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Characterization of innovative enamel with luminescent properties

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Enamelling is one of the oldest decoration technique

Kurium sceptre
San Marco in Venice (1000-1200 AD.)

With industrial revolution
a very good coating: corrosion protection, resistance to heat, to abrasion, hygiene.
No aesthetic reasons

Technical properties of vitreous enamel

Excellent corrosion protection properties

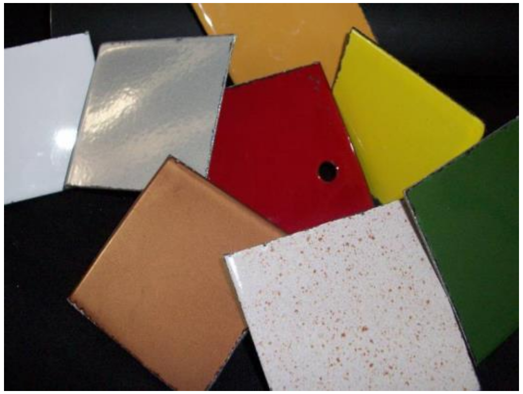
one or more layers of vitreous material →

- chemical inertia of the vitreous material
- high thickness of the coating

weathering and chemical resistance

impermeability to liquids

High temperature and fire resistance


In recent years:

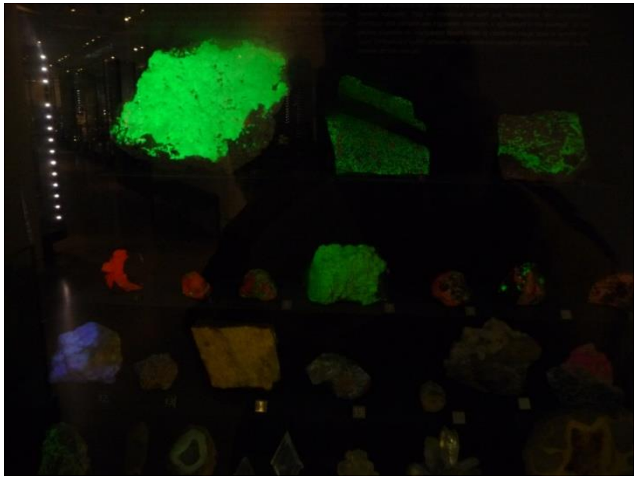
- improved quality of the enamel coatings
- reduction of the surface aesthetic defects
- possibility of various sensory effects: texture effects, very gloss coatings
- high colour palette
- combine different functional properties, such as antibacterial properties and optical properties with corrosion and high temperature



Luminescent materials

Emission of light when excited by cathode rays, UV radiation or visible light.
A matrix doped with activators, which are transition metal or rare earth ions that act as emitting centers.

When irradiated the activators absorb the energy reaching an electronic excited state (unstable condition). The system goes back to the ground state with **radiation emission.**



Luminescent materials, such as polymers, organic coatings, and inks are already on the market.

Organic pigments: no resistance to natural weathering, UV radiation, and chemicals;
Not suitable for HT application.

Tendency: **combine in a material more properties of different nature: smart coatings!!**

luminescent enamels

In enamel: luminescent effect by addition of pigments containing rare earths (europium Eu and dysprosium Dy).

Luminescence effect: electronic transitions of europium ions;
Long afterglow: dysprosium ions as hole traps capturing the gaps formed by the excitement of the Eu ions.

luminescent enamel layer: interesting possibility to have a deposit with functional and aesthetic properties of the traditional enamels with the new characteristics.

→

possible commercial applications: components of outdoor furniture and interior design, architecture, applications in the safety field.

Applications in fields in which luminescent paints are not suitable

Aim of work

obtain luminescent enamels ad study the influence of the presence of Eu and Dy ions

The luminescent properties are maintained after thermal curing and during exposure to aggressive environments?

?

The addition of luminescent pigments could reduce or modify the excellent properties of traditional porcelain enamel?

Effect of different amounts of europium and dysprosium.
Highlight the optical properties of these layers.
Weathering accelerated tests and mechanical damage one to evaluate the durability of luminescent properties

A more extensive and complete discussion

Chapter 7

Innovative Luminescent Vitreous Enameled Coatings

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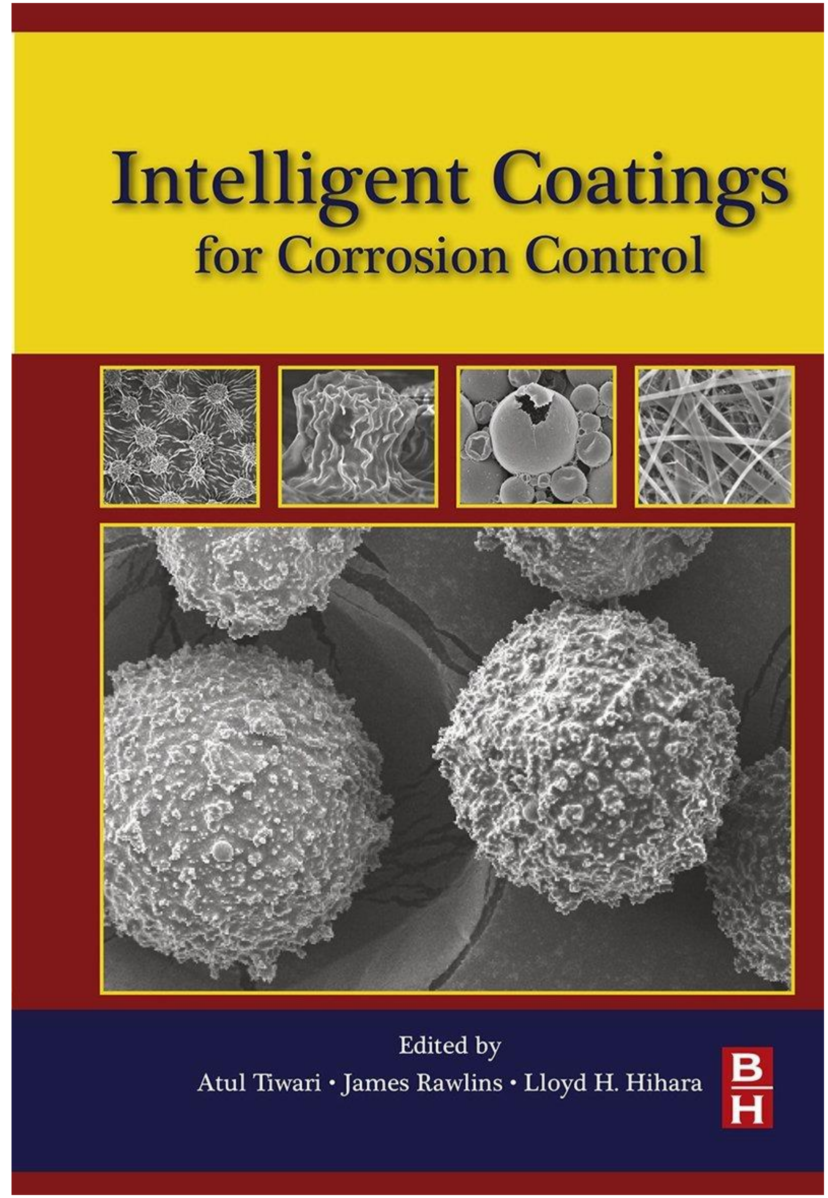

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Materials

<u>Substrate</u>: low-carbon steel panels

<u>Enamel system</u>: 3 layers: ground-layer for adhesion; the second for corrosion protection; top layer for luminescent properties.

<u>Application</u>: wet spraying. Drying and firing treatments (850°C).

First two layers composition: typically based on SiO_2, B_2O_3, Na_2O. TiO_2 was added in the intermediate layer as an opacifier agent. 220 µm total thickness of both layers.

Top layer: adding of 50% wt. of **luminescent pigments**, made of a vitreous matrix, 50% Al_2O_3, 25-30% SiO_2, 30 SrO, 10-15 MgO, 2% CaO,1-2% B_2O_3 wt, addition of Eu_2O_3 and Dy_2O_3.

5% clay, 0.5% sodium aluminate and 50% water added to produce applicable slurry

different Eu/Dy ratio, dimension of pigments (smaller for 1 and 2 samples)

	Ref	1	2	3
ratio Eu/Dy	--	1.2	4	0.6
Visible color	white	white/light yellow	Light blue	yellow
Luminescent emission color	---	sky blue	sky blue	blue green
Thickness of luminescent layer [µm]		170	240	195

Experimental details

Microstructure analysis using a Philips XL30 ESEM.
Luminescent properties characterized by Jasco FP6300 spectrofluorimeter.
Color measured by spectrometer Konica Minolta CM-2600d, (international CIELab method).

Durability of the luminescent effect and the optical color
exposition to 500h of UV-A radiation (ASTM G154).
Evaluation of change of luminescence and color.

Maintenance of the luminescent properties after cycles of loading and unloading (stimulants day and night): cycled accelerated test (1h of UV-A radiation and 1h without) for total 24 cycles.
Continuous monitoring of luminescence of surface as a function of time by spectrometer Ocean Optics USB4000-UV-VIS Miniature Fiber Optic.

Mechanical damage on luminescent and protective properties by Taber abrasion tests, following ASTM D4060 standard,
Electrochemical impedance measurements to follow the decrease of protection properties during mechanical damage

Chemical resistance: immersion in 10%wt acid citric (pH 2 RT, 24h) and alkaline solution (52.64 g/l tetra potassium pyrophosphate, pH 10 for 6 h at 96 °C)

Damage evaluation

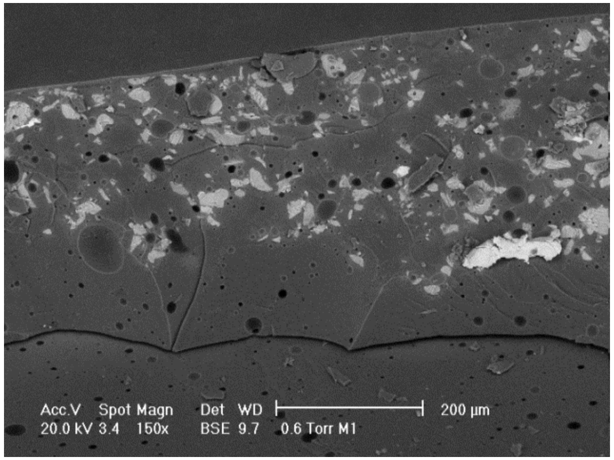
•Luminescent layers: smaller and not frequent pores. Very good adhesion between the luminescent layer and intermediate one; no cracks at the interface.

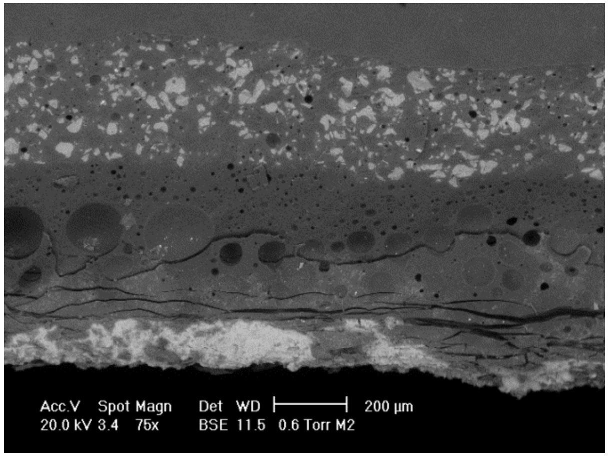
•Different microstructures and the distribution of rare earth particles.

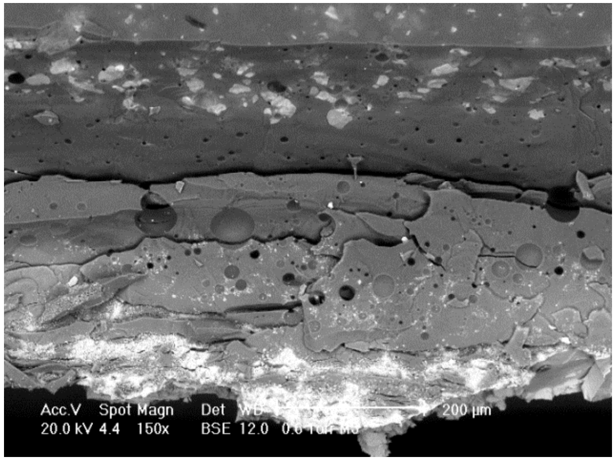
•Particles of strontium oxide, light particles, more concentrated in some areas with variable size.

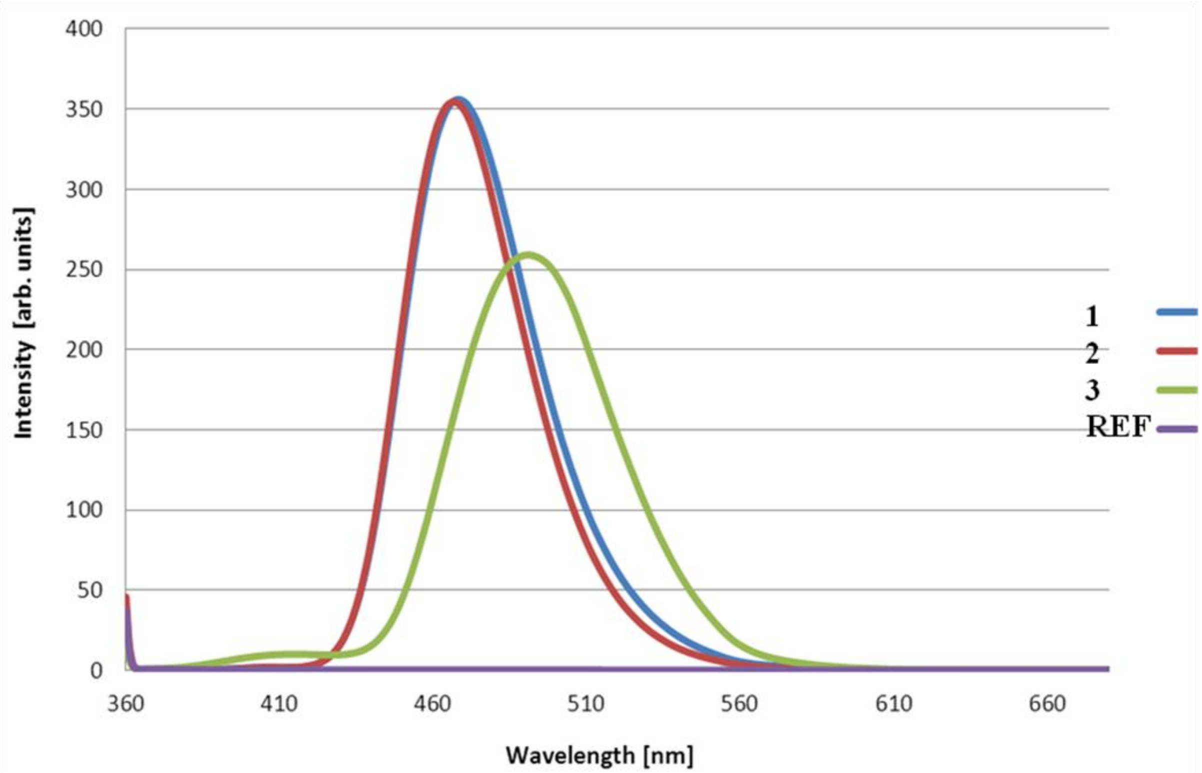
•sample 3: not homogeneously distribution of particles; in some cases the pigment particles emerged on the surface, probably due to the higher dimension of the pigment.

•The EDXS analysis: homogeneous dispersion of europium and dysprosium.





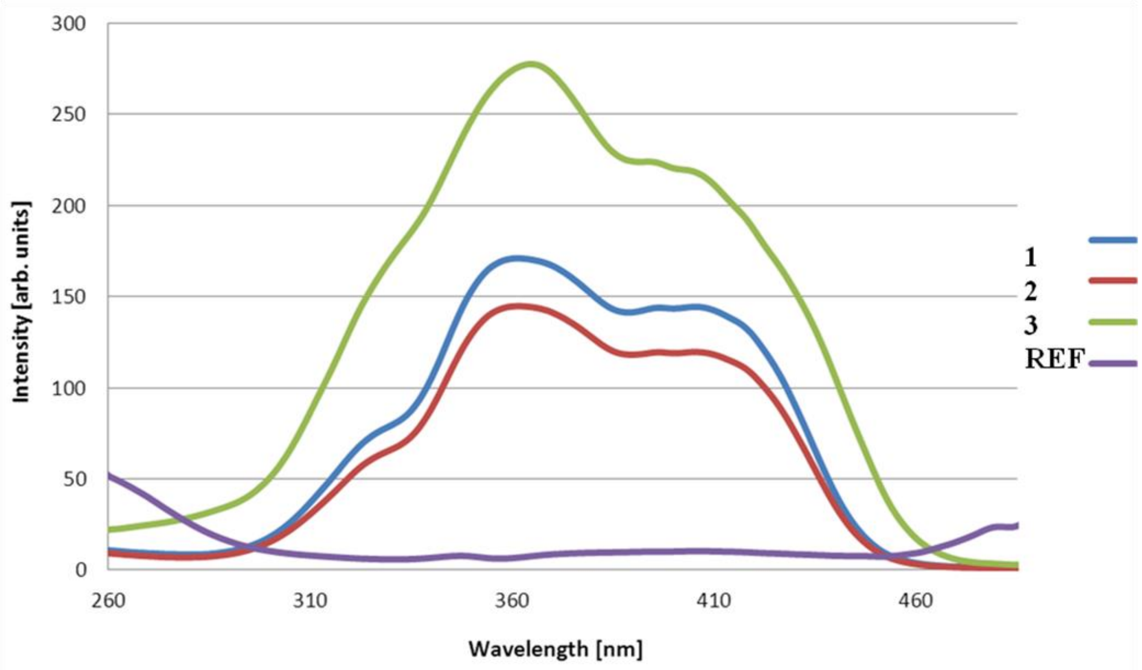




Emission spectra of the luminescent enameled layers and reference one excited by a radiation with 350 nm wavelength

• presence in the emission spectra of two broadbands, peaked at 467 nm (blue) and 491 nm (green).

•**increasing of the dysprosium presence** (2 < 1 <3): the contribution of the peak in the green increases.



Excitation spectra of the luminescent enameled layers and reference one

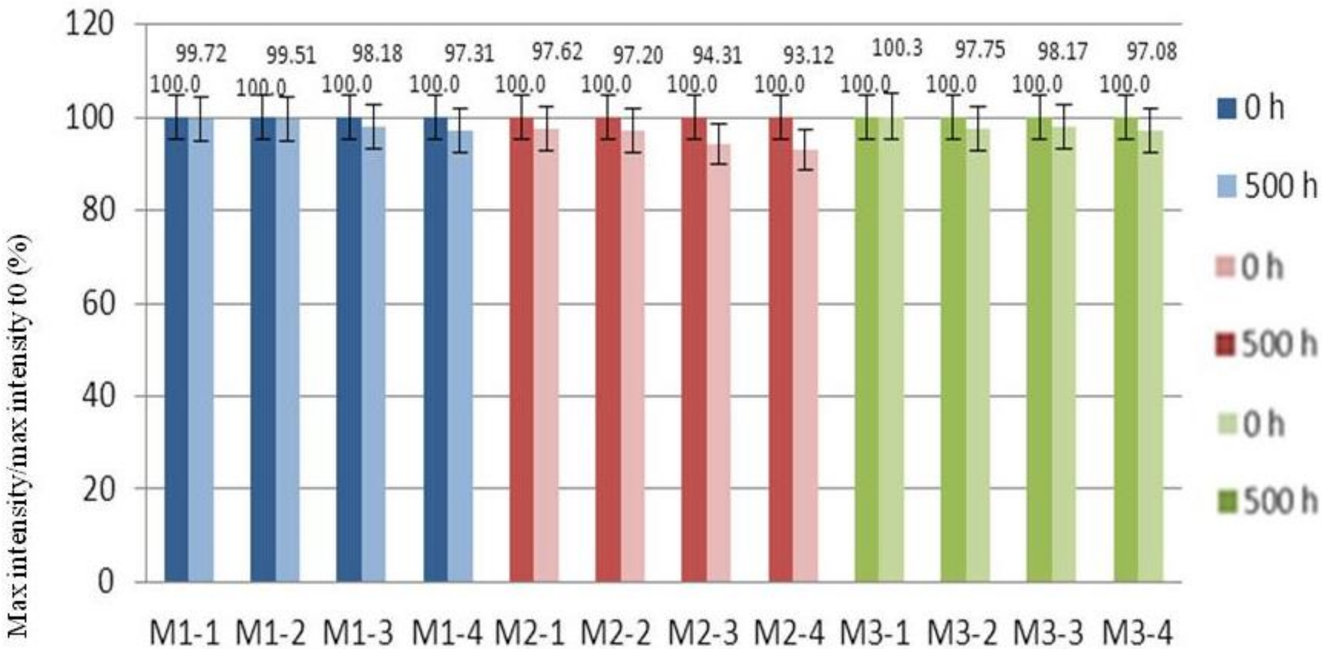
•From the excitation spectra: presence of three peaks.

•Samples 1 and 2: spectra with the same shape; sample 3: a slightly different.

•Reference sample: not show luminescent effects.

•These spectra used as reference starting point to evaluate the trend of the luminescent behavior after weathering and degradation accelerated test.

Luminescent effect behavior in function of the accelerated weathering test

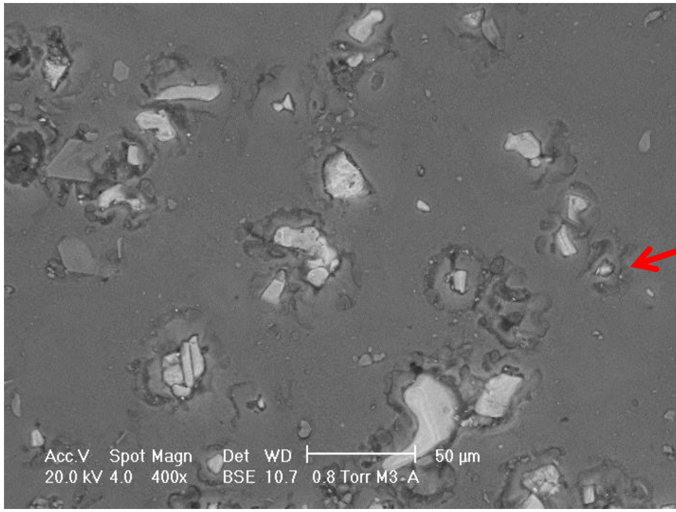


intensity of mean peak of the excitation spectrum ***after 500 hours of UV*** *exposure normalized to the intensity of the initial peak 0*

- **500 hours of UV-A exposure**: a total change of visible colour comprised between 2 and 2.6 points, hardly appreciable by the human eye.
- **Luminescent effect does not present any modification**.

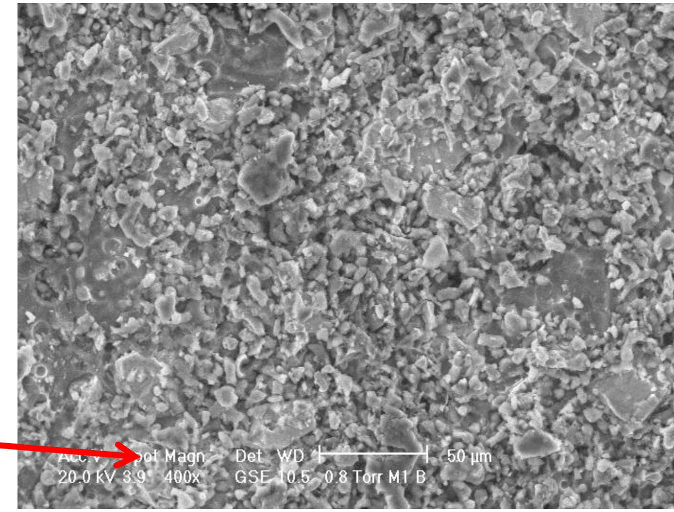
- **Cyclic test:** no produced damage or deterioration on the luminescent pigments; the intensity of the emission feature remained constant.
- no change in the form and position of the peaks in the emission and excitation spectra.
- The intensity remains unchanged.

Chemical resistance



sample 3 after 24 hs of immersion in ***citric acid solution***

sample 1 after 24 hs of immersion in ***alkaline solution***



Immersion in acid citric solution

•samples 1 and 2: very good behavior without changes in surface gloss, colour and roughness;

sample 3: damaged surface with localized attacks mainly close to emerged particle with consequent roughness increasing and gloss decreasing: dimension of the pigments and their present on the surface could be favor the localization of the acid attack.

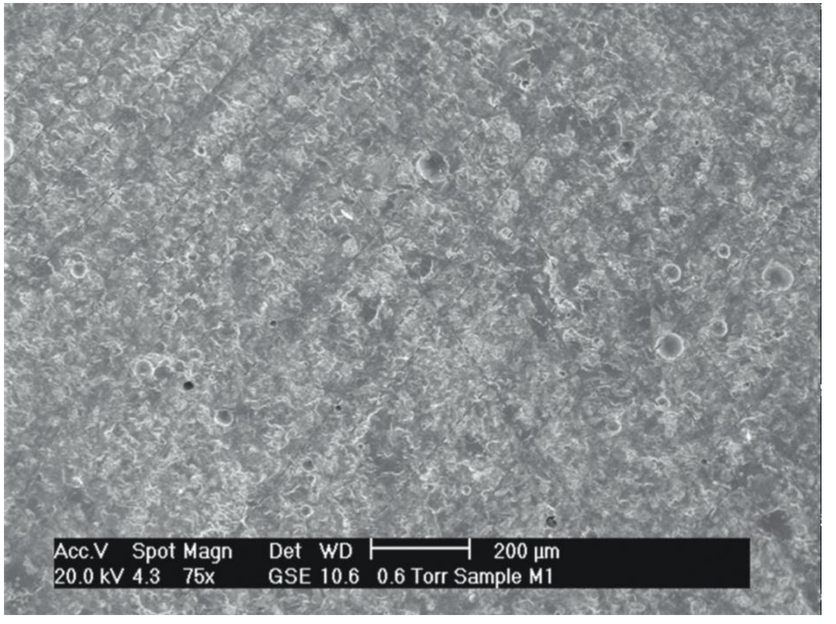
no change in the excitation and emission spectra. Probably the localized damage with possible removal of some pigments is not enough to modify the luminescent effect.

•immersion in acid alkaline solution

•The presence of the pigment on the surface of sample 3: shielding effect for the glassy: slightly attacked; samples 1 and 2: totally damaged.

•samples 2 and 3 change in the intensity of the peaks of emission and emission probably due to the higher roughness.

Luminescent properties



•abrasion behavior: a great surface modification with the removal of part of the luminescent enamel layer and with a formation of a widespread defectiveness.

•A remarkable increase of roughness, color and gloss changes.

Maintenance of corrosion protection of the substrate: only the more external layer damaged without cracks till to substrate.

Decrease in the luminescent properties due to high surface damage.

CONCLUSION

It is possible to obtain a vitreous enamel coatings with luminescent properties with addition of rare earth compounds such as europium and dysprosium to glass frit

These deposits show very interesting properties permits to think to a very intersting application.

The modification of the frit necessary for the optical effect do not change the very good properties of a traditional enamel (chemical resistance, adhesion and corrosion protection, aesthetical aspects).

The dimension and the position in the layer of luminescent pigments has effect on these behaviors in particular for chemical resistance.

Future research: optimization of dimension and quantity of luminescent pigments to obtain the best performance.

publications

books

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- S. Rossi, et al., cap 7 “Innovative Luminescent Vitreous Enameled Coatings” in “Intelligent Coatings for Corrosion Control” edited by A. Tiwari. Elsevier 2015, ISBN-9780124114678

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Research?

EU grant?

network?

PhD position?

University Collaboration?