USE OF THE HOT STAGE MICROSCOPE TO EVALUATE THE CHARACTERISTICS AND BEHAVIOUR OF FRITS AND GLAZES AT DIFFERENT HEATING RATES

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The hot stage microscope (HSM) is a useful instrument in following the behaviour of frits and glazes during firing. Different phenomena such as shrinkage, sintering, softening and melting can be observed and the measuring of critical temperatures, contact angles and other parameters are also possible. A very interesting evaluation of surface tension and viscosity is also possible. All these phenomena are influenced by sample preparation, grain size distribution and the heating rate to which the sample is subject.

The behaviour of frits and glazes changes drastically when the microscope's heating rates resemble those of industrial fast firing processes (single fast firing, double fast firing, monoporosa in the ceramic tile industry).

A new instrumental method and new equipment permit us to follow better the behaviour of frits and glazes in fast firing conditions where traditional methods are not suitable.

1. INTRODUCTION

Ceramic frits and glazes need to be technically investigated during their firing to identify the major phenomena which occur evaluating general behaviour, physical properties, reactions, development of gas by using optical microscope, SEM, X- ray analysis, viscosity determination of the molten glass and all the thermal analyses such as thermal expansion (T.D.), differential thermal analysis (D.T.A.) and, finally, the HSM.

With the HSM we are able to determine information such as sintering of grains (starting from milled material), softening of the glaze sample and, obviously, the temperatures or intervals of temperature where these phenomena take place.

By means of these observations and temperature data it is easier to judge whether frits and glazes are suitable for specific firing conditions (double traditional firing, DTF, double

and single fast firing, DFF, SFF, monoporosa, MOP) at specific heating rates.

Unfortunately, most of the instruments for thermal analysis have been designed to work at a heating rate of 10°C/min (which means they reach 1200°C after 2 hours) whilst most of the modern fast firing processes take place in 30 - 40 mins, reaching maximum firing temperature in about 15 - 20 minutes only (abt 60°C/min). This means that most of the information obtained with thermal analysis is not sufficiently reliable because it does not refer to effective firing conditions.

Differences in behaviour and characteristic points and temperatures can be observed with the HSM when analyses are made at different heating rates. The most significative transformation can be described.

A) Sintering: By firing glassy material, frits, glazes, their very high viscosity decreases strongly, the transition point (Tg) is reached (visible also with thermo-dilatometric analysis) and if the material is finely milled its particles sinter together. It is very important to determine at what temperature (Ts) this phenomenon takes place, especially for the fast firing process.

B) Softening: With a further increase in temperature and decrease in viscosity the glaze sample tends to smooth its edges and round its profile. We indicate this phenomena as softening and the softening temperature (Tw) can also be related to that shown during the thermal dilatometric analysis. The glass behaves like a high viscosity liquid and two physical parameters start to be important: surface tension γ and viscosity η. Depending on composition and heating rates, the glass can also develop a more orderly structure which can lead to separation of phases and crystallization which influence the next softening and melting steps.

C) Melting: With the progressive decreasing of the viscosity the glass becomes more movable and tends to form drops, minimizing its free surface energy. An exact melting temperature for glass does not exist so a melting interval has to be considered. With the help of the HSM it is possible to determine at which temperatures the profiles of a sphere, semisphere or 1/3 of a sphere of the glass sample appear. These are used as characteristic melting temperatures.

At its maximum firing temperature, a glaze has reached its minumum viscosity in the range of about $\log \eta = 2 - 3$ d Pa s. At this temperature all the single drops are already sealed together, the surface tends to become flat and smooth and the defects tend to be sealed.

D) Crystallization: For those frits and glazes for which crystallization occurs the behaviour of the glaze changes drastically. The reorganization of the glass structure, the separation of the crystals and the system nonhomogeneities strongly affect all the relevant parameters and all the characteristic temperatures may change according to the different heating rates.

As these phenomena greatly influence the surface quality of the fired tiles we studied different types of ceramic frits which are intended for different firing cycles. For this work a new HSM enabling any heating rate up to 80 °C/min was used to investigate different phenomena such as shrinkage, sintering, softening and melting. (The HSM analyses were compared to X-ray diffraction to detect the presence of crystallized phases, if any. Dilatometer measurements were also used to estimate Tg and Tw). The HSM provides very useful information regarding phenomena during firing, provided that it is used at the same heating rate as under industrial firing conditions, especially when firing is very fast.

2. THEORETICAL CONSIDERATION

In general, gravity and surface tension forces act on the sample when temperature rises and viscosity decreases. The shrinkage of the glass sample is related to the sintering effect of the glass particles and can be described by (1).

(1) $$\alpha = \frac{\Delta L}{L} = \frac{3\gamma}{4\eta r} t$$

α= linear shrinkage of a glass sphere model under the action of surface tension (η) viscosity (γ) and time (t).

At a fixed temperature, formula (1) shows shrinkage correlated to time, while viscosity and surface tension are considered to be constant. To describe the real dynamics of the firing conditions the heating rate has also to be considered. This appears from formula (2) which is deducted from formula (1) using partial differentiation of the shrinkage versus T and t.

(2) $$\frac{\delta\alpha}{\delta T} = \frac{(3\gamma) / (4\eta r)}{(\delta T) / (\delta t)}$$ Influence of heating rate ($\delta T/\delta t$) on dynamic shrinkage ($\delta\alpha/\delta T$)

Viscosity η depends on temperature T and is expressed by VFT equation (3)

(3) $\log \eta = A + B/(T - T°)$ where A, B, T° are constant.

From (2) it is shown that the differential ($\delta\alpha/\delta T$) lowers with an increase in the heating rate.

Consequently, at higher heating rates during firing cycles, sintering will take place at a higher temperature. This effect can be seen from the images of the HSM analyses when they are made at faster heating rates as under industrial conditions (see figures).

Beyond the softening point (Tw) the forming of glaze drops (spheres) can be observed on the glazed tiles when a very thin glaze layer is applied. At the highest firing temperature the glaze will normally flow and spread well but, particularly under fast firing conditions, time is insufficient to obtain a smooth surface and so some hammering and wavy effects can be observed.

In general, the gravity and surface tension forces influence the glaze sample: when the viscosity of the glaze decreases, the surface tension tends to change the sample into a spherical shape whereas the force of gravity and the specific gravity of the glass contrast with this thereby flattening the surface of the glaze. As during industrial firing, also in HSM analyses the samples are not in a condition of real equilibrium so the viscous flow has to be considered. Equation (4) describes the interaction of the dynamic forces acting on the glass.

(4) $2\gamma/b - \rho g h - 2v/r = \eta (\delta v/\delta x)$

The viscous flow is represented by sharing speed ($\delta v/\delta x$) which is clearly in relation with the surface tension (γ), viscosity (η), specific gravity (ρ) and force of gravity (g).

As described in formulas (3) and (4) the shape of the images visualized and measured with the HSM depends on surface tension, density and viscosity. The temperatures at which the major phenomena such as sintering, sphere, semisphere, 1/3 of a sphere occur and the evaluation of the related graphs give fundamental information about the behaviour of the glass and about the expected final surface quality.

3. HOT STAGE MICROSCOPE EQUIPMENT (HSM)

Determination of the characteristic transformation points of the frits was made by means of the new HSM (*) (Fig.1). This traditional instrument has been totally innovated and uses a digital system of analysis for imaging. This enables us to follow the behaviour of the sample and measures its physical parameters at every firing stage and firing rates. Even at rapid heating speeds it is possible to control and collect data with the computer which is otherwise impossible with the naked eye. Acquisition and recording of images, identification and calculation of specific points, the elaboration of graphs and final printing are made by a special programme.

The instrument has a platinum heated kiln with an automatic power unit and microprocessor capable of subjecting the sample to heating gradients of up to 80°C/minute, reaching a maximum of 1600°C. The temperature is read with a 2°C resolution, is measured by means of a Pt/Pt-Rh thermo-element placed directly under the sample and digitalized.The image is obtained by means of an electronic video camera and a special optical lens designed to obtain maximum resolution (10 μm). Diagrams, values and images can be printed out when the HSM analyses have been completed.

4. INVESTIGATIONS

The analyses with the HSM were conducted systematically on a group of very representative transparent and white frits for the tile industry suitable for several firing conditions such as monoporosa (MOP), double fast fire (DFF), double traditional firing (DTF) and single fast firing (SFF). Each analysis was conducted at 3 different heating rates: 10°K/min, 30°K/min, 50°K/min. In this work special attention was given to the comparison between four frits (white and transparent) for MOP and DTF cycles. Indicative oxide formulas are given in Table 1 and characteristic points of the investigated frits are given in Table 2.

TAB.1: Chemical Composition of the Investigated Frit Systems

Frit	SiO2	ZrO2	B2O3	Al2O3	MgO	CaO	ZnO	Alcal
MOP W	56	7	3 - 5	5	10	10	3 - 5	
MOP T	55	-	3 - 6	10	5	10	10	3 - 6
DTF W	60	10	9 - 14	5	-	5	2	3 - 5
DTF T	65	-	9 - 14	7	-	5	2	5 - 8

TAB 2 Characteristic Points of the Investigated Frits

From:	Dilatometer		Hot Stage Microscope					
Frit	Tg	Tw	dT/dt	Ts	Tr	Ts	T1/2	T1/3
MOP WHITE	627	825	10	930	1070	1110	1190	1241
			30	916	1010	1116	1212	1248
			50	923	1002	1097	1194	1216
MOP TRANS	644	803	10	921	1020	1060	1140	1160
			30	864	1032	1092	1164	1200
			50	897	993	1088	1172	1208
DFF WHITE	670	810	10	791	890	990	1181	1240
			30	789	915	1032	1224	1296
			50	787	912	1079	1224	1301
DFF TRANS	577	648	10	710	840	920	1130	1210
			30	745	857	1032	1104	1177
			50	754	872	1010	1150	1250

The HSM shows us automatically: a) the height of the sample and the sintering diagram, b) maximum width of the sample compared to its height so as to determine the sintering and melting ranges, c) image form to determine the point in which the sample has the closest resemblance to a sphere, semisphere and 1/3 of a sphere, d) the roughness of the sample's surface is controlled to determine initial softening, e) contact angle between the ceramic support and the molten glass (tangent).

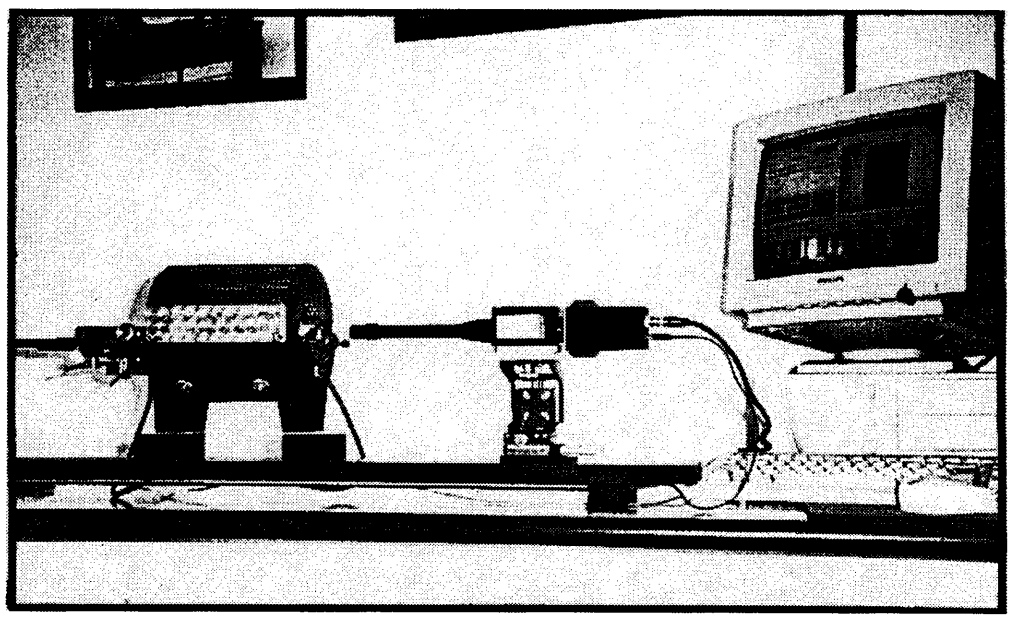

Fig. 1: Hot Stage Microscope (HSM) * Tradename MISURA designed by M. Paganelli comercialized by Expert System - Modena

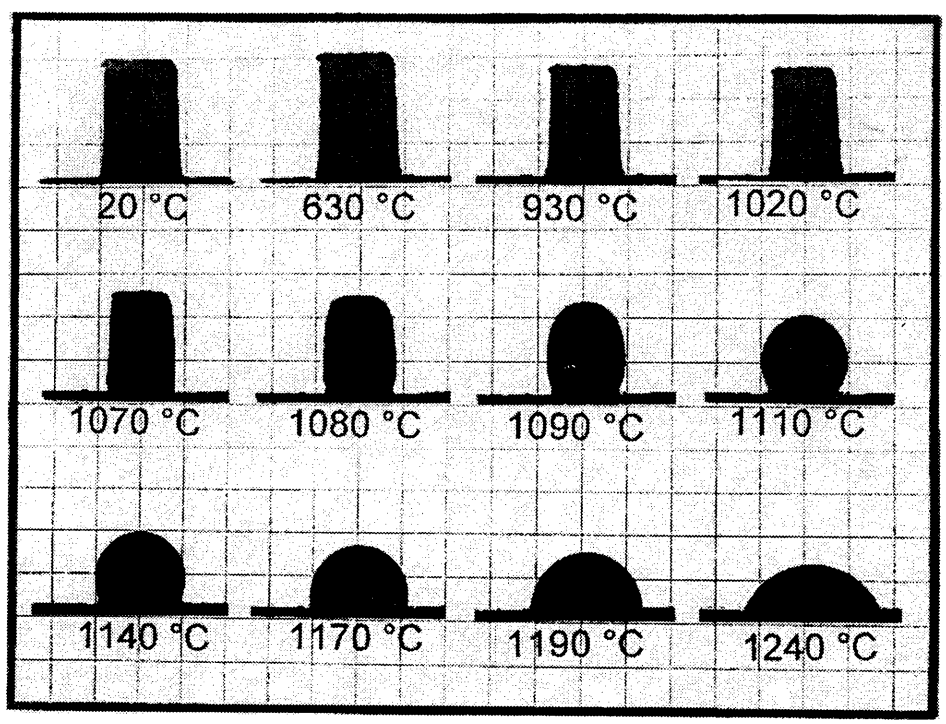

Fig. 2: HSM images of white monoporosa frit during frit

MOP frits are poor in alcali and boron content but high in CaO and ZnO content compared to frits for DTF. The change in composition of the MOP frits has been dictated by the following requirements:

- delay as much as possible the sintering and softening of the glass so as to allow the escape of the gas from the body without being trapped by the molten glass
- avoid possible crystallization or phase separation during fast firing (whereas this can occur during longer firing cycles)
- have the appropriate viscosity and surface tension so as to avoid gas bubbles reaching the surface and thus obtain a smooth surface at the end of the process.

Plotting the height in percentage (of the samples) versus temperature following the analyses made with HSM on some frits, it is possible to highlight the most important changes which occur at different heating rates. Some graphs are included as follows.

Fig. 3: Monoporosa Transparent Frit. Heating rates at 10-30-50°C/min.

Fig. 4: Monoporosa White Frit. Heating rates at 10-30-50°C/min.
In both cases the shift of the softening point (Tr in Table 2) and the melting conditions are very evident. When the heating rate is lower, frits can organize some crystallization and delay their softening. When the heating rate is high, as in monoporosa production firing conditions, the softening of the frit is anticipated (no time for crystallization but continuous shrinkage and progressive flattening of the glass).

Fig. 5: Double Traditional Firing White Frit. Heating rates at 10-30-50°C/min.
Phenomena as described for Fig. 3 and 4, but the situation is less critical. Due to their composition traditional frits begin to sinter and soften at much lower temperatures and the influence of different heating rates is less evident.-

Fig. 6: Comparison between a Monoporosa White Frit heated at 10 and 50°C/min and a Double
Traditional Firing White Frit heated at 10°C/min.
The drastic delay of all sintering, softening and melting parameters related to the Monoporosa Frit versus the traditional one are highlighted.

Fig. 7: Single Fast Firing Ca-Matte frit.
The graphs H/T and the derivative dH/dT highlight the very typical behaviour of this frit which has an eutectic composition. After sintering, just when softening begins, the frit develops a very strong crystalline structure (see also Fig. 7 - XRD patterns of C) and stop hrinking for a long time between 920°C and 1160°C. Then, in a very short temperature interval, the frit samples collapse passing through a very rapid softening and melting stage (sphere, semi-sphere, 1/3 of a sphere).

Fig. 8: X-Ray Diffraction.
X-Ray analysis highlights the crystalline structure which develops inside a Monoporosa Transparent Frit when heated for a sufficient time (30 mins at 850°C). Diopside crystallization occurs (B) whereas no crystals are in the non heated glass (A). What is also very evident is the crystallization of the wollastonite inside a Ca-matte frit for Single Fast Firing when thermally treated in the same way (C).

5. CONCLUSIONS

Many important phenomena related to the heating of frits and glazes can be studied by means of HSM analysis. Not only thermal properties but also the interesting evaluation and determination of the glass viscosity and change in reaction and wettability of different frits on different types of body can be studied. A Hot Stage Microscope with adjustable heating rates and temperature programmer, with electronic image acquisition and data elaboration, is becoming a necessity in order to have reliable data and be able to forecast the physical behaviour of frits and glass, especially under the current fast firing conditions.

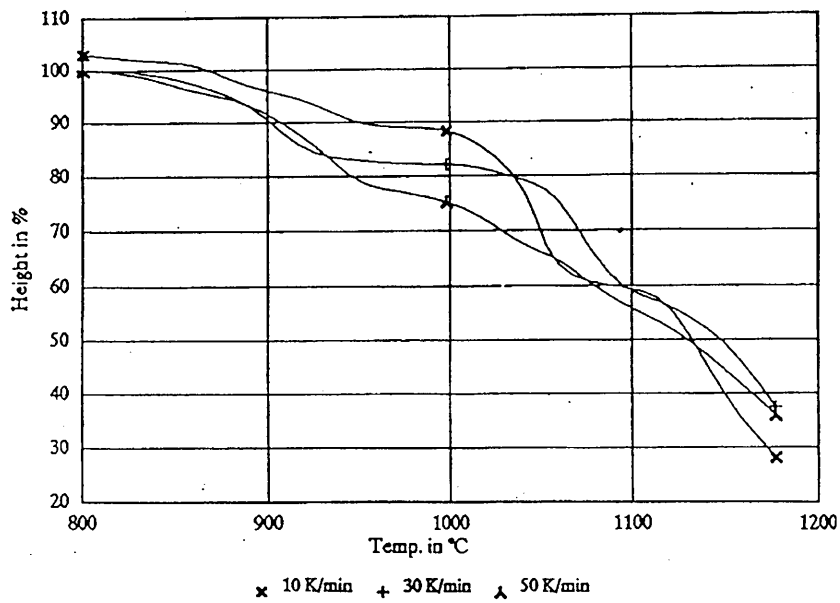

Fig. 3: Monoporosa Transparent Frit.

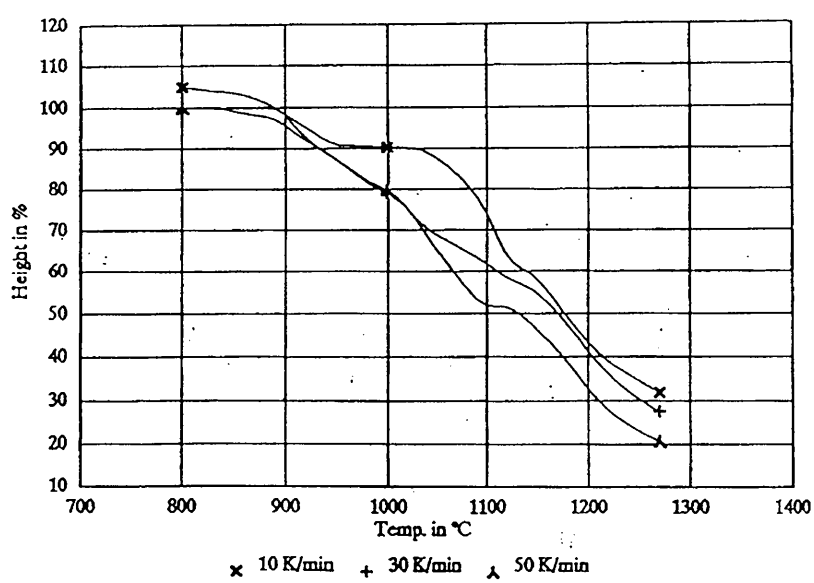

Fig. 4: Monoporosa White Frit

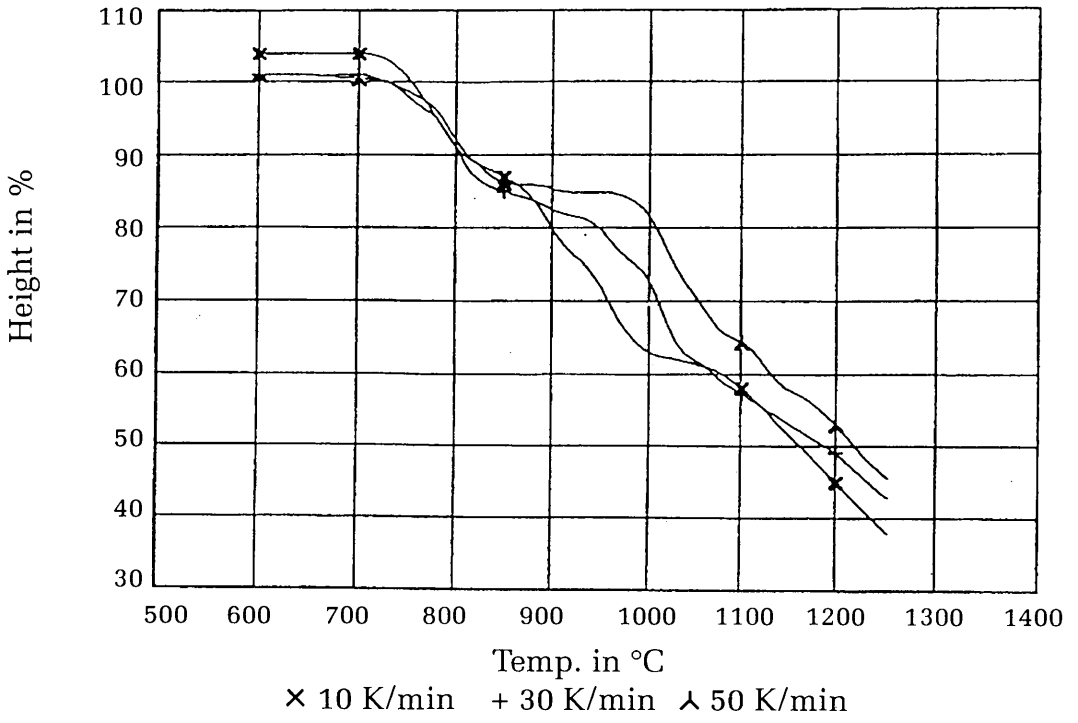

Fig. 5: Double Traditional Firing White Frit

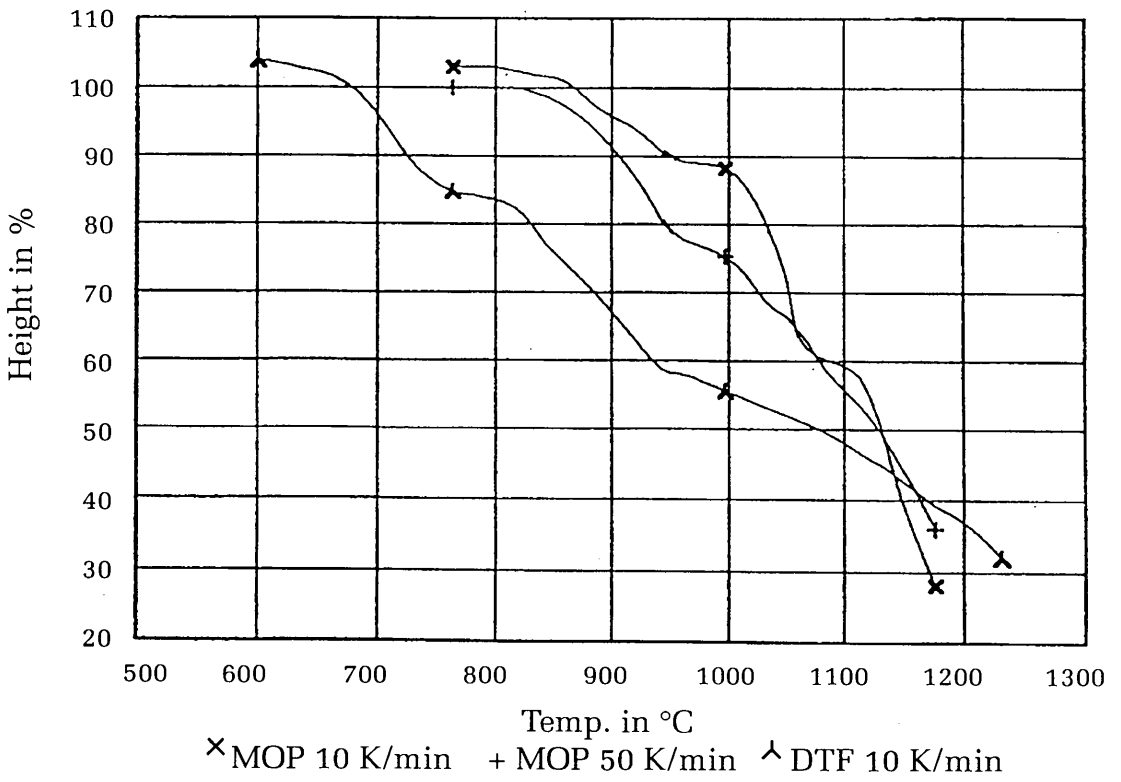

Fig. 6: Comparison between a Monoporosa and Traditional White Frit

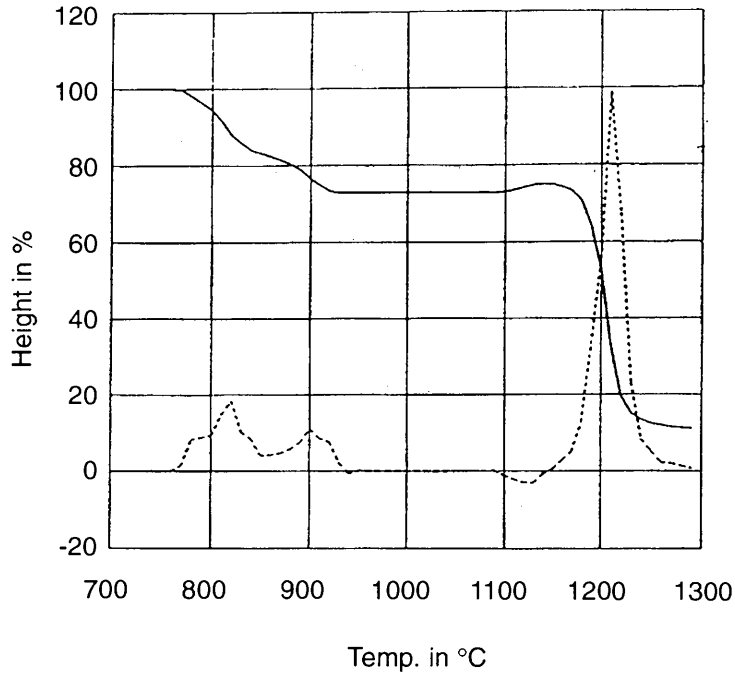

Fig. 7: Single Fast Firing Ca-Matte frit.

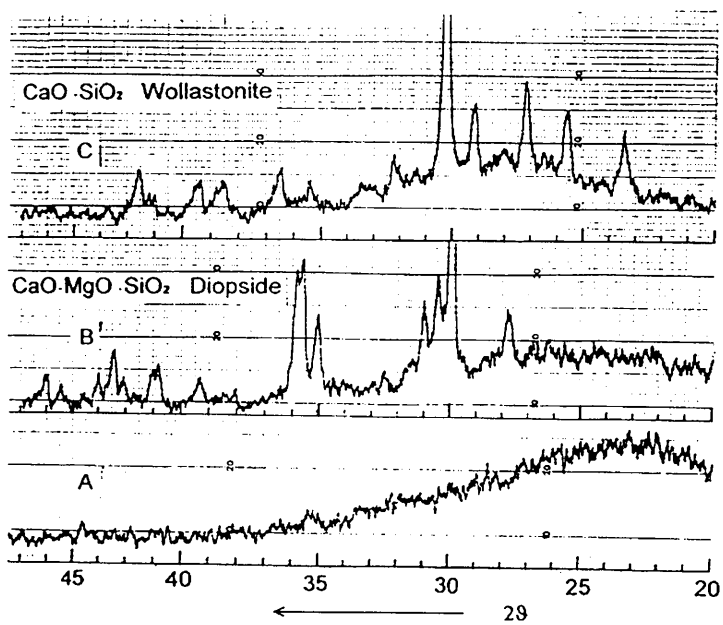

Fig. 8: X-Ray Diffraction: A) Monoporosa Transparent Frit without thermal treatment - B) Treated at 850°C for 30 mins - C) Single Fast Firing Frit, treated at 850°C for 30 mins