

LOW TEMPERATURE LUMINESCENT ENAMELS FOR GLASS ART APPLICATIONS

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ABSTRACT

A liaison between art and science was explored. The discovery and use of new knowledge, with a close relationship between scientists and artists, was encouraged through the development of novel materials, such as luminescent glass enamels.

The use of materials with special optical properties is commonly explored in contemporary glass art and design. Over the centuries, many artists have used glass to produce unique objects, but the luminescence effect in glass is being explored only recently. Luminescent glasses are usually produced by using anemissive center in the batch composition; therefore, all the glass bulk is luminescent. The application of luminescent coatings in the final phase of glass production can be more advantageous, saving time, effort, and costs. These coatings can be applied at temperatures near the glass transition temperature, avoiding glass deformation.

Novel luminescent glass enamels that can be fired at low temperatures, ranging from 550 to 630°C, with an appropriate consistency for glass painting is here presented. Five enamels were obtained by using as emissive centers several lanthanide oxides that under UV light showed different luminescent colours. The combination of these enamels gave rise to a diversified colour palette. Several luminescent coloured enamels under daylight were also produced by doping the developed enamels with 3 d transition metals to enlarge the palette of products to paint on glass. The produced enamels were applied on different glass substrates to study their potential in future artworks.

The developed objects and art works illustrate the dichotomy between transparency and opacity, monochrome and polychrome and their application into fine arts and architectural glass.

Keywords: luminescent glass; low firing enamels; lanthanides; colour palette, glass art, art and science

INTRODUCTION

Luminescent materials can be assumed as "smart materials", which have changeable properties, meaning that they can reversibly modify their shape or colour in response to physical and/or chemical influences [1]. In addition to having applications in different technological fields, as photonics, lighting and smart windows, several authors also integrated these materials in architecture, design and art projects.

Many artists explored light using neon tubes, acrylics and textiles [2].Luminescent glasses can also have a fascinating effect for artists to explore, as the different luminescent colours can only be observed under UV-light [3]. The light effects obtained can improve the visual value of art works since the observed colours, are not the reflected part of the incident white light, as in the usual coloured glasses, but simply the colours emitted by the luminescent glass. Susan Lie bold is one of the glass artists who work with luminescent borosilicate glass and often integrates her flame worked pieces into installations using UV light. Teresa Almeida is another example of a glass artist who generally explores the luminescent effect and the combination of different luminescent colours [2-4]. Luminescence in glass can be obtained by doping the glass composition with lanthanide oxides [5-8]. Although the luminescent properties of the

lanthanide oxides have been studied for several years for different applications [9-12]they have only been used more recently in artworks [8,13]. Luminescent soda-lime silicate and borosilicate glasses for application in the art field have already been developed by using various lanthanide oxides, which gave rise to different luminescent colours under UV light:red-orange "(Eu2O3, Eu3+ and blue and Eu2+, respectively), green (Tb4O7), vellow (Dy2O3), orange (Sm2O3), blue (CeO2) and violet (Tm2O3) [14]. The exhibition "Within Light/ Inside Glass", which took place in 2015 in Venice and Lisbon, included several artworks by different artists who used this type of glasses [15]. Several d transition elements are commonly used to colour glass, namely copper, cobalt, iron and manganese [9]. Glasses doped with both d transition elements and lanthanides oxides may exhibit two different colours when observed under daylight or UV light, being this optical effect valuable for artistic installations, offering a wide colour palette. However, a luminescence quenching may occur due to the presence of 3d transition metals [16-18], which depends on its coefficient of absorption and concentration. Therefore, it is imperative to have careful control of the d transition elements concentrations used for the enamel production. The application of luminescent films in the final stage of glass production to colour the glass surface may have several advantages compared to the traditional production of luminescent glass, which is made by adding the desired emissive centers in the glass composition. These coatings can be applied at low temperatures after producing the glass objects, giving rise to a less time-consuming expensive and process. Contemporary glass artists are constantly exploiting unique optical properties and the development of innovative materials can have a high impact on their works. Therefore, in this study, low firing luminescent enamels were developed to obtain glass objects with different luminescent colours. Compositions of low firing enamels are well described in the literature [19-21], but to the best of our knowledge, there is no work reporting the synthesis of low temperature luminescent enamels, with a vitreous surface [22]. We synthesized a luminescent vitreous enamel using a composition based on 50% Al2O3, 25-30% SiO2, 30% SrO, 10 15% MgO, 2% CaO and 12% B2O3 (wt.%), having Eu2O3 and Dy2O3 as emissive centers [22]. However, this enamel composition is applied at high firing temperatures, around 850 °C, which will cause a deformation of the glass

pieces. In order to avoid shape distortion of the art works, the applied enamels should be fired at temperatures closer to the glass transition temperature, generally below 565 °C [23]. Low firing luminescent enamels using lanthanide oxides in their composition were developed in this study and a first set of paintings were made in small objects. To optimize the application of the developed enamel to artistic applications, such as in architectural glass applications and larger scale pieces, a residency was made at Derix glass studios. Derix Glass studios is a family business that runs since 1866 located in Taunusstein, Germany. With a long tradition in architectural art glass, The Derix studio works together with famous artists such as Johannes Schreiter, Patrick Reyntiens, Gerhard Richter, Alexander Beleschenko, Graham Jones, Narcissus Quagliata, Markus Lüpertz, Ed Carpenter and John K. Clark, among others. Derix Glass studios produces large scale commissions using several techniques - traditional glass painting (stained glass), acid etching, spraying (airbrush), screenprinting, sandblasting, fusing and gluing (laminating or lamination). Some of these techniques, such as airbrush, screen-printing and sandblasting were made in this residency.

EXPERIMENTAL PROCEDURE

Several low melting enamels with different compositions were prepared, being the first experiments made with europium oxide. Eu3+ displays a red-orange luminescence under UV light and has been chosen due to its unique optical properties such as an intense luminescence and high quantum efficiencies [24-26]. Based on the composition reported by Roret, Vieil and Chiti [20-22]a low firing enamel was synthesised, enamel A, with the following composition in wt.%: 59.2% Pb3O4, 16.3% SiO2, 16.5% B2O3, 2.5% Na2O and 5.5% R, where R correspond to different lanthanide oxides (Sm2O3, Eu2O3, Tb4O7, Dy2O3 or Tm2O3). Reagent grade SiO2 (p.a., Fluka), Pb3O4 (Barracha F.T.T. Lda.), Na2CO3 (p.a., Riedel de Haen) and B2O3 (Barracha F.T.T. Lda.) were used as starting materials. To this composition 5.5wt. %of different lanthanide oxides Sm2O3, Eu2O3, Tb4O7, Dy2O3 or Tm2O3(Rare Earth Limited) were added. The obtained luminescent enamels were applied to glass substrates using different media such as water, gum Arabic solution and decoflux (WB41) at temperatures ranging from 540 °C to 565°C. To obtain luminescent enamels with two different colours, when exposed to daylight or UV light, several 3d transition metal oxides

(MnO2, Fe2O3, Cr2O3, CoO, and CuO) were added in various concentrations to the above mentioned composition, enamel A, doped

already with 5.5 % of lanthanide oxides (Table 1).

Table1. 3d transition metals oxides concentrations (% wt.) added to enamel A doped with 5.5wt. % of a lanthanide oxide

Enamel A + 5.5wt.%	3d transition metals oxides concentrations (wt. %)				(0)
lanthanide oxide	MnO ₂	Fe ₂ O ₃	Cr ₂ O ₃	CoO	CuO
Sm ₂ O ₃	1.00 0.25				
Tb ₄ O ₇	0.50 0.25	0.075 0.05			
Dy ₂ O ₃	0.50 0.25	0.075 0.05			
Eu ₂ O ₃	0.375 1.00	0.10 0.075 0.05	0.025 0.015 0.0075	0.05 0.01	0.25 0.15 0.05

Batches of 10 g were melted in Pt/Rh crucibles using an electric furnace at 1250°C for 30 minutes in air. The melt was poured into water and the frits obtained were milled in different mills (Retsch PM 200 and PM 100). Subsequently, the frits were sieved using a Vibratory Sieve Shaker AS 200 from Retsch and batches of frits with different grain sizes were obtained (32-45, 25-32, < 25 microns). Luminescence spectra were obtained using a SPEX Fluorolog-3 Model FL3-22 spectr of luorometer and glass transition temperature (Tg) was determined using a differential scanning calorimeter Pegasus® DSC 404 F (DSC) in the temperature range of 20 to 840 °C with a heating rating of 5 K/min. For this measurement, the sample was previously crushed in an agate mortar and placed ina platinum crucible. For compatibility tests, a polariscope, Sharple SenarconStrhin, was used to check for tensions inside the glass pieces." A space was missing.



FIGURE1. Teresa Almeida. (2008). Enamel A doped with 5.5 wt. % Eu_2O_3 under (a) daylight and (b) UV light (ca. 370 nm) after being fired at 560 °C. (c) Five examples of synthesised luminescent enamels under UV light (ca. 370 nm) doped with different lanthanides after being fired at 560 °C. (from left to right Eu^{3+} , Tb^{3+} , Sm^{3+} , Dy^{3+} and Tm^{3+}).© Teresa Almeida.

RESULTS AND DISCUSSION

Luminescent enamels

Different compositions were prepared to obtain low melting enamel with luminescent properties. The first prepared enamels were similar to those produced by Merigaud and Shinkanova [27, 28], who reported low firing enamels with zinc. They were doped with Eu2O3, and a low firing enamel was obtained (550 °C), however, they were not luminescent. Other low firing compositions based on silicon, lead and boron doped with Eu2O3 were then studied and a low firing enamel was synthesised, enamel A. A combination of these different glass network formers and network modifiers doped with 5.5% of Eu2O3, gave rise to a luminescent glass enamel. A colourless

layer under daylight with luminescence under UV light (ca. 370 nm) obtained at temperatures below 565 °C, was produced, see Figures 1 (a) and (b). The glass transition temperature (Tg) ca 424°C, indicates that the produced enamel melts at low temperatures so that it can be applied to any common glass surface without glass deformation. Enamels with different lanthanide oxides were prepared by adding to the batch composition 5.5% of europium oxide (Eu2O3), terbium oxide (Tb4O7), samarium oxide (Sm2O3), dysprosium oxide (Dy2O3) or thulium oxide (Tm2O3). The luminescent colours obtained were respectively, orange-red, green, orange, yellow, and violet, as shown in Figure1 (c), which are in agreement with the colours found in the literature for each lanthanide in the trivalent state [5, 29].The emission spectraof the enamels doped with each lanthanide oxide also correspond to the trivalent state (Figure2)[5, 11, 29-32]."



FIGURE2. Andreia Ruivo. (2018). Emission spectra of the luminescent enamels doped with 5 wt. % of the following lanthanide oxides: Eu_2O_3 , Tb_4O_7 , Sm_2O_3 , Dy_2O_3 and Tm_2O_3 ($\lambda exc=393$, 370, 400, 385, and 355 nm, respectively). © Andreia Ruivo"

These enamels were applied in glass substrates using different painting techniques, such as brush painting, screen-printing (direct and using decals) and spraying. The enamels produced have also been tested on several types of glass used inutilitari an and decorative applications,

namely, soda-lime silicate glass(including float glass) and borosilicate glass. Concerning the float glass it is crucial to perform the enamels application on the non-tin side, as our tests have shown that if we paint on the tin side the colour, under daylight, changes substantially into grey. On the opposite if the enamel is applied on the other side of the glass, colourlesse namels are achieved. Subsequently, the developed enamels were applied to various objects made by using different techniques, namely casting, lampworking, slumping, pâte de verre and glassblowing. It was possible to obtain multiple paintings by applying the produced luminescent enamels on glass substrates, using any of the techniques described above and all the experiments gave rise to a vitreous surface. Regarding screen-printing it was necessary to make four applications of the enamels to obtain a good luminescence. It is important to note that the visual effect depends on the numbers of layers applied. Figure3 shows the increase of the luminescence intensity with increasing number of layers.



FIGURE3. AndreiaRuivo. (2018). Optical spectra of luminescent enamels applied by screen-printing, with europium oxide (A) and with terbium oxide (B) excited at 393 nm and 370 nm, respectively, with several layers (1, 2, 3 and 4).© AndreiaRuivo

Several firing schedules were tested to avoid devitrification of the glass surface. The best result was obtained by heating the enamel with a temperature rate of 150 °C / h until reaching 560 °C and remaining at this temperature for 15-30 min. If a faster rate, e.g. 300° C / h, was used, the enamel would not attach completely to the glass surface. To achieve new luminescent colours, several mixtures of two different enamels were made and fired, extending the luminescent colour palette to magenta, green, pink, yellow, and other colours, as can be seen in Table 2. The heterogeneities observed when

these mixtures were applied to the glass substrates occurs because the paintings were performed with a brush, and in some cases, the dripping technique was used. Compatibility tests have been done to analyse if all the developed glass frits with different colours could be mixed. These compatibility tests included firing a mixture of two or more luminescent frits into a single glass at 560 °C, or the application of more than one layer of different frits, followed by firing it at the same temperature. After firing, all the glass pieces were observed in the polariscope and no stress was detected.

Table2. Enamel A doped with different lanthanide $oxides(Eu_2O_3, Sm_2O_3, Tb_4O_7, or Dy_2O_3)$ mixed in different weight proportions, such as 25%+75%, 50%+50%, 75%+25%.

Two luminescent enamels (Enamel A + lanthanide oxide) mixed in different proportions	Image $(\lambda_{exc} ca. 370 \text{ nm})$
$Eu_2O_3 (25\%) + Tb_4O_7 (75\%)$	1.51
$Eu_2O_3 (50\%) + Tb_4O_7 (50\%)$	
$Eu_2O_3 (75\%) + Tb_4O_7 (25\%)$	St.

$Tb_4O_7 (25\%) + Sm_2O_3 (75\%)$	- A
$Tb_4O_7 (50\%) + Sm_2O_3 (50\%)$	
$Tb_4O_7 (75\%) + Sm_2O_3 (25\%)$	
$Tb_4O_7(25\%) + Dy_2O_3(75\%)$	から
$Tb_4O_7 (25\%) + Dy_2O_3 (75\%)$	A Star
$Tb_4O_7 (25\%) + Dy_2O_3 (75\%)$	100
$Dy_2O_3 (25\%) + Sm_2O_3 (75\%)$	
$Dy_2O_3(50\%) + Sm_2O_3(50\%)$	2131
$Dy_2O_3(25\%) + Sm_2O_3(75\%)$	60

Luminescent enamels doped with 3d transition elements

The colour in glass is commonly associated with the addition of 3 d transition metals. Ions have characteristic electronic states, so different ions give rise to different colours[34] The most common elements used in the glass industry are Fe, Cu, Cr, V, Mn, Ti, Co and Ni [35].

In previous research developed by the authors, glasses doped with several metal oxides of 3d transition elements and lanthanide oxides were prepared to obtain luminescent glasses that, instead of being colour less, can exhibit different colours under visible light [3].

Considering these results, luminescent enamels doped with the same oxides were also prepared to obtain the same optical properties. However, the presence of some 3 d metal oxides can attenuate or suppress luminescence. This phenomenon in photo physical terminology is named quenching [36]. Therefore, the concentration ratios of lanthanide oxides/3d transition element oxides were tested to determine the practical value to obtain the best coloured enamels. Table 2 shows the various concentrations of the 3d transition elements added to enamel A composition containing different lanthanides.

"In Figure4 it can be observed the emission spectra of the glass samples painted with the enamel doped with Eu2O3 and with different concentrations of Fe2O3. A decrease in the luminescence intensity with Fe2O3 content is shown. However, by controlling the Fe2O3 concentration, it was possible to achieve luminescent glass enamels with two different colours, one under daylight another under ultraviolet light. The described optical effect was obtained for the samples doped with Eu2O3 and with 1% MnO2, 0.15% CuO, 0.1% Fe2O3, 0.015 % Cr2O3, or 0.01% CoO. Higher concentrations of these elements significantly suppress the luminescence



FIGURE4. AndreiaRuivo (2019). Emission spectra of enamel A doped with 5.5 % Eu₂O₃ and Fe₂O₃ (black line - 0.075%; grey line- 0.1% (wt. %), excited at 393 nm.© AndreiaRuivo



FIGURE5. Teresa Almeida. (2009). Enamel A doped with metal oxides (a, b) with 0.1% of Fe_2O_3 and (c, d) with 1% MnO₂, under daylight and UV-light ($\lambda_{exc}ca$. 370 nm). © Teresa Almeida.

In Figure5 two examples of enamel A doped with europium oxide and with metal oxides (a) and (b) with 0.1% of Fe2O3 and (c) and (d) with 1% MnO2, are observed, showing coloured samples not only under daylight and but also under UV light. Observing the concentrations needed to obtain a suitable coloured luminescent enamel, comparatively, they generally agree with the values of the absorption coefficient of each colourant ion taken from the literature for a soda-lime-silicate glass [10]. For example, Co2+ has a high absorption coefficient value, between 32 and 48, therefore the quantity of CoO needed to obtain an intense colour is very low. Using Cu2+ and Mn3+, higher concentrations of these elements are required to obtain coloured samples, since they have absorption coefficients of 3.0 and 4.0, respectively. Concerning Cr3+, which has an absorption coefficient of 5.9, the quantity of Cr2O3 used to colour glass and, at the same time to obtain a luminescent enamel was extremely low since the luminescence was strongly quenched by chromium addition. This luminescence intensity decrease with the increase of Cr2O3 concentration is probably due to the formation of Cr6+ in the glass matrix [37]

Luminescent enamels application using different techniques

'To understand a work of art we must have some idea of the limitations, technical and conventional, within the artist works' [38] It was essential attest the enamels' application to evidence their feasibility onto the glass surface, exploring the art and science interface.

Different painting techniques, such as painting with a brush, screen-printing (direct and using decals), and spraying were applied onto the glass surface. The enamels were also tested using different glass techniques, such as casting, lampworking, slumping, pâte-de-verre, and blowing. It was alsovitalto understand if the use of the luminescent enamels can be applied not only for painting on float glass as a canvas base in a two-dimension application but also on three-dimensional glass objects. The primary application, such as painting with a brush in different glass compositions were conducted in the research unit VICARTE (Glass and Ceramic for the Arts) installations. The screen-printing was performed at the Faculty of Fine Arts, Porto University (FBAUP) in the glass workshop.

The first application of the enamel was on float glass and it was done by painting as mentioned previously. After the first tests demonstrated promising results, the enamels were also applied on asoda-lime silicate glass object obtained using the glassblowing technique. Thisthreedimensional test piece was subjected to two firings, which means that there are parts in the sample with two layers of luminescent enamels. The results obtained show that there was no deformation of the glass shape, and the luminescent intensity varies with the applied layers. Subsequently, the experiments were conducted on objects obtained using other glass techniques, such as slumping, casting and pâtede-verre and the results obtained were identical to the previous ones. Screen-printing was the second application to be performed. The screenprinting was done using 90 and 120 size frames at the installations of the FBAUP, using waterbased medium and also an oil medium. Since the results did not show any substantial difference, the water-based medium was elected for future applications. This medium was chosen

as it is easier to clean and is an eco-friendly material. Tests using decals were also designed and applied in slumping pieces. The testes started on float glass following the described process and subsequent specificities. To each sample were performed four applications, with enamel coatings from 1 to 4. The number of layers of the luminescent application is crucial for the visual effect. Under UV light the luminescence is more intense if the enamel is applied more than once, however under day light more layers translate into less transparency To attest if the developed enamels could be applied on a bigger scale, to Architectural glass and Public glass, different test pieces were made at Derix Glass studios using several types of glasses such as OptiWhite float glass, antique glass, and Artista ®glass. The primary applications were made with brush painting. Regarding the antique glass it was used mouthblown Lamberts Glass®, clear and coloured, and several types of flashed glasses, transparent, opal and opaque, clear and with different colours (blue, red, green, and yellow). Flashed glass is categorised as a glass that has a coating of clear glass with one, or more layers of coloured glass. These layers are thin and are normally produced on mouth-blown sheet glass. This glass can be acid-etched to present several graduations. In the glass used at Derix Glass studios, four gradations were obtained, where the luminescent enamel was painted. The tests made with these types of glass confirmed that the enamels luminescence maintains their intensity in the different colour gradients. At Derix Glass studios screen-printing is one of the techniques used for the enamel's application on glass surfaces with a larger scale. Considering the good results obtained on screen-printing at FBAUP, it was also decided to make some test pieces. Figure 6 illustrates the test pieces made with the enamels doped with terbium oxide, after applying one layer (6 a) and two layers (6 b) to maintain their transparency. In the obtained samples, we can observe that the enamels are almost invisible under day light. The results obtained are decisive for proving the subtle application of these luminescent enamels the screen-printing technique with in architectural glass.



FIGURE6. Teresa Almeida. (2013). Test pieces made with terbium oxide. The test piece on the right is illuminated with UV light and the piece on the left with day light. The pieces had one layer (a) and two layers (b). © Teresa Almeida.

Regarding the spraying technique (airbrush), the first applications were made with the europium doped enamels using a water-based medium and oil-based medium (for oil-based medium it was used turpentine as thinner) with the application of multiple layers. This research has shown that the best results have been achieved with the oil medium and turpentine. The enamels dried faster, and it was possible to apply more layers of wet paint over wet paint. In a water-based mixed paint, we observed that the medium and paint separated during spraying, and that the application was not even and smooth enough. The following tests were made with terbium, dysprosium, and samarium doped enamels with an oil-based medium, using a SATA mini jet, with a 1.1 nozzle. Figure 7 shows the result obtained by using 25 ml of europium enamel.



FIGURE7. Teresa Almeida. (2013). Test piece made with europium oxide enamel. The same test piece on the right is illuminated with UV light and on the left with day light. © Teresa Almeida.

After the initial tests, more experiments were made by using sandblasting with a "resist", in this case a film print. Resist is 'a substance that resists or prevents a particular action. During the process of acid etching or sandblasting, parts of the surface are protected with a resist" [39]. The samples were made by the following procedure: (1) spraying europium and terbium doped enamels on the glass surface;(2) firing the samples at the temperature range of 555-610 °C; (3)applying photo resist film on glass; and (4) finally sandblasting (sand or corundum). The results obtained were identical to the previous ones since the luminescent enamels hold the "resist" and remained luminescent.

All the obtained results demonstrate that the developed luminescent enamels are suitable to be applied in three dimensional shapes and also on different types of glass.

Application of luminescent enamels in art

As previously mentioned, this study on luminescent enamels was made focused on their application in artworks. The different colours emanated from the luminescent glass objects, under UV-light, modify their perception compared to the colourless/coloured objects observed under daylight, changing the observer's mind, with regard the surface, colour, and shape of the object. This optical change raises the inquisitiveness of the observer, who can visualize the object in its two distinct visual impacts. The developed enamels were suitable to be used on float glass and other types of sodalime silicate glasses, most commonly for utilitarian or decorative applications, and borosilicate glass. The glass surfaces showed good enamel vitrification and no craquelé was observed. This indicates that the produced luminescent enamels are suitable for painting on float glass as canvas, in two-dimension applications, and for three-dimensional glass objects made using various techniques such as glassblowing, casting, lampworking, and pâte de verre.

The use of UV light is mandatory to observe the object's luminescence, however, in these cases, is not a concern when exhibiting an artwork, as the UV-light can be an integral part of the artistic installation. It does not conflict with the aesthetical purpose of the glass artwork and should be seen alternatively in two different ways depending on the light used, UV or daylight, allowing the artist to play with colours. An example of the same enamels applied in a glass substrate under daylight and UV light can be found in Figure 8.



FIGURE8. Glass panels painted with luminescent enamels under day light (left side) and UV light (right side), ca. 370 nm. (detail of the work little organism that glow in the darkness)[©] Teresa Almeida.

Art Work development 1: Little organism that glow in the darkness

The work presented, such as little organism that glow in the darkness (Figure 9), offers a multiplicity of different concepts that come together in several projects, and where luminescent enamels are the primary medium in the work of art. The use of UV light is not a concern since it is an integral part of the installations. It does not clash with the aesthetical purpose of the glass pieces and should be seen on paired with the similarly keen interest in the polychromatic surfaces as the monochromatic. The inspiration comes from the corals, colourful and organic forms. Through ultraviolet lighting, it was able to recreate this in pieces with the white light the colour fades in the depth of the ocean, where the colourlessness takes form. The solar beams which propagate through the surface of the waters act as an

analogy of the ultraviolet light. Here the solar light reveals the intense colours of the corals. while in the pieces where the luminescent enamels were used, it is in the darkness with the help of dark light that colours are visualised, that they get colour. Its intensity is related to the intensity of light that we introduce on the pieces of art. The colour changes with the luminescent enamels and shift the attention of the observer to a profound vision of a completed new art piece. The absence of colour in the art piece presents a dissimilar formal composition than a colourful piece, even though it is only one work of art. Both colour and the light fulfil this duality, they convey expression and allow the observer to obtain new perceptions about the work of art.

The pieces were conceived for a gallery space and displayed at the exhibition Vidro [arte] Luminescência at São Paulo, Brazil in 2011.



FIGURE9. Painted Float glass, using the produced

Art Work development 2: far-fetched view

In the piece far-fetched view (figure 10) flashed glass was used and several techniques, such as, etching, spraying and painting were incorporated. This small piece aims to be a bridge between art and architecture, and it was created in the residency of Derix studios, so this case study presents an example for architectural space. The principal idea was to introduce the luminescent enamels and create a stained glass window that "never sleeps". Glass always had a strong connection with light. The stained glass is the best example of this analogy. 'The immaterial glow of stained glass gave colour a new mystical dimension in the Early Middle Ages' [40]. Stained glass lived through the day light, creating a symbiosis of light and colour that illuminate the dark cathedrals.At twilight, they rest in the darkness of the night, only to wake up on the first rays of the dawn. With the development of new technologies, we have artificial light and artificial windows emerge in the architecture landscape, but in the works produced the idea was to recreate a false window and an approach to day light.

With the introduction of the lanthanide oxides in the glass painting and the utilization of an ultraviolet light during the night the stained glass awakes from the darkness and can acquire a new composition. The colours painted on the glass are colourless during the day and colourful during the nigh. The architectural place is no longer astounding as it was in medieval times; it is now a space of light and contemplation [2].

The colourful windows will interact with the architecture surroundings, creating new shadows and a new luminosity. The glass presented in the piece far-fetched view is almost monochromatic, having only the blue colour. At night with the UV light the blue glass obtains a new composition.

Josef Albers said "In visual perception a color is almost never seen as it really is - as it physically is. This fact makes color the most relative medium in art" [41].



FIGURE10. Teresa Almeida. (2013). Far-fetched view. Painted with luminescent enamels. The piece on the right is illuminated with UV light and the piece on the left with day light. © Teresa Almeida.

FINAL REMARKS

The relationship between artists and scientists has been explored for a long time. It is not only science that influences art, but art also influences science, it is a mutual relationship, and collaboration is crucial for the evaluation of new materials and new artistic concepts. Strosberg, consider that collectively, art and science develop pioneering concepts, often using the same subjects to the same end. Originating new ideas and forms is what makes an artist or scientist [42]. This research demonstrates this relationship promptly.

This work aspired to demonstrate a practicebased research where it was scrutinized the development of new materials, low melting luminescent enamels, for application in art. These products can be applied to glass art pieces glassblowing. made bv kiln casting, lampworking and using different techniques such as painting on a flat surface as a canvas or in any three-dimensional object with a brush, screen printing or spraying. A low temperature, around 560 °C, was used to melt the developed enamels, demonstrating that they can be applied to any type of commercial glass without deformation.

In addition to the common five luminescent colours, obtained by using five different lanthanides, an innovative and increased colour palette was obtained by mixing two enamels doped with different lanthanides. Moreover, luminescent glass enamels that change colour if observed under daylight or ultraviolet light were obtained, by adding 3d metal oxides in the luminescent enamel compositions, with an adequate concentration, to avoid the luminescence quenching. As the compatibility tests have shown that enamels with different colours can be mixed, artists can make their own colours.

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REFERENCES

[1] Ritter, A. Smart materials in architecture, interior architecture and design,Birkhäuser; 2007

- [2] Almeida, T. O vidro como material plástico: transparência luz, cor e expressão, [doctoraldissertation], Aveiro University; 2011
- [3] Almeida, T., Ruivo A., Matos A.P., Oliveira, R. & Antunes A., 'LuminescentGlasses in Art', J. Cult. Herit.2008; 9: 138-142. Elsevier Science.
- [4] Almeida, T. 'Art and Science: New Approaches in the Making, Process, and Development of New Materials', The International Journal of New Media, Technology and the Arts. The International Journal of the Arts in Society. 2013;1 (1):1-14.
- [5] Gorller-Walrand, C. Binnemans, K. 'Spectral intensities of f-f transitions', Gschneidner Jr KA, Eyring L, Handbook on the physics and Chemistry of Rare Earths Vol. 25 (Elsevier Science B.V.). 1998: 101-264
- [6] Ruivo, A.; Muralha, V. S. F.; Águas, H.; Pires de Matos, A.; Laia, C. A. T.; 'Time-resolved luminescence studies of Eu3+ in soda-lime silicate glasses' J. Quant. Spectrosc. Radiat. Transfer.2014; 134: 29-38
- [7] Johnson, J. A; Benmore, C. J.; Holland D.; J. Beuneu, Du, B.; Mekki, A.
- [8] 'Influence of rare-earth ions on SiO_2 -Na₂O-RE₂O₃ glass structure', J. Phys: Condens. Matter.2011; 23, 065404
- [9] Anjaiah, G.; Nayab Rasool, S. K.; Kistaiah, P. 'Spectroscopic and visible luminescence properties of rare earth ions in lead fluoroborate glasses'J. Lumin. 2015; 159:110–118
- [10] Binnemans, K. 'Lanthanide-Based Luminescent Hybrid Materials', Chem. Rev.2009;109: 4283– 4374.
- [11] [Bamford, C.R. Colour Generation and Control in Glass (Glass Science and Technology), Elsevier. 1977
- [12] Bünzli, J.C.G.; Chopin, G. R., Lanthanide probes in life, chemical and earth sciences, Elsevier. 1989; 432
- [13] Eliseeva, J.C.; J Bünzli,C. G. 'Lanthanide luminescence for functional materials and biosciences', Chem. Soc. Rev.2010;39: 189-227
- [14] Laia, C.A.T; Ruivo, R. 'Photoluminescent Glasses and Their Applications', Pedras B. (ed.) Fluorescence in Industry. Springer Series on Fluorescence (Basel, Springer Nature Switzerland AG). 2019; Available from: doi:10.1007/4243_2019_1
- [15] Ruivo, A.; Almeida, T.; Quintas, F.; Wiley, R.; Troeira, M; Paulino, N.; Laia, C. A. T.; Queiroz, C. A.; Pires de Matos, A. 'Colours of Luminescent Glasses for Artworks'. 12th International AIC Colour Congress, Proceedings, ed. by L. Mac Donald, S. Westland and S. Wuerger.2013: 885-888.
- [16] Pires de Matos; Ruivo, A; Godilho, I Within Light/ Inside Glass. 2015

- [17] Kessler M. A. 'Determination of copper at ng ml-1-levels based on quenching of the europium chelate luminescence', Anal. Chim. Acta. 1998; 364: 125.
- [18] Nery, S. M.; Pontuschka, W. M.; Isotani, S.; Rouse, C. G. 'Luminescence quenching by iron in barium aluminoborate glasses', Phys. Rev. B. 1994; 49: 3760-3765.
- [19] Rao, G.V.; Veeraiah, N.; Reddy, P. Y. 'Luminescence quenching by manganese ions in MO–CaF₂–B₂O₃ glasses' Opt. Mater. 2003;22: 295-302.
- [20] Roret, M. Nouveau Manuel Complet de la peinture sur verre sur porcelaine& sur et émail des émaillagesindustriels et de la fabrication dexémaux et des couleurs vitrifiables, Paris: nouvelle edition, fac-simile. [1866] 1977
- [21] Vieil, P. L'art de la Peinture sur verre et de la vitrerie, Paris: Minkoff Reprint, Genéve, facsimile.[1774] 1973
- [22] Chiti, J.F.Manual de esmaltes cerâmicos, Buenos Aires: CondorhuasiEdition. 1987
- [23] Rossi, S.; Quaranta, A.; Tavella, L.; Deflorian, F.; Compagnoni, A. M. 'Innovative luminescent vitreous enameled coatings' In: A Tiwari, J Rawlins, L. H. Hihara, Intelligent coatings for Corrosion Control, Butterworth-Heinemann, Elsevier.2015
- [24] Stone. G. Firing Schedules for Glass, (First Edition), Melbourne. 2000
- [25] Silva, G.H.; Anjos, V.; Bell, M.J.V. Carmo, A.P.; Pinheiro, A.S.; Dantas, N.O. 'Eu³⁺ emission in phosphate glasses with high UV transparency' J. Lumin. 2014; 154: 294–297.
- [26] Kindrat, I.I.; Padlyak, B.V. 'Luminescence properties and quantum efficiency of the Eu-doped borate glasses' Opt. Mater.2018; 77: 93-103
- [27] Yamane, M.; Asahara, Y. Glasses for Photonics, (UK, Cambridge University Press.2000
- [28] Merigaud, B.;Claus, M. Zinc- containing, lead and cadmium-free glass frits, method of their production and their use. United States patent 5342810.1994
- [29] Shinkanova, E.V.; Bychko, G. V. 'Chemical resistance of low-melting enamels for decorating glass products' Glass and ceramics. 2005; 62: 293-294
- [30] Carnall, W.T. 'The absorption and fluorescence spectra of rare earth ions in solution'. K.A. Gschneidner, Jr and L. Eyring (Eds), Handbook on the physics and Chemistry of Rare Earths, Vol. 3. North-Holland Physics Publishing.1979
- [31] Babu, P;Seo, H. J.; Jang, K. H.;Balakrishnaiah, R.;Jayasankar, C. K.; Joshi, A. S. 'Optical spectroscopy and energy transfer in Tm³⁺ doped metaphosphate laser glasses'J. Phys.: Condens. Matter.2005; 17: 4859–4876

- [32] Elisa, M.; Sava, B. A.; Vasiliu, I. C.; Monteiro, R. C. C.; Veiga, J. P.; Ghervase, L.; Feraru, I.; Iordanescu, R'Optical and structural scharacterisationof samarium and europiumdoped phosphate glasses' J. Non-Cryst. Solids. 2013; 369: 55–60
- [33] Padlyak, B. Drzewiecki, A. 'Spectroscopy of the CaB₄O₇ and LiCaBO₃ glasses, doped with terbium and dysprosium', J. Non-Cryst. Solids. 2013; 367: 58–69
- [34] Hemmilä, I.; Laitala V. 'Progress in Lanthanides as Luminescent Probes', Journal of Fluorescence.2005;Vol 15 (4): 529-542
- [35] Valeur, B. Molecular Fluorescence: Principles and Applications. Weinheim, Wiley VCH. 2001
- [36] Weyl, W.A. Coloured Glasses, Sheffield, Society of Glass Technology. 1951
- [37] Ronda, C. Luminescence, From Theory to Applications. Weinheim, Wiley VCH. 2008

- [38] Paul, A. Chemistry of Glasses, 2nd edition, New York: Chapman. 1990
- [39] Dutton, Denis.The Art instinct, beauty, pleasure, and human evolution. First edition, Bloomsbury Press. 2009: 186
- [40] Price, R. W (ed) Glass. A pocket Dictionary of Terms Commonly Used to Describe Glass and Glassmaking, Revised Edition, The Corning Museum of Glass. 2006:72
- [41] Gage, John.Color and culture. Practice and meaningfromAntiquity toAbstraction. University of California Press, Thames & Hudson Ltd, 1999: 64
- [42] Albers, Josef. Interaction of color. London: Yale University. 1976
- [43] Strosberg. E. Art & Science, New York: Abbeville Press Publishers. 2001

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