PHYSICAL—CHEMICAL CHARACTERISTICS OF CERAMIC GLAZESAND THEIR INFLUENCE ON THE QUALITY OF CERAMIC SURFACING AND FLOORING

Julio García Sainz

A.— PHYSICAL—CHEMICAL CHARACTERISTICS OF CERAMIC GLAZES AND THEIR INFLUENCE ON THE QUALITY OF CERAMIC SURFACING AND FLOORING

Ceramic products for flooring and surfacing have a series of characteristics directly related to the kind of glaze used.

A.1.— RESISTANCE TO CHEMICAL AGENTS

Ceramic products support the action of the most varied chemical agents: detergents, lyes, acids, etc., it being necessary that they remain under any circumstances unaltered over time.

The fundamental variables which affect chemical resistance are:

1.1.— Composition
1.2.— Treatment of the product: firing temperature and cycle.
1.3.— Chemical attack variables: Surface area of attack pH of the chemical agent
Temperature
Time of exposure to attack.

1.1.— The effect of composition on chemical resistance

— Alkalines: these generally reduce chemical resistance in the order K_2O, Na_2O, Li_2O, owing to the weakness of the link formed between the cation and the silicon network.
— Alkali—earths: these also reduce the resistance of the glaze, although their effect is weaker than that of alkalis. The order would be BaO, SrO, CaO, MgO.
— Alumina: in general increases chemical resistance.
— Boron: normally reduces chemical resistance, although in alkaline silicate glazes inclusion of boron has positive effects up to 12% of B_2O_3.
— Silicon: this is the formative agent of the main silicon network. It has excellent resistance to acids.
— Titanium and Zirconium: these are stabilizing elements, with zirconium being much more effective than titanium.

— Lead: its effect is negative in an acid medium and variable in alkaline medium, for it depends upon the elements which accompany it.

— Zinc: its effect is normally negative, although in calcic glazes it has a stabilizing effect at low percentages.

1.2.— Treatment of the product: firing temperature and cycle A ceramic glaze is composed of frits and additives. Firing temperature and cycle have a decisive influence on glaze formation, for the quantity of raw material which forms part of the glaze network, and therefore its resistance to acids, depend upon these factors. Furthermore, in glazes which undergo phase separation during cooling, we can observe that in rapid firing we obtain better chemical resistance results than in slow firing.

1.3.— Chemical attack variables

The basic variables are:

a) Surface area of the attack. It is obvious that, all other variables being equal, the larger the surface area in contact between the glaze and the medium the greater will be the attack. Glazes which present a porous appearance are therefore more susceptible to attack, due to unsuitable adaptation to the base or to the firing cycle.

b) pH of the medium. The more acidity or basicity, the more aggressive will be the medium and therefore its effect.

c) Temperature and time. Both variables are directly proportional to the chemical attack.

A.2.—RESISTANCE TO ABRASION

Abrasion may be defined as the change undergone by a surface due to the action of a mechanical medium which produces coming away of particles. A great variety of methods can be found in the bibliography for determining resistance to wear; thus we may point to:

—Sand—drop method (Scott type)
— Striking method (Scharum type)
— Loose—grain polishing method (PEI type)
— Linked—grain polishing method (Taber type).

With these systems we can determine loss of appearance or quantify loss of weight, shine, surface edge, etc.

If we leave aside aspects such as product tonality, which have a determining influence on loss of appearance (the appearance of dark products suffers more rapidly than that of light ones), there are two factors which condition the resistance of a glaze to abrasion:

2.1.— Composition
2.2.— Treatment of the product during firing.

2.1.— Composition

— Frits with high lead content present low resistance.
— Frits with $ZrO2$ or $TiO2$ present the best resistance.
— Frits with high $B2O3$ content or alkalines also present low resistance.
— The addition of raw materials produces a positive effect on resistance to abrasion, the most notable amongst them being: zirconium silicate, anatase and alumina.

2.2.—Treatment of the product during firing.

A glaze which presents a compact appearance, without occlusion of bubbles, will clearly have better performance against abrasion. These bubbles which form in the glaze normally originate from the gases produced by reactions involving loss of weight in the base. It is therefore useful to find out the T.G.A. (thermogravimetric analysis) of the base in order to thus be able to choose the type of glaze and the type of firing curve.

A.3.— RESISTANCE TO QUARTATION

The appearance of quartation in a ceramic product is in function of several parameters: Composition of the glaze

— Composition of the base
— Interphase between base and glaze. glazes consist of one or more frits milled finely with some raw material.

This mix, in suspension in water, is applied to the ceramic base. During the firing process, while undergoing heating, the glaze follows the movements of the base without developing any force, until it melts. The forces appear when the glazed product cools down, and the temperature at which this occurs will depend on the composition of the glaze. These forces will be of compression or tension according to the expansion coefficient of the base and the glaze. When the expansion coefficient of the glaze is greater than that of the base there appear forces of tension. Depending on their intensity, these forces can either be absorbed by the elasticity of the glaze or else lead to quartation. In order to avoid quartation problems, glazes have to work under compression, so they must have a lower thermal expansion than the ceramic base to which they are applied. We often find in practice that over time compression in the glazes decreases, and eventually tensions are created which produce quartation.

This "delayed" quartation is caused by humidity

—induced expansion of the base. Expansion due to humidity is produced by the existence of amorphous phases in the base, due either to CaO and MgO defect in the case of bases for surfacing or to insufficient temperature in the case of bases for single

— firing flooring. Furthermore, one of the most important factors for perfect attachment of the glaze is the formation of an interphase layer between base and glaze.

The properties of this layer are a mixture of those of the base and those of the glaze, so that it acts as a sort of "shock absorber".

A.4.— RESISTANCE TO SLIP

The slip—resistance of ceramic flooring depends upon two factors:

— Type of surface of the base
— Type of glaze used

Friction coefficient (according to TORTUS method)
Glaze typeDry surface
Wet surface
Semi—gloss 0.65 - 0.29
Granular 0.49 - 0.34
Leather 0.47- 0.44
Corundumed 0.56 - 0.47
Rustic 0.64 - 0.59

The classification of flooring according to slip coefficient is:

less than 0.19 dangerous
from 0.20 to 0.30 borderline
from 0.40 to 0.74 satisfactory
over 0.75 excellent

A.5.— SURFACE ASPECTS

Surface aspects of ceramic products, such as shine, drawing, opacity, will clearly be in function of the reaction of the glaze during firing. The covering capacity of the glaze will depend upon its surface tension, high—temperature viscosity and opacity. A glaze with high surface tension will have a tendency to lead to the appearance of cracks (contraction of the glaze) and occlusion of bubbles. Nevertheless, when the surface tension is excessively low the malt presents an appearance with lower drawing. Within certain limits, surface tension may be considered as an additive property, and several researchers have proposed factors which represent the characteristics supplied by various oxides.

Surface tension = $a1p1 + a2p2 + a3p3 +$
... where:
a = Dietzel constant
p = percentage by weight of the various components.

Oxide component
Dietzel constant

Li_2O	4.6
Na_2O	1.5
K_2O	0.1
MgO	6.6
CaO	4.8
BaO	3.7
PbO	1.2
ZnO	4.7
B_2O_3	0.8
Al_2O_3	6.2
SiO_2	3.4
ZrO_2	4.1

The melted viscosity gives us some idea of the capacity of the glaze to bathe the base by spreading in the form of a regular layer. The viscosity of a glaze depends basically on temperature and composition. In general, alkaline oxides, of lead, of barium and B_2O_3 lower the viscosity at any temperature. Oxides of magnesium, zinc, zirconium and alumina provide glazes of high viscosity.

B.—CONTROL SYSTEMS

From the previous aspect we can deduce that the fundamental characteristics to be taken into account in frits and enamals are:

— Composition
— Expansion coefficient
— Sealing temperature
— High—temperature viscosity
— Opacity
— Surface aspect (gloss, drawing).

We shall now look at control systems for these variables.

B.1.— COMPOSITION

There are two ways of controlling the composition of a frit:

1.— Direct systems

Chemical analysis (atomic absorption spectrophotometry)

2.— Indirect systems such as expansion coefficient, viscosity, colour development, opacity, etc.

B.2.— EXPANSION COEFFICIENT

A bar of frit is subjected in a dilatometer to heating with previously established velocity. The expansion coefficient is then determined between 20 and 320°C.

B.3.— SEALING TEMPERATURE

With controlled—granulometry powdered frit, pressed globules of frit or master glaze and frit which we wish to control are prepared. Firing is carried out in a gradient kiln.

B.4.— HIGH—TEMPERATURE VISCOSITY

Globules are prepared as in the previous section, and these are placed on a plate which is put into the laboratory kiln (crucible furnace) at an approximate inclination of 45°. Firing is carried out with a previously established heating curve. The length of the fusion globule is then determined.

B.5.— OPACITY

A colorimeter is used to determine the opacity and colour deviation (L, a, b) of the pieces glazed and fired with master glaze and control.

B.6.— SURFACE ASPECT (Gloss, drawing, etc.)

Milling, application and baking according to previously established mixture of sample of master and of frit or glaze to be controlled. Texture, gloss, absence of defects, etc., are compared visually.

C. - PARAMETERS OF PRODUCTION. STATISTICAL QUALITY CONTROL

If the control of quality is important, so much more so is the manufacturing of it. Statistical quality control is a procedure for taking and measuring samples during the manufacturing process, and by statistical analysis, checking if the process is under control, and producing material within the customer's requirements.

It is designed to prevent machinery defects rather than defects in quality control. As conditions in the production process are checked, rapid adjustments can be made to the machine if it is detected that the process in getting out of control. In the production process of frits there are various parameters which we can submit to this statistical quality control.

a) With reference to raw materials:

- Granulometry
- Chemical composition
- Control of impurities

b) With reference to the process:

- The weighing or measuring out of the components

- The mixing of raw materials. Acheving a homogenous mixture as well as avoiding the development of later separations in the mixture.
- Melting temperature
- Pressure in the kilns
- Combustion control (relation gas/air)
- Length of time of the frit in the kiln, can be checked indirectly measuring the timed production of the frit.
- Defecting control such as the contamination by refraction of the kiln, wastes and resto of fuel residues, etc...