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***Corresponding author**

Guillermo Monrós, Department of Inorganic and Organic Chemistry, University Jaume I, Castelló, Castelló, Spain

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Opinion

Black Inorganic Pigments: From Black to Ultra-Black Behaviour, A Microstructural Approach

Guillermo Monrós*

Department of Inorganic and Organic Chemistry, University Jaume I, Castelló, Spain

Opinion

There are different methods for an "objective" measurement of colour such as the developed by CIE (Comission International de l´Eclairage) [1] colorimetric method referred to a standard lighting (e.g., D65) and an observer's field of view (e.g., 10º) L*a*b* and C*h* colour On this method, L* is a measure of lightness (100=white, 0=black) and a* and b* of colour parameters (-a*=green, +a*=red, -b*=blue, +b*=yellow). According to Albert Munsell [2] the optimal chroma is obtained when Lightness L* (measured by the L*a*b* method) is high for yellow (80-90), cyan (75-85) and green (70-80), middle for magenta (50-60) and red (45-55) and low for blue (25-35) hues, for a pure black L* is zero. The values of C* (chroma), h* (hue) and the tolerance ΔE* based can be estimated from L*, a* and b* parameters by the equations 1-3 respectively:

$$C^* = (a^2 + b^2)^{1/2} \text{ (eq. 1)}$$

$$h^* = \arctan(b^*/a^*) \text{ (eq. 2)}$$

$$\Delta E^* = \sqrt{\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2}} \text{ (eq. 3)}$$

On the other hand, the total solar reflectance is evaluated from UV-Vis-NIR diffuse reflectance spectra as the integral of the measured spectral reflectance and the solar irradiance divided by the integral of the solar irradiance in the range of 350 to 2500 nm for R, 700 to 2500 nm for RNIR or 350-700 nm for R_{Vis} as in the equation 4:

$$R = \frac{\int_{350}^{2500} r(\lambda) i(\lambda) d\lambda}{\int_{350}^{2500} i(\lambda) d\lambda} \text{ (eq. 4)}$$

Where, (λ) is the spectral reflectance (Wm^{-2}) measured from UV-Vis-NIR spectroscopy and $\boldsymbol{i}(\lambda)$ is the standard solar irradiation ($Wm^{-2}nm^{-1}$) according to the American Society for Testing and Materials (ASTM) Standard G173-03. For a pure black L* and R_{Vis} are zero and for a cool black pigment, which reflects efficiently NIR radiation [3], R_{NIR} should be maximised.

Coloured solids can act as pigments for paints and for polymers if its chemical stability withstands the temperature and aggressiveness of the polymeric conforming process. However, as Woldemar Weyl [4] defined, a ceramic pigment is a coloured solid stable in the Si^{4+} tetrahedral media of glazes at its relative high temperatures of maturation (from 800 ºC for soda lime glass to 1200 ºC for porcelain paste). Usually, are octahedral chromophore cations in solid solutions in highly stable crystals with a high refractive index such as spinel (n=1.8) zircon (n=1.9), cassiterite (n=2) or rutile (n=2.8). However, there are other mechanisms of colour based on heteromorphic or mordant pigments (e.g., the pink koral of hematite encapsulated in zircon or the red of cadmium sulfoselenide, also in zircon) and structural pigments (e.g., green Victoria of uvarovite garnet $Ca_3Cr_2Si_3O_{12}$) [3].

Carbon Black is the amorphous polymorph of elemental carbon produced by incomplete combustion of hydrocarbons such as petroleum, coal tar as raw material, it shows fine particle size with very low crystallite size (3 nm for studied sample), and high refraction index (2.3) which shows L*a*b*=20.2/0.1/0.1 and $R_{Vis}/R_{NIR}/R$ (%) =3/3/3. On the other hand, graphite is a black crystalline hexagonal allotropic form of carbon which is an efficient conductor of electricity [5,6]. Colour characteristics of nanographite samples with increasing crystallite size of 30.2, 40.8 and 64.3 nm measured by Scherrer method [3] shows L*=40.0, 44.0 and 41.0 respectively, and R_{Vis}=7.3, 8.2 and 9.0 % respectively, indicating a decrease of dark shade with the crystallite size of the material. Around 2003 was reported the called NPL Super Black surface prepared by electroless process. This Ni-P ultra-black shows an integrated absorptance (α) between 90-93 % stable up to 200 °C. The chemical composition of coatings shows Ni and Zn particles embedded in a suitable matrix of NiO, Ni_2O_3 and Ni_7P_3 [7]. Coatings absorb 99.7% (R_{Vis}=0.3%) of the visible light incident upon them are routinely produced. In July 2014, Ben Jensen, founder of Surrey Nano Systems (a spin-out from the University of Surrey's Advanced Technology Institute in 2006), reports the Vantablack coatings: the name joints the acronym VANTA (vertically aligned nanotube arrays) and black. The coating was grown from a Chemical Vapour Deposition process (CVD) and absorbs 99.965% of visible light (R_{Vis}=0.035%) with a very dark colour L*a*b*=0.2/0.9/-1 [8]. Some darker coatings are possible but only Vantablack is a commercial sprayable paint. Microstructure of both Ni-P ultra-black and Vantablack coatings are critical for the absorbing light [7,8].

If carbon black is the reference of black pigments for paints, the elegant fond noir of Sèvres [3,9] is the reference for black ceramic pigments. It is a blue-black pigment based on $CoFe_2O_4$ spinel, sometimes modified by Mn addition, associated to the interest in creating porcelain that resembled lacquer of furniture around 1769, and shortly after the manufactory began producing hard-paste porcelain. This pigment obtained from oxides, chemically modified by Zn addition, and fired at 1000 ºC for 3 h shows L*a*b*=30.0/7.8/7.7 and $R_{Vis}/R_{NIR}/R(\%)$ = 7.8/36.5/20.3. The pigment shows a good black cool performance in 2wt% addition to porcelain paste (1190 ºC) with L*a*b*= 40.9/3.3/5.0 and $R_{Vis}/R_{NIR}/R$ (%) = 12.0/31.6/20.6, with relatively low R_{Vis} and high R_{NIR}. From the chromium introduction in Sévres by Brogniart in 1802 [10], the iron-chromium black (a solid solution of iron in eskolaite Cr_2O_3) can be prepared in the factory, where a palette of 138 pigments numbered between 10001 and 10138 was established at the Sèvres laboratory, among which 76 pigments are composed of chromium oxides including probably Fe-Cr_2O_3 eskolaite black (trigonal, R-3c) and/or $FeCr_2O_4$ spinel black (cubic, Fd-3m) [11,12]. This pigment obtained from oxides, chemically modified by Si addition, and fired at 1000 ºC for 3 h shows L*a*b*=22.1/1.7/0.2 and $R_{Vis}/R_{NIR}/R$ (%) = 4.3/24.2/13.1 close to carbon black value (ΔE* = 2.5). The pigment shows a good black cool performance in

2wt% addition to porcelain paste (1190 ºC) with L*a*b*= 64,79/-3,42/-13,05 and R_{Vis}/R_{NIR}/R (%) = 8/49/28. In a previous work, we analysed other novel published black ceramic pigments such as $YMnO_3$ (hexagonal, $P6_3cm$), $Sr_4CuMn_2O_9$ (trigonal, P321) and Melilite $Sr_2(Mg_{0.5}Mn_{0.5})Ge_2O_7$ (tetragonal, P-42_{1m}) with ΔE* = 3.6, 25.5 and 14.3 respect Carbon Black, but all these pigments produce colourless porcelain paste when are 2wt% added to paste. However, cuprates such as $CuFe_2O_4$, with ΔE* = 23 respect Carbon Black, remains stable in porcelain paste with L*a*b*=37.6/-2.9/1.5 and R_{Vis}/R_{NIR}/R (%) = 6.7/15.9/11.2. The microstructure of ceramic pigments designed by Sol-Gel or other non-conventional procedures [4,12], can improve the colour of powder and its coloured paints, but the aggressivity of glazes and ceramic matrices difficult the preservation of microstructure for produce veritable ultra-black ceramic pigments.

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