

Modification of the rheological properties of screen printing ceramic paints containing gold

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Abstract. This work presents the results of modification of rheological properties of screen printing paints containing gold. 15 wt% glossy gold paste and 15 wt% glossy liquid gold were used as modifiers containing gold. The study showed that the gold paint for screen printing can be obtained by evaporation of the 15 wt% liquid gold and the golden luster. The compaction process of liquid gold by evaporation is slow and easy to perform in industrial conditions.

The second way to adapt the 15 wt% gold ceramic paint for screen printing application depended on adding the aniseed oil and the pine oil. The course of the flow curve of the gold paste without modification indicates that it is shear thinning and shows the desired effect of thixotropy, and even anti-thixotropy, at low shear rates ($<50^{-1} \text{ s}^{-1}$). The introduction of the essential oils eliminates this phenomenon and the paste converts itself from the non-rheostable to the rheostable liquid.

1. Introduction

From the rheological point of view, typical screen printing paints based on nonaqueous solvents show Newtonian or pseudoplastic behaviour, i.e. they are shear-thinning and have yield point [1-8]. Flow curves courses and equation models of typical rheostable fluids are shown in Fig.1 [4].

Flow curves are usually presented as a change in shear stress or a change of apparent viscosity versus shear rate gradient. These courses are equivalent.

As the practice shows, screen-printing pastes should also have little thixotropy, which protects them of spreading on the printed surface [6-9]. However, the courses of flow curves of rheo-unstable fluids (time dependent rheologies) are more complicated and it is not possible to describe them using simple mathematic formulas (Fig.2) [4].

Generalization of these curves by plotting of the so-called equilibrium curves or by the averaging of their courses at increasing and decreasing shear rates allows these typical rheostable fluid models to characterize the non-rheostable fluids (see also Fig. 1).

The second important aspect consists in adjusting the measurements conditions (shear rate) of these fluids to the conditions occurring during printing.



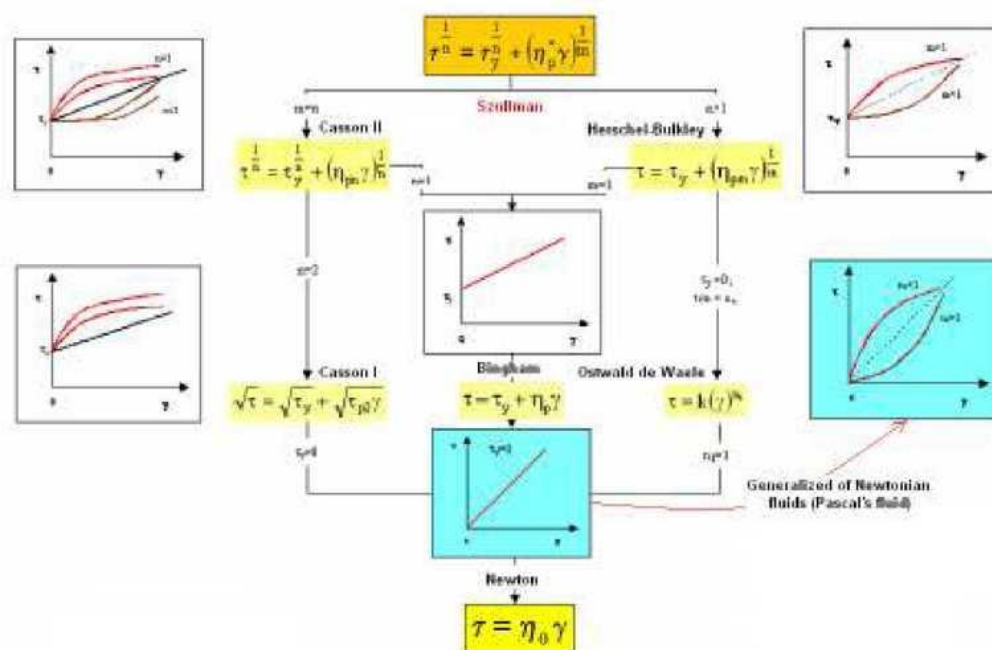


Figure 1. Flow curves courses and equation models of typical rheostable fluids [4]

By addition of the so called additives and other simple technological procedures (thickening, dilution) the rheological properties of ceramic paints (yield point, flow curves courses, thixotropic properties etc.) can be changed significantly, and thus the print quality [9- 13]. Non-polar surface-active substances, various drying retardants, antistatic agents, hardeners etc. are used as auxiliary agents. Such paints cannot be usually used after drying and/ or curing (cross-linking). The problem of drying during printing becomes more important when it concerns expensive gold-based paints. This applies both to the changes in rheological properties of paint and, above all, when the reuse of ore is taken into consideration.

2. Materials and method

The aim of this study is to determine the adjustability of the rheological parameters of paints containing gold in terms of using them for screen printing. The following materials were used for tests:

- 15 wt% glossy gold paste - used for painting strips (PMP);
- 15 wt% liquid glossy gold - used for hand stamping (PMP);
- gold luster (Degussa- Gold Bronze 36);
- anise oil- colourless essential oil with a characteristic odour; melting temperature 1519 °C; containing 80-95 wt% of anethole; received from water distillation of Pimpinello anisum; soluble in alcohol and ether but practically insoluble in water;
- pine oil- colourless essential oil; containing pinene, kanfen, felandrem, kuminal, anisaldehyde and barneol; received from the water distillation of pine needles; soluble in alcohol.

The industrial practice has shown that screen printing paints in operating conditions should have apparent viscosity in the range 600 - 1000 Pas, and shear rate in the range 5001000 s⁻¹. Because liquid gold has its viscosity of 94.8 Pas and gold luster has its viscosity of 7.9 Pas, they were thickening by evaporation at 100 °C. In contrast, gold paste with viscosity of 2606 Pas was diluted by the addition of essential oils.

Apparent viscosity measurements were performed on Rheotest II viscometer, equipped with a cone-plate system, in the wide range of shear rates.

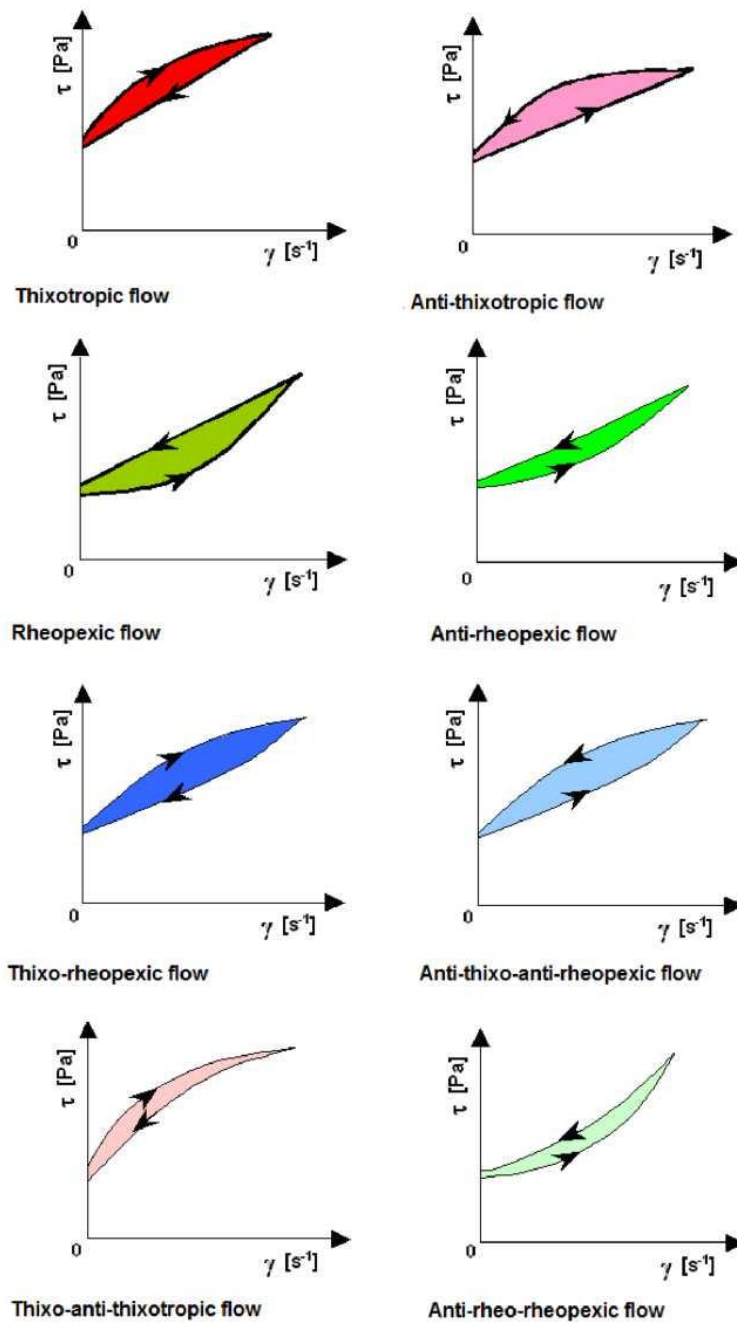


Figure 2. The flows of rheo-unstable fluids and their generalizations [4]

3. Results and discussion

Flow curves of the screen printing gold paints before and after drying are shown in Fig. 3, while the changes of apparent viscosity during drying are shown in Fig. 4. Ceramic liquid gold with the concentration of 15 wt% was labelled as Au15%fluid and Au15%fluid.eva after evaporation. Consequently, the ceramic golden luster was labeled as Au6% luster and Au6% luster.eva after drying.

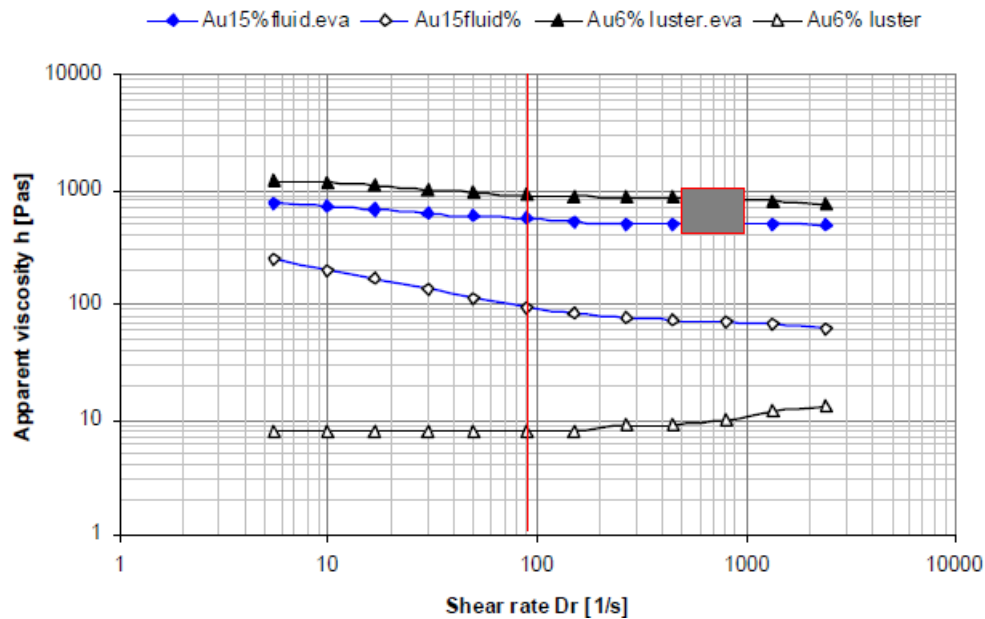


Figure 3. Flow curves of the screen printing paints before and after drying

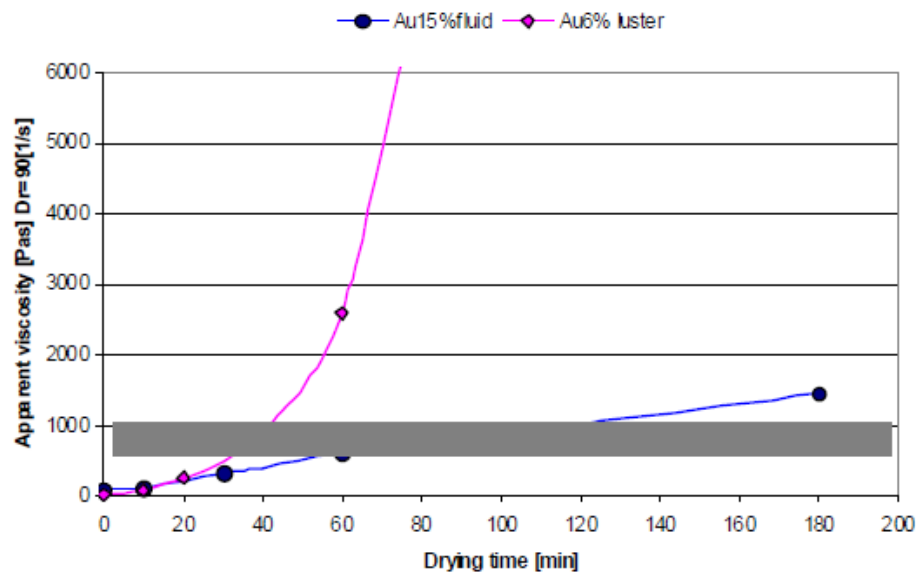


Figure 4. Changes of apparent viscosity of the screen printing paints during drying

The tests have shown that gold paint for screen printing obtained by evaporation can be made of 15 wt% liquid gold and gold luster. The densification process of liquid gold by evaporation is slow and relatively easy to carry out in industrial conditions. Such effects were not obtained during densification of the luster paints because in this case the evaporation process is fast and it is difficult to obtain the screen printing paint of the required viscosity. This also means that under manufacturing conditions, i.e. at 18-25°C, gold paint is constantly compacted by evaporation. From the technological point of view, if this process is slow, it is a positive phenomenon. During the fast evaporation, in addition to the changes in the rheological properties, also the content of ore changes, which can affect the properties of decorated products.

The rheological measurements have shown that flow curves of both slurries, i.e. 15 wt% liquid gold as well as 6 wt% gold luster, after densification by evaporation are similar to the Newtonian flow with

a slight yield point. Generally speaking, before and after densification by drying they are still rheostable fluids with constant apparent viscosity as a function of shear rate. The drying process of gold paints causes an increase in flow resistance without any significant changes in the courses of flow curves.

Table 1 shows the fitting of the curves to the Newtonian/Bingham and Ostwald de Waele flow models before and after drying.

Table 1. Parameters of rheological equations of paints containing gold

Sample	Rheological equation	
	Newton/Bingham	Ostwald de Waele
Au15%fluid	$T = 0.62y + 31.71$ $R^2 = 0.9969$	$T = 3.11 Y^{0.77}$ $R^2 = 0.9934$
Au6%luster	$T = 0.10 Y$ $R^2 = 0.9928$	$T = 0.16 Y^{0.92}$ $R^2 = 0.9931$
Au15%fluid.eva	$T = 7.47 Y + 218.64$ $R^2 = 0.9969$	$T = 13.23 Y^{0.93}$ $R^2 = 0.9997$
Au6%luster.eva	$T = 4.82 Y + 61.64$ $R^2 = 0.9997$	$T = 8.36 Y^{0.92}$ $R^2 = 0.9992$

It should be noticed that both rheological equations, Newton/Bingham and Ostwald de Waele describe very well the flow curves of the tested paints. Fitting power of the measurement results to the equations is above 99%. The practical choice of a model depends on the expected parameters of the rheological equations (consistency, flow index, yield point, viscosity).

Before evaporation the ceramic paint with liquid gold exhibits shear-thinning behaviour. It originates from the fact that during shearing of the liquid gold, polymer chains of the so-called mordant change their conformation. After densification by evaporation this phenomenon practically disappears and the flow coefficient increases from 0.77 to 0.92. During drying in 100°C probably a partial degradation of the organic mordant occurs, which changes the courses of the flow curves. These changes may also result from increasing of the concentration of suspensions containing gold. The luster ceramic paint, as opposed to the liquid gold, practically does not change the properties of thinning. In this case flow coefficients are about 0.92.

It should be noticed that consistency coefficients of the tested paints increased a couple of times (about 10). Consistency is the measure of the internal structure of the paint slurry, i.e. polymer conformation of the mordant, grains aggregation, concentration etc., which affects the course of the flow.

It can be also noticed that the gold luster paint dries faster and because of that it is harder to obtain proper apparent viscosity for the screen printing purposes.

The second way to adapt 15 wt% gold ceramic paste for the screen printing application was based on the addition of aniseed and pine oils. Depending on the amount and nature of additives, the authors obtained liquids with different apparent viscosities (Fig. 5).

The initial glossy gold paste containing 15 wt% of ore has high viscosity, about 2600 Pas, which hinders the screen printing application on the decorated surface.

The investigations have shown that suspensions of lower viscosity can be obtained from the ceramic gold paints of high viscosities by the addition of oils and they can be adapted to the screen printing. The flow curve of the gold paste without any modification shows that it is shear-thinning and has a desirable thixotropy and even anti-thixotropy at low shear rates ($<50 \text{ s}^{-1}$) (Fig. 6). From the point of view of non-rheostable fluids such a flow curve course is classified as thixotropic-anti-thixotropic.

The introduction of essential oils eliminates this phenomenon and the non-rheostable fluid is

converted into a rheostable liquid. It may be also noticed that in the shear rate range of 100 s^{-1} the paste modified with aniseed oil gets slightly concentrated and is shear-thinned above 1000 s^{-1} . In the case of pine oil the flow curve does not change in all the range of shear rates. Because of their structure, essential oils probably do not allow the change of the conformation of the mordant polymer chains in the paste to occur, and thus alter its rheological properties. Perhaps the reason is the mutual insolubility of polymers, i.e. the so-called mordant and oil. There is, however, no detailed information about this.

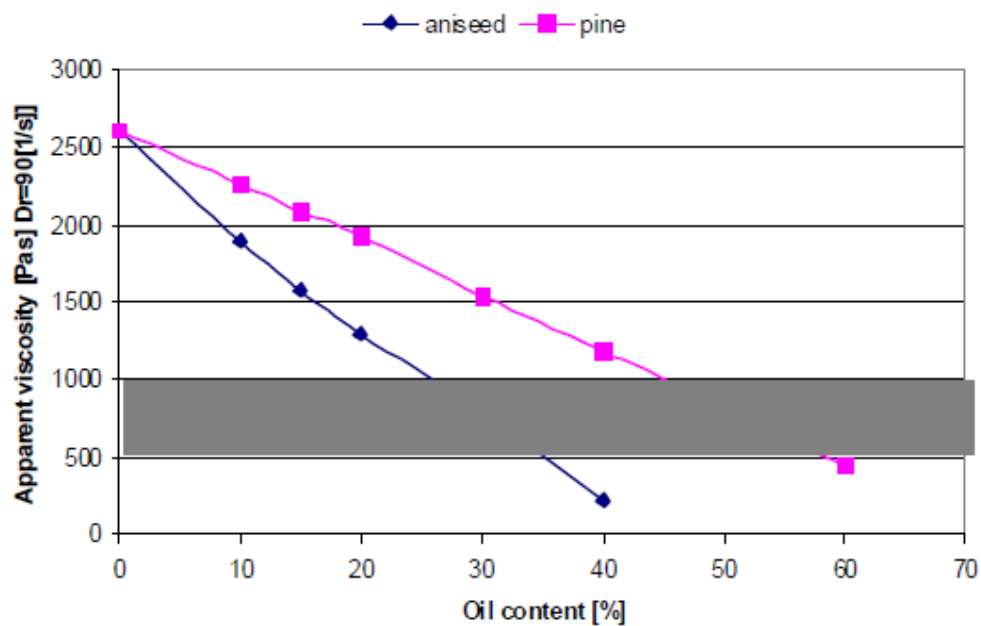


Figure 5. Changes of apparent viscosities of the gold paint modified with aniseed and pine oils

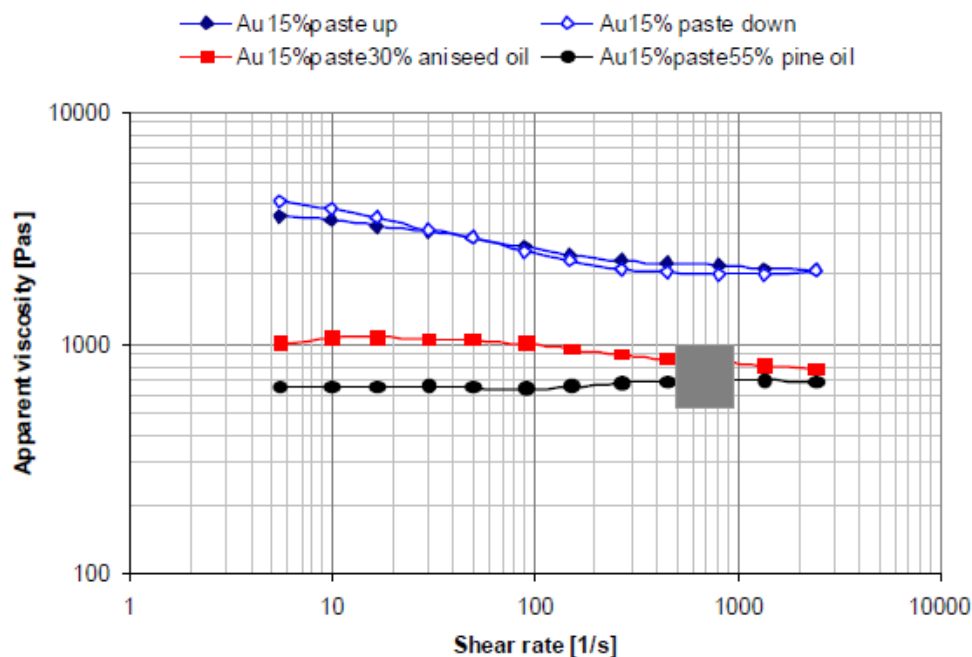


Figure 6. Flow curves of the screen printing paints after modification with essential oils

The tests have shown that the addition of the essential oils reduces the effect of shear- thinning. Flow coefficient increases its value from 0.88 to 0.94 in the case of aniseed oil and to 1.00 in the case of pine oil. Diluting the gold paste with the essential oils reduces the consistency coefficient several times. This also applies to the yield points (Table 2).

Table 2. Parameters of the rheological equations of the gold paint modified with essential oils

Sample	Equations of the rheological models	
	Newton/Bingham	Ostwald de Waele
Au15%paste (equilibrium)	$T = 20.11y + 374.54$ $R^2 = 0.9995$	$T = 45.21 Y^{0.88}$ $R^2 = 0.9999$
Au15%paste 35% aniseed	$T = 7.59 Y + 218.97$ $R^2 = 0.9980$	$T = 12.14 Y^{0.94}$ $R^2 = 0.9995$
Au 15%paste 55% pine	$T = 6.30 Y + 39.38$ $R^2 = 0.9992$	$\gg, 1.00 T = 6.37 Y$ $R^2 = 0.9999$

Generally, screen printing paints with pine or aniseed oil do not have thixotropic properties. It is known that the most favorable technological effects are obtained when the screen printing inks are shear-thinning with slight thixotropy [10]. In practical terms aniseed oil is a friendlier solvent because it dries more slowly. Hence, it should be recommended for screen printing techniques, although at higher contents in the paste it can cause characteristic microcracks of the gold layer applied to the ceramic product (Fig. 7) and may change the colour of gold (Fig.8).

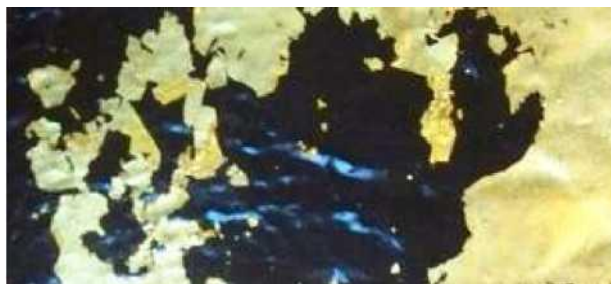


Figure 7. Microcracks of the diluted gold paint after burning (magnified 100-times)

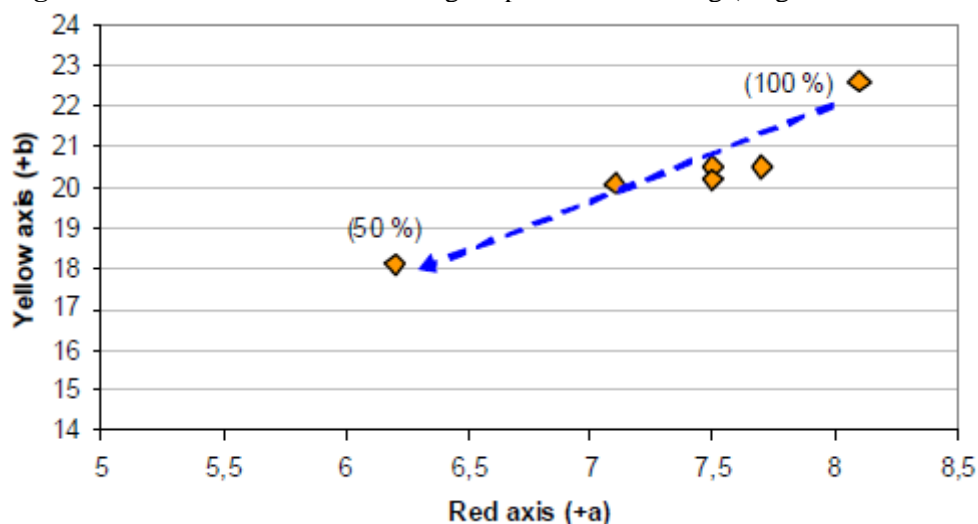


Figure 8. The change of gold paste colour after dilution

It was mentioned that at low shear rates a small effect of dilatancy occurs for the suspension of the gold luster. This phenomenon is unfavourable because it makes difficult correct clarity of an outline drawing to be obtained. When printing with such inks the speed of the squeegee should be reduced, because undesirable characteristic textures of the screen can be obtained. This demonstrates the inability to melt-in-time during printing (Fig. 9).

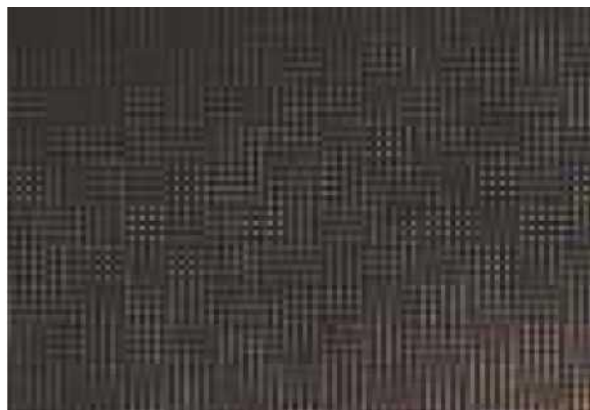


Figure 9. Screen texture on the flat surface caused by dilatancy (magnified 100 times)

It is worth noting that apparent viscosities of the tested paints at shear rates of $500 - 1000 \text{ s}^{-1}$ are about $600\text{-}1000 \text{ Pas}$. If the speed of the squeegee corresponds with the shear rates of the ceramic paint during the measurement, the obtained results will be useful for screen printing purposes. Otherwise, the results will not be sufficient to assess the suitability of screen printing inks.

The presented methods of adjusting the viscosity of the inks for screen printing, however, change the gold content in the paint. These results are shown in Table 3.

Table 3. The content of gold in a defined area of printing

Sample number	Content of gold [%]
Au15%fluid	15
Au15fluid eva	16
Au 6% luster	6
Au6%luster eva	8
Au15%paste	15
Au15%paste +30% aniseed	9
Au15%paste + 55% pine	7

To determine this effect, thickness of the gold layer on the fired product was measured. The test was performed by the colorimetric method, using the formation of a complex of trivalent ions of gold with Rhodamine B. Gold was taken into the solution from a well-defined surface of the product (1cm^2) with the use of aqua regia.

The use of essential oils to reduce viscosity of screen printing gold inks is associated with a reduction in gold content. In particular, the biggest reduction can be seen with the use of pine oil (over 45%).

Abrasion resistance of gold coatings is the most representative parameter to assess their properties [14]. Increased susceptibility to abrasion was shown by the paint with pine oil, which directly corresponds to the content of gold (Fig. 10).

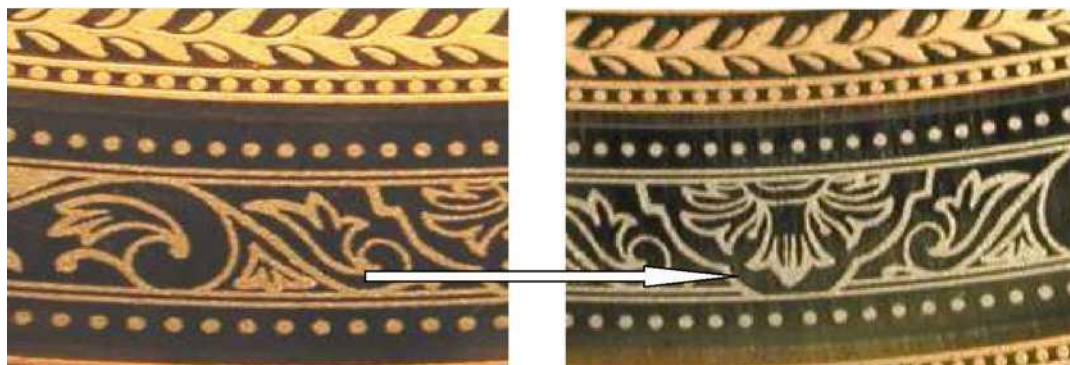


Figure 10. Effect of abrasion of the gold coating after 40 cycles according to the BN-69/7822-01 [14]

Similar effects were obtained for modified gold luster.

4. Conclusions

1. Ceramic glossy gold paints of different viscosities can be adjusted to the screen printing purposes both by thermal thickening and by dilution with the use of essential oils.
2. In the case of dilution the best results are achieved by the use of aniseed oil. Paint dilution leads to the lower content of gold and adversely affects gold coating abrasion.
3. Due to the high drying rate the thermal thickening technique is not recommended for gold lusters.
4. The addition of essential oils changes the rheological properties of screen printing paints. In particular, it eliminates the beneficial effects of thixotropy and pseudoplasticity.
5. Apparent viscosity of the screen printing paints should be adjusted to the speed of the squeegee shift.

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