CUPRORIVAITE BLUE PIGMENTS WITH HIGH NIR REFLECTANCE OBTAINED BY COLLOIDAL METHODS

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1. INTRODUCTION

Cuprorivaite ($CaCuSi_4O_{10}$) is the basis of the Egyptian blue pigment and can be modified with strontium to enhance its stability (Sr-$CaCuSi_4O_{10}$ solid solutions) (1). Egyptian blue was the first calcined inorganic pigment, and it was the most widely used from the first Egyptian dynasties to the end of the Roman period in Europe. From the standpoint of colour, many over 3000-year-old specimens have remained unchanged to the present day. Its luminescent properties, long service life, and high intensity photoluminescence at 910 nm make it a promising candidate for use in biomedical applications: the IR photons can penetrate deeply into human tissue and the pigment emission minimises light absorption by the tissues in a refreshing effect. In addition, the pigment is extremely stable, exhibiting bright luminescence even after millennia (2). To prepare inkjet inks, one can opt for ultramilling of calcined pigments or for generation of water-dispersible colloids by non-conventional chemical procedures using aqueous or hydroalcoholic methods (3). This study describes the obtainment of colloids and calcined pigments generated by aqueous methods: CO (colloidal sol–gel) and MOD (metal–organic colloid with polycarboxylate acids) of $Ca_{1-}Sr_xCuSi_4O_{10}$ x=0 (Egyptian blue) and x=0.4 (strontium-modified Egyptian blue) compositions.

2. EXPERIMENTAL

Using aqueous methods, CO (colloidal sol–gel) and MOD (metal–organic colloid with polycarboxylate acids) samples of compositions $Ca_{1-}Sr_xCuSi_4O_{10}$ x=0 (Egyptian blue) and x=0.4 (strontium-modified Egyptian blue) were prepared from nitrates of cations dissolved in water and peptised in an ammonia solution in the case of the CO samples; in the MOD method, at the same nitrate solution, O.5 moles of citric acid/mol cuprorivaite were added prior to ammonia peptisation. Figure 1 shows the appearance of the dispersions and the results and characterisations obtained by the deposition and glazing indicated.

3. RESULTS AND CONCLUSIONS

The results (Fig. 1) indicate the obtainment of black colloidal powders (example: L*a*b*=47.1/-1.4/0.5 for CO x=0.4) with the presence of tenorite in XRD at 500ºC/1h of relatively high NIR reflectance (of the order of 30% in the CO and lower in the MOD samples). Calcination at 800ºC maintained the tenorite, wollastonite also appearing. At 1050ºC the blue pigment was obtained (example: L*a*b*=37.11/-3.63/-7.13 for MOD x=0), cuprorivaite crystallising, which produced turquoise blue colorations in monoporosa glazes (example: L*a*b*=74.2/-15.4/-9.4 for MOD x=0) and high NIR reflectance (36% for MOD x=0), though residual formation of cuprite (Cu2O) was observed that in reduction could give rise to pinholing problems in the fired glazes, this being avoided by calcining at lower temperatures as may be observed in the ceramic sample (1000ºC)(Fig. 2).

<table>
<tr><th>DISPERSIONS
(pH 7)</th><th>500ºC/1h</th><th>800ºC/1h</th><th>1050ºC/1h</th></tr>
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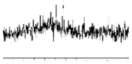
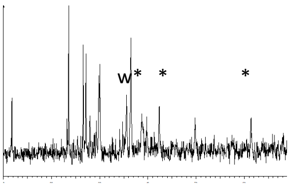
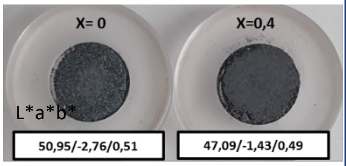
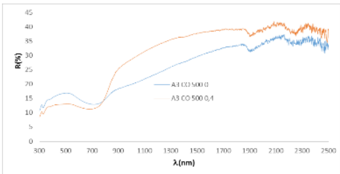
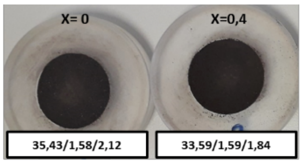
x=0 0.4

XRD: 500 and 800ºC tenorite CuO

1050ºC cuprorivaite, Cu_2O*, wollastonite w</td>
<td>
$R_{vis}/R_{NIR}/R$=15/23/19
12/30/20
</td>
<td>
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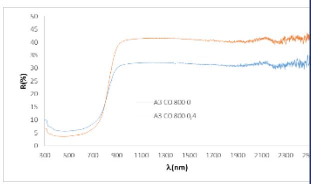
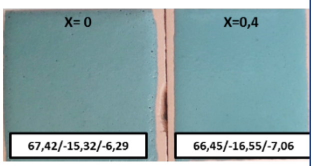
5/37/19


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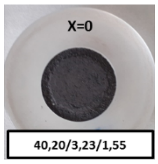
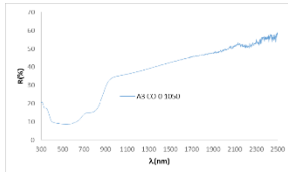
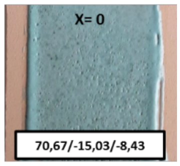
32/21/27</td>
<td>
$R_{vis}/R_{NIR}/R$=11/34/12
x=0.4 melts


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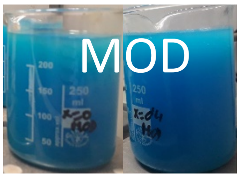
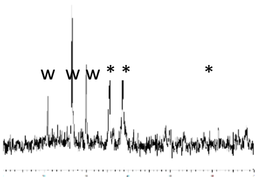
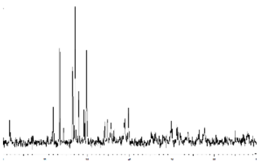
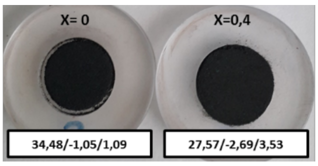
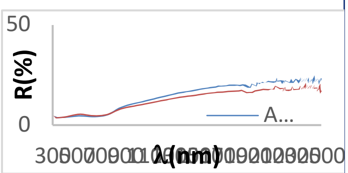
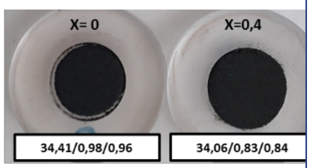
<td>
x=0 0.4

XRD 800º
Cu_2O*,wollastonite w

1050ºC cuprorivaite,</td>
<td>
$R_{vis}/R_{NIR}/R$=5/13/8
5/12/8
</td>
<td>
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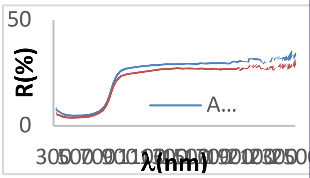
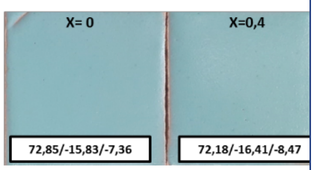
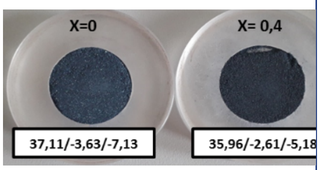
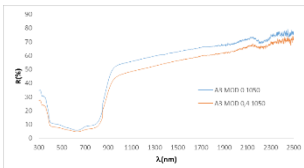
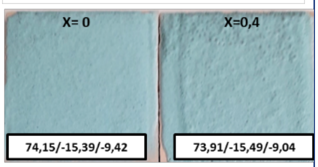
5/23/13


$R_{vis}/R_{NIR}/R$=40/27/35
39/27/34</td>
<td>
$R_{vis}/R_{NIR}/R$=9/48/27
x=7/42/23


$R_{vis}/R_{NIR}/R$=47/36/43
46/33/41</td>
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Figure 1. *Results described for the colloids*

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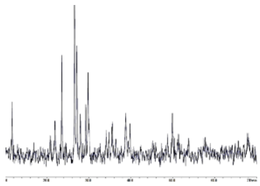
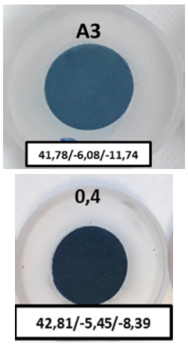
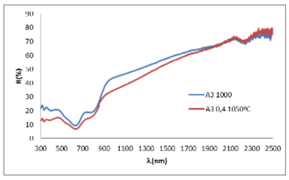
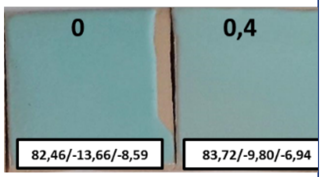
<td>
XRD cuprorivaite</td>
<td></td>
<td>
$R_{vis}/R_{NIR}/R$=16/45/29
12/40/24</td>
<td>
$R_{vis}/R_{NIR}/R$=49/41/46
54/45/50</td>
</tr>
</table>

Figure 2. *Results described for the the ceramic sample.*

4. REFERENCES

[1] E. Kendrick, C.J. Kirk CJ, S.E. Dann, Structure and colour properties in the Egyptian Blue Family, $M_{1-x}M'_xCuSi_4O_{10}$, as a function of M, M' where M, M'=Ca, Sr and Ba. Dyes and Pigm 73 (2007) 13-18.

[2] http://www.webexhibits.org/pigments/indiv/overview/egyptblue.html (accessed 30/05/2019)

[3] Zhidong Pan, YanminWang, HuiningHuang, ZhiyuanLing, Yonggang Dai, ShanjunKe, Recent development on preparation of ceramic inks in ink-jet printing, Ceramics International, 41(2015)12515–12528.

5. ACKNOWLEDGEMENTS

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