

Characterization of innovative enamel with luminescent properties

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Introduction

Porcelain enamel is used both for decorative purposes and for corrosion protection of some metals. Due to its glassy nature, this kind of layer shows excellent resistance to high temperatures and excellent corrosion protection properties [1-2]. In recent years, the research is trying to combine different functional properties, such as antibacterial properties and optical properties with corrosion and high temperature. The luminescence is the optical properties of materials, which consists in the emission of visible light radiation under irradiation with UV radiation. Luminescent materials, such as polymers, organic coatings, and inks are already on the market. However, these products are based on organic pigments that do not often present resistance to natural weathering, UV radiation and chemicals. In addition, the organic layers are not suitable for application at high temperatures. The development of luminescent enamel layer could be an interesting possibility to have a deposit which presents, in the same time, functional and aesthetic properties typical of this traditional type of coating together with the luminescence characteristics.

This paper deals with luminescent enamels with interesting possible commercial applications (components of outdoor furniture and interior design, architecture, applications in the safety field). These deposits could be very interesting in applications in which luminescent paints are not suitable. In enamel the luminescent effect is obtained by the addition of inorganic pigments containing rare earths, such as europium and dysprosium. The luminescence in the pigments is guaranteed by the electronic transitions of europium ions; while dysprosium ions guarantee a long afterglow [3]. The characteristics of layers with different amounts of europium and dysprosium were analyzed. Several testing methods are used to highlight the optical properties of these layers. Weathering accelerated tests and mechanical damage one were used to evaluate the durability of these particular properties.

In this paper the most important aspects of the research will be illustrated. A more extensive and complete discussion is present on the book "Intelligent Coatings for Corrosion Control" in press [4].

Methods/Discussion

Luminescent enamels were applied on a low carbon steel substrate by wet spray technology and subsequent curing at 850°C. The enamel system is made by three layers. The first and the second deposits are classical enamel, deposited to guarantee good adhesion with the metallic substrate and corrosion protection properties. The first two layers present a typical commercial composition based on SiO₂, B₂O₃, Na₂O and other oxides; TiO₂ was added in the intermediate layer as an opacifier agent. The total thickness of both layers together is 220 µm.

The top layer shows the luminescent properties. A standard enamel frit was used with the addition of 50wt% of luminescent pigment (Al₂O₃, SiO₂, SrO, MgO, Eu₂O₃ and Dy₂O₃), containing europium (Eu) and dysprosium (Dy). Also 5 wt% of clay, 0,5wt% of sodium aluminate and 50 wt% of water were added, in order to produce applicable slurry. 3 luminescent enamels were produced modifying the ratios of Eu/Dy, as reported in table 1. In addition, the dimension of luminescent pigments used for the first two samples are smaller than those used for sample 3. A reference sample was produced using the same composition of frit without the addition of luminescent pigments.

The microstructure was studied using a Philips XL30 ESEM. Luminescent properties were characterized by Jasco FP6300 spectrofluorimeter.

Table 1: produced samples

Samples name	REF	1	2	3
Ratio Eu/Dy	--	1,2	4	0,6
Visible color	White	White/light yellow	Light blue	Yellow
Luminescent color	--	Sky blue	Sky blue	Blue green

To evaluate the durability of the luminescent effect and the optical color, the samples were exposed to 500 hours of UV-A radiation (ASTM G154). The luminescence and color before and after exposure were measured. The color was measured using a spectrometer Konica Minolta CM-2600d, following international CIELab method. To highlight the maintenance of the luminescent properties after cycles of loading and unloading (stimulants day and night) a cycled accelerated test (1 h of UV-A radiation and 1h without) was carried out for total 24 cycles. The luminescence of surface as a function of time was monitored in continuous using a spectrometer Ocean Optics USB4000-UV-VIS Miniature Fiber Optic. To evaluate the effect of mechanical damage on luminescent and protective properties abrasion tests using Taber Abraser with H22 abrasion wheels and 1 kg imposed weight, following ASTM D4060 standard, were made. Electrochemical impedance measurements were carried out to follow the decrease of protection properties during the increase of mechanical damage.

Results

Figure 1 shows the cross section (brittle fractures) of the samples. Considering that the first two layers are made by traditional enamels composition and the aim of this work, the attention will be focused only to the luminescent layer.

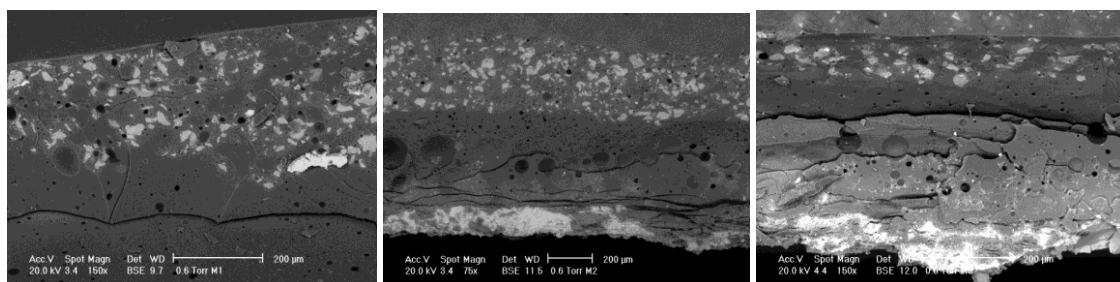


Figure 1: Cross section of the samples: from the left sample 1; 2 and 3.

The finish luminescent layers show smaller and not frequent pores. The adhesion between the luminescent layer and intermediate one is very good and no cracks are present at the interface. The different microstructures and the distribution of rare earth particles were highlight in the samples.

Observing the luminescent deposit, the particles of strontium oxide, light particles, are concentrated more in some areas and show a variable size. Considering sample 3 the distribution of particle is not homogeneous within the thickness and, in some cases, the pigment particles emerge on the surface, probably due to the higher dimension of the pigment compared to those used for the other two samples. The EDXS analysis highlights a homogeneous dispersion of europium and dysprosium in the luminescent deposits.

Considering the luminescent behavior it is possible observe the presence in the emission spectra (figure 2) of two broadbands peaked at 467 nm (blue) and 491 nm (green). With the increase of the dysprosium presence ($2 < 1 < 3$) the contribution of the peak in the green increases. From the excitation spectra (Figure 3) it is possible to observe the presence of three peaks. Samples 1 and 2 show spectra with the same shape; sample 3 presents a slightly different spectrum. The reference sample without luminescent pigment does not show luminescent effects. These spectra will be considered as reference starting point to evaluate the trend of the luminescent behavior after weathering and degradation accelerated tests.

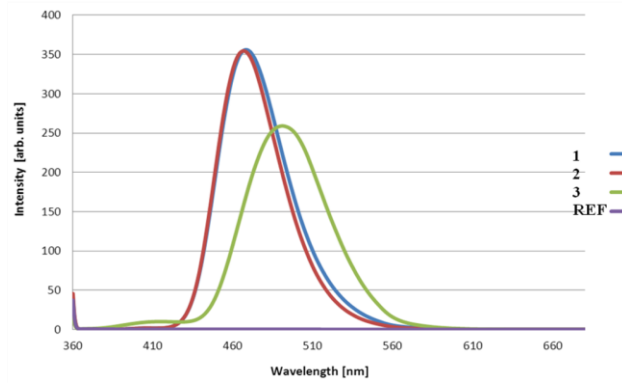


Figure 2: Emission spectra of the luminescent enameled layers and reference one, excited by a radiation with 350 nm wavelength.

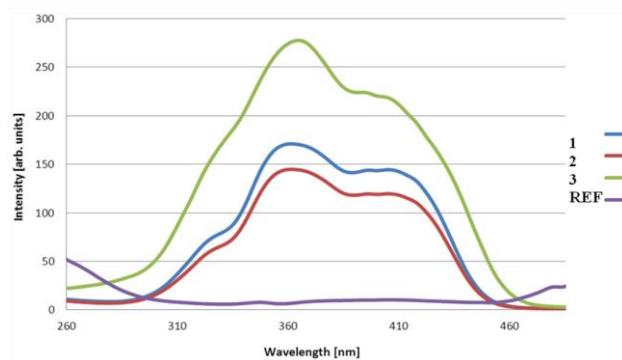


Figure 3: Excitation spectra of the luminescent enameled layers and reference one.

Now the luminescent effect behavior in function of the accelerated weathering test will be considered.

After 500 hours of UV-A exposure all samples show a total color change comprised between 2 and 2,6 points, hardly appreciable by the human eye. On the contrary, the luminescent effect does not present any modification. For example, in figure 4 is reported the intensity of mean peak of the excitation spectrum, normalized to the intensity of the initial peak.

Also the UV-A cyclic test did not produced damage or deterioration on the luminescent pigments highlighted by the constant of the intensity of the emission feature. In all cases no change in the form and position of the peaks in the emission and excitation spectra is observed. The intensity remains unchanged too.

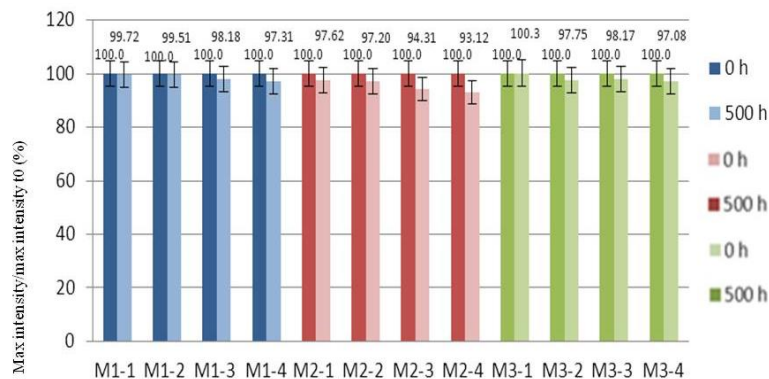


Figure 4: intensity of mean peak of the excitation spectrum after 500 hours of UV exposure normalized to the intensity of the initial peak.

Considering the test to evaluate the resistance to acid matter, after 24 hours of immersion in citric acid solution, samples 1 and 2 highlight a very good behavior without changes in surface gloss, color and roughness. On the contrary, sample 3 degrades in the acid solution showing localized attacks mainly close to the surface emerged particle with consequent roughness

increase and gloss decrease. The higher dimension of the luminescent pigment and their presence on the surface is likely to promote the localization of the acid attack, as reported in figure 5.

The presence of the pigment on the surface of sample 3 has a shielding effect for the glassy matrix in the immersion in alkaline solution. In fact in this case the behavior of the 3 samples is the opposite compared to the previous solution. The sample 3 is slightly attacked while the surfaces of the samples 1 and 2 are totally damaged (figure 5).

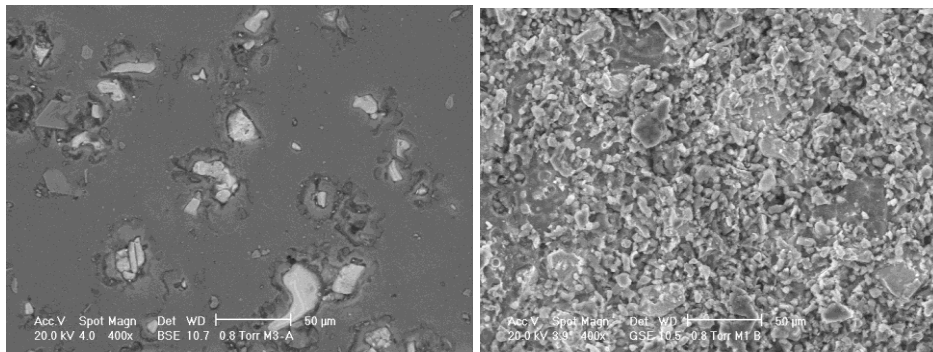


Figure 5: surface of sample 3 after 24 hours of immersion in citric acid solution (on the left) and surface of sample 1 after 24 hours of immersion in alkaline solution (on the right).

The immersion of the samples for 24 hours in citric acid solution does not cause any change in the excitation and emission spectra in sample 3 too. Probably the localized damage with possible removal of some pigments is not enough to modify the luminescent effect. Considering the alkaline attack, only for sample 2 and, to a lower extent, for sample 1 a change in the intensity of the peaks of emission and emission is observed. Probably, the higher roughness, produced during the aggression alkaline, hinders the absorption and emission process.

Finally the abrasion behavior is illustrated. 1000 cycles of Taber abrasion test produce a great modification of the samples surface with the removal of part of the luminescent enamel layer and with a formation of a widespread defectiveness. In all samples a remarkable increase of roughness, color and gloss changes are observed. The corrosion protection of the steel substrate is maintained because of only the more external layer results damaged and no cracks till to the substrate are observed. As one might expect, this high surface damage produces a decrease in the luminescent properties.

Conclusions

This research shows the possibility to obtain a vitreous enamel coatings with luminescent properties. The luminescent effect was obtained by rare earth compounds addition, such as europium and dysprosium.

These deposits show very interesting properties, which permits to think to very interesting applications.

The modification of the frit, which is necessary to obtain the optical effect, does not change the very good resistance properties of a traditional enamel (chemical resistance, adhesion and corrosion protection, aesthetical aspect). It was highlighted that the dimension of luminescent pigments and their position in the enamel layers affects the resistance behaviour of the deposits. Future research will be aimed to optimize the dimension and quantity of luminescent pigments to obtain the best performance of these smart coatings.

References

1. S. Rossi, E. Scrinzi, Chem. Eng. Process. 68 (2013), 74-80.
2. A.I. Andrews, S. Pagliuca, W.D. Faust, Porcelain (Vitreous) Enamels and Industrial Enamelling Processes. The International Enamellers Institute; Mantova, 2011.
3. Y. Lin, Z. Tang, Z. Zhang, J. Zhang, Q. Chen, Mat Sci & Eng B86, (2001) 79–82.
4. S. Rossi et al. chap. 7 “Innovative luminescent vitreous enameled coatings” in “Intelligent Coatings for Corrosion Control” eds. A. Tiwari, L. Hihara and J. Rawlins, Pub. Elsevier 2014 ISBN: 978-0-12-411467-8.