MULTIFUNCTIONAL NANOSTRUCTURED GLAZES BY MEANS OF PROTECTED AND DISPERSED NANOPARTICLES

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ABSTRACT

New glazes with innovative characteristics have been developed for the ceramic floor and wall tile industry by the dispersion of nanoparticles. Matrix particles of sepiolite clay have been prepared to support and protect different types of dispersed nanoparticles of a metallic or oxide nature. The developed glazes are nanostructured and multifunctional, since different properties can be combined in a single glaze, such as a metallised appearance, and hydrophobic, bactericidal, fungicidal, and self-cleaning properties.

The concept of supported nanoparticles uses, efficiently, current processes of nanoparticle technology, providing an innovative ceramic product and greater added value.

The developed glaze also addresses issues of great topicality, such as sustainability and the reduction of environmental impact throughout its life cycle, since it requires much smaller quantities of functional metallic oxides and assures their immobilisation thanks to encapsulation. The fact that these metals remain fixed in the sepiolite matrix, avoiding agglomeration and enhancing their stability during the production process, reduces manufacturing costs and minimises occupational risks in the use and handling of nanoparticles.

1. INTRODUCTION

Traditionally, ceramic floor and wall tiles have had to fuse strength and durability characteristics in order to be able to perform as wall and floor coverings and thus, finally, enter the world of architecture and decoration, in which they are currently considered to be building elements that can be used to define either an internal or an external environment. This has led to progressively more sophisticated ceramic materials and applied technologies for fabricating these.

Other different covering materials have also progressed significantly in that same direction, however, reducing the edge that ceramic products had in a scenario with a great variety of possible alternatives in flooring or wall cladding. As a result, present market demands are looking for new effects and functionalities that complement traditional ones [1,4] for ceramics, such as the development of specific products that are able to reduce surface slipperiness without constraining aesthetic qualities, products with greater scratch hardness and wear resistance, products that provide enhanced cleanability and prevent the appearance of mould or incorporate biocidal capabilities, products that can be integrated into the latest domotic solutions or that extend the excellent aesthetic qualities already achieved by current ceramics.

With the help of nanomaterials, feasible alternatives can be found in the quest to resolve current problems in the ceramic sector and obtain the above effects and functionalities in ceramics since, on a general level, nanotechnology opens up new avenues for the development of unusual properties in materials. The interest in these materials resides in the fact that when their size decreases, their properties change drastically [5,6].The research currently being undertaken in relation to the new nanometric sizes enables the development of new electric, optical, magnetic, and catalytic functionalities, etc. But these also entail problems when it comes to their practical embodiment, which must be solved [7]. For example, nanoparticles display strong agglomeration, there is instability with regard to the chemical oxidation of metallic nanoparticles, and risks appear in relation to nanoparticle handling and the effect of nanoparticles on the environment [8,9] due to their small size and high reactivity during chemical treatment. Moreover, in the ceramic sector, it may be noted that the potential use of nanoparticles also faces the unavailability of nano-charges on a large scale, owing to the lack of repetitiveness of the scaling processes for obtaining nanoparticles and the health issues involved in handling nanoparticles.

This study has sought to obtain nano-functional glazes by a conventional ceramic process, applying nanotechnology, necessarily overcoming the difficulties presented by the nano-charges mentioned above. For this purpose, as a technological instrument, it was proposed to use nanoparticles supported on fibres of a laminar clay known as sepiolite to obtain supported nanoparticles that are dispersed and protected. Thus, the present development of multifunctional nanostructured glazes addresses the solution of the above difficulties and opens up a new field of research that takes an enormously promising step forward with regard to the enhancement of ceramics properties and the incorporation into these materials of functional nanoparticles.

2. INCORPORATION OF NANOPARTICLES INTO THE GLAZE

With a view to resolving the constraints regarding the use of nanoparticles in the ceramic industry, the heterogeneous nucleation of nanoparticles in nano-porous matrices was addressed, so that the nanoparticles remain embedded in the matrix, and are thus dispersed and environmentally protected.

Sepiolite is a clay with the molecular formula ($Mg_8Si_{12}O_30(OH).4(H_2O)_4.8H_2O$) and consists of sheet silicates that are stacked, generating octahedral voids that house Mg^{2+} (figure 1). This structure has particles with a fibrous shape, 20-40 nm in diameter and 2 µm long, with zeolitic channels of 0.36 x 1.6 nm in which water is housed. The size of the channels prevents cations from positioning themselves there, making leaching necessary by chemical attack on Mg^{2+} in order to generate octahedral sites that can be replaced with other metal cations, which are finally reduced in order to obtain metallic particles protected by the sepiolite [10,11]. As a result of subsequent thermal treatment, the clay loses water and its structure folds, transforming itself into an anhydrous sepiolite and protecting the nanoparticles.

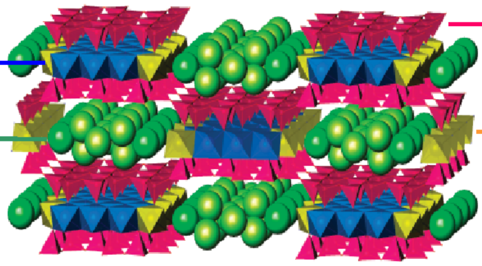


Figure 1. Sepiolite clay structure: silica tetrahedra, magnesium octahedra, and zeolitic water.

Using this innovative product, the following work methodology was applied to develop the glazes:

- Selection process of the nature of the supported nanoparticles, depending on the functional characteristics to be developed, as well as copper and silver [12, 14] for metallised or silver glazes as biocidal element [15].
- Study of the compatibility mechanisms with the phases present in floor and wall tile glazes during the ceramic process.
- Adaptation of glaze rheology after the addition of the nanoparticles, determining the optimum metal concentrations. The sepiolite clay assures the non-agglomeration of the particles in the glaze and keeps them dispersed,

so that the appropriate rheology is achieved. Figure 2 shows a reduction in viscosity with shear rate, which means that they display a plasticising behaviour (fluidisation by shear).

- Glazing of tiles on a laboratory scale by different techniques: airbrush, spray gun, or bell waterfall. Adjustment of the optimum grammage and selection of the most favourable glazing technique.
- Study of the samples and new constituents with a view to functionalising the resulting glazes, providing them with innovative characteristics, and enhancing their properties.
- Development of an industrial production process in which sepiolite incorporates metallic or oxide particles.
- Study of the industrial feasibility of the ceramic process and initiation of its industrial implementatio.

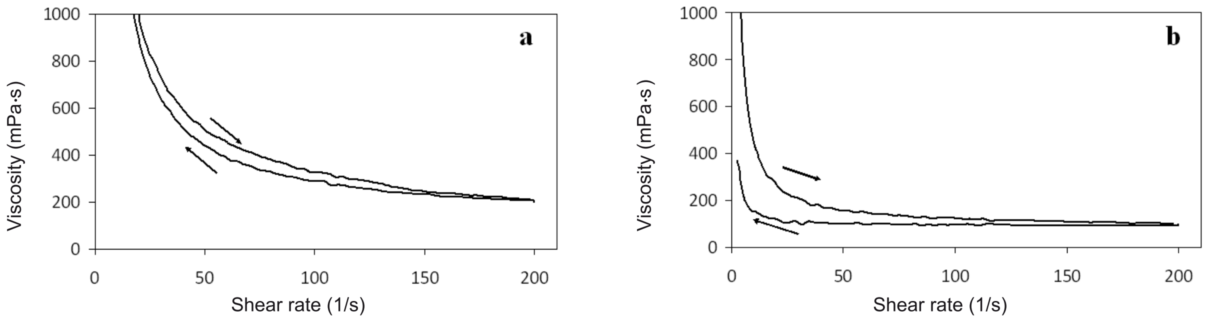


Figure 2. Rheological curves of
a) a usual crystalline glaze, and b) a glaze containing sepiolite with metallic nanoparticles.

3. GLAZE CHARACTERISTICS

Different effects have been obtained depending on glaze layer thickness and the metal concentration in the glaze. These aesthetic effects also vary according to the type of nanoparticles dispersed in the glaze. Variations of colour, glosses and striking reflections in the coloured glazes, glossy metallic appearances, metallised matts, and matt-rough finishes can be obtained, thus also enabling the use of screen printing and overglazes. That is, the glaze behaves just as a standard glaze for a conventional ceramic process. Thus, for example, when copper is incorporated into the glaze (figure 3) by means of sepiolite, glazes with different characteristics were obtained:

- Green colour, owing to the cation exchange of Cu^{2+} with Ca^{2+} cations in the lattice.
- Green colour with metallic reflections because part of the copper is reduced at high temperature, thanks to the protection offered by the sepiolite, while the other part remains as Cu^{2+} exchanging with Ca^{2+}.

- Metallised appearance because a large part of the copper present in the glaze is found as Cu^0.
- Metallised matt appearance owing to excess copper in the glaze, which ends up by forming copper oxide (CuO).
- Rough appearance owing to the formation of CuO at the surface.

Tests were conducted with different nanometric and micrometric metallic copper sizes. The rheology of the system for micrometric particles was inappropriate for the application, because of particle decantation in the glaze, while the desired metallised reflection was not obtained either. This is probably because the sepiolite does not protect these particles, so that they oxidise readily, and because of the lack of reactivity of the copper particles owing to their large size, since they cannot be reduced like the nanoparticles. Thus, micrometric copper particles produce matt effects because copper oxide (II) appears more readily at the surface, while nanoparticles yield a glossy metallised effect.

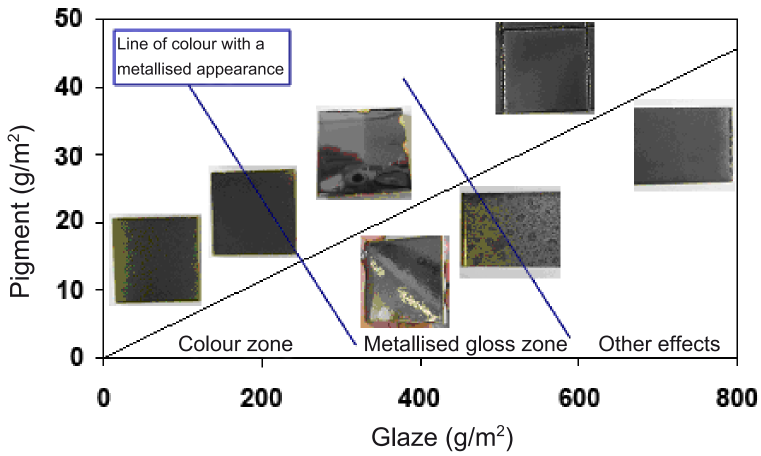


Figure 3. Different effects obtained by the incorporation of copper nanoparticles into the glaze with sepiolite.

One functionality found in the glazes was that of hydrophobicity, in addition to a glossy metallised appearance with a feeling of depth (figure 4). A thorough study of the samples revealed the nanostructured nature of the entire glaze and the existence of a concentration gradient of metal cations that increased near the surface. This effect was mainly obtained by the following two mechanisms, which occur in glazes of a crystalline nature:

a) A migration process of the metal cations to the surface owing to the greater solid-liquid interface energy in relation to that of the liquid-gas interface. It is at the surface that the redox processes occur, which are needed to reach the oxidation states responsible for the metallised appearance, yielding glazes with an intense gloss and feeling of depth with a specular reflection.

b) A thermodynamic spinodal decomposition process, which occurs during the cooling of the sintering cycle which leads to phase separation that generates the nanostructured appearance of the glaze. This nanostructure produces the hydrophobicity of the glaze. In fact, a 'cellular' type of microstructure actually appears that in turn is nanostructured (figure 5) in a similar way to that of the Lotus Flower, this being the first completely inorganic glaze that is hydrophobic in addition to displaying a metallised appearance. The metallic nanoparticles (responsible for this metallised appearance) are coated with a nano-rough crystalline glaze layer, so that the water does not remain anchored to the surface. A conventional crystalline glaze has contact angles of ~35º, without water repulsion, while in the case of the glazes made, a value of 95º was reached, with a hydrophobic effect [16].

Figure 4. Test in which the tile with a metallised appearance displays hydrophobicity.

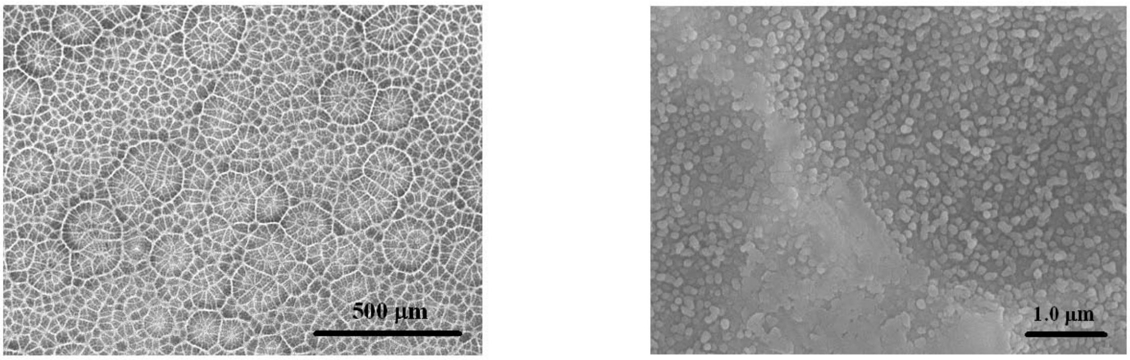


Figure 5. a) MOLP image of the microstructure with a cellular appearance in the glaze with a metallised appearance. b) SEM image of the nanostructure generated by spinodal decomposition at the surface of the microstructure with a cellular appearance.

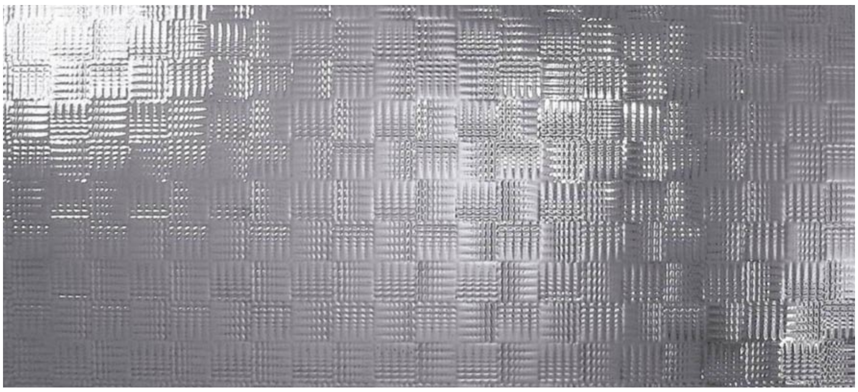
On the other hand, with this method, new colour ranges based on metallic nanoparticles were achieved in which a plasmon effect [17] occurred, located at the surface. When a ray of light of appropriate frequency strikes the metallic particles, plasmon takes place, i.e., the electrons of these particles begin to vibrate at a certain frequency in all directions of the space, producing dispersion or scattering of the radiation at this frequency, giving rise to a colour. For this to occur, the particle size must resemble or be smaller than the radiation wavelength. Chromatic flexibility was achieved depending on the concentration and type of chosen metal. High colour yield was obtained owing to the small size of the metallic particles, by the resulting scattering. Thus, only 0.15% gold [18] in a conventional glaze leads to bright violet colours.

Another of the functionalities displayed by the glazes is its biocidal quality. The tests conducted using glazes with silver nanoparticles, introduced by means of the previously mentioned sepiolite method [15], evidence their biocidal quality in relation to the *Escherichia Coli* bacteria.

The encapsulation of the nanoparticles by the sepiolite fibres has meant a step forward in the application of nanoparticles on an industrial level in the ceramic industry, since the barriers posed by nanoparticles have been surmounted, thus enabling advantage to be taken of the advantages that nanotechnology offers. To date, multifunctional and nanostructured glazes have been achieved, such that the functions of each glaze can be varied depending on the metal involved and the quantity introduced. Thus, glazes can be designed with characteristics that meet the client's needs, with a better pigment yield, entailing savings in relation to the quantity of material and lower demand on existing resources.

With this method of nanoparticle protection using phyllosilicates, the incorporation of nano-charges into ceramic matrices has been achieved, obtaining glazes on an industrial scale called **Nanoglaze** (figure 6), such that they contribute the following advantages to the world of ceramics:

- The nano-charges are not agglomerated, so that after the incorporation processes they keep the properties corresponding to the nano-scale, and not to the micro-scale, as occurs in the case of agglomerates.
- The environmental impact is reduced because smaller product quantities are required. Since nanoparticles are used, the same effects can be achieved by reducing the quantity of material.
- Using standard ceramic technologies, it has been possible to obtain innovative aesthetic effects and functionalities.
- Safety is favoured in the handling of nano-charges and in manufacturing processes because they are fixed in the sepiolite.
- The industrial scalability of the process is possible owing to the non-agglomeration and safety provided by the encapsulation of nano-charges in the sepiolite.



** The processes of obtaining nanoparticles supported on phyllosilicates and multifunctional nanostructured glazes are protected by the corresponding international patents and exploitation licence contracts [19,20].*

Figure 6. Effects obtained by nanoparticle dispersion in the glaze: hydrophobic glaze with a metallised appearance; Industrial application: ***Nanoglaze****.*

4. CONCLUSIONS

The development presented satisfactorily addresses the problematic issues relating to the industrial application of nanoparticles in the glaze sector and, therefore, opens up a new field that constitutes an extremely appealing challenge for the ceramic sector. The developed glazes offer the following characteristics: compatibility with the composition and processing of a standard glaze; great uniformity in the glaze owing to good dispersion of the nanoparticles; a nanometric, ordered structure with fractality of the resulting glaze; multifunctional properties; new glazes of a metallised appearance with hydrophobic properties that can provide self-cleaning ceramic surfaces; new colours based on optical plasmon effects; and glazes with fungicidal and bactericidal properties, all obtained by conventional ceramic application processes.

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REFERENCES

[1] A. Escardino, La innovación tecnológica en la industria cerámica de Castellón, Bol. Soc. Esp. Ceram. V. 40 ,1, 43-51 (2001).

[2] A. Moreno, Ceramic tiles: above and beyond traditional applications, Bol. Soc. Esp. Ceram. V. 45, 2, 59-64 (2006).

[3] E. Tortajada, D. Gabaldón, I. Fernández, La evolución tecnológica del distrito cerámico de Castellón: la contribución de la industria de fritas, colores y esmaltes, Bol Soc Esp. Ceram. V., 47, 2, 57-80(2008).

[4] E. Criado, Reflexiones sobre el futuro de la Industria Europea de la Cerámica, Bol. Soc. Esp. Ceram. V. 46, 39-46 (2007).

[5] T. Raming, et al., Densification of Zirconia-Hematite Nanopowders, J. of the Eur. Ceram. Soc. 23, 1053-1060 (2003).

[6] M. Mayo, Int. Mater. Rev. 41 85 (1996).

[7] R. Dowdin, D. Durham, Summary of the Workshop on Structural Nanomaterials, National Materials Advisory Board. National Research Council. National Academy Press Washington, D.C. (2001).

[8] A. Dowling, R. Clift, N. Grobert, D. Hutton, R. Oliver, O. O'Neill, J. Pethica, N. Pidgeon, J. Porritt, J. Ryan, A. Seaton, S. Tendler, M. Welland, R. Whatmore, Possible Adverse Health Environmental and Safety Impacts, Nanoscience and Nanotechnologies: Opportunities and Uncertainties, The Royal Society & The Royal Academy of Engineering. 35–51 (2004).

[9] M. Auffan, J. Rose, M. R. Wiesner, J. Bottero, Chemical stability of metallic nanoparticles: A parameter controlling their potential cellular toxicity in vitro, Environ. Poll. 157, 1127-1133 (2009).

[10] A. Esteban-Cubillo, Obtención de nanopartículas metálicas soportadas o embebidas en matrices oxídicas Alúmina-Sepiolita, Tesis doctoral, UAM (2007).

[11] J. Santarén, A. Álvarez, Monodisperse and corrosion-resistant metallic nanoparticles embedded into sepiolite particles for optical and magnetic applications, J. Am. Ceram. Soc. 89, 10, 3043-3049 (2006).

[12] J. Molera, C. Baye´s, P. Roura, Key Parameters in the Production of Medieval Luster Colors and Shines, J. Am. Ceram. Soc., 90 [7], 2245–2254 (2007).

[13] J. Roqué, J. Molera, J. Pérez-Arantegui, C. Calabuig, J. Portillo, M. Vendrell-Saz, Lustre colour shine from the Olleries Xiquets, Workshop in Paterna (Spain), 13th century ad: nanostructure, chemical composition and annealing conditions, Archaeometry 49 , 3, 511–528 (2007).

[14] J. Roqué, T. Pradell, J. Molera, M. Vendrell-Saz, Evidence of nucleation and growth of metal Cu and Ag nanoparticles in lustre: AFM surface characterization, Journal of Non-Crystalline Solids 351, 568–575 (2005).

[15] L. Esteban-Tejeda, F. Malpartida, A. Esteban-Cubillo, C. Pecharromán, J. S. Moya, The antibacterial and antifungal activity of a soda-lime glass containing silver nanoparticles, Nanotechnology 20, doi:10.1088/0957-4484/20/8/085103 (2009).

[16] P. Jaquotot, A. Campillo, J. J. Reinosa, M. A. Bengochea, A. Esteban-Cubillo, C. Pecharroman, J. S. Moya, J. F. Fernández, Desarrollo de esmaltes nanoestructurados multifuncionales, Bol. Soc. Esp. Ceram. V. 48, 2, 95-98 (2009).

[17] P. Cheyssac, V.A. Sterligov, S.I. Lysenko, R. Kofman, Scattering of surface plasmon-polaritons and light by metallic nanoparticles, Optics Communications 175, 383–388 (2000).

[18] M. Francoeur, P. G. Venkata, M. Pinar, Sensitivity analysis for characterization of gold nanoparticles and agglomerates via surface plasmon scattering patterns, Radiative Transfer 106, 44–55 (2007).

[19] J. Santaren, J. Limpo, E. Aguilar, A. Alvarez, J. S. Moya y C. Pecharroman, Procedimiento para preparar nanopartículas metálicas y materiales obtenidos por el procedimiento. Patente Española ES2229940 de 01 junio 2006.

[20] A. Esteban, J. S. Moya, C. Pecharroman, J.F. Fernandez, R. Pina, J. J. Reinosa, Procedimiento de obtención de esmalte cerámico con brillo metálico y su aplicación en pavimentos cerámicos. Solicitud de Patente nº.ES200701612 de 12 junio 2007 y PCTES2008070107 de 29 mayo de 2008.