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Rheological Behaviour of Gold Containing Screen Paints

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Abstract

A technique of silk-screen printing is the most of all used technology of decoration of ceramic articles. It is still developing in the direction of automation process and manner of bringing, fixing and the other useful properties of decoration. In the article, the results of rheological behaviour of both gold colours belong to the so-called screen paints no-water systems and lustre gold screen paints that due to their special behaviour are practically used in ceramic industry have been presented.
Keywords: Screen paints, Gold, Rheology, Lustre gold screen paint

ZACHOWANIE REOLOGICZNE FARB DO SITODRUKU ZAWIERAJĄCYCH ZŁOTO

Sitodruk jest najczęściej wykorzystywaną techniką zdobienia artykułów ceramicznych. Jest wciąż rozwijana w kierunku automatyzacji i sposobu przeprowadzenia, utrwalania i innych użytkowych właściwości dekoracji. W pracy zaprezentowano wyniki badań nad właściwościami reologicznymi zarówno farb złotych należących do tzw. niewodnych układów farb do sitodruku, jak i lustrzanych farb złotych do sitodruku, które ze względu na swoje specjalne zachowanie stosowane są przemyśle ceramicznym.
Słowa kluczowe: farby do sitodruku, złoto, reologia, lustrzana farba złota sitodrukowa

1. Introduction

From the rheological point of view, screen-printing pastes work in non-aqueous systems and have pseudoplastic behaviour [1–6]. Practice shows that the screen-printing paste should also possess little thixotropy, which protects it from spreading on the printed surface. [7-9]. However, the courses of flow curves of rheo-unstable fluids (time dependent rheology) are more complicated, and it is not possible to describe them using simple mathematic formulas [8].

Flow curves are usually illustrated as changes of shear stress or viscosity versus shear rate. The courses of these curves are equivalent. An addition of organic agents can considerably change rheological properties of the screen printing paste (yield point, course of flow curve, thixotropy *etc*.) as well as quality of print [9].

Surface-active and non-polar substances, drying moderators, antistatic substances are commonly used as an auxiliary agent, because after drying and hardening (cross-linking) paints cannot usually be used. The problem of drying during printing acquires a special meaning in the paints containing gold, because of rheological properties changes and impossibility of ore recycling.

2. Materials and methods

The purpose of this work is to describe the possibility of regulation of rheological parameters of suspensions which contain gold, applied in screen printing. In the research the following materials were used:

– glossy gold paste 15 % (for painting stripes - PMP),
– glossy gold liquid 15 % (for hand stamp - PMP),
– lustre gold (Degussa – Gold Bronze 36).
– anisum oil (ethereal oil, colourless with characteristic smell, melting point 15-19°C), which contains 80-95 % anethol; is soluble in alcohol and ether, practically insoluble in water; obtained in distillation of pinpinella anisum.
– Pine oil (colourless, soluble in alcohol), which contains pinen, kanfen, felandrem, kuminal, anisium aldehyde, barneol; obtained in distillation of pinus silvestris needles (productivity 0.25-0.5 %).

Industrial practice shows that screen-printing pastes should have a viscosity interval between 600-1000 Pa·s. There were two methods to obtain suitable paints, by evaporating (liquid gold and lustre gold) and diluting gold paste. As a raw material, liquid gold (viscosity of 94.8 Pa·s) and gold lustre (viscosity 7.9 Pa·s) have been used; these substances were thickened by evaporating at 30°C. The additive of ethereal oils has diluted the gold paste with initial viscosity of 2606 Pa·s.

The measurement of apparent viscosity was provided using a Brookfield DV III+ rheometer.

3. Results

The investigations show that gold paste useful for screen printing can be obtained from liquid gold 15 % by evaporating. The liquid gold thickening process by evaporating is very slow, but quite easy to provide in industrial conditions. This effect cannot be obtained for thickening lustre paints because this evaporating process is fast, and it is difficult to produce the screen-printing paste with suitable viscosity. This means that in industrial conditions (temperature of 12-25°C) gold for painting gives in to permanent thickening.

The evaporating process is slow what, from the technological point of view is a positive phenomenon but, on the other hand, it changes the contents of ore, as well as the useful parameters of decorating products.

Flow curves of paints before and after evaporating are show in Fig. 1, and apparent viscosity changes during evaporating in Table 1.

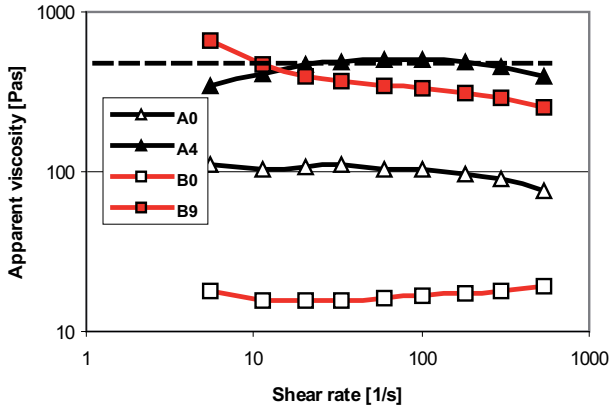

Fig. 1. Flow curves of screen-printing pastes containing gold before and after evaporating process.

Flow curves of non-modified gold are marked by symbol A0, and evaporated samples by A4, consistently for initial gold lustre B0 and after drying sample B9. The investigations show that flow curves of 15 % ceramics liquid gold thickened during evaporating are closed to Newtonian flow and show insignificant changes of the course, contrary to the paints based on gold lustre. So they are rheo-stable liquids with constant apparent viscosity in the shear rate function; moreover, the drying process causes only an increasing flow resistance. Whereas lustre paint after thickening displays a clear effect of shear–thinning flow behaviour, moreover it has quicker evaporation. During the evaporation, the chain of degradation of organic agent follows. This phenomenon causes the effect of thinning during shearing, because of changes in the polymer conformation.

In the case of gold ore the content in lustre paints (5 % level) for rheological investigations the set number 9 has been typed (with higher appearance viscosity). Both paints A and B do not show thixotropy and rheopexy phenomena.

The second method of gold ceramics paste adaptation for screen printing was the addition of anisum and pine oils to the suspension. Depending on the quality and quantities

Table 1. Changes of apparent viscosity during evaporating in temperature 30°C.

Sample number	Evaporating time [min]	Apparent viscosity [Pa·s]
A1	0	94.8
A2	30	212.4
A3	60	328.4
A4	120	592.3
A5	180	1005.2
B0	0	17.9
B7	10	72.5
B8	20	120.4
B9	40	900.2
B10	60	2053
B11	90	10050

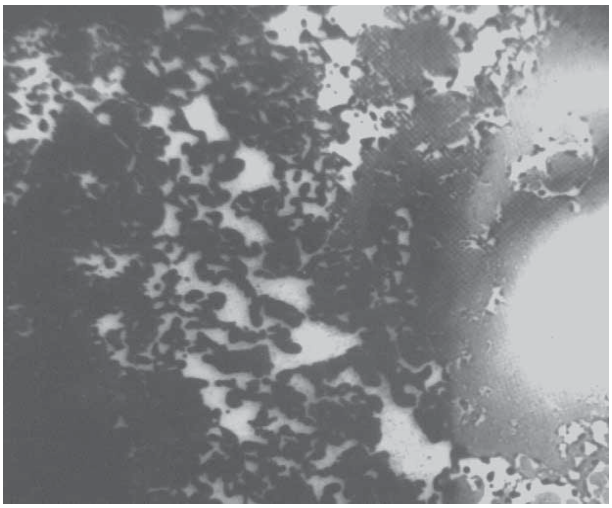

Fig. 2. Microcracks of gold coat after heat treatment.

Table 2. Changes of apparent viscosity diluted by glossy gold paste.

Sample number		Content [wt%]	Apparent viscosity [Pa·s]
–	C0	0	2606
Anisium oil	CA10	10	1897.2
	CA20	20	1297.7
	CA30	30	989.7
	CAN40	40	224.5
Pine oil	CS15	15	2132.0
	CS30	30	1921.1
	CS40	40	1184.0
	CS55	55	631.8
	CS60	60	372.4

of agents, liquids with different apparent viscosity have been obtained (Table 2). As investigations show, from ceramics gold paints with high viscosity (modified by ethereal oils), it is possible to obtain screen-print pastes. From the practical point of view, anisum oil is a more effective diluter, because of slower drying, although overdosing can cause characteristic microcraks (Fig. 2).

The courses of flow curves (Fig. 3) show that gold paste 15 % without modifications is shear-thinning and displays advantageous rheopexy in a lower shear rate (< 50 s^{-1}). Additions of ethereal oils eliminate these phenomena, and the liquid transforms from rheo-unstable to rheo-stable. It can be noticed that, in the shear rate interval 100-1000 s^{-1}, the oils modified paste is thickened, and over than 1000 s^{-1} paste is shear thinned. This is the proof of ethereal oils domination in rheological properties of screen printing pastes. Probably the structures of ethereal oils inhibit confirmation of polymers agents also added to gold pastes, as well as rheological behaviours. It is surely the result of mutual insolubility of polymers, but detailed information about these processes is unknown.

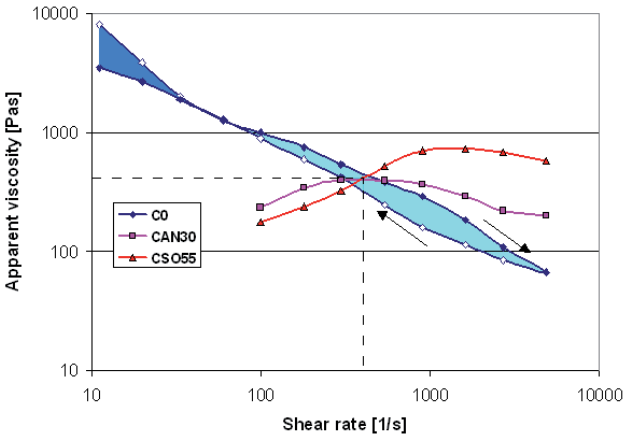

Fig. 3. Flow curves of screen-printing paints after modification by ethereal oils.

Fig. 6. Effects of gold coat abrasion after 40 cycles acc (BN-69/7822-01).

As mentioned above, the addition of pine and anisum oils adequately 30 and 55 wt% in lower shear rate shows dilatant behaviour. This is a disadvantage because of contours sharpness. During printing the squeegee speed decreasing is necessary. It is important to notice that apparent viscosities of pastes (shear rate 300 s^{-1}) are similar and amount ~700 Pa·s. In this case, glossy gold paste (15 %) can be used in screen printing without modifications, under one condition that the squeegee shift speed is the same at the shear rate ~300 s^{-1}. This means that screen printing pastes viscosity measurements in static conditions cannot be sufficient for suitability estimation.

Generally, screen printing suspensions, modified by pine and anisum oils, are characterized by no thixotropy properties. The best technological effects are obtained where screen printing pastes have pseudoplastic flow behaviour, which is the shear–thinning flow behaviour and low thixotropy properties [10]. That is why during further measurements, after heat treatment very characteristic print texture were obtained, because the paste has no ability to flow during printing. The methods used for screen printing paints viscosity adaptation can change content of gold in paint. The measurement of gold content in the print and burnt coat shows fundamental differences. Table 3. shows the results of investigations.

Table 3. Content of ore in print surface.

Sample number	Content of gold [wt%]
A0	15
B0	5
A4	16
B9	6
CAN 30	8
CSO 55	7

The addition of ethereal oils principally decreases the content of ore, especially pine oil (more than 45 %).

Gold coats abrasion resistance is the most representative parameter of usage properties estimation. The paint modified by pine oil shows enlarge inclinations to abrasion, which directly correlate with the content of ore in the coat (Fig. 4). Similar effects were obtained using the modified gold lustre.

4. Conclusions

Glossy gold ceramic pastes with different viscosities can be used in screen printing, both through thermal thickening and ethereal oils diluting.

The addition of ethereal oil changes the rheological behaviour of pastes; it especially eliminates good phenomena such as thixotropy and rheopexy.

Apparent viscosity of screen-printing pastes should be adjusted to squeegee shift speed, especially when the paste shows time dependent rheology phenomena.In the case of the thermal thickening process this techniques is not recommended for gold lustres because of the high evaporation process. In the case of diluting, better effects for obtaining high quality pastes is constituted by a dosage of anisum oil, although overdosing causes characteristic microcraks. Dilut-

ing of pastes provides the decreasing content of ore and has a negative influence on coats abrasion.

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