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Preparation and characterization of high NIR reflective pigments based in ultramarine blue

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ABSTRACT

Buildings are responsible for at least 40% of energy use in most countries. High reflectance outdoor coatings can bring significant energy savings for building applications. In this context, ultramarine blue pigment (UB) has been modified to increase its near infrared reflectance by depositing a reflecting film based on TiO_2 containing different types and concentrations of nanoparticles (alumina, titania and a mixture of them). The developed pigments were characterized by X-ray diffraction (XRD), field emission scanning electron microscopy (FE-SEM) and laser dispersion.

For testing the performance of the modified pigments, they have been dispersed in a conventional waterborne paint at different percentages and characterized by UV–Vis-NIR spectrophotometry (measuring Total Solar Reflectance and CIE L × a × b ×). All the obtained paints increased the TSR in 2.65% when adding nanoparticles but the maximum value was obtained for an addition of 6 wt.% of titania nanoparticles. Higher contents of nanoparticles led to agglomeration reducing the reflectance in the final paint.

1. Introduction

Buildings are responsible for more than 40 percent of global energy use and one third of global greenhouse gas (GHG) emissions. This fact has made energy efficiency and savings strategies a priority for energy policies at world level [1,2].

Especially important has been the intensification of energy consumption in Heating, ventilation and air conditioning (HVAC) systems accounting for around 40% of total building consumption [3,4] and being the largest energy end use both in the residential and non-residential sector.

The EPBD (European Directive o the Energy Performance of Buildings) [5] was adopted with the objective of "promote the improvement of the energy performance of buildings within the community taking into account outdoor climatic and local conditions, as well as indoor climate requirements and cost-effectiveness". Building sector has the greatest potential to deliver quick, deep and cost effective reductions in GHG emissions [6,7].

The majority of the building stock in Europe is pre-1990 and 40–50% is pre-1960. In order to address the huge challenge of affordable building refurbishment, different solutions are being explored with the aim of obtaining substantial energy savings at an acceptable investment [8,9].

Solutions from the chemical and materials science can bring significant energy savings for building applications being the *high reflectance outdoor coatings* one of the most promising ones [10]. These coatings reflect sunlight radiation in the infrared part of the spectrum. Since nearly half of the solar radiation consists of near-infrared (NIR) radiation (700–2500 nm) which is a direct consequence of heat, the use of NIR reflective materials aids to preserve lower exterior surface temperatures of buildings [11,12]. The amount of heat conducted to the interior decreases being possible to save up to 15% of air conditioning energy consumption depending on the climate region. Costs of applying these coatings are affordable and offer reasonable payback times [10].

These high reflectance coatings mainly refer to paints containing cool pigments. Although white pigments such as titanium dioxide (TiO_2) have a high solar reflectance, they cannot always satisfy the consumer's demand as they are white. One strategy for non-white cool pigment production is the use of complex inorganic colored pigments (CICPs). One barrier for the use of these pigments is their

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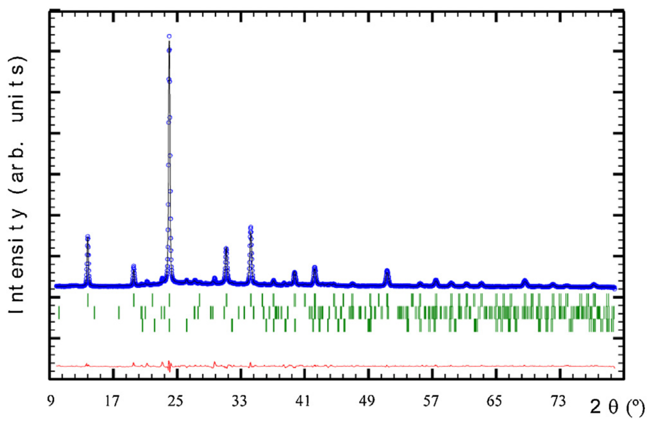

Fig. 1. X-ray diffraction refinement for the Ultramarine pigment. Circles denote experimental points; upper solid line is calculated profile. Theoretical peak positions (vertical sticks) and difference line are shown in the bottom of the pattern.

toxicity character as most of them contain toxic metal elements (Co, Cd, Pb, Cr) restricted by the environmental regulations [13,14].

Ultramarine blue pigment (UB) is an inorganic pigment having a sodium aluminum silicate sulfide structure ($Na_8Al_6Si_6O_{24}S_2$) similar to Sodalite. Ultramarine blue are a family of low-cost mineral pigments (cost 3–5 times lower than a CICP) and with high pigmentary properties commonly used in construction sector.

The aim of this study is to develop a cool pigment based on ultramarine blue. The strategy to modify this conventional pigment into a high reflecting pigment is to coat the pigment with a coating containing nanoparticles with a crystal structure of rutile or corundum (structures used for the CICP development).

Dispersed nanoparticles in the pigment coating will provoke multiple scattering effects achieving high reflection between 700 and 2500 nm. The suitable nanoparticles and the amount of particles in the coating are one of the most important parameter that must be optimized to achieve the fixed goal. Alumina (having a size of 13 nm) and titania (having a size of 21 nm) nanoparticles were selected due to their high diffraction index and strong light scattering.

2. Experimental part

2.1. Materials

2.1.1. Ultramarine pigment

A standard ultramarine blue pigment produced by Nubiola Pigmentos S.L. was used. Ultramarine pigment compositions are based on the crystal chemistry of the royal blue Sodalite mineral Lazurite [$Na_6Ca_2Al_6Si_6O_{24}(S_n,SO_4)_2$].

The particle size distribution of the pigment was analyzed using a Malvern Mastersizer 2000 at the same conditions explained above. A stable and mono-modal distribution was obtained for this system being the main particle size d_{50} of 1.2 μm.

The scanning electron microscope (SEM) micrograph indicates rather irregular shape of the pigment particles with a particle size in the range from 1 μm to 2 μm in good agreement with the particle size distribution results.

The purity of the sample was evaluated by standard X-Ray diffraction measurements. The identification of the pattern was evaluated, in all the cases, using the Powder Diffraction File (PDF) database. PANalytical XíPert High Score program was used for identification and Miller indexing of all the observed maxima. Moreover, the selected patterns used for the identification of the

Table 1
Processed pigments (nanoparticle type and concentration added to the titania coating).

Pigment	Added nanoparticles to the coating solution	%wt. nanoparticles[a]
Pigment 1	Al_2O_3	2
Pigment 2		4
Pigment 3		6
Pigment 4		8
Pigment 5	TiO_2	2
Pigment 6		4
Pigment 7		6
Pigment 8		8
Pigment 9	50%	2
Pigment 10	Al_2O_3 + 50%TiO_2	4
Pigment 11		6
Pigment 12		8

[a] related to the coating solution weight.

Table 2
DL and TSR of processed pigment.

Alumina (Al_2O_3)			
Pigment	%wt. Pig	TSR (%)	DL
1	5	62.95	72.57
(2 wt%)	10	55.72	61.04
	15	51.87	53.59
2	5	63.08	73.35
(4 wt%)	10	56.87	61.44
	15	51.58	53.84
3	5	66.69	73.74
(6 wt%)	10	56.8	61.62
	15	51.64	54.54
4	5	66.43	74.26
(8 wt%)	10	55.72	62.42
	15	51.81	54.22
Titania (TiO_2)			
Pigment	%wt. Pig	TSR (%)	DL
5	5	62.41	71.86
(2 wt%)	10	56.15	62
	15	51.88	54.97
6	5	64.9	72.37
(4 wt%)	10	56.47	61.44
	15	49.95	52.14
7	5	65.73	73.28
(6 wt%)	10	56.51	60.85
	15	51.7	53.68
8	5	66.22	72.57
(8 wt%)	10	55.4	61.96
	15	52.82	55.14
Mixture (50%Alumina + 50%Titania)			
Pigment	%wt. Pig	TSR (%)	DL
9	5	64.45	72.55
(2 wt%)	10	55.95	60.44
	15	52.03	54.36
10	5	66.27	73.39
(4 wt%)	10	56.01	61.22
	15	52.36	54.49
11	5	66.27	73.16
(6 wt%)	10	58.15	62.44
	15	51.81	55.11
12	5	65.45	73.96
(8 wt%)	10	56.6	61.97
	15	52.89	55.26
Reference (un-modified blue)			
Pigment	%wt. Pig	TSR (%)	DL
Original	0	80.98	94.61
	5	58.26	64.54
	10	53.86	58.94
	15	51.26	57.03