The Development of New Types of Glass Frits with Special Optical Properties for the Incorporation of Luminescent Materials

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1. Introduction

An enamel has been developed which has been made visually functional by incorporating inorganic luminescent pigments. This enamel finish exceeds conventional emergency signs made of synthetic material both in intensity and duration of afterglow. The use of luminescent enamel therefore represents a viable alternative in the fields of signage and safety.

2. Basic Principles

2.1 Radiation

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). 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 phosphorescence or afterglow.

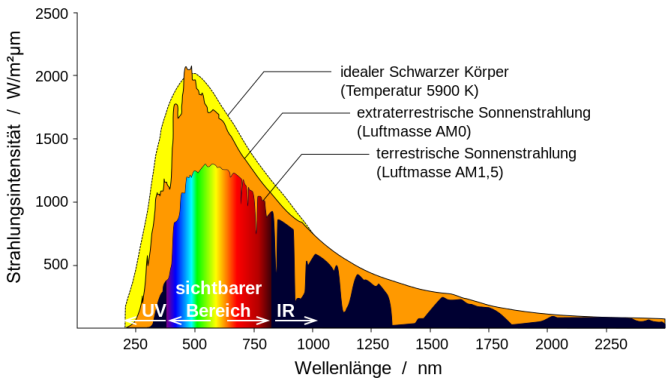

Figure 1

2.2 Luminescent Pigments

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.
For several years there has been a new group of luminescent pigments on the market. Alkaline earth aluminates e.g. strontium aluminate ($SrAl_2O_4$: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.

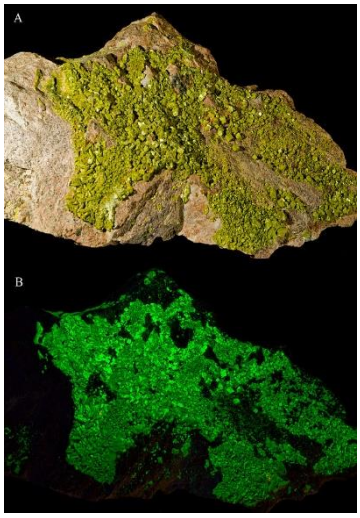

Figure 2

2.3 Enamel

Since the industrial availability of zinc sulphides they have also been used in enamel. Various frits in combination with this luminescent pigment have been empirically tested. Compared to signs made of synthetic material, however, the luminosity was too weak and the afterglow too short, even with the best results. Additionally the processing of the enamels was relatively complicated and there was a very strong reaction to contamination. In order to avoid enamelling defects such as black spots the work was carried out in designated rooms. Furthermore an additional glaze was necessary in order to prevent the decomposition of the zinc sulphide on the surface of the enamel outdoors. In turn the glaze further weakened the intensity and afterglow duration. Time and time again attempts have been made to manufacture and market enamelled signs with these luminescent pigments. These enamelled signs were not able to win through against painted signs and those made of synthetic material. The development of new luminescent enamels is presented below, whereby the frits developed for use with doped strontium aluminate as the luminescent pigment have been changed and optimized to the greatest possible extent.

3. Experiments

3.1 Selection of Luminescent Pigment and Enamel

The requirements of the luminescent enamel with regard to optical properties are very high. Above all a luminescent enamel must demonstrate the highest possible permeability for UV radiation as well as for visible light. 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.
During the enamelling process the fluorescent substance used must not be changed or attacked chemically and physically by the enamel. In the development of such an enamel both aspects play an important role. Different optical measurements were drawn on for these purposes. By cooperating with the University of Applied Sciences Münster it was possible to carry out the appropriate measurements of the frits. The transmission values of various test frits at 370 nm are listed in Table 1.
One can see how different the permeability is of the various frits for UV light. The frits used up to now as luminescent enamels indicate very poor values. Likewise test frit 01 was also used up to now as luminescent enamel, however, it shows a relatively high permeability. In contrast, test frit 07 (titanium white frit) has very poor optical prerequisites due to crystallization and is therefore unsuitable as a luminescent enamel. Based on these results the development was commenced.

Fritte	Brenntemperatur	Reflexion bei 370 nm
Testfritte 01	860 °C	75 %
Testfritte 02	700 °C	72 %
Testfritte 03	700 °C	68 %
Testfritte 04	700 °C	45 %
Testfritte 05	700 °C	33 %
Testfritte 06	600 °C	20 %
Testfritte 07	860 °C	15 %

Table 1

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. To facilitate comparison the transmission values of the individual luminescent enamel frits at 370 nm are listed in Table 2.

Fritte	Brenntemp.	Reflexion bei 370nm
Fritte 03	820 °C	85 %
Fritte 06	820 °C	83 %
Fritte 02	820 °C	80 %
Fritte 07	820 °C	79 %
Fritte 00	820 °C	76 %
Fritte 01	820 °C	75 %
Fritte 05	820 °C	57 %
Fritte 04	820 °C	49 %

Table 2

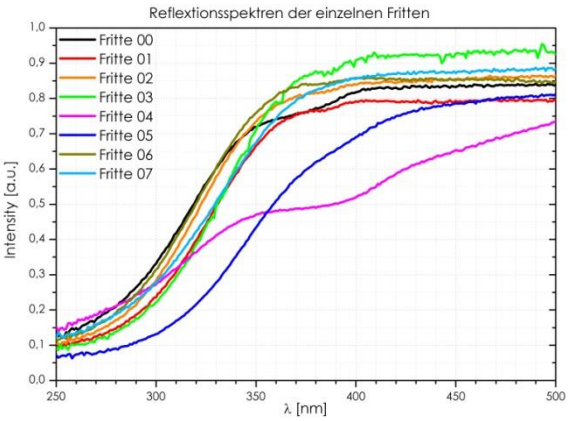

Figure 3

Because the luminescent pigment is attacked chemically in a different way according to the frit, based purely on the reflection measurement of the frit a reliable statement cannot be made about emission intensity and afterglow duration from the luminescent pigments used in the respective frit. For this purpose x-ray diffraction diagrams (XRD) were taken in order to assess the crystallinity of the luminescent pigments in the enamel. The crystalline phase of strontium aluminate ($SrAl_2O_4$:Eu,Dy) in the respective frit is depicted in Figure 4. The reflexes of the pure luminescent pigment and their whereabouts in the individual frits can be seen. 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. In the glass matrix there is consequently scarcely any luminescent pigment in crystalline form.

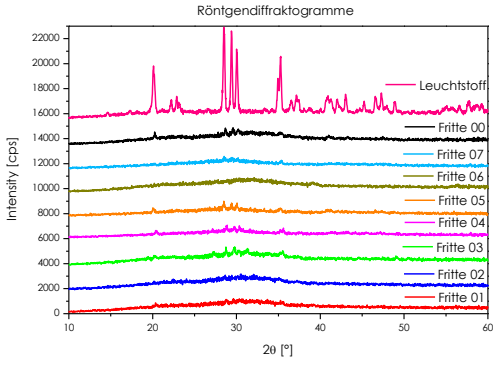

Figure 4

From the excitation and emissions spectra further quantitative and qualitative statements can be made about luminescent pigment bound in the enamel.
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 ($\lambda > 340$ 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.
These findings from the excitation and emissions spectra correlate with those of the x-ray diffractometry. The more crystalline the strontium aluminate ($SrAl_2O_4$:Eu,Dy) is in the glass matrix after the firing process, the more efficiently the irradiation of the luminescent pigment can occur.
Based on these findings further experiments were carried out with frit 05.

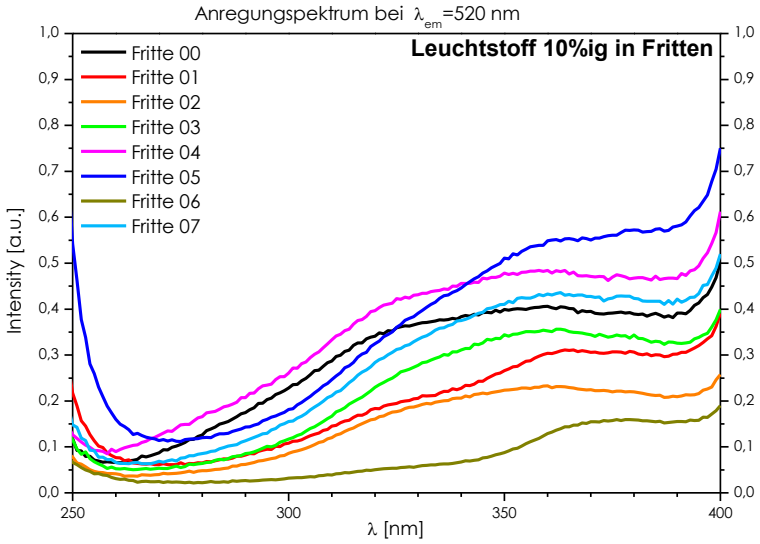

Figure 5

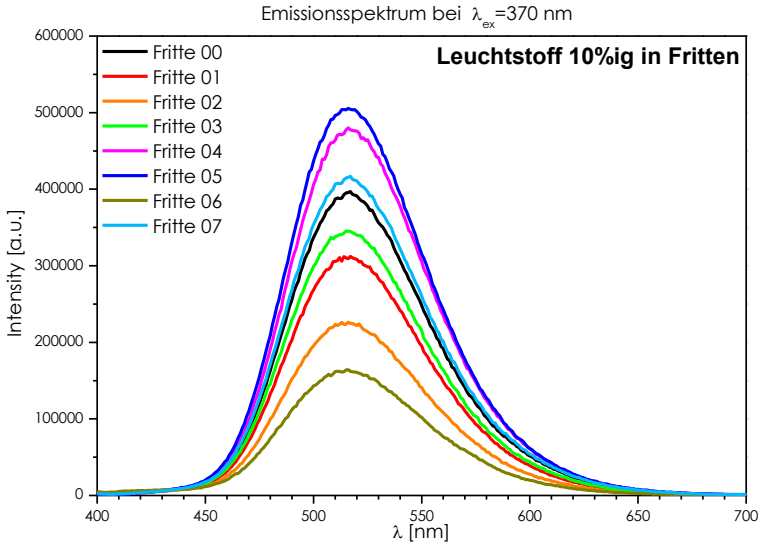

Figure 6

3.2 Concentration

In order to clarify selection of the correct concentration of luminescent pigment different amounts were used and tested in frit 05. The test samples produced containing differing concentrations of the luminescent pigment were measured for their duration of afterglow. 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.

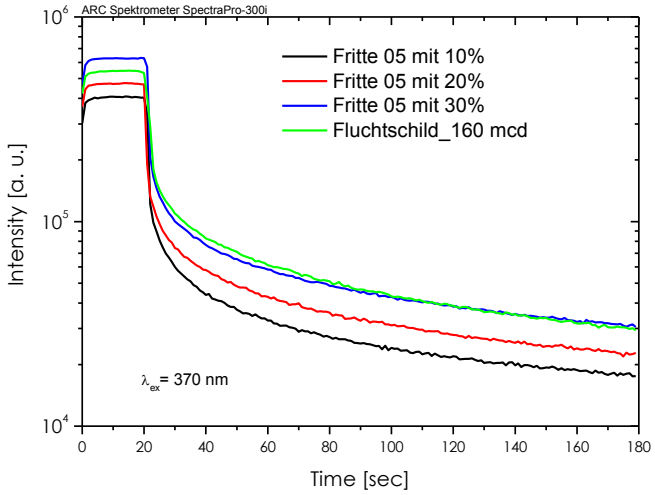

Figure 7

3.3 Practical Application

Based on the results shown above some enamelled emergency signs were produced as prototypes. Frit 05 and strontium aluminate doped with europium were used for this. The luminescent pigment concentration was 30% for production of the prototypes as in doing so the performance of commercial emergency signs was matched. Test sample 2D(5) was enamelled twice in order to achieve better homogeneity of the luminescent enamel. In contrast, test sample 1D(5) was manufactured with a single coating of the luminescent enamel.

Measurements of the duration of the afterglow were made in a time-resolved manner with the help of an integrating sphere. The irradiation was carried out with UV light (370 nm). The intensity value for the emission was taken at 520 nm. For comparison a commercial emergency sign made of synthetic material was used (to DIN 67510-1).

The results of the afterglow measurements are depicted in Figures 8 and 9. 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.

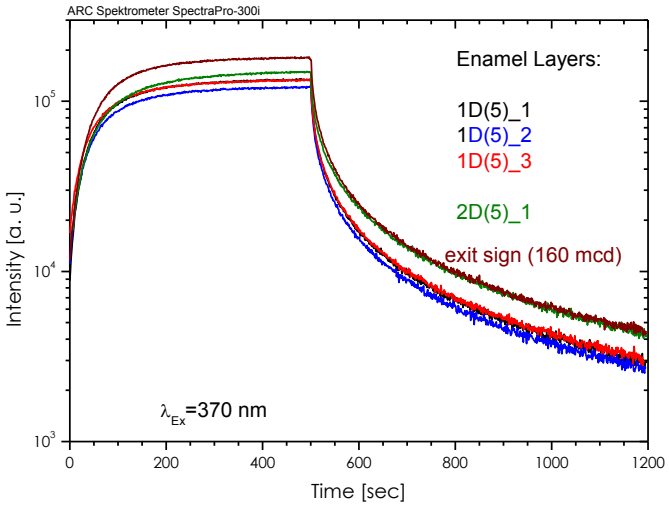

Figure 8

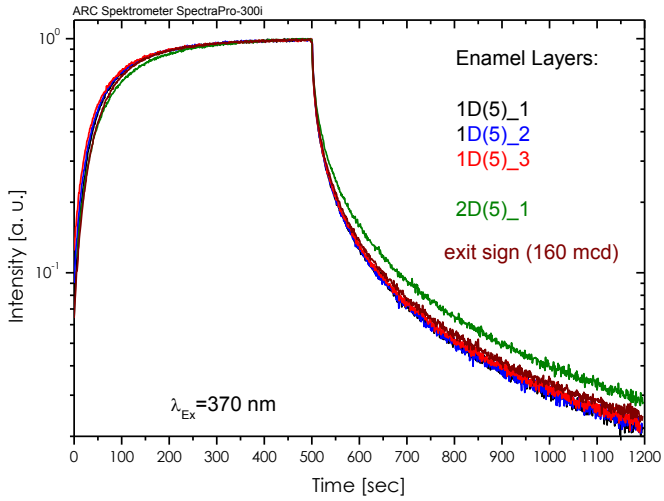

Figure 9

4. Summary

Many aspects had to be taken into consideration in the development of a luminescent enamel. Depending on the type of fluorescent material or luminescent pigment used a wide variety of measurements, described here, were necessary in order to suit the frit to the fluorescent material. A reliable statement cannot be made regarding the emission intensity of a luminescent pigment in the frit based purely on the reflection measurement. The reflection measurement alone is not enough to select the frit as the luminescent pigment is attacked chemically in a different way according to enamel composition. If we consider frit 05 then the transmission values were rather low compared to other frits which had been developed. Nevertheless, combined with strontium aluminate as the luminescent pigment this frit achieved the best results in the emission and afterglow measurements.
Prototype enamelled signs have been successfully manufactured with the developed frit 05 fulfilling the German Industry Standard DIN 67510-1.

Sources:

Figure 1: *http://de.wikipedia.org/wiki/Datei:Sonne_Strahlungsintensitaet.svg von Degreen at de.wikipedia. Later version(s) were uploaded by Quilbert at de.wikipedia. (Transferred from de.wikipedia;) [CC-BY-SA-2.0-de (http://creativecommons.org/licenses/by-sa/2.0/de/deed.en)], vom Wikimedia Commons (Abgerufen am 03.12.2014)*

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