ASSESSMENT OF THE DEGREE OF DISPERSION IN SCREEN-PRINTING INKS

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ABSTRACT

Suitably dispersing the solid particles (frit and pigment) that make up screen-printing inks, within the suspending liquid, is a fundamental processing step of such inks. A dispersion, which is lacking in the mix's solids constituents, can give rise to variations in the dispersion's properties during production, as well as yielding inappropriate behaviour of the ink in its screen-printing application, thus producing a flawed glaze coating.

There are currently no established methods of quantifying the degree of dispersion of the solids constituents in the screen-printing inks usually employed in ceramic tile manufacture.

In the present study, different methods have been designed and developed for quantifying the level of dispersion of the solids constituents in industrial inks. On the one hand, laser diffraction techniques were employed to verify the overall solids dispersion in the solids mix. On the other hand, a novel image analysis technique for glazed surfaces has been prepared, allowing quantification of the degree to which the pigments used have been dispersed.

Applying these techniques has enabled the degree of dispersion to be determined, on using screen-printing ink preparation systems that involve applying different dispersing energies. It was shown, that the most widely adopted dispersion method currently employed in industry does not provide the required levels of dispersion.

1. INTRODUCTION

At present, ceramic tile manufacturers have adopted screen printing as the major tile decorating technique.

Screen printing involves depositing ink through a mask held over a stretched fabric, which only lets ink through certain areas, thus reproducing the design in the mask.

Successive applications of different colours using masks with differing designs, allow relatively complicated decorations to be obtained. Moreover, this technique makes it possible to obtain quite thick depositions of ink, and produce large production batches economically.

The screen-printing inks that are currently employed consist of concentrated solids suspensions with highly varying compositions (Fig. 1). The solids, which make up round 50-70 wt% of the paste, are basically frits and pigments. As far as the suspending liquid is concerned, the traditionally used vehicles based on mineral oils have been replaced by different kinds of polyglycols in recent years. Nowadays some additives are also being included by directly mixing them with the vehicle, thus contributing certain specific functions.

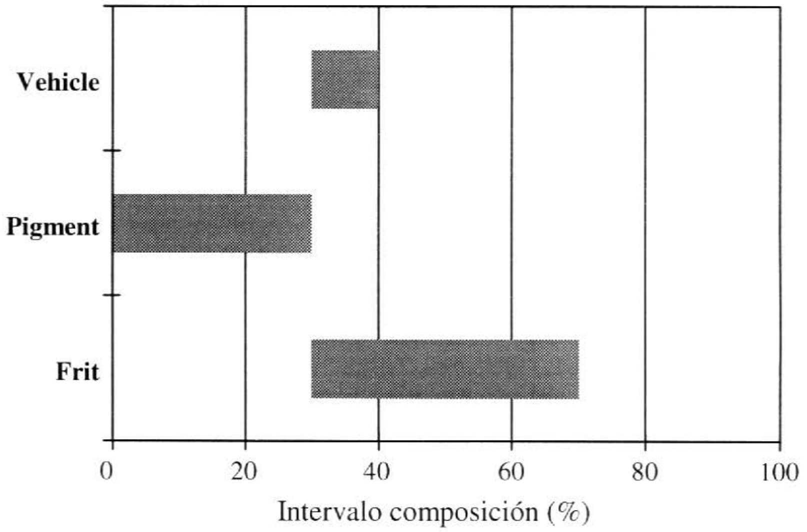

Figure 1. *Composition interval of industrial screen-printing inks*

The general screen-printing paste preparation method [1] has been schematically depicted in Fig. 2. The frit is first wet milled in a ball mill to a targeted particle size, with subsequent drying. The pigments are fabricated by calcination and then ground and dried. These steps are usually carried out by the frit and pigment producers. The tile manufacturer directly prepares the screen-printing paste by adding these solids to the suspending liquid, according to preset loading formulas. After mixing the constituents, with a view to removing the coarsest particles from the paste, a refining process is often run using different systems: screening, three-roll mill, colloid mill, bead mill, etc.

In order to assure the reproducibility of the screen-printed coating across time, it is necessary to maintain highly constant operating conditions and materials characteristics. To do so, it is vital to obtain printing pastes with perfectly dispersed solids in the suspending liquid or screen-printing vehicle.

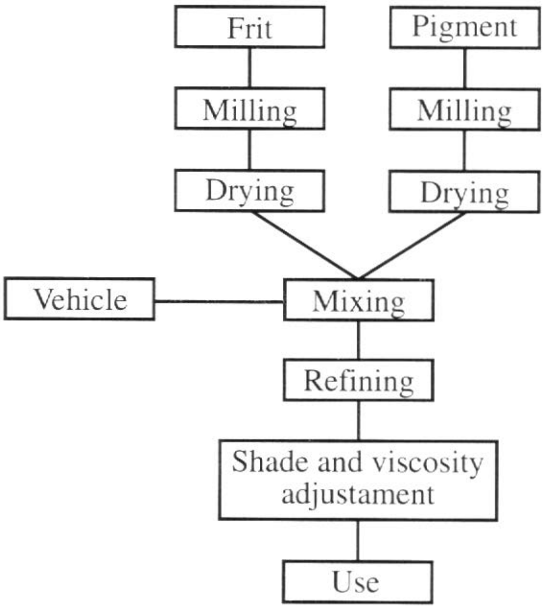

Figure 2. *General preparation process for screen-printing inks.*

1.1. SOLIDS DISPERSION IN LIQUIDS

The term dispersion refers to the whole process of incorporating a particulate solid in a liquid medium and obtaining a suspension in which each particle behaves independently, completely surrounded by the medium [2].

The overall dispersion process may be schematically divided into three stages [2][3], in which different physical processes arise (Fig. 3):

a) Particle wetting.
b) Breakup of particle groups (aggregates and agglomerates).
c) Stabilization of dispersed particles.

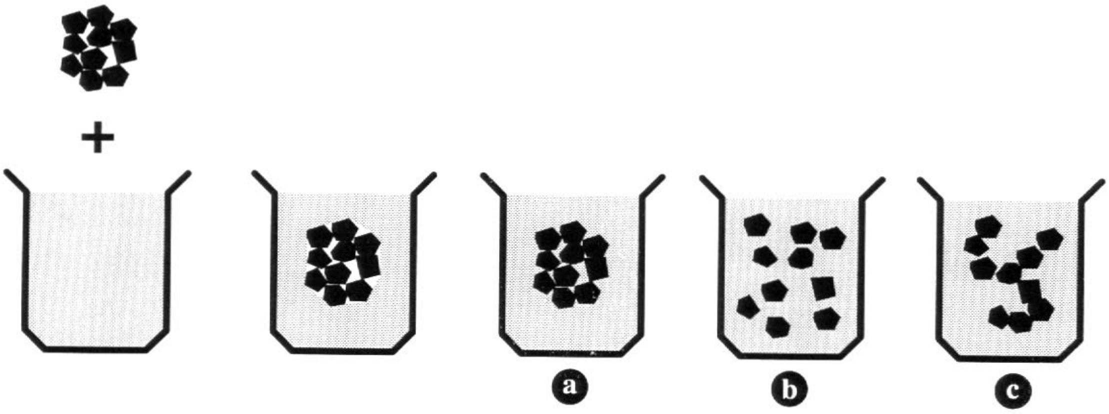

Figure 3. *Solids dispersion stages: (a) wetting, (b) agglomerate breakup, (c) stabilization.*

In practice, these stages overlap and may be hard to identify, however, on separately analysing them, more may be learnt about dispersion, enabling the overall process to be optimized.

Before analysing the principles involved in dispersing a solid, a series of concepts needs defining, which will be used repeatedly in this study. *Aggregates* are groups of primary particles linked at their faces, exhibiting a significantly lower specific surface area than the sum of the surface areas of their constituent particles, which is why much energy is required for their breakup. *Agglomerates* are primary particle groups and/or aggregates that are linked at their edges and corners, in which the specific surface area of the group approaches the sum of the surface areas of the group's constituents. Finally, *flocs* are particle groups in which the bonding forces are weaker than those in the agglomerates, and much weaker than those in the aggregates. Flocs can therefore be easily destroyed, but may form again just as easily if the force separating them is removed.

These three stages will be considered separately below, identifying the physico-chemical principles involved.

1.1.1. Particle wetting.

The wetting process in a powder made up of solid particles, consists of bringing the whole solid surface into contact with the liquid [4]. This includes both the external surfaces and the internal ones of the aggregates and agglomerates [1].

Placing a solid in a liquid produces a series of changes in the solid-liquid-gas interfaces, which involve changes in the energy of the system, and which control the wetting process. This process is usually represented schematically by dividing the process that arises when a cubic particle is introduced into a liquid, into three stages (Fig. 4):

- *Adhesion*: The solid is brought into contact with the liquid, producing a new solid-liquid interface that replaces the gas-solid and solid-gas interfaces.
- *Immersion:* The gas-liquid interface is kept constant, whereas the solid-gas interface is replaced by a solid-liquid interface.
- *Spreading*: Substitution of the solid-gas by the solid-liquid interface is completed, and the original liquid-gas interface is formed again.

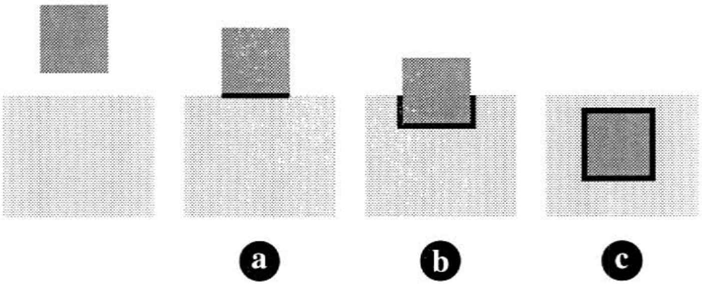

Figure 4. *Stages involved in wetting a solid : (a) adhesion, (b) immersion, (c) spreading.*

The total work involved in wetting a solid will be the sum of the work associated with each of the three processes, and may be calculated by means of the following equation:

$$W = W_a + W_i + W_s = \gamma_{L/V}(\cos\theta + 1) - 4\gamma_{L/V}\cos\theta - \gamma_{L/V}(\cos\theta - 1) = -6\gamma_{L/V}\cos\theta \qquad (1)$$

The wetting work depends on interfacial tension and the contact angle. This may be positive or negative according to the value of cosθ, which means, respectively, that the wetting process may be spontaneous or require the application of a certain energy. In practice, adding surface-active agents lowers liquid surface tension and ensures that θ approaches zero, thus encouraging the particle surface wetting process.

However, it has been indicated above that the wetting process also includes the penetration of liquid into the inner aggregate and agglomerate channels. The pressure required for a liquid to enter a pore is:

$$P = \frac{-2\,\gamma_{L/V}\cos\theta}{r} \qquad (2)$$

Therefore, penetration will only be spontaneous when $\theta<90^{\circ}$. However, the greater surface tension $\gamma_{L/V}$ is, the greater will the pressure be for the liquid to enter the pores.

Surface-active agents provide easy, good surface wetting of a solid (by reducing θ), however they also lower surface tension, which reduces capillary pressure and hinders the process by which liquid penetrates inside the solid. Furthermore, for a given solid, the wetting rate is proportional to the product $\gamma_{L/V}\cos\theta$ and inversely proportional to the viscosity of the liquid. Adding surfactants lowers this product, so that the penetration velocity drops. It is therefore necessary to select a surface-active agent that assures surface wetting of the solids without excessively lowering surface tension, since that hinders wetting of the inner surfaces.

1.1.2. Breakup of particle groups

The breakup of aggregates and agglomerates into their particle constituents involves breaking bonds and generating new surfaces, which means increasing the energy of the system. The main mechanisms employed in applying such energy to bear on these groups are impact and shear (Fig. 5).

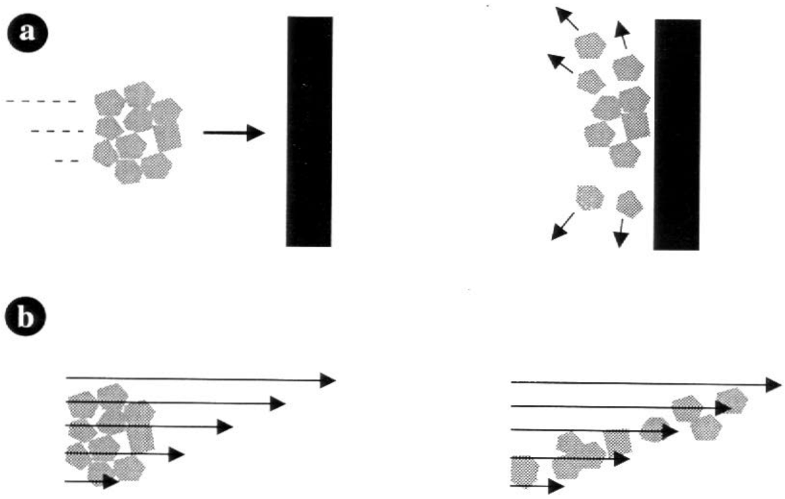

Figure 5. *Agglomerate breakup mechanisms: (a) impact, (b) shear.*

Impact dispersion is based on transmitting high kinetic energy to particles or groups, capable of causing them to break up into smaller fragments. Impact dispersion systems are based on making particles hit an element that has a different velocity to theirs. The efficiency of such impacts largely depends on the viscosity of the suspension, owing to viscous damping, so that they are only operative while the suspension has low viscosity.

Shear dispersion is based on a viscous drag mechanism. As a result of differences in velocity among the various suspension layers across which the agglomerate lies, shear stresses arise that tend to separate agglomerate constituents. The greater the medium's viscosity, the greater will the shear rates be that can form, and the greater will the shear stresses applied to the agglomerate be. The kinds of equipment that work via this mechanism operate using highly viscous suspensions.

1.1.3. Stabilization.

After particle wetting and aggregate and agglomerate breakup, it may be of interest to suppress floc formation in the suspension, and keep individualized particles. This can be done by ensuring that the interparticle repulsion forces prevail.

It is common practice to use salts and polymers that modify electrostatic and steric forces for stabilizing suspensions.

1.2. INFLUENCE OF DISPERSION IN SCREEN-PRINTING INKS

The dispersion state of the solids comprised in a screen-printing ink has a marked effect on ink behaviour during application as well as on the characteristics of the resulting coating [5].

The presence of large particle groups, which have difficulty in getting through the mesh, makes them accumulate on the printing screen, clogging it up and not letting part of the ink through. Furthermore, the gloss of the resulting coating is also related to the size of such groups, so that the larger they are, the lower will gloss be.

The size distribution of particles and existing groups directly impacts the viscosity of the suspension, and the intensity of the resulting colour.

On the other hand, having an incompletely dispersed system makes it keep on evolving to achieve greater dispersion. This gives rise to stability problems, both with regard to the viscosity of the ink and to the resulting decoration colour.

Owing to the manifest importance of the degree of solids dispersion in screen-printing inks, the present study has attempted to establish the most suitable laboratory methods for assessing the dispersion of the various ink constituents. These methods were subsequently used to study how using different industrial facilities affected dispersion in several kinds of ink.

2. EXPERIMENTAL

2.1. MATERIALS.

Table I shows the simplified composition of the inks used.

Table I. *Ink compositions used.*

Composition (%)	Ink L1	Ink L2	Ink L3	Ink L4	Ink I1	Ink I2
Polyglycol	38.0	40.0	34.3	38.9	41.3	39.3
Frit	36.5	57.2	38.0	60.8	43.5	60.5
Pigment	25.5	2.8	27.7	0.3	13.2	0.2

Inks L1-L4 were prepared in the laboratory, whereas samples I1 and I2 were taken from inks that were prepared industrially for use in production.

2.2. EQUIPMENT.

The inks were mixed and dispersed by means of the following equipment:

Laboratory stirrer. This apparatus involves a propeller-type stirrer, which does not produce any appreciable shear. Rotating speed was 270 r.p.m..

Laboratory disperser. This apparatus consists of a disk impeller blade with rim serrations, having a 10 cm diameter, set at right angles on a rotating shaft. The design yields relatively high shear in the region between the disk and the bottom of the container. Rotating speed was 3000 r.p.m..

Industrial disperser. The design of this facility and that of the laboratory disperser were alike. The disk used had a 25 cm diameter, with a rotating speed of 900 r.p.m.

Three-roll mill. This facility consists of three metal cylinders, arranged in parallel, which have various rotating speeds. The closeness of the cylinders allows generating very high shear stresses, exceeding those of the dispersers described above. The facility operates at a roller pressure of 13 bar, with an output of 110-130 kg/h.

Laboratory bead mill. A laboratory bead mill was used with a milling chamber volume of 0.5 litre. This apparatus basically consists of a conical drag rotor, which fits a container having the same conical shape (stator). The milling beads are located in the space between the rotor and container wall, and are moved by the turning rotor. The sample was pumped into the space where milling takes place. The direct action of the beads upon the particles or groups (by friction and compression) enables enough energy to be transferred to mill them. A flow rate of 30 kg/h was used, with a bead load that occupied 50% of chamber volume.

Industrial bead mill. This mill is a scaled-up model of the laboratory bead mill. A flow rate of 40 kg/h was used, with a bead volume that took up 50% of milling chamber volume.

3. RESULTS

3.1. ASSESSMENT OF THE DEGREE OF DISPERSION

3.1.1. Particle-size analysis

Particle-size analysis methods can be a valuable tool for studying the degree of dispersion [6]. They directly measure the size of the units present in the suspension, regardless of whether individual particles of groups of particles (aggregates, agglomerates or flocs) are involved. The technique employed in this study was laser diffraction.

Particle-size analysis techniques always work with highly diluted suspensions. The inks must therefore be diluted before running the measurements. The sample dilution process could raise its degree of dispersion. In order to prevent any such alteration, the following precautions were taken. Dilution was carried out on the same carrier that contained the inks, since any change in the nature of the liquid involved could have seriously affected the degree of actual particle dispersion in the original ink. Furthermore, this dilution was carried out slowly, without producing any appreciable shear that might have broken up the agglomerates.

In order to verify whether the procedure described for diluting the inks had been conducted without producing any excessive change in the degree of dispersion in the sample, comparative testing was done by applying ultrasonics after diluting (Fig. 6).

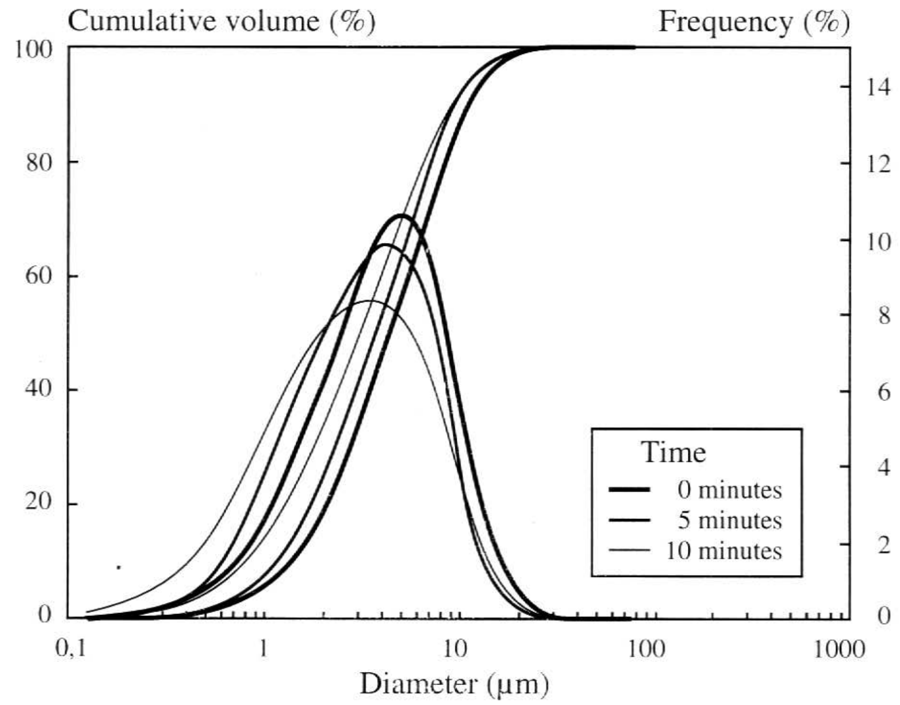

Figure 6. *Effect of applying ultrasonics on a partially dispersed ink.*

Applying ultrasonics yielded a progressive reduction of the largest groups, raising the fine distribution fraction. This behaviour indicates that the dilution procedure did not unduly affect the degree of particle dispersion in the ink and that the particles were not fully dispersed, since applying energy by means of ultrasonics allowed breaking up a significant fraction of the existing groups. The technique involved may therefore be used to assess ink dispersion.

Screen-printing inks can be prepared with different types of equipment, which may provide varying degrees of dispersion. In order to examine the dispersion resulting from the use of different kinds of equipment, three inks were prepared using three types of preparation equipment on a laboratory scale, namely: a stirrer, a disperser and a bead mill.

The plots of the particle-size distribution curves of inks L2 and L4 (Figs. 7 and 8), prepared with these different types of equipment, show considerable variations. The ink prepared with the disperser yields a much finer particle-size distribution that of the ink prepared with the stirrer. On the other hand, the size distribution found with the bead mill is the finest, since a milling system is actually involved, capable of applying enough energy to reduce particle sizes, or break up the most resistant aggregates.

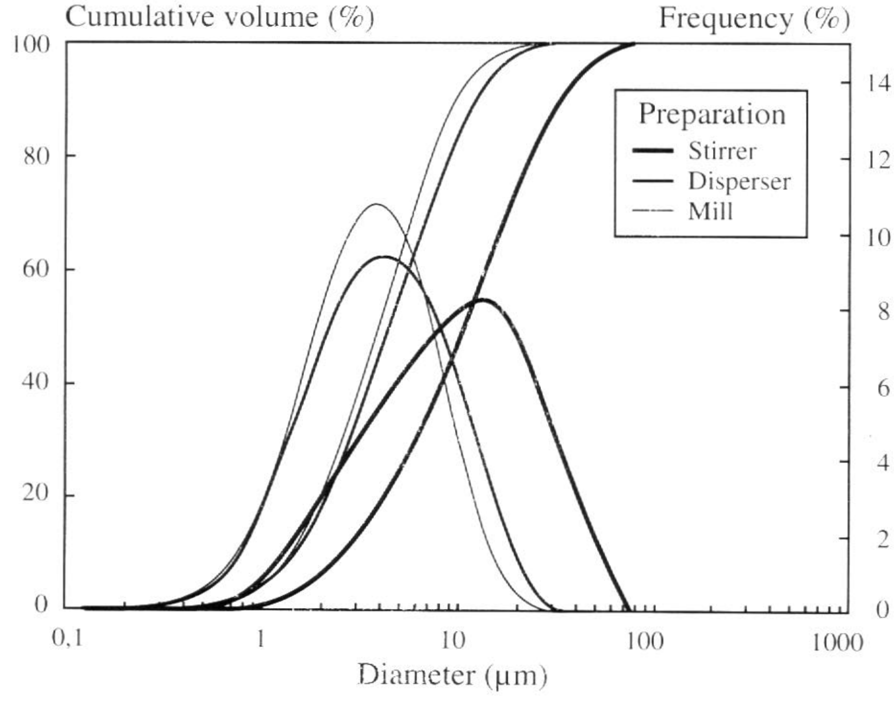

Figure 7. Ink L2 particle-size distribution with different preparation systems.

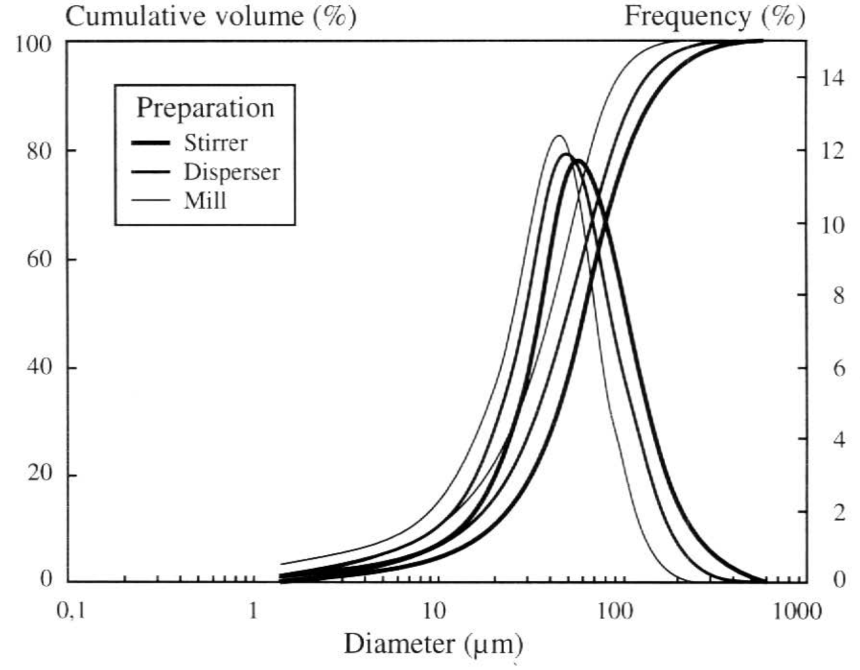

Figure 8. *Ink L4 particle-size distribution with different preparation systems.*

However, ink L3 (Fig. 9) showed differing behaviour. The particle-size distribution found on preparing this ink with the disperser was only slightly finer than the one obtained with the stirrer. This is because the particle groups that existed after mixing were resistant enough to withstand the shear stresses generated by the disperser. On the other hand, the bead mill did allow reducing the proportion of aggregates and agglomerates, as it can reduce particle size.

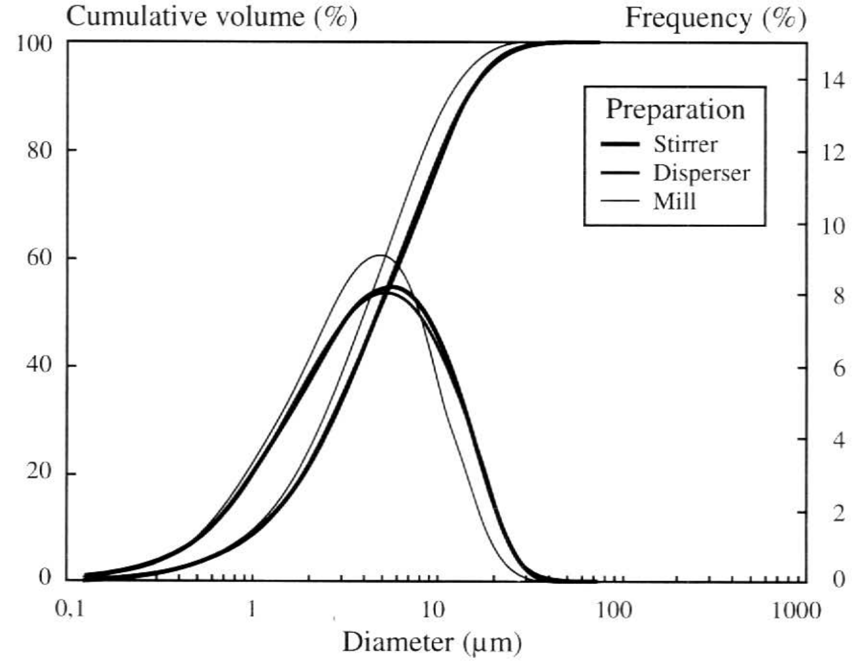

Figure 9. *Ink L3 particle-size distribution with different preparation systems.*

The behaviour observed may be explained as a result of the differing nature of the frit and pigment particle groups. Frit agglomerates are formed in the drying stage, so that they are much more brittle than the pigment aggregates formed by calcination. Thus, frit particle agglomerates are dispersible on applying sufficiently high shear. However, the highly resistant pigment particle groups do not disperse under low shear stresses and require such shear to be very high, or even need the action of a mill to disperse them. This explains the behaviour of inks L2 and L4 that have a low pigment content, and ink L3 that has a high pigment proportion.

This technique does not distinguish between ink constituents, but yields an overall size distribution of sample constituents. Consequently, if a low pigment proportion is involved, it will not be possible to know whether it is well-dispersed or not, although this may be of considerable importance optically, later on.

3.1.2. Microscopy and image analysis.

An examination of the pigment at the surface of a fired tile, by means of optical microscopy, allows directly appreciating its state of agglomeration when the ink was applied, which makes this technique of the greatest interest.

The accompanying figures depict photographs taken of the tile decorated with ink L2 (Fig. 10), showing the presence of particle groups. Inks L3 and L4 showed too little contrast to allow identifying the pigment.

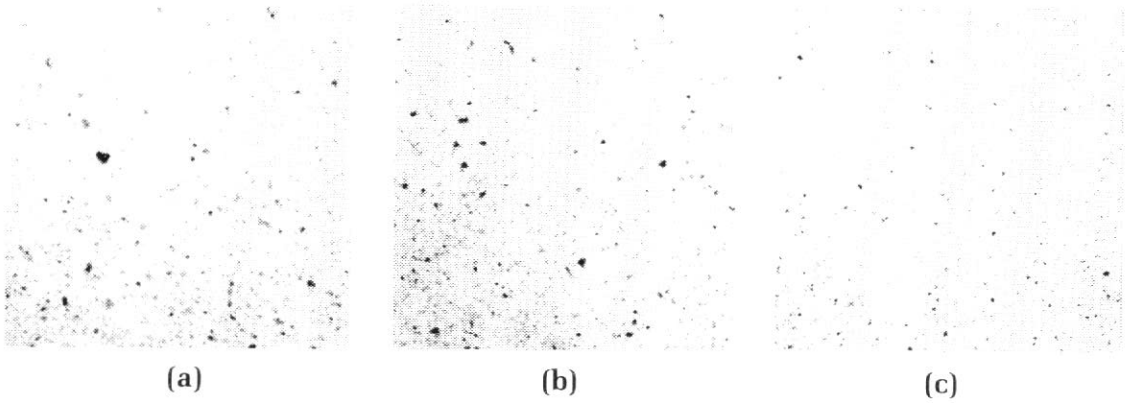
(a) (b) (c)

Figure 10. *Photographs taken with an optical microscope of the screen-printed surface using ink L2, with different preparation methods: (a) stirrer, (b) disperser, (c) bead mill.*

In order to quantify the images afforded by the microscope, these images were run through a computerized image analyzer, which counts the existing groups and determines their size. The resulting data for each dispersion process have been summarized in Table II.

Table II. *Pigment aggregate mean diameter in ink L2 with different preparation equipment.*

Ink L2	Mean diameter (µm)
Stirrer	2.64
Disperser	2.52
Bead mill	2.12

It can be clearly observed that pigment group size was lowered on using dispersion or milling systems. However, this reduction was small when only shear was applied, as a result of the resistance of pigment aggregates.

In this test, only data referring to the degree of pigment dispersion were obtained, as frit fusion during firing impeded any further appraisal. Thus, the image analysis test solely assessed the degree of dispersion and/or milling of the pigment.

3.1.3. Rheological behaviour.

The methods set out in the foregoing sections directly measured particle or agglomerate sizes, so that they are considered direct methods. However, ink agglomerate size directly influences a multiplicity of properties that might be used for indirectly assessing or controlling the degree of dispersion.

The size of the hydrodynamic units within the suspension has a marked impact upon the rheological behaviour of the inks, which is why they can be used for controlling rheological behaviour.

Inks L2 and L3 (Figs. 11 and 12) exhibited similar behaviour. Using a high shear disperser left the flow curves unaltered, and only slightly reduced viscosity. However, when the bead mill was used, the slope of the viscosity curve climbed noticeably. As a result of the breakup of agglomerates with low compactness, viscosity dropped at high shear rates, while increasing at low rates owing to the increase in forces of a colloidal nature on lowering particle and aggregate sizes. Such behaviour was not observed on employing shear-driven dispersion systems, as particle and aggregate size remain unchanged.

Ink L4 (Fig. 13), which had a much larger particle size than the foregoing ones, exhibited virtually constant viscosity in the studied viscosity intervals. This is because the colloidal forces were practically negligible. The reduction in particle size resulting from bead milling yielded a drop in viscosity across the whole measured range.

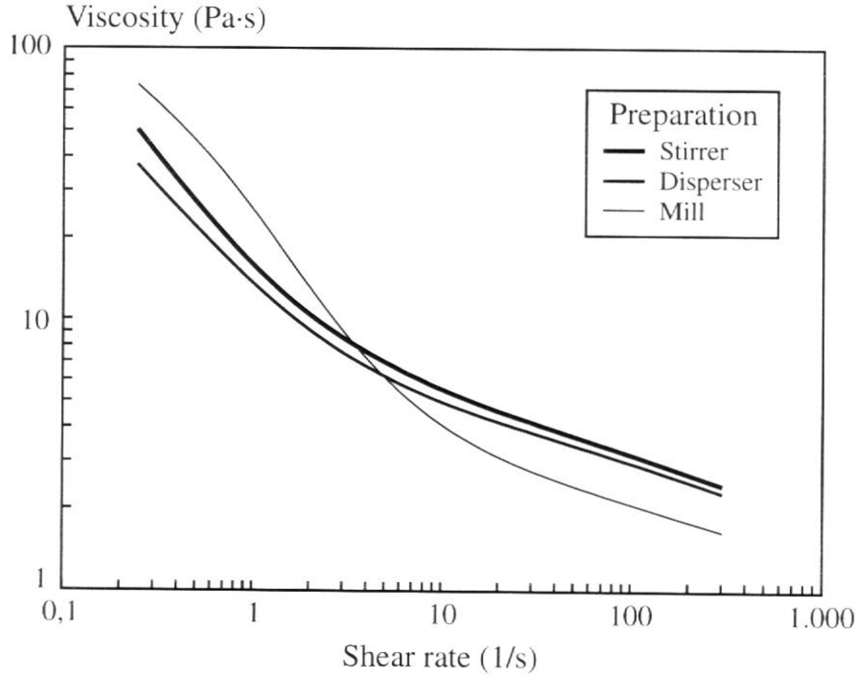

Figure 11. *Ink L2 viscosity curve with different preparation systems.*

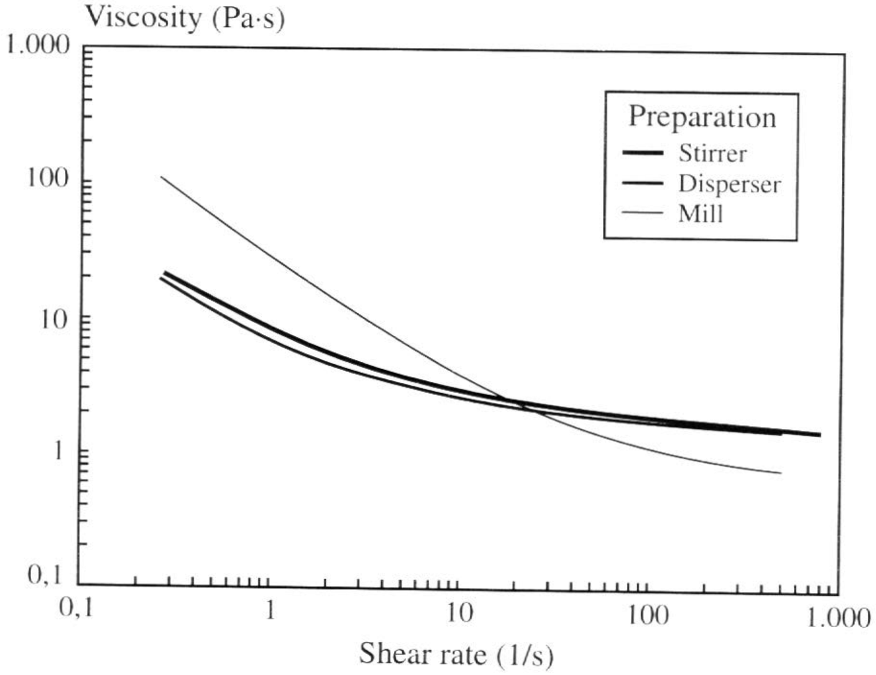

Figure 12. *Ink L3 viscosity curve with different preparation systems.*

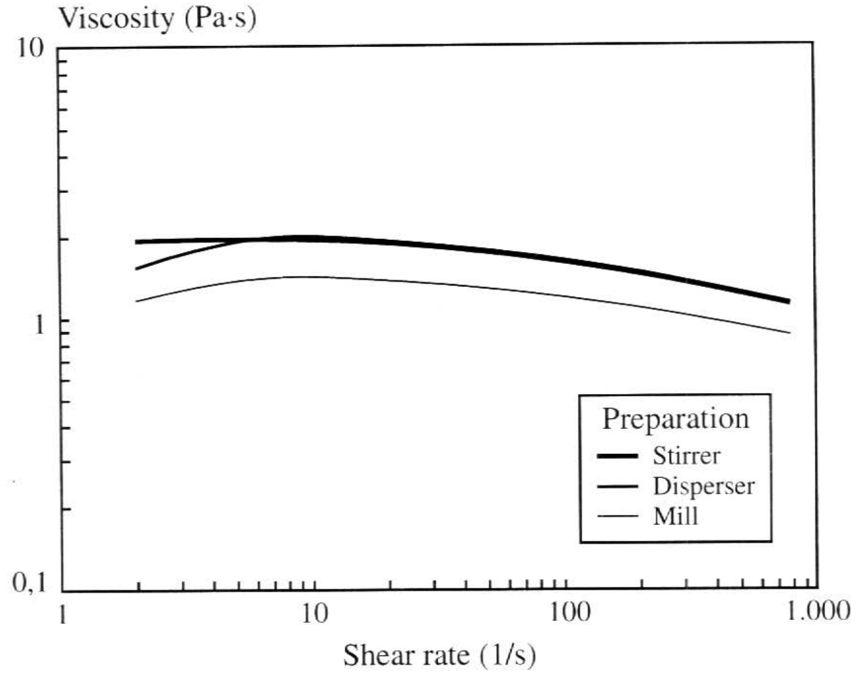

Figure 13. Ink L4 viscosity curve with different preparation systems.

3.2. DISPERSION OF INDUSTRIAL SCREEN-PRINTING INKS

In order to substantiate the laboratory results on an industrial scale, a series of tests were programmed, which would allow the degree of dispersion to be determined, arising in some industrially used facilities, and the importance that this might have in respect of ink behaviour in production.

The behaviour of two industrial inks was studied, with different pigment proportions. These inks were prepared industrially in a disperser, a three-roll mill and a bead mill. The findings have been detailed below.

3.2.1 Particle-size analysis.

Ink I1 (Fig. 14), containing a large proportion of pigment, showed no appreciable variation of its particle-size distribution on being treated in the three-roll mill, possibly because the arising shear stresses were incapable of breaking up the pigment aggregates. Such was however not the case with ink I2 (Fig. 15), which exhibited a slight drop in the proportion of coarse particles on being treated in this facility.

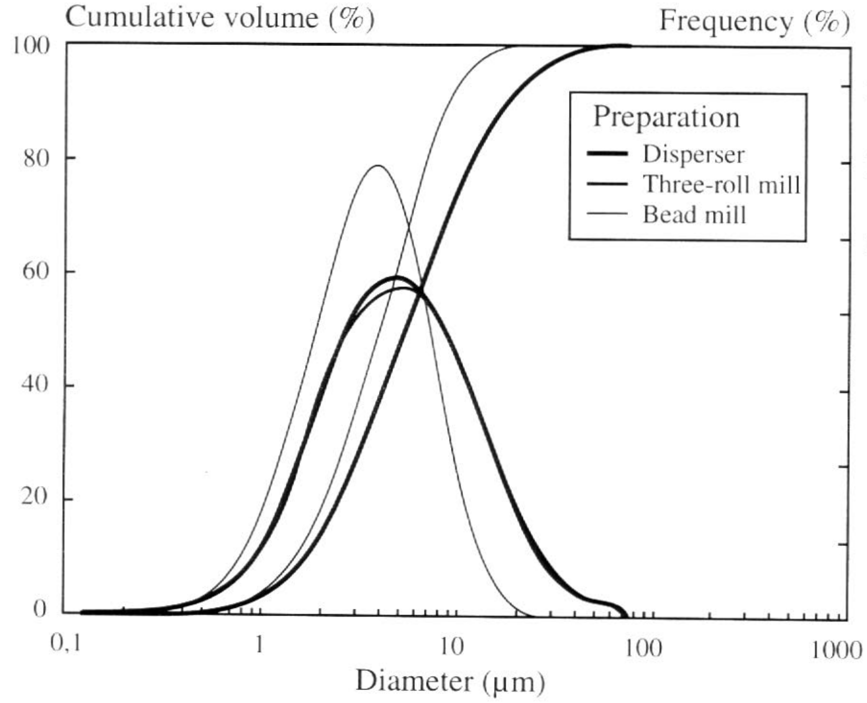

Figure 14. *Ink I1 particle-size distribution with different preparation systems.*

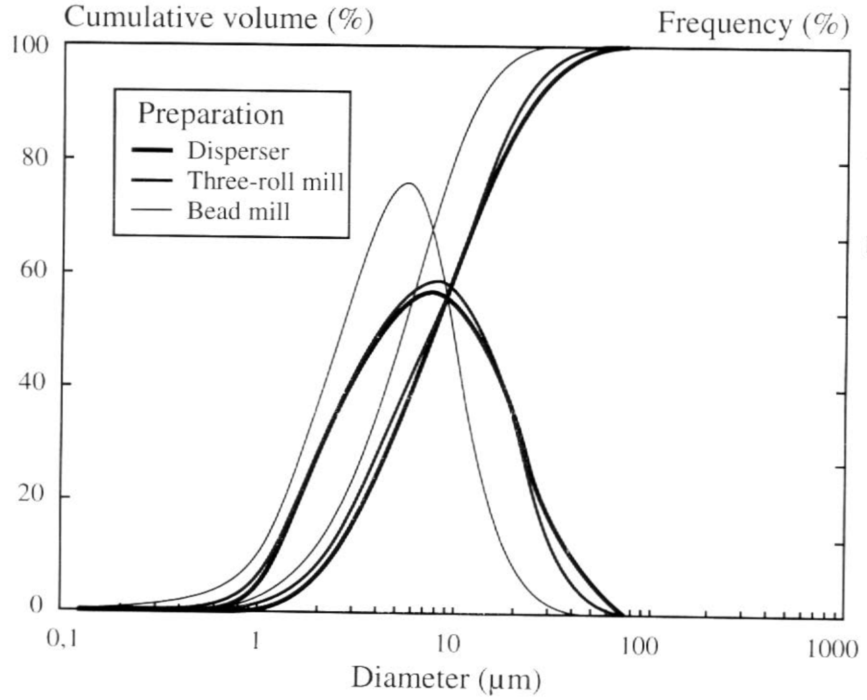

Figure 15. *Ink I2 particle-size distribution with different preparation systems.*

When these inks underwent the action of the bead mill, particle size was observed to undergo significant reduction, as the whole distribution shifted towards smaller sizes. This system was able to completely eliminate all the agglomerates and/or aggregates, and even effectively reduce particle size.

The resulting size reduction with the bead mill must obviously affect ink behaviour, however, it was necessary to verify whether the variations observed on using the three-roll mill were significant as far as the ink's industrial behaviour was concerned. For this purpose, and with a view to having a parameter that would be directly related to particle size, the oversize fraction was determined on a 40 μm screen of the material that accumulated on this screen after different operating times. This test was not run with the bead mill because there were no starting oversizes of the inks prepared in the bead mill.

Table III. *Oversize at 40 μm (wt%) of inks I1 and I2 on starting and after operating for 90 min.*

Ink	Preparation	Initial oversize	Final oversize
I1	Disperser	5.5	14.1
	Three-roll mill	4.7	12.3
I2	Disperser	6.2	17.0
	Three-roll mill	5.8	14.4

The results obtained are summed up below. The inks prepared with the three-roll mill have slightly lower initial oversize fractions compared to those of the inks processed solely with the disperser. Thus, after operating for 90 min, the cumulative coarse particle amount on the screen was greater in the case of the ink prepared with the disperser, so that the differences in oversize fractions became progressively more significant.

In order to ascertain whether the agglomerates held back were frit or pigment agglomerates, the ink prepared with the three-roll mill, found on the screen, underwent chemical analysis at the start and after 90 min operation. The test run involved boron analysis, since this element was contained in the frit but not in the pigment. The frit boron percentage was also determined, in order to set up the relevant correlations. The resulting data have been set out in Table IV.

Table IV. *B_2O_3 content.*

Sample	B_2O_3 (%)
Frit	3.30
Start	2.70
Oversize after 90 min	2.50

It can be observed from the table, that there was a 0.2% drop in boron (corresponding to 6.1% frit), after a 90 min ink residence on the screen during the screen-printing operation. This means that the three-roll mill lowered frit agglomerate size, enabling them to pass through the printing screen better than the pigment aggregates.

3.2.2. Image analysis

On examining the screen-printed surfaces by microscopy, with the different inks prepared on an industrial scale, it was observed that only the inks ground in the bead mill had an appreciably smaller pigment particle size.

Ink I1, with a high pigment proportion could not be subjected to image analysis. However, when this ink was ground in the bead mill, the resulting texture was more uniform. Ink I2 yielded the data shown in Table V. They show that although the three-roll mill slightly reduced pigment aggregate size, this reduction only became noticeable on using the bead mill.

Table V. *Ink I2 pigment particle and aggregate mean diameter with different preparation systems.*

Ink I2	Mean diameter (μm)
Disperser	5.81
Three-roll mill	5.75
Bead mill	4.63

4. CONCLUSIONS

The determination of particle sizes or particle groups is a useful technique for assessing the degree of solids dispersion in an ink, as long as a suitable sample diluting procedure is used, so as not to bias the sample unduly. The method can be employed for any type of ink, and yields reproducible results. It is important to point out that the resulting particle-size distributions correspond to the solids contained in the sample (both frit and pigment).

The examination of screen-printed surfaces by optical microscopy allowed differences to be appreciated in pigment particle size and coating uniformity. These differences could be quantified by statistical analysis of the resulting images, though this was only applicable to inks containing small quantities of pigment. The determination by image analysis, of the mean diameter of the agglomerates present in the fired screen-printed coating, is a direct measurement of the agglomeration state of the pigment contained in the ink.

Ink viscosity is a parameter that is very sensitive to variations in the degree of dispersion. Just as in the foregoing method, it can be used with any kind of ink, and yields reproducible results.

Of the preparation methods studied, the only one that gave rise to an appreciable drop in the existing particle group sizes was the method involving bead mill processing. It was also the method that yielded the lowest amount of solids accumulation on the screen.

The three-roll mill only produced agglomerate breakup when the agglomerates were large and/or had low resistance, as was the case with the frit agglomerates, without however noticeably affecting pigment aggregates. The result was a drop in the solids quantity that accumulated on the screen, compared to the oversize fraction resulting from the ink which had only been mixed in the disperser.

5. REFERENCES

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