RHEOLOGIE – COMPLEX

BY INTERACTION

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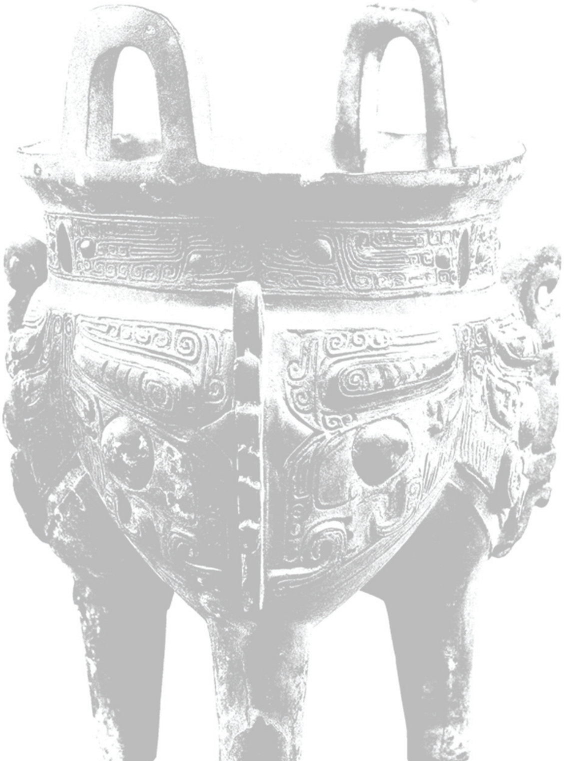

Rheologie – Complex by Interaction

J. Wendel

Wendel-Email, Dillenburg, Germany

Abstract The properties of the slurry are very important in enamel business. Especially in sheet steel business and aluminium enamelling with wet application the quality of the final product depends very much from the properties of the slurry. But also in cast iron business the slurry properties are very important. For the application for pipes and valves the style is very similar to sheet steel business. But also for powder business like cast iron bathtubs where the final application is a dry process the slurry properties are requested for the ground coat.

Rheology is a branch of physics dealing with affairs which happen by deformation and flow of liquid, colloid and solid systems due to the effect of external forces. The target of this work has been to determine the interactions within a rheological system. To be sure to find effects the item was studied in the system with the factors: water – clay – borax – boric acid – kaolin and an enamel frit. The observed responses haven been the shear stress, the thixotropy, the milling fineness, the density, the pH-Value and the viscosity of the slurry. In order to be able to calculate the responses it is necessary to find out about the up to now unknown interactions. Very interesting are the found interactions between clay and borax and borax and boric acid. As it is known that the rheological parameters depend also on the frit [1], the system was enlarged by a second frit and the differences of the factor effects on the responses have been determined. The investigation was done by the means of design of experiments. The effects of the factors on all responses have been determined by multiple linear regression using a model valid for all responses. Now it is possible to calculate the rheological properties in advance and to optimise the slurry properties within this system for any application chosen.

Fundamental

It is the target of slurry production to have a preparation of the enamel frit as a creamy liquid which may be applied on the metal in a thin film. Due to the high differences regarding density the milled enamel frit (density $\rho \approx 2,5$ g/cm³) will deposit fast in water (ρ=1,0 g/cm³) if there aren't any additives.

To understand the surface processes it is recommendable to look at the mechanisms which have been studied at the model substance quartz. As a result of crushing quartz, breaks of chemical bonding appear within the siloxane (≡Si-O-Si≡) groups, forming the radicals ≡Si· and ·O-Si≡ respectively. As the suspension is made in water the recombination of those radicals plays only an inferior role. Rather than that the free bondings are saturated forming silanole (≡Si-OH) and another silanole (HO-Si≡) respectively. Accompanied by hydroxide (OH^- -Ions) the weak base silanole (≡Si-OH) is giving away it's proton easily:

$$\equiv Si\text{-}OH + OH^- = (\equiv Si\text{-}O\text{-})^- + H_2O \quad (1)$$

Forming the silicate $(\equiv Si\text{-}O\text{-})^-$ groups at the quartz surface, hence the particles are charged negatively [2].

Compensating this charge positively charged ions are located close to the surface, forming a diffuse electrical double-layer at the surface of the particles. This mechanism is valid similarly also for enamel frit particles. Regarding a vitreous enamel slurry these positively charged counter-ions are usually sodium ions (Na^+), which may be exchanged by other ions. This is especially important for clay containing systems. For the different affinity regarding cation-exchange the Hofmeister-series is valid. In ascending order

$$Li^+ < Na^+ < K^+ < NH_4^+ < Rb^+ < Cs^+ < Mg^{2+} < Ca^{2+} < Sr^+ < Ba^{2+} < Al^{3+} < H^+ \qquad (2)$$

adsorptive capacity is increasing. The more right the position of a cation in this series is, the worse it will be exchanged [3].

Concerning hydrophilic colloids it is rather the wrapping up with water molecules (hydration) whether the solvation of the particles than the electrostatic charge. Hydrophilic colloids are showing a high endeavour to adsorb water molecules which later inhibit coalition of the colloids to bigger particles [4]. The thickness of the double-layer determines the hydration ability of the particles and hence their tendency to sediment.

The thickness of the double-layer is reciprocally proportional to the field strength of the cations within the double-layer. The stronger the cation is the more the double-layer is drawn tight. Strong cations are leading to a coagulation of the particles forming bigger aggregates and therefore precipitation occurs. Compared to silica gel the milled vitreous enamel frit particles are relatively big and the obtained charge density is much too low — therefore to prepare a slurry of vitreous enamel we are obliged to use of substances with a much bigger specific surface, these colloids are used then as an agent for suspension. Regarding a vitreous enamel slurry with a content of 5% clay one enamel particle faces 10^4 to 10^5 clay particles [5].

In between the two extremes, the coagulating and the low viscous clay suspension exists the field of thixotrop colloidal systems. A thixotrop slurry stiffens while relaxation and while motion it becomes fluid. For a vitreous enamel slurry this behaviour is welcome: while motion they are fluid – they can be pumped and sprayed, but after the application they shall not drain, instead of that they shall stop and stay with a certain thickness on the substrate. The correct adjustment of a vitreous enamel slurry is a tightrope walk between liquefaction and precipitation. For the actual modern manufacturing process it is necessary to limit all tolerances especially those of the clay and the water. The use of de-ionised water in the enamelling plants became self-evident and the compositions of enamelling clays are strictly controlled concerning amount and nature of the clay minerals. To satisfy the requirements of ready to use vitreous enamel slurries in full amount, it is necessary to know more about the interactions of the additives to the slurry in order to react fast and efficient to the changing requirements of the different uses.

Suspensions of vitreous enamel in water behave thixotrop, admittedly for that a very fine milling of the enamel frit is needed. Pure kaolin clay – water systems behave rheopex – which means while stiring up the viscosity increases. While adjusting a vitreous enamel slurry with clay the thixotropic vitreous enamel system is superposed by the rheopexy clay system. The use of set-up salts allows to reduce the amount of clay considerably [6]. This sequels their effect onto the diffuse double-layer which surrounds the clay particles.

Investigation of the System: clay – Kaolin – Boric acid – Borax – Water

Design of experiments

DOE is a method to design worksheets for investigations in that way to maximise the information to be obtained and to minimise the number of trials to do so. To choose the factors the first two – clay and water - are for vitreous enamel slurries almost obligatory. Concerning the set-up salts the combination borax – boric acid was chosen to observe also the effect on the pH-value and interactions involved with the neutralisation reaction respectively. The choice of kaolin finishes the list of factors to determine the effect of the enameling clay more easy. In order to find interactions it is necessary to make the design at least with three levels. For the picked system we would have to do 3^5 trials to receive a full factorised plan. Including repetitions for the centered trial that would be 245 trials. Box-Behnken designs neglect the trials in the centre of the cube faces and at the cube corners. Figure (1) shows the design region for a three factor design graphically.

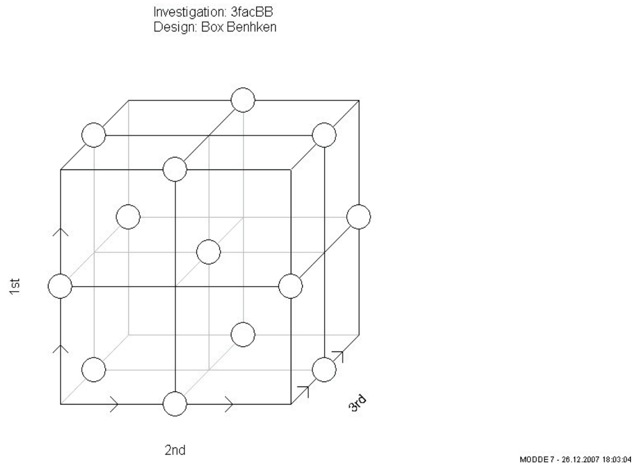

Fig. 1 Three factor Box-Behnken DOE

Using this reduction of the trials the DOE could be finished with 73 trials totally. To find out about the effect of a frit onto the rheological system another plan with 34 trials was done.

Trial execution

All factors not included in the DOE have been kept constant. The slurries were prepared always using the same milling station, the same mill, the same mill balls and constant milling time. All measurements have been taken one day after the preparation of the slurry at room temperature (20 – 25°C) with always the same acceleration ($1{,}1/s^{-2}$). The variation of the additives is always relatively to 100 parts of vitreous enamel frit, the rust protection was kept constant and also does not contribute to the plan.

Results of the plan with one frit

Figure (2) shows one of the rheograms with the typical structure viscous behaviour. The obtained curves for building up the structure and breaking down the structure have been fitted using a potential law. This fit following the Ostwald de Waele flow law for the expected dependence between the shear stress τ the shear rate D (former deformation-speed) and with the viscosity η^*, and a substance specific parameter *n* (equation 3) mostly worked well.

$$\tau = \eta^* \cdot D^n \tag{3}$$

Up to now couldn't be formulated a universal flow law for non-newtonian liquids. Therefore for the description different types of curves are used to define the observed [7]. Most of the flow laws are derived from empirical approaches [8,9]. The flow law of equation (3) delivered up to 150 Hz pretty good fits. For higher frequencies – potentially for a special spraying application it would be recommendable to use another flow law. For all trials the factor *n* was smaller than 1, like it is expected for structure viscous flow.

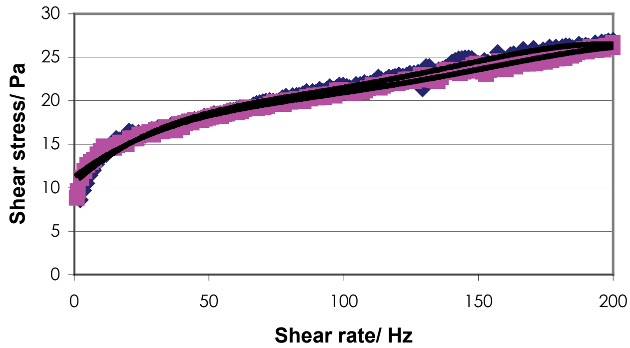

Fig. 2 Typical rheogram of a slurry

The blue curve shows the measurement for the structural degradation (increasing frequency) and the pink curve shows the measurement for the way back. The area between the two curves is giving a value for the thixotropy [10].

All results may be explained by a linear combination of the chosen factors and the two interactions clay*borax and borax*boric acid which have been found.

Figure (3) shows the detected interaction between boric acid and borax for this system.

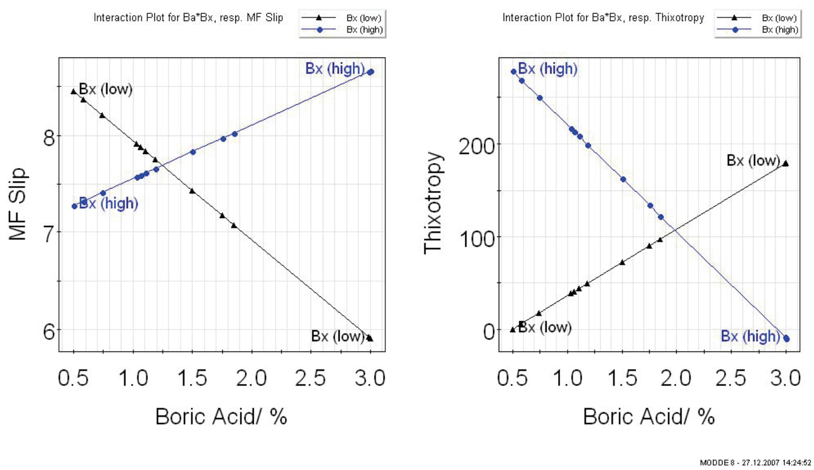

Fig. 3 The effect of the interaction between boric acid and borax for the responses milling fineness and thixotropy

Interactions are present when the effect of one factor (here: substance) depends from another factor present at the same time. In our example an increasing amount of borax in the slurry is working in the opposite direction depending from the amount of boric acid present in the slurry. In the case of a low boric acid content the addition of borax increases the thixotropy. In the opposite case of a high boric acid content in the slurry the addition of borax is lowering the thixotropy. By the means of interaction apparently contradictory results may be explained easily.

Figure (3) is just showing the extreme cases. In figure (4) the effect of this interaction may be seen over the whole range of the factors.

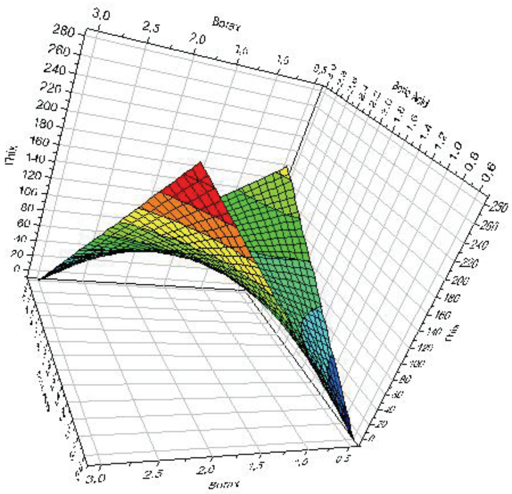

Fig. 4 Effect of the interaction between boric acid and borax over the whole range of the factors.

The one straight line for a low boric acid content complies in this figure with the front edge of the plane and the other straight for a high boric acid content complies with the rear edge of the plane.

The analysis of all results is giving the effects (or the coefficients) of the factors for the different responses. Figure (5) shows the results which will be discussed now.

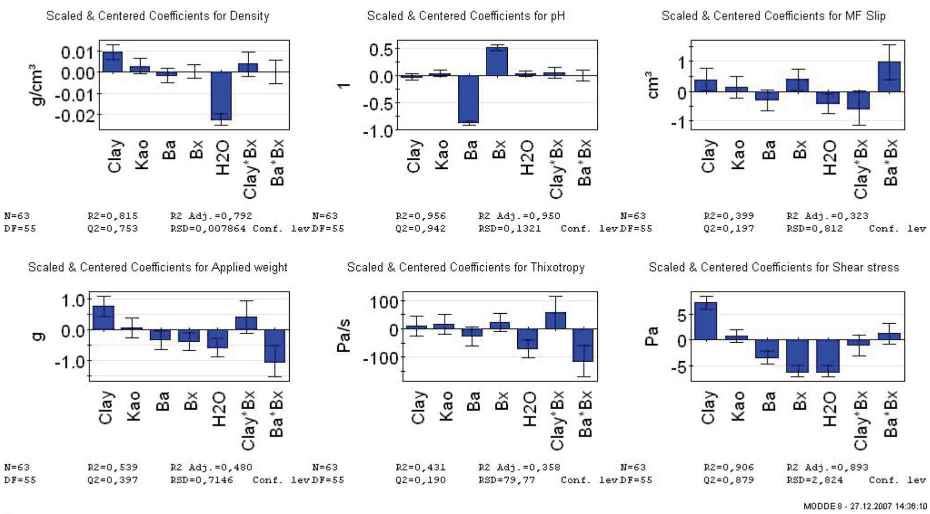

Fig. 5 Factor coefficient plot

The density of the slurry results from the effects of clay and water. All the other effects aren't significant for this response.

The pH-value of the slurry results just as expected from the acid-base-balance boric acid and borax. The only thing which might surprise is that there is no interaction between these factors regarding the pH-value response. The found ratio for the neutralisation corresponds in about with the reaction shown in equation (4):

$$[B_4O_5(OH)_4]^{2-} + 2\ H_3BO_3 = 2\ [B_3O_3(OH)_4]^- + H_2O \qquad (4)$$

The difference can be explained by the effect of adsorption of borax at the clay. Also this interaction between clay and borax is realisable even when it is not significant for that response yet.

The milling fineness of the slurry is determined mainly by the interaction of boric acid and borax which seems to hinder the crushing process. But the results for this response don't have the statistically provided security like the results for the density, the pH-value and the shear stress which may be shown with the analysis of variance. (Fig.(6): ANOVA-Plot).

The applied weight is a fast and easy to achieve test result for the applied thickness of the slurry on the substrate. Increasing the amount of clay corresponds with an increase of thickness, besides that factor only the interaction between clay and borax increases the applied weight – with more trials this interaction would be most probably significant too. Not surprising is the liquefying effect of water and the salts boric acid and borax, but also the interaction between these two factors increases the effect.

The response thixotropy is mainly decreased by the factor water and the interaction between boric acid and borax. The interaction effect of the neutralisation (eq. 4) is valid which means that the product of this neutralisation - the complex polyborate ion $[B_3O_3(OH)_4]^-$ - must be responsible for this effect. The interaction between clay and borax is also already valid (this will be seen also by the good analysis of variance) and it increases the thixotropy.

Also precise are the results for the maximal shear stress (value at the end frequency of 200 Hz). Only clay increases this response, the factors water, borax and boric acid lower the result. There is some correlation between the results of the responses for the shear stress and the applied weight – only the effect of the interaction between boric acid and borax differs.

Figure (6) shows the analysis of variance plot. Each left column shows the variation of the response explained by the model. The column in the middle shows the variance of the response not explained by the model. In the case the third column is smaller than the first one the reproducibility of the trials using this model is already within the 95% confidence level.

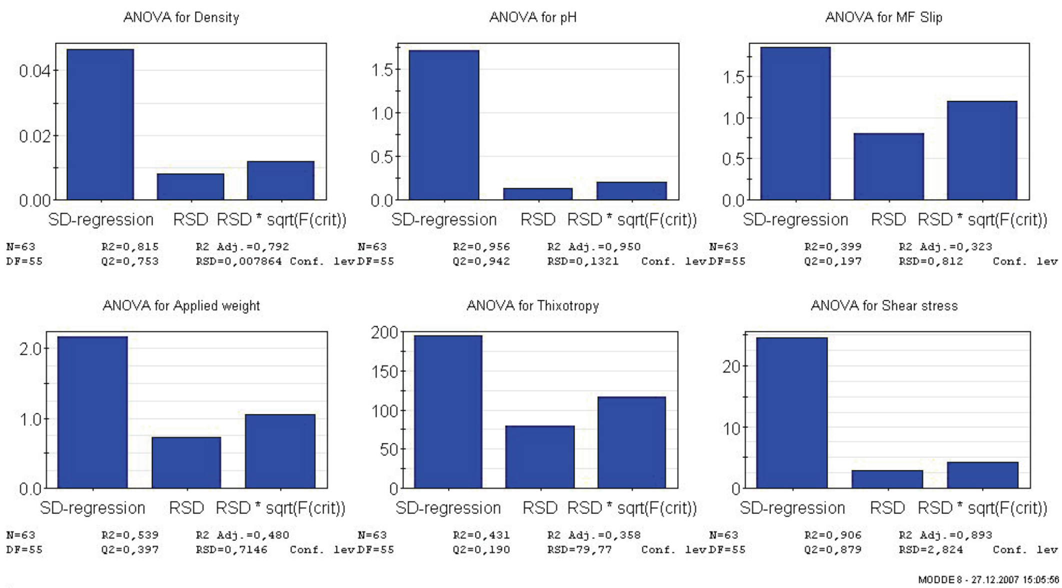

Fig. 6 Analysis of variance for the responses

It was told before that the curves for the shear stress could be fitted with the Ostwald de Waele law. Now the target was to calculate the rheograms from the factors. Figure(7) shows the effects for the viscosity and the exponent *n*.

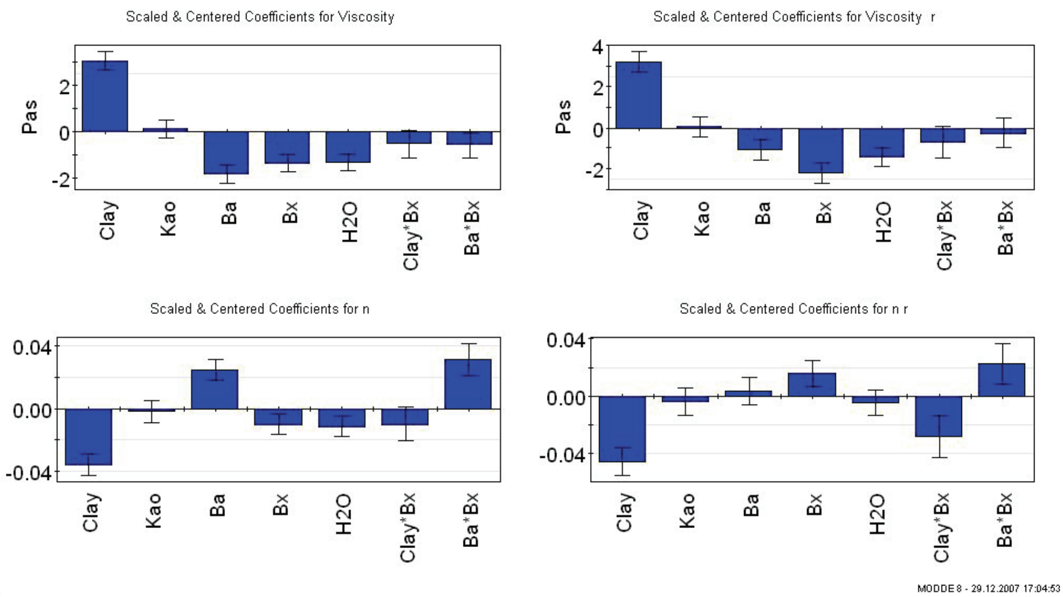

Fig. 7 Factors for viscosity and exponent *n*.

First of all this approach is interesting to achieve the result for the apparent viscosity – which was between 1,6 and 13,7 Pas for the range of the trials – but further more the analysis of the factor effects onto this response will allow to calculate the rheograms later. That worked well and now it is possible to calculate the rheogram from the factors (fig.(9)). Additionally it is also possible to calculate the other way around the rheologic factors for a desired rheogram. The two found interactions are significant also for these responses – especially for the exponent n (fig(8)).

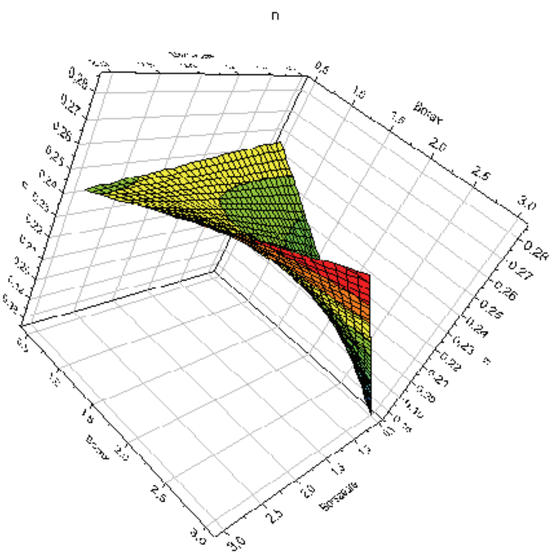

Fig. 8 Interaction of boric acid and borax for the exponent *n*.

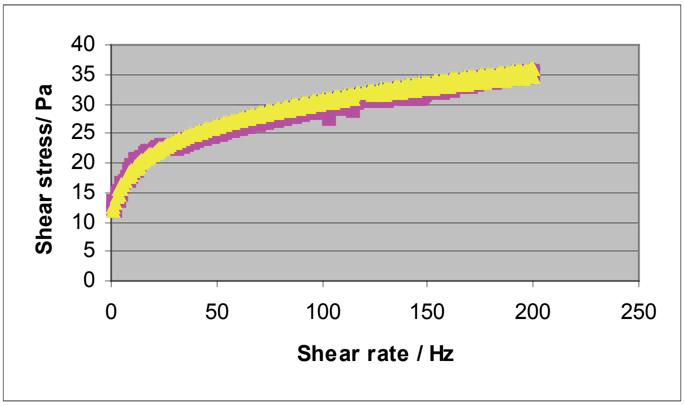

Fig. 9 Comparison of measured data (pink) and calculated data (yellow)

This analysis also points out that the differences of the viscosity for the structural degradation and the building up of the structure are based on a different effect of boric acid and borax for the two cases. This is valid for the apparent viscosity as well as for the exponent *n*. Also this effect might be explained by phenomena of adsorption of the diffuse double-layer.

Figure (10) shows the ANOVA-plot for the responses viscosity and exponent *n* out of the factors.

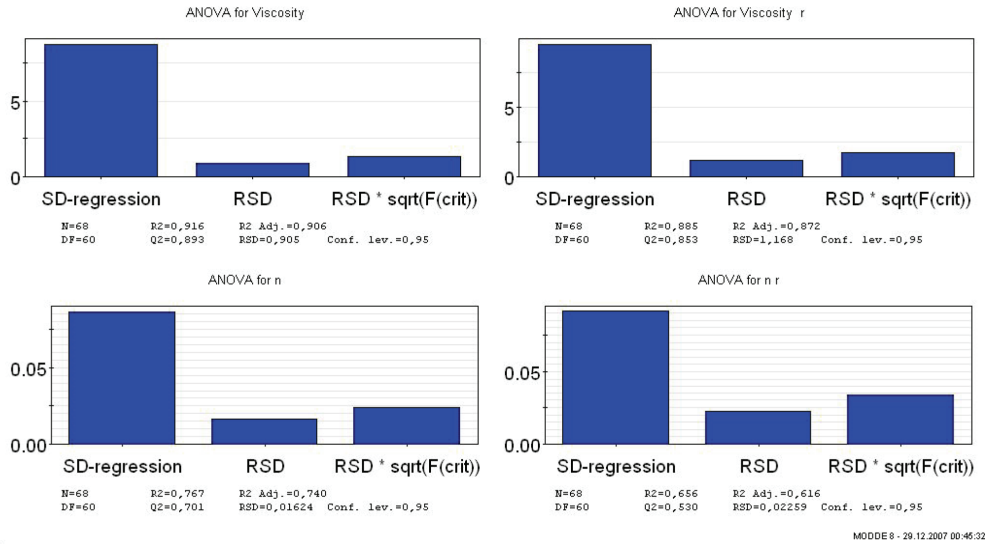

Fig. 10 Analysis of variance for the viscosity and the exponent *n*

The results allow the desired calculation without any restrictions.

Results for the plan with two frits

It is well known that the set-up salts for different frits have a different effect. Additionally to the first frit which has a acid resistance according to EN-ISO 14483-1 class „AA“ a second frit with a lower acid resistance “A“ is used. Figure (11) shows the determined coefficients.

The results verify the first plan. For the response pH-value an increasing effect of the „A“ frit is visible. This must be the effect of leaching out the alcali ions from the frit. Consequently the effect is existing as well for the flow out time of the ford-cup 6mm, the applied weight and the shear stress.

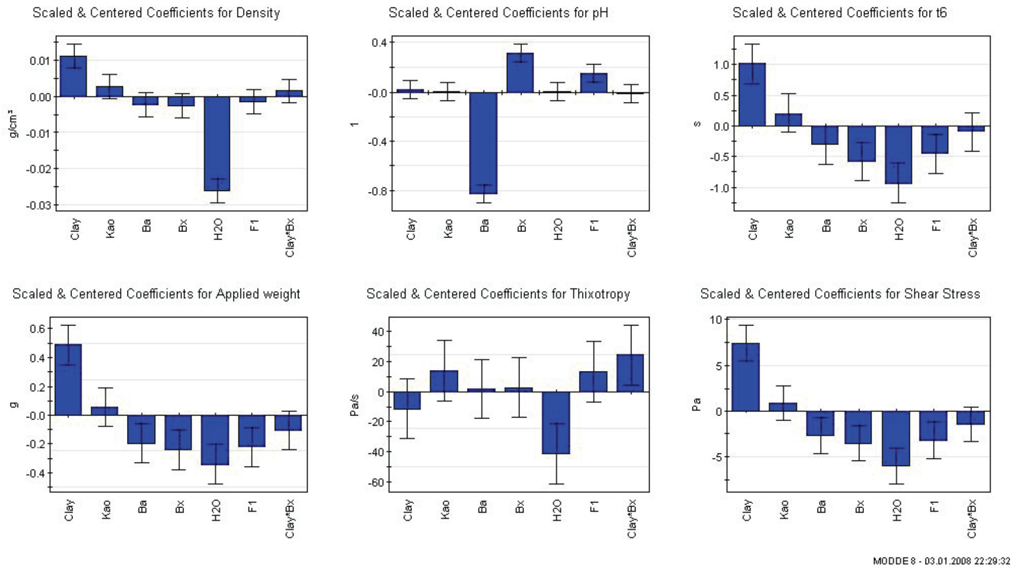

Fig. 11 Coefficient plot for two frits.

By the way during this investigation we also realised that the results for the ford-cup with a 6mm drain hole are much more reliable than those with the drain hole of 4mm. The 4mm drain hole is only usable for a narrow band of the viscosity.

The effect of the frit is less than expected, maybe one must choose a frit which is leaching out a lot more to find a stronger effect.

The „AA“-frit isn't set as an own factor, because in the mixture system it would only be a pseudo factor having exactly the opposite properties which are found for the „A“-frit. This is a consequence of the balance of the model.

Figure (12) shows the confirmed interaction effect of clay and borax in the system with two frits. Due to the interaction effect the plain is twisted. Without interaction there would be only a more or less tilted straight plane in the diagram.

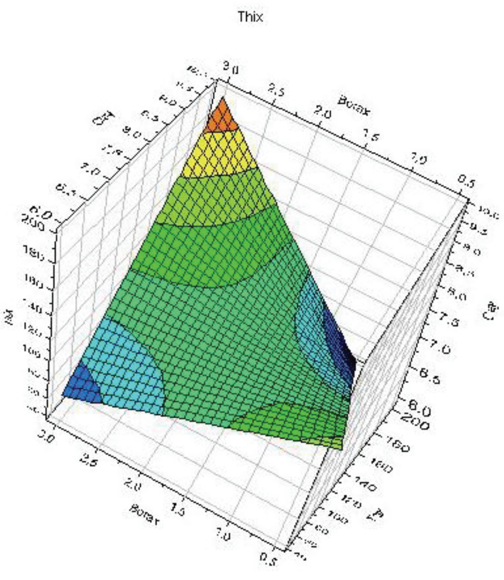

Fig. 12 Effect of the factors clay and borax for the response thixotropy

Within the investigated system the low setting effect of kaolin attracts attention. But compared to the used white clay this is not astonishing as this white clay contains a higher amount of illite. The setting effect illite – a hydro-muskovite – is comparable with montmorillonite.

Summary

Looking from material view the vitreous enamel slurry contents of the dispersion agent water with the dissolved salts and of the dispersed material which is the in water insoluble vitreous enamel frit and the clay with it's content of feldspar and quartz. The flow rating of such a suspension is difficult to seize as it is influenced by many factors. It was the target of this work to make this flow rating calculable in order to find for different applications like spraying, dipping and flooding always an optimised rheology. The problem is now reduced to define what someone wants. To adjust the rheology is when we know the factors and the interactions no more problem.

A vitreous enamel slurry must additionally be optimised for more responses. Just to name some of them:— the biscuit strength — a small drying shrinkage to prevent drying cracks — the brilliance of the surface which may not be reduced — the resistance to aging of the slurry to have a stable rheology for a longer period and — it's wetting ability for the substrate.

Acknowledgement

Thanks to Ms. N. Köker who did all the practical work for this investigation for her Bachelor thesis at the institute for applied material science from the University of Duisburg in our lab.

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