

Basis of glaze rheology

1. Introduction

The preparation of glazes has experienced increasing amounts of automation and growing demands on quality with an associated rise in productivity. This means that the following requirements are placed on the preparation of glazes with respect to their rheological properties:

- constant viscosity versus time
- temperature stability
- good coverage and no running
- high output with low pump achievement

The rheological properties of the glazing slip also influences the surface quality of the final product, whether it is tiles, sanitaryware or tableware articles.

Thus considerable emphasis is placed by the ceramics industry on optimizing the processing properties of the glazes by controlling their flow properties.

The flow properties (structural viscosity and thixotropy) and the yield point can be useful for simple evaluation in practical applications.

2. Explanation of the rheological properties to be evaluated

Flow characteristics

The terms structural viscosity and thixotropy are used to describe the flow characteristics of substances. Fig. 1 shows the flow properties of a structurally viscous and a thixotropic system.

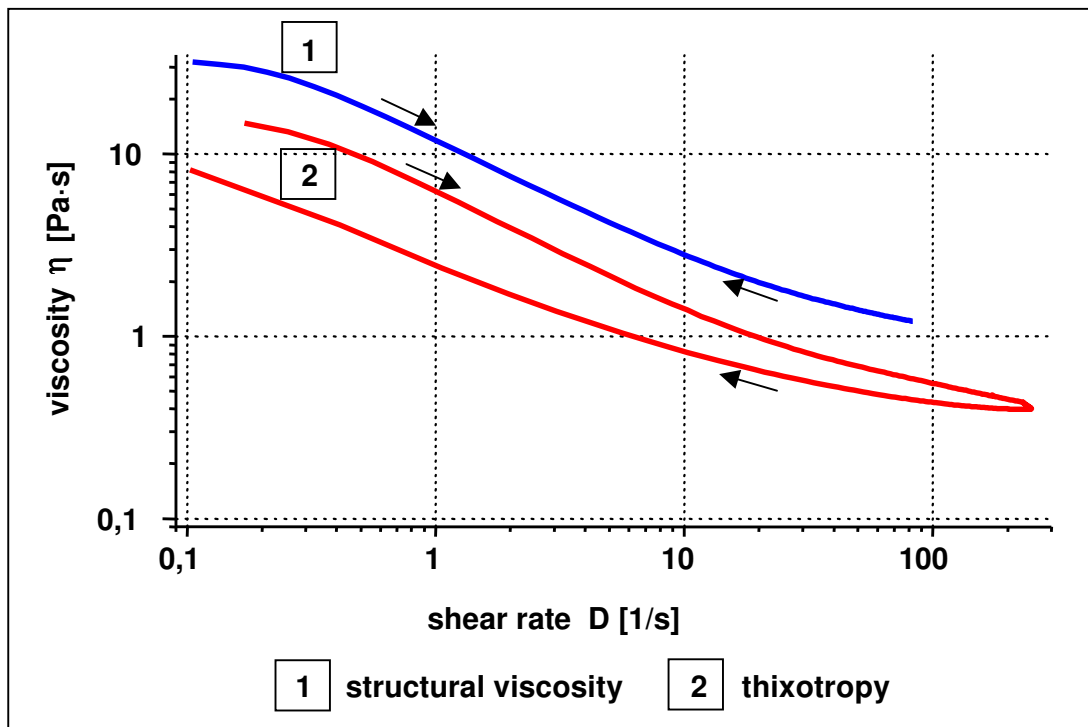


Fig. 1: Flow characteristics of a structurally viscous and a thixotropic system

In structurally viscous systems (curve 1), the viscosity sinks as the shear rate increases, and again rises by the same amount as the shear decreases, without time delay.

In thixotropic systems (curve 2), the viscosity sinks with increasing shear rates and increases, dependent upon time, as the shear is reduced. The viscosity of a thixotropic system is therefore dependent on shear stress *and* time.

Yield Point

The yield point is the resistance that needs to be overcome in order to cause a substance to flow. There are materials with or without yield point. The two variations are shown in Fig. 2.

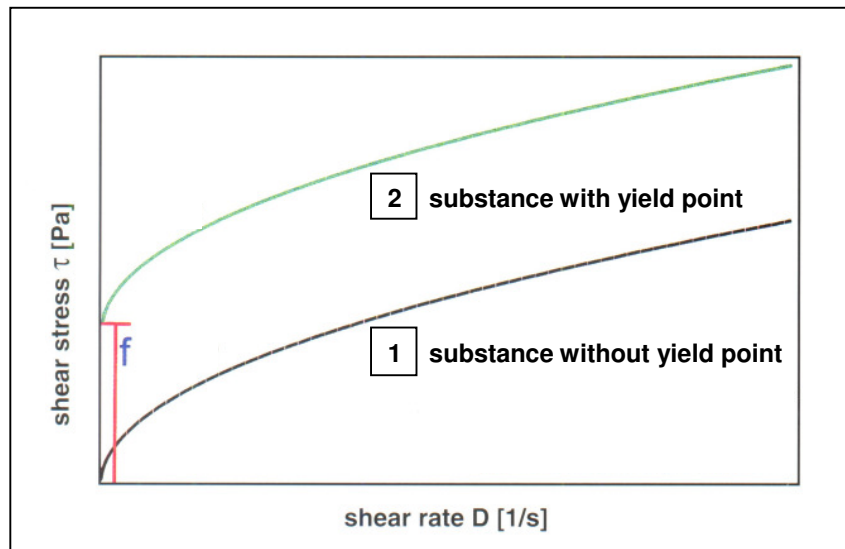


Fig. 2: Schematic representation of the presence of a yield point

Curve 1 describes a substance that does not have a yield point. With the smallest of outside influencing forces, these substances begin to flow.

A substance having a yield point is shown in curve 2. This material first begins to flow when the outside influencing forces (e.g., gravity when glazing vertical surfaces) are greater than the structural forces of the substance which work against flow.

This is once again clarified in Fig.3.

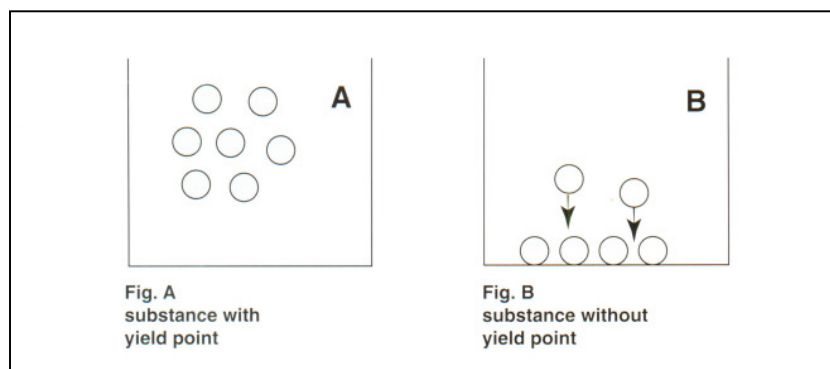


Fig. 3: Example of the yield point effect

Two different substances strewn with coarse grains of sand are schematically represented.

In part A of the figure the grains of sand remains in suspension; i.e., a yield point exists. The solid particles do not sediment.

In part B of the figure the grains of sand sink to the bottom; i.e., although high viscosity exists, a yield point does not. The solid particles sediment.

The following should clearly show the principle relationship between the yield point and the achievable layer thickness of the glaze. In addition, Fig. 4 shows a model of a glaze layer on a vertical surface.

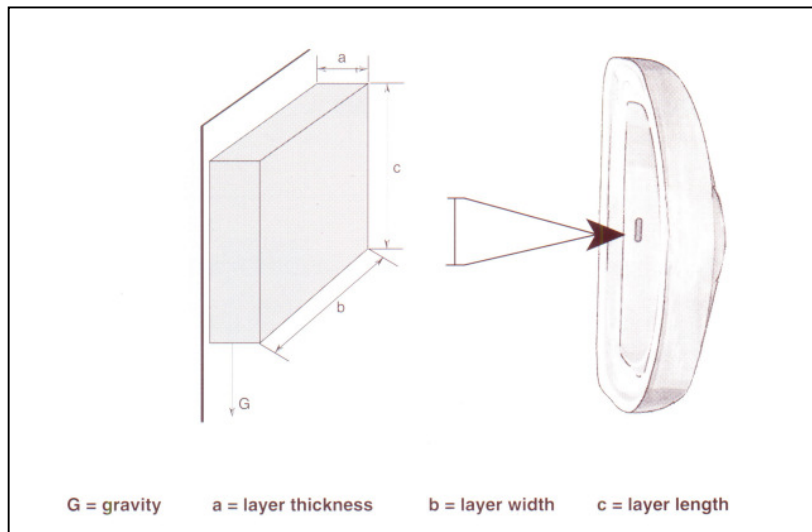


Fig. 4: Volume element of a glaze layer on a vertical surface

The yield point is characterized by the limiting shear stress at which a glaze still remains on a vertical surface without running. For the limiting shear stress, the following applies:

$$\tau = F / A$$

τ : limiting shear stress
 A : shear surface = $b \cdot c$
 F : = G = gravity

$$G = m \cdot g$$

m : mass of the volume element

$$G = V \cdot \rho \cdot g$$

g : acceleration due to gravity = 9.81 m/s²

$$G = a \cdot b \cdot c \cdot \rho \cdot g$$

V : volume of the volume element = $a \cdot b \cdot c$
 ρ : density of the glaze

Thus the yield point f results:

$$f = G / A = \frac{a \cdot b \cdot c \cdot \rho \cdot g}{b \cdot c} = a \cdot \rho \cdot g$$

The formula shows that the yield point is independent of the layer width b and the layer length c . With respect to the measurement of the glaze layer, the layer thickness a is the only variable to be used in the formula.

The thickness of the glaze layer which theoretically stays on the non-absorbent background without running, is calculated as follows:

$$a = \frac{f}{\rho \cdot g}$$

For a glaze with a density of $\rho = 1.7 \text{ g/cm}^3$, following layer thickness can be calculated using various existing yield points:

$f = 20 \text{ Pa}$	$a = 1.2 \text{ mm}$
$f = 15 \text{ Pa}$	$a = 0.9 \text{ mm}$
$f = 10 \text{ Pa}$	$a = 0.6 \text{ mm}$

Since an absorbent background is used in practice, greater layer thicknesses can be achieved with comparable yield points.

3. Transferring the fundamental rheological terms onto a practical application

If a glaze is supposed to have a smooth, even surface, the viscosity has to remain low long enough to allow good spreading to occur. On vertical surfaces, however, this can lead to running.

Conversely, to completely prevent the glaze from running, a fast recovery of the viscosity after a shear stress (e.g., spraying process) is required so that no more flow, and therefore no more spreading, takes place.

The rheological additives (PEPTAPON types) from Zschimmer & Schwarz are optimized compounds with binders that encourage spreading, and which are appropriate for both conditions. They guarantee:

- good levelling
- no running

Fig. 5 shows a schematic representation of the build up in viscosity and the thereby resulting condition of the glaze surface after a shear stress (e.g., spraying process).

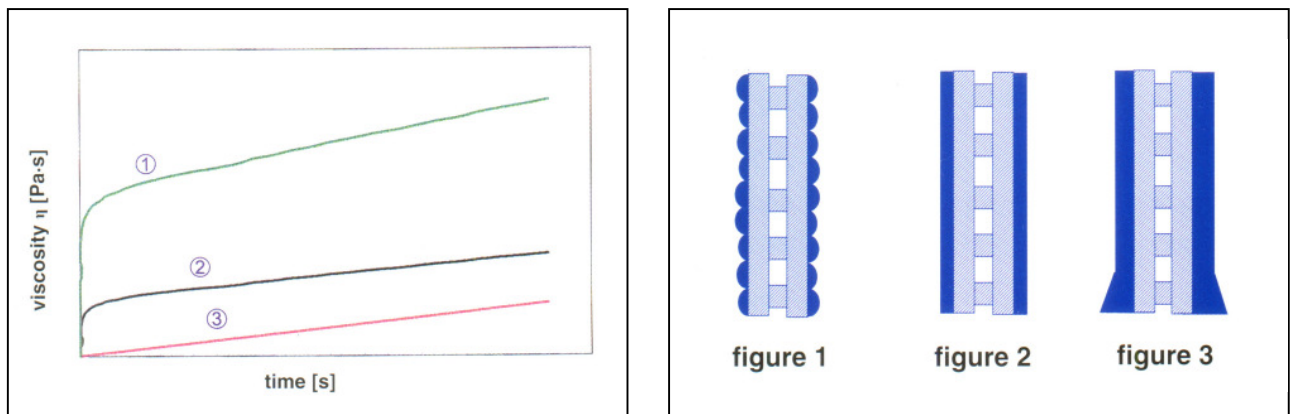


Fig. 5: Schematic representation of the build up in viscosity after shear stress

In curve 1, a very rapid increase in viscosity is seen after the shear stress ends. The glaze behaves structurally viscous (pseudo-plastic). Thus no running occurs, however, the glaze does not spread either (figure 1).

A well-balanced viscosity increase is shown in curve 2. The rise of the viscosity over time is optimal, guaranteeing good spreading while prohibiting running (figure 2).

Curve 3 shows a glaze with a very slow increase in viscosity after high shear stress. Good spreading is seen, but the glaze displays strong running tendencies as well (figure 3).

The optimal glaze model in figure 2 was, in addition to the bond and the drying time of the glaze, of paramount importance during the developmental work on the PEPTAPON types.

4. Comparison of the application possibilities of CMC and Peptapon

The following explanation shows the differences of glazes bonded by PEPTAPON types compared to carboxymethylcellulose (CMC). The advantages with regard to the viscosity and flow curves as well as the temperature stability are distinctly seen here. It is clear that the use of CMC (due to its characteristics) is limited by the high demands placed on the processing properties of glazes.

Figure 6 shows the flow curves of a glaze containing CMC (OPTAPIX KG 1000) as well as glaze containing PEPTAPON 44.

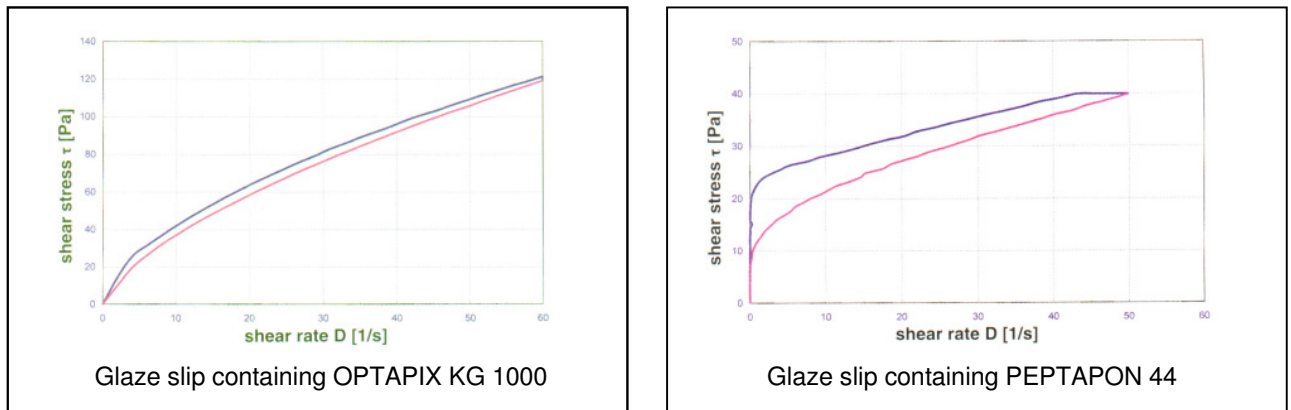


Fig. 6: Flow curves

The flow curve for the glaze containing CMC clearly shows that this substance does not have a yield point; conversely, the glaze with PEPTAPON 44 displays a yield point.

That means that greater layer thicknesses are possible using the CMC only by multiple glazing; i.e., glazing with interim drying. The productivity is therefore considerably lower than in single-layer glazing. Furthermore, the solid particles in the glaze slip containing CMC can sediment, which is not the case when using PEPTAPON, due to the existing yield point.

Figure 7 shows the viscosity curves of a glaze containing CMC (OPTAPIX KG 1000) and a glaze containing PEPTAPON 44.

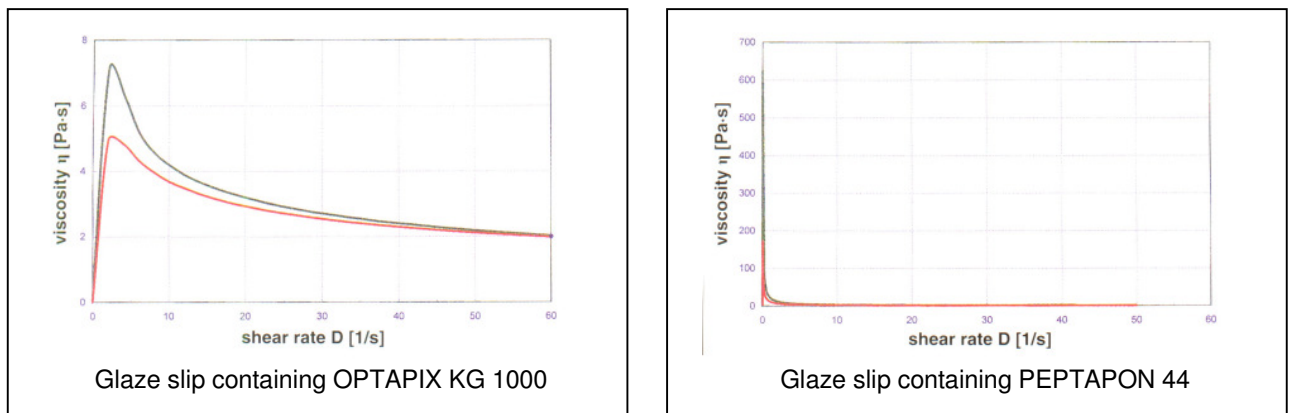


Fig. 7: Viscosity curves

The viscosity of the glaze bonded with PEPTAPON 44 decreases rapidly to a low end viscosity given increasing shear rates. With reduced shear rates, it quickly increases again.

The decrease and increase in viscosity with the CMC-containing glaze proceeds slowly. The final viscosity at the greatest shear is higher than with PEPTAPON.

That means the PEPTAPON-bonded glaze can be processed in a manner that is easier on the pump. The glaze can be conveyed with a more little expenditure in power. This can be confirmed by comparing the pump rotation frequency (rounds / minute) at equal shear rates.

The progression of the viscosity curve as well as the low end viscosity of the PEPTAPON bonded glaze makes an increase in the amount of glaze throughput per unit of time possible. A productivity increase equal to that of single-layer glazing can be achieved.

It should be noted that the PEPTAPONs have a further advantage in their increased temperature stability compared to CMC. The viscosity of a 1 % solution was recorded with respect to temperature. The samples were continuously heated over 5 hours.

For the recorded temperature range of 14 to 45 °C, significant difference resulted, as shown in Fig. 8.

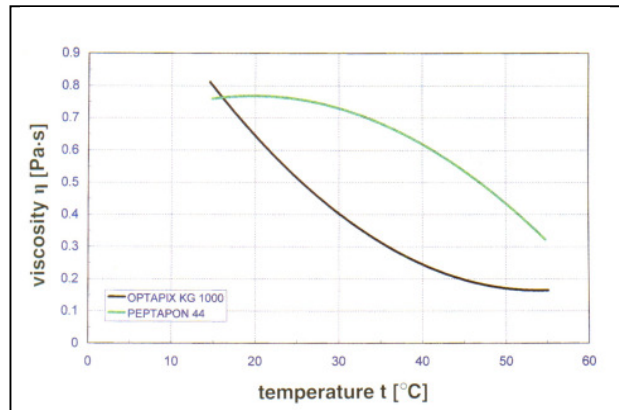


Fig. 8: Viscosity changes in a glaze slip versus temperature

CMC has very low temperature stability. The variations in viscosity are extremely evident even with small temperature differences. This deviation range is a distinct disadvantage for an automated glazing process.

In contrast, the insignificant viscosity deviations of the PEPTAPON-bonded glaze allow a complete automation of the glazing process using robotics.

The requirement of stable viscosity over time is also fulfilled by using the PEPTAPON types. Storage tests over several weeks show constant values.

Due to the stable viscosity of the PEPTAPON types, the glaze slip shows the same glazing results (smooth surface, no glaze runs) after several weeks, as if the slip was freshly produced.