Rheological study to test a new formulation of silk screen paint

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A study was carried out to evaluate a new formulation of silk screen paint developed with the objective of changing the traditional, expensive milling process as well as replacing the organic milling medium with a water-based solution. The new and traditional formulations are compared on the basis of their rheological properties. Some oscillatory tests were found to be useful to study milling conditions that simulate the industrial preparation process.

Key words: rheology, yield stress, thixotropy, oscillatory tests, viscoelastic region

Estudio reológico para la preparación de una nueva fórmula de pasta serigráfica

Se ha llevado a cabo un estudio para evaluar una nueva fórmula de pasta serigráfica desarrollada con el objetivo de cambiar el proceso tradicional de molienda cuyo coste es más elevado y para reemplazar el vehículo serigráfico de molienda orgánico por uno acuoso. Las dos fórmulas, la nueva y la tradicional, se han comparado en función de sus propiedades reológicas. Las mediciones en régimen oscilatorio han resultado muy útiles para obtener las condiciones de molienda en laboratorio que mejor simularan las condiciones a nivel industrial.

Palabras clave: reología, punto de fluencia, tixotropía, test de oscilación, región viscoelástica.

1. INTRODUCTION

Silk screen paints are suspensions with two phases: a solid phase (coloured pigment) and a liquid phase (medium). The coloured pigments are oxides and the medium is generally an organic mix of polymers or mineral oils. Rheological properties of suspensions are strongly influenced by the medium and by the content of solid particles. The composition of suspensions for silk screen paints (1) is quite similar to the composition of ceramic glazes; the most important difference is the high oxides content of the silk screen paints.

In the case of silk screen paint it is fundamental to know and be able to control the density and rheological properties such as viscosity, thixotropy and yield stress because in the application process the rheological parameters of silk screen paints (2) are more critical than in the case of glazes. Silk screen paints are traditionally obtained in three steps: wet milling the solid phase with deflocculant, drying the milled suspension, and adding the organic medium (3). There is also a direct method which consists in wet milling directly all the components of the paint.

Today 90-95% of factories buy raw materials which have been milled and dried. These kinds of raw materials must then be milled with the medium in a fine grinding mill and the resulting suspension is ready to be used after only 50-60 minutes. The problem with this method is the high cost of milled raw materials. Indeed, industries prefer to buy the raw material (oxides, frits etc.) not milled and mill them together with a small quantity of medium using a drum ball mill (Alsing mill). With this method a large quantity of slurry at

high density is prepared which must be stored. This slurry is then prepared for use by the addition of the organic medium and other additives necessary to achieve the desired rheological properties and density required for the industrial application process. The objective of the present study was to evaluate a new formulation of silk screen paint developed with the aim of reducing the cost of the milling process as well as replacing the traditional organic milling medium with a water based solution.

2. EXPERIMENTAL

2.1 Materials and methods

In this study two samples prepared in laboratory are considered: the traditional formulation (PS1-Lab) and the new formulation (PS1N-Lab). In order to evaluate if laboratory conditions reproduce adequately the industrial conditions, another sample as reference is considered: PS1-Ind, a traditional formulation obtained directly from the factory. The laboratory samples were made using the industrial raw materials and mixing with a laboratory milling process. Rheological characterisation was carried out to control the milling level of the laboratory sample (comparison PS1-Ind and PS1-Lab). As a good laboratory milling is chosen the PS1N-Lab is prepared at the same conditions and the rheological behaviour of this new formulation in comparison

to the traditional formulation (PS1-Lab) is performed.

Formulations for studied samples are reported in Table I. The raw materials and medium (F for PS1 and A for PS1N) were mixed together for 22h in a ball mill (ball-powder weight ratio, 1:1). In the case of PS1N, after milling, media B and C were added and the density was determined. The raw materials for PS1 were pre-milled and the particle size was about 1mm, whereas the average particle size of the raw materials for PS1N was about 1cm. The milling medium was different for the two formulations. In the case of PS1 "medium F" was employed; in the case of PS1N a mix of three different additives in a water based solution was employed. Medium F is a solution of diethylene glycol, Medium A is a solution of 25% of a mix of diethylene glycol, Medium B is a mix of resins and polyglycols and Medium C is a mix of carboxyl resins and polyglycols. Medium B is a binder which must be used to increase the viscosity and Medium C must be added to obtain the required density.

The rheological measurements were carried out at 25°C using a RS50 Haake rheometer (CS-CR) equipped with two different sensors (plate-plate for steady state measurements and cone-plate for oscillatory tests) (4). Before testing, all samples were subjected to preshearing at 1000 s⁻¹ for 60s (at 10 s⁻¹ for oscillatory tests) with a rest for 180 s in order to have the same conditions for all samples.

2.2 RESULTS AND DISCUSSION

The oscillatory tests were carried out to determine the best laboratory milling conditions to reproduce industrial conditions. The PS1-Lab sample prepared in the laboratory were tested by oscillatory measurements after the ball milling and compared with the industrial sample (PS1-Ind). A preliminary stress sweep is performed to evaluate the linear viscoelastic region (see Figure 1) for the two samples. In this region, where modules are constant, the frequency sweep is performed successively.

Figure 2 shows the frequency sweep results of the industrial reference slurry PS1-Ind compared with the same laboratory formulation PS1-Lab. The trend of the modules which indicates the degree of dispersion of slurry is the same for both the industrial and laboratory samples, indicating that the laboratory milling process is suitable for the purposes of this study.

Since the laboratory milling system (PS1-Lab) simulates the industrial conditions (PS1-Ind) quite well, the other laboratory sample (PS1N-Lab) is prepared in the same conditions and rheological characterisation was carried out to compare the behaviour of the two laboratory formulations (PS1 - Lab and PS1N - Lab).

The new formulation exhibits a lower viscosity at high shear, while at low shear the viscosity of the two formulations is the same.

Flow curves are reported in Figure 3. The measurements were made at the equilibrium condition between shear rate=0 and shear rate=300 s⁻¹ in control rate mode.

The shear behaviour is described well by the Herschel-Bulkley model:

$$\tau = \tau_0 + k\dot{\gamma}^n$$

TABLE I: FORMULATIONS OF SAMPLES STUDIED.

FORMULATIONS	RAW MATERIALS	MEDIUM	MILLING PROCESS
PS1 - Ind (traditional)	frit (1) 87.0 wt% clays (1) 4.3 wt% pigment 8.7 wt%(ZrO ₂ based)	F 52.2 wt%	INDUSTRIAL FINE GRINDING MILL 50'
PS1 - Lab (traditional)	frit (1) 87.0 wt% clays (1) 4.3 wt% pigment 8.7 wt%(ZrO ₂ based)	F 52.2 wt%	LABORATORY PREPARATION
PS1N - Lab (new)	frit (2) 87.5 wt% clays (2) 4.0 wt% pigment 8.7 wt%(ZrO ₂ based)	A 44.2 wt% B 6.2 wt% C 20.0 wt%	BALL MILL 22h

(1) particle size: <1mm

(2) particle size: <1cm

Figure 1. Stress sweep test to find viscoelastic region.

Figure 2. Oscillatory test for the comparison between the industrial mill and the laboratory one.

Figure 3: flow curves of the two formulations of laboratory samples PS1 and PS1N.

the corresponding fitting curves are also shown in Figure 3. The values of shear stress evaluated from the model are quite different as reported in table II. The yield stress was evaluated from the flow curve in mode control stress (5) in the range 0-10 Pa for 180s too. The curves are fitted by power law model and the results are reported in table II. Contrary to what we found from the flow curve in shear rate the yield stress measured does not change significantly with the new formulation.

Finally in order to compare the stability of the two formulations, an oscillatory test was carried out ($\nu = 10\text{-}0.1$ Hz) in the viscoelastic region ($\tau = 0.2$ Pa) previously found with a stress sweep for the PS1-lab slip.

As seen in Figure 4, the trend of the moduli is the same, indicating that the slurries are quite "stable".

The elastic response indicated by G' exceeds the viscous one of G'' for the two formulations but this difference in the case of PS1N-Lab is greater. It seems that PS1N-Lab is more elastic than PS1-lab. The level of the G' -curve is said to coincide with the number of crosslinks in the structure of the slip.

To complete the rheological characterisation, thixotropic tests were carried out at constant shear rate (shear rate = 0 s^{-1} for 100-200-250s and shear rate = 50 s^{-1} for 100-150-200s) (5).

The time dependency is correlated with floc formation and breakdown during time under shear (6). Since a silk screen paint is usually stored for long time before use (high volume production is more economical), it is important that the slurry does not exhibit a high level of structural build-up after a rest time. At the same time, some thixotropic behaviour is important because after application it should not take too long a time for the silk screen paint to dry.

Both formulations exhibit some thixotropic behaviour and the trend is the same (Fig. 5), but the new formulation seems to have a higher level of structural build-up ($\tau_{\max}/\tau_e$ is higher for PS1N-lab) after a rest time (Fig. 6 and Table III). This behaviour is confirmed by the oscillatory tests which evidence the presence of a crosslinked structure.

3. CONCLUSIONS

The new formulation has been produced on an industrial scale and the results are very good. Due to the reduced content in organic compounds, occurrence of the black core defect after firing is also reduced.

The study of rheological properties (oscillatory tests) was found to be a quick and easy approach to evaluate laboratory conditions of milling in order to simulate industrial processes.

TABLE III: VALUES OF $T_{\max}$ AND T_{eq} TO EVALUATE THE TIME DEPENDENCY.

PS1-Lab			PS1N-Lab		
$\tau_{\max}$ (Pa)	τ_e (Pa)	$(\tau_{\max}/\tau_e)$	$\tau_{\max}$ (Pa)	τ_e (Pa)	$(\tau_{\max}/\tau_e)$
58.1	51.7	1.12	45.1	35.4	1.28
59.4	54.1	1.10	44.7	37.7	1.19
69.0	57.9	1.19	53.8	42.6	1.26
76.6	62.3	1.23	65.6	47.0	1.39

TABLE II: VALUES OF THE MODEL APPLIED AND VALUES OF YIELD STRESS MEASURED DIRECTLY WITH A FLOW CURVE IN MODE SHEAR STRESS.

PS1-Lab			PS1N-Lab		
Model data		Measured	Model data		Measured
k	τ_0 (Pa)	τ_0 (Pa)	k	τ_0 (Pa)	τ_0 (Pa)
3.5	0.2	1.2	2.4	10.3	1.1

Figure 4. Oscillatory tests to evaluate the stability of the new formulation in comparison with the old one for laboratory samples PS1 and PS1N.

Fig.5: On-off cycle to evaluate the time dependency for laboratory samples PS1 and PS1N.

Fig.6: build-up phenomena after a rest time for laboratory samples PS1 and PS1N.

The new formulation developed was found to be very similar to the traditional formulation with regard to stability but better than the traditional formulation with regard to time dependency and elasticity.

Indeed the new formulation exhibits greater values of G' . This means that the new system is subject to slow deformation as confirmed by the higher values of structural build-up after a rest time.

The new formulation can be moved easier than the traditional one and it is easier to drain the mill as its viscosity is lower. Although the rate of the structure regeneration of the new sample is higher than the old one and it could be a problem in case of prolonged time of storage, a re-thickened can be important anywhere to prevent sagging phenomena.

BIBLIOGRAPHY

1. "La smaltatura", Società Italiana per la Ceramica Assiceram, Faenza Editrice S.p.A., 1979.
2. P. Prampolini, "Le paste da serigrafia", in "La reologia dei materiali ceramici tradizionali", Ed. P. Pozzi e C. Galassi, Faenza Editrice, pp 187-203, 1994.
3. G. Guarnieri, "La serigrafia", Faenza Editrice S.p.A., 1980.
4. G. Schramm "A practical approach to rheology and rheometry", Gebrueder Haake, 1994.
5. A. Albertazzi, E. Rastelli, "Valutazione della tistotropia e del limite di scorrimento di barbotine ceramiche industriali con viscosimetro rotazionale", Cer. Acta, 9, [4], 5-11, 1997.
6. C. Galassi, E. Rastelli, R. Lapasin "Time dependent properties of ceramic suspensions", Cer. Trans.- Science, Technology and Applications of Colloidal Suspensions, Vol. 54.

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