



Durability of vitreous enamel coatings and their resistance to abrasion, chemicals, and corrosion: a review

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Abstract Vitreous enamels represent a class of coatings with different technological properties, mainly appreciated for the protection they guarantee to the covered substrates. This review introduces enamel coatings, describing their production technologies and presenting the main properties affecting the enamel's durability. Firstly, this review article introduces the most important studies regarding the improvement in abrasion resistance, highlighting both successes and failures. Afterward, the work reveals an outlook about the resistance to chemicals, underlining the good resistance of enamels toward acidic chemicals and discussing the results of studies aimed to improve their performances toward alkaline solutions. This review also considers the corrosion protection property of enamels, highlighting the high barrier effect they provide against the absorption of aggressive substances toward metal substrates. Finally, new perspectives and possible future research paths are presented, being aware that this kind of coating offers both good product protection and functional integrity over time.

Keywords Vitreous enamel, Abrasion, Corrosion, Durability

Introduction

Enameling has its origins in ancient times and can be considered the oldest technique used by ancient civilizations to decorate precious objects. The Mycenaean civilization was the first to employ this technique for decorative purposes about 4500 years ago.¹ The decorative role of enamel became more and more

important in the following centuries, until reaching its climax around the fourteenth century, when its decline began. Only with the advent of the industrial revolution, in the nineteenth century, this type of coating began to be used also for technical purposes.^{2,3}

Enamel coatings combine aesthetically pleasing colors and glossy finishing with excellent technical properties, such as corrosion protection and durability: this was the main reason for vitreous enamel success in many fields, such as household and industry.^{4–6} This vitreous coating still represents an extremely modern coating, with high-performance characteristics, mainly attributable to the glassy nature of the matrix.

The vitreous enamel is obtained starting from many different raw materials found all over the Earth: quartz, soda ash, borax, and metal oxides.⁷ They are ground together in the appropriate proportions to make a fine powder, which is melted at temperatures between 1100 and 1450°C and rapidly quenched to obtain the most important component in the enamel making process: the frit.^{1,2,5}

The frit composition is a key aspect to be taken under consideration as it determines most of the engineering properties of the coating. The major constituent of the frit is the silicon oxide, a glass-forming component, but many other oxides are usually added together.^{2,7} B₂O₃ is employed as a glass-forming element, while Na₂O, K₂O, and Li₂O are used to control the melting temperature of the frit. Aluminum oxide is introduced as an opacifying agent and anticorrosive element,⁸ whereas zirconium oxide, lead oxide, and titanium oxide are useful to improve the resistance to acids and alkali. Nickel and cobalt oxides were used to improve adherence between the enamel coating and the metallic steel substrates,^{1,9} but now they have been replaced by nontoxic compounds. In recent years, particular attention has been devoted to the production of environmentally friendly frits, trying to replace toxic elements such as lead and vanadium

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with more sustainable substitutes, such as titanium dioxide, iron trioxide, and bismuth oxide.¹⁰

At this step, the frit must be milled until reaching a suitable granulometry, which is usually in the range of 100–250 μm .⁷ The frit can be milled in dry or wet procedure, with the addition of mill additives and color pigments. In the more common wet process, the frit is ball milled together with a dispersing medium (water), colloidal clay (used to keep the frit particles into suspension), and other additives.^{1,3,7} The obtained mixture is commonly referenced as “torbida” or “slip.” Every frit is tailor-made for a specific application, and its composition is adjusted to address specific production and technological issues.¹¹ The ready-to-use frit can be applied to the substrates to be covered by dry or wet methods.³ Dry deposition methods, such as the powder electrostatic application technique, also allow high-quality deposits to be obtained on complex-shaped objects, where the charged powder can adhere to the substrate up to 10 min before the firing process. Despite these positive aspects, conventional wet application methods, such as dipping and spraying, are prevalent in the enameling industry worldwide, as they are easily carried out on many different substrates.⁵ The wet spraying technique does not allow an optimal control of the deposition process as it really depends on the operator experience.⁵ In addition to the conventional wet spraying method, the electrostatic wet spraying technique represents a simple way to deposit homogeneous enamel coatings. In this case, the particles to be sprayed possess an electrostatic charge opposite to the one of the ware to be covered; the obtained deposits are very thick, but it is possible to obtain important overspray savings. In the last years, besides the classical deposition techniques, electrophoresis is gaining more and more importance as an effective method to obtain high-quality deposits.¹² The electrophoretic deposition method has been firstly applied in the enameling industry around the 1960s to deposit ground coats layers and nowadays it is known as EPE (“electroporcelain enameling”). The starting material is water-based slurry in which an electrical direct current is used to drive charged frit particles to an electrode. Most of the EPE processes work in anodic configuration. Thanks to the electrodeposition technique, it is possible to effectively control the thickness of the coatings, obtain a complete coverage of the edges, and improve the efficiency of the process, with a high level of utilization of the coating materials.^{13,14} After enamel application, the covered substrate is fired in an oven at very high temperatures in order to obtain the vitrification of the porcelain enamel.

Vitreous enamel coatings can be applied on different substrates, ranging from glass to steel, cast iron, aluminum alloys,^{15–17} Ti-based alloys,^{18,19} TiAl-based alloys,^{20,21} and Ni-based superalloys^{22,23} for oxidation protection at high-temperature purpose. Nowadays, enamel coatings are mainly used to protect steel components for high-duty technological applications,

such as flue pipes, chemical reaction vessels, and gas turbines.^{5,8,9,11} In recent times, the application of enamel on aluminum alloys has generated increasing interest as this coating can guarantee optimal resistance to corrosion and heat, not affecting the lightness of components¹⁶ usually employed in buildings and automotive industries. The main difficulty in the enameling of aluminum is the correct choice of the frit composition because it is necessary to work at temperatures lower than 600°C and have a good superficial distension of the vitreous flakes at the same time.¹⁷ Both the microstructure of the enamel deposit and structure of the coating–metal interface are crucial for the final characteristics of the deposits.^{24–29} If we could cut an enameled material in section, we would see a complex coating structure,³⁰ as shown in Fig. 1.

Porosity and bubbles are common features of the enamel structure^{2,31} and are mainly due to gas evolution during the firing treatment.^{2,3,5} The pore distribution and size can be tailored and controlled, changing the firing temperature, the viscosity of the slip, and adding both organic and inorganic additives.²

Independently on the substrate, enamel coatings possess very good engineering properties. They are not significantly affected by UV exposure, so their aesthetical properties remain unchanged in time,^{32,33} differently with respect to organic matter such as paints and polymers. They have good resistance to heat, direct flame, and thermal shock,^{2,7,16} enamels withstand chemical attack from acids and alkali maintaining gloss, color, and surface properties.^{3,5} Thanks to the strong adhesion between the enamel and the metallic substrate,^{24,25,34,35} enameled materials possess an intrinsic optimal corrosion resistance and can withstand a certain amount of bending without detach-

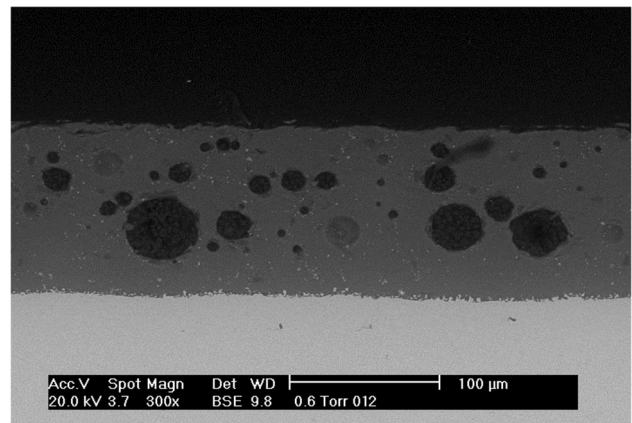


Fig. 1: Scanning electron microscope cross-sectional image of a standard enamel (3 wt.% quartz + 3 wt.% feldspar) deposited on an aluminum alloy substrate.³⁰ Modified from Wear, 332–333, S. Rossi, N. Parziani, C. Zanella, Abrasion resistance of vitreous enamel coatings in function of frit composition and particles presence, 703, Copyright (2015), with permission from Elsevier

ment or chipping. Figure 2 graphically illustrates these characteristics.

Despite all the positive aspects previously underlined, some issues limit the application of this type of coating in many industrial fields. Vitreous enamel shows nonexcellent abrasion resistance, despite its superficial hardness, and this is mainly due to its brittle behavior.^{36,37} Abrasion is a very common mechanism of degradation of enameled surface, as fracture may occur and propagate,³⁶ leading to loss of aesthetical properties, disclosure of the intrinsic enamel porosity, and loss of mass through the formation of flakes. Degradation due to abrasion negatively affects corrosion protection properties, as cracks can reach the metal substrate and allow a direct contact between the substrate and the aggressive environment.

This review focuses on the durability and degradation of enamel coatings, taking into consideration the external agents that can cause a relevant loss of their protective properties. Each section will consider a different property that makes vitreous enamel a coating of industrial interest, focusing on abrasion resistance, resistance to chemicals and detergents, and resistance to corrosion. The work highlights how these properties can be improved and examines the main scientific studies published in this regard. The review makes a critical analysis of the methods that are currently used to characterize these properties, highlighting their positive aspects and limitations as well. In conclusion, a discussion about the future perspectives of scientific research on enamel coatings will be introduced, showing possible research paths to be followed.

Enamel properties affecting durability

Vitreous enamel represents a particular type of coating as it is made from low-cost materials, but at the same time it entails interesting technological properties. The degradation and durability of this coating are key aspects to be taken into consideration when thinking about industrial applications. It is then necessary to investigate the external agents influencing the loss of properties of these coatings and to study possible ways to improve their resistance and durability.

Resistance to abrasion

Among all the possible damage mechanisms due to an external mechanical action, abrasion is one of the most frequent that enamel coatings must withstand. Enamel coatings possess high hardness, but the low fracture toughness of the glassy matrix reduces their resistance to abrasive wear, with consequent brittle fracture happening in the coating.³⁰ Thus, many authors pointed out that a high hardness in combination with a high fracture toughness is required for high abrasion resistance of ceramic materials.³⁸ Moreover, the study of enamel coatings abrasion resistance is very important in order to understand the damage mechanisms that lead to a decrease in both functional and aesthetic properties. In addition, this topic has arisen great interest in the scientific and industrial community as it could be valuable to develop enamel coatings with improved mechanical properties. There are many possible ways to address this issue, thus improving the abrasion resistance of enamel coatings. First, it is possible to modify the chemical composition of the frit, but often the best results are obtained by the addition of mill additives. The crystallization of enamel coat-

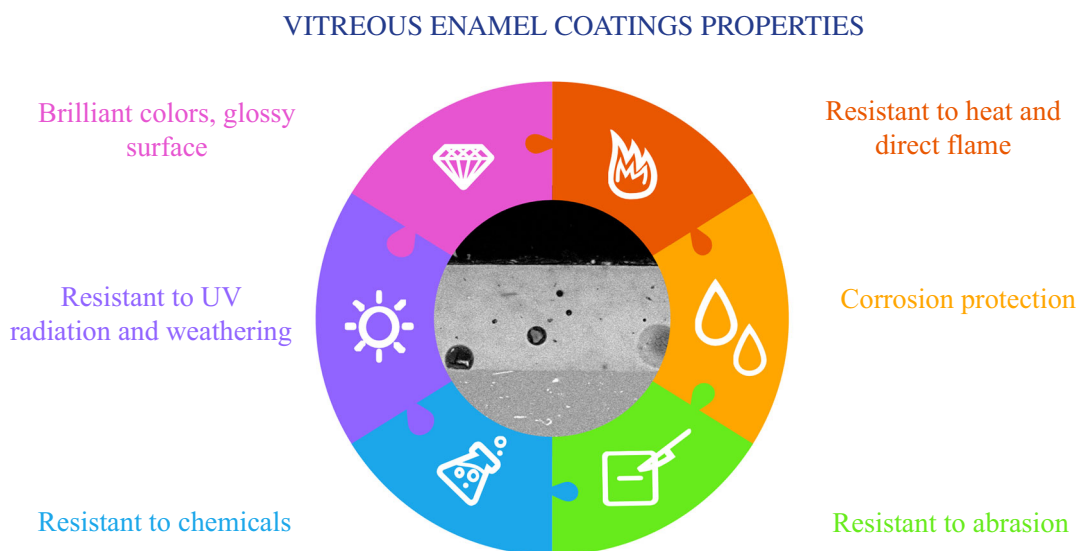


Fig. 2: Graphical illustration of enamel coatings properties

ings³⁹ also represents an interesting opportunity to improve the overall properties of the glassy-ceramic layer, such as the abrasion resistance, hardness, and impact resistance.⁴⁰ The crystallization of enamels, which can be controlled both by thermal treatment⁴⁰ and by using a suitable frit composition,⁴¹ can have positive effects on the improvement in enamel abrasion resistance as well.⁴¹ Other ideas, probably more innovative, consider the addition of hard or auto-lubricant particles in the enamel matrix. However, the choice of the right approach to be followed is not so easy, as many factors must be taken under consideration. Some of these aspects regard, for example, the particle resistance to process temperatures to which enamel is subjected during firing, the compatibility of the particles into the enamel matrix, as well as the dimension and quantities of the added filler. The addition of particles and mill additives embeds a cost for industries; therefore, it is necessary to find solutions that can improve the abrasion resistance of the coatings without producing negative effects. Figure 3 summarizes the main results published in recent times about this topic, giving the reader an overview on the possible ways to improve the abrasion resistance of enamel coatings.

The first and probably one of the easier approaches consists of the modification of the frit composition by the addition of mill additives, as studied extensively.^{30,42,43} One of the first attempts is attributable to Rossi and Scrinzi⁴³ which investigated the effect of potassium feldspar ($KAlSi_3O_8$) and zirconium silicate ($ZrSiO_4$) on the abrasion resistance of enamel coatings. These chemical compounds are usually employed to promote the pyrolytic properties, in the case of enamel coatings subjected to high temperatures, and improve flame resistance avoiding loss of aesthetic properties.³ The addition of these compounds in a 30 wt.% quantity resulted in negatively influencing the abrasion resistance of enamel coatings because it led to an increase in the surface roughness in both cases. Moreover, the mismatch stress between additive and parent glass may cause the decrease in the overall mechanical properties of enamel coating, causing lower abrasion behavior. This is because the mismatch stress may lead to spontaneous crack in enamel,^{44,45} reducing the coating's properties. In addition, it was demonstrated that the solubility of the additive has an important effect on the coating microstructure and on its abrasion resistance too. Zirconium silicate does not dissolve completely in the matrix and this negatively influences the abrasion behavior.³ Moreover, the agglomeration of the filler may introduce

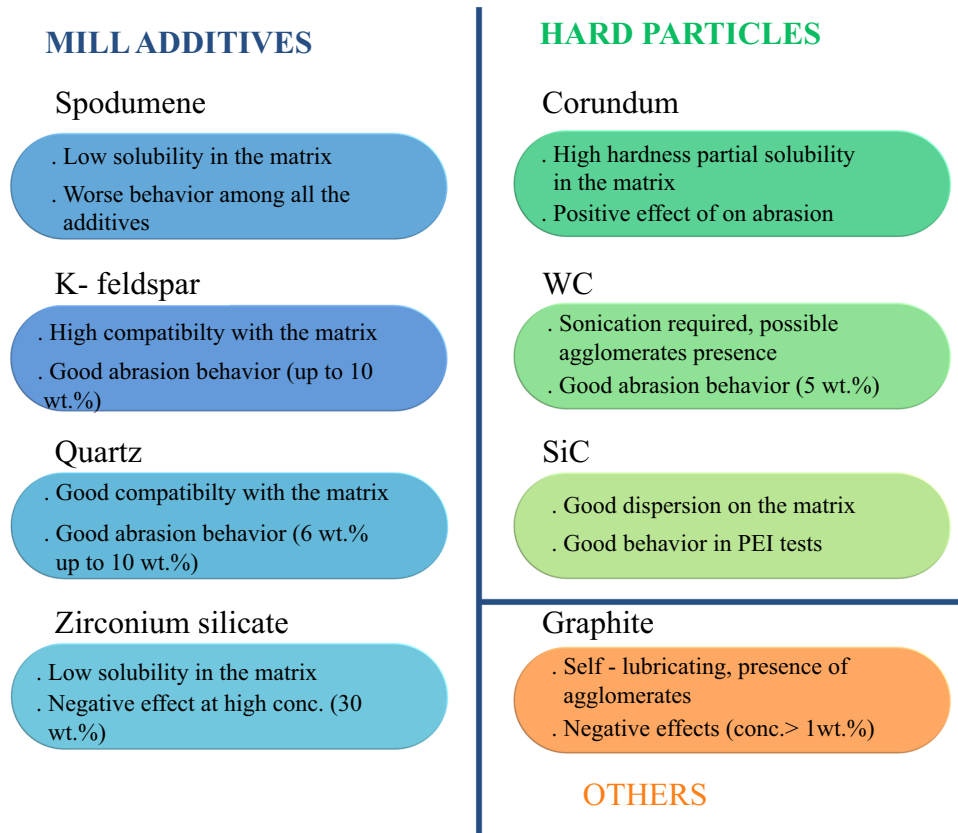


Fig. 3: Illustration of the main results achieved of the improvement in enamels abrasion resistance

large internal stresses, representing crack trigger and propagation sites.⁴⁶ The chemical reactions between the additive and the glassy matrix play a fundamental role in improving the enamel mechanical resistance. Chen et al.,⁴⁶ for example, investigated the effect introduced by the addition of NiCrAlY platelets in a glassy matrix. During the firing process, the oxidation of the platelets produces nichromite, which diffuses into the glassy matrix, improving the adherence of glass to the NiCrAlY alloy platelets, as suggested by previous works about the adherence of glasses to metals.^{47,48}

More detailed studies followed in 2014 and 2015^{30,42} regarding the effect of different types of mill additives on enamel coating properties. They examined the effect of different compounds, ranging from potassium feldspar, zirconium silicate, and quartz (SiO_2) to spodumene ($\text{LiAl}[\text{Si}_2\text{O}_6]$), comparing the obtained results with the performances of a standard enamel coating (usually made with the addition of 3 wt.% quartz and 3 wt.% feldspar).

It is important to point out that the characterization of the enamel coatings properties must be carried out adopting an all-round approach, as single technique measurements and analysis are not able to provide useful information on the behavior of the coatings. This is the reason why a complete study regarding the wear behavior of this type of coating should first include a deep microstructural characterization and then it should include gloss⁴⁹ and roughness⁵⁰ measurements in order to see how the presence of mill additives influences the surface properties of the coating. In addition, it is necessary to exploit abrasion experiments recording mass loss, gloss, and roughness changes at appropriate cycle multiples. The necessity to exploit abrasion tests recording both mass loss and changes in gloss and roughness arises from the enamel structure itself. The abrasion mechanisms could lead to the disclosure of the enamel intrinsic porosity and the debris could fill these pores, altering the mass loss measurements. The abrasion resistance of enamels can be studied using two different tests, each one characterized by different abrasion conditions. The first one is the Taber test, used to evaluate the two-body abrasion process according to the ASTM 4060-10 standard,⁵¹ and the latter is the PEI test, used to study three-body abrasion process, according to the ISO 10545-7 standard.⁵² The two methods operate in different ways and cause a very different abrasion action on the sample surface. In the Taber test, the abrasion action is produced by the contact of the specimen with two abrading wheels. As the sample rotates, the wheels are driven in opposite directions and the resulting abrasion marks form a pattern of crossed arcs in a circular band. This technique involves a severe and localized damage due to a more abrasive medium and higher contact stresses, thus leading to a superficial and sub-superficial abrasion mechanism.^{43,53–57} On the other side, the PEI test is exploited imparting a circular horizontal motion to the sample and using an abrasive medium constituted by water, alumina, and steel balls of different

dimensions. Thus, the PEI test produces a more uniform damage, avoiding the production of localized defects and cracks that could reduce the protection properties of the coatings.^{3,58} Figure 4 shows the different damage mechanisms produced by PEI test and Taber test.

It is important to point out that these two tests give the researchers different information on the abrasion resistance of the coatings and are influenced by different factors. In older studies, Taber test was the preferred method to investigate the behavior of many types of coatings,^{53–57,59–61} among which there were also enamel coatings.^{42,43} On the other hand, in the last years some studies exploit both PEI and Taber tests, reflecting the industrial importance the PEI test embeds.^{43,58}

The previously cited studies by Rossi et al.^{30,42} analyze the effect of mill additives exploiting only Taber test, but the general approach seems to provide the reader a complete overview on the coating behavior. The effect of the different additives was studied in different concentrations up to 10 wt.%. The addition of any additive leads to a reduction in the total porosity and pore dimensions, thus reducing the probability that porosity could act as a crack initiator and propagator. The positive action an additive can have on the abrasion resistance of the coating also depends on its compatibility in the enamel matrix. It has been demonstrated that feldspar has an optimal solubility and leads to an increment in abrasion resistance, whereas zircon silicate and spodumene have low solubility and cause an increase in surface roughness, lowering the ability of the coating to withstand wear.^{30,42} These studies have also highlighted the importance to take under consideration different parameters, as the gloss mostly depends on the additive concentration, whereas the surface roughness is mainly dependent from the type of the used additive.⁴² Those considerations point out the importance of balancing the composition of the enamel coating to obtain the desired properties. It is possible to increase the concentration of an additive to improve the abrasion resistance of the coating, but this choice could lead to a marked loss of aesthetical properties in terms of gloss and color as well.

Another possible way to improve the resistance of enamel coating could be the addition of hard particles. Some studies investigated the possibility of using tungsten carbide (WC) and silicon carbide (SiC) as reinforcing fillers.^{42,58} The positive effects of these particles are only exploited at high concentrations, from 5 wt.% up to 10 wt.%,³⁰ but in the case of WC addition, an ultrasound sonication step is necessary to avoid the formation of clusters and aggregates that could have a detrimental effect on the abrasion resistance. In 2016, Rossi et al.⁵⁸ showed that the homogeneous distribution of the carbides is beneficial to obtain an improvement in the abrasion resistance, as previously highlighted,⁴¹ and showed that the shape of the added particles deeply influences the abrasion mechanism. When the samples are subjected to Taber test, encouraging results have been obtained only with

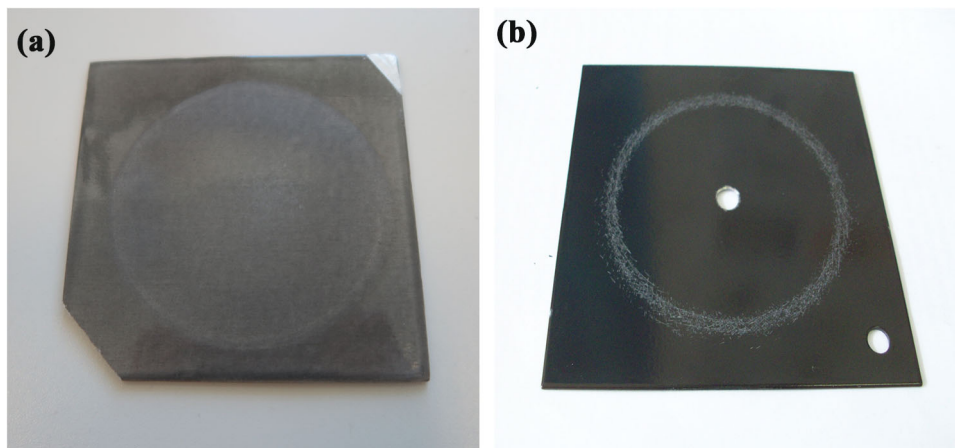


Fig. 4: Image of the abrasion damages caused by (a) PEI test, (b) Taber test

the addition of WC, because the sharp shape of SiC particles could be a point of initiation of cracks and fractures. An opposite behavior was observed in the samples subjected to PEI test, as the main factor influencing the abrasion behavior is the distribution of the particles in the enamel matrix: WC always shows some aggregation phenomena, despite the sonication process underwent.

Regarding the possibility of adding hard particles to the enamel matrix, another way was recently investigated. The addition of small corundum (Al_2O_3) particles in high concentrations could have a positive effect on the abrasion resistance of enamel coatings, as these particles are very hard, and even if some of them are exposed on the surface of the coating, they provide optimal resistance to abrasion. Rossi et al.⁵⁸ demonstrated that the partial solubilization of small corundum particles could lead to areas with higher hardness and improved resistance to mechanical damage.

Another way to improve the properties of this type of coating could be represented by the addition of particles with self-lubricating properties, such as graphite. PTFE and MoS_2 used in composite coatings as solid lubricants cannot be used because they degrade at the enamel firing temperatures. The first attempts, made to investigate the possibility to use graphite as a reinforcing filler, failed mainly because graphite tends to agglomerate and to form flakes, leading to a great mass loss during abrasion tests.³⁰ Recent studies⁶³ pointed out the possibility to add graphene nanoplatelets to the enamel matrix, avoiding the formation of large agglomerates and opening new perspectives on the use of graphene in enamel coatings. Thus, the addition of graphene could have a positive effect on the abrasion resistance of enamel coatings.

So, up to now, many roads have been tried to improve enamel abrasion resistance, but no definite solution has been found. In this field, the experience of enamellers has an important value, as it is necessary to forecast the effects a specific addition would cause.

Resistance to chemicals

The protective performances of vitreous enamel coatings, as well as their intrinsic properties, strongly depend on the frit's chemical composition. The frit can be defined as a complex alkali-metal alumino-borosilicate, and its structure can be visualized as a network of SiO_4 tetrahedra and BO_3 triangular configurations containing alkali metals such as lithium, sodium, and potassium or alkaline earth metals, especially calcium and barium, in the network interstices.⁶⁴ Enamel coatings do not show the same acid resistance as glass, mainly due to their internal structure and chemical composition. The presence of high concentrations of alkali and alkaline earth metals oxides causes the modification and breakdown of the SiO_4 network, with a consequent decreased resistance to acids. The acid hydrogen ions, in fact, are involved in an ion exchange with the metal ions of the network modifier.¹ The resistance to acids therefore strongly depends on the chemical composition of the frit of which the enamel is composed, but it can also be influenced by external agents such as pH and temperature values. Furthermore, resistance to acids can be modified by mill additions, with the beneficial effect of adding bentonite, quartz, and zirconium oxide² and also by the degree of firing and the furnace atmosphere. Nowadays, vitreous enamel coatings possess good resistance to acids, thanks to the measures and modification of the frit studied over the years.

On the other hand, enamels suffer most when they come in contact with alkaline agents.^{3,7} The frit is often modified through the addition of alumina and zirconia, or barium, calcium, lead, and zinc oxides in order to improve enamel coatings' resistance to alkali. These compounds are added to the frit as they can strengthen the bond of the silica network, forming insoluble silicates. The use of milling clay also promotes the increase in alkaline resistance of the enamel. As happens for the resistance to acids, also in this case, there are many different factors influencing vitreous

enamel coatings' resistance to alkali. Among these factors, we can appoint, for example, the temperature and concentration of the alkaline solution. The chemical attack is more severe as the temperature and concentration of the alkaline agent increase.

Over the years, various studies have been carried out to improve the protective performance of these materials, in contact with both acidic and basic substances. The chemical resistance of enamel coatings has been always improved mainly following two different ways: increasing the chemical-resistant frit portion on the total enamel formulation or adding resistant mill additives. One of the most used additives is quartz, as it gives the enamel good resistance to chemicals. An increase in quartz concentration could be beneficial to improve resistance to chemicals, but it could also lead to an increase in enamel viscosity and therefore to the necessity of using higher firing temperatures. Thus, there is a threshold concentration of quartz that can be added to the enamel formulation that cannot be overstepped; otherwise, the production of the enamel itself could be very difficult or impossible to complete, as too high firing temperatures would be needed. A possible way to address this issue could be represented by the addition of different quartz additives, such as liquid colloidal silicon dioxide.⁶⁵ This type of quartz additive has nanometric dimensions and can guarantee good surface finishing together with high resistance to boiling acids.

Rossi et al.,⁴² for example, studied the influence of type and quantity of different mill additives on the chemical resistance properties of a standard enamel coating, exposing the different samples to acidic and alkaline solutions. The gloss value at 20° was chosen as the main parameter to define the level of degradation of the coatings, as the gloss is very sensitive to surface modification phenomena.² The reaction with a 10 wt.% citric acid solution at pH = 2, according to the ASTM C282-10 standard,⁶⁶ caused minimal variations in gloss, as the enamel generally offers good resistance to acid attacks. However, an increase in the enamel performance was assessed thanks to the addition of spodumene, potassium feldspar, or quartz. The beneficial effect of these additives was found to be more marked by increasing their concentration up to 8 wt.%. On the other side, when the samples were tested with alkaline materials, by immersion in a tetra potassium pyrophosphate solution at pH = 10 (ASTM C614-10 standard⁶⁷), an important gloss decrease was observed. Even in this case, however, an increase in the additive concentration up to 10 wt.% counteracted the degradation of the enamel; in particular, samples with the addition of spodumene managed to retain up to around 30% of the initial gloss. Furthermore, by observing the samples with the scanning electron microscope, it was possible to observe the attack morphology and study the attack mechanisms. In acid solution, a localized attack occurs near the grain boundaries, which was more severe in the presence of accumulations of mill additives or in the presence of additives containing

easily diffusible cations such as Li⁺, Na⁺, and K⁺. In alkaline solution, on the other hand, the attack always takes place in a generalized way,⁶⁸ causing the dissolution of the glassy matter. This phenomenon, however, was found to be partially limited by large spodumene crystals. In general, Rossi et al.⁴² showed that quartz addition could provide good property improvement without any specific weakness. Figure 5 shows the enamel surface morphology after immersion in acidic and alkaline solution for samples containing 10 wt.% feldspar and 10 wt.% quartz.

The use of hard particles, exploited to increase the enamels abrasion resistance, can have a detrimental effect on the performance of enamel coating both in acid and alkaline environments. Rossi et al.⁵⁸ studied the effect of silicon carbide (SiC) and tungsten carbide (WC) addition on the coating's resistance to chemicals. The immersion of the samples in citric acid⁶⁶ and potassium pyrophosphate⁶⁷ caused a severe degradation of the coating. The addition of SiC and WC resulted in a significant decrease in the performance of the enameled matrix. The interface between the particles and the vitreous material represents a preferential site for the acid and alkaline attacks. Therefore, carbides are used to promote the abrasion resistance of enamel coatings, but, on the other side, they also tend to favor their degradation in the presence of acid and alkaline solutions. Thus, this work⁵⁸ highlights the need to consider the interface between the glass matrix and the filler as a preferential attack path.

Besides the quantity of filler, the size of the particles introduced into the glass matrix also influences the performance of enamel coating. Recently, a study was carried out regarding the addition of Al₂O₃ powders of micro- and macro-dimensions⁶² and the evaluation of their addition on the enamel coatings properties. Considering the various industrial applications to which the enameled products are subjected, the chemical resistance properties of the samples under examination were characterized by the Kesternich test.⁶⁹ The coatings were therefore exposed to an atmosphere containing SO₂, which simulates aggressive industrial environments.^{70,71} The exposure to several test cycles highlighted the negative effect caused by aluminum oxide based fillers. As previously described, the reinforcing effect of hard particles regarding abrasion resistance collides with an inevitable decrease in the enamel chemical resistance. Even in this study, in fact, the interface between the filler and the glass matrix represents a critical site for triggering of degradation phenomena, which become more severe with the increase in mill additives concentration. Finally, smaller particles offer greater matrix-additive interfaces, causing a marked decrease in coating performances. The Kesternich test, supported by electron microscopy analysis, therefore represents an effective method for assessing the chemical resistance and degradation phenomena of enamel coatings.

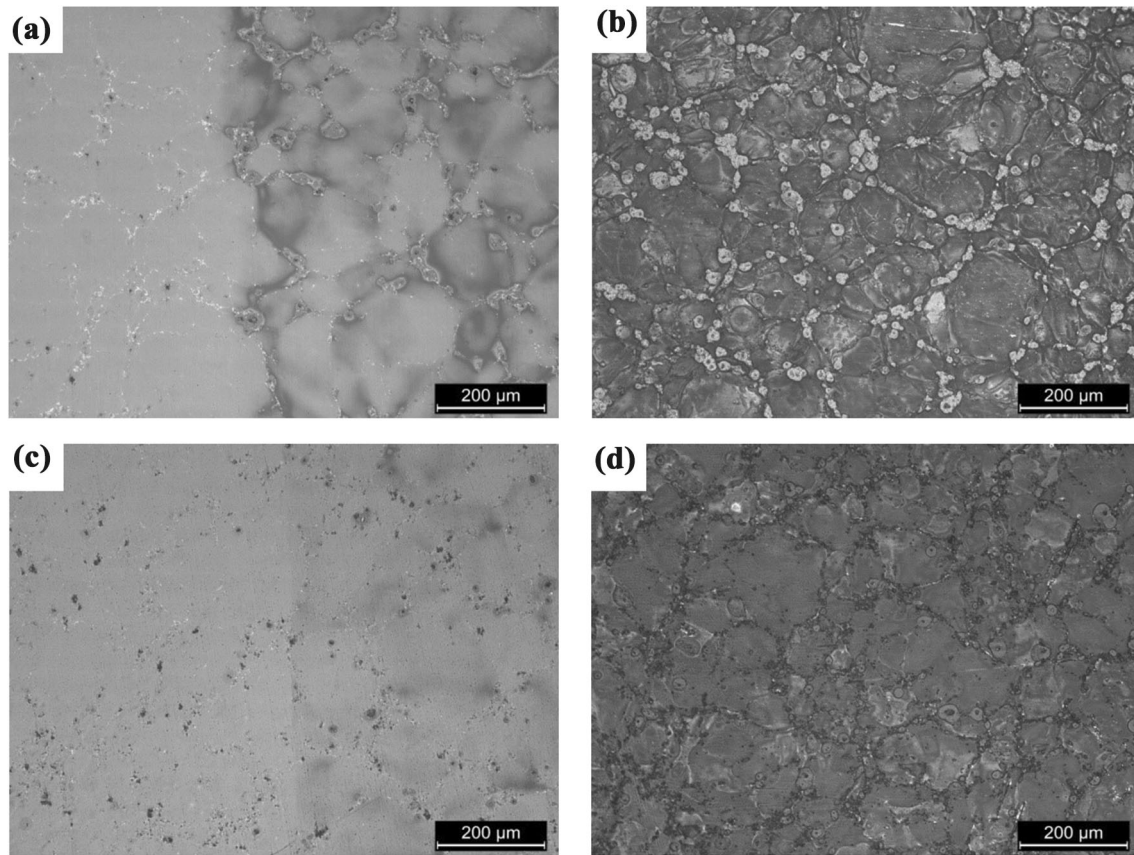


Fig. 5: Optical images of the surface of enameled samples after 24 h immersion to test chemical resistance: (a) 10 wt.% feldspar immersed in acidic solution, (b) 10 wt.% feldspar immersed in alkaline solution, (c) 10 wt.% quartz immersed in acidic solution, (d) 10 wt.% quartz immersed in alkaline solution.⁴² Modified from Materials and Design, 55, S. Rossi, C. Zanella, R. Sommerhuber, Influence of mill additives on vitreous enamel properties, 885-886, Copyright (2014), with permission from Elsevier

One of the main critical aspects of the vitreous enamel materials remains their low resistance to alkali. In recent decades, some studies have employed lithium oxides instead of sodium oxide, in order to improve the performance of enamel coatings,² or a combination of SiO₂ and ZrO₂ has proved to be effective in the case of exposure to weakly alkaline solutions.⁷² Izgagina et al.,⁷³ instead, studied different and complex combinations of additives on the enamel alkali resistance, immersing the samples in 0.1 N NaOH solution for 4 h at 80°C, according to the DIN EN 14483-4 standard⁷⁴ and calculating the subsequent mass loss. The combination of zirconia and lithium oxides, with the addition of milling additives based on quartz, has shown a significant increase in the protective performance of the glass matrix toward attacks of alkaline solutions.

Finally, the performances of enameled materials are often associated with their aesthetic properties, like in the application to stoves and kitchenware. Scrinzi and Rossi³³ studied the chemical resistance of different enamel coatings, evaluating their gloss and color variation after immersion in acidic or alkaline solutions. All the samples taken into consideration showed high resistance to acid attack, as their color and gloss

did not change, but the attack caused by alkali led to an important decrease in their aesthetical properties. Electron microscopy observations showed that the SiO₂ matrix is the most sensitive component of the coating,⁷⁵ but the presence of pigments with big dimensions and localized distribution could also represent preferential chemical attack sites. The pigmentation of the coatings therefore represents a delicate aspect, as an excessive quantity of pigments could cause agglomeration phenomena and lead to a decrease in the protective and aesthetic properties of vitreous enamel coatings.

It is possible to conclude that enamel coatings show good resistance to acid chemicals but their resistance to strong or, even worse, hot alkali solutions can hardly be significantly improved.

Resistance to detergents

Resistance to detergents is an often overlooked property, but it has some important implications when enamel coatings are used for application in washing machine tubs, bath tubs, shower floors, and hobs. In

these cases, the need to produce enamel coatings with an optimal resistance to alkali is limited with respect to the usefulness that proves to have detergent-resistant enamels.

An optimal resistance to detergents does not directly imply good resistance to alkali and vice versa, whereas acid-resistant titania enamels generally show good resistance to detergents as well.⁶³ It was demonstrated that an increase in milling clay concentration in the enamel formulation has positive effects on improving detergent resistance too.⁶⁴ The degradation phenomenon carried out by the aggressive action of detergents is strongly dependent on temperature and it becomes more and more severe as the temperature increases.⁶⁴

Several studies^{76,77} analyzed the effect of different type of detergents on enamel degradation, considering mass loss and aesthetical properties changes, such as gloss and roughness shifts. It was demonstrated that liquid detergents, which are increasingly gaining market, possessing acid pH ranging from 5.6 to 6.8 have a negative effect on enamel durability with respect to general powder synthetic soaps with pH values of about 10, and their action is even stronger if coupled with high temperatures and high concentrations of detergents.⁷⁷

The study of the aggressive action of detergents on enameled materials is probably not so important when enamel coatings are applied on materials or objects of industrial use, but is certainly interesting for the characterization of enameled objects used in daily life, such as kitchenware, stoves, shower floors, and bath tubs.

Corrosion protection properties

Like any type of coating, the vitreous enamel layers are first required to provide corrosion protection to the metal substrate on which they are deposited. Even before the aesthetic, mechanical, and chemical resistance properties, a coating must in fact possess excellent corrosion resistance features. The glassy nature of enamel makes this material a perfect candidate for applications where the product must withstand exposures to particularly aggressive environments for any metal component.

Nowadays, many different tests are available to evaluate a material's corrosion protection. One of the most used is the salt spray fog test. This test is a popular and standardized (ASTM B117-19 standard⁷⁸) accelerated corrosion method, usually exploited to check the corrosion protection properties of a coating on a metal substrate. The testing apparatus consists of a closed chamber, where a saltwater (5 wt.% NaCl) solution is introduced using pressurized air. This produces an aggressive environment of dense saltwater fog to which the samples are exposed. Some recent examples of the application of salt spray test in the assessment of enamel coatings corrosion protection

properties are given by Yan et al.⁷⁹ and by Reis et al.⁸⁰ Despite the ease-of-operation of these accelerated tests, the obtained results are usually qualitative and used only to make a comparison among different specimens. For this reason, the scientific community is increasingly using electrochemical methods to characterize the protection properties of coatings and have more precise and reliable results. Among all the available electrochemical techniques, electrochemical impedance spectroscopy (EIS) is one of the most used methods worldwide.

The electrochemical impedance spectroscopy (EIS) technique has been used to characterize degradation processes in a wide variety of coatings,^{81–83} from metallic layers⁸⁴ and organic coatings⁸⁵ to ceramic materials.⁸⁶ This technique, being nondestructive and very sensitive, can therefore be used in the characterization of defects in vitreous enamel coatings, as observed by Conde and De Damborenea⁸⁷ Indeed, with this work the scientists have managed to establish a relationship between the loss of the enamel coating's protective properties and the mechanism by which the corrosion process takes place. This mechanism changes from a diffusion-controlled process, which takes place during the first moments of immersion, to a charge transfer controlled process only after 24 h of immersion in the test electrolyte. Therefore, the EIS technique enables the in situ evaluation of very resistive materials, like enamel, avoiding material damaging and being able to discriminate the occurring corrosion mechanism. Another very effective but less conventional method to study the corrosion resistance of enamel coatings is represented by the electrochemical noise technique (EN), as established in a previous work.⁸⁸ This study established that the onset of surface defects, due to chemical attack, leads to changes in the system electrical activity, with a consequent increase in both current and potential noise. The EN technique allowed evaluation in real time of the moment of the development of defects in the coating, with a subsequent decrease in its protective properties. Although this method is quite complex and refined, it has proven to be a valid alternative to more standard techniques, as it has shown results in accordance with EIS measures. All these studies showed that vitreous enamel coatings possess high intrinsic corrosion protection properties, if free of defects, as also assessed by Bukovec et al.⁸⁹

The insulating nature of the glass matrix is well suited to applications that require high protection against corrosion of the metal products. Enamel coatings therefore offer a valid alternative to the use of the most standard polymeric coatings. As an example, Fan et al.⁹⁰ compared the protective performance of vitreous enamel with an epoxy based coating. They carried out open-circuit potential, electrochemical impedance spectroscopy, and potentiodynamic polarization tests, highlighting the excellent resistive properties of vitreous enamel coatings. In addition to that, they showed that enamels offer a high barrier

effect against the absorption of aggressive solution, also with respect to the epoxy coating.

Just as the protective properties of a coating strongly depend on its integrity, so the performances of a vitreous enamel layer can be influenced by its structure^{34,91} and morphology.^{92,93} Tang et al.,⁹⁴ in fact, assessed the protective performance of mono- and double-layer enamel coatings by means of electrochemical techniques and showed that the protective properties of enamel coatings strongly depend on their degree of porosity. If the porosity inside the coating is interconnected, the protective features of the glass matrix may disappear. On the other hand, if the enamel, single- or double-layer system, possesses pores disconnected from each other and no cracks are present, it can offer high corrosion protection to the covered substrates.

In addition to its defectiveness, the morphology of the glassy matrix can also influence the protective properties of the coating. Wang,⁴⁰ for example, studied the effect of the thermal crystallization process on the protective properties of enamel coatings. The rise in the process temperature caused an increase in the level of crystallization of the glass matrix. This association with better adhesion between the enamel and the substrate led to a higher corrosion resistance. Also, Yan et al.⁹⁵ evaluated how the crystallization phenomena modify the enamel corrosion resistance. Oxidation processes could favor the precipitation of complex oxides form the glass phase: oxygen diffuses via an exchange between the oxygen of amorphous silicate glass network and dissolved O₂ molecule.^{96,97} The crystallized precipitates not only consume the oxygen of amorphous silicate glass network, but also block the oxygen diffusion path,⁹⁵ improving the corrosion protection provided by the enamel coating. These works highlighted the fundamental role that enamel structure plays a role in determining the protective performances of these coatings. Therefore, the integrity and defectiveness of enamel coatings are not the only factors to be taken into consideration during the production process.

However, the most important difference with respect to organic coatings is the insulating nature of the glass matrix. The enamel coating can face three types of degradation reactions, such as the ion exchange between ionic species in water (particularly H⁺) and ionic components in the enamel (primarily alkali), the hydrolysis of network-forming species, and the dissolution of hydrolyzed species into solution.^{98–100} The rate of these reactions is controlled by temperature, solution pH, and concentration of dissolved solution species, but is slower with respect to metal degradation phenomena.¹⁰¹ As a matter of fact, the glassy matrix acts as strong barrier to aggressive ions. The available literature offers some related examples. Xiong et al.¹⁸ studied, for example, the protective behavior of vitreous coatings at high temperatures in oxidizing environments. Their work highlighted that the uniform and dense enamel layer could

provide oxidation protectiveness to Ti60 titanium alloy at high temperatures, thus protecting the substrate from oxygen embrittlement for long-term oxidation. On the other hand, Tao et al.¹⁰² concentrated their studies on the ability of enamel coatings to counteract the passage of hydrogen ions by means of hydrogen charging tests and deuterium penetration experiments. Their results proved that enamel coating represented an effective barrier against hydrogen isotope penetration, thanks to the loss of shortcut of hydrogen diffusion and the formation of the bonds like the O–H and Si–H ones. On the other hand, previous other works had confirmed that enamel coatings are good candidates for the barrier to hydrogen isotope penetration for titanium and its alloys.^{25,103,104} In addition to the effective barrier effect also exhibited by other ceramic coatings, enamels possess several other advantages. First of all, the deposition process is cheaper than the realization of ceramic coatings based on aluminum and chromium oxides. Moreover, the enamel can be easily deposited even on large-sized products with complex geometries, avoiding the risk of incurring significant defects. From a purely aesthetic point of view, the enamels also enable the deposition of coatings with high aesthetic performances, with a wide choice of colors and visual effects. Finally, the good adhesion of enamel coatings to the substrates hinders under-film corrosion phenomena.¹⁰⁵

In conclusion, it possible to state that enamel coatings guarantee optimal corrosion protection to the covered metallic substrates. The insulating enamel matrix, if dense and free of macroscopic defects, represents a valid alternative to standard organic coatings because it provides a strong barrier effect against the passage of ions and aggressive solutions that can alter the nature of the metal substrate.

Conclusions and future outlook

Enameling of metals is an antique art, and it allows a new material to be created, which combines the features of glass together with the characteristics of metals. Rarely in the history of materials science, the coupling of two such different materials has given such versatile results, both by an aesthetical and technological point of view. This is the reason why the spread of porcelain enamel has always been continuously growing, in parallel with the search for new application sectors and the improvement in frit formulations.

As described in this review article, many attempts have been made to improve the intrinsic protection properties of enamel coatings, such as abrasion resistance, protection to corrosion, and resistance to chemicals. Many methods have been tried in order to address these issues, starting from the modification of the enamel frit composition, to the addition of mill additives or hard particles. Some of them were successful, while others highlighted the limits of some

additives and approaches. Considering the innumerable possibilities that could still exist regarding the improvement in enamel properties, it seems more useful to focus on improving some technical specifications in a timely manner for individual technological applications, rather than exploring the effects that a given compound will bring on overall enamel characteristics. In this context, it is important to highlight that enamel coatings characterization is currently carried out using simple and well-established methods or techniques; thus, regarding this aspect no development is expected. On the other side, it is necessary to evidence the necessity to adopt an all-inclusive approach, in order to consider the different factors on which the results of scientific investigations depend, as concerns, for example, abrasion measurements.

Certainly, the world of enameled coating does not seem to potentially bring major scientific innovations or to be a field in which science can make an essential contribution, to which industries cannot already make up for independently. Unlike what it is possible to imagine, there are still many issues waiting to be settled for further development and many applications to which enamel coatings could bring help.

Two lines of research very active in this historical moment are, for example, those regarding the development of highly reflective coatings for low-energy impact buildings and that of self-cleaning and catalytic coatings.¹⁰⁶ Modified enamel coatings have been considered as suitable candidates to address these issues as many encouraging results are published in the literature on these topics,^{107,108} even if further developments are needed to make this type of technology mature. We are expecting more research on these topics, and we really believe that new applications will be developed soon, probably being able to degrade organic pollutants¹⁰⁹ or even kill viruses or bacteria.

Moreover, enamel coatings could find an important position in technological and design fields in which the importance of color, color effects, and finishing is fundamental. Luminescent enamels are an example of an innovative smart enamel coating with unique optical properties. They are obtained with an addition of rare earth compounds and they show particular optical properties, which can be useful in the safety field, in architecture, and for outdoor furniture.¹¹⁰

At this point, the authors really believe the time has come to focus attention on the possibility to improve enamel fracture toughness as well. Several studies about composite ceramic materials and coatings including graphene sheets and carbon fibers were published in recent years, highlighting an impressive improvement in composite properties. It would be interesting to verify how these additives can improve the strength and toughness of enamel coatings as well, thus opening a way to nonbrittle enamels. If the chipping and cracking tendency of enamel coatings was significantly reduced, a new era of application for these coatings would start soon.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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