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Functionalized enamel of ceramic tiles by sol gel technique (review)

Deposición de capas funcionales sobre esmaltes cerámicos mediante la técnica sol-gel (revisión)

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Abstract

The function of enamels for the ceramic tile industry has been a research topic for the past 15 years. Different researchers have focused their efforts on achieving surfaces with functional attributes that increase product value and provide solutions for the technological needs of our times. This article presents a review of the scientific literature dedicated to obtaining functional surfaces by means of the sol-gel technique, which provides a means for deposition and formation of thin layers on traditional ceramic enamels in order to provide functional characteristics. The document presents: typically used alcoxidic solutions, the different deposition techniques emphasizing the experimental findings obtained by the authors, and a synthesis of the functional effects obtained by means of the technique.

Keywords: Ceramic enamel - Functional enamel – sol gel - ceramic

Resumen

La funcionalización de esmaltes para la industria de las baldosas cerámicas ha sido un frente de investigación importante en los últimos 15 años. Diferentes investigadores han centrado sus esfuerzos en conseguir superficies con atributos funcionales que incrementen el valor agregado del producto y a su vez aporten respuestas a las necesidades tecnológicas de nuestros tiempos. El presente artículo se centra en hacer una revisión de la literatura científica dedicada a la obtención de superficies funcionales por medio de la técnica de sol-gel, la cual es apta para la fabricación de soluciones que se depositan formando capas finas sobre los esmaltes de cerámica tradicional con el fin de aportar características funcionales al mismo. El documento presenta las principales soluciones alcóxidicas usualmente empleadas, las diferentes técnicas de deposición haciendo énfasis en los hallazgos experimentales obtenidos por los diferentes autores, y presenta una síntesis de los efectos funcionales hasta la fecha obtenidos por medio de la técnica.

Palabras clave: esmaltes cerámicos, esmaltes funcionales, sol-gel, cerámica.

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1. Introduction

The ceramic enamel is a layer of glassy nature that is deposited on the surface of different substrates, of ceramic nature in general, to provide beautiful attributes and protect the surface due to its physical properties. A vast field of enamel applications include ceramic tiles, which are used for flooring and facing in the construction sector [1, 2]. As shown in Figure 1, three clearly defined layers can be distinguished in the tiles: i) the bisque, which serves as support and has the highest thickness and body in the tile, ii) the engobe, which has a thickness between 100 and 200 µm, and joins the enamel and the bisque and iii) the enamel, which is a layer of very low porosity, with a thickness between 75 a 300 µm and the aforementioned characteristics [3].

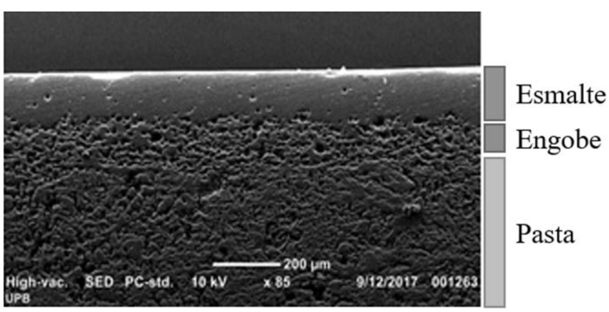


Figure 1. Cross section of a ceramic tile

Besides providing aesthetic and decorative characteristics, the enamels on such tiles can be used for other functional features. Some of the features that it is desired to improve or implement on these surfaces include: self-cleaning, energy storage, photocatalytic, antibacterial, fungicidal, high scratch resistance, inhibiting ice formation, absorb or emit substances, luminescent surfaces and even coating that can change properties when subject to a certain stimulus [4]. Nevertheless, many of the parameters which are necessary for an application at industrial scale are not sufficiently stable yet, and are still under research [5]. Therefore, this constitutes a big challenge for industry, since incorporating new technologies implies adaptation of production cycles and of routine manufacturing conditions which entails high economic investments.

To the best of our knowledge, there are various techniques available to provide functional attributes to the enamel, which include: i) modification of the enamel composition by means of incorporating substances in the enamel mix prior to the burning, ii) physical modification of the surface using plasma or chemical deposition means in vapor phase, and iii) chemical deposition of liquid solutions; the sol-gel technique is one of the most representatives of this family.

The sol-gel technique for material synthesis has been extensively proven for obtaining glassy and ceramic materials [6–10]. Wet chemistry reactions of hydrolysis and condensation produce the transformation of molecular precursors into oxide networks [11].

The following review is specifically focused in gathering scientific information, about the use of the sol-gel technique for deposition of chemical solutions in glassy enamels of ceramic tiles, in order to improve properties or provide functional attributes to the enameled surface. Figure 2 presents a graphical report of the yearly evolution of the publications about the subject, in online scientific databases and specialized books cited in the consulted literature, among which Google Scholar, Science Direct, Wiley Online Library, Springer Link, UN Institutional Repository, American Institute of Physics, Taylor & Francis Online, ACS Publications can be mentioned.

The review was carried out considering publications between 2000 and 2017, with the greater number of works being reported in the period 2009-2017. First. The report focuses on presenting the different types of alkoxides typically used. Then, it describes the different deposition techniques, emphasizing in the experimental findings obtained by different authors. At last, it presents a synthesis of the functional effects.

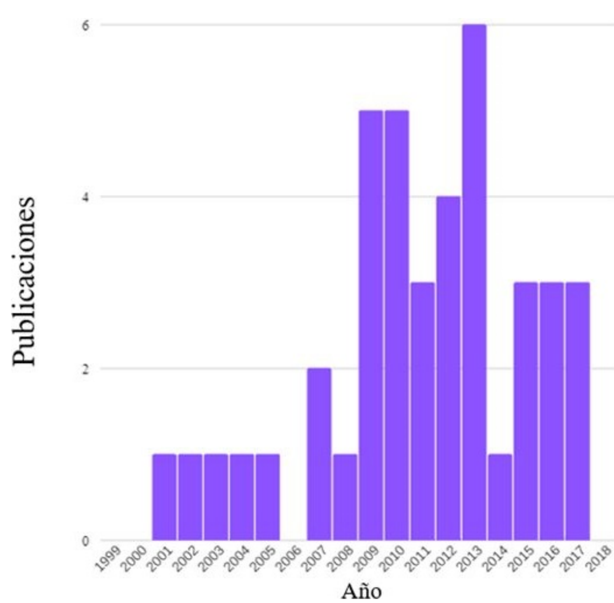


Figure 2. Report of publications per year.

2. Precursors

Table 1 presents the chemical precursors commonly employed for coating enamels using the sol-gel technique, and their corresponding structures. The precursors (starting reagent) are an alkoxide of typical chemical formula R-O-M, which are compounds that comprise a metallic ion (or another cation) represented by letter M, an oxygen molecule represented by letter O and an alkyl group R. The general reactions are expressed in Table 2, according to [12].

Table 1. Precursors

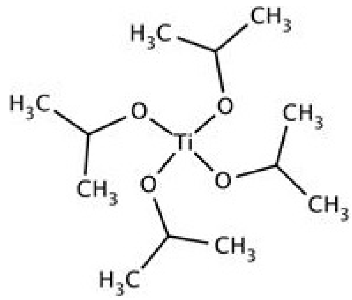
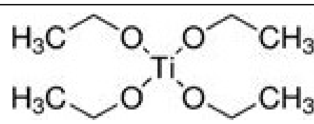
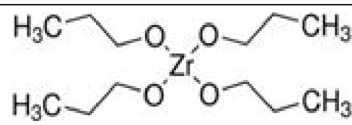
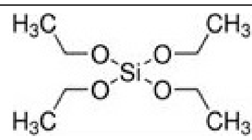
Name	Molecular formula
Titanium Isopropoxide	
Titanium Ethoxide	
Zirconium propoxide	
Tetra-ethyl-orthosilicates	

Table 2. General reactions of the sol-gel process

Hydrolisis
M-(OR)$_x$ + H-O-H → HO-M(OR)$_{x-1}$ + H-OR
Condensation
Alcoxolation (OR)$_{x-1}$ –M-OH+RO-Me-(OR)$_{x-1}$ → (RO)$_{x-1}$ –Me-O-M-(OR)$_{x-1}$ +ROH *Oxalation* (RO)$_{x-1}$ –M-OH+HO-M-(OR)$_{x-1}$ → (RO)$_{x-1}$ –M-O-M-(OR)$_{x-1}$ +HOH *Conventions:* M: Si, Ti, Zr, Hf, Ta, Nb, Al, Zn, etc. R: CH_3, C_2H_5, C_3H: 7, etc.

Once the reaction has occurred, the precursors form colloids, which are suspensions with a small dispersed phase (1-1000 nm), negligible gravitational forces and interactions being dominated by short range forces (Van der Waals attraction forces and surfaces loads). The sol is a colloidal suspension with solid particles inside a liquid.

The gel point is the moment in which the oxide bounded particles spread through the vessel that contains the colloid. During the gelation reaction, the viscosity increases until constituting a solid which adopts the form of the mold. At this point, the pore fluid mainly comprises alcohol and water, and the colloid becomes an alcogel, which can be removed from the container and can stand by itself [13].

Figure 3 is a schematic representation made by [6]. The aerogels are obtained when the liquid-filled pore is replaced by air, without altering the structure or the volume of the gel body.

In the sol-gel process, the reactions depend upon various parameters such as:

- Composition and concentration of the precursors (alkoxide and solvent)
- Amount of water added
- Type and concentration of the catalyst employed
- Additional additives such as desiccants
- Sequence in which the components are added
- Mixing time
- Aging time
- Mixing conditions (efficiency of the mixture, agitation by ultrasound, atmosphere)
- Temperature

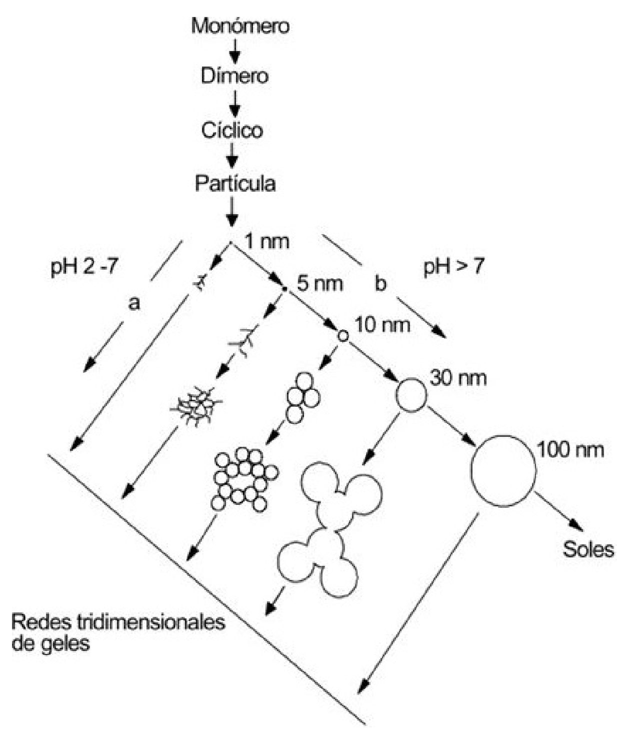


Figure 3. Schematic representation of the sol-gel process [6].

3. Deposition techniques

Regarding the deposition techniques, this sections presents the remarkable findings reported in the reviewed literature, which are complemented with the information presented in Table 3 that summarizes characteristics of the reported techniques.

3.1. Spin

This technique is based on the deposition of small amounts of solution on the surface of a substrate that spins at a high speed, such that the solution disperses due to the centrifugal force, forming a homogeneous liquid film. The solution quickly evaporates the solvent and the oxide molecules are deposited on the substrate. The thickness of the film directly depends on the following variables: speed of rotation, viscosity, contents of solvent and its properties when evaporating.

There are mathematical models of the variation of the thickness, which are described in detail in [12–17]. Thin layer coatings, with a thickness between 0,1 and 10 µm, can be obtained with this technique [18].

This technique has been extensively used in applications which require the formation of uniform films, namely with homogeneous thickness and low rugosity [19]. For this reason, it is employed in manufacturing electronic micro components and has been of interest to obtain highly glossy enamels for tiles, since a reduction of the rugosity of a surface increases its gloss [2].

3.2. Dip

The dip coating deposition technique involves totally immersing the substrate in the solution, and further removing it at a controlled speed [20, 21] under environmental conditions. According to some researchers, it is considered the simplest technique to deposit films on the surface of a substrate, which may be either flat or curved [11]. Indeed, they state that it can be implemented on surfaces with areas in the order of square meters.

The thickness of the film directly depends upon the velocity of substrate retraction and the viscosity of the solution; low velocities are appropriate to obtain thin films, with a thickness between 0.3 and 3 µm, and rugosity between 60 and 690 nm [18].

In 2007, Kuisma *et al.* [22] studied the cleaning capacity of ZrO_2 and TiO_2 thin films, deposited using the dip coating technique on the surface of enameled ceramic tiles of dimension 3.0 x 3.0 cm. Using topographic measurements, this work showed that for higher roughness of the ceramic enamel, more organic material gets adhered to the surface.

On the other hand, Piispanen *et al.* [23] characterized the effects of the resistance to a chemical attack (stained) and cleaning of two tiles, one with dull finish and the other with glossy finish, with TiO_2 and ZrO_2 films deposited using the dip coating technique. It was determined that the TiO_2 coating has greater cleaning and self-cleaning capacity after being exposed to UV light. The authors indicated that the cleaning capacity of glossy glassy surfaces was not steep, and the zirconium coatings could negatively affect the enamels self-cleaning capacity.

Hofer *et al.* [24] studied the thermal stability and the active photocatalytic property of titanium, deposited on ceramic surfaces (enameled substrates and non-enameled corundum substrates) with a coated area of dimension 2.5 × 4.0 cm, using a dip coating process. It was found that the thermal stability reduction depends on the composition of the substrate, thus making evident a slight variation on the electronic structure of the titanium, which indicated weak interactions between the silica and the titanium.

Similar results were reported in a study of the coating of ceramic tiles and window glasses with thin films of nano TiO_2, using dip and spray deposition techniques, showing a good self-cleaning performance of the coatings [25].

In addition, it has been used to obtain antibacterial effects on glassy substrates of ceramic tiles against *Escherichia coli* y *Staphylococcus aureus*, using solutions of Ag/SiO_2 [26] deposited on the enameled surface of the tiles by means of a dip coating technique. They achieved an excellent antibacterial performance against both types of bacteria related to a high synthetizing temperature of the deposited layer, since after this treatment the silver ions are constantly released, which generates variations in their concentrations thus inhibiting the growth of these bacteria.

Soares *et al.* [27] used the sol-gel technique for producing thick coatings of silica and silica/zirconium colloidal particles, on glassy-ceramic substrates of the system Li_2O-Al_2O_3-SiO_2, in order to increase if resistance to scratch and wear. The deposition was carried out at a retraction speed of 5 cm/min. Compared with the results obtained with the substrate without coating, it was found an improvement in the final look of the surface for the functional coatings; nevertheless, the resistance to wear kept constant compared with the samples without coating.

In addition, Zhang *et al.* [28] studied the effects of incorporating titanium nano particles to solutions of tetraethyl orthosilicate (TEOS) deposited on commercial white glassy ceramic tiles (25 × 25 × 5 mm), by means of a dip coating technique in which the substrates were submerged during 3 minutes and further removed at 1 mm/s. This research verified a better dispersion for the particles of P25-TiO_2/TEOS, with a greater surface area and rugosity, and a smaller particle size compared to the particles of P25-TiO_2, which produced a better hydrophilicity and a greater photocatalytic activity, under irradiation of visible light.

López *et al.* [29] examined the effect of different types of substrate, on the morphology of the surface and the photocatalysis of a great scale TiO_2 film. The impregnation was carried out by dip coating; specifically, for the cases of a glassy substrate of soda-lime ground with acid (12 × 21.5 cm), a SiO_2 barrier layer was deposited with a retraction velocity of 5 cm/min.

On the other hand, the substrates (12 × 21.5 cm) of sodium-lime glazed with acid, glassy soda-lime glazed with acid previously coated with a SiO_2 barrier layer, enameled ceramic tile and 6061 aluminum alloy, were impregnated with a TiO_2 film. These tests determined that the phase and microstructure of the TiO_2 film are exclusively anatase. Additionally, it was found a significant variation in the growth of the TiO_2 crystals and the morphology and thickness of the film with respect to the substrate being used, which in turn affects the photocatalytic activity.

The studies carried out by Hazmaliza *et al.* [30] showed the antibacterial performance of the anatase mixed with enamel applied on ceramic tiles, using two different sizes of anatase powder (micrometric and nano). For conducting these experiments, the concentration by weight of the anatase powder in microns was varied, while the size nano anatase was established on a fixed value. The results obtained show a slight variation in the color of the manufactured tile, which becomes more yellowish as the anatase composition increases. Similarly, it is evident that the antibacterial properties increase when the composition of nanometric anatase is greater compared to the micrometric, due to larger area of antibacterial agents on the tile. Likewise, as the composition of anatase powder is greater, the enamel viscosity will be larger.

It is important to note that research has been also conducted related to the application of this technique, in the TiO_2 self-cleaning coating of clay roof tiles (1 × 1 × 0.8 cm) [31]. The authors demonstrated that a TiO_2 photocatalytic coating in the anatase nanocrystalline phase applied under industrial conditions for thin film (0,399 mg of suspension/tile surface cm^2), has a better photocatalytic activity in the decomposition of methylene blue, hydrophilicity and antimicrobial activity, than a thick (0.885 mg suspension/ cm^2) photocatalytic coating.

3.3. Spray

This deposition technique consists of a process of spray or vertical atomization of a stationary liquid solution or in linear movement, where a fluid beam driven by compressed air is fragmented into disperse drops that collide on a substrate. There are many variables associated to the correct operation of the spray, namely flow of solution, pressure of the compressed air, type of nozzle and nozzle-substrate distance, among others [32]. Such variables influence on the size, shape, velocity and drop strength of collision; these are also related to fluid properties (surface tension, density and viscosity).

After the collision, a heat transfer occurs between the drops and the surrounding air, thus evaporating the solvent through the boundary layer around each drop. At the end of the evaporation, the drops adhere to the glassy surface creating a thin layer coating with a thickness between 0.1 and 3 μm [18].

This deposition technique does not have limitations in terms of the substrate size, since the aperture angle of the application gun can be adjusted. It requires a small amount of solution because the deposition is carried out only on the enameled surface, thus reducing costs and minimizing the environmental impact since it is not necessary to use a vacuum to eliminate the gases emerging from the process [33–35].

Bondioli *et al.* [36] studied the functionalization of the surfaces of industrial ceramic tiles by means of the sol-gel technique, to improve the cleaning capacity of non-enameled thin porcelain stoneware, preparing TiO_2-SiO_2 coatings with different concentration of titanium that were deposited using an airbrush. This work reports that films are transparent, they do not modify the stoneware gloss and show good adhesion. In addition, they yield a greater catalytic effect at high synthetizing temperatures, which produces a self-cleaning and self-sterilizing ceramic surface that may also degrade various organic contaminants in the surrounding environment.

Savvova *et al.* [37] developed TiO_2 coatings on ceramic enamels, determining the multi-functionality of this material by reporting its substantial (70-90 %) antibacterial and antifungal properties. Once again Bondioli *et al.* [38, 39] reported the functionalization of the surfaces of ceramic tiles, but this time focusing on soluble salts (alternative coloring processes of ceramic materials without enamel) to improve mechanical properties (resistance to scratch and wear) and the conductivity.

For that purpose, solutions with different concentrations of zirconium, titanium and silver were prepared, and 300 g/cm^2 were applied with airbrush on green unfired bisque. It was visualized that the addition of zirconium soluble salts increased the scratch resistance, while simultaneously maintaining the final aesthetic appearance of the ceramic tiles. The results obtained for titanium and silver were similar to the results already mentioned for zirconium, with the difference that a multi-functional layer is generated.

3.4. Screen

The serigraphy or screen imprinting enables the realization of two-dimensional designs, which makes it useful in industrial processes [40]. The serigraphic processes require a knitting material, that may be synthetic fiber of steel mesh tensioned and bonded to a frame, which is covered with an emulsion that is impermeable to the coating solution in the area in which no printing should appear.

It is a technique that virtually does not cause losses of the coating solution during printing, because the frame goes across the screen at a constant velocity, and after performing the application it goes backwards in order to repeat the procedure.

Due to its versatility, this method has been utilized for 50 years in the ceramic industry to deposit enamels and decorate tiles [18]. For this type of substrates, processes that generate a TiO_2 thin layer using the sol-gel technique, produce thicknesses between 5 and 35 µm, taking into account that both the thickness and the amount of applied material can vary according to the application percentage of the screen, which includes the volume between the screen threads and the thickness of the emulsion [40].

Since not all the material is deposited on the screen, the thickness of the wet layer also depends on the strength and the trawl speed of the frame, the screen-substrate distance, and the viscosity of the deposited solution [40].

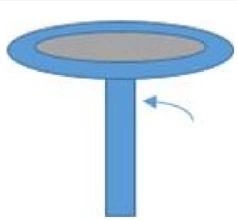
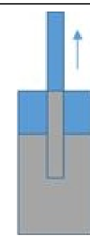
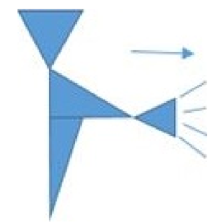
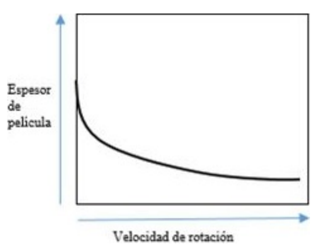
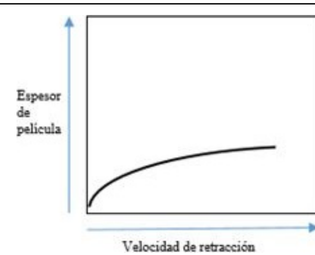
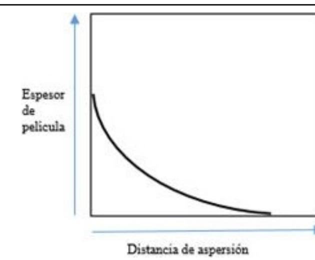
In 2008, São Marcos *et al.* [41] studied the TiO_2 layers deposited by means of serigraphy (55 and 136 µm sifting) at 25 and 50 g/m2 on enameled single-pore tiles. They determined that the layers gave more than 90% efficiency 6 to 8 h after performing the Orange II discoloration, under visible artificial light without layer deactivation; this yielded acceptable levels of discoloration in reasonable periods of time.

In the following year, these researchers [42] characterized and determined the photocatalytic degradation of Orange II, for active ZnO layers deposited at 25 and 50 g/m^2 by means of different sifting screens (55 and 135 µm), using single-pore tiles with glossy enamel (20 × 10 cm from Revigrés, PT); in this case, results revealed a considerable discoloration performance of Orange II (more than 50% efficiency after 6 to 8 h, with a maximum attenuation degree of 72%), under artificial visible light or by direct exposure to sun light. For this effect, the TiO_2 and ZnO layers avoid the elimination of the photocatalyst at the end of the process.

For the same year, Rego *et al.* [43] used the materials previously described to determine the photocatalytic degradation of the Orange II coloring in aqueous solutions, under direct exposure to sun light. For this purpose, TiO_2 and ZnO layers were deposited with 50 g/m^2 on ceramic tiles of single-pore glossy commercial enamels (20 × 20 cm from Revigrés, PT) by means of a serigraphic process where sifting screens were used (136 µm).

This layers exhibited a greater performance for the TiO_2, besides a maximum degree of color attenuation of 90%. On the other hand, in 2011 Seabra *et al.* [44] evaluated the photocatalytic behavior of titanium layers deposited by spray and serigraphy, and the former gave a better coverage with small rugosity levels.

Table 3. Characteristics and publications per deposition technique

Technique	**SPIN**	**DIP**	**SPRAY**	**SCREEN**
Graphic representation				
Typical curve of behavior of thickness as a function of the process variables				
Thickness range	0,1-10 µm	0,3-3 µm	0,1-3 µm	5-55 µm
AntibacteriaL		[26, 30]	[45–47]	
Photocatalysis	[29]	[21–25, 28, 29, 31]	[25, 35, 36, 48–58]	[40–44, 48]
Scratch resistence		[27]	[36–39]	

4. Applications

Figure 4 illustrates the distribution of the consulted literature according to the desired application. It is clearly seen that the applications associated to photocatalysis and antibacterial effect have mainly received the attention. Less than 10% of these researches have focused in increasing the scratch resistance of the surfaces. A brief description of this type of applications is presented in the following.

4.1. Photocatalysis

The absorption of photons coming with light with enough energy (equal or greater than the energy band of the catalyst), promotes catalytic reactions in the surface of the material, generating excitons (pairs e^- – h^+). Such excitons can be used to produce redox reactions [59].

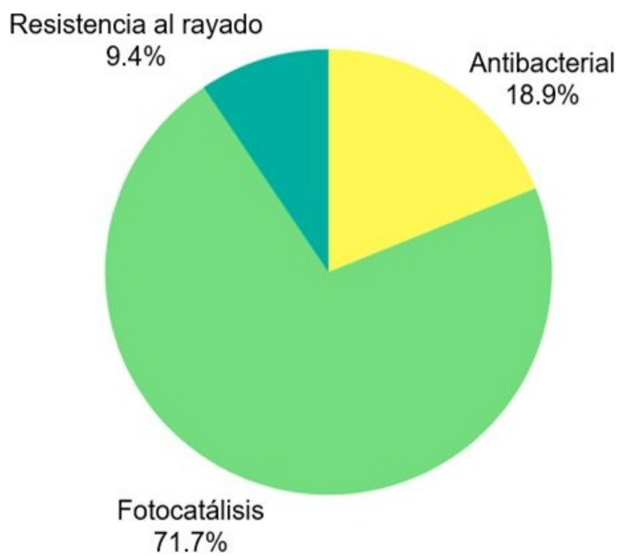


Figure 4. Distribution of research works according to applications.

The main purpose of obtaining coatings with catalytic functions using titanium and its variations on enameled ceramic surfaces, is the self-cleaning such as it is reported in the revision conducted by [18]. This characteristic is the combination of two phenomena: the catalyst action on particular substances (CO_2, COVs) and the superhydrophobicity of the titanium. Some authors also ensure the possible elimination of NO_x, CO, SO_x from the air [60, 61].

4.2. Antibacterial

One of the effects of the interactions between the free radicals (ions and excitons) deposited on the surfaces, is the significant reduction of the growth of microorganisms. The reduction mechanism is based in blocking the aerobic activity of the microorganism, due to the absence of oxygen in the medium.

This application has been of great interest in public places highly exposed to conditions of growth of microorganisms, such as health facilities (clinics, hospitals, surgery rooms), schools and colleges, as it has been proposed in [62].

4.3. Scratch resistence

Behind the improvement of this property, underlie aspects related with the improvement in other properties such as the useful life of the surfaces and their attributes, namely: gloss, color, texture, hardness, among others, which are affected by the wear due to friction phenomena to which the ceramic products are subjected.

The possibility of forming nano and micrometric ceramic layers with crystalline structure, instead of the amorphous structure typical of the glassy enamels, has demonstrated notorious increments in the response of the surface regarding scratch resistance [63].

5. Conclusions

After conducting this revision, it was found that the sol-gel technique has been employed for manufacturing solutions that are deposited in thin layers on traditional ceramic enamels, in order to provide it with functional characteristics. The reported literature mainly corresponds to researchers located in Italy, Brazil and Portugal. The surfaces with photocatalyst (self-cleaning) functional attributes have been a major axis that has motivated the research works in this area. In addition, the broad market and the potential positive effect have driven innovations for the industry.

Even though this is a research topic from 2000, with a strong boost from 2007, the researches in other functionalities seem to be susceptible of being studied, because it is possible to coat enamels with alkoxidic solutions using the sol-gel technique.

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