the other hand light given off from the luminescent pigment must in turn be able to be emitted through the enamel as intensively as possible and without loss. Various production enamels are seen in Table 1.

| Fritte | Brenntemperatur | Reflexion bei 370 |
|---|---:|---:|
| Testfritte 1 | 860 °C | 75 % |
| Testfritte 2 | 700 °C | 72 % |
| Testfritte 3 | 700 °C | 68 % |
| Testfritte 4 | 700 °C | 45 % |
| Testfritte 5 | 700 °C | 33 % |
| Testfritte 6 | 600 °C | 20 % |
| Testfritte 7 | 860 °C | 15 % |

*Table 1:* Testfritte means various produktion enamels

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The reflection spectra of various luminescent enamels developed are shown in Figure 3. The reflection spectra of the individual frits show very **different transmission behaviour for light** with a wavelength between 250 nm to 500 nm. The cause of this could be down to the differing chemical composition of the individual frits. Frit 03 shows the greatest permeability above 370 nm, whereas initially frit 04 has the best permeability at 250 nm, however, with increasing wavelength exhibits relatively strong absorption between 350 nm and 500 nm.

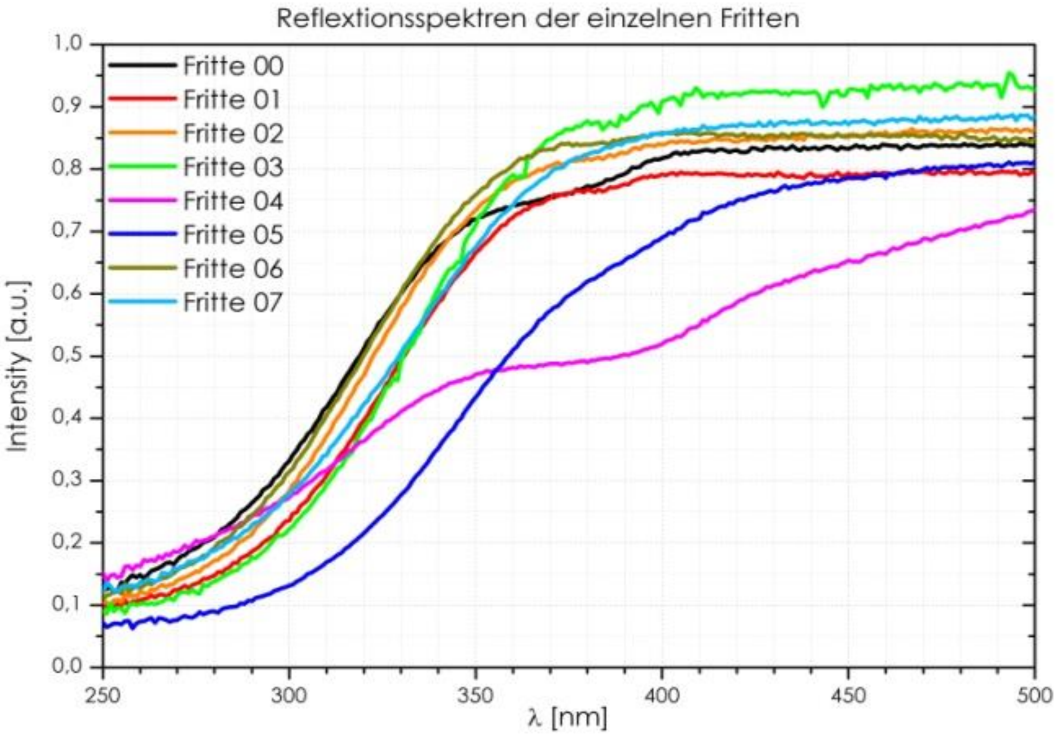

*Figure 3*

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The reflexes of the pure luminescent pigment and their whereabouts in the individual frits can be seen in Figure 4 . At this point it should be mentioned that the content of luminescent pigment in the frits is 10% and the intensity of the reflexes is accordingly lower than the intensity of the pure luminescent pigment. It is therefore **evident that the luminescent pigment is well preserved as crystal** compared to the amorphous phase of the glass in frit 00, frit 04 and frit 05 and was attacked the least by the melt. If we compare this with frit 01 or frit 06 for example it can be clearly seen that the pigment has been almost completely disintegrated by the melt during the firing process.

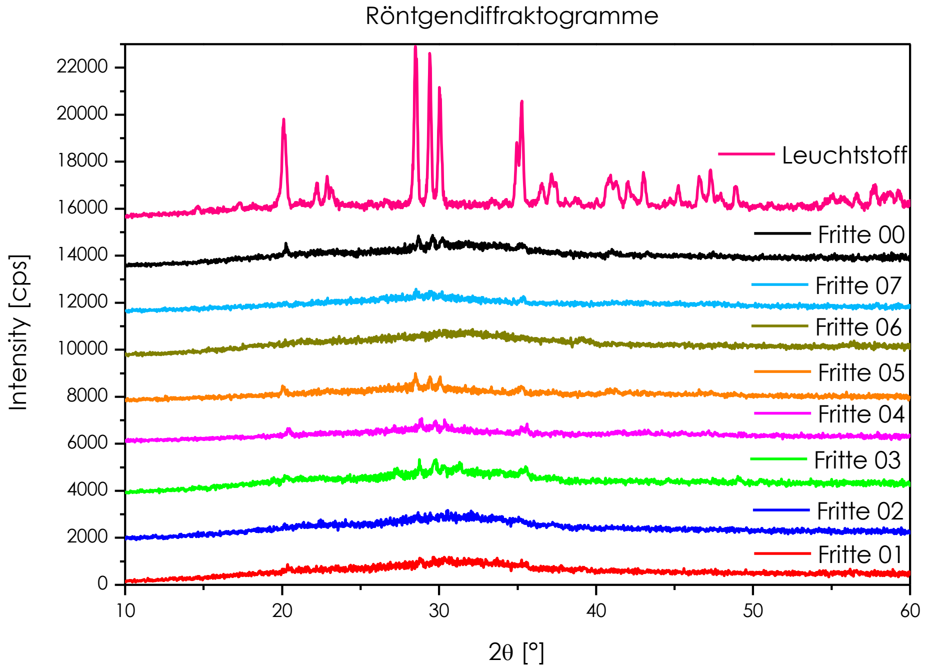

*Figure 4*

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The excitation spectrum and the emissions spectrum of the individual frits can be seen in Figures 5 and 6 respectively. As with the XRD measurements the **luminescent pigment concentration in all test samples is also 10%** here.

It is clearly evident in both spectra that the intensity of the individual test samples differs greatly. When looking at the excitation spectrum at 520 nm (Figure 5) it can be noticed that between 270 nm – 340 nm frit 04 shows the highest intensity. In the near UV range (λ > 340 nm) however, frit 05 is substantially higher in intensity. Thus the corresponding result is that, in the emissions spectrum at 370 nm (Figure 6), frit 05 shows the highest emissions values here.

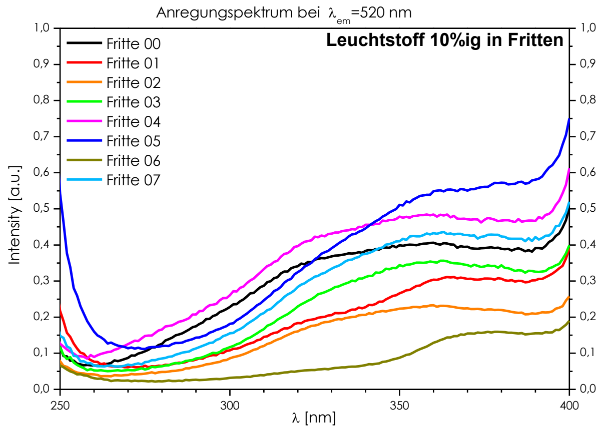

Figure 5

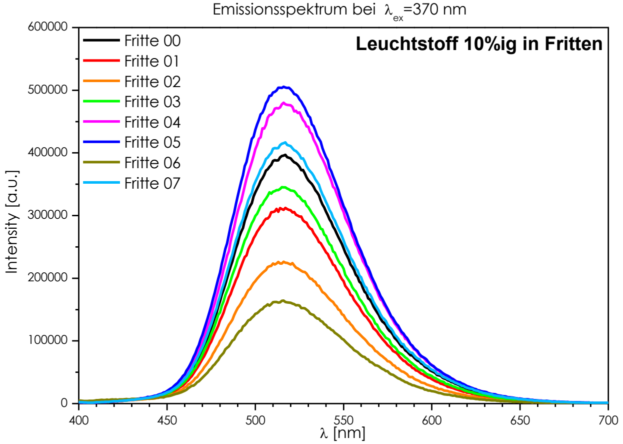

Figure 6

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A commercial emergency sign made of synthetic material which likewise contains luminescent pigments and satisfies the legal requirements of DIN 67510-1 served here as a guide.

Figure 7 shows the chronological sequence of luminescent intensity after irradiating the test samples with UV light (370 nm). Test samples with 3 different luminescent pigment concentrations were produced for this purpose (10%, 20%, and 30%). It can be clearly observed that, with increased concentration of the fluorescent material, the intensity of the light emitted during irradiation (t < 20s) and after irradiation (t > 20s) increases. Therefore the test **sample with 30% luminescent pigment has the highest intensity**.

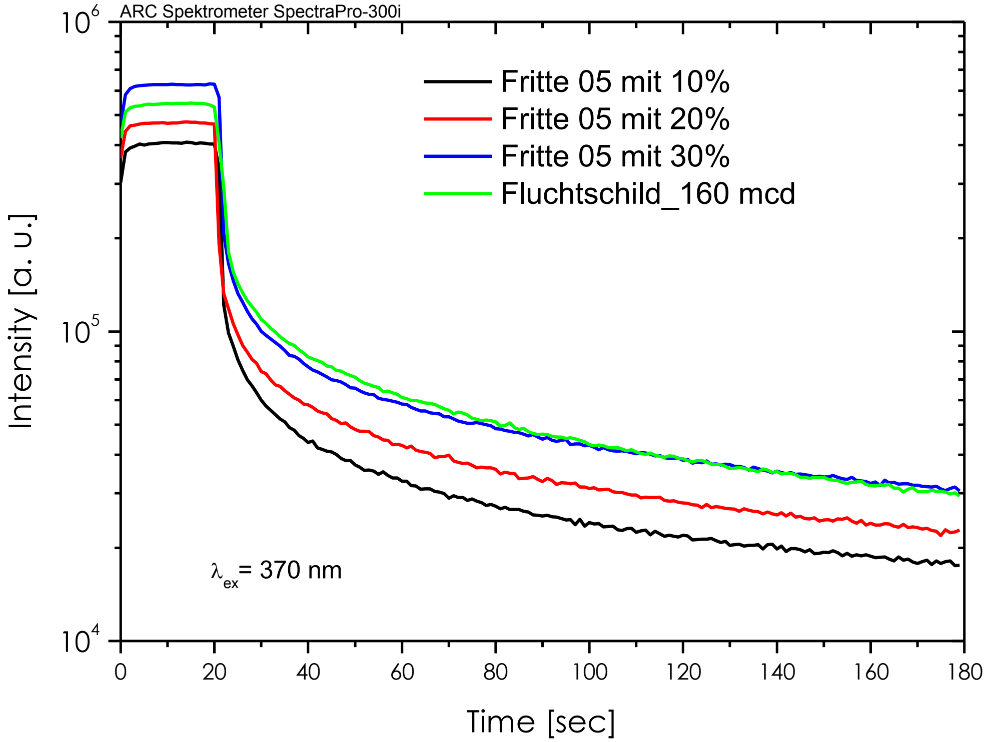

*Figure 7*

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For comparison a commercial emergency sign made of synthetic material was used (to DIN 67510-1).
The absolute intensity, achieved after approximately 6-7 minutes irradiating, is still better in the commercial product, however, the intensity even after some seconds of afterglow is not distinguishable from the enamel coat of test sample 2D(5). The normalized decay curves in Figure 9 show that the 2D(5) test **sample with a double coat has more potential than the commercial emergency sign**.

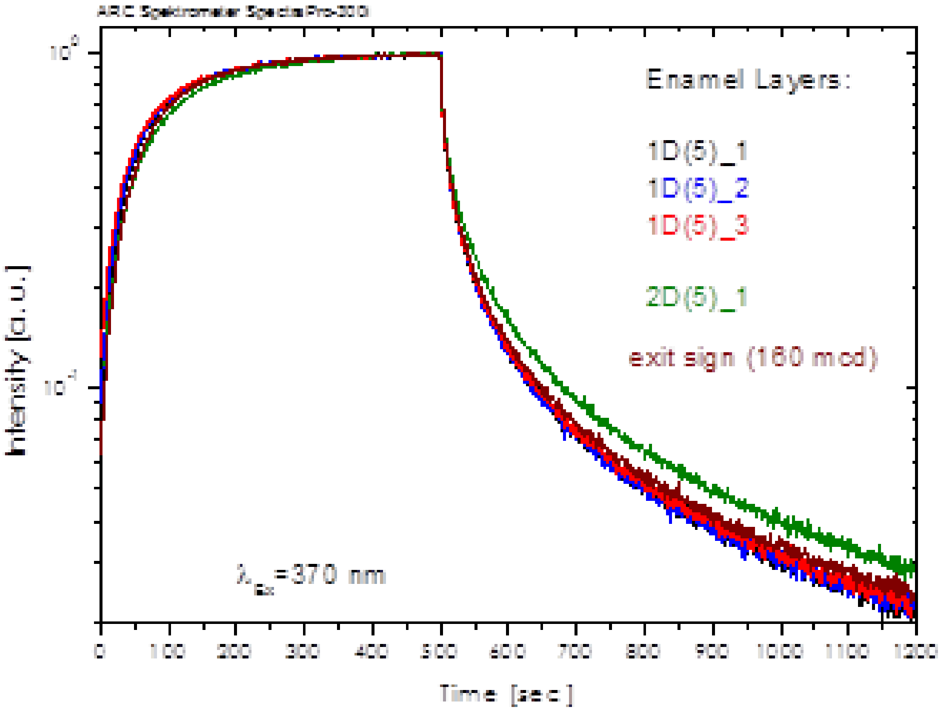

*Figure 9*

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Sings from left: Enamelled zinc sulphide, new developement, paint. Daylight, 1 minute dark, 30 minutes dark