GLAZES FOR CERAMIC WALL AND FLOOR TILES. EVOLUTION AND PERSPECTIVES

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ABSTRACT

Over the last thirty years, the technical and aesthetic characteristics of ceramic glazes for ceramic wall and floor tiles, glaze and frit elaboration procedures, techniques for applying these materials on a green or fired ceramic body, as well as the firing cycle to which the glaze is subjected, have all undergone and continue to undergo extraordinary evolution.

In this exposition, after highlighting the close relationship between the characteristics of the glazed surface and the manufacturing process, the different kinds of glazes, their elaboration processes and glazing techniques as well as their evolution during the last few years, are analyzed and discussed. Two lines of action for developing new glazes are proposed and some surface-coating techniques at present used in other sectors are described.

1. INTRODUCTION

The ceramic wall and floor tile industry has undergone profound technological transformation in the last thirty years, both with regard to the manufacturing process as to the characteristics of the finished product. Many of these steps forward, such as the implementation of single firing first of all in floor tile and later in wall tile production, and the progressive reduction of the firing cycle could not have been carried out if suitable glazes had not been developed at the right time.

Similarly, the widespread use of glazed ceramic wall and floor tiles would not be as extensive as it is nowadays, were not the technical and aesthetic characteristics of the glazed surfaces suited for their different applications.

In order to achieve these aims, new frits and glazes have had to be developed, manufacturing processes improved, new techniques and glaze application facilities incorporated in the glazing line and ever more rigorous monitoring systems established, both with regard to raw materials as to the manufacturing process.

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2. RELATION BETWEEN THE CHARACTERISTICS OF THE GLAZED SURFACE AND ITS MANUFACTURING PROCESS

The properties of a glazed surface, just as that of any ceramic product, depend, beside the physico-chemical characteristics of the starting materials, on the development of each of the stages involved in its manufacturing process (Figure 1). In fact it has repeatedly been shown that incorrect execution of any of the process stages (fritting, grinding, etc.), not only affects development of the following ones (glazing and firing), but also the characteristics of each intermediate product (porosity, permeability of the dry glaze layer), as well as those of the end product (bubbles, etc.). Wall tile manufacture must be considered as a set of interconnected stages which progressively transform some raw materials into a finished product. This basic axiom of the ceramic materials manufacturing process results in a series of more specific considerations of great interest:

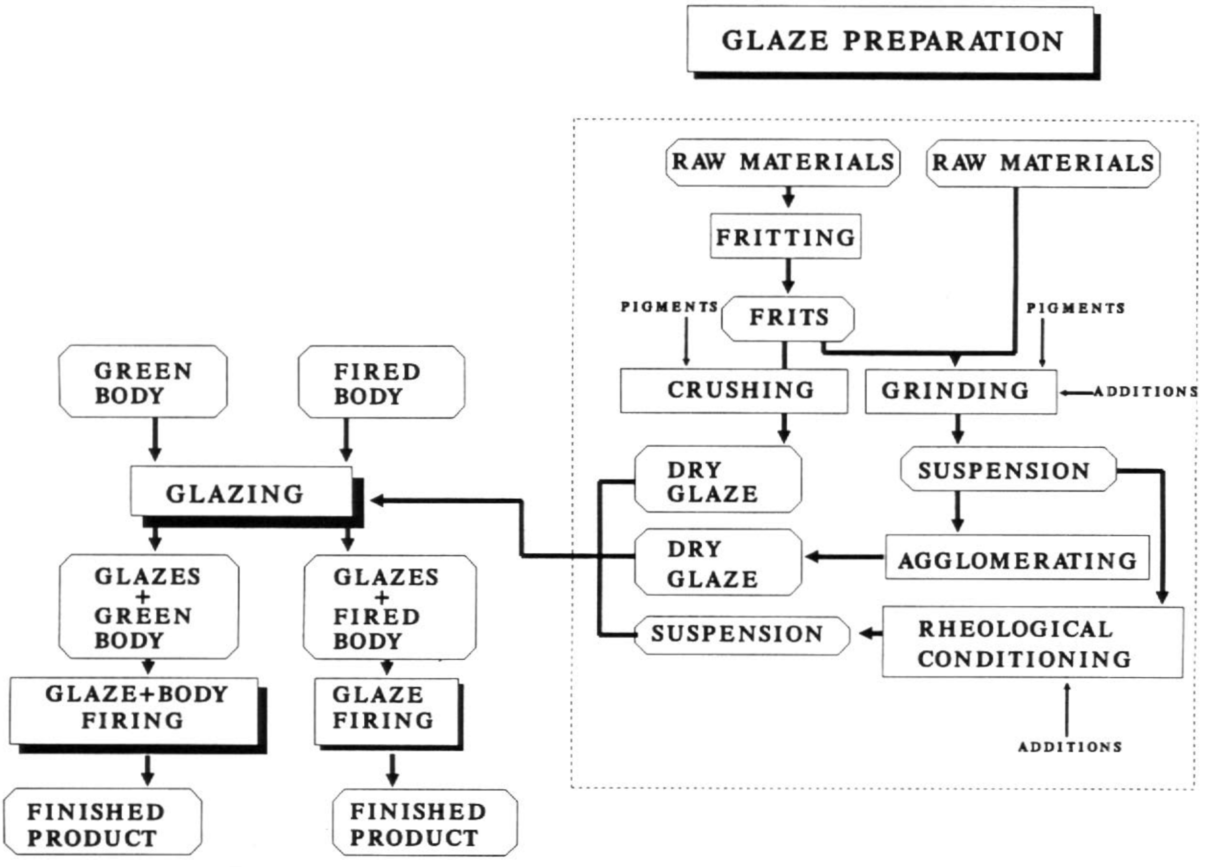


Figure 1.- Scheme of the glazed wall and floor tile manufacturing process.

i) Change in any process variable, intentionally or fortuitously, which modifies the characteristics of a material resulting from an operation (frit, suspension, applied glaze layer, etc.), will alter the development of the following stages and very probably the characteristics of the finished product.

ii) All the process operating variables must be strictly controlled as all influence the characteristics of the finished product.

iii) A good quality glazed surface can only be obtained from a suitable formulation and the correct execution of each stage according to a preestablished scheme.

3. WALL AND FLOOR TILE GLAZES

3.1 Considerations on their formulation.

The material applied during the glazing operation, in one or several successive layers on a green or fired body, is made up of several components (frits, additives, etc.), each of which fulfills a specific task, either for the orrect execution of one or more process stages, or to confer certain technical and aesthetic characteristics to the finished surface. The choice of these constituents and the amounts involved in formulating each of the layers to be applied must be carried out with both aims in mind.

Optimizing a formulation often turns out to be complicated as many of the components improving some product characteristics (gloss, texture, etc.) are detrimental to others (hardness, resistance to acid attack). The optimal formulation is therefore the one behaving most appropriately throughout the whole manufacturing process and conferring the desired technical and aesthetic characteristics to the end glaze.

3.1.1 Characteristics determining glaze composition.

The following requirements may be highlighted among the most important ones a formulation has to fulfill (Figure 2):

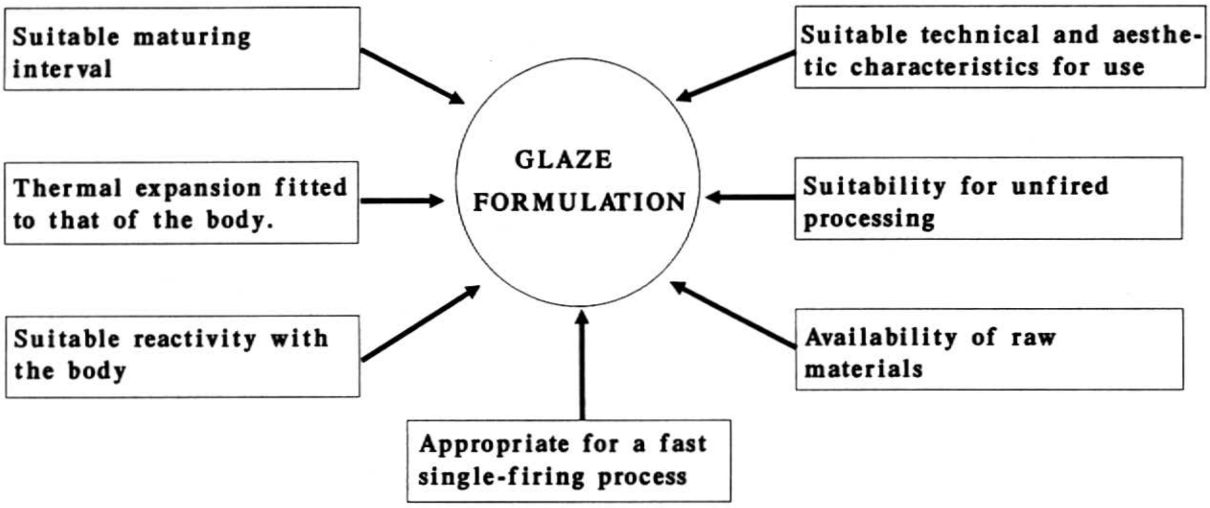


Figure 2.- Requeriments determining glaze composition.

i) Suitable maturing interval.
During firing of the glaze, a series of physical transformations (sintering, phase transformations) and chemical reactions (dissolution of components, immiscible phase separation, crystallization) take place which determine the technical properties and appearance of the glazed surface. It is not only vital that glaze porosity should be minimal and that the above-mentioned transformations take place to the extent required at the firing temperatures and cycles used, but that all the glaze properties hardly change with slight firing temperature changes, in order for the glazed surface to possess the desired characteristics. This results in values for viscosity, surface tension and liquid-phase amounts at firing temperature being suitable and their variation with this variable being limited (1) (2).

ii) Suitable thermal expansion.
If the thermal expansion curves of the fired body and glaze are different enough, stresses develop between both layers during cooling of the ware in the kiln which will result in curvature or even in crazing and shelling of the glaze. As ceramic glazes are more resistant to compressive stress than tensile stress, glazes are usually utilized having slightly lower coefficients of expansion than the body, so that the glaze is held under compressive stress.

Moreover, in this case, retard crazing as a result of moisture expansion of the body and/or shrinkage undergone by the mortar layer in contact with the glazed wall tile, is deferred or its possible manifestation even impeded (3).

iii) Appropriate reactivity with the body.
During firing, the glaze must react with the surface of the body (or with the engobe and this in turn with the body), to form an intermediate bonding layer (4). This interaction is vital in preventing crazing and shelling. On the contrary, excessive reactivity between both layers can impair surface quality.

iv) Suitability for processing of the unfired components.
To obtain stable suspensions with the rheological characteristics required by each kind of application and in order for the layer to have the appropriate properties as it develops during glazing (adhesion, permeability, porosity, etc.), it is vital that the relation plastic material (clays, kaolins)/ non-plastic material should be suitable, besides the use of the corresponding rheological additions. Furthermore, both the fritted and the unfritted components should be completely insoluble in water. Solubility in water, even though to a highly limited extent, considerably alters the rheological conditions of the suspension and therefore of its behaviour during glazing and firing.

v) Technical and aesthetic characteristics.
The appearance (glossy, matt, opaque, transparent) and the technical properties of the glazed surface are characteristics which although affected by the glaze applications and firing stages, largely depend on the starting composition.

These are, ultimately, the characteristics determining performance of a glazed surface used for different purposes (Figure 3).

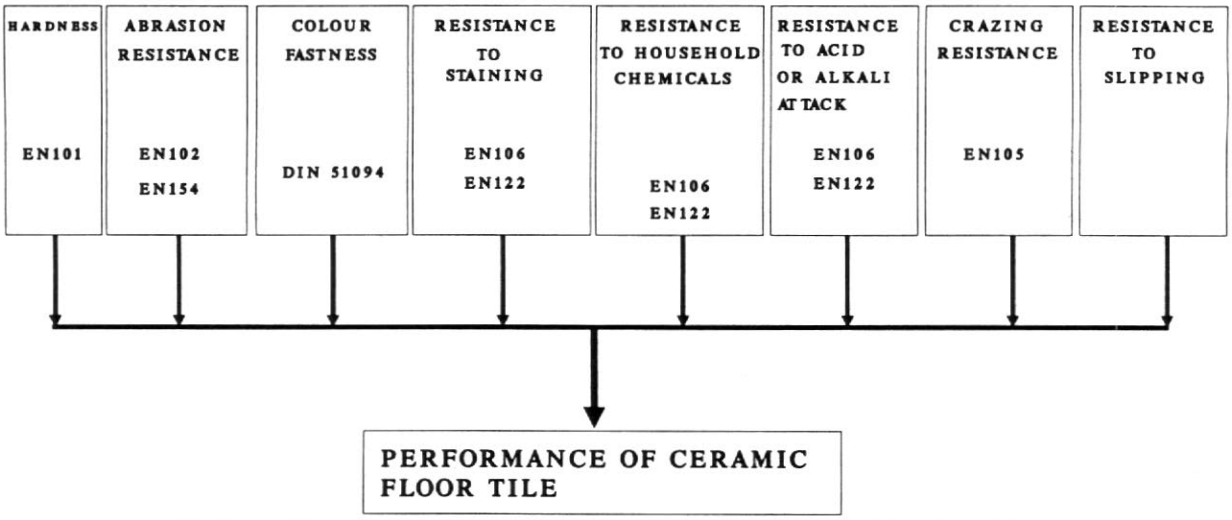


Figure 3.- Characteristics of the glazed surface defining ceramic floor tile performance.

vi) Availabiliy of raw materials.
The price of raw materials used in elaborating glazes should not be high if the product is to be competitive. Homogeneity and continuity in raw material quality and supply are likewise fundamental.

vii) Fitting the ware to the single-firing process.
The glaze must seal the body surface (sealing temperature) at temperatures where the breakdown reactions of the clay minerals and carbonates, and oxidation of the ware have ended, so that the glazed surface will not be impaired by pinholing caused by gaseous releases from the body and facilitate internal oxidation of the ware, thus avoiding formation of the black core defect (5) (6).

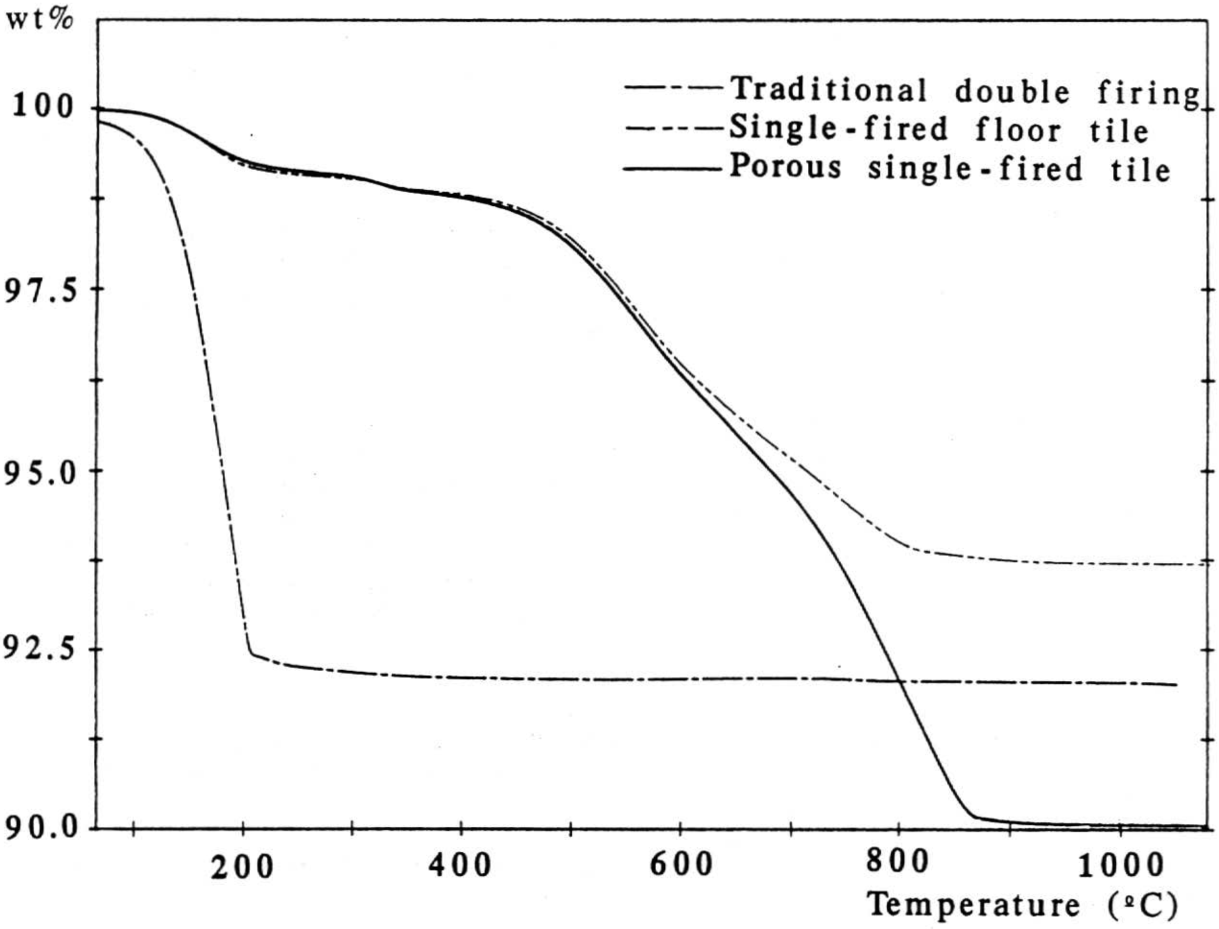


Figure 4.- Thermograms of different bodies.

On comparing the thermograms (Figure 4) of a moisture-saturated double-fired body, with a low porosity single-fired body, and a third porous single-fired body, with the exception of the previously fired body, the remainder all show gaseous releases at high temperatures. In fact, carbonate decomposition in the porous single-fired body is not completed until temperatures close to 900°C and in the stoneware composition about 800°C, are reached.

3.1.2 Effect of the composition on glaze properties.

Thoroughgoing analysis and discussion of the influence of each oxide in a glaze composition on its behaviour or on the characteristics of the finished product (hardness, thermal expansion, etc.) would be long and tedious, and therefore lies beyond the scope of this exposition. Even in the most favourable instance of the glazes being fritted, analysis would be complicated and would have to be conducted by grouping them in families of similar compositions, as in general, the effect of each oxide on some of the above-mentioned properties depends among other factors on the overall composition of the system. Obviously, if the glaze is not fritted, besides the above constraints other factors such as the mineralogical nature of the components and physical characteristics (particle size, etc.) complicate this analysis even further.

However, with a view to analyzing the glaze compositions and their evolution, the effect of certain fluxing oxides which are or were very widely used in glazes, on some glaze properties will very briefly be described next.

Figure 5 reports the plot of the effect which substitution of 10% silica by a fluxing oxide has on variation in viscosity of the melt with temperature, for a glaze fritted with a high Si02 content. The curves in this figure were assessed by means of the Bremond correlation (7).

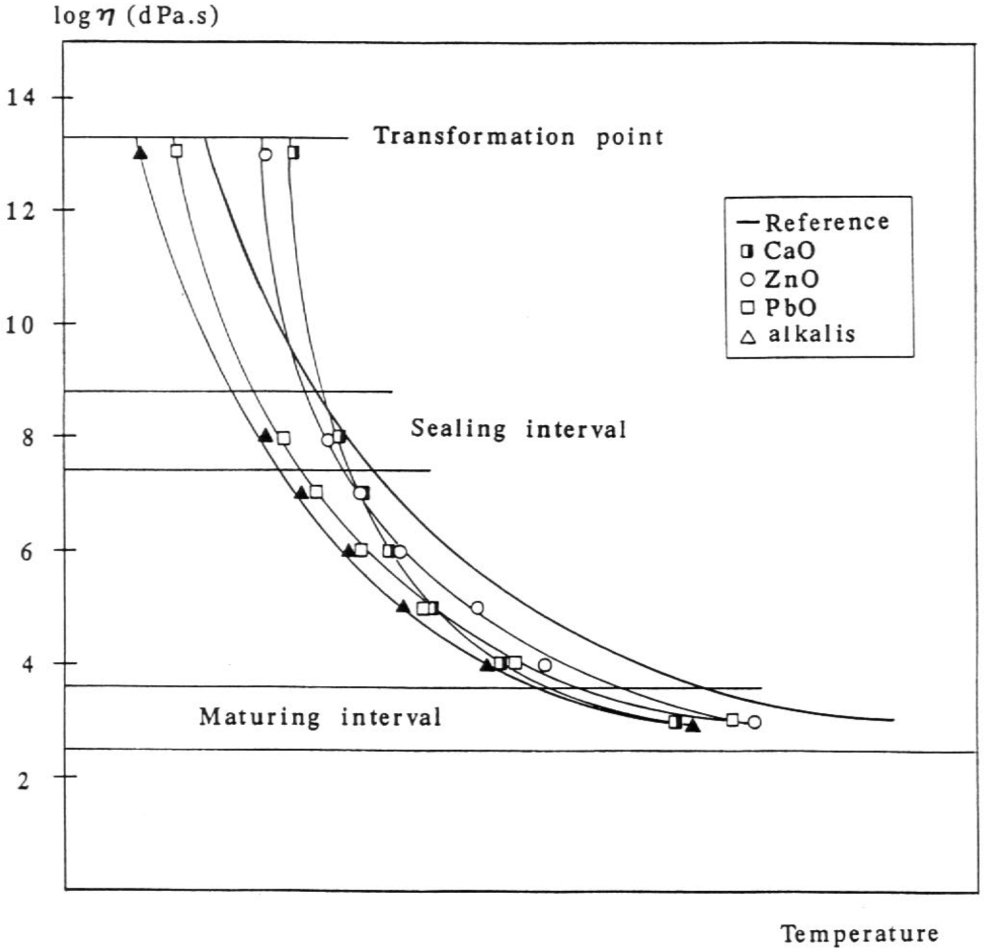


Figure 5.- Variation of the viscosity of a melt with temperature. Effect of some fluxing oxides.

Although replacing silica by any of these oxides lowers glaze maturing temperature (log η= 3-4), variation in viscosity with temperature, on which glaze behaviour largely depends during firing, is shown to vary from one oxide to another. In fact, whilst substitution of silica by alkaline oxides and PbO lowers viscosity of the original glaze in the whole temperature interval (the behaviour of B_2O_3 is similar), CaO and ZnO only lower temperatures close to glaze maturing temperature, increasing it at low temperatures. The reduced melting interval some glazes have with high amounts of CaO and ZnO, with high sealing temperatures and maturing temperatures like those of glazes with a high B_2O_3, Na_2O, K_2O and PbO content, is the main reason for using these glazes in single-fired porous wall tile manufacture, as will be seen below.

The effect some of the above-mentioned oxides have on the coefficient of thermal expansion (α), Young's modulus (E), refraction index (n), and surface tension of the molten glaze (σ) can be observed in Table I. It details the factors with which each oxide contributes to each of the properties above, assuming these can be considered additive. This assumption has been experimentally confirmed, within certain limits, for glazes with an exclusively vitreous nature (8) (9).

As far as other glaze properties are concerned such as hardness or chemical resistance, although it is quite clear that substitution of a lattice forming oxide (SiO_2, $A_{12}O_3$) or a lattice stabilizing oxide (ZrO_2, TiO_2) by any of the above-mentioned fluxing oxides, worsens these glaze properties, setting up comparisons between all of them is very complicated. However, generally speaking, glazes with a high lead content are recognized as being softer than those formulated with alkaline oxides and these in turn are not as hard as those containing alkaline earth oxides and ZnO (10). The behaviour to be expected from these glazes with regard to acids, is quite similar to that described above (11).

Oxide	$\alpha_i \times 10^8$ (°C^{-1})	E_i(Kbar)	σ_i(mN/m)	$n_i \times 10^4$
PbO	13.00	4.6	1.2	0.0179
CaO	16.67	7.0	4.8	0.0177
ZnO	6.00	5.2	4.7	0.0168
Na_2O	33.33	6.1	1.5	0.0159
K_2O	28.33	4.0	0.1	0.0155
B_2O_3	0.33	---	0.8	------

$\alpha = \sum \alpha_i \cdot p_i$ — Range 20-100 °C —— Winkelmann-Schott

$E = \sum E_i \cdot p_i$ —————— Winkelmann-Schott

$\sigma = \sum \sigma_i \cdot p_i$ — at T=900 °C —— Dietzel

$n = \sum n_i \cdot p_i$ —————— Dietzel

$p_i \longrightarrow$ wt %

Table 1.- Additive factors for calculating glaze properties.

On comparing the effect each oxide has on the characteristics analyzed, those, whose introduction in the glaze composition is justified because glaze behaviour during fusion or some final properties improves, generally turn out to be detrimental to other properties. As a result, recourse is had to compromise solutions in glaze formulation which globally optimize glaze behaviour during processing and the properties of the resulting product, making it therefore necessary to often use complex oxide mixes.

3.2 Compositions.

The high degree of both aesthetic as well as technical diversification the glazed surface of wall and floor tiles has progressively attained and the different firing techniques which have been implemented together with the need to adapt each glaze to the manufacturing variables and composition of each body, are the causes justifying the great number of compositions formulated.

This is why it has been considered preferable, when analyzing and discussing compositions and their evolution to do it in a general manner, classifying the glazes in groups based on the firing cycle they undergo and on the use to which the finished product is to be put. Reference will therefore be made to:

- Glazes for single-fired wall tile.
- Glazes for traditional double-fired wall tile.
- Glazes for fast double-fired wall tile.
- Glazes for fast single-fired floor tile.

On the other hand, although most glazed surfaces are obtained by application (dry, wet or by means of serigraphy) of different materials, in this section we mainly refer to the composition of the so-called basic glaze or basic layer, generally by the wet method. Not only is this layer the thickest, but starting from the same basis and combining or modifying the remaining applications leads to different glazes being obtained.

Moreover, within each group of glazes, for the sake of briefness, reference will generally be made to those basic glazes which are or were most commonly used.

3.2.1 Wall tile glazes.

The most commonly used bases for obtaining these glazes were and are still transparent (crystalline) and opaque (mainly white) glazes, both of which are glossy. At present, about 90% of wall tile glazes being fabricated are elaborated by applying serigraphs to these bases. These glazes are made up of one or more frits with the necessary additions to obtain suspension and are subsequently applied, usually by bell glazing.

3.2.1.1 Glazes for traditional double-fired wall tile.

In the beginning, frits mainly with a high lead content were used as this oxide had traditionally been used since ancient times (12) and also because of the advantages it bore (Table II) compared to other fluxes, for obtaining glazes whose hardness is not a fundamental characteristic and which are fired at low temperatures (approx. 950°C) according to slow cycles.

Advantages	Disadvantages.
- Vigorous flux, similar to alkaline oxides but providing the glazes with lower thermal expansion. - Gives the glazes a wide maturing interval. - Provides the glaze with low surface tension and a high refraction index, wich promotes flow, gloss and colour performance of the glazed surface. - Reduces the tendency to surface crystallization of the glazes.	- High volatility at temperatures over 1150°C. - Lowers glaze hardness. - Glazes are highly soluble in acid medium. - Toxicity of raw materials and some frits.

Table 2.- Advantages and drawbacks of lead oxide compared to other fluxes.

Among the frits with the highest lead content, lead silicates and borosilicates (Figures 6 and 7) are to be highlighted. Owing to their high reactivity (these are the most fluxing frits), they have been extensively utilized during the seventies in achieving decorative effects such as "reactive serigraphs", "electric blue", "parchment effect".

There has been a progressive trend in reducing glaze lead content, mainly owing to its toxicity, replacing this flux by boron oxides, alkaline and alkaline earth oxides. In Figures 8 and 9, the transparent frit composition interval is represented, with and without lead, at present being used as basic glaze for wall tile.

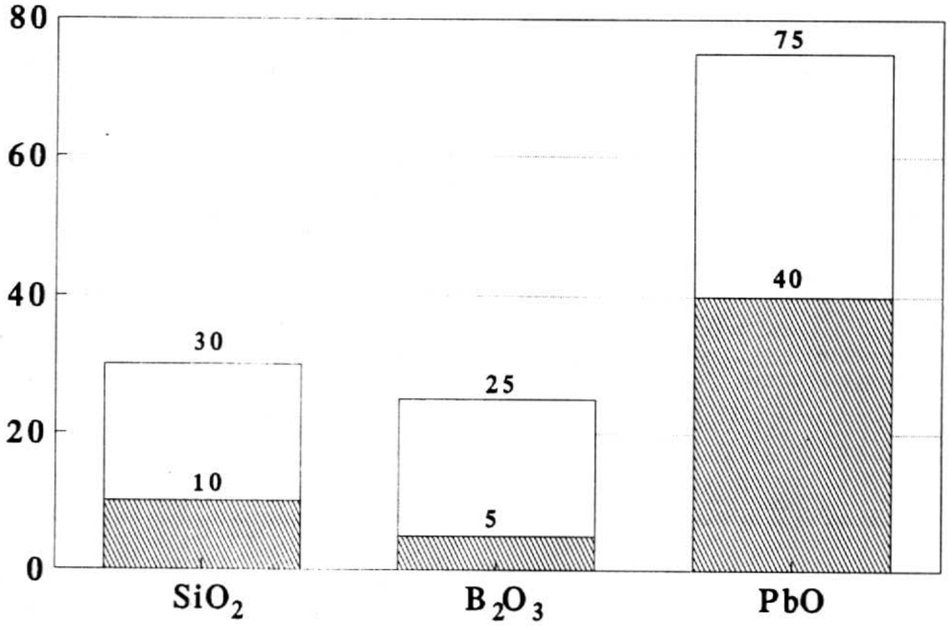


Figure 6.- Lead borosilicate frits. Composition interval (wt%).

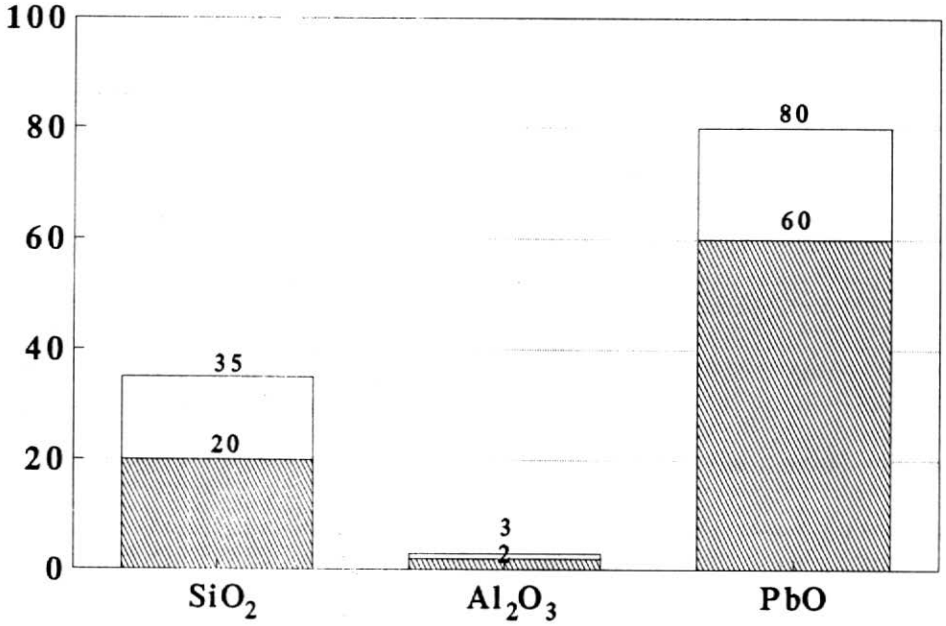


Figure 7.- Lead silicate frits. Composition interval (wt%).

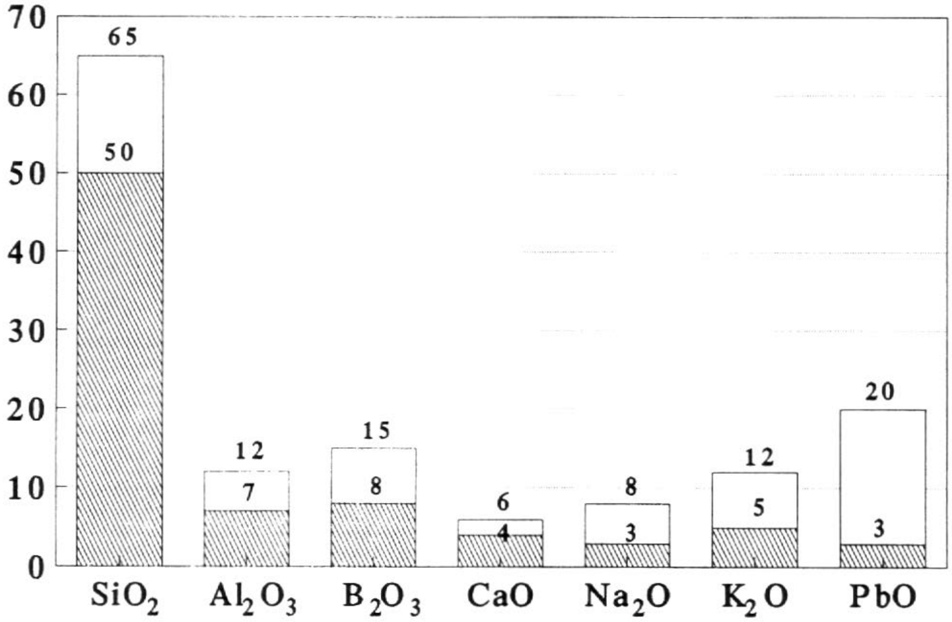


Figure 8.- Boracic crystalline frits with lead oxide. Composition interval (wt%).

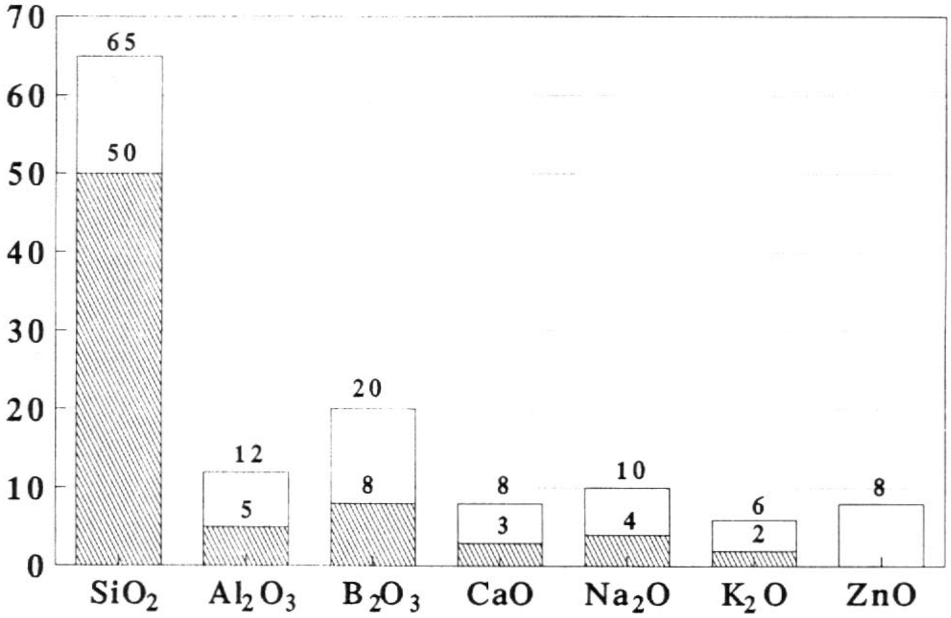


Figure 9.- Transparent lead-free frits. Composition interval (wt%).

Opaque glazes, the most commonly used in previous decades (13) (14), have been obtained since the sixties by means of zirconium frits. Their composition interval is like that of transparent frits mentioned above, with a zirconium oxide content ranging from 8 to 14% (in wt). Opacity is obtained during firing of the glaze mainly by zirconium silicate crystallization which had previously been dissolved in the frit during fusion (12). Zirconium frits completely replaced opaque glazes obtained by adding tin oxide on grinding to transparent frits (13), as well as those obtained from frits with a high arsenic and fluorine content (14).

3.2.1.2 Glazes for fast double-fired wall tile.

These glazes, fired with such short firing cycles (30-50 min), dispose of extremely short maturing intervals (2-4 min). As a result, the frits used must soften at moderate temperatures and present low viscosities on melting at peak firing temperature (approx. 1050°C). To achieve these aims, alkaline oxides (Na_2O and K_2O) and B_2O_3 were at first widely used as fluxes. More recently, there has been a trend toward increasing the amount of alkaline earth oxides (mainly CaO) and ZnO to the detriment of alkaline oxides (mainly Na_2O).

Figure 10 shows the composition interval for transparent frits used at the moment in fast double firing (crystalline). In order to obtain opaque glazes, frits with a very similar composition to that of transparent frits are utilized, with zirconium oxide percentages ranging from 8 to 14%.

3.2.1.3 Glazes for single-fired porous wall tile.

As already pointed out above (Section 3.1.1), CO_2 release from carbonate breakdown in the body during fast firing, involves temperatures at which the raw glaze seals the body (sealing temperature) being higher than that at which this reaction is completed, and melting and maturing of the frit taking place in an extremely short space of time.

It is vital, in order to fulfill both requirements, to use alkaline earth oxides (mainly CaO) and ZnO as principal fluxes in high proportions, since as observed above, introducing them in the frit formation, besides raising sealing temperature, provides the glaze with a sufficiently low viscosity at firing temperature for maturing to be rapidly completed (Figure 11). Obviously, the alkaline oxide and B_2O_3 percentage in this kind of frit must be lower than that of frits for traditional fast double firing, as these fluxes, like PbO, lower sealing temperature.

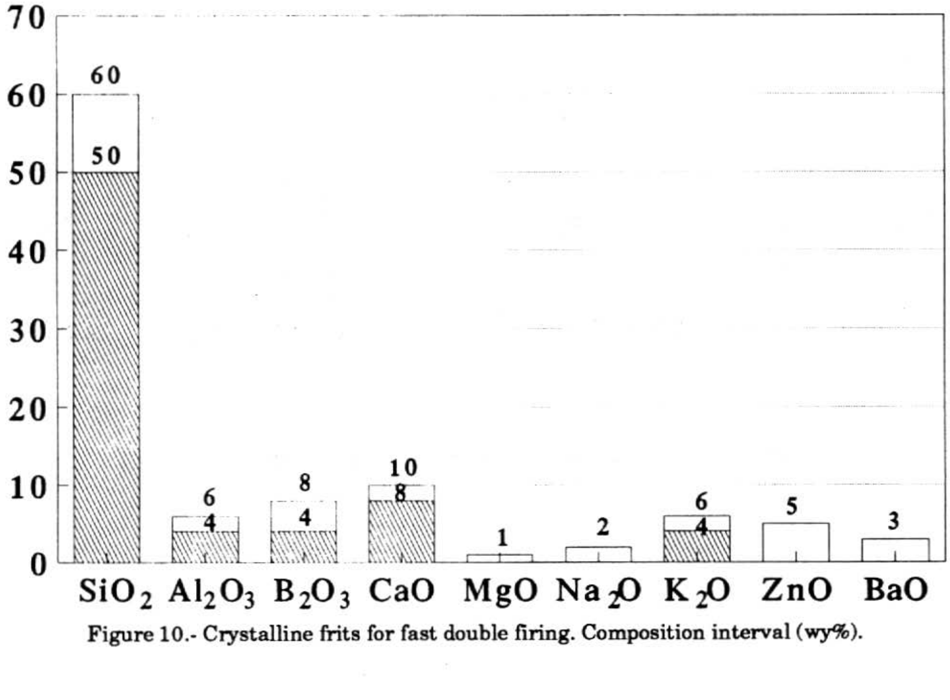


Figure 10.- Crystalline frits for fast double firing. Composition interval (wy%).

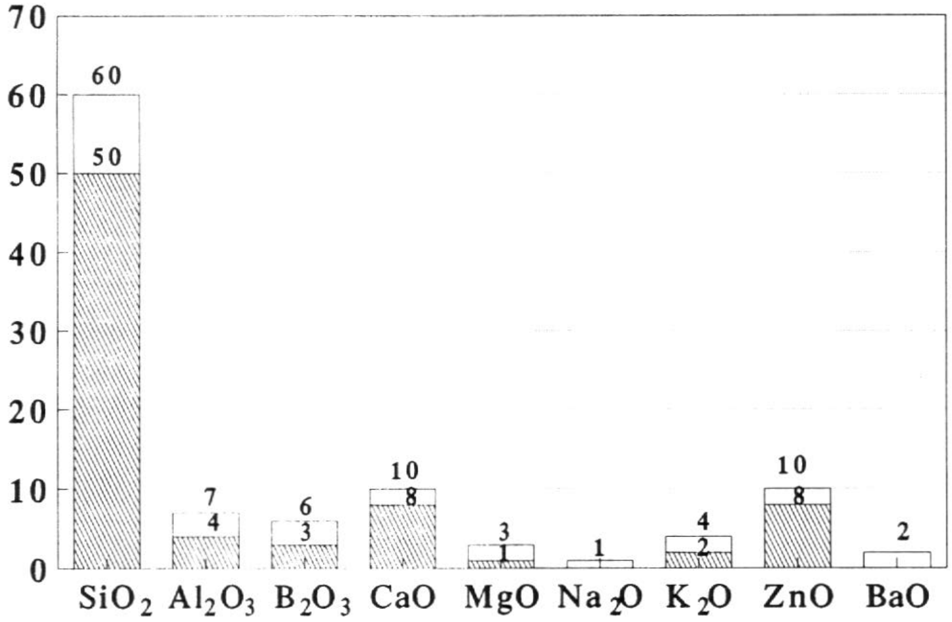


Figure 11.- Crystalline frits for porous single firing. Composition interval (wt%).

Figure 12 shows the fusion diagram of a frit used in porous single-fired tile manufacture (A) and one for traditional double firing (B). Although both frits show the same fluidity at the maximum temperature tested, the fusion interval for the porous single-fired frit is much narrower.

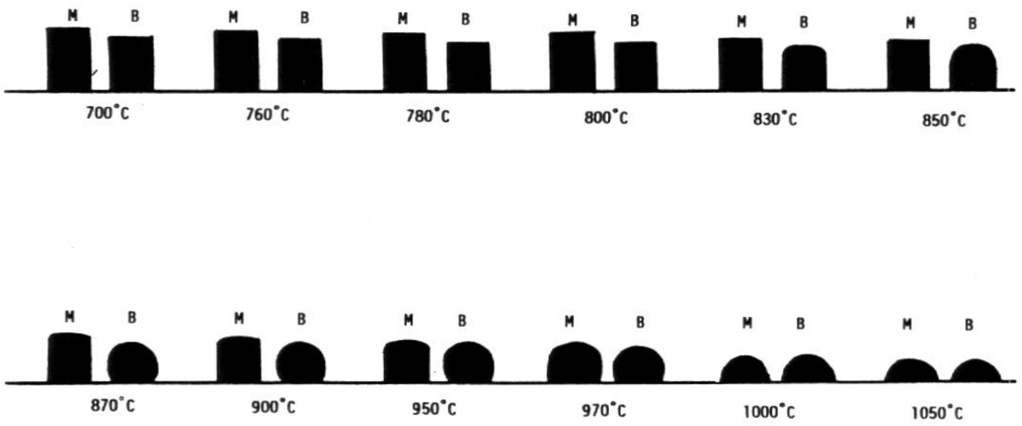
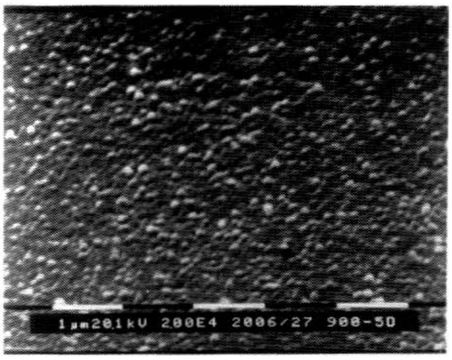


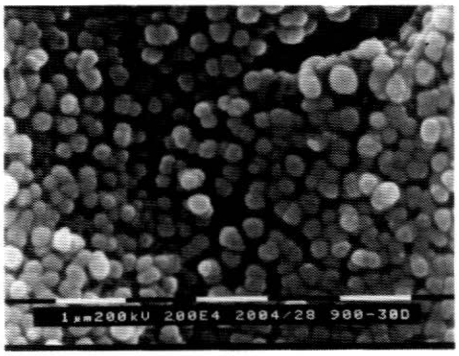
Figure 12.- Fusion diagrams of a traditional double firing glaze (B) and a glaze for porous single firing (M)

One of the main drawbacks in the use of these compositions for obtaining transparent glazes, stems from the tendency these vitreous systems have of separating into immiscible liquids during firing, which can give rise to problems with colour differences in the finished product (15).

In fact, on studying the evolution of the chromatic coordinates of glazes with different compositions, on modifying the cooling cycle, changes in colour were observed to be associated to growth and/or coalescence of immiscible phases separated by nucleation. Furthermore, colour in the finished product was shown to depend to a considerable extent on the thermal cycle used (Figure 13).



Thermal treatment: 10 min. at 1050°C. Transparent.



Thermal treatment: 10 min. at 875°C. Blue colour.
Figure 13.- Microstructure of a porous single-fired glaze with liquid immiscibility.

On determining the influence frit composition has on the rate at which this transformation develops and on end colour of the glaze, it has been observed that although frits have been developed with little tendency to change in colour as a result of slight alterations in the cooling cycle, minor variations in frit composition considerably affect this behaviour.

The above is a clear example of the fact that in order to obtain good glazes in porous single-fired wall tile it is essential to set up even more rigorous control systems than those required when using other firing techniques. This control must be applied not only to frit elaboration but also to glaze application and firing. In fact, development of these last two stages is very often more decisive with regard to final product quality than the characteristics of the frit itself.

As far as opaque glazes for porous single-fired wall tile is concerned, these have been shown to be more opaque than those resulting from the use of other compositions with smaller amounts of alkaline earth oxides and ZnO, while having the same zirconium oxide content in their formulation. This increase in opacity with increasing amounts of the above-mentioned oxides in the composition, is due to immiscible liquid-phase separation taking place during firing of these vitreous systems (Figure 14).

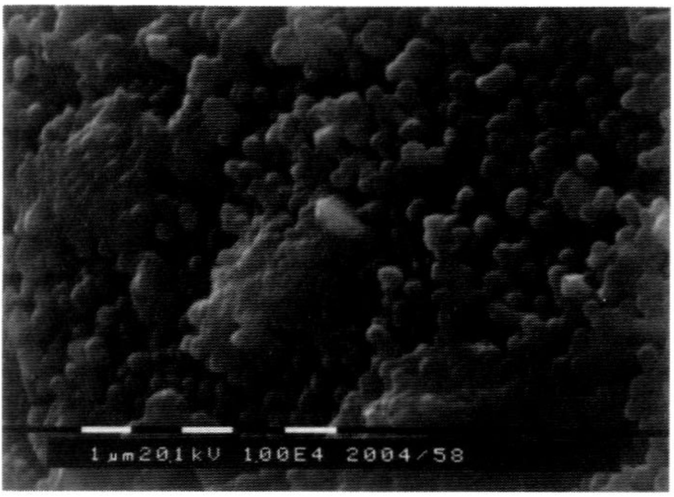


Figure 14.- Porous single-fired opaque glaze.

It must however be pointed out that the recent development of this kind of frit has had positive repercussions on formulating other glazes both for wall and floor tiles.

3.2.2 Glazes for single-fired floor tile.

As already highlighted above, the characteristics of the glazed surface (Figure 3) determine performance of ceramic floor tile on use in different surroundings, in terms of the surface deterioration it undergoes. Consequently, glazes have been developed and are still being developed with mechanical and chemical properties which, although superior to those required for wall tile, vary greatly from one glaze to another.

In general, these glazes are obtained by applying different layers of material by a wet method (dropping, spraying, silk screen printing) or by a dry method (crushed frits, agglomerates) on a white, opaque basic glaze. Others are virtually made up of one basic glaze with variable colour and texture (matt, satin, granular, rustic, semi-glossy), according to its formulation. In both cases the glaze surface never has specular gloss, since any other texture is more suitable for obtaining the characteristics required by these glazes (abrasion resistance, scratch hardness, slipping resistance etc.).

From the start, frits of a different nature in varying proportions (30 to 60%) and other non-fritted components with a highly distinct character have been used in formulating basic glaze, according to the glaze texture and properties desired.

Some of these non-fritted components such as feldspars, nephelines and zinc oxide contribute together with the frits to forming the glassy matrix of the glaze. Others, on the contrary, such as zirconium silicate and corundum hardly dissolve in the vitreous phase, whilst improving abrasion resistance of the glaze within certain limits, as well as opacifying ($ZrSiO_4$) or increasing matting (Al_2O_3).

Other constituents often included in these glazes are anatase, which besides increasing matting positively affects the chemical and mechanical properties of the glaze, and minerals bearing alkaline earth oxides (wollastonite and calcium carbonate and/or magnesium carbonate), which raise matting and also form part of the glassy matrix.

The most common trends adopted in elaborating these glazes may be summarized as follows:

- Reducing the number of bases, thus simplifying glaze elaboration.
- Introducing the frits which have been developed (fast double-firing, porous single firing) in the basic glaze formulation and increasing frit content which improves glaze properties.
- Incorporating new decorating techniques (dry applications).
- Product diversification, making it ever more suitable for its final purpose.

As far as this last aspect is concerned, although at present glazes with high mechanical performance (high abrasion resistance and scratch hardness) are available, there is a clear trend toward obtaining glazes with a smoother surface than before and which behave suitably on use in highly transited areas.

To achieve this aim, glazes must lack porosity (internal and external) and contain a high proportion of high hardness microcrystals strongly bonded (without any mechanically or thermally induced stresses), to a glassy matrix which is also hard and resistant. At present, research is being conducted in this direction at our Institute, by means of state projects and projects concerted with private enterprises, and the findings look very promising.

3.3 Specific consumption.

The trend in consumption in each kind of glaze described in the foregoing, may be analyzed from the evolution glazed ceramic tile production has undergone in Spain (Figure 15).

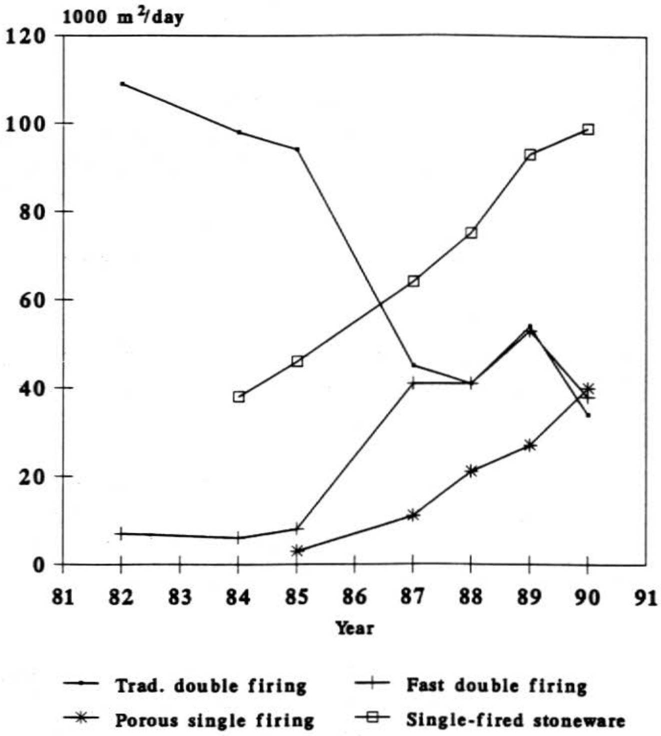


Figure 15.- Evolution of ceramic tile production in Spain (Figures suppied by ASCER).

Generally speaking, progressive increase in single-fired wall and floor tile production can be observed since this technology was implemented. However, in 1990, floor tile production increased much less than porous single-fired wall tile production.

Production of traditional double-fired wall tile, which had already dropped considerably with the implementation of fast double firing and porous single firing, after an incidental increase in 1989, has clearly fallen behind.

As far as fast double-fired wall tile production is concerned, its evolution is observed to be parallel to that of traditional wall tile since 1988.

3.4 Some considerations on the development of new glazes and improvement of present glazes.

The spectacular increase which has taken place in recent years in research, development and fabrication of new materials with an exclusively vitreous or glass-crystalline matrix, and excellent mechanical, chemical and optical properties (16) (17), must have positive repercussions on the field of ceramic glazes.

At the outset, immediate application of fabricating techniques as well as of compositions used in elaborating these materials cannot be directly carried out (because of economic or technical reasons), for glaze production. However, it has been shown that some of these procedures, such as the elaboration of glass-ceramics and/or certain vitreous systems with a great tendency to crystallize, can be used on suitably adapting them, for obtaining good floor tile glazes (18) (19).

On the other hand, the knowledge acquired in elaborating the most advanced vitreous or glass-crystalline materials, is to be taken advantage of, in developing new glazes and improving present ones. Study methods, experimental techniques and state-of-the-art knowledge available concerning such important transformations as phase separation, nucleation and crystal growth, all belong to this line of action.

A good example of the foregoing, is the study conducted on liquid-phase separation in glazes for porous single-fired wall tile (15).

The incorporation of experimental techniques (roughnessmeter) reserved for other materials, in the study of the variation glaze surface texture undergoes on abrading it, also fits in with this line of action (20).

In short, the adaptation of compositions and/or manufacturing procedures of special glass-crystalline and vitreous materials and the use of the knowledge acquired in elaborating these materials, are two highly promising work lines in developing new glazes and improving present ones.

4. MANUFACTURE OF FRITS AND GLAZES

The elaboration of frits, ceramic pigments and glazes at the turn of the century was carried out at the firm manufacturing the wall tiles itself. In the forties, this situation had changed substantially, since in 1946, of a production totalling more than 3700 TM/year, 35% was fabricated by specialized enterprises. This trend grew and led to the growth of a powerful industrial sector which produced more than 45000 TM in 1969. However, some wall tile factories still existed which elaborated their own frits and glazes (14). At present, all frits and and pigments are manufactured by firms exclusively devoted to this activity. Only a few wall tile factories obtain their own glazes from already elaborated frits and pigments. The economic importance the frit, ceramic pigment and glaze sectors have reached in the last decade, is to be seen in Figure 16.

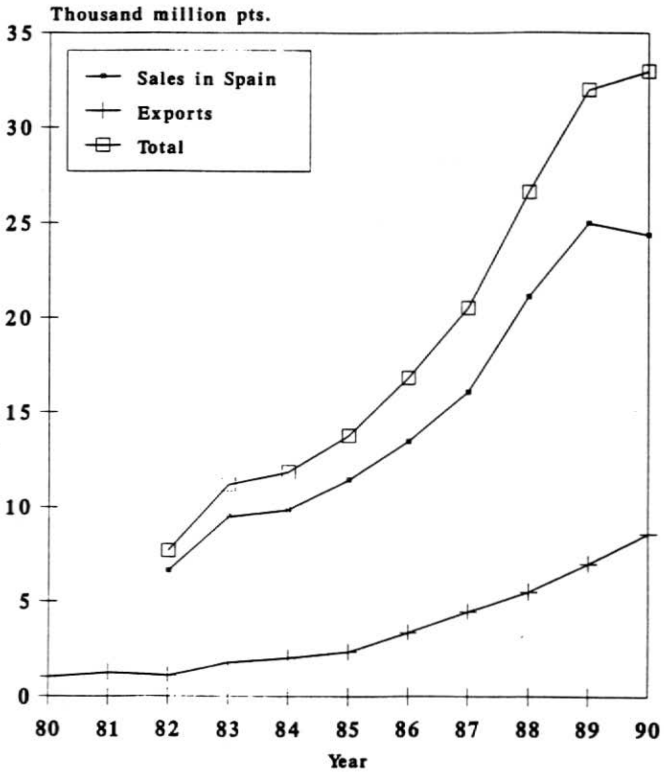


Figure 16.- Spanish frits, ceramic colours and glazes subsector. Sales evolution (Figures supplied by ANFFECC).

4.1 The frit fabrication process.

4.1.1 Reasons justifying the use of frits.

The main reason for the fritting operation is converting water-soluble components of a composition into an insoluble glass by fusion with other components. Fritted glazes bear certain advantages with regard to non-fritted ones which justify their exclusive use in wall tiles and the trend to increase frit content in floor tile glazes. The most important reasons are as follows (21):

i) It allows PbO to be used in the composition, as its solubility and therefore its toxicity is reduced to minimal values, when utilized in suitable frit compositions.

ii) Fritted glazes with the same composition as non-fritted glazes, fuse and mature at lower firing temperatures and/or times than the latter, and besides, provide the finished product with a smoother and glossier surface texture.

iii) The fritting operation, on reducing glaze temperature and/or firing time makes it possible to use compositions with greater SiO_2 and Al_2O_3 contents. This allows glazes with better mechanical and chemical properties to be obtained.

iv) Quality of glazes obtained from ZrO_2-bearing frits is better and they are more opaque than those obtained by adding an equivalent amount of zirconium silicate during glaze milling.

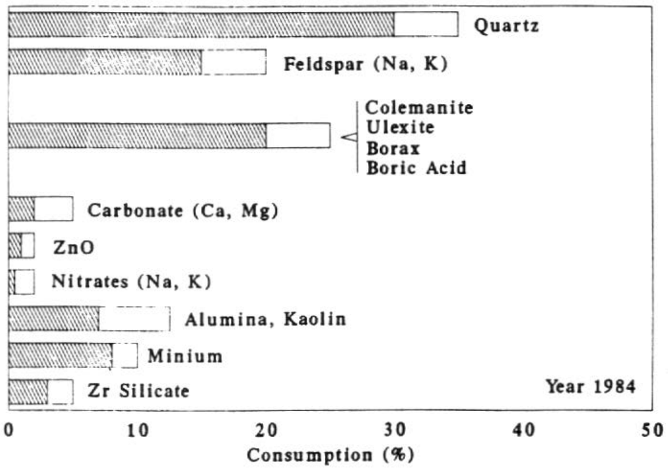
v) The tendency to settle and/or segregate, shown by raw glazes containing ingredients with great differences in article sizes and densities, is reduced.

4.1.2 Raw materials.

In fabricating ceramic frits, widely varying raw materials are utilized, both with regard to composition as to physical and mineralogical characteristics. The most important criteria usually used in choosing the raw materials involved in the frit recipe are:

- Overall costs of the formulation.
- Impurities deteriorating frit quality (iron compounds and other colouring oxides).
- Physico-chemical and mineralogical characteristics determining behaviour of the mix during fusion and quality of the frit obtained.
- Homogeneity and continuity in quality and supply.

Assessed relative raw materials consumption corresponding to the period from 1984 to 1991, is shown in Figure 17(*).



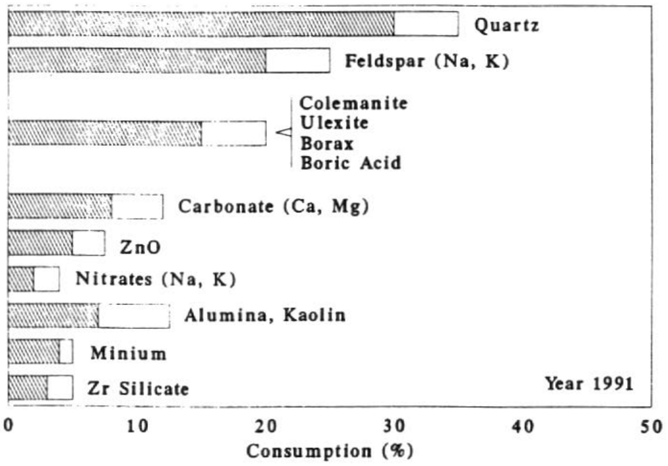


Figure 17.- Relative consumption of raw materials for frit manufacture.

In this figure, a considerable drop in the relative consumption of minium and a slight decrease in the boracic materials percentage is to be seen. On the contrary, ZnO, alkaline earth carbonates, feldspars and alkaline nitrates (these last two mainly potassic), consumption percentages increased.

This change in raw materials consumption corresponds to that undergone by the relative production of different kinds of frits.

(*) Assessed from data supplied by different firms.

4.1.3 Fritting.

Dosing and mixing raw materials and subsequent fusion of the mix, initially in reverberating kilns and later in rotary kilns, are traditionally discontinuous operations.

The incorporation of tank furnaces represented the first step in achieving a continuous and automated frit manufacturing process as used at present (Figure 18).

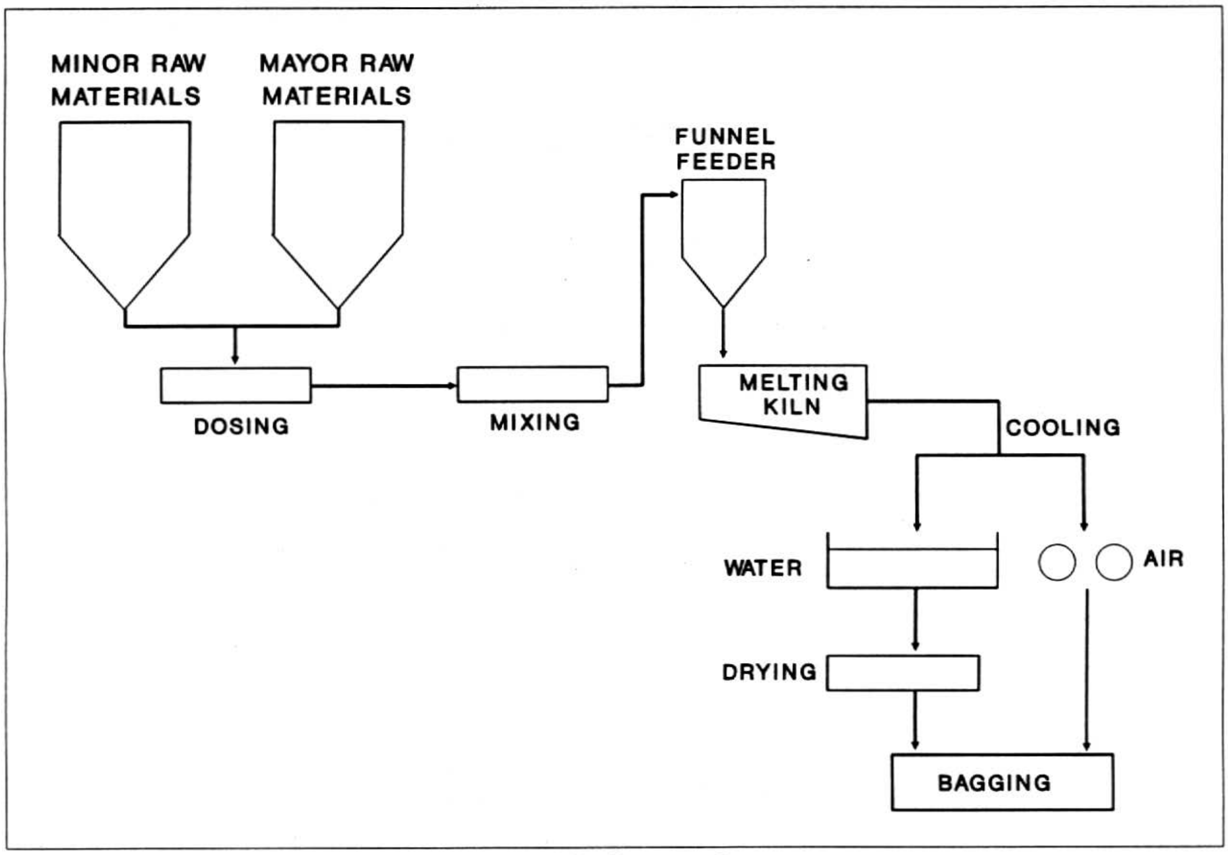


Figure 18.- Scheme of the frit manufacturing process.

Powdered raw materials are proportioned gravimetrically and transported by vacuum pneumatic circulation to a mixer, obtaining a homogeneous mix of the components in a few minutes. The resulting material is stored in a funnel and fed at a uniform rate (varying according to the frit) into the smelting furnace by an auger. In the heap of material which starts forming at the kiln entrance, decomposition reactions in the raw materials begin to take place with gaseous release, liquid-phase formation between the most fluxing components and dissolution of the most refractory constituents (quartz, alumina, zirconium silicate) in the melt. The partial fusion of some of the components allows the surface layer of the pile to slide continuously. The foregoing reactions must be completed as the kiln is crossed, to obtain a good frit. The fused material is quenched rapidly by pouring water on it or by means of water-cooled rollers.

The corrosion the refractory undergoes, mainly owing to partial dissolution of some of its components in the molten glass, has been and continues to be one of the most serious problems affecting glaze and frit fabrication. In fact, on the one hand this permanent deterioration of the kiln lining requires periodic reparation, whilst on the other, the particles most resistant to chemical attack are pulled out and drawn away by the molten glass, contaminating the resulting frit.

The rate at which this corrosion process develops mainly depends on the following factors:

i) Fritting temperature and rate at which the melt flows through the kiln. Increasing the value of these variables raises corrosion rates.

ii) Chemical composition, surface tension, and viscosity of the melt. A decrease in viscosity and surface tension of the glass and an increase in basicity of the composition raise the rate of refractory deterioration.

iii) Capillary texture of the refractory (apparent porosity, permeability and pore size) and its microstructure (percentage, size and nature of the vitreous and crystalline phases).

In order to reduce these drawbacks to the utmost, frit manufacturers have followed a parallel route to that of glass manufacturers, progressively replacing traditional (sintered) refractories by new advanced (electrosmelted) refractories, with virtually no apparent porosity and progressively more suitable composition, as these developed.

Fritting of many compositions used nowadays, could not be adequately conducted in more traditional kilns, owing to high melting temperatures (1500°C) required by these mixes and their high viscosity.

Incomplete dissolution of the most refractory components of the mix in the viscous liquid, as it forms during fritting, gives rise to unfused particles. The presence of these particles or refractory elements in the frit, often impairs quality of the resulting glaze. However, its negative effect is even more striking if the frit is applied dry in crushed form. In order to minimize the presence of these unfused particles, not only must composition and grain size of the raw materials mix be optimized and controlled, but so must all the process operating variables (mixing and melting).

Contamination of the frit during the process by metal particles (iron, steel) is another source of defects which has entailed installing iron particle removal facilities in frit and glaze manufacturing plants.

Frit quality as at present required in new wall tile manufacturing processes has reduced the tolerated variation intervals even further, as far as raw materials and process operating variables are concerned. Figure 19 details controls at present carrried out in frit and glaze manufacturing plants.

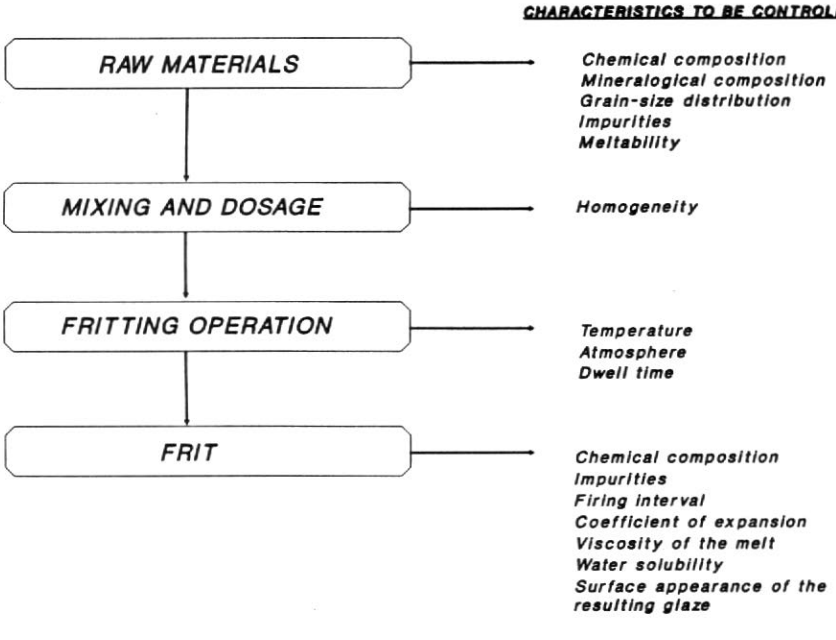


Figure 19.- Controls carried out in frit manufacture.

4.2 The glaze elaboration process for dry application.

Glaze application in the form of dry powder whose use commenced at the beginning of the eighties, reached its greatest dissemination and diversification after 1988 (22) (23). This technique, which was mainly developed to obtain new, more attractive decorating effects than those available at that time, is at present considered one of the most suitable for obtaining glazed surfaces with high technical performance, such as high wear resistance and Mohs scratch hardness.

On the basis of grain size of the material applied and the procedure involved in obtaining it, these products may be classified in powders, crushed frits and agglomerates.

4.2.1 Powders.

These have a small particle size, between 60 and 200μm and are generally made up of a mix of pigments and frits. Although these products were the first to be used in this kind of application (marble effect), after an initial boom, they have progressively been replaced by others. It is of utmost importance for its correct application that grain-size distribution of the powder should be highly controlled (there should be no very coarse particles or agglomerates of fine particles), and fluidity should be acceptable.

4.2.2 Crushed frits

These are frits that have been subjected to crushing and screening in order to obtain appropriate grain sizes. Depending on the end effect desired, grain-size distribution will be very narrow or wide. Generally, the most common intervals range from 0.15-0.5 mm and 1-2 mm.

Coloured grainy material is obtained from coloured frits by fusion or by coating the already crushed frit particle with a ceramic pigment. In the latter instance, the pigment must be regularly distributed over all the frit grains.

In order for the resulting glaze layer to show the required characteristics (lack of porosity, suitable thermal expansion, texture), the different grains used must be compatible with each other and with the remaining glazes which can be applied wet. Inappropriate choice of grains and/or basic glaze frequently gives rise to pores between different granules or between granules and base, in the fired glaze, which considerably impairs product quality. However, as mentioned above (Section 4.1), the main problem in manufacturing crushed frits is the presence of unfused material leading to the appearance of specific localized defects on the fired glaze surface.

4.2.3 Agglomerates

These products originally arose from the need to overcome the problem of unfused material in a frit, as fine grinding of the unfused particles practically eliminates the defect. Although in the beginning the main component of the agglomerate was a sole frit, at present these products are generally made up of different ingredients, as also occurs in floor tile glaze compositions.

The manufacturing process of an agglomerate includes the following basic stages: preparation and grinding, agglomeration, at times crushing of the agglomerates and classifying by sizes. Grinding is generally conducted by the wet method to achieve suitable particle size and close mixing of the constituents.

The procedures used in obtaining agglomerates can be classified according to the kind of bond between the particles, into the following two large groups:

- Procedures based on sintering.
- Procedures based on binder additions.

Besides the procedure employed, the resulting agglomerates must have sufficiently high mechanical strength to allow mechanical manipulation without undergoing deterioration, especially on transporting and applying them.

i) Procedures based on binder additions.
Some of these processes are based on adding an organic binder to the ground, dry glaze powder. Agglomeration takes place by continuous and discontinuous granulation.

Another very common practice is to add the binder to the slip suspension and simultaneously carry out particle drying and agglomeration at high temperature in a granulating facility, thus obtaining highly resistant granules. A variant of this procedure involves drying the slip by means of a belt dryer with subsequent crushing of the sections obtained, choosing suitable sizes.

ii) Procedures based on partial sintering.
In all of these, the previously shaped material, generally by pressing, is subjected to a thermal cycle allowing partial sintering of the piece by fusion of some of its components.

Plastic components are included in the formulation, as are small amounts of binders sometimes, so that the shaped piece (in ovoid, rectangular form, etc.), will acquire the necessary consistency for manipulation before firing. Partial sintering of the piece is conducted in fast-firing kilns (of the single-layer third fire kind). Sintering temperature varies from one glaze to another, and ranges from 550 to 800°C.

The sintered piece is crushed and the appropriate size interval is then chosen.

5. PRESENT GLAZE APPLICATION TECHNIQUES FOR WALL AND FLOOR TILES.

Glazing has gone through a considerable evolution with regard to both operation control and to application equipment and techniques. These changes have arisen on trying to lower production costs, improve product quality or achieve new aesthetic effects.

From ancient times to the present day, glazes as well as engobes have been applied in a suspended state (wet application). Only silk screening techniques require the material to be applied, to behave plastically. Techniques such as monopressatura and dry application of the glaze in powder, crushed frit and agglomerate form, have been developed only very recently. These dry applications, with the exception of monopressatura, have been incorporated in traditional glazing lines.

5.1 Wet application techniques.

The incorporation, throughout history, of new application equipment for glazes, engobes and serigraphs, the way these are combined in the glazing line, the development of additions to accurately prepare the rheological conditions of the suspension, together with quality controls for this operation, are some of the main factors which have led not only to lower production costs, but also to evolution of the technical and aesthetic characteristics of the glazed surface.

From its origins to well into the beginning of this century, glaze application and wall tile decoration were manually conducted, thus making quality largely depend on the craftman's skill. However, two decorating techniques were developed between the XIVth and XVth century: decoration by the "cuerda seca" and the "arista" or "cuenca" wall tile techniques. Both procedures involved a considerable reduction in manufacturing costs and the latter was the first mechanized decoration process for wall tile in series (24).

Another decorating procedure which, although already being used in our country in the XVIth century, replaced the foregoing techniques reaching its greatest development toward the end of the XIXth and turn of the XXth century, involved applying perforated templates. By means of this technique, wall tiles were decorated in series, with great aesthetic quality in the modernist era and later decades when they were widely used in tiled dados and low wainscoting. This decorating technique survived until the sixties (1965), when mechanical silk screen printing first appeared in Spain. Nevertheless, since the fifties polychrome, decorated wall tile production dropped in favour mainly of single colour or white wall tiles (24).

Development of the glazing line after the Second World War(*) brought about a tremendous mechanization of the glaze application process, which had until then been manual. The first glazing lines developed were waterfall curtain glazing units, (bell glazing was developed later). A continuous curtain of glaze suspension, with constant thickness and rate of fall, is obtained with this equipment. Later, glaze drop application equipment was developed such as sprayguns (airbrushing) or dropping and turning cup equipment for dripping and mottling. The disc-spraying booth is also to be included in this group although it was developed later, toward the end of the sixties.

In the following years, as existing facilities were improved such as disc spraying and silk screening units, other equipment was developed (rotary silk screening machine). Besides these more or less widely used facilities, new ones were developed with a view to creating or obtaining other ceramic effects.

Appropriate combination of some of these units in the glazing line, together with the development of new frits, glazes and pigments, made it possible for the surface appearance of wall tiles (texture and decoration) to undergo considerable evolution. In fact, glazing went from single-layer glaze application (ususally one frit) by waterfall or bell glazing on a previously fired body, to application of successive layers of different frits and/or glazes according to a preestablished sequence.

Mechanizing the glazing operation on the one hand, and the considerable effect the characteristics of the applied glaze layers (porosity, surface roughness, etc.) have on the properties and appearance on the other, have been decisive factors in establishing suitable application conditions, and setting up the required in-works tests for glazing control. Actually each kind of application produces texture in the layer formed and requires certain rheological conditions of the suspension which must be held within a preestablished interval for glazing to be correctly carried out, and for the characteristics of the layer formed to be suitable (Table III) (25).

During glazing of biscuited bodies, water migrates from the slip to the body as a result of capillary suction by the pores of the fired piece. This suction capability of the piece allows glaze to be applied and is responsible for adhesion of the raw glaze to the piece, for the texture obtained in the layer formed, as well as for the drying time of this layer. This entails the need to control the suction rate of the biscuited body, a property that largely depends on the raw materials utilized and the process variables used in fabrication (26).

On implementing single firing, the glazing operating variables to be controlled have increased, their tolerated variation interval has narrowed and new drawbacks inherent to glazing green ware (low mechanical strength of the green ware, glaze adhesion to the body, curvature of the green ware, etc.) have appeared. All this has led to establishing even stricter control of the rheological conditions of the suspension, functioning of glazing equipment, characteristics of the ware after drying (mechanical strength, moisture content, compactness), its temperature, etc.

As set out above, when single firing began, the number of successive layers applied during glazing were few, neither waterfall curtain glazing nor serigraphs were used, so that the range of decorative effects and surface textures was limited. This situation has changed drastically, as it now possible to obtain decorated surfaces by single firing which were formally reserved for double-firing processes.

(*) In 1956, when the first survey was carried out in the wall tile industry in Spain, a glazing machine had already been installed.

Application	Rheological parameter		Surface texture of the ware	Suspension control	Equipment control
	Solids content (%)	Viscosity (c.p.)			
AIRBRUSH	55-65	5-15	good	systematic	systematic
DISC	55-65	10-30	good	systematic	systematic
BELL	65-75	100-400	very good	thorough	thorough
SERIGRAPHY	55-65	1000-7000	-	accurate and constant	thorough

Table 3.- Some characteristics of different applications used in ceramic wall and floor tile production.

On implementing the single-firing technique in wall tile manufacture, it was necessary to improve the unfired surface finish of the glazed ware. At present, the glazing line is virtually reduced to two bell applications (engobe and basic glaze) and silk screening.

Nevertheless, owing to the great number of variables involved in glazing in the single-firing process, it is vital to establish optimal application conditions and strictly maintain them to guarantee the quality of the finished product.

Figure 20 schematically shows the in-works controls at present conducted during glazing.

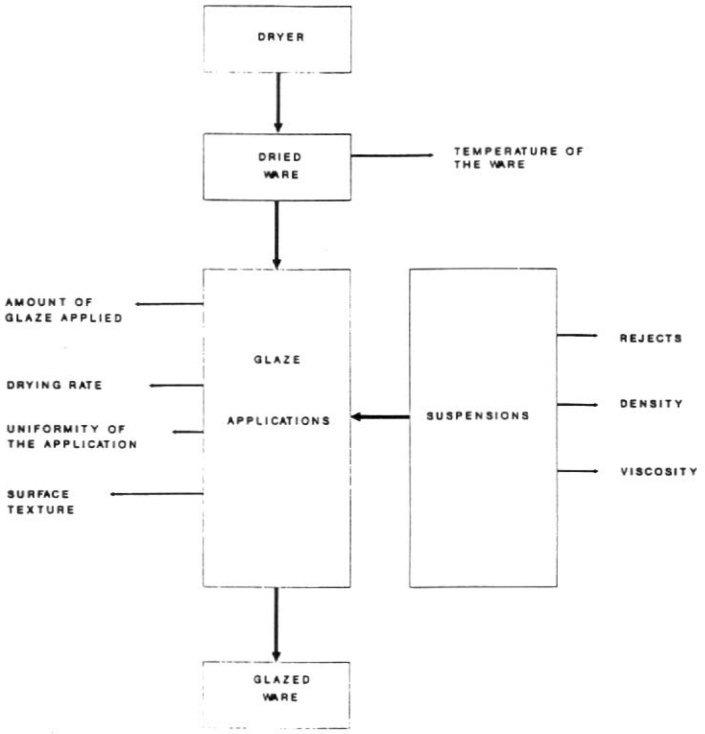


Figure 20.- Controls carried out during the glazing operation.

5.2 Dry method techniques.

5.2.1 Dry glaze application.

This procedure basically involves scattering dry glaze (in the form of powder, crushed frits or agglomerates) on a recently applied still liquid basic glaze, so that the dry grains will cling to the surface of the ware. At times, fixatives are used or a second glaze coating is applied, generally by disc application, to make the scattered granular material adhere better to the surface. In order to obtain specific decorative effects, a glue is often applied by serigraphy over the already dry basic glaze so that on scattering the dry granules over the piece, only those are retained which are deposited on the fixative. By using different kinds of agglomerates or crushed frits (coloured, transparent, opaque) and suitably combining dry application with the wet application techniques mentioned above, untold decorative effects can be achieved (22) (23).

During dry glaze application, no segregation owing to granule size differences, or material accumulation in different areas of the ware should take place, since such phenomena may lead to undesired irregularities on the surface of the piece. This makes it not only vital for the material applied to have suitable grain size distribution and good fluidity, as indicated above, but also to dispose of appropriate facilities.

5.2.2 Monopressatura.

The procedure consists of depositing a granulate glaze layer, during the pressing operation, on the slightly compacted powder bed of the body and subsequently applying sufficiently high pressing pressure for the piece to acquire the desired mechanical properties. To facilitate mainly die filling, as this is the most critical part of this operation, pressing powder preparation for both glaze and body is carried out by the wet method with subsequent spray drying.

Although this technique was first developed in the mid seventies (27) (28), implementation has been scarce. There are very few production units operating in the world at the moment (22), and none in Spain.

The greatest or most obvious advantages of this technique lie in simplification and greater automation and control of the manufacturing process, which occurs on eliminating the glazing line and those deriving from dry glaze application, such as the reduction of liquid effluents and polluting suspensions. On the contrary, although die-filling equipment has evolved substantially, the aesthetic effects at present obtainable on the glazed surface, are much more limited than those to be obtained by other glaze application techniques. This is probably one of the main disadvantages of monopressatura, impeding widespread implementation.

6. DRY GLAZE ELECTROSTATIC APPLICATION.

The electrostatic application of dry glaze particles on metal plate found first industrial utilization in 1975, after some years of laboratory scale research and development (29) (30).

Factors contributing considerably to implementing and developing this procedure are the low material loss involved in this kind of application compared to the wet process, and the fact that no polluting suspensions and/or liquid effluents are produced (31).

Recently, attempts have been made to apply this technology to wall tile manufacture (22), with a view to eliminating wet glaze application and grinding, and the polluting effluents and suspensions. Different kinds of bodies have been tested with this aim: green, fired with or without engobe, by traditional double- or single-firing, etc. In these experiments, this type of coating has been shown to considerably favour outgassing of the body, mainly due to glaze particle packing being less dense than that obtained by traditional wet applications (22).

6.1 Brief process description.

The basis for electrostatic dry glaze application is the strength of the attraction formed on electrostatically charged powdered material, when applied onto a body charged to opposite polarity. Figure 21 schematizes this application procedure (29).

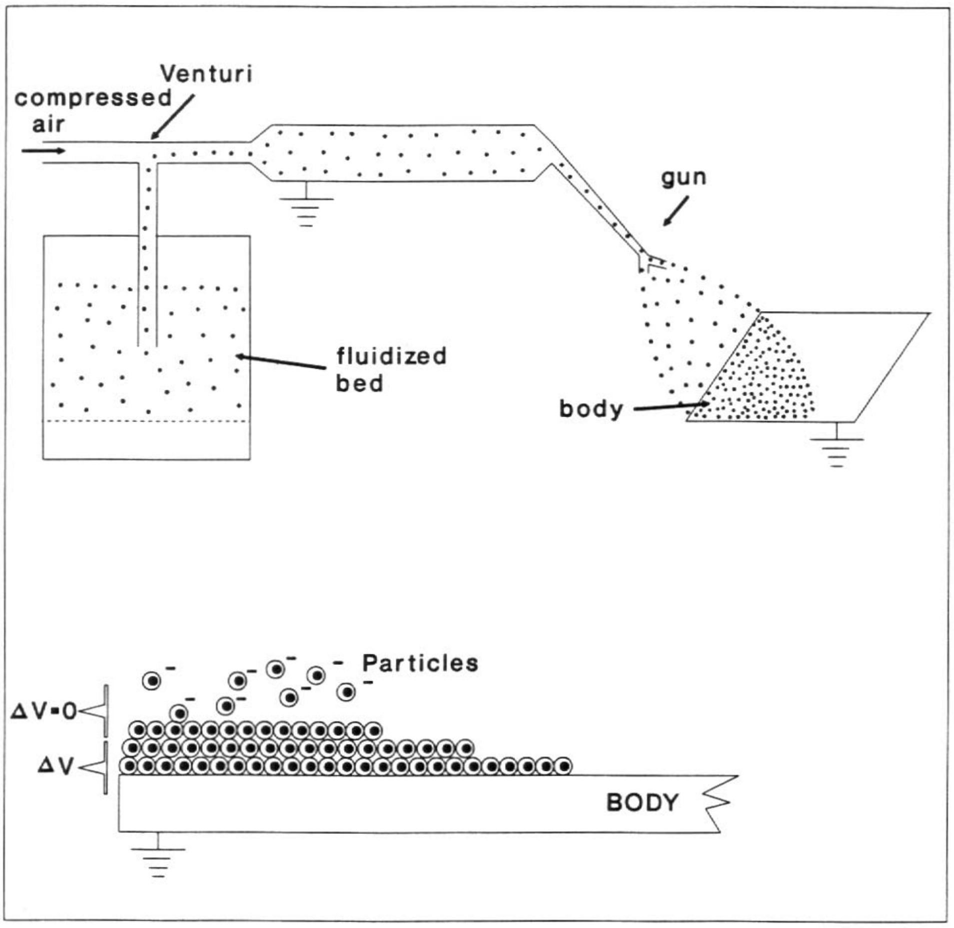


Figure 21.- Dry electrostatic application.

Initial powder treatment involves grinding the frit together with an organic agent encapsulating the particles formed with a hydrophobic surface which, besides reducing atmospheric moisture absorption, raises frit resistivity, which tends to improve application efficacy and bonding to the substrate to which it is applied.

A basic stage in this process is powder fluidization. In the fluidized bed, the agglomerates in the powder are broken into separate particles, which greatly enhances powder fluidity. The powder suspended in the air is transported by a venturi pump; the powder flow is regulated by means of compressed air across an area where high electrical voltage is maintained, producing charged air particles, which in turn charge the powder particles by ion or electron bombardment. In general, negative polarity charged powder particles are preferred, as their mobility in air is greater than if they were positively charged. As the gun-sprayed particles reach the substrate, they are retained because of the electrostatic attraction brought about between the negative surface charge the frit particles keep and the substrate with its opposite charge (29).

As powder is deposited on the substrate, the outer frit layer retains more and more of its negative charge. Gradually, the difference in potential between the deposited powder and that which is being deposited decreases to a zero point. From this moment onwards, the glaze particles reaching the surface are repelled by those already deposited, impeding further deposition. This self-controlling mechanism guarantees uniform glaze thickness, even on irregular surfaces (32).

6.2 Factors influencing application development and coating quality.

The rate at which this kind of application takes place, as well as the thickness and quality of the coating obtained, depends to a great extent on powder characteristics and process parameters, which must be strictly controlled. Among the latter the following deserve to be mentioned: moisture content and ambient temperature, gun-substrate distance, voltage application, gun type, air flow, powder-air ratio, etc. (32).

The powder characteristics most influencing application development and coating quality are: fluidity, electrical resistivity and particle size distribution (34) (35). In fact, good powder fluidity is essential for uniform application and suitable finished surface quality. Likewise, to achieve the foregoing aim and avoid applied materials waste during pre-firing transport and storage, the glaze must adhere strongly to the body and have high resistivity. This is why the frit is usually encapsulated by an organic medium during grinding, as indicated above.

Particle size distribution of the raw glaze has been observed to considerably influence its fluidity and adhesion to the body, as well as rate of deposition and thickness of the coating. In fact, when the powder is coarser, electrostatic adhesion strength and fluidity have been observed to drop, whilst coating thickness and rate of deposition grow. In industrial glaze application on metal plate, particle size must lie between 10 and 80 µm. If the particle fraction under 10 µm is over 10-15%, problems usually arise involving impaired coating quality (30) (33).

Table IV summarizes the main advantages and drawbacks of this kind of application compared to wet glazing (22). Although no real economic data is available, as no information has been forthcoming concerning the industrial use of this process in wall tile glazing, it is highly likely that operating costs at present are greater than those of other commonly used techniques.

Disadvantages	Advantages
- More delicate manipulation of the unfired ware. - The glazed surface cannot be decorated by silk screen painting. - Difficulty of appliying successive layers of different glaze. - Only regular smooth surfaces and light "fumé" effects can be obtained. - Great attraction of ambient dust onto the glazed surface. - Ambient air conditions (mainly moisture content) must be highly controlled.	- No glaze milling is required. - Glaze losses are reduced. Excess applied powder is easily recovered by recirculating in a closed circuit. - More constant thickness of the glaze layer applied. - No control of the physico-chemical parameters of the suspension is required. - Completely automated glazing process. - No liquid effluents or polluting suspensions are produced.

Table 4.- Advantages and disadvantages of dry electrotatic glazing compared to wet glaze application.

7. OTHER SURFACE-COATING TECHNIQUES

A series of very recent techniques (Table V) is included in this section which are at present being used in coating different kinds of materials industrially (from plastics to ceramics materials), with a view to improving the tribological properties of the surface coated (hardness, wear resistance, etc.) (36). The excellent coating properties stem from the final microstructure and hardness of the material applied (Figure 22). Almost all these procedures (with the exception of CVD), are characterized by ambient substrate temperature during treatment.

At present these techniques are only used to obtain ware with high added value for specific purposes, owing to high operating costs, as a result of which industrial application to wall tile production in the near future does not look ery likely.

Moreover, the aesthetic effects which might in principle be obtainable by means of this kind of treatment would be more restricted than those achieved by common techniques.

	PVD(*)	CVD(*)	Flame spraying	Plasma spraying
Layer thickness (e) or deposition rate (v).	1< v <100 (μm/min.)	1< v <100 (μm/min.)	0.01< e <2 (mm)	0.01< e <2 (mm)
Porosity of the layer	very low	very low	can be considerable	low
Adhesion to substrate	normal	very good	good	good
Ambient	10 a 10^{-3}Pa	Reacting gas	air, inert	air, inert
Body temperature during treatment	low	600< T <1400°C	T< 100°C	T< 100°C

(*) PVD = Physical vapour deposition
(*) CVD = Chemical vapour deposition

Table 5.- Characteristic of some surface-coating methods.

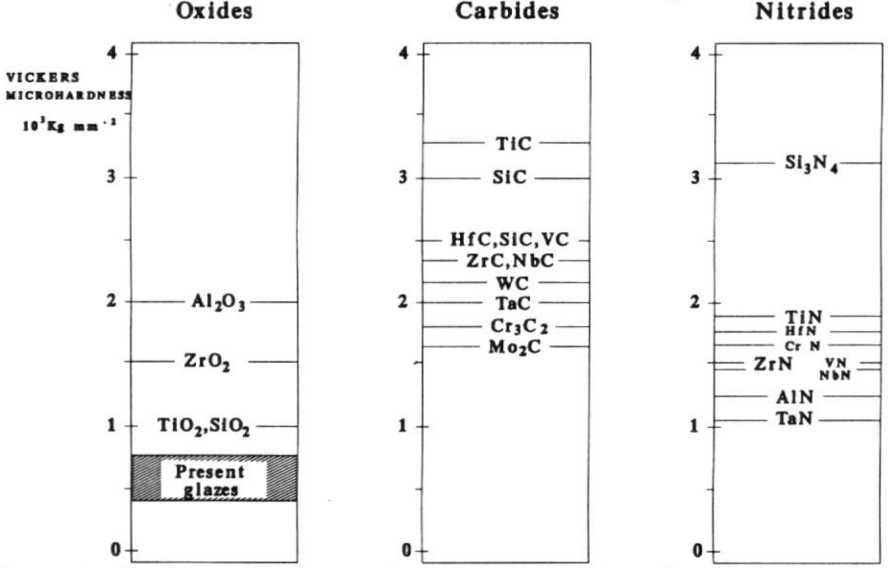


Figure 22.- Vickers microhardness of some ceramic materials used for surface coating by advanced technogy.

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