Foam Enamel- Matching up highest reactivity of foaming agents with the most suitable viscosity of enamel

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Abstract

Foam enamel is highly porous enamel, a material which is little investigated in research and not yet applied in industry. Ongoing investigations pursue the target of implementing foam enamel in various fields to make use of the characteristic advantages offered by the material. Previous research focused on finding the optimum parameters to foam up one certain type of enamel. To develop transferable and widely applicable knowledge it is necessary to understand the fundamentals of foam enamel technology. The findings described herein give an introduction into the fundamental understanding.

Introduction

In enamel technology bubbles are seen as significant defects. On one hand bubbles reduce the mechanical strength, may lower the chemical resistance or even be the reason for emerging cracks [1], on the other hand bubbles have positive effects like arresting the development of cracks and increasing the elasticity of the coating.

Still there is motivation to create highly porous enamel, so called foam enamel. Foam enamel behaves similarly to foam glass as thermal and acoustic insulation. Since it can be applied in thick layers (around 10 mm) it also minimizes vibration of enamel products. Thus it can replace materials which are combined with enamelled products to provide stiffness. So far this is often done on a base of organic material (e.g. glue) which represents a particular fire risk.

Production of porous enamel at lab scale is described in the literature [1–4] but no practical implementation has been reported so far. Enamels are mixed with foaming agents such as silicon carbide, carbon or carbonates and fired between 700°C and 900°C. During firing the enamel melts and foaming agents produce gas, so a foam structure is produced. As soon as the foamed enamel is cooled down, the structure becomes stable.

The production of foam glass follows the same procedure. The biggest difference is the relatively dry batch for foam glass compared to the watery slurry for enamel production. Since these processes are so similar, the existing knowledge of foam glass production can be transferred to foam enamel production. The influence of several process parameters on the foaming result is reported in the literature. The following table gives a summary of the literature.

Process parameter	Reference
Foaming agent	[5–15]
Grain size distribution	[7, 16]
Temperature regime	[8, 9, 16–18]
Atmosphere	[17]
Water content and hydration time	[1, 9, 17]

The literature about foam enamel follows similar methods and approaches as literature about foam glass. In general it is shown that different enamel compositions can be foamed up if appropriate parameters, mainly regarding foaming agent and temperature regime, are defined. In foam glass science such approaches lead to some statements which can be generalized within certain limits. In enamel technology the feasibility of generalization is limited due to substantial variations in composition; this is especially true of foam enamel.

This background strengthens the motivation to create a structured manual which enables enamellers to investigate the foaming parameters required to foam up their own enamel composition by carrying out only a few focused experiments.

To create such a universally valid manual it is not effective enough to run more foaming experiments with a range of combinations of different compositions, foaming agents and firing parameters. It is more expedient to understand the fundamentals of the process of foaming up enamel. Therefore the first step of examining the fundamentals is to study the correlation between the temperature-viscosity-behaviour of the enamel, the reaction rate of the foaming agent and the resulting foam structure.

Methods

Differential Scanning Calorimetry (DSC): Netzsch's STA 409 was used to carry out DSC measurements on several carbon blacks. All samples were heated from 20 °C to 1000 °C with a ramp of 10 K/min. Exothermal heat was measured and plotted against temperature.

Viscometric fixed points: Following DIN ISO 7784-1 VFT-equations were calculated for the enamel compositions investigated. To calculate the constants of the VFT-equation fibre elongation viscometry (DIN ISO 7884-3), measurement of softening point (ISO 7884-6) and dilatometric measurements (DIN ISO 7884-8) were carried out following the respective standards.

Foaming experiments were carried out on pre-enamelled steel samples. The samples were cleaned with ethanol before slurry was spread on them with several thicknesses. The slurry was a standard mixture plus foaming agents. After spreading, the samples were dried at 120 °C to constant weight and then fired at different temperatures in muffle furnaces.

Discussion and Results

In the present literature about foam glass and foam enamel lots of examinations are reported which show optimum combination of foaming agent and enamel make up a certain density. The results of those examinations are only valid for the glass or enamel compositions regarded. The results suggest that it is not necessary to perform more. It is more useful to develop structured guidance that can be followed to find the optimum parameters for foaming up the enamel that would be applied to the product anyway. This is particularly advantageous since that enamel is optimized for best adhesion on the substrate.

The advantages of using the same enamel for foam enamel are diverse. No additional working step is necessary which makes foam enamel very efficient compared to other reinforcement methods. The application of the slurry can be done by conventional application methods, like spraying or dip coating. Since the enamels on both sides have similar chemical compositions the enamel at the product edges will merge smoothly.

Figure 1 shows how such an enamel product could be assembled. On one side of the steel plate standard enamel is applied. On the other side of the plate foam enamel having the same composition, but with the addition of foaming agent, is applied. For most applications the second side would not be exposed to environmental or chemical attack or seen by customers.

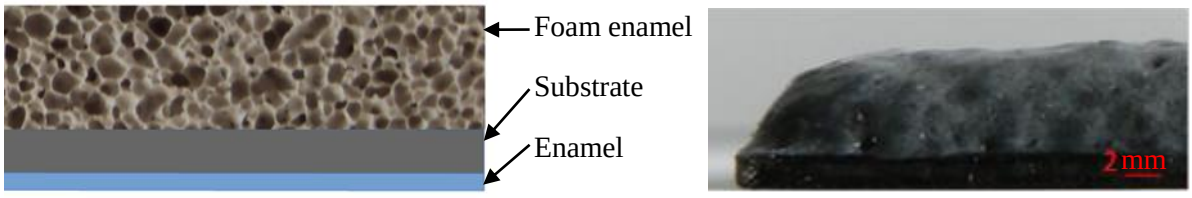

Figure 1 assembly of possible foam enamel products

In enamel technology it is well known that metal sheets always need enamel layers of equal thickness on both sides. If the thickness differs too much the metal sheet will warp due to the different expansion coefficients of the materials. However, this theory is based on enamels having the same density as the substrate. The emerging force caused by different expansions is manly correlated to mass not thickness. This makes it possible to create assemblies which show no warping despite one side being covered by a thicker layer (of lower density). This was confirmed by samples with 7 mm thick foam coatings on metal sheets of 0.5 mm thickness.

An important goal of the investigation is to find parameters to adjust foaming behaviour while firing temperature and time are maintained at the levels used to process existing enamel and product combinations. Thus the following parameters are considered predominantly: type and percentage of foaming agent, grain size distribution of foaming agent, additives e.g. oxidizing agent.

One approach to find the optimum foaming parameters is to observe the physical and chemical processes. To create foam via a direct foaming method, two parameters are crucial. On the one hand the gas-forming reaction should have a high reaction rate to produce gas for foaming up the melt. On the other hand the melt itself needs to have just the right viscosity to be foamed up. If the viscosity of the melt is too high the pressure of the gas needs to be very high to create bubbles; only a few and very small bubbles will evolve. If the viscosity is too low emerging bubbles will rise up, join together (coalescence) and leave the melt. In this case the foam structure will be very coarse, with a broad range of pore size distribution and therefore poor mechanical strength. On this basis foam enamel should be produced most successfully by matching the temperature of the optimum foaming viscosity and a high reaction rate in the gas-forming reaction since both characteristics can be controlled by several parameters (Figure 2).

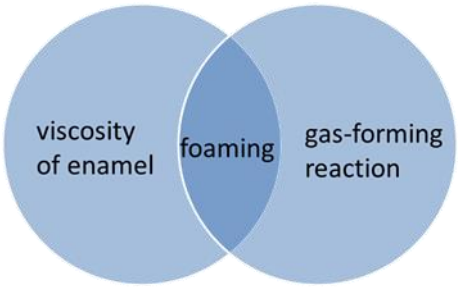

Figure 2 Correlation of temperature fields of viscosity and gas-forming reaction

Figure 3 shows the result of DSC measurements (Differential Scanning Calorimetry) of several carbon blacks. Thermal black, lamp black and furnace black were compared. It shows that choosing an appropriate type of carbon black is crucial. The temperatures of maximum reaction rate of the carbon types tested vary between 630 °C and 700 °C. It also shows that the temperature ranges of high reaction rates are quite narrow. The differences between the carbon blacks are due to grain size distribution, grain morphology and surface chemistry, which are all related to the production method of those carbon blacks. All in all it demonstrates that selecting a single type of carbon as a foaming agent is never enough.

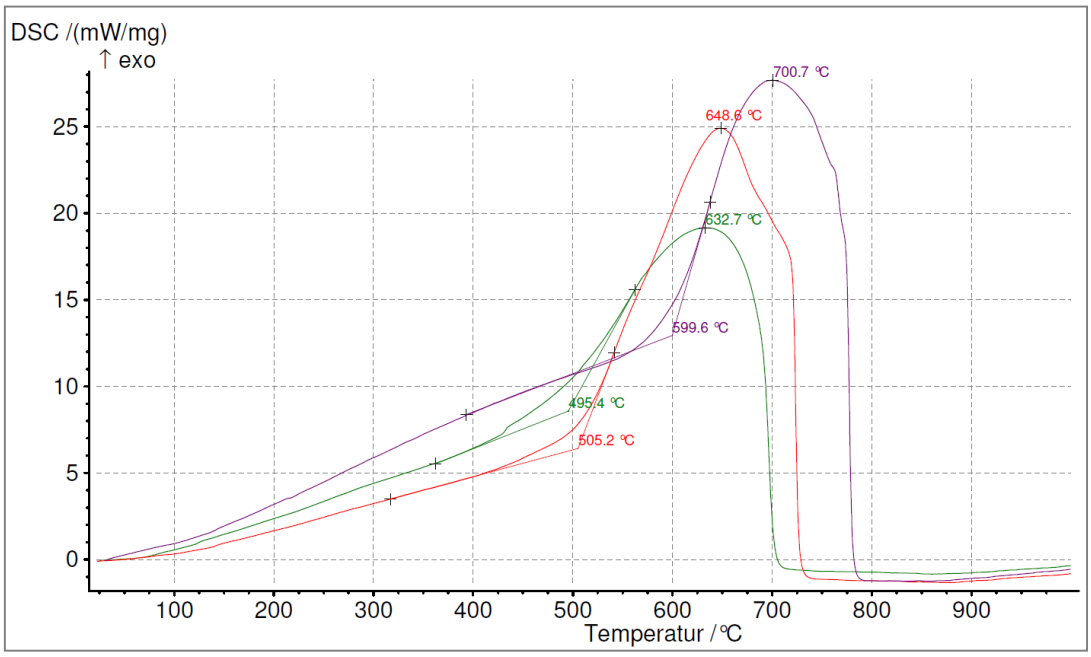

Figure 3 Results of Differential Scanning Calorimetry of several carbon blacks

To follow the theory shown in Figure 2, the optimum viscosity of the enamel is needed to match both temperatures. Therefore VFT constants were measured and equations calculated. The results are plotted in Figure 4.

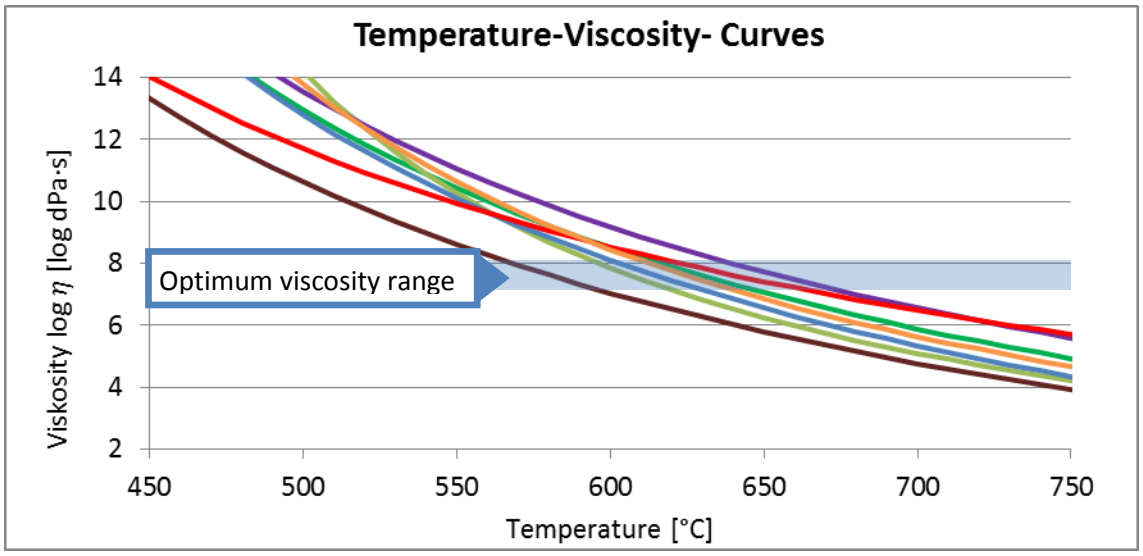

Figure 4 Temperature-Viscosity-curves of several enamels

Figure 4 demonstrates the great variety in viscosity possessed by enamels at foaming temperature. The temperatures range between 580 °C and 650 °C, matching the possible temperatures of highest reaction rates shown in Figure 3.

Foaming experiments with matched enamels and foaming agents were carried out but the results were unsatisfactory. This led to the conclusion that matching the two relevant temperatures of reactivity of the foaming agent and the suitable viscosity of the enamel in theory alone was not enough. In practical implementation both were influenced by each other. The reactivity depends on the surrounding glass system providing the potential reaction partners. Furthermore the viscosity of the enamel changes when foaming agents are introduced. For example the use of carbon leads to a chemical reduction of the glass network which results in a change in viscosity and surface tension – both critical in the foaming process.

The direct foaming method also needs to be seen as a time-dependent process. Before the enamel can be foamed up by the evolving gas, it needs to be molten.

Conclusions

All in all the investigations have shown that there is a need to examine the fundamentals of the enamel foaming process. Results from different research publications performing foaming experiments cannot be taken into account to directly generalise knowledge. One approach to find the optimum foaming parameters by matching the appropriate viscosity of enamel with the highest reaction rate of foaming agent was investigated and appeared to be insufficiently comprehensive.

The foaming experiments performed confirmed that it is possible to produce foam enamel samples with desirable characteristics. Prospective fields of application could be heat insulation, sound absorption or strengthening of enamelled panels. Improving the acoustic behaviour of wash and shower basins is conceivable. Good heat resistance, non-inflammability, high porosity and the potentially profitable coupling with steel plates are advantages which could be exploited.

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