NEW GENERATIONS OF PIGMENTS FOR THE THERMAL EFFICIENCY OF BUILDINGS

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1. ABSTRACT

The requirements in terms of energy efficiency in buildings are increasingly stringent, since buildings are responsible for 40% of energy consumption and 36% of CO_2 emissions in advanced countries, according to the Green Building and LEED Core Concepts Guide (U.S.Green Building Council). One of the critical aspects of energy efficiency in the climate change strategy, because of global warming, is the low solar reflectivity of building envelopes as well as of public urban spaces (streets and roads). The global albedo effect is being reduced not only by the reduction in snow-covered area (owing to climate change) but also by the colossal increase in low solar reflective urbanised (asphalted) area. In the field of paints, intensely coloured but unstable organic pigments are used to obtain coloured layers: the CMYK four-colour system based on copper phthalocyanine cyan (blue pigment 15: 4), quinacridone magenta (red pigment 122), diarylated yellow (yellow 12) and carbon black, have an optimum intensity and reflectivity although with low reflectivity in the cases of cyan and black. Inorganic pigments are an alternative to organic pigments because of their durability and stability. Standard four-colour inkjet printing today has a significant reflectivity, except for black. This paper presents a CMYK four-colour system based on Co-Celsian, Cr-pseudobrookite, Ni-geikielite and Cr-hematite with a similar colorimetric behaviour (L*a*b*) but with higher solar reflectivities, which can be developed in situ from colloidal dispersions for DoD inkjet applications. Finally, a CMYK four-colour system based on compositions with lanthanidesis discussed.

2. INTRODUCTION

Energy efficiency requirements for buildings are becoming increasingly stringent since buildings are responsible for 40% of energy consumption and 36% of CO_2 emissions in advanced countries, according to the Green Building and LEED Core Concepts Guide(U.S. Green Building Council) (1). The State of California prescribes a minimum Solar Reflectivity Index,SRI,of 75% (with a minimum of solar reflectance at 3 years aging of 0.63 and a minimum solar emittance of 0.75) (2). On November 30, 2016, the European Commission proposed an update of Directive 2012/27/EU on energy efficiency, under which all new buildings must have buildings with almost zero energy consumption by December 31, 2020 (public buildings have a deadline of December 31, 2018) (3). One of the critical aspects of energy efficiency in the climate change strategy, because of global warming, is the low solar reflectivity of building envelopes as well as public urban spaces (streets and roads). The global albedo effect is being reduced not only by the reduction of snow-covered area (because of climate change) but also by the colossal increase in low solar reflective urbanised (asphalted) area. In addition, indoors, the engineering society of American lighting recommends minimum values of total floor reflectance of 25% (in this case in the visible spectrum) that results in an increased light energy savings of up to 25% and is rewarded in LEED certification with 2 credits.

In this sense, in the field of paints, organic pigments with low solar reflectivityare used to obtain coloured layers: it’s typical to find the CMYK four-colour system based on copper phthalocyanine cyan (blue pigment 15:4), quinacridone magenta (red pigment 122), diarylated yellow (yellow 12) and carbon black (4), which all have an optimum intensity and reflectivity although with low reflectivity in the cases of cyan and black. Inorganic pigments are an alternative to organic pigments (5). In the four-colour inkjet printing process, cobalt-doped gahnite (alone or mixed with cobalt olivine) is used for cyan (actually a blue), spinel (Zn-Fe-Cr-Al) for magenta (actually a bright brown), praseodymium yellow in zircon and spinel black in (Co-Cr-Fe-Mn) (6). This four-colour systemproduces a significant SRI, except in the case of black.

3. OBJECTIVES

In this paper, the new generations of inorganic pigments with high NIR reflectivity are discussed and a four-colour CMYK system based on Co-Celsian, Cr-pseudobrookite, Ni-geikielite and Cr-hematite of similar colorimetric behaviour (L*a*b*) is presented but with greater solar reflectivities, which can be developed in situ from colloidal dispersions for DoD inkjet applications. A four-colour system of pigments based on lanthanides is also proposed.

4. EXPERIMENTAL

Cool pigments are highly-reflective pigments in the near infrared (NIR, 780-2100 nm), that protect the building with a cladded envelope highly reflective to infrared rays, which has several interesting environmental advantages:(a) Significant thermal conditioning savings for the building, (b) Improved air quality, as the temperature is tempered by cooling coverings, (c) Decreased greenhouse gas emissions and (d) Mitigation of the urban heat island effect (7).

When solar radiation hits the roof and walls of a building, part of the radiation is reflected and part is transferred to the interior of the building. The total solar reflectivity (TSR or simply R) of the surface is measured using the UV-Vis-NIR diffuse reflectance spectrometry technique (300-2500 nm) relative to the standard solar spectrum (total fraction of solar energy reflected in the standard atmospheric conditions described above). The solar spectrum used is that of the American Society for Testing and Materials (ASTM G173-03, 2003). By this method, the total solar reflectivity of the surface R is calculated by equation 1.

$$R = \frac{\int_{300}^{2500} r(\lambda) i(\lambda) d\lambda}{\int_{300}^{2500} i(\lambda) d\lambda} \text{ (equation 1)}$$

Where r(λ) is the measure of the spectral reflectance at each wavelength of the studied surface and i(λ) is the spectral irradiance at the considered wavelength of the standard solar spectrum of the American Society for Testing and Materials (ASTM G173-03, 2003) (8).

In the present work four CMYK four-colour systems have been analysed:

a) Four-colour organic CMYK using the four basic organic colours based on those already mentioned, copper phthalocyanine cyan (blue pigment 15: 4), quinacridone magenta (red pigment 122), diarylate yellow (yellow 12) and carbon black.

b) In the Standard Ceramic Four-colour CMYK inkjet process, the cobalt-doped gahnite (alone or mixed with cobalt olivine) is used for cyan (actually a blue), spinel (Zn-Fe-Cr-Al) for magenta (actually a bright brown), praseodymium yellow in zircon and spinel black in the (Co-Cr-Fe-Mn) system.

c) Four-colour Ceramic high SRI CMYK based on Co-Celsian, Cr-pseudobrookite, Ni-geikielite and Cr-hematite that can be developed in situ from colloidal dispersions for DoD inkjet applications. The structural characteristics of this four-colour system are summarised below:

- Co-Celsian cyan: based on the cobalt doping of the Celsian feldspar $(_{0.9}Co_{0.1})Al_2Si_2O_8$(monoclinic, Space group $I2_1/c$).Cobalt replaces barium. The barium configuration in the celsian has avery close oxygen with a significant effect on the Si-O-Si bond angles (9).In fact, in the Celsian, Al and Si present a partially ordered lattice and the Ba presents an irregular configuration with 10 neighbouring oxygens not equidistant from Ba. This disorder induces low symmetry and increases the kinetic barrier of crystal nucleation. $BaCO_3$ (Panreac), Co_3O_4 (Aldrich), $Al(OH)_3$ (Panreac), and SiO_2 (quartz, Sibelco)were used as precursors. The mixture was calcined at 1,200°C maintaining the temperature for 3 hours.

- Cr-pseudobrookite Magenta based on chromium doping of pseudobrookite Fe_2TiO_5(Orthorhombic, Cmcm Space Group) with an extraordinary structural flexibility to accommodate different cations (with varied valences +2, +3 or +4) in its two different and distorted octahedral positions, A (4c) andB (8f), producing broad solid solutions with the general formula $[M^{3+},M^{2+},Ti]^A[Ti,M^{2+},M^{3+}]^B{}_2O_5$.This ability together with its high melting point and high refractive index makes the titanium pseudobrookites excellent candidates for the development of ceramic pigments (10). Cr_2O_3, anatase TiO_2 and hematite Fe_2O_3 (all supplied by Panreac) were used as precursors. The mixture was calcined at 1,000°C maintaining the temperature for 3 hours.
- Ni-geikielite yellow based on the nickel doping of geikielite $(Mg_{0.5}Ni_{0.5})TiO_3$ that belongs to the ilmenite group ($FeTiO_3$) (trigonal, Space Group R3).The stability and crystallisation of the Co-ilmenite phase ($CoTiO_3$) is well known in the literature as ceramic pigment. Related to this system, the Mg_2TiO_4 compounds with spinel structure and $MgTi_2O_5$ with pseudobrookite structure are considered in the literature as structures stabilised by entropy: their relatively high entropy is associated with mixing different cations in specific crystallographic positions (11).$MgCO_3$, anatase TiO_2 (Panreac) and NiO (Prolabo) were used as precursors. The mixture was calcined at 1,000°C maintaining the temperature for 3 hours.
- Black Cr-hematite based on chromium doping of Fe_2O3 hematite (Trigonal, space group R-3c), isomorphic hematite to corundum presents a structure with iron in the centre of a distorted octahedron with three oxygens at a distance and another three at a shorter distance readjusting the Bragg (father and son) measurements, who considered that the Al was surrounded by 6 equidistant oxygens in the ruby (solid solution of chromium in corundum) (12). This solid solution (13) is different from another pigment in the chromium-iron-oxide system based on chromium $FeCr_2O_4$ although both undergo colour changes towards the yellow-brown when they interact with the Mg and Zn ions of the glazes (14). They were used as Cr_2O_3 and Fe_2O_3 precursors (Panreac). The mixture was calcined at 1,000°C maintaining the temperature for 3 hours.

d) Latest generation four-colour system, based on pigments containing lanthanide elements in their formulation.

In the ceramic samples the precursors were mixed in a ball mill using acetone as a dispersant;when the acetone had evaporated, the powdersobtained were calcined at the indicated temperature. To obtain nano-colloidal dispersions, a method of coprecipitation from the precursor nitrates (Aldrich) was used, except for Si and Ti, for which silicon teratoxide TEOS and titanium n-butoxide were used as precursors,respectively. The nitrates were dissolved in water, then the alkoxides were added (if necessary) and ammonia was slowly added, continuously stirred until pH 7 at 70°C. The powders were glazed at 5% in a double-firing frit (1,050°C).The samples were characterised by the following techniques:

a) The powder samples were characterised by X-ray powder diffraction of therandomly oriented powder in a Siemens D5000 diffractometer with Cu $K_\alpha$radiationin the range 10-70°2θ, scan speed 0.05°2θ/s, time constant 10 s and conditions of 40 kV and 20 mA. Glazed pieces were obtained from the powders with glazes at 5% by weight in a conventional double-firingfrit of composition ZnO-SiO_2-CaO (1,050°C).

b) The colorimetric characterisation of the small glazed slabs was carried out by measuring the L*a*b* colour parameters following the CIE methodology (Commission International de l'Eclairage) using the Jasco V670 spectrometer, with D65 illuminant and 10°observer. In this method, L* measures lightness (100 = white, 0 = black), a* and b* measure chroma (-a*= green, + a*= red, -b*=blue, + b*=yellow) (15).The microstructural characterisation of the powders was carried out with a LEYCA Leo-440i electron microscope (SEM, Scanning Electron Microscopy).

c) The total solar reflectivity (TSR or simply R) of the surface has been evaluated using the UV-Vis-NIR diffuse reflectance spectrometry technique (300-2,500 nm) relative to the standard solar spectrum, using a Jasco V670 spectrometer of the powder samples and glazed pieces according to the method described above. To compare the TSR of two pigments it is necessary that their performance or dyeing strength (evaluated through L*) be similar, so it is convenient to extrapolate TSR values to a value of L*, usually 65 (R_{65}) (16).

5. RESULTS AND DISCUSSION

5.1. ORGANIC PIGMENTS

Fig. 1 shows the organic-based pigments chosen for their optimal intensity and solar reflectivity and black carbon powder marketed in emulsion form applied in 10% vinyl paint and their CIEL*a*b* values (Fig. 1.a). The application in paint produces very bright colours and with low reflectivity values in cyan and above all black (Table 1).The pigments are not stable and when calcined at 500°C, the phthalocyanine copper cyan becomes greenish, the carbon disappears and a white residue of calcium carbonate remains, added as inert material to the emulsion, as observed in the X-ray diffraction of the white powders obtained (Fig.1.b) The diffuse reflectance spectra Vis-NIR of the samples in Fig.1.c show the different reflectivities noted.

5.2. INORGANIC PIGMENTS USED FOR INKJET INKS

Table 1 shows the results obtained with inorganic pigments used in powder in inkjet inks, added at 10% in vinyl paint and added at 5% in porcelain stoneware frit (e) with their CIEL*a*b* values and corresponding Vis-NIR spectra.The application in paint presents less vivid colours than in the case of organic paints (b* less negative in cyan, a* lower in magenta, b* lower in yellow and higher values of a* and b* in black); however, the R and R65 reflectivity values improve to those of organic, except in magenta.

5.3. INORGANIC PIGMENTS WITHOUT LANTHANIDES

Figure 2 shows the results obtained with the proposal of a new CMYK palette of pigments prepared in the form of colloidal dispersion based on the aforementioned systems. In the case of Celsian-based cyan doped with cobalt $Ba_{0.9}Co_{0.1}BaAl_2Si_2O_8$ (Figure 3.a): with the colloidal method we obtain dispersions that produce acceptable blue films by screen printing (Fig.3.a), in the powder no residual quartz observable to X-ray diffraction is detected (not shown) presenting the clean Celsian phase, the colour of the powders is more intense than that obtained by the traditional method, although with lower b* (L*a*b*= 64.9/0.4/-35.1 for CE and 47.7/-2.1/-19.0 for CO).In the glaze, the CO sample shows more intensity of L*colour and better blue saturation (L*a*b* =59.8/0.1/-16.6 for CE and 57.4/1.8/-22.4 for CO)

In the case of the proposed magenta of pseudobrookite doped with chromium $(Fe_{1,9}Cr_{0,1})TiO_5$ (Fig.3.b), the colloidal deposition by screen printing generates homogeneous brown films (L*a*b* =60.9/7.1/12).The calcined powder presents pseudobrookite as a single phase without the presence of residual hematite detected in the XRD (not shown) of the ceramic sample. The powder has a red hue a* higher than the ceramic powder (L*a*b* = 43.8/5.8/6.2 in CE and 46.2/6.8/7.6 in CO).The behaviour in the glaze is similar to the ceramic in intensity L* and red hue a* (L*a*b* = 43.6/18.8/12.4 for CE and 41.2/16.1/15.6 for CO)

In the yellow based on ilmenite geikielite doped with nickel $(Mg_{0,5}Ni_{0,5})TiO_3$(Fig.3.c), the colloidal deposition by screen printing generates homogeneous yellow films (L*a*b* = 71.6/6.8/40.3) with a much higher value of b* than the results discussed below for the glaze. The calcined powder (L*a*b* =61.7/4.5/27.0 in CE and 70.6/15.4/44.0 in CO) is a much higher yellow than the colloidal sample with b* 44 versus only 27 of the CE powder and with red to a* high tone.The colloidal powder CO presents almost solely the ilmenite geikielite crystalline phase, while the counterpart CE powder has residual diffraction peaks (not shown) associated with the karrooite pseudobrookite (MTi_2O_5) of relative intensity and little significant in CO.

In the case of the black, based on the solid solution of chromium in hematite $Cr_{0.5}Fe_{1.5}O_3$ (Fig.3.d), the colloidal deposition by screen printing generates homogeneous brown films (L*a*b* = 54.1/6.3/4.5).The calcined powder (L*a*b* = 42.3/-0.3/0.6 in CE and 41.5/0.0/0.6 in CO) has an excellent black colour and similar to that obtained with the CE method. X-ray diffraction (not shown) indicates the single phase hematite in both samples. The glaze composition in the double-fired glaze becomes brownish (L*a*b* = 34.1/11.6/4.0 in CE and32.9/2.7/-3.9 in CO), although it does so less than its ceramic counterpart (a* = 2.7 versus 11.6 in CE).The browning of this solid solution is considered in the literature due to the entrance into the surface structure of the Mg (II) and Zn (II) ion particles coming from the glaze (13).

Figure 4 summarises the results of the Vis-NIR spectroscopy of the powdered and glazed CO colloidal samples of the proposed palette without lanthanides. In Table 1, the results of this palette can be compared with the usual inkjet results. A greater reflectivity is observed, both in direct R and in the extrapolatedreflectivity at L* = 65 (R_{65}) in all colours except yellow, both in the powder and glaze measurements.

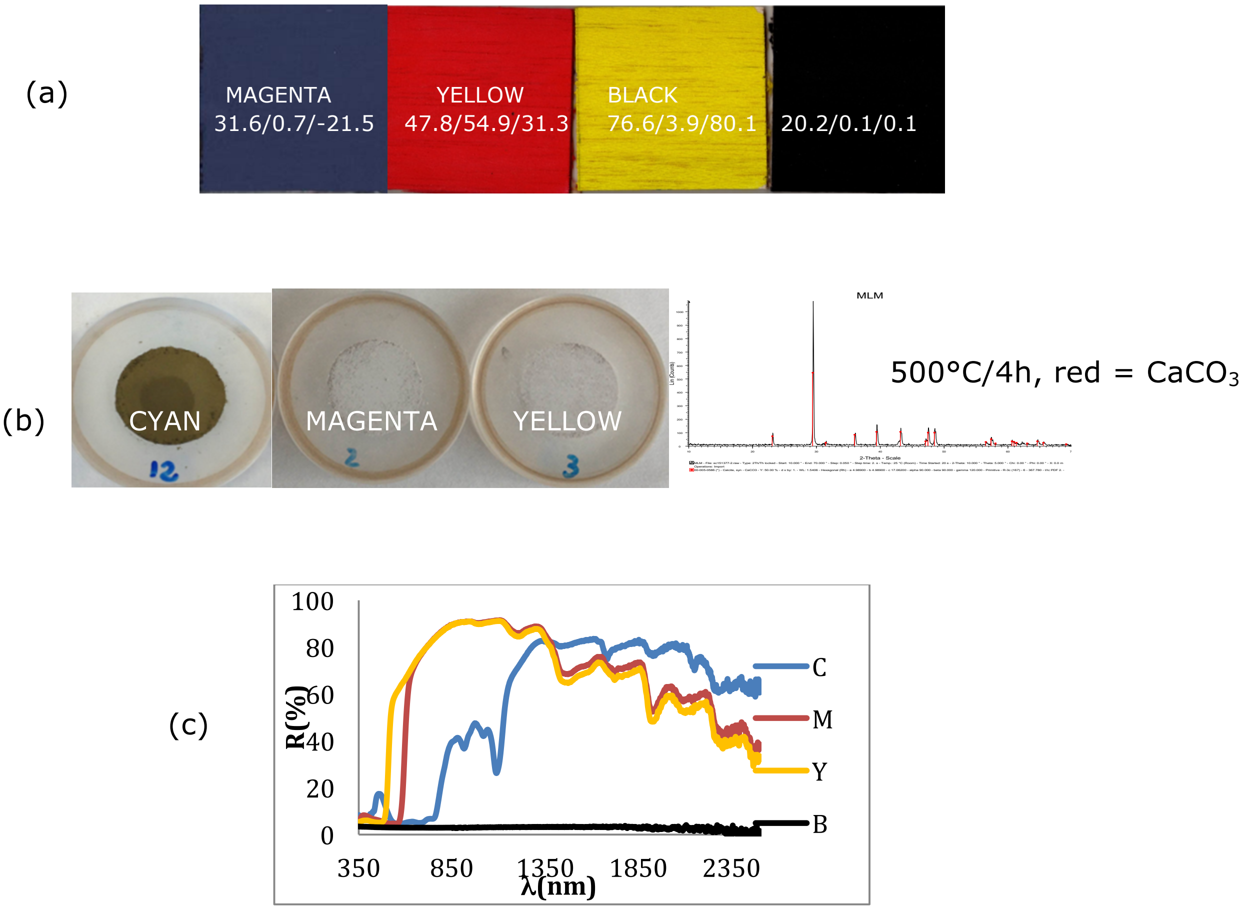

Figure 1._Organic Pigments and Carbon Black:(a) In vinyl paint at 10% and CIEL*a*b*, (b) Calcined at 500°C/3h and X-ray diffraction of the white powders obtained, (c) Vis-NIR diffuse reflectance spectra of the samples._

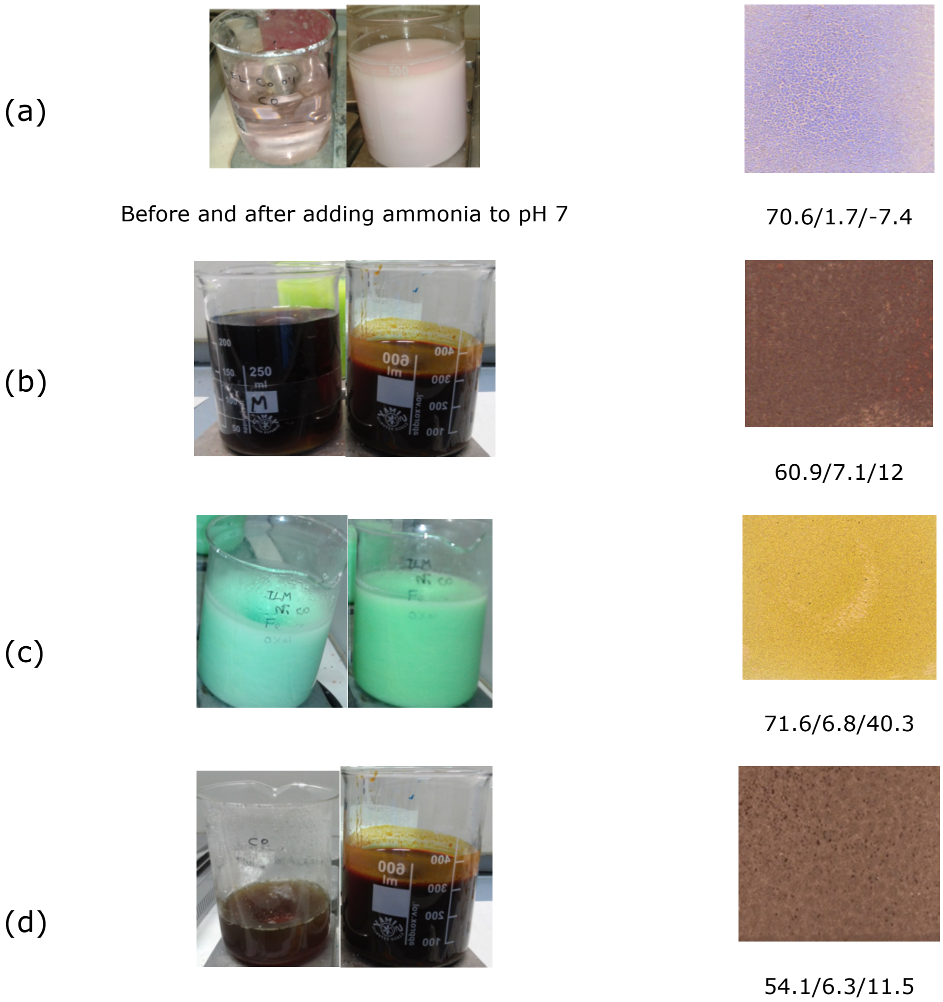

Figure 2.*Preparation of the Nanocolloid Dispersion (left) and Direct Screen-printing Application (48 threads/cm) on Monoporous Body (right):(a) Celsian* $Ba_{0.9}Co_{0.1}BaAl_2Si_2O_8$*(b) Pseudobrookite* $(Fe_{1.9}Cr_{0.1})TiO_5$*, (c) Geikielite* $(Mg_{0.5}Ni_{0.5})TiO_3$*.*

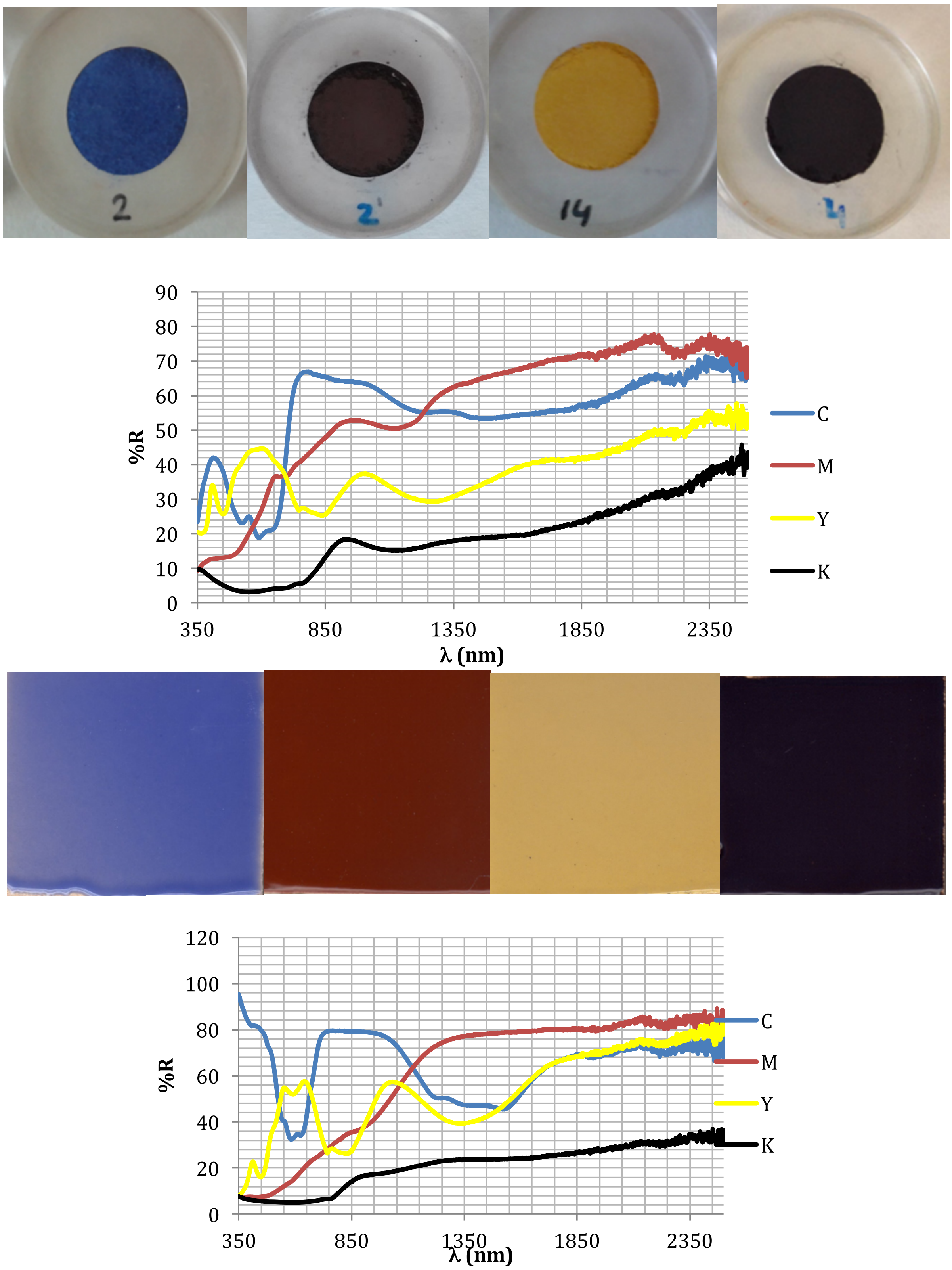

Figure 4.*Vis-NIR Spectrum of the CMYK Colloidal Samples Studied: a) Of the powders, b) Of the tiles glazed at 5% in double-firing frit (1,050°C)*

SAMPLE	L*a*b*	R	R_{65}	R (Vis)	R(NIR)	R_{65}(NIR)
ORGANIC (paint 10%)						
CYAN	31.6/0.7/-21.5	29	59	8	51	100
MAGENTA	47.8/55.0/31.3	58	78	34	84	100
YELLOW	76.6/3.9/80.1	65	55	48	82	70
BLACK	20.2/0.1/0.1	3	9	3	3	10
INKJET (paint 10%)						
CYAN	44.6/-8.9/-16.2	34	50	23	63	92
MAGENTA	32.5/11.2/7.5	23	46	8	33	66
YELLOW	85.0/-1.6/56.9	73	56	63	79	60
BLACK	27.8/-0.5/-1.3	7	16	2	10	24
INKJET (Powder)						
CYAN	52.6/-6.4/-13.5	35	43	25	42	52
MAGENTA	42.5/5.2/6.1	23	35	7	33	51
YELLOW	90.2/-1.9/47.2	67	48	61	71	51
BLACK	39.7/-0.3/0.2	6	10	2	9	15
INKJET (Double firing 5%)						
CYAN	27.5/5.9/-12.8	12	21	4	16	28
MAGENTA	32.6/13.0/9.2	30	60	6	46	92
YELLOW	80.6/-7.1/45.3	64	52	54	72	58
BLACK	27.7/0.1/0.8	6	14	1	11	26
CMYK Palette (Powder)						
CYAN	47.7/-2.1/-19.0	64	87	60	69	94
MAGENTA	46.2/6.8/7.6	35	49	15	55	77
YELLOW	70.6/15.4/44.0	42	39	40	45	42
BLACK	41.5/0.0/0.6	13	20	5	19	30
CMYK Palette (Double firing 5%)						
CYAN	57.4/1.8/-22.4	46	52	32	62	70
MAGENTA	41.2/16.1/15.6	39	62	24	54	85
YELLOW	71.1/6.0/19.3	35	32	37	33	30
BLACK	32.9/2.7/-3.9	11	22	4	17	34

Table 1. *CIEL*a*b* and R Values Compared.*

5.4. INORGANIC PIGMENTS WITH LANTHANIDES

There are a large number of high reflectivity NIR pigments (cool or cooling pigments) in the literature that usually have stoichiometries with lanthanide components that make the product more expensive but which have a higher NIR reflectivity in addition to similar tonalities, and in many cases eliminate or decrease the use of heavy metal transition cations of proven toxicity, such as Co, Cr, Mn, Zn, Ni on which the 3.1 and 3.2 palettes previously discussed are based.

In the case of cyan (actually a blue in standard inkjet practice), E. Aranzabea et al.(16) designed a process to increase the reflectivity of ultramarine blue based on sodalite ($Na_8Al_6Si_6O_{24}S_2$), a low cost inorganic pigment compared to when they have to use cobalt. For this they deposit TiO_2 nanoparticles and/or Al_2O_3 on the sodalite particles using a sol-gel method with controlled hydrolysis of titanium butoxide, increasing the R_{65} of 58.16 for additions in sodalite paint of 5% to values around 59.7.Sodalite is unstable in ceramic environments. Smith AD, et al.(17.18) developed an intense blue pigment based on the solid manganese solution in the perovskite by calcining of the oxide mixture at 1,200°C (ceramic route with or without pelletizing)an intense blue pigment based on the manganese solid solution in perovskite$YInMnO_3$ (the best blue is the stoichiometry $YIn_{0.8}Mn_{0.2}O_3$ with L*a*b* = 34.1/11.7/-44.4 and R = 34% R_{65}=65% in powder and in vinyl paint at20% 77.9/-2.9/-19.3 and R (NIR) = 62%, R $(NIR)_{65}$=65 (17)).The pigment protected by patent (18) indicates that it can be applied in glass and ceramics but the patent does not provide data for these applications, though it does in cement and in vinyl paint. Sheethu et al.(19) describe a blue that is based on lanthanum and lithium solid solution in the tetragonal network $SrCuSi_4O_{10}$ (the best blue is $Sr_{0.3}La_{0.7}Cu_{0.3}Li_{0.7}Si_4O_{10}$ with L*a*b* = 49.6/10.4/-51.7 obtained by calcination of the oxides at 950°C/16h and with a R(NIR)=66, $R(NIR)_{65}$=86); however, the stability in aggressive matrices is not verified. Zhang et al. study a similar system with europium although they use a MOD method or citrate route (20); the best blue is $Sr_{0.8}Eu_{0.2}Cu_{0.3}Si_4O_{10}$ with L*a*b*=46,6/-4,6/-28,1 obtained by calcination of the oxides at 900°C/2h and with R(NIR)=72.3, $R(NIR)_{65}$=100).

For magenta (brown for standard practice) Vishnu et al.(21) obtain red-brick and brown pigments with the solid solution of Pr (IV) in a cerate with cubic fluorite structure $Y_2Ce_2O_7$; the best red is $Y_2Ce_{1.7}Pr_{0.3}O_7$ with L*a*b* = 32.6/18.1/12 obtained by calcination of the oxides at 1,500°C/18h and with R(NIR)=57.5,$R(NIR)_{65}$=100.The same authors obtain yellows by doping the same structure with Mo(V); the best yellow is $Y_2Ce_{1,5}Mo_{0.5}O_7$ with L*a*b* = 90.2/-4.5/62.4 obtained by calcination of the oxides at 1,500°C/18h and with R (NIR) = 80.5, R $(NIR)_{65}$=58.Thongkanluang et al.(22) obtain brown pigments using hematite composites $Fe_2O_3$with high reflectivity oxides such as Sb_2O_3, SiO_2, Al_2O_3 or TiO_2 (the most reflective powder composite L*a*b* = 35.6/15.9/11.2 reaches R (NIR) = 46.7%, $R(NIR)_{65}$= 58, glazed at 5%, fired glaze and resulting colour not described, reaches R (NIR) = 41.3 in glaze firing at 1,100°C).Jovani et al.(23)describe reds with lanthanides with a reddish-orange pigment based on the solid solution$Y_{2-x}Tb_xZr_{2-y}Fe_yO_{7-\delta}$with L*a*b* = 64/34/33 in an industrial frit at 4% for x = 0.35 with low absorption in the NIR zone.García et al. and Llusar et al. describe in 2001 the obtaining of pigments of cerium oxide doped with lanthanides (24.25) such as Pr or Tb; being clean semiconductors, they produce red colourations in monoporosa and porcelain tile glazes in solid solutions $Ce_{1-x}Pr_xO_2$ with R(NIR)=82.3, $R(NIR)_{65}$= 81 for the sample of Fig.8 x = 0.05 (L*a*b* = 66/20/24) in the case of monoporosa; at higher temperatures (porcelain stoneware) the system is unstable and pinholing occurs due to the emission of oxygen by partial decomposition of the dioxide in the sesquioxide:

$$CeO_2\ (s) \rightarrow Ce_2O_3\ (s) + 1/2O_2(g)$$

In the case of yellow, Gargori et. al (26) obtain yellow colourations by the ceramic route that improve a lot in the described colloidal CO path of double-dopedsolid solutions with V^{5+} and Ca^{2+} in pyrochlore $Y_2Sn_2O_7$ with mineralisers ($Ca_xY_{2-x}V_ySn_{2-y}O_7$) using treatments of 1,200°C/6h with L*a*b*values of the ceramic powder x = y = 0.16 of 85.7/1.1/34.5; the glaze at 5% in double-firing frit (1,000°C) yields yellows L*a*b* = 80/5/43.7 (the EC sample gives 79.3/2.6/35) with R(NIR)=81, $R(NIR)_{65}$=66.However, the pigment is not stable against higher temperature glazes and does not render colour in monoporosa glaze (1,080°C). Lili Liu et al.(27) develop interesting high-reflectivity pigments by doping perovskite $LaFeO_3$ with aluminium ($LaAl_xFe_{1-x}O_3$), calcining at 700°C/6h and using a citrate route: with low dopings x = 0 renders brown powdersL*a*b*=62.6/17.1/30.4 with R(NIR)=65.4, $R(NIR)_{65}$=68, at high dopingvalues x = 0.7 yellow powders are obtained L*a*b*=71,2/2,8/10,0 withR(NIR)=56.7,$R(NIR)_{65}$=52.

In black, the applications of lanthanides are scarcer and only one black of perovskite $CrNdO_3$ has been described modified with fluorides (28) L*a*b*=43.4/2.4/4 in powder R(NIR)=21, $R(NIR)_{65}$= 31 and glazed at 5% in double-firing frit 1,050°C 55/-1.8/3.3 gray shades R (NIR)=15, $R(NIR)_{65}$=18.Smith AD, et al.(17.18) also describe obtaining black powders that are most likely of high reflectivity in the undoped $YInO_3$, powders although they do not study them in this sense, neither in the publications nor in the patent, just glossing the blue ones obtained with manganese.

6. CONCLUSIONS

From the point of view of solar reflectivity, coloured layersof optimal organic pigments in this sense were compared:a four-colour CMYK system based on copper phthalocyanine cyan (blue pigment 15: 4), quinacridone magenta (red pigment 122), diarylated yellow (yellow 12) and carbon black, all of them with a high SRI except for cyan and black. Inorganic pigments are an alternative to organic pigments. In the inkjet process, the cobalt-doped gahnite (alone or mixed with cobalt olivine) is used for cyan (actually a blue), spinel (Zn-Fe-Cr-Al) for magenta (actually a bright brown), praseodymium yellow in zircon and spinel black in (Co-Cr-Fe-Mn).This four-colour system produces a significant SRI, except black that improves carbon black.Here we present a four-colour CMYK system based on Co-Celsian, Cr-pseudobrookite, Ni-geikielite and Cr-hematite with a similar colorimetric behaviour (L*a*b*) but with higher solar reflectivities that can be developed in situ from colloidal dispersions for DoD inkjet applications. Finally, a CMYK palette of high reflectivity with pigments containing lanthanides in their composition has been discussed.

7. ACKNOWLEDGMENTS

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