SYNTHESIS OF A RED PIGMENT FROM GOLD NANOPARTICLES

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ABSTRACT

A simple method of synthesising red pigments for ceramic glazes, based on gold nanoparticles protected by a refractory oxide capsule, was developed. Gold nanoparticles of an appropriate size were obtained by reaction in an aqueous medium between an Au(III) solution and an ammonium bromide solution, keeping the Br^- concentration low during the process.

The gold nanoparticles were encapsulated by adding the protective oxide in colloid form and subsequently coagulating it, alkalinising the medium. Diethylentriamine was then added to encourage the interaction between the gold nanoparticles and the oxide nanoparticles. This was followed by adding carboxymethylcellulose to raise medium viscosity, and to avoid segregation and subsequent agglomeration of the gold nanoparticles during drying. The dry residue was directly usable as a glaze pigment without requiring further thermal treatments.

Three protective oxides, namely SiO_2, Al_2O_3, and SnO_2, were tested. In the three cases, pigments with a high colouring strength were obtained, which gave rise to reds of different shades in the resulting test glaze.

1. INTRODUCTION

One of the most difficult colours to obtain in ceramics is red, particularly in high-temperature glazes. At present, zircon-encapsulated cadmium sulphoselenide is an acceptable solution, from both a colour yield and a stability standpoint. However, the high toxicity of Cd(S,Se) entails an environmental risk. Alternative red pigments are therefore needed, particularly in view of the foreseeable restrictions to be imposed by the REACH regulations, at least in Europe.

Decorations based on colloidal gold have been used in ceramics and glass for centuries (known as Purple of Cassius)[1], but they are difficult to obtain and, in particular, cannot be used as pigments in the classical sense of the term, owing to their liquid nature. The physical base of Purple of Cassius is the presence of gold nanoparticles (AuNPs) that exhibit the so-called surface plasmon resonance (SPR) phenomenon, which causes very intense absorptions of certain electromagnetic spectrum frequencies (maximum about 530 nm)[2]. This phenomenon generates very strong reddish colorations when the AuNPs are dispersed in a glass, so that they might be considered inorganic chromophores[3].

A variety of alternatives have been proposed for obtaining solid pigments from Purple of Cassius. The initially developed craft process consisted of numerous stages (precipitation of the purple in the form of a gel, mixing of the gel with milled glass, calcination of the solid, and final milling) and it was characterised by the scarce reproducibility of the pigment colouring strength and its lack of stability at high temperatures. As a result, numerous improvements have been put forward throughout the 20th century. The first investigations focused on facilitating the precipitation stage, and in this sense it was suggested that the gold colloid should be coprecipitated with Al or Sn[4] oxyhydrates, as well as performing the precipitation in the presence of inert materials of the kaolin or feldspar type[5]. A second research route was the direct deposition of the gold colloid on the solid that would constitute the protective capsule, the proposed protective materials being frits[6] or oxyhydrates of elements whose oxides were stable in silicate glasses[7].

In addition to the improvements with regard to the traditional method, completely different approaches were also proposed. The most sophisticated approach may perhaps be deemed the method put forward by Brandes *et al.*[8] for obtaining a purple pigment in the form of spherical particles by the joint pyrolysis of solutions containing the gold precursor and the protective capsule precursor.

The present investigation originated on considering that there was no wet process that could be readily scaled up to an industrial scale, which would allow pigments to be synthesised in a range of reds and purples that exhibited high colouring strength in different ceramic glazes, including those that required high firing temperatures (for white stoneware tile or porcelain tile). The starting point was the relative ease with which a suspension of AuNPs in aqueous medium could be obtained by reducing a soluble gold salt[9,10]. The problem lay in encapsulating the AuNPs with a refractory oxide that would protect them from dissolution in the glaze. In order to attempt to resolve this, commercial refractory oxide colloids were used, since their nanometric particle size would facilitate capsule formation.

Gold surfaces have little affinity for oxide surfaces. The incorporation was, therefore, studied of additives that could act as bridges between the AuNPs and the oxide nanoparticles to facilitate encapsulation. Ideally, one end of the molecule would need to display an affinity for gold and the other for oxides. Thiols bind strongly to AuNP surfaces and are, therefore, the recommended option in the literature for controlling nanoparticle growth[11]. On the other hand, amines can also bind to AuNP surface[12], as well as to oxide surfaces. The tests were conducted by choosing a representative of each group. In the case of the thiols, 6-mercaptohexanol was chosen so that the OH group present at the other end of the chain would facilitate the interaction with colloidal oxide particles. In the case of the amines, diethylentriamine was chosen, which on having several amino groups allows the same molecule to bind to different particles.

2. EXPERIMENTAL PROCEDURE

The raw materials used to synthesise the AuNPs were tetrachloroauric acid trihydrate (Heraeus) and ammonium bromide (Fluka). The following additives were used in certain experiments: 6-mercaptohexanol (hereafter 6MH, Fluka), diethylentriamine (hereafter DTA, Fluka), and a 1 wt% carboxymethylcellulose solution (hereafter CMC, Hercules). In the research conducted, the precursor used to generate the protective silica capsule was an industrial SiO_2 colloid in water (30% by weight). In addition, in order to evaluate whether the encapsulation method could be extended to other oxides, commercial Al_2O_3 (20% by weight, Alfa Aesar) and SnO_2 (15% by weight, Alfa Aesar) colloids were used. The colouring strength of the different synthesised pigments was evaluated in a transparent single-fire glaze, obtained from a crystalline-type industrial frit.

Generally speaking, the different pigment samples were synthesised starting with 100 ml distilled water and quantities of tetrachloroauric acid and ammonium bromide that kept a molar ratio of about 0.53 (Table 1). Both reactants and the water were combined in various modes to maintain different precursor concentrations during the reaction (Table 2) and they were kept in contact for a certain time (t_R) with a view to obtaining a stable suspension of appropriately sized AuNPs. The oxide colloid selected in each case was then added to the freshly prepared suspension, after which ammonia was added to produce colloid gelling and formation of the protective capsule (0.6 ml of NH_3 at 35% was added for each ml of colloid addition). In the course of the study, the foregoing additives were tested, and the general procedure was readjusted as a function of their nature and behaviour.

Ref.	$HAuCl_4$ (mmol)	NH_4Br (mmol)	SiO_2 (ml)	Al_2O_3 (ml)	SnO_2 (ml)	NH_3 (ml)	6MH (µl)	DTA (µl)	CMC (ml)
A1	0,76	1,43	5	-	-	3	-	-	-
A2	1,52	2,86	20	-	-	12	-	-	-
B1	0,76	1,43	5	-	-	3	100	-	-
B2	0,76	1,43	5	-	-	3	100	-	-
B3	0,76	1,43	5	-	-	3	100	-	-
C1	0,76	1,43	5	-	-	3	-	100	-
C2	0,76	1,43	5	-	-	3	-	100	30
D1	0,76	1,43	-	10	-	3	-	100	32
D2	0,76	1,43	-	-	13	3	-	100	32

Table 1. Raw materials used in pigment synthesis.

Ref.	SPECIFIC SYNTHESIS CHARACTERISTICS	t_R (min)	CALCI-NATION
A1	Addition of solid NH_4Br to the $HAuCl_4$ solution	5	Yes
A2	Identical to A1	60	Yes
B1	Dropwise 50 ml addition of a solution containing NH_4Br and 6MH on 50 ml of a solution containing $HAuCl_4$.	5	Yes
B2	Dropwise 50 ml addition of a solution containing $HAuCl_4$ on 50 ml of a solution containing NH_4Br and 6MH	5	Yes
B3	Dropwise simultaneous addition of 10 ml of two solutions, one containing $HAuCl_4$ and the other NH_4Br and 6MH, on 80 ml of H_2O	5	Yes
C1	Dropwise 50 ml addition of a solution containing NH_4Br on 50 ml of a solution containing $HAuCl_4$. Addition of DTA after the ammonia	5	Yes
C2	Dropwise 50 ml addition of a solution containing NH_4Br on 50 ml of a solution containing $HAuCl_4$. Addition of DTA and CMC after the ammonia	5	No
D1	Identical to C2	5	No
D2	Identical to C2	5	No

Table 2. Operating conditions used in pigment synthesis.

The suspension obtained in each case was dried under infrared lamps and was optionally subjected to calcination for 30 minutes at 900ºC to strengthen the protective capsule on the AuNPs. The pigment obtained was disaggregated in an agate mortar and sieved on a 200 µm mesh, but it was not milled in order to avoid breaking the resulting oxide capsule. In selected samples, the size and morphology of the AuNPs present in the pigment particles were investigated by scanning electron microscopy (FEG-SEM Quanta 200F, FEI Co, USA).

The first block of experiments (A1 and A2) was designed to evaluate the effect of reaction time and the Au/SiO_2 ratio on pigment colouring strength, as well as the feasibility of obtaining the pigment without incorporating any organic additives since, if this were feasible, it would be much simpler to scale up the process.

The second block of experiments (B1, B2, and B3) was designed to investigate the effects of two parameters: in the first place, the precursor concentrations during the AuNP formation; secondly, the incorporation of 6MH as an agent to control the size of these nanoparticles and to encourage their binding to the silica nanoparticles. The experiments were conducted using the same quantities of reactants as in A1, but adding 6MH in an equimolar quantity with respect to gold. In B1, the concentration of NH_4Br was kept low with respect to that of $HAuCl_4$ during the reaction; in B2, the concentrations were reversed and in B3 the concentrations of both precursors were held low.

The third block of experiments (C1 and C2) was essentially designed to analyse the effects of the DTA addition on the formation of the protective capsule. The effects of the viscosity of the medium during the drying and final calcination were analysed in parallel. In both experiments, synthesis was performed by keeping the NH_4Br concentration low during the reaction and incorporating 10 mole per cent of DTA with respect to the initial gold content. However, the DTA was introduced after adding the ammonia to encourage bridge formation between the AuNPs and the silica and to avoid, as far as possible, bridge formation between the AuNPs themselves. In the C2 experiment, the CMC solution was also added to the medium to increase its viscosity and to make it more difficult for the particles to segregate during drying, while calcination was not performed in order to evaluate whether AuNP growth took place during calcination.

The fourth block of experiments (D1 and D2) was designed to evaluate whether the process that led to the C2 pigment could be generalised to capsules of other oxides, for which Al_2O_3 and SnO_2 colloids were tested as protective capsule precursors, though it was necessary to readjust the colloid volumes as a function of the colloid concentration in order to keep an approximately constant Au/oxide ratio (by weight).

The pigments were incorporated into the transparent glaze, the glaze slips being applied to fired white-body biscuits using a glaze applicator with a 600 µm aperture. After the test pieces had dried, they were fired with a typical thermal treatment used for single-fired floor tile, characterised by a peak temperature of 1120 ºC and a 6-minute hold at peak temperature. The CIELab chromatic coordinates of the resulting fired glazes were measured with a diffuse reflectance spectrophotometer (Color Eye 7000A, X-Rite Inc. USA), using the CIE standard illuminant D_{65} and CIE 10º standard observer.

In this investigation, the pigments were incorporated into the glaze in variable quantities, since the available quantity of sample varied notably in the different experiments. In addition, as the quantity of gold in the pigments exhibited a relatively wide range of variation, the theoretical percentage of gold introduced into the dry glaze in each case was taken as a reference (this varied between 0.05% and 0.2% depending on the experiment), since this element was the real chromophore. This was similarly the reason that an estimation of the yield of the incorporated gold was defined in order to compare the colouring strength of the synthesised pigments. The gold development factor (Ψ) was defined as the quotient between the increase in the red component generated in the fired glaze and the theoretical percentage of gold, by weight, contained in that glaze.

$$\Psi = \frac{a^* - a^*_{base\ glaze}}{\% Au}$$

The relationship between the chromatic coordinates and the percentage of gold was obviously not linear, since colour saturation was reached beyond a certain percentage of gold. During the investigation, however, very low chromophore concentrations were used, which were thus deemed to be within the range in which the relationship was approximately linear, so that ψ would therefore be significant in order to differentiate between the results of the different experiments.

3. RESULTS AND DISCUSSION

3.1. Pigment synthesis

During the synthesis of the first two pigments (A1 and A2), it was noted that the yellow $HAuCl_4$ solution quickly turned to intense red after the NH_4Br addition, without losing transparency. This change might have stemmed from the appearance of AuNPs, owing to a reducing effect of the bromide, but there was also the possibility that a certain quantity of the Br_4Au^- complex had formed, this being characterised by a reddish colour (though it could not have been the major component, since not enough NH_4Br had been introduced for that to occur). After the addition of the silica colloid and the ammonia, the reddish colour remained, without the formation of any heterogeneities being detected, which indicated that both reagents were compatible with the already formed coloured product. When the suspensions had dried, materials of a homogeneous appearance were obtained, which acquired a pink colour after calcination.

In the three experiments of the second block (B1, B2, and B3), the presence of 6MH altered the evolution of the system, tending to generate a suspension that was rather opaque, with different shades of brown. This suggested that 6MH could favour AuNP coagulation before the AuNPs could interact with the silica colloid. The heterogeneity of the suspension was maintained in the reddish-brown materials obtained after drying; however, calcination yielded materials with a relatively homogeneous pink colour.

In pigment C1 synthesis, the behaviour was identical to that described for pigment A1, and suspension appearance did not vary when the DTA was finally incorporated. During the drying of suspension C1, no heterogeneities were observed to develop in the solid, and calcination yielded a pink material. Pigment C2 behaved identically during the reaction, without any changes in suspension appearance being noted after the addition of the CMC solution, which indicated that this additive did not affect the stability of the silica and AuNP suspension either. However, drying yielded a dark purple material, completely different from the materials that had been previously obtained.

In the synthesis of pigments D1 and D2, the sequence of events was identical to that observed in C2 pigment synthesis, indicating that the change in the nature of the protective oxide did not affect the development of the process. In both cases, drying produced a dark purple material.

3.2. Colour development

All the synthesised pigments were incorporated into the transparent glaze, yielding a range of reddish tones with very different saturations, as shown in their chromatic coordinates (Figures 1 and 2). In addition, Ψ also displayed a very wide range of variation.

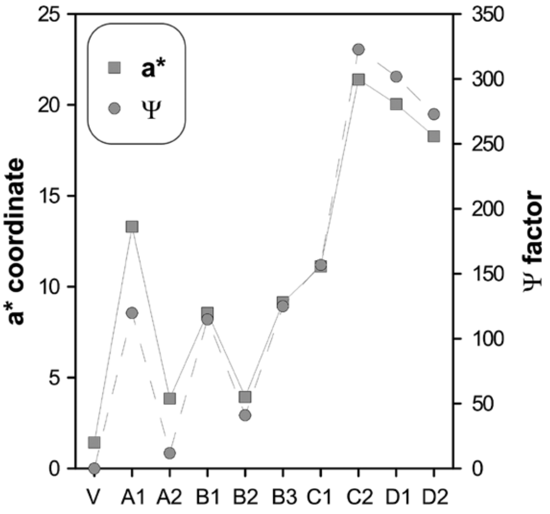

Figure 1. a coordinate and Ψ factor of the fired transparent glaze (V) and of the pigment-containing fired glazes.*

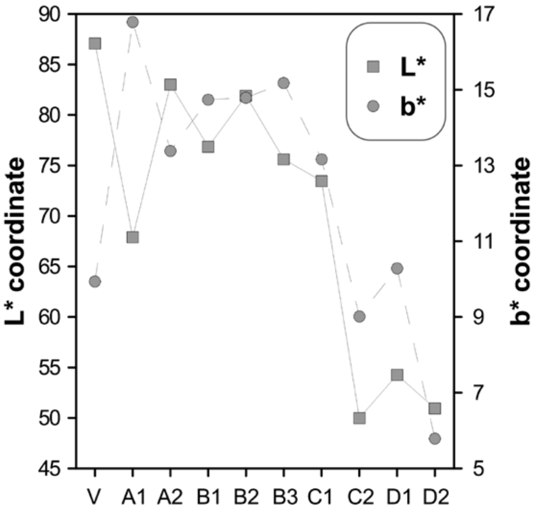

Figure 2. L and b* coordinates of the fired transparent glaze (V) and of the pigment-containing fired glazes.*

The evolution of the chromatic coordinates (as well as that of Ψ, which was practically parallel to that of a*) shows that pigment colouring strength was very sensitive to the synthesis conditions. The results obtained allow the following effects of the studied variables to be inferred:

- It was possible to synthesise the pigment without incorporating any organic additives. However, the colouring strength was relatively low and the use made of the gold, in particular, was limited. Under these conditions, an increase in the SiO_2/Au ratio or in the reaction time appeared to have an adverse effect on pigment colouring strength.

- The incorporation of 6MH parallel to NH_4Br apparently slightly improved pigment colouring strength, as shown by the values of Ψ for pigments B1 and B3, which resembled that obtained with pigment A1 (though a* was lower, as a smaller quantity of pigment was introduced). On the other hand, it appeared to be appropriate to keep the NH_4Br concentration low during the AuNP synthesis reaction in order to produce a pigment with greater colouring strength, whereas high NH_4Br concentrations did not appear advisable.
- The incorporation of DTA at the end of the process to facilitate the interaction between the colloid silica and the AuNPs appeared to have a favourable effect, since a notable increase in Ψ was achieved with respect to that of pigment A1. However, the most significant contribution to pigment colouring strength was the addition of CMC and the suppression of the calcination step, since this almost tripled the value of Ψ with respect to that of pigment A1, while also yielding very high values of a*.
- Once certain acceptable processing conditions had been identified, the nature of the oxide that formed the protective capsule was not the determining factor of pigment colouring strength, since the replacement of SiO_2 with Al_2O_3 or SnO_2 as encapsulating material also generated pigments with high colouring strength, albeit a little lower than that of pigment C2.

The lightness of the resulting colours was strongly correlated with a*, such that the pigments that produced the most reddish colours also produced the colours with the lowest lightness (Figure 3), though in view of the trend defined by the experimental data there appeared to be a limit to the value of a* that could be attained in the glaze.

The yellow component of the fired glazes exhibited no clear correlation with a* (Figure 4). When the colouring strength of the pigment was low or moderate, the b* of the colour obtained in the fired glaze was always greater than that of the fired base glaze. In contrast, when the pigment colouring strength was very high, values of b* were reached that were similar to or lower than those of the fired base glaze, the most notable case being the D2 pigment, in which the combination of the nanoparticles with the SnO_2 capsule gave rise to the lowest value of b* and, therefore, the purest red.

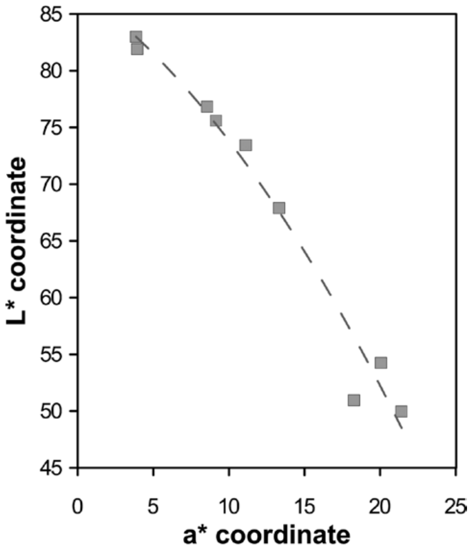

Figure 3. Relationship of a to L* in the pigment-containing fired glazes.*

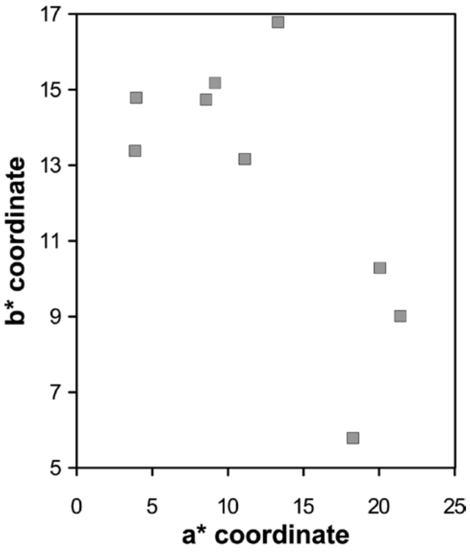

Figure 4. Relationship of a to b* in the pigment-containing fired glazes.*

The reflectance spectra of the resulting glazes (as examples, those of the fired base glaze are compared with the corresponding ones of the fired glazes containing pigments A1, B1, and C2 in Figure 5, while those of the fired glazes containing pigments C2, D1, and D2 are compared in Figure 6) indicate that the red colour was due to a reduction in reflectance below 650 nm, produced by a very intense absorption band centred at about 540 nm, but which was only clearly defined in the case of pigment C2. This result was consistent with the characteristic strong absorption of the SPR phenomenon generated by the AuNPs (the wavelength of the maximum absorption of the AuNPs dispersed in water varied between 517 and 575 nm when their diameter increased from 9 to 99 nm)[13].

The spectra explain the lack of a clear correlation between b* and a*, since in the area of the spectrum corresponding to yellow, the curves displayed the greatest slope and, therefore, small alterations affected b* to a greater extent.

The SPR absorption band hardly varied when silica was replaced with alumina (Figure 6); however, in the case of SnO_2 there was a certain shift towards higher wavelengths, which was the cause of the lower yellow component generated in the glaze. Assuming that the size of the nanoparticles was similar in pigments C2, D1, and D2, this variation may be interpreted by assuming that the SPR absorption depended on the refractive index of the medium surrounding the AuNPs and that the greatest difference was between the refractive indices of SiO_2 and of SnO_2 (1.54 as opposed to 2.00, respectively)[14].

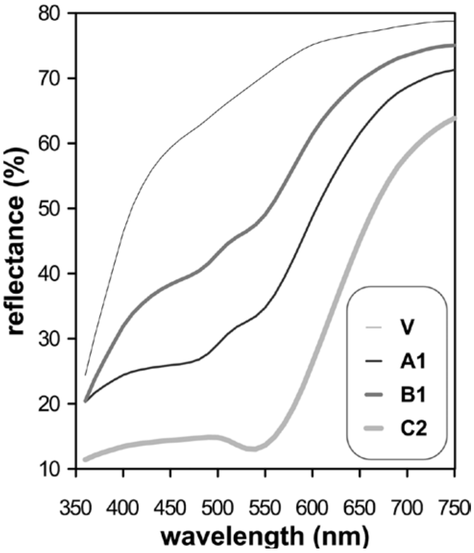

Figure 5. Reflectance curves of the transparent fired glaze (V) and of the fired glazes containing some of the synthesised pigments.

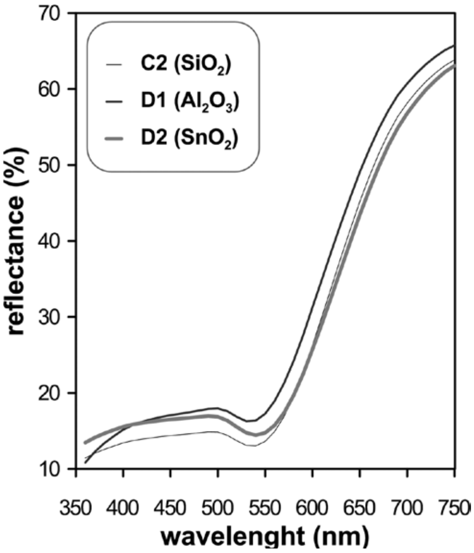

Figure 6. Reflectance curves of the fired glazes containing pigments synthesised with different oxides.

3.3. Pigment microstructure

Though the spectrophotometric curves of the fired glazes were consistent with the presence of AuNPs in the pigments, scanning electron microscopy was used to confirm their presence. In the case of pigment B1, approximately spherical gold particles dispersed in the silica were identified (Figure 7, left) which, however, displayed a quite wide size distribution. Most of the gold particles had a size close to a micron and only a very small fraction had a size below 100 nm, which is required for SPR to occur. This was consistent with the pigment pink colour and its low colouring strength.

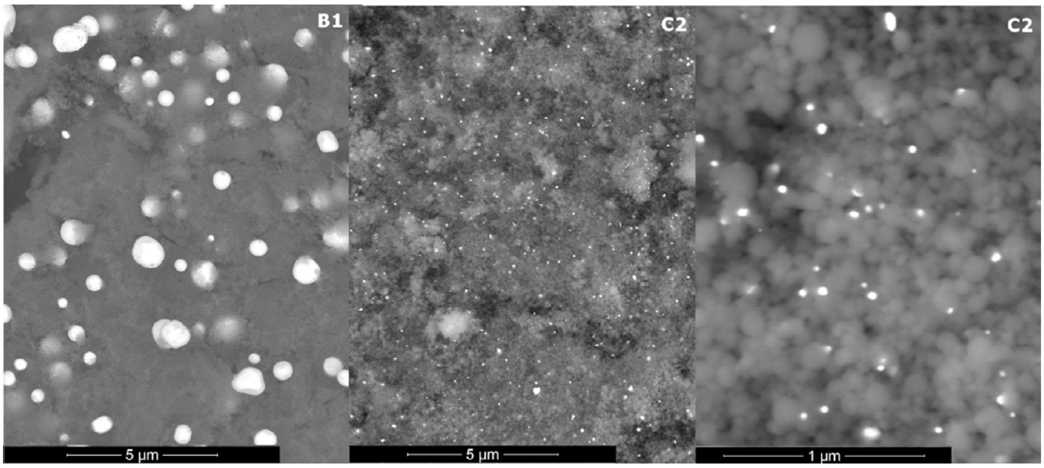

Figure 7. Photographs of pigment B1 and C2 particles at the same magnifications (left and centre), and of the C2 pigment particles at higher magnifications (right). The white areas correspond to gold particles.

In the case of the C2 pigment, the AuNPs sized smaller than 100 nm were the most numerous fraction (Figure 7 centre and right) and were very well dispersed in the silica, which was consistent with their purple colour and high colouring strength.

On the other hand, it may be noted that the silica matrix in the B1 pigment exhibited a very high degree of sintering owing to the thermal treatment that it had undergone, while in the C2 pigment the silica matrix consisted of clearly differentiated nanoparticles, among which the AuNPs were distributed. The thermal treatment that allows the silica to sinter may also favour AuNP growth (it might produce mass transport by the gas phase owing to the greater pressure of the vapour in equilibrium with the nanometric particle surfaces), so that most of the particles present in the final pigment would have a larger diameter than the required diameter.

4. CONCLUSIONS

Red pigments were synthesised for glazes by encapsulating AuNPs in a refractory oxide matrix. To achieve a high colouring strength, it was necessary for the AuNP nanoparticle diameter not to exceed 100 nm during their synthesis or encapsulation process.

AuNPs with the desired characteristics were synthesised by reaction between aqueous solutions of $HAuCl_4$ and NH_4Br, operating in such a way that the NH_4Br concentration was kept low during the reaction.

AuNP encapsulation was achieved by adding the protective oxide in the form of a colloidal dispersion to the AuNP suspension (Si, Al, and Sn oxides being appropriate for the process), and alkalising the medium by coagulating the oxide nanoparticles. It was verified that the presence of diethylentriamine during the coagulation improved the encapsulation process. Suspension drying was a critical factor in obtaining the pigment. It was therefore helpful to increase the suspension viscosity by adding CMC in order to avoid AuNP segregation and subsequent agglomeration. On the other hand, it was not advisable to subject the pigment to thermal treatment at high temperature, since this led to AuNP growth and decreased their colouring strength.

The developed pigments exhibited very high colouring strength in transparent fired glazes, generating different intense red shades, depending on the oxide used in the protective capsule.

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