GLAZE

Introduction

A glaze is a specially formulated glass applied to ceramics. It involved the coating of the fired objects with an aqueous suspension consisting of finely ground quartz sand mixed with sodium salts (carbonate, bicarbonate, sulfate, chloride). The ware would then be refired, usually at a lower temperature, during which the particles would fuse into a glassy layer.

Application of glaze

In the case of electrical insulators the glaze must maintain specific electrical properties even in inclement weather. For chemical porcelain it must have high chemical durability. For fine china, porcelain, and semi-vitreous china, it must have high gloss and be resistant to dish washing chemicals. In all cases it must be resistant to thermal shock.

Raw materials of Glaze

1- Lead Glaze: the addition of lead reduces the melting or fusion point of the glaze mixture, which allows the second firing to be at an even lower temperature. Lead is a component of fine china glazes because it “fixes” many of the application and flow problems of glazes and adds high gloss. Lead is not used as it once was, in the white lead form, which was desired in dipping glazes. All most all lead is now contained in frits. A frit is a special glass used in compounding glazes. It ties up toxic and soluble materials and sometimes coloring oxides. Clays and insoluble oxides and or carbonates may be added to the frit to form the glaze composition.

2- Potassium feldspar: is a single-component high-temperature glaze for chemical porcelain.

Classifications of Glaze

1- porcelain process the body is porous after a low-temperature fire. Therefore it is easy to dip. This process is automated for dinner plates and such in modern factories.
2- china process the ware is vitrified and it must be heated during the glazing process. This is usually done by burners in the first section of the glazing tunnel.

3-electrostatic spraying this is a good way to put enamel on household appliances. Glazes can be applied in powder form by electrostatic praying

**Defects of Glazing**

1- Rough Foot-unglazed

If the glazed ware is fired on refractory setters glaze may cause sticking during firing. The solution is to clean the foot carefully after glazing, often using a sponge belt. The foot can be waxed prior to glazing. This can be done by melting paraffin in a flat electric frying pan with a sponge bottom. Waxing belts are also available. After firing, the foot should be checked for roughness and smoothed using a burnishing stone or a foot burnishing machine.

2- Pinholes Pinholes can be caused by over firing, impurities in the glaze, or contaminants in the body. Closed setters can be used to protect the ware from flame impingement during firing.

3- Crazing Cause by a glaze / body mismatch where the coefficient of expansion of the glaze is higher than that of the body. Addition of silica or a low-expansion frit usually corrects the problem.

4- Crawling crawling of the glaze from the substrate can occur before or during firing. During firing viscous glaze can pool and overcome surface tension forces binding the glaze to the ware. Over-grinding can increase the tendency to crawl due to the formation of colloidal factions that tend to shrink more cracking the glaze on drying. The glaze formula may have to be changed to reduce or increase the fired viscosity of the glaze. Too-fluid glaze may extract silica and alumina from the body during firing changing the glaze composition. Fine clays can cause excessive drying shrinkage. Opacifiers and some underglaze colors can cause crawling. Ware should be clean before glazing. Binder additions can help crawling. PVA can also be used.
5- **Peeling** caused by the opposite of the above. The glaze is in so much compression that it shivers off. Curved or sharp surfaces enhance the effect. This is not a common default and is the easiest fault to resolve simply by increasing the thermal expansion coefficient of the glaze. Simply lowering the flint content (or grinding the flint coarser) is the common cure. A more fluid glaze also can reduce peeling.

6- **Blisters** fast firing or incomplete firing. Non oxidation of carbon compounds from organic binders due to too little heat in the preheat zone and or non-oxidizing conditions. Impurities such as limestone or SiC from grinding or clay storage operations. Hardening of the glaze may help.

7- **shivering** caused by too low a thermal expansion coefficient for a glaze.

**Firing Conditions of Glazing**

The firing curve naturally has heat up and cool down periods. In between these slopes is a flat or modified soaking time/temperature. During heat up, the binders are removed from the glaze. They must be completely removed and they must not be reduced to carbon during heat up (preheat). This does not mean that you can’t approach reducing conditions. Some compounds like MnO and FeO can greatly improve melting although they are often in the glaze only in tiny amounts as impurities. These compounds do not form under oxidizing conditions.

**Cooling Conditions of Glazing**

Cooling is important to both the glaze and ceramic ware. You can cool quickly to just above the silica phase transition and then cool slowly through the transitions. This may not be good for the glaze which is trying to get rid of the bubbles created after the glaze melted. This can put you between a rock and a hard place. You have to be able to control the whole cooling zone of a tunnel kiln from the minute the ware comes out of the hot zone.
Notes on Glaze Formulation

1- It is interesting that silica can raise the thermal expansion of a body and lower the thermal expansion of the glaze.

2- For all practical purposes the thermal expansion coefficient of the glaze must be lower than that of the body. This keeps the glaze in compression after firing. Glazes always fail in tension. Keeping the compressive forces higher than the tensile forces.

3- Kiln contamination can be a problem in some operations. Pits, pin holes, and pocks caused by impurities dropping on the glaze during firing can be removed by grinding. The ware is resprayed with a thin coat of glaze and then refired.

4- If body impurities are still releasing gases on refiring.

5- Every element you add to a glaze impacts the final-glaze properties. For example, too much alkali content will increase the solubility of a glaze, raise its thermal expansion, and in general raise havoc. A minimum amount of alkali content will give the glaze fusibility. Also, individual alkalis act differently in extent. Therefore one would use more than one alkali and the minimum amount of each that yields the best balance in properties.
Slip Casting

Slip casting is the most conventional method of producing varied pieces that can have complex forms (culinary, sanitary, refractory materials, technical ceramics). This method consists of casting a suspension (slip) in a porous mold, generally made of plaster. The capillary migration of the liquid into the pores of the mold results in the formation of a consolidated layer of particles on the mold surface. The main advantages of slip casting are:

i) the complexity of the forms that can be produced

ii) its low cost

iii) the use of perfectly dispersed suspensions in technical ceramics leading to dense and homogenous green microstructures.

Its major disadvantage is its low production capacity.

Aqueous suspensions are the most common materials (MgO, CaO, La2O3, etc.) and non-oxides (SiC, Si3N4, AlN, etc.) are cast in an organic environment (alcohol, ketone, trichlo-r ethylene). The surfaces of these non-oxides can nevertheless be “hydrophobated”.

Slip Casting Mechanics

Some of the early analyses treated the mechanics of slip casting in terms of a diffusion process. The slip casting process involves the flow of liquid through a porous medium.

\[ J = \frac{K \left( \frac{dp}{dx} \right)}{\xi L} \]

where \( J \) is the flux of liquid, \( K \) is the permeability of the porous medium, \( dp/dx \) is the pressure gradient in the liquid, and \( \xi \) is the viscosity of the liquid.

In slip casting, the pressure gradient that causes flow arises from the capillary suction pressure of the mold. As the consolidation of the particles proceeds, the filtrate(i.e., the liquid) passes through two types of porous media: (1) the consolidated layer and (2) the mold.

The zeta potential (\( \xi \))

A charged particle constituting an electrokinetic entity and subjected to an electric field (E), will move at a speed (v) (electrophoretic velocity).
The electrophoretic mobility ($\mu$) ($\mu$ in $m^2 s^{-1} V^{-1}$) is defined, for spherical particles, by:

$$\mu = \frac{v}{E}$$

The zeta potential is calculated using the following expression:

$$\xi = \frac{f_h \mu \eta}{\varepsilon_r \varepsilon_0}$$

where $\eta$ is the viscosity of the solution and $\varepsilon_r$ the dielectric constant of the liquid, $\varepsilon_0$ the dielectric constant of the diffuse layer.

The Henry constant $f_h$ is a function of the ratio of the particle radius to the thickness of the diffuse layer. The $f_h$ constant is equal to 1.5 for a value of this ratio lower than 1 (broad diffuse layer). The particle is then regarded as an isolated charge. If the contrary happens (ratio higher than 100), which is the case of environments with low dielectric constant, the diffuse layer is regarded as a plane state and the $f_h$ dielectric constant is equal to 1.

The value of the zeta potential is often correlated with the stability of the suspensions.

**Molds**

The mechanism of absorption of the liquid in the suspension is linked to the capillary suction effect of the porous mold. The porous network of the mold is therefore of vital importance for the setting rate and the characteristics of the green part. The most widely used molds are made of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) formed by reaction of plaster ($\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$) and water. Plaster presents an inter-connected network of gypsum needles and plates which confer on it its mechanical strength. Plaster allows the easy and low-cost manufacture of complex molds with good surface quality, high porous volume (40 to 50%) and pore size lower than 5 $\mu$m. On the other hand, plaster has a low abrasion resistance and high solubility in water, as well as a drop of its mechanical properties due to dehydration, above 40°C, which limits its necessary drying between two castings so as not to increase the setting time. The surface of the mold can be covered to facilitate the demolding and to reduce attacks by acid suspensions (silica) or by organic suspensions (alcohol), using alginates, talc or by graphite.

Other materials are used for the production of casting molds with high mechanical strength and high hardness, for instance, epoxy resins filled or with ceramic powders.
Casting suspensions

Obtaining ceramic parts, with satisfactory properties in a reproducible way by slip casting requires a judicious choice of the grain size and the control of the particle surface chemistry. The behavior and the viscosity of the suspensions in fact depend directly on the grain size of the powders, the inter-particle interactions (state of dispersion) and the particle concentration. The powder grain size distribution, which will influence the arrangement of the particles during the consolidation, varies considerably according to the type of ceramic and the final properties desired.

In the case of technical ceramics, the particle size is generally low with a narrow distribution to ensure satisfactory sintering reactivity and a homogenous microstructure. On the other hand, in the case of traditional ceramics, the mixture is typically made up of fine clay platelets, as well as silica and feldspar particles of about a few tens of micrometers.

Traditional clay ceramic suspensions and technical ceramic suspensions differ by the degree of particle dispersion. A high viscosity at low shear rate and/or a sufficiently high yield stress is favorable for avoiding the sedimentation of the particles at rest, before the casting, but especially in the mold during the setting. The minimal value of the threshold stress $\tau_s$ which balances the sedimentation forces of particles with diameter $d$ and density $\rho_p$ in a suspension of density $\rho_s$ is expressed by:

$$\tau_s = \frac{2}{3}d (\rho_p - \rho_s)$$

Emptying–demolding

The consolidated layer must have sufficient mechanical strength so that it will not flow out with the suspension during the emptying of the mold and allow its demolding. In partially coagulated systems containing clay (traditional ceramics), the coagulation forces give a sufficient cohesion on the piece. The cohesion of pieces realized with dispersed suspensions (technical ceramic) can be increased by the addition of binders (carboxymethyl cellulose, ammonium or sodium alginate) which can also contribute to the dispersion. The addition of binders nevertheless presents the disadvantage of increasing the setting time through an increase in the viscosity of the suspension and a reduction in the permeability of the consolidated layer.
Flaws
The main flaws encountered in a green part obtained by slip casting are:

i) the presence of large pores (pinholes) due to a poor degassing of the suspension.

ii) a preferential orientation of anisotropic particles (clay platelets, mica) to a low thickness on the piece’s surface which results in a differential shrinkage and stresses during drying and sintering.

iii) a non-homogenous microstructure due to a sedimentation of coarse particles.

Pressure casting
The supply of an additional pressure, compared to the low capillary pressure of the mold (< 0.2 MPa for plaster), decreases the setting time. In this respect, the pressure casting consists of applying a pressure, generally lower than 5 MPa, to the suspension in the porous mold. The pressure gradient thus created (ΔP) will force the fluid through the porous network and the formed layer, considerably reducing the setting time compared to slip casting. Pressure casting reduces the water content in the green part and increases its density and its cohesion. The mono- or multi-cavity molds are made of plaster or polymer with a mechanical strength and porosity greater than plaster, as well as an elasticity allowing a water tightness of the mold under low clamping force.

Pressure casting able process provides high productivity. It is now quite widely used in the industry for production of ceramic sanitary ware and tableware. On the other hand, the application of this process to technical ceramics is still relatively new. Elastic stress-strain relation of the form:

\[ p = \beta \varepsilon^{2/3} \]

where \( p \) is the stress, \( \varepsilon \) is the strain, and \( \beta \) is constant for a given particulate system.