Journal of Building Engineering

Impact of SiO_2, TiO_2 and ZnO nanoparticles incorporation on the thermo-optical properties of dark-coloured façade coatings

--Manuscript Draft--

Manuscript Number:	
Article Type:	Research Paper
Section/Category:	Coatings and claddings
Keywords:	Thermo-optical Properties; Colour Properties; Spectrophotometer; Nanoparticles; Façade
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Abstract:	In pursuing energy-efficient construction and reduced environmental impact, this study explores the integration of TiO_2, SiO_2, and ZnO nanoparticles into finishing coats for thermal-enhanced façade systems. Buildings account for a substantial portion of energy consumption, with façades playing a pivotal role. The impact of nanoparticle type, size, and material combination on thermo-optical performance was investigated through systematic analysis. Our findings reveal significant improvements in near-infrared (NIR) reflectance, a crucial factor in minimising heat absorption. Notably, TiO_2 nanoparticles demonstrate a 50% enhancement in NIR reflectance with ΔE of 3.4, followed by ZnO (28%, ΔE 3.2), and SiO_2 (22%, ΔE 4.61). Application-specific variations highlight the improved behaviour of TiO_2 in finishing coats for ETICS (Exterior Thermal Insulation Composite Systems), SiO_2 in acrylic paints, and ZnO in dye formulations. These results allow architects and builders to incorporate dark colours into façade aesthetics while maintaining thermo-optical efficiency and durability. As the demand for sustainable building practices grows, our work contributes to the evolving landscape of energy-efficient construction materials and design strategies. Investigating the long-term durability of these nanoparticle-enhanced coatings remains an important future research avenue.
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07. September. 2023

Dear Editors-in-Chief,

Herewith we send you the manuscript of a paper entitled "Impact of SiO_2, TiO_2 and ZnO nanoparticles incorporation on the thermo-optical properties of dark-coloured façade coatings", by Rita Carvalho Veloso, Joana Maia, Rodrigo Praça, Andrea Souza, João Ventura, Nuno M. M. Ramos and Helena Corvacho, which we would ask you to consider for publication in Journal of Building Engineering.

This work contributes to studying the nanoparticle type, size, and material combination on thermo-optical performance through a systematic analysis in pursuing energy-efficient construction and reduced environmental impact. An extensive laboratory characterisation comprising the nanoparticles' structural and morphological analysis and the thermo-optical performance was performed. This resulted in an integrated analysis of the different properties by measuring the solar reflectance, colour parameters and emissivity and contributed to the increase in knowledge of ETICS, the most commonly used thermal insulation system in Portugal, particularly in renovation actions. The significant improvements in near-infrared (NIR) reflectance, a crucial factor in minimising heat absorption, may allow architects and builders to incorporate dark colours into façade aesthetics while maintaining thermo-optical efficiency and durability.

I hereby certify that this paper consists of original, unpublished work which is not under consideration for publication elsewhere. I hope for your favourable consideration for publication in the Journal of Building Engineering - Elsevier.

Sincerely yours,

Joana Maia

Research highlights:

- Thermo-optical performance depends on the type and size of nanoparticles
- TiO_2 nanoparticles improve NIR reflectance by 50% with a colour change of 3.4
- Nanoparticles can enhance façade coatings for better thermo-optical properties
- The use of nanoparticles can meet dark colour aesthetic requirements
- Improved thermo-optical performance reduces thermal stress, improving durability

Impact of SiO_2, TiO_2 and ZnO nanoparticles incorporation on the thermo-optical properties of dark-coloured façade coatings

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Abstract

In pursuing energy-efficient construction and reduced environmental impact, this study explores the integration of TiO_2, SiO_2, and ZnO nanoparticles into finishing coats for thermal-enhanced façade systems. Buildings account for a substantial portion of energy consumption, with façades playing a pivotal role. The impact of nanoparticle type, size, and material combination on thermo-optical performance was investigated through systematic analysis.

Our findings reveal significant improvements in near-infrared (NIR) reflectance, a crucial factor in minimising heat absorption. Notably, TiO_2 nanoparticles demonstrate a 50% enhancement in NIR reflectance with ΔE of 3.4, followed by ZnO (28%, ΔE 3.2), and SiO_2 (22%, ΔE 4.61). Application-specific variations highlight the improved behaviour of TiO_2 in finishing coats for ETICS (Exterior Thermal Insulation Composite Systems), SiO_2 in acrylic paints, and ZnO in dye formulations.

These results allow architects and builders to incorporate dark colours into façade aesthetics while maintaining thermo-optical efficiency and durability. As the demand for sustainable building practices grows, our work contributes to the evolving landscape of energy-efficient construction materials and design strategies. Investigating the long-term durability of these nanoparticle-enhanced coatings remains an important future research avenue.

Keywords: Thermo-optical Properties, Colour Properties, Spectrophotometer, Nanoparticles, Façade.

1. Introduction and background

Energy consumption has become a significant concern in economic development and an important issue to solve in the decarbonisation pathway.

According to the European Commission [1], 40% of the energy consumption is attributed to buildings, highly related to the operation stage for indoor space comfort, heating or cooling needs, as stated by several authors [2-7]. This fact dramatically impacts greenhouse gas emissions, where buildings are responsible for 36% [1]. Furthermore, the durability requirement applied to construction materials and components is crucial to ensure sustainable construction, reducing the need for new resources and reducing waste.

Unavoidably, when exposed to solar radiation, buildings absorb a large portion of the radiation reaching their exterior surface [8]. Building envelope may reach very high temperatures depending on its surface properties, such as reflectance and emissivity. Studies focusing on the search for mechanisms that increase solar reflectance in the near-infrared region (NIR) are being conducted with increasing intensity [9-11].

Reducing the building envelope exterior surface temperature may reduce indoor cooling energy needs, especially in old buildings with a low level of thermal insulation, thus promoting thermal comfort for building users [12]. However, as stated in Cánovas-Saura et al. [13], including additional thermal insulation in a realistic building design makes possible savings due to the use of reflective finishing negligible, especially for colder climates. Thus, in new buildings, with a higher level of thermal insulation, the main concern is not related to indoor thermal comfort or energy consumption but to the fact that the outer layers of the façade, when exposed to solar radiation, are particularly prone to thermal stress, which means higher surface temperatures and greater temperature variations. This may have a significant impact on their durability.

The colour of building façades plays an essential role due to its influence on the temperature reached by the coating layers when exposed to solar radiation. The temperature is usually higher on a dark tone façade than on a light tone façade [14]. Consequently, the dark tone façades are more prone to degradation due to high-temperature variations. Cánovas-Saura et al. [13] studied how to improve the efficiency of building thermal control without limiting envelope aesthetic options. Their study focused on using coloured bilayers, where the inner layer ensured solar absorptance or reflectance and the colouration was provided by the outer layer. Twenty different bilayers were studied, representing a broad palette of colours in static and dynamic configurations. Nineteen locations worldwide were chosen for the simulations carried out to investigate the performance of the bilayers in different climates. Using bilayers allowed for a wider envelope colour range while achieving energy savings, particularly in hot climates and for a low level of thermal insulation [13].

In countries where summer overheating is a concern, painting the façades with light or white colour is widespread and an old practice. White effectively reflects solar radiation in the visible region as well as in the NIR region, as well as absorbing a very low amount of the incident total solar radiation [15]. A smooth, opaque and white surface can reach 85% of solar reflectance [16]. However, such a high reflectance value corresponds to a clean and white surface. Over time, the reflectance of an exposed façade tends to decrease due to dust deposition and the natural ageing of the paints.

Besides, sometimes architects show a preference for dark colours for façade coating layers. Some of the reasons that influence this choice are related to the aesthetics and the ease with which dark tone façades disguise dirt and pollution caused by atmospheric agents [15, 16]. Furthermore, a façade with light colours can increase the risk of external surface condensation in colder periods, accelerating degradation due to biological growth [17, 18].

To our knowledge, only a few studies focused on dark NIR-reflective pigments. Suwan et al. [19] described a Co-doped $ZnFe_2O_4$ black pigment synthesis with a 48-50% NIR reflectance. Wang et al. [20] prepared a $MnTiO_3$ powder with a good solar use performance.

However, these pigments require complex syntheses with difficult implementation in the industry and high energy demand (due to calcination processes) and solvents that are not considered environmentally friendly.

Cozza et al. [21] presented a study on the possible formulation of exterior building paints as smart coatings with high IR-reflectance to decrease energy use for cooling buildings. The goal was to investigate the possibility of extending the range of building colours to dark ones. The study focused on black pigments. Increments of 30% were found for total solar reflectance [21].

Another possibility for improving the thermo-optical properties of building surfaces is using thermochromic coatings. Thermochromic materials, which change colour in response to temperature fluctuations, have been investigated and applied mainly for glazed areas. However, the need to control the surface temperature of opaque elements increased the interest in searching for the same effect in those elements. An innovative thermochromic mortar based on ordinary white Portland cement and organic microencapsulated thermochromic pigments is presented in Perez et al. [22]. The optical properties of the mortar change with temperature at the transition value of the pigments (31°C). The material presents a light colour and high reflectance for higher temperatures in the visible range. It shows a dark grey colour for lower temperatures and low reflectance [22].

In later research, concrete tiles were coated with a thermochromic mortar. As in the former study, the mortar was prepared by adding organic microencapsulated thermochromic pigments to its composition. Although some encouraging results for non-exposed surfaces, the study identified a clear need for further research to improve the durability of thermochromic opaque materials in outdoor conditions exposed to solar radiation [23].

When thermo-optical properties of façades are studied, researchers have to keep in mind that, besides their effect on the indoor conditions and their durability, there may also be an effect on the outdoor environment. The urban heat island (UHI) phenomenon is well-known, and several strategies applied to façades can contribute to its mitigation, such as highly reflective building envelopes [24].

Directional reflective materials, particularly retro-reflective (RR) materials, were tested for use in addition to traditional diffusive cool materials. Different-sized glass beads were incorporated into a typical Italian exterior paint. The experimental study showed that RR materials could be effectively applied as coatings on the building envelope, reducing the UHI effect [25].

In another study, the paint was obtained by depositing four different RR microspheres on a traditional plaster for exterior applications [26]. Two full-scale vertical surfaces, one covered with RR plaster with glass microspheres and the other with diffusive plaster, were built to assess the visual comfort of pedestrians. The Daily Glare Probability indicator and surface temperature for the RR wall were always lower than those for the diffusive wall. At 42ºN latitude, it was found that the best-performing configuration is the combination of RR façade and RR pavement for glass spheres [26].

Given the choice of dark tones, incorporating nanomaterials in the façade finishing layer is one of the possible solutions to avoid excessive solar absorptance. Thus, since one of the purposes of including nanomaterials in exterior finishing coatings is to improve solar reflectance, the nanomaterials chosen are generally metallic oxides, given their great capacity to selectively reflect solar radiation in the visible and near-infrared region [27]. Organic materials can have the same capacity, although these materials tend to suffer photodegradation with UV exposure [27]. Titanium dioxide (TiO_2) is a metal oxide that effectively contributes to solar reflectance [28]. Besides TiO_2, another promising nanomaterial is zinc oxide (ZnO). Due to its stability in harsh chemical and mechanical conditions and low toxicity, it is widely used in decorative paints. However, it does not have the ability to scatter light as TiO_2 [29].

Nanomaterials are distinguished by their optical properties, particularly those related to emissivity and reflectance, which are strongly connected with particle size. As the particle size decreases, the density of the sample changes and consequently, the reflectance is affected [30, 31]. Besides providing an effect on the thermal performance of façades, nanomaterials may help to improve the physical properties of materials such as mortars, enhance the durability of composite materials, allow for materials weight reduction, and provide antimicrobial, anti-corrosive and self-cleaning properties [27, 32, 33].

To test the application of titanium dioxide (TiO_2) on travertine stones, research was carried out on their durability. The results showed that using nanoparticles of both TiO_2 polymorphs (rutile and anatase) dispersed in resin significantly increased the durability of the surfaces of the stones during the ageing tests. No colour change in the sample surfaces is another advantage of the resin-TiO_2 nanoparticle hybrid coating. The best results were obtained with anatase TiO_2 nanoparticles since they are colourless powder [34].

An article on photocatalytic TiO_2-based thin layers to be applied on mortars in façades, which concerns coating efficiency (which encompassed their self-cleaning ability, depolluting effect, and antimicrobial properties), confirms the beneficial photocatalytic activity of the coating and identifies the needs for further research. The latter would be mainly on specific evaluations that may be needed for each coating composition and testing condition to understand their performance. The type of contamination agents, TiO_2 dispersion and characteristics, dopants, nanocomposites and type of substrate are among the principal agents influencing the results [35].

Lu et al. [36] also used nanoparticles to develop a colourful superhydrophobic coating of silicon dioxide nanoparticles (SiO_2), quartz sands, silicone sealant, and latex paint. The produced coating meets both durability and aesthetic requirements and shows mechanical stability, anti-corrosion characteristics and high UV resistance [36].

In the scope of a broader research project, Circular2B, the present study investigates the influence of three reflective nanomaterials (TiO_2, SiO_2 and ZnO) on the thermo-optical properties of façade coatings, aiming to assess the suitability of newly formulated coatings with nanoparticles incorporation, to enhance the reflectance of dark surfaces without changing their colour. Those coatings are applied to an External Thermal Insulation Composite System (ETICS), the most commonly used thermal insulation system in Portugal, particularly in renovation actions, and a cladding panel. This panel is made of an alkali-activated (AA) mortar mainly composed of industrial and construction and demolition wastes (CDW), which are being studied and optimised to respond to the growing need for applying circular economy principles to the construction sector.

2. Materials and methods

Two distinct façade systems were studied: an External Thermal Insulation Composite System (ETICS) and a cladding panel produced from an alkali-activated mortar. The finishing coat of the ETICS consists of a commercial acrylic-based product incorporating a black colourant and the cladding panel of black water-based acrylic paint. Both finishing coats were doped with different types and concentrations of nanoparticles to access their optimised thermo-optical behaviour.

2.1. Materials and sample preparation

The first façade system consists of certified and commercial ETICS. Four samples were produced and tested based on the EAD 040083-00-0404 [37]. The ETICS, according to the information provided by the manufacturers, have EPS (expanded polystyrene, 20 kg/m^3) as thermal insulation with a thickness of 60 mm and a base coat composed of cement, synthetic resins and mineral additives, with density between 1700-1800 kg/m^3, applied with 1-2 mm.

The base coat layer was reinforced by a glass fibre mesh. The finishing coat is an acrylic-based material with organic additives, incorporating 6% of a black colourant doped or not with nanoparticles. The manufacturers frequently use this percentage of the black colourant to provide the black tone to the finishing coatings.

Regarding the second façade system, four cladding samples were produced from industrial, construction, and demolition wastes. Mainly, they are constituted of fly ash (90 % w/w), polyurethane (% 5 w/w), timber (% 5 w/w) and aluminium powder (< 0.1% w/w). The mixtures were alkali-activated with sodium hydroxide (NaOH, 3M) and sodium silicate (ratio of NaOH/silicate was 0.3). A 0.6 solid/liquid ratio was chosen to provide mechanical strength. After adding the activator, the specimens were cured in a controlled ambient (85ºC, 40% HR) for about 20h. The finishing coat consists of black water-based acrylic paint.

Silicon dioxide (SiO_2) with 20-30, 60-70 and 400 nm nanoparticles, as well as titanium dioxide (TiO_2) with 30 nm nanoparticles and zinc oxide (ZnO) with 10-30, 100, 500 and 1000 nm nanoparticles, were purchased from an external supplier. All nanopowders used in this study were ≥ 99.9% trace metals basis and were employed as obtained without further purification.

The standard matrices are a commercial black iron oxide-base dispersion colourant (PBk11 index) for the ETICS finishing coat and an acrylic water-based paint (PBk7 index) commonly used on façade systems for coating the cladding panel. The properties of such black coating are described in Table 1.

Table 1: Colourant and paint characterisation.

Name	Pigment	Colour	Index	Opacity	Density (kg/m^3)
Black colourant	Fe_2O_4 (magnetite)	Dark grey or black w/ bluish to yellowish undertones	PBk11	2-3	1911

Black water-based acrylic paint	Amorphous carbon black	Deep black, brown undertone	PBk7	1-2	1364

In the first phase, the commercial nanoparticles were dispersed directly in the matrices in different concentrations (1, 3, 5, 8, 12, 16 and 20% w/w) to explore the performance of the doped coatings on the near-infrared region. All the doped samples were mixed at room temperature until obtaining a homogeneous mixture and then applied on 35×35×3 mm^3 acrylic substrates with a spatula.

After the production and subsequent analysis of solar reflectance and colour, despite all samples increasing the total and NIR reflectance when compared to the conventional colourant and to the acrylic paint, it was found that the adequate percentage to dope the commercial finishing coatings was 8% (% w/w). As such, ETICS and cladding samples were produced with nanoparticles incorporated in their finishing coatings, as shown in Table 2, allowing a second phase of testing, considering the façade systems.

Table 2: Composition of the finishing coatings applied to the façade systems.

Façade system	Sample	Dimensions of specimens (mm)	Nanoparticles	Size (nm)	% w/w nanoparticle	% w/w colourant
ETICS	M1	200×200×60	TiO_2	30	8% (1)	6% (2)
	M2		ZnO	500		
	M3		SiO_2	60-70		
Cladding panel	N1	100×100×30	TiO_2	30	8% (3)	Non-applicable
	N2		ZnO	500		
	N3		SiO_2	60-70		

(1) Percentage relative to colourant weight;

(2) Percentage relative to the organic coating weight.

(3) Percentage relative to acrylic-paint weight

The visual aspect of both types of samples is presented in Figure 1.

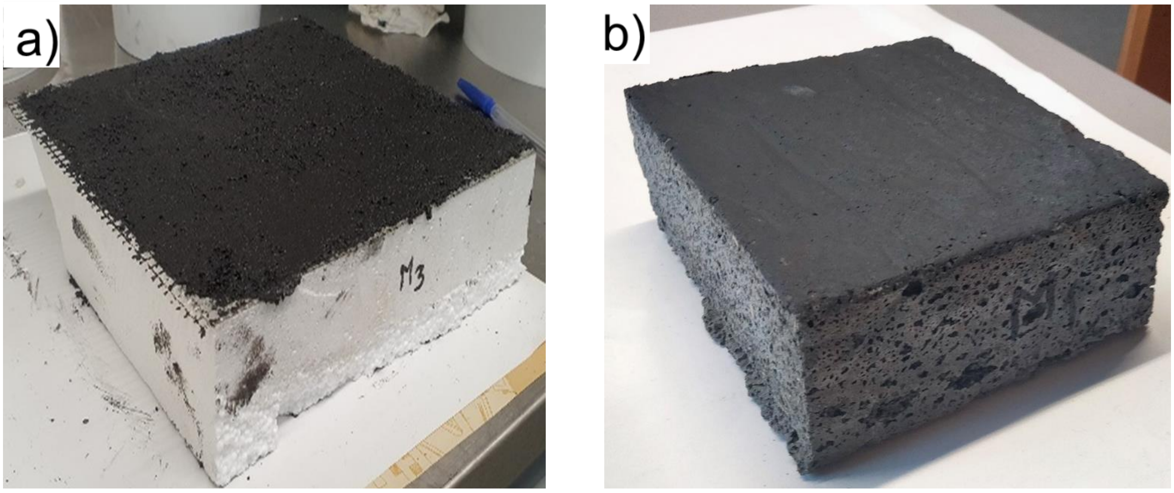

Figure 1: Samples of (a) ETICS and (b) Alkali-activated cladding.

2.2. Nanoparticles characterisation

The morphology and crystalline nature were carried out by Scanning Electron Microscopy (SEM) with analysis of Secondary Electron (SE) and Electron Backscattered Diffraction (EBSD) analysis (Quanta 400 FEG ESEM/ EDX Genesis X4M) using an acceleration voltage of 15 kV. The SEM images were taken at ×20000, ×50000, ×100000 and ×200000 magnifications.

2.3. Thermo-optical assessment

Solar reflectance measurement can be carried out by measuring the solar spectrum properties such as absorbance, reflectance and transmittance of a material using a spectrophotometer. As such, a portable modular spectrophotometer was used coupled with different wavelengths (FLAME-T (UV-VIS) and FLAME-NIR) with an integrating sphere in the 200-1650 range (measured at 5 nm wavelength intervals along a spectrum, UV-VIS and NIR). The weighted average of three samples was used to calculate spectral reflectance using the ordinates Direct Normal Irradiance for air mass of 1.5 defined in ASTM G197 [38] and following the procedure established in ASTM E903 [39]. Through this calculation, it is possible to determine the total reflectance (SR) given by equation (1):

$$SR = \sum_{i=1}^{100} R(\lambda_i)/100 \quad (1)$$

while the NIR Solar Reflectance (SR_{NIR}) was calculated using the equation (2):

$$SR_{NIR} = \sum_{i=46}^{100} R(\lambda_i)/55 \quad (2)$$

where the subscript *i* is the ordinate number derived from the tables of ASTM G173 [40] in Appendix X2 of ASTM E903 [39], and R is the spectral reflectance given by the spectrophotometer at a given ordinate wavelength (λ_i).

The colourimetry parameters of all samples were studied using the same modular spectrophotometer, only in the UV-VIS region (400 – 700 nm). The CIE L*a*b colour coordinates were calculated as recommended by the Commission Internationale de l'Eclairage (CIE) [41] for the visible range, with the observer 10 degrees under a D65 illuminant. According to the CIE methodology, the lightness (L*) ranges from black (zero) to white (100), the a* coordinate ranges from green (-128*) to red (+128*), and the b* of blue (-128*) to yellow (+128*). The average for the colour properties (L*, C*, H) was calculated considering three measurements for each sample.

The chroma (C^*_{ab}) is the colour intensity (i.e. light red, pastel red, dark red, etc.) perceptible to the human eye, whose value is defined in equation (3). The hue (H_{ab}) gives the colour type and identity for a dominant wavelength (red, blue, yellow, etc.) where the colour position is calculated by equation (4), corresponding in a circle position to red (0 or 360º), green (120º) and blue (240º).

$$C^*_{ab} = [(a^*)^2 + (b^*)^2]^{1/2} \quad (3)$$

$$H_{ab} = \text{arctang}(a^*/b^*) \quad (4)$$

The colour difference (ΔE) is a parameter expressing the perceived magnitude of the difference between two objects. The calculation of ΔE can be performed using the equation (5) given on ISO 11664-4 [41]:

$$\Delta E^*_{ab} = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2} \quad (5)$$

Human eyes can perceive colour differences in different conditions (illuminant source, observed angle, and human psychological perceptibility). Several studies [42-44] defined a benchmark of the ΔE value between 2 and 3 for human perceptibility. This study considered the perception levels given in Table 3.

Table 3: Colour perception levels (after Xie et al. [45]).

Level	ΔE	Perception
0	≤ 1.0	Not perceptible by human eyes
1	1 – 2	Perceptible by close observation
2	2 – 10	Perceptible with a glance
3	11 – 49	Colours are more similar than opposite
4	100	Colours are the exact opposite

The emissivity of a material surface is its effectiveness in emitting energy as thermal radiation. The emissivity is the ratio between the thermal energy emitted by a real body and the thermal energy emitted by a blackbody at the same temperature. The emissivity measures were carried out using the standard procedures described in ASTM C1371 [46], which conceals a technique for determining the emissivity of typical material near room temperature using a portable differential emissometer. By measuring emissivity, it is possible to quantify the amount of long-wave electromagnetic radiation that a body emits and on which the surface temperature of the body depends. Thus, the values of emissivity can vary from 0 to 1.

3. Experimental Results and Discussion

3.1. Nanoparticles structural and morphological analysis

Scanning Electron Microscopy (SEM) images of the different nanoparticles are displayed in Figure 2. Such images show that 30 nm TiO_2 present a homogeneous and cubic shape [Figure 2(a)]. As for the SiO_2 nanoparticles, some agglomeration with spherical and homogenous morphology is observed for the smaller sizes, i.e., 20-30 and 60-70 nm [Figure 2 (b) and (c)], some agglomeration with spherical and homogenous morphology. However, for the 400 nm size, SiO_2 has an irregular shape and a large size distribution [Figure 2(d)]. The ZnO particles present polydispersity in terms of size and shape [Figure 2(e)-(g)]. The nanoparticles are spherical in Figure 3(e) concerning the 10-30 nm size. For the <100 nm [Figure 2(f)], the particle presents a shape of faceted crystals with homogeneous sizes. As for the 500 and 1000 nm [Figure 2(g) and (h)], the particles are mixed in the form of nanorods and irregular size and shape.

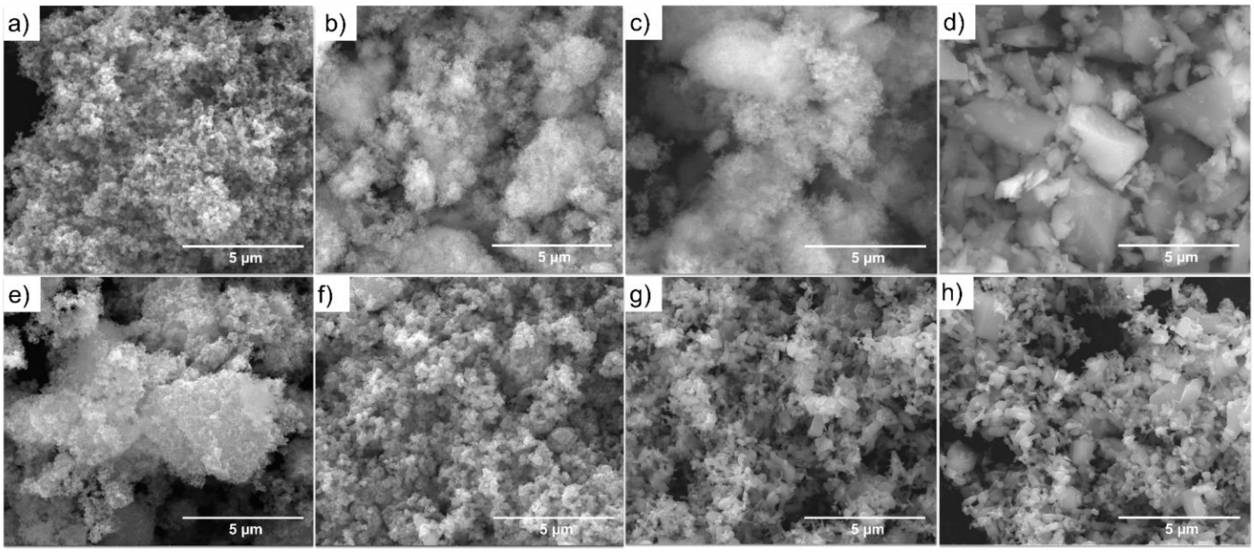

Figure 2: Scanning electron microscopy (SEM) images of (a) the TiO_2 rutile 30 nm, (b) SiO_2 20-30 nm, (c) SiO_2 60-70, (d) SiO_2 400 nm, (e) ZnO 10-30 nm, (f) ZnO <100 nm, (g) ZnO 500 nm and (h) ZnO 1000 nm. Scale bar: 5µm.

3.2. Thermo-optical performance of the doped finishing coats

The goal of this study was to analyse the effect of the selected nanoparticles incorporation in two distinct stages: firstly, to investigate the impact on a black commercial colourant commonly used to formulate finishing coatings, and second, to choose the most suitable nanoparticle (and better percentage of incorporation) which revealed the best performance in the near-infrared region and, simultaneously, maintaining the visual aesthetic, i.e. the colour, of the surface.

3.2.1. Nanoparticle-doped colourant

The optical properties of the nanoparticle-doped colourant samples were carried out to choose from each group of nanoparticles which size and percentage were suitable to incorporate in the ETICS finishing coating. As such, Figure 3 presents the spectral reflectance of the colourant-doped samples in acrylic substrates. Observing the results, it is possible to notice that all samples show an analogous performance in the UV-VIS region by partially absorbing the visible light. Concerning the near-infrared region, the specimens present significant differences since the nanoparticles-doped samples improve the reflectance of the colourant.

The results of the reflection in Figure 4 show that an increase in the NIR reflection leads to an increase in the total reflectance in all cases and gives a correlation of 80% for the studied samples. However, this behaviour of total reflectance versus NIR reflectance depends on the particle type, size, and incorporation ratio.

For TiO_2 (Figure 4a), the total and NIR reflectance decrease with increasing particle incorporation. The best results for these particles are obtained at 1% incorporation, where the total reflectance increases by 20% and the NIR reflectance by 95%.

When evaluating the SiO_2, Figure 4b, it can be seen for all particle sizes that a kink in the behaviour of the two reflections occurs at 12%. The best concentration is related to the particle size for this type of particle. Small particle size is expected to lead to a higher reflectance [47, 48], but the best results are obtained with a 20% admixture of particles with a size of 60-70 nm, leading to an increase of 21% overall and 52% of the NIR reflectance.

The ZnO (Figure 4c) shows the most inconsistent results when increasing the proportion of incorporated particles and decreasing the size. The best performance is seen with a ratio of 3% of 1000 nm particle size, an overall increase of 35% and 87% in NIR reflectance. This result has an opposite effect to that expected for size, as several studies indicate that reducing particle size can lead to a better reflection result [48, 49]. Yet, the behaviour in the NIR region is similar to the results found by [50].

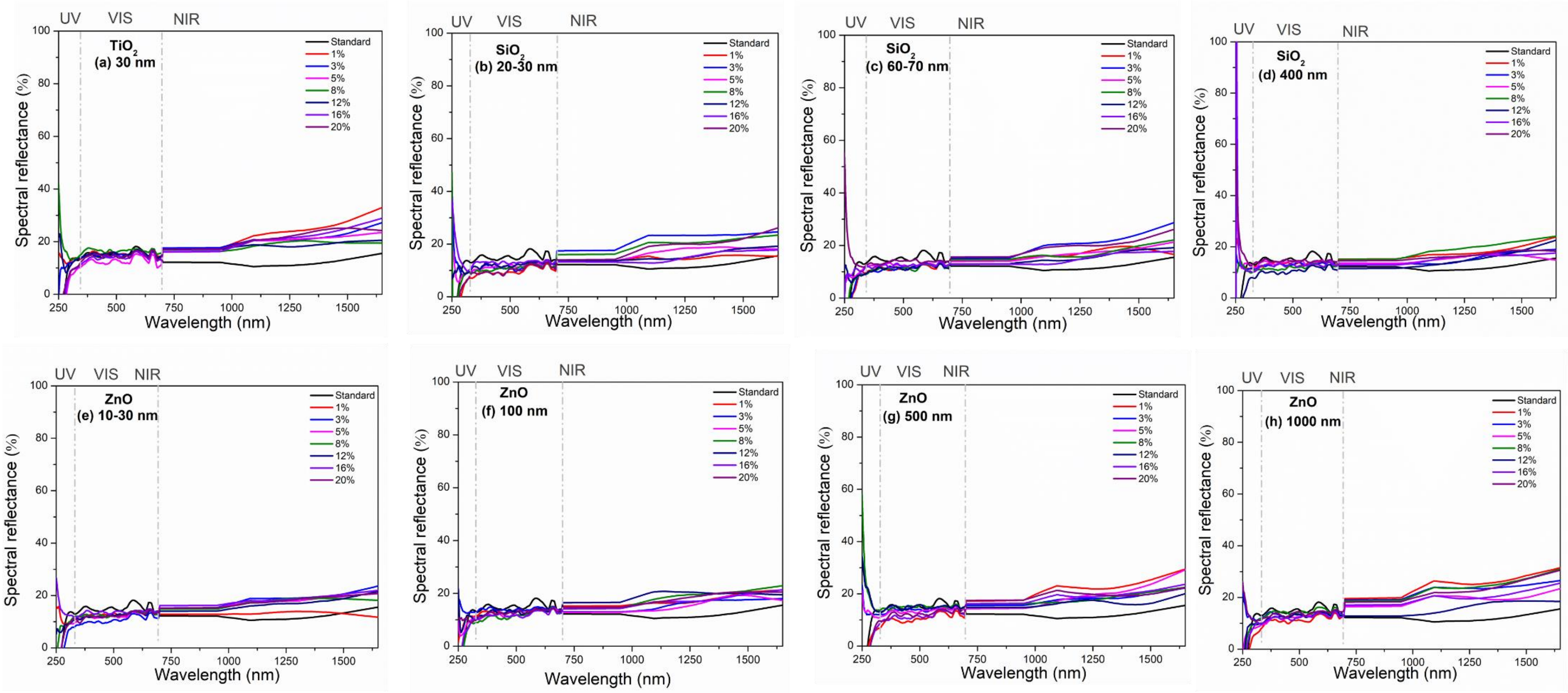

Figure 3: Spectral reflectance behaviour for the black colourant doped with (a) the TiO_2 rutile 30 nm, (b) SiO_2 20-30 nm, (c) SiO_2 60-70 nm, (d) SiO_2 400 nm, (e) ZnO 10-30 nm, (f) ZnO <100 nm, (g) ZnO 500 nm and (h) ZnO 1000 nm samples.

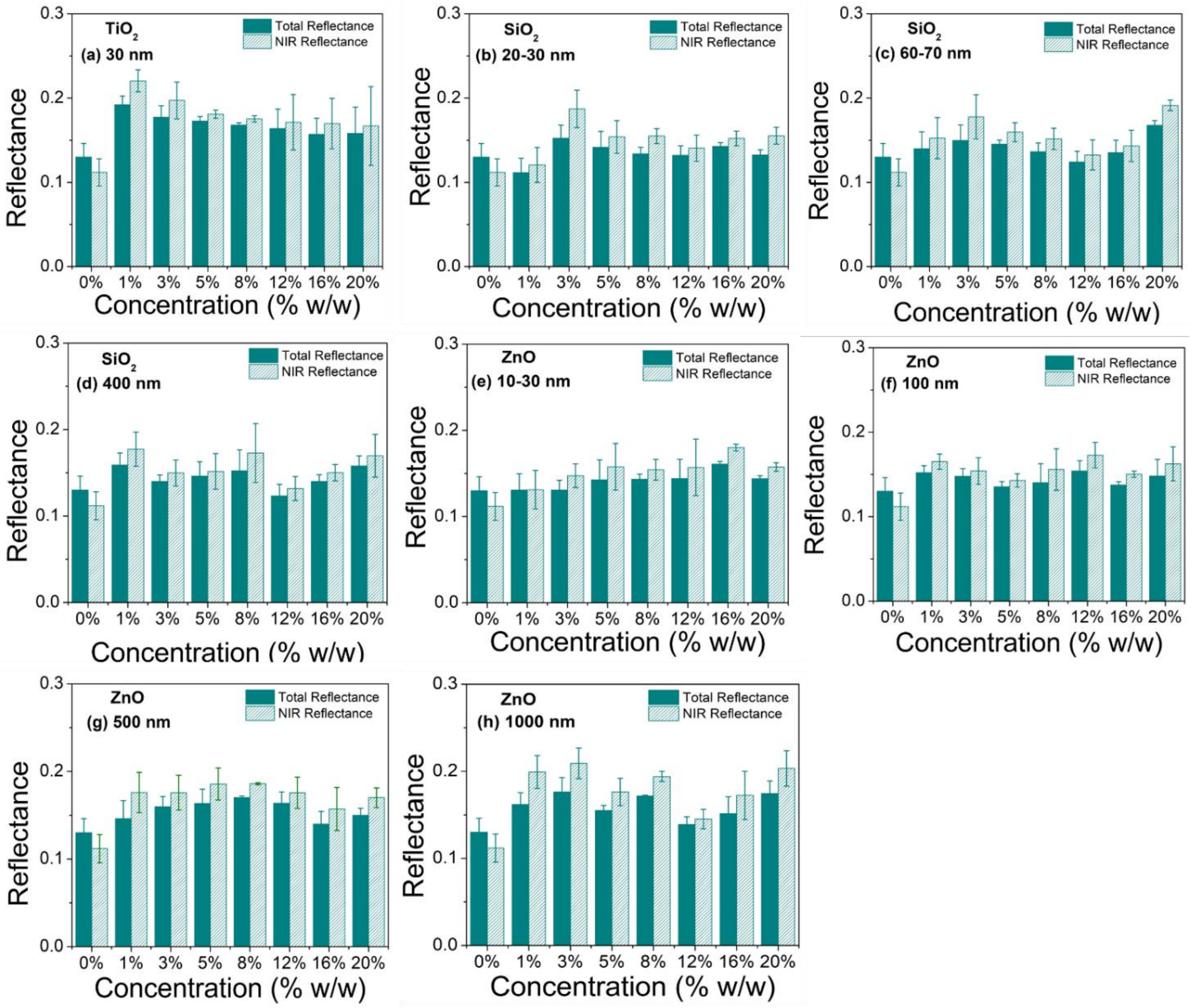

Figure 4: Calculated total average and NIR reflectance using ASTM E903 for the black colourant doped with (a) the TiO_2 rutile 30 nm, (b) SiO_2 20-30 nm, (c) SiO_2 60-70, (d) SiO_2 400 nm, (e) ZnO 10-30 nm, (f) ZnO <100 nm, (g) ZnO 500 nm and (h) ZnO 1000 nm samples.

As expected, titanium oxide performs best in improving reflectance [47, 51]. Nevertheless, the best combination between particle type, size, and content for application in architectural coatings also depends on the aesthetic evaluation; this study uses the CIELab colour space evaluation. Figure 5 shows the a*b* coordinates for the colourant samples doped with nanoparticles, while Figure 6 shows the colour parameters hue and chroma assessment. The comparison of the visual aesthetics of the doped samples with the standard black colourant is shown in Figure 7.

The a* and b* coordinates indicate the colour shades [52]. For the standard results, the values of these coordinates are related to the pigment used in the black dye (Table 1). The PBk11 has a bluish-to-yellowish hue [53], seen in Figure 5a, with a b* value of almost zero and a positive value of a* and a hue value between 120º and 240º (Figure 6a). The low value for chroma in Figure 6a is also a characteristic of black colour. Similar results were obtained for all standard samples for SiO_2 (Figure 5b and Figure 6b) and ZnO (Figure 5c and Figure 6c). The black, white, and grey colours are considered achromatic, meaning that the difference between a* and b* should be minimal [52].

When evaluating the incorporation of the nanoparticles, the best results are expected to be obtained for the samples with the smallest a*b* difference [54]. In the case of titanium oxide (Figure 5a), the best incorporation rate would be 5%. 16% and 20%, but when evaluating the chroma and hue difference (Figure 6a), the 16% leads to the lowest deviations. The best candidates for the SiO_2 (Figure 5b) could be the samples doped with 400 nm or 60-70 nm, with 20% incorporation due to the lower difference from the standard in hue and chroma value (Figure 6b). Similarly, when analysing reflectance, the results for the zinc oxide coordinates (Figure 5c) are the most inconsistent, with the best achromatic values at the highest levels of incorporation, 16% and 20%. When looking for the minor differences in hue and chroma (Figure 6c), the candidate for the best formulation is at 1000 nm with 20%.

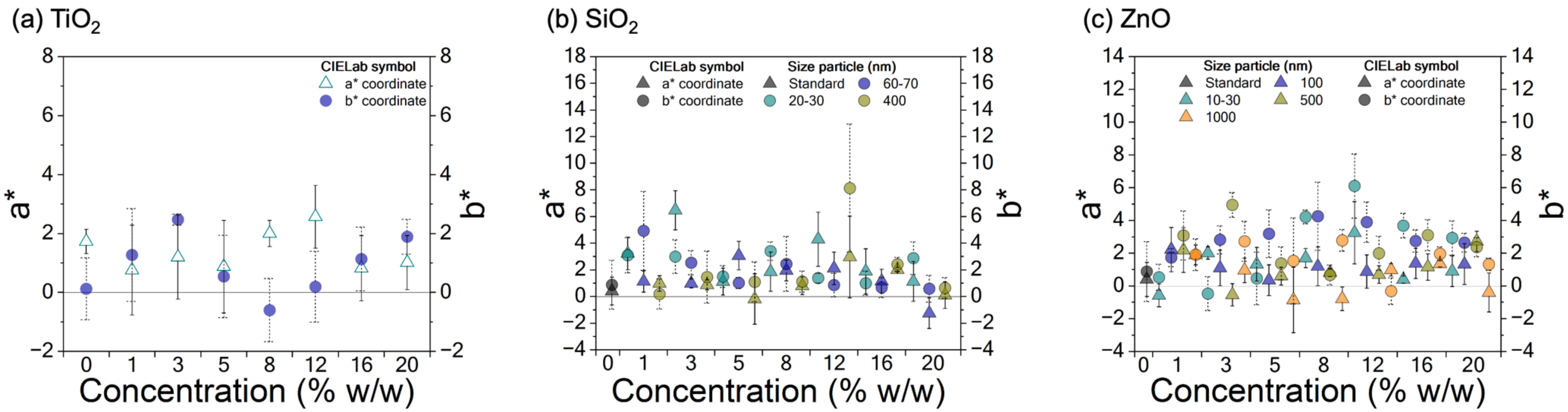

Figure 5: CIELab space coordinates for black colourant doped with (a) the TiO_2 rutile 30 nm, (b) SiO_2, and (c) ZnO nanoparticles.

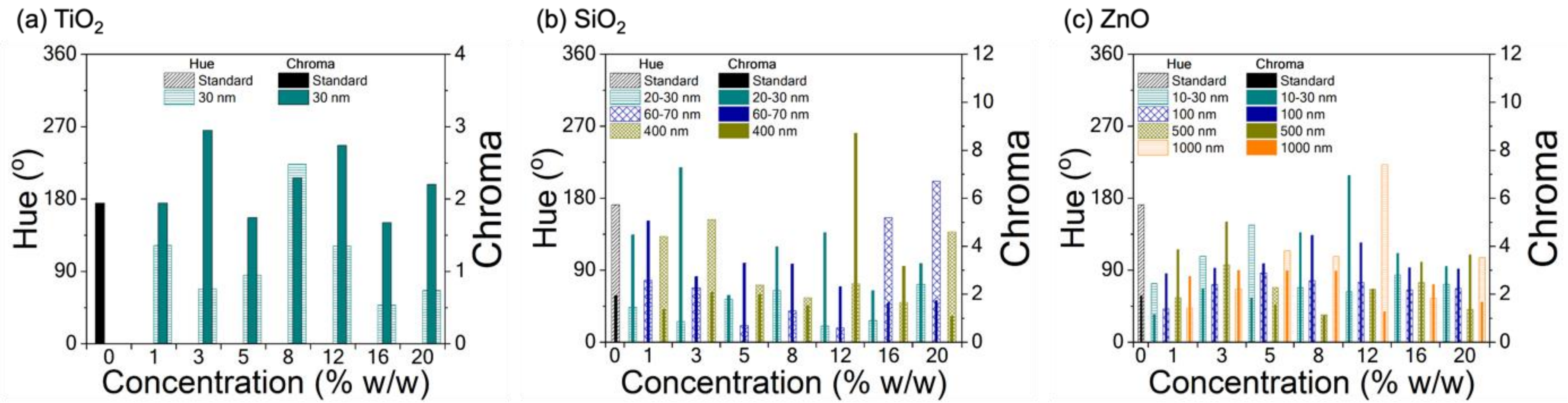

Figure 6: Hue and chroma assessment for black colourant doped with (a) the TiO_2 rutile 30 nm, (b) SiO_2 and (c) ZnO nanoparticle, when compared with the conventional colourant.

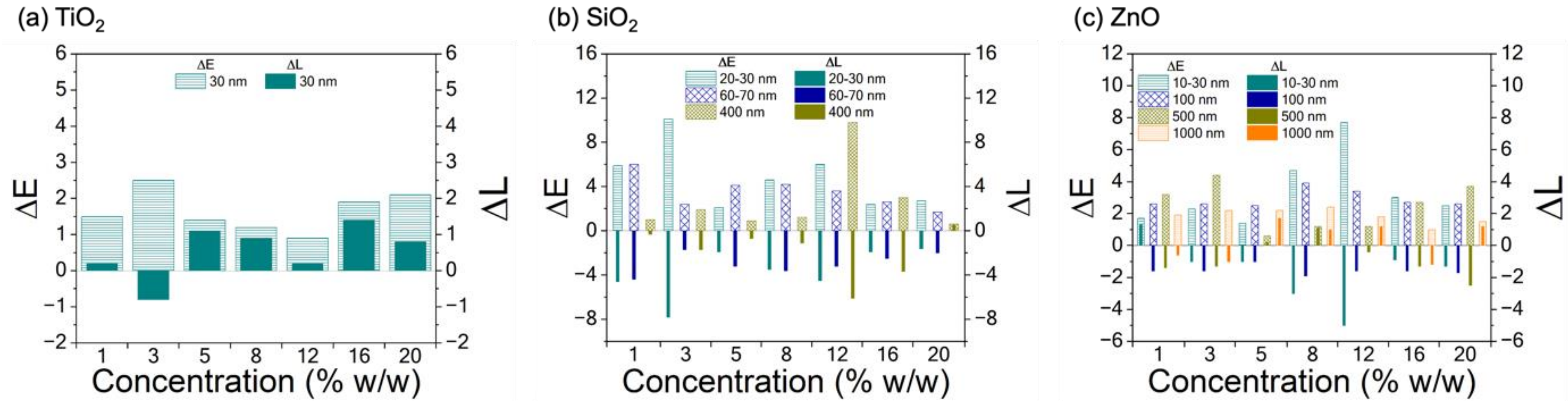

Figure 7: Total colour difference and lightness variation for black colourant doped with (a) the TiO_2 rutile 30 nm, (b) SiO_2 and (c) ZnO nanoparticle, when compared with the colourant without nanoparticles.

The hue and chroma values are based on the a* and b* coordinate measurements and form the basis of colour perception. However, the human eye and the psychological perception of colours do not recognise these properties [55]. For this, ISO 11664 [41] proposes to indicate the comparison between colours by the parameter of total colour difference (ΔE) and brightness difference (ΔL). Figure 7a shows the colour difference and lightness for the doped samples compared to the black colourant without nanoparticles.

When analysing Figure 7a for the samples doped with TiO_2, it is noticeable that most of the samples have a colour difference of less than 2, corresponding to perception level 1, i.e. the difference is only noticeable when looking closely (description of the levels in Table 3). The inclusion in the 3% content is the only one where the variation in lightness is negative, which was not expected as the negative values indicate that the sample is darker than the standard. This effect produces a higher colour difference than in the other samples (Figure 7a). The best concentrations in terms of variation of brightness and colour are 8% and 12%.

As far as SiO_2 incorporation is concerned (Figure 7b), the 60-70 nm and 400 nm sizes show the slightest colour variation (ΔE). For SiO_2, all samples became darker than the standard samples, which means negative values for ΔL in Figure 7b, with the best doping combination found at the high incorporation levels, namely 16% and 20%, for all sizes.

The ZnO (Figure 7c) sample shows the most significant variation in the change in results compared to the other nanoparticles. The best result for the ZnO nanoparticles is for the 1000 nm, where almost all samples show a colour difference of less than 2.

The results on colourant show that, as expected, the effect of the nanoparticles on the thermo-optical properties of the dye depends on the type, size, and content of the incorporated nanoparticles [47]. For example, looking at the performance in reflection (total and NIR) and colour difference, it can be seen that the best nanoparticle is TiO_2. However, the zinc oxide could be more effective than the titanium oxide of level 1 in improving the NIR reflectance with level 2 colour differences. At the same time, the silica shows the worst performance in both criteria (colour and reflectance). Nevertheless, the total reflectance increased for all nanoparticles tested due to the effect of NIR reflectance, as shown in Figure 8.

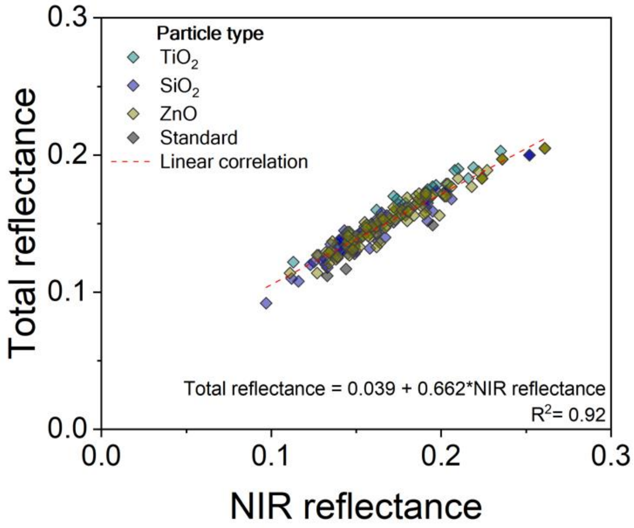

Figure 8: Correlation between the NIR reflectance and Total reflectance.

For the next phase, i.e. incorporation into the acrylic paint and the ETICS finishing coat, three nanoparticles with a size of 30 nm, 60-70 nm and 500 nm for TiO_2, SiO_2 and ZnO were selected for the paint and the ETICS, respectively. A concentration of 8% was adopted for the final ETICS coating, as shown in the results of the decision matrix in Table 4.

Table 4: Decision matrix for best performance for thermo-optical properties for doped colourant samples.

Variable			Modification against standard			
			Total reflectance	NIR reflectance	|DL|	DE
Particle	TiO_2		31%	41%	0.8	1.7
	SiO_2		9%	33%	2.8	3.7
	ZnO		16%	50%	1.5	2.7
Particle size	TiO_2	30	31%	41%	0.8	1.7
	SiO_2	20-30	4%	17%	3.7	4.8
		60-70	10%	42%	2.7	3.5
		400	12%	41%	2.0	2.8
	ZnO	10-30	10%	38%	1.9	3.3
		100	12%	41%	1.6	2.9
		500	20%	57%	1.2	2.4

	1000	24%	66%	1.1	2
Content	1%	15%	45%	1.8	3
	3%	19%	50%	2.1	3.6
	5%	16%	41%	1.4	1.9
	8%	17%	45%	2.0	2.9
	12%	10%	32%	2.8	4.3
	16%	12%	37%	1.8	2.7
	20%	19%	49%	1.2	2.2

3.2.2. Nanoparticle-doped acrylic paint

Similar to the former study, the same procedure and measurements were carried out for the acrylic paint nanoparticle-doped in acrylic substrates to find the most suitable concentration of nanoparticles to be incorporated in the finishing coating of the alkali-activated cladding panel. Considering the previous results, the acrylic paint was doped with TiO_2 30 nm, SiO_2 60-70 nm and ZnO 500 nm size. Using this methodology, it is possible to compare total and NIR reflectance behaviour in two distinct coatings (colourant and acrylic paint) for the same substrate with the adequate size and percentage of the selected nanoparticles. Typical spectral reflectance variations are displayed in Figure 9. Figure 9a shows that TiO_2 nanoparticles increase the reflectance in both regions, particularly in the visible regions, which consequently will cause a colour change in the paint. The behaviour of the other two nanoparticle groups is similar since both absorb light in the visible region, although less than TiO_2. Analysing the SiO_2 nanoparticles, it is observed that there is an improvement in the near-infrared reflectance, specifically for concentrations between 1% and 12%. Likewise, ZnO nanoparticles cause an enhancement in the reflectance but only at the lowest concentrations (1% and 3%), as verified in Figure 9c.

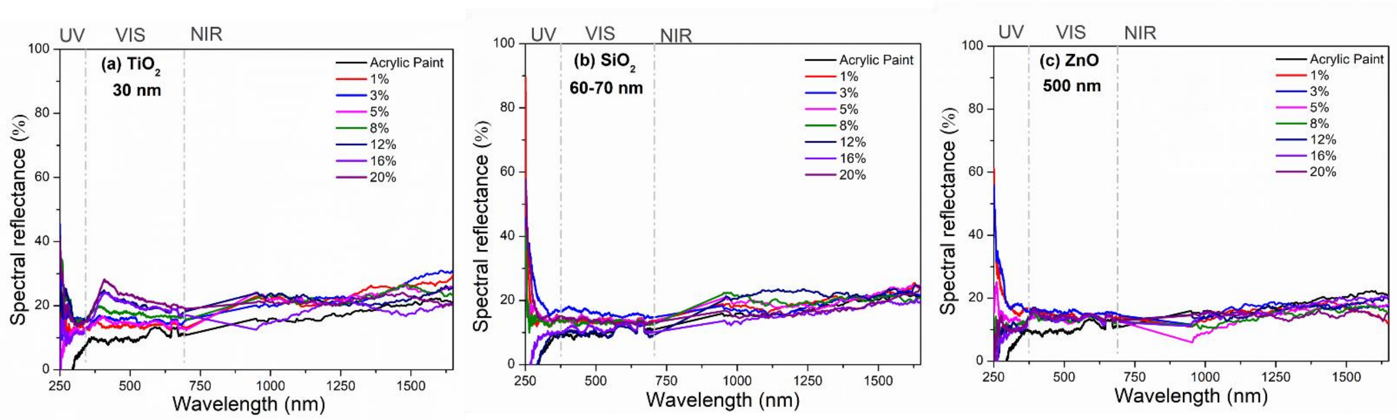

Figure 9: Spectral reflectance behaviour for the acrylic paint doped with (a) the TiO_2 rutile 30 nm, (b) SiO_2 60-70 nm and (c) ZnO 500 nm samples.

Following the ASTM E903 procedure [39], total and NIR reflectance was calculated for the tested nanoparticles, as shown in Figure 10. The results demonstrate that the incorporation of nanoparticles in the acrylic paint, in general, causes an increase in both values of reflectance. Acrylic paints have more components in their composition when compared to colourant, which has a simpler composition. This factor could influence the amount of radiation the nanoparticle-doped samples reflect once a carbon-based pigment is incorporated into the acrylic paint. Through the sample production, it was verified that the nanoparticles' incorporation was more straightforward compared to the commercial colourant. In general, both average values of reflectance for each group tested are higher in acrylic paint when compared to the previous study. ZnO nanoparticles are an exception. Even so, these samples show improved reflectance than the non-doped acrylic paint. Clearly, the TiO_2 nanoparticles show an improvement on both total and NIR results of 20% and 22%, respectively, for 20% concentration, when compared to the 13% of the non-doped paint, followed by the SiO_2 nanoparticles, which achieves the best result for 3% concentration with 17% of total reflectance. As for the ZnO, the doped samples present lower reflectance with 16% of total reflectance for 3% concentration.

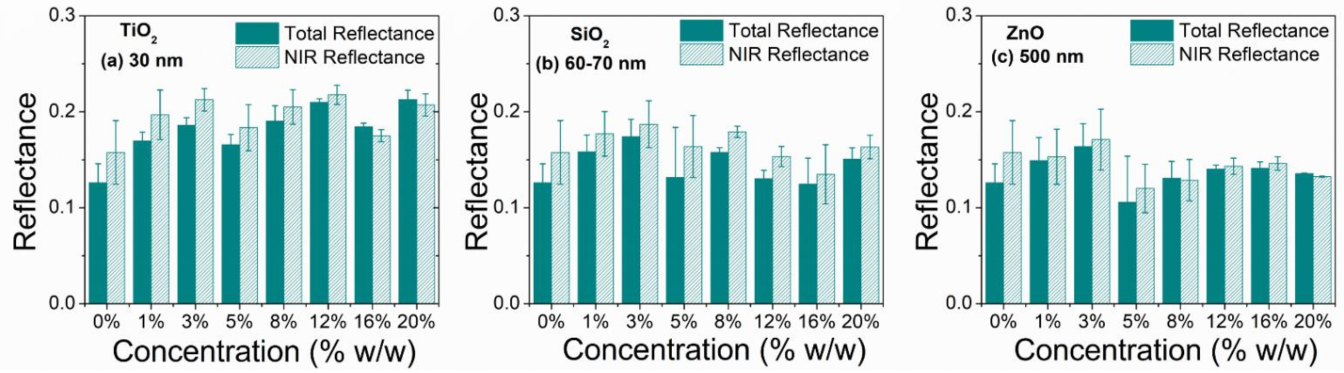

Figure 10: Calculated total average and NIR reflectance using ASTM E903 for the acrylic paint doped with (a) the TiO_2 rutile 30 nm, (b) SiO_2 60-70 nm and (c) ZnO 500 nm samples.

As described for the colourant, the effect of the nanoparticles in the acrylic paint depends on the colour pigment. In this study, the paint has a PBk7 pigment index classified as a deep black-brown undertone [53]. The brown is classified as an orange hue (+a* and +b* coordinates, Figure 11a) with low lightness [52]. As soon as the hue/chroma of the black acrylic paint deviates from the black colourant, the admixture of the nanoparticles shows a different behaviour, as can be seen from the hue and chroma values (Figure 11b) and the total colour difference and lightness variation (Figure 12).

Incorporating the nanoparticles into the acrylic paint substantially influences the colour coordinates more than the black colourant. The acrylic paint has more components than the pigment, which could explain the variations in the incorporation of nanoparticles [42].

The deviations in the CIELab coordinates affect the hue and chroma of the samples (Figure 11b). All samples with 16% and 20% TiO_2 have a negative effect on the hue, meaning that the colours take on a greyish tone and become brighter [52, 56], which is confirmed by the variation in brightness in Figure 12.

For the TiO_2, the 1% and 3% may be the best candidates as they show less variation in a* coordinate (Figure 11a) and less total colour variation and lightness increase (Figure 12). For the silicate, the higher concentrations, 8%, 12% and 16%, show the best results and evaluate the hue and chroma (Figure 11b). When considering the ΔL, the best concentration should be

16% with a minimal change (Figure 12). The ZnO shows the most achromatic CIELab values, with the lowest a*b* difference, but has the most significant impact on the hue (Figure 11b). The best candidates are those with a content of 8%, as they show less variation in total colour difference and brightness (Figure 12).

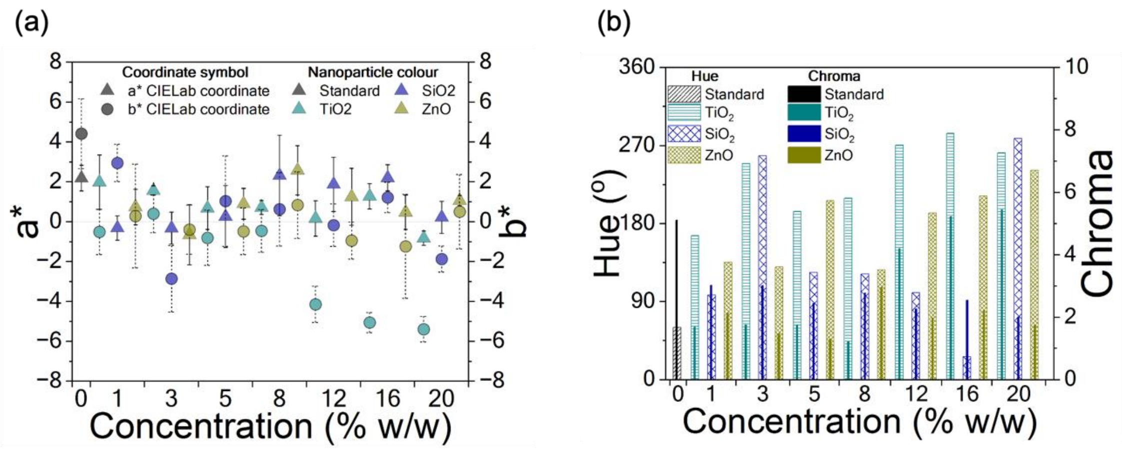

Figure 11: CIELab space coordinate (a) and hue and chroma assessment (b) for the acrylic paint doped with the selected nanoparticles.

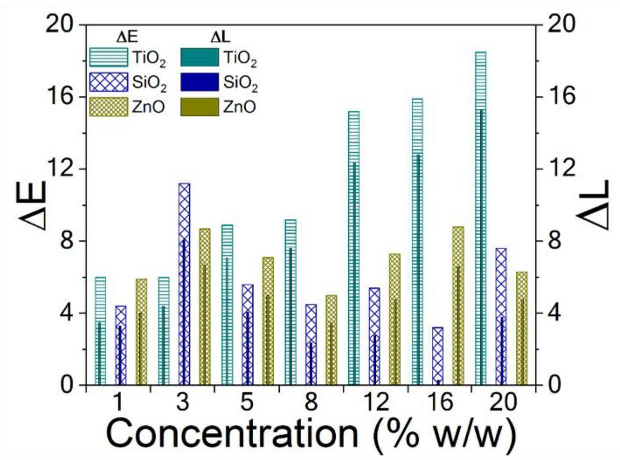

Figure 12: Total colour difference and lightness variation of acrylic paint doped with the selected nanoparticles.

None of the samples doped with acrylic paint has a total colour difference (ΔE) of less than 2. For SiO_2–3%, TiO_2 at 12%/16% and 20%, the ΔE was above 10. The other samples have a colour perception at level 2, meaning the colour difference can be perceived at a glance.

Doping the black acrylic paint also shows a good result in increasing the total reflectance by changing the NIR range. However, the effect on colour aesthetics was more pronounced than with the black colourant. Therefore, a new decision matrix, Table 5, was created to define the best concentration for applying the paint to the façade samples.

Table 5: Decision matrix for best performance for thermo-optical properties for doped acrylic paint samples.

Variable		Modification against standard			
		Reflectance	NIR reflectance	|DL|	DE
Particle	TiO_2	58%	68%	9.0	11.4
	SiO_2	23%	39%	3.5	6.0
	ZnO	16%	12%	5.1	7.0
Content	1%	34%	45%	3.6	5.5
	3%	47%	57%	6.4	8.6
	5%	13%	29%	5.4	7.2
	8%	34%	41%	4.5	6.2
	12%	34%	41%	6.7	9.3
	16%	26%	25%	6.5	9.3
	20%	40%	38%	8.0	10.8

Applying the criteria to increase NIR reflectance and total reflectance without changing colour aesthetics, the best-applied concentration in colour is 8%, which increases NIR reflectance by 41%, with a lower total colour difference (4.5).

3.3. Thermo-optical performance of façade systems with doped finishing coats

3.3.1. ETICS

The thermo-optical properties, such as colour and reflectance, are considered surface properties, so an ETICS commercial finishing coat was doped with nanoparticles (Table 2). Figure 13 shows the spectral and calculated reflectance for the ETICS samples, where the standard is considered to be the final coating doped with the black dye (6% w/w), M1 is considered to be the standard doped with 8% TiO_2 30 nm, M2 is considered to be 8% ZnO 500 nm and M3 is considered to be 8% SiO_2 60-70 nm.

The results of Cozza et al. [42] and Levinson et al. [57] indicate that dark colours have a reflectance in the visible range (VIS) of less than 20%. As shown in Figure 13a, all ETICS samples could be classified as a dark basis of the VIS reflectance, and a change in the UV and NIR range could also be detected in the doped samples (M1, M2 and M3).

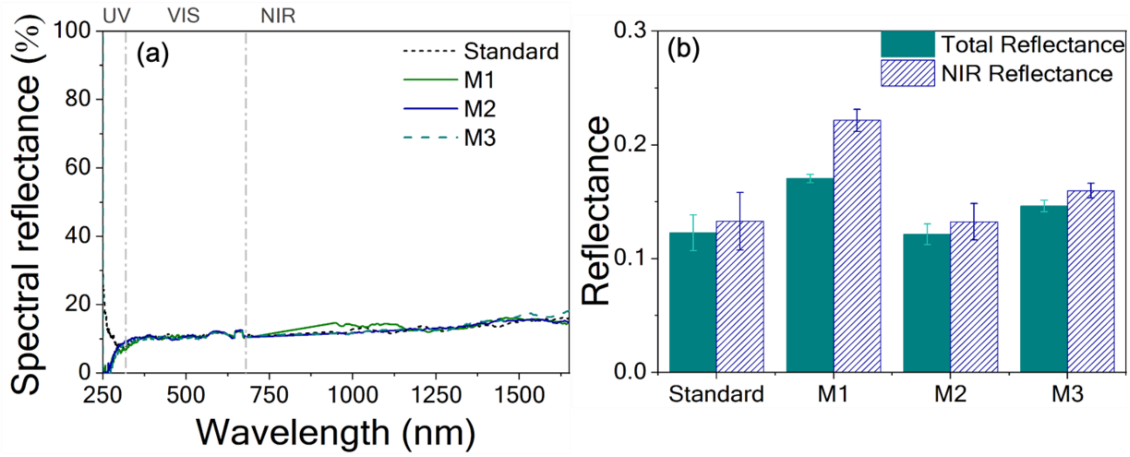

Figure 13: (a) Spectral and (b) total and NIR averaged reflectance calculated by ASTM E903 for the ETICS samples with nanoparticles incorporation (M1 – TiO_2; M2 – ZnO; M3 – SiO_2).

The black standard ETICS sample (Figure 13b) has a higher NIR reflectance than the total value. This behaviour contrasts with the standard samples with a colourant (Total: 0.130 and NIR: 0.112, Figure 4), where the improvement in NIR reflectance due to the coating type was 98% (colourant vs finishing coat). Similar results for the same colours on different coatings were observed by Alchapar and Correa [58].

Figure 13b shows that TiO_2 (M1) performs best in the NIR with an improvement of 65%, followed by SiO_2 (M3) with an improvement of 20% and ZnO (M3), which does not change the reflectivity in the NIR. The best performance of the M1 samples might be related to the high reflectance of the titanium oxide and the size of the nanoparticles [48, 51]. The increase also affects the behaviour of the total reflectance in the NIR and agrees with the results of the samples doped with a colourant (Table 4).

The aesthetic evaluation of the ETICS was based on the CIELab coordinates, Figure 14a, and hue and chroma colour properties (Figure 14b). The a*b* for the ETICS standard sample is similar to the colourant (Figure 5) with a low a*b* value and a hue value between 120º and 240º but with a higher chroma value than the colourant (Figure 6). If only CIELab coordinates are evaluated, titanium oxide (M1) and silicon dioxide (M3) are the best candidates for improving the thermo-optical properties.

The higher chroma values in Figure 14b show that the ETICS samples are darker than the coloured ones [56], as M1 maintains the chroma value compared to the standard and M2 and M3 increase the value by almost 50%. This chroma improvement can also be seen in the brightness variation in Figure 15.

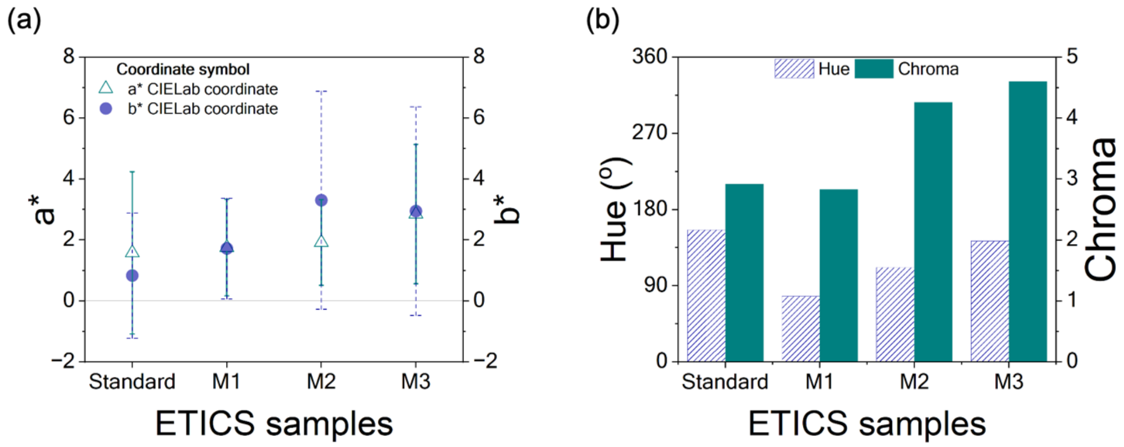

Figure 14: Colour parameters of ETICS samples coated with doped finishing coat.

The levels of colour perception for ETICS are level 1 for the M1 samples and level 2 for the M2 and M3, as shown in Figure 15. The doped sample became darker than the standard. Here, the best performance was demonstrated by the titanium oxide doped M1 samples, an opposite effect from the 8% TiO_2 inclusion in the colourant.

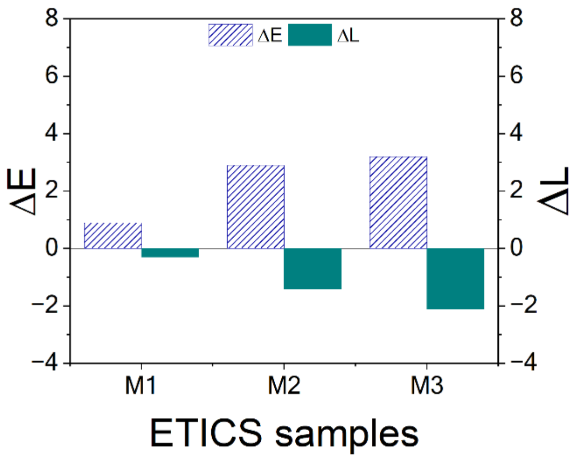

Figure 15: Colour and lightness difference of ETICS samples coated with doped finishing coat.

Another surface property essential to evaluate the surface temperature and the thermal behaviour of ETICS systems is the emittance, with results shown in Figure 16.

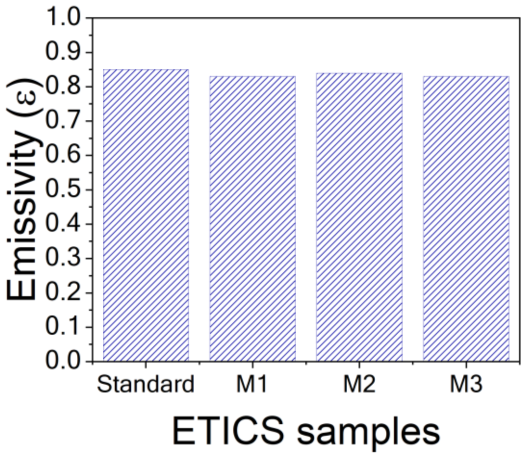

Figure 16: Emissivity of ETICS samples coated with doped finishing coat.

The found emissivity values, with an average value of 0.84, are consistent with the materials used for façade coatings [59]. The slight deviations in the results show that incorporating nanoparticles into the final coating of ETICS does not influence the emissivity, which is consistent with the results of Sharma et al. [60].

According to the criterion of improving the NIR reflectivity without changing the colour of commercial mortar for the final coating of ETICS, M1 is the best formulation as it increases the NIR reflectivity by 65% and has a colour difference of 0.9, while sample M2 is the worst as it reduces the reflectivity by 1% and results in a colour difference of 2.9.

3.3.2. Cladding panel

The thermo-optical properties, such as colour and reflection, are considered surface properties. Therefore, a cladding panel made of industrial/construction waste was painted with the acrylic paint with and without incorporated nanoparticles (Table 2).

Figure 17 shows the spectral and calculated reflectance for the cladding samples, considering the black acrylic paint as the standard, the 8% TiO_2 30 nm doped standard as N1, 8% ZnO 500 nm as N2 and 8% SiO_2 60-70 nm as N3.

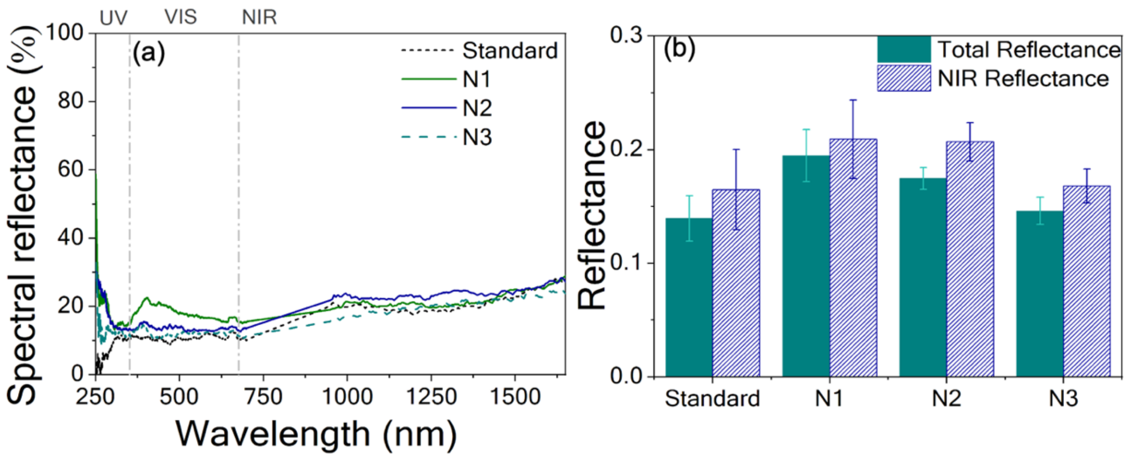

Figure 17: (a) Spectral and (b) total and NIR averaged reflectance calculated by ASTM E903 for the alkali-activated cladding samples with nanoparticles incorporation (N1 – TiO_2; N2 – ZnO; N3 – SiO_2).

As expected for dark colours in the visible range (VIS), 20% should be lower [42, 57]. Conversely, sample N1 (doped with TiO_2) has a higher visible reflectance, Figure 17a, while samples N2 and N3 can be classified as dark based on the VIS reflectance. The doped samples (N1, N2 and N3) also showed changes in the UV and NIR range.

Like the ETICS assessment, the standard black cladding sample (Figure 17b) shows higher reflectance than the acrylic paint, with a 30% improvement in NIR reflectance due to the coating type (acrylic paint vs. painted cladding). However, all inclusions increase reflectivity at a lower intensity for cladding than ETICS. N1 (TiO_2) is the best cladding formulation, increasing NIR reflectance by 27%, while N2 causes an increase of 25% and N3 has the smallest gain of 2%.

According to the criterion of colour aesthetics, the CIELab coordinates (Figure 18a) of the standard samples have a similar value to the standard acrylic paint (Figure 11a), while the admixture of nanoparticles, samples N1 and N2, decrease the coordinate values and change the hue from orange to blue, as can be seen in Figure 18b for the hue value above 90°.

On the criteria of colour aesthetic the CIELab coordinates (Figure 18a), the standard samples have a similar value of the acrylic paint standard (Figure 11a), while the incorporation of the nanoparticles, sample N1 and N2, reduce the coordinate values modifying the colour shade from orange to blue, as seen in Figure 18b for the hue value higher than 90°. The best candidate under the colour parameters is N2 and N3 due to the lower hue and chroma variation.

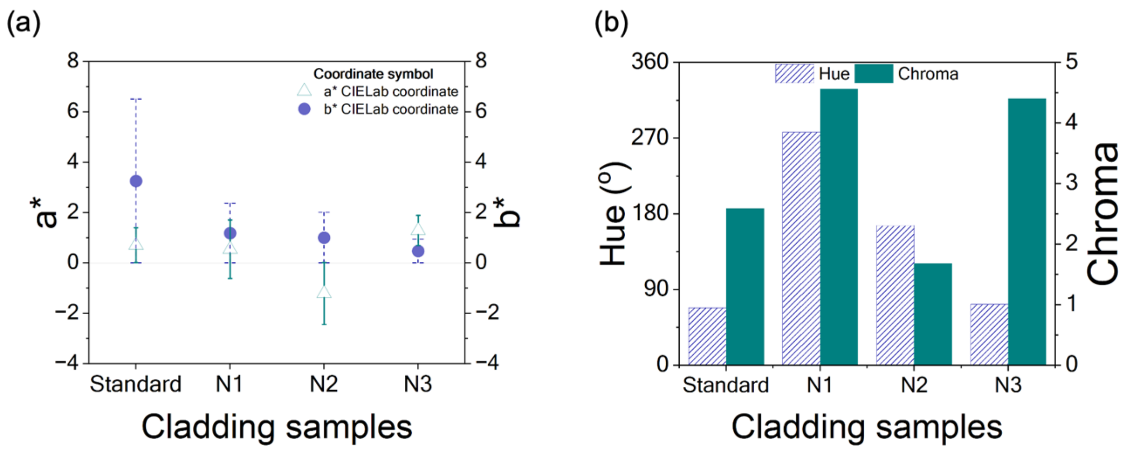

Figure 18: Colour parameters of cladding samples painted with doped acrylic paint.

Despite the colour parameters for aesthetic performance, evaluating the total colour difference (DE) and lightness (DL) is necessary, Figure 19. In the case of the doped paint, the cladding becomes lighter with the incorporated nanoparticles, with the worst result for titanium oxide (N1) and the best for silica (N3). The levels of ΔE are higher than the ETICS rating, with the N1 and N2 formulations having level 2 and N3 having level 1 perception.

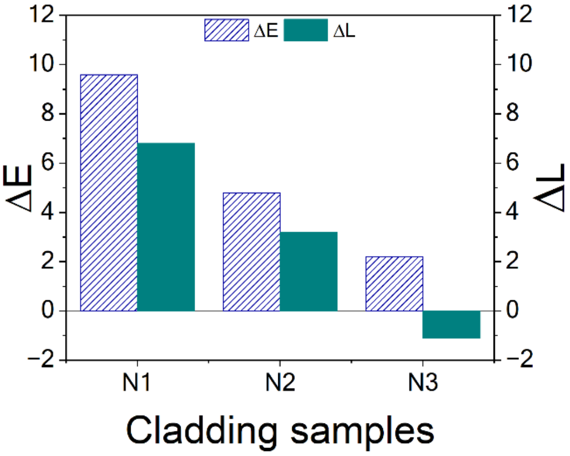

Figure 19: Colour and lightness difference of cladding samples coated with doped finishing coat.

Emissivity is a thermal property that depends on surface characteristics, such as roughness and colour glow. In the case of the cladding samples, Figure 20, no significant variation was found between the formulations, and an average value of 0.84, the same value as that of the ETICS and in the range of the façade materials.

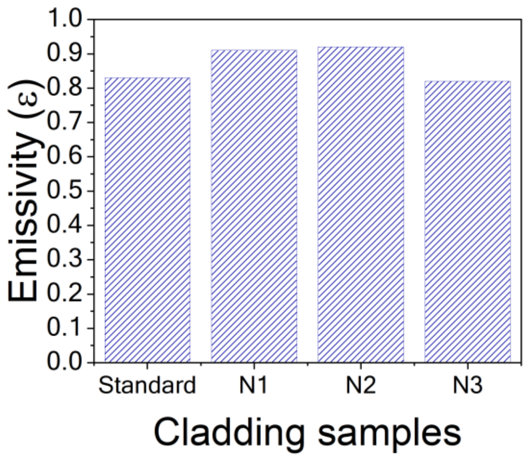

Figure 20: Emissivity of cladding samples coated with doped finishing coat.

According to the criterion of improving the NIR reflectance without changing the colour of the painted cladding, N1 is the best formulation as it increases the NIR reflectance by 25% and has a colour difference of 2.2. In comparison, sample N2 increases the reflectance by 25%, resulting in a colour difference of 4.8, and the worst formulation, N3, at a 2% increase in the NIR range and a colour difference of 9.6.

4. Conclusions and Perspectives

This work studied the effect of incorporating TiO_2, SiO_2 and ZnO nanoparticles on the thermo-optical properties of finishing coats for thermal enhanced façade systems, such as ETICS and waste-based cladding panels. It was found that:

- The thermo-optical performance depends on the type and size of the nanoparticles in a combination of the incorporated material;
- Comparing the same formulations for different applications, TiO_2 shows the best performance in ETICS, SiO_2 in acrylic paints and ZnO in colourant formulations;
- The titanium oxide is the best particle, improving NIR reflectance by 50% with a ΔE of 3.4, while the zinc oxide improves NIR reflectance by 28% with 3.2 from ΔE, and the SiO_2 improves NIR reflectance by 22% with a total colour difference of 4.61;
- The colour aesthetics depend on the incorporated material, the lower ΔE for the colourant and the application of the pigment in the ETICS system; on average, the incorporation of the nanoparticles makes the colours lighter than the standard formulations in all cases studied.

These results show that it is possible to use different nanoparticles to meet the aesthetic requirements of using dark colours, to improve the thermo-optical behaviour and consequently to improve the durability of the different façade systems concerning thermal stress.

Building façades are susceptible to various wear and tear phenomena. Therefore, further evaluations of the durability of these doped top coatings for façade systems are needed and are also under development.

Author statement

Rita Carvalho Veloso: Conceptualization; Data curation; Formal analysis; Investigation; Resources; Writing - original draft. **Joana Maia:** Conceptualization; Formal analysis; Funding acquisition; Investigation; Methodology; Project administration; Supervision; Writing - original draft; Writing - review & editing; **Rodrigo Praça:** Data curation; Investigation. **Andrea Souza:** Conceptualization; Formal analysis; Investigation; Writing - original draft. **João Ventura:** Funding acquisition; Writing - review & editing; **Nuno M. M. Ramos:** Funding acquisition; Writing - review & editing. **Helena Corvacho**: Conceptualization; Funding acquisition; Supervision; Writing - original draft; Writing - review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

This work was financially supported by Project PTDC/ECI-CON/28766/2017—POCI-01–0145-FEDER-028766 funded by FEDER through COMPETE2020—Programa Operacional Competitividade e Internacionalização (POCI) and by national funds (PIDDAC) through FCT/MCTES, Project Circular2B - 37_CALL#2 - Circular Construction in Energy-Efficient Modular Buildings financing under the Environment, Climate Change and Low Carbon Economy Programme within the scope of the European Economic Area Financial Mechanism EEA Grants 2014-2021 and by Base Funding—UIDB/04708/2020 of the CONSTRUCT—Instituto de I&D em Estruturas e Construções—funded by national funds through the FCT/MCTES (PIDDAC). R. C. Veloso and A.R. Souza would like to acknowledge the support of FCT - Fundação para a Ciência e a Tecnologia for the funding of the Doctoral Grant SFRH/BD/148785/2019 and DFA/BD/8418/2020, respectively.

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Declaration of interests

☒The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: