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Preparation of aqueous pigment slurry for decorating whiteware by ink jet printing

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Ink-jet printing technology is used in many applications, including personal printing, commercial printing, product marking and rapid prototyping, and is an attractive option as a direct printing technology and in the manufacture of micro parts. The ink-jet printing system is a relatively inexpensive means of achieving accurate direct reproduction of patterns or pictures stored digitally. Recently, in ceramic processing, ink-jet printing systems have been applied for three-dimensional printing [1–3] and solid freeform fabrication using ceramic powders [4–7]. The inks used for three-dimensional printing are organic materials (binder etc.), while those used for solid freeform fabrication are typically suspensions of ceramic powders. The ceramic inks are normally dispersed in non-aqueous media, however, the preparation of suspensions of ceramic powders in aqueous media represents a desirable advancement in terms of environmental and personal safety [4–6]. For decorating whiteware, ink-jet printing is an attractive technology offering benefits such as simultaneous multicolor printing, elimination of the need to make plates, and speedy, low-cost processing [8]. However, the success of this technology will be strongly dependent on the preparation of suitable ceramic inks, slurries that are particularly well-dispersed, fluidized and thickened. A key factor in this process is the rheological behavior of the ink slurry. The purpose of the present study is to elucidate the optimum preparation conditions for such slurries, such as pH, apparent viscosity and dispersion, as suitable for ink jet printing in application to the decoration of whiteware.

The four color pigments examined were yellow (1541 Yellow, Kawamura Chemical Co., Ltd., Japan), pink (SP-75 Pink, Nitto Sangyo Co., Ltd., Japan), blue-green (M-33 Nando, Nitto Sangyo Co., Ltd., Japan) and black (M-800 Black, Nitto Sangyo Co., Ltd.). Pigments with narrow particle-size distribution were prepared by attrition milling for 8 h. Table I lists the densities and particle size distributions of these pigments. Ammonium polyacrylate (Celuna D-305, Chukyo Yushi Co., Ltd., Japan) was used as the dispersant, and screen-printing oil (water-soluble medium 80683, Ferro Japan Co., Ltd., Japan) was used as the thickener. The main chemical constituent of the thickener was hydroxypropylcellulose ethanol solution. The pH of the slurries was adjusted with tetramethyl ammonium hydroxide and HNO_3. Slurries containing ion-exchanged water, pigment, thickener and dispersant were prepared by ball milling for 24 h at room temperature. The dispersant was then added to the slurries in a fixed amount of the dry weight base (dwb) of the pigment (wt%), followed by the addition of the thickener in weight fraction of the solvent.

The apparent viscosities of the slurries were measured at 100 s^{-1} using a rotational viscometer (VT550, Haake, Germany) at 25 °C. Sediment volume measurements were employed to evaluate the dispersion stability of the slurries. The sediment volumes were measured after pouring 100 ml of each slurry into a graduated cylinder, which was then sealed and left to stand for 24 h prior to measurement. The electrokinetic behavior was determined for slurries containing 2 vol% pigment and 10^{-2} M KCl as a supporting electrolyte using an acoustophoretic spectrometer (DT-1200, Dispersion Technology Inc., USA). A drop-on-demand ink-jet printer (Michelangelo, LAC Co., Japan) with a nozzle having a solenoid coil was employed to decorate a tile. The resolution of the ink-jet printer was about 40 dpi, which was not superior to other ink jet printing systems with piezoelectric actuators. Although ink viscosities of up to 10 mPa · s and ink solid-loading of less than 10 vol% are considered suitable for other ink jet printers, the printer employed in this study was capable of using inks with higher viscosity and higher solid loading. The apparent viscosity of the typical ink applied in this study was around 80 mPa · s at 100 s^{-1}.

Fig. 1 shows the electrokinetic behavior of yellow pigment particles and the effect of pH on apparent viscosity for slurries with 65 wt% solid loading. The yellow pigment particles have an isoelectric point (iep) at pH 2.5, above which the zeta potentials of the particles become negative, and become gradually more negative with increasing pH. The velocity rapidly decreases with increasing pH up to pH 6, above which the viscosity becomes constant, corresponding to the region where the particles have high negative surface charge. In the acidic region, the increase in apparent viscosity represents the formation of a flocculate structure due to the weak electrostatic repulsive potential of the particles with small negative surface charge. However, these structures collapse in the neutral to basic region as the electrostatic repulsive potential overcomes the van der Waal's attractive potential.

TABLE I Characteristics of pigment powders

		Particle size distribution (μm)		
Pigments	Density (g/cm^{-3})	10%D	50%D	90%D
Yellow	4.2	0.45	0.88	2.0
Pink	4.0	0.48	0.92	2.1
Blue-green	4.8	0.40	0.62	0.92
Black	5.2	0.60	1.7	3.0

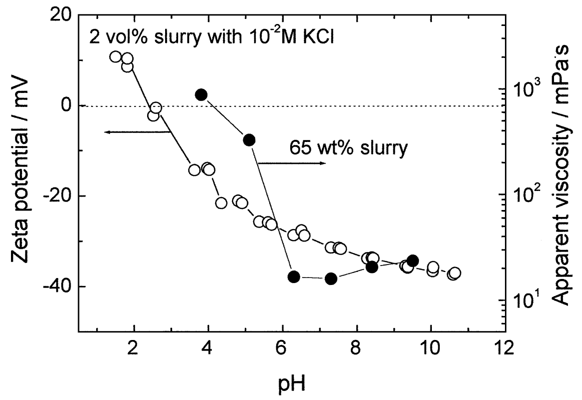

Figure 1 Electrokinetic behavior of yellow pigment particles and apparent viscosity for slurries with 65 wt% solid loading.

The flow behavior of the pigment slurries was dependent on the electrostatic properties of particles in the aqueous media, and the flow behavior of all pigment slurries could be enhanced by appropriately controlling the pH. The pH required to enhance the fluidity of the slurries was in the basic region.

Fig. 2 shows the electrokinetic behavior of the yellow pigment particles for various amounts of dispersant. The iep values of the particles do not shift after the addition of the dispersant. At pH 4–7, the surface charge of the particles decreases with increase in the amount of dispersant, but the surface charge is constant at pH > 7, with values about 10 mV more negative than without dispersant. The increase in surface charge indicates an improvement of surface properties due to adsorption of the dispersant on the surface of pigment particles. The dispersion of pigment particles in aqueous media was enhanced by the increase in electrostatic repulsive potential due to the adsorption of dispersant on the particles.

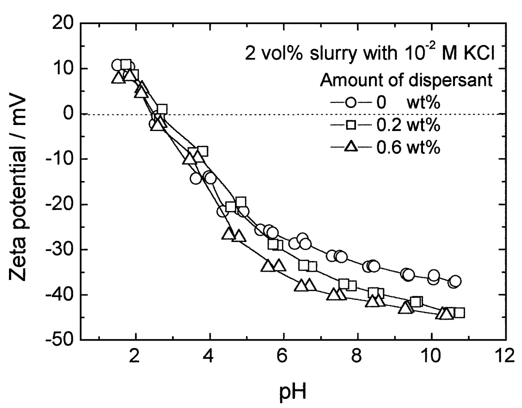

Figure 2 Electrokinetic behavior of yellow pigment particles as a function of dispersant concentration.

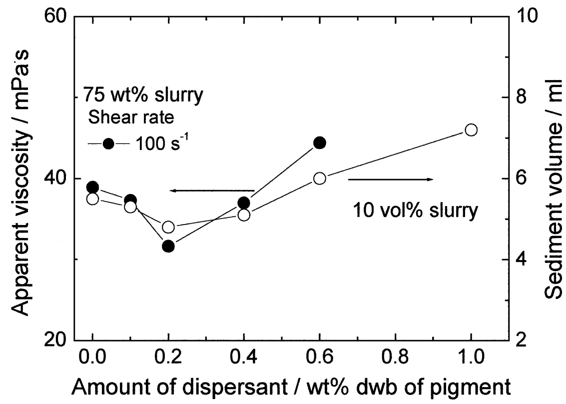

Figure 3 Variation in apparent viscosity and sediment volume of yellow pigment slurries with dispersant concentration at pH 8.

Fig. 3 shows the effects of dispersant concentration on the apparent viscosity for slurries with 75 wt% solid loading and the sediment volume for 10 vol% slurries. These slurries were adjusted to pH 8. The apparent viscosity decreases gradually down to a minimum at 0.2 wt% dispersant, and then increases with the dispersant amount. This enhancement of fluidity can be explained by promotion of the adsorption of the dispersant on the surface of the pigment powders due to the higher electrostatic repulsive potential. The optimum amount of dispersant with respect to achieving the optimum fluidity of the pigment slurries, was around 0.2 wt% dispersant (dwb pigment powder). The sediment volume exhibited a similar trend, becoming minimum at 0.2 wt% dispersant. Therefore, a slurry with 0.2 wt% dispersant is considered to be well-dispersed and fluidized. It should be noted, however, that even well-dispersed slurries tend to form dense sedimentation when stored for extended periods through the coagulation of particles. Avoiding the formation of dense sediment is desirable for ink-jet printing because such sediment is extremely difficult to re-disperse compared to loose, flocculated sediment.

In order to avoid the sedimentation of pigment particles, the viscosity of the dispersion media can be controlled by the thickener. Fig. 4 shows the effect of thickener concentration on the apparent viscosity of slurries with 50 wt% solid loading and the sediment volume for 10 vol% slurries. These slurries contained 0.2 wt% dispersant and were adjusted to pH 8.

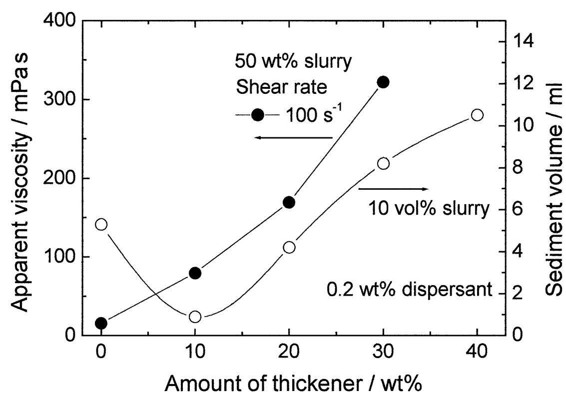

Figure 4 Variation in apparent viscosity and sediment volume of yellow pigment slurries with thickener concentration for 0.2 wt% dispersant and pH 8.

Figure 5 Photograph of tile decorated using the optimized aqueous pigment slurries.

The apparent viscosity of the pigment slurries gradually increases with the amount of thickener, while the sediment volume decreases to a minimum at 10 wt% thickener, and then increases gradually. If the role of the thickener is to increase the viscosity of the media, the particle sedimentation rate should become slower with increasing thickener content due to the increased friction resistance at the interface between the particles and dispersion media. At thickener concentrations of up to 10 wt%, the sediment volume was effectively reduced by the increased viscosity of the media. However, excess amounts of thickener were found to accelerate the flocculation of the slurries. It is expected that the ethanol contained in the thickener is responsible for this flocculation by reducing the dielectric constant in the media [9]. The optimum amount of thickener for preventing sedimentation of pigment particles is therefore around 10 wt%. At this level, the apparent viscosity of the slurry is 78 mPa · s, which is equivalent to that of the typical inks used for ink-jet printing.

The dispersion and fluidity of the other pigment slurries were evaluated in the same way. The solid loading of the four pigment slurries were prepared so as to be less than the typical ink viscosity. Table II lists the optimum preparation condition for the four kinds of pigment slurries. Four aqueous pigment slurries were prepared under these conditions of pH, solid loading, and amount of dispersant and thickener, and applied in the decoration of a tile (300 mm $\times$ 200 mm) using the present ink-jet printing system. The result is shown in Fig. 5. No blockages occurred during printing.

TABLE II Optimum preparation conditions for pigment slurries suitable for ceramic decoration by ink-jet printing

Pigments	pH	Dispersant (wt%)	Thickener (wt%)	Solid loading (wt%)
Yellow	8	0.2	10	50
Pink	11	0.2	10	40
Blue-green	10.5	0.3	10	40
Black	10–11	–	10	35

In summary, four kinds of pigment slurries were well dispersed and fluidized in basic region. In the basic region, the addition of 0.2–0.3 wt% dispersant of dwb of the pigment powders more enhanced the dispersion and fluidity of the four kinds of pigment slurries. The optimum amount of the thickener for preventing the sedimentation of pigment particles was around 10 wt% of the solvent. Applied in the decoration of a tile by present ink-jet printing system was achieved by the four kinds of pigment slurries under the optimum preparation condition.

References

1. E. SCHS, M. CIMA, P. WILLIAMS, D. BRANCAZIO and J. CORNIE, *J. Eng. Ind.* **114** (1992) 481.
2. J. GRAU, M. CIMA and E. SACHS, *Ceram. Ind.* **7** (1996) 22.
3. J. MOON, J. E. GRAU, V. KENZEVIC, M. J. CIMA and E. M. SACHS, *J. Amer. Ceram. Soc.* **85** (2002) 755.
4. S. J. KIM and D. E. MCKEAN, *J. Mater. Sci. Lett.* **17** (1998) 141.
5. J. WINDLE and B. DERBY, *ibid.* **18** (1999) 87.
6. H. YOKOYAMA, N. KATO, T. HOTTA, K. NAKAHIRA, M. NAITO and S. HIRANO, *Ceram. Trans.* **112** (2001) 363.

7. W. D. TENG, M. J. EDIRISINGHE and J. R. G. EVANS, *J. Amer. Ceram. Soc*. **80** (1997) 486.
8. P. R. JACKSON, in "Science of Whitewares," edited by V. E. Henkes, G. Y. Onoda and W. M. Carty (The American Ceramic Society, Ohio, USA, 1996) p. 395.
9. A. KITAHARA and A. WATANABE, "Electrical Phenomena at Interfaces" (Kyoritsu Shuppan, Tokyo, 1972) p. 122.

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