

Dispersion and stability of silver inks

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Different dispersants were used to develop ethanol-based silver inks for continuous ink-jet printing. Inks were made using varying amounts of dispersant and silver. Various parameters, such as sedimentation behaviour, sediment volume, half-value time and viscosity, were used to assess the dispersion and stability of these inks over 10 days.

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1. Introduction

In recent years, there has been a drive to achieve higher densities in electronic circuit packaging and assembly [1]. Increasingly, more manufacturers are turning to surface mount technology (SMT) which permits fine conductive tracks with narrow spacing between them and higher device populations on circuit boards [2].

Conventionally, the conductive track on the printed circuit board (PCB) is formed by etching away a layer of copper foil from the insulating substrate or plating a thick film of conductive metal on a chemically prepared insulating substrate [3]. In another development, sub-micrometer particles suspended in a well-dispersed ink was dispensed using a commercially available ink-jet printer to form structures layer by layer [4]. Although focus of this technique, which is known as Direct Ceramic Ink-Jet Printing, has been on ceramics and their composites [5–8], it can also be adapted for liquid metal ink to print circuitry. Jet printing has previously been used in the metallisation of hybrid microcircuits [9], solar cells [10, 11], superconducting circuits [12] and large area electronic structures [13] as well as printing of solder and flux for microelectronics packages [14] and flat display panels [15].

The advantages of direct ink-jet printing for circuitry are many. Solder bumps of 24 μm in size and 25 μm in line width have been made with a 100% yield [15]. In addition, jet printing, being a data driven and computer controlled operation, will result in a shorter lead time in design and production and more flexibility during manufacturing as it employs material addition rather than removal. These will inadvertently provide a higher degree of automation with better reproducibility and reliability. The low temperature during printing also minimises any unwanted reactions during processing. Moreover, with direct ink-jet printing, many of the processing steps can be eliminated with savings in devices and processing. Like the recently developed conductive lithographic film, this purely additive process can avoid the expensive and potentially polluting photo-resist and etching process [16, 17].

As in freeforming ceramic parts by jet printing, the development of ink-jet printing circuit tracks depends

critically on the formulation of metallic inks with good printing characteristics. The properties of the ink such as viscosity, electrical conductivity, surface tension and powder content, will affect deposition [18, 19]. The ink must also conform to the printer specifications and display stability throughout the printing process. The principle of handling of the ink is also applicable here, i.e., de-agglomeration of the powders and preparation of a stabilised suspension [20, 21]. The metal particles may be stable in the suspension because of their charge and consequent repulsion (electrostatic stabilisation) or because of the presence of adsorbed dispersant layers (steric stabilisation) [22]. Electrostatic stabilisation is thought to be most effective in high dielectric constant media, e.g., water. However, it is also important in non-aqueous solvents and it has been recognised that by manipulating the pH value in the solvent, the degree of dispersion and stabilisation can be altered [22, 23]. Steric stabilisation is more commonly used to create a stable suspension although it is not always possible to predict which forces dominate under a given set of circumstances [24]. It will be influenced by temperature, pressure, solvent composition, solvent quality, molecular architecture, number of anchoring groups, active surface site density, and colloid and organic concentrations in solution [25, 26]. The state of a sterically stabilised system can also be changed by manipulating the thickness of the adsorbed layer, the affinity of the dispersant to the surface, the amount adsorbed and the solubility of the dispersant in the medium [27].

Care also needs to be exercised during handling of metallic powders such as silver which is susceptible to oxidation and explosion in air. Of particular concern to conductive circuitry is low resistivity. This is related to the current carrying capacity of the track and it reduces with a decrease in the width of the conductor. After firing, the conductor on a finished PCB should exhibit good current-carrying capability and this is affected by the materials and processes used to form the conductors [28].

In this paper, we discuss our investigations on the dispersion and stability of silver ink prepared for printing in a continuous jet printer. Different amounts of

dispersants were used and the sedimentation behaviour and viscosity of the inks were studied.

2. Experimental procedure

The Ag powder used is Silver NanoPowder 562 (NanoPowders Industries, Kfar-Saba, Israel) which is an ultrafine powder used for conductive coatings, conductive inks and thick conductive pastes. The purity of the powder is 99.73% (by weight); the average particle size (d_{50}) and specific surface area are $1.6 \mu\text{m}$ and $3.62 \text{ m}^2 \text{ g}^{-1}$, respectively.

Three different dispersants, Atphos 3202 (density = 1097 kg m^{-3}), Atphos 3205E (density = 1097 kg m^{-3}) and Zephyrym PD7000 (density = 1020 kg m^{-3}) were used to disperse the Ag powder in industrial methylated spirit, IMS (Grade 74 OP, Fisher Scientific, Leicestershire, UK). All the dispersants were supplied by Uniqema (Everberg, Belgium) and are soluble in industrial methylated spirits (IMS).

Both Atphos 3202 and 3205E are phosphate ester-based, anionic dispersants with good stability in water and organic solvents. In addition, Atphos 3202 contains a higher content of phosphoric acid. When used in a polar solvent, the dispersant adsorbs onto the particles which electrostatically repel one another and this helps in achieving a stable colloidal suspension. However, in a non-aqueous medium with a low dielectric constant such as ethanol, the electrical barriers preventing aggregation are largely ineffective as the medium has a low ionic concentration and steric stabilisation prevails [22, 29]. By adjusting the ionic strength of the solution, it is possible to create substantial surface charge density in order for electrostatic stabilisation to predominate [23]. This can be done by adding an acid or a base [22].

Zephyrym PD7000 is primarily a polymeric dispersant made from a polyoxyalkene amine derivative. It is weakly cationic, which is attributed to the amine group, but behaves more like a non-ionic dispersant in terms of its dispersing mechanism [30]. As any polymeric dispersant, a molecule of Zephyrym PD7000 contains an anchor group and a polymeric chain. The anchor group is adsorbed onto the particle surface where a weak bond is formed; while the polymeric chain penetrates into the solvent and provides a barrier that prevents strong interactions between the particles.

In this study, the amount of dispersant used (*WPD*) in the Ag ink was varied as given in Table I. *WPD* is expressed as the percentage weight ratio between dispersant and the Ag powder and was varied between 0.5 and 5. The recommended usage of the dispersant is 0.5–0.9 wt% for optimum dispersion [30]. The dispersant was first subjected to ultrasonic disruption (Branson Sonifier 250, Branson Ultrasonic Corporation, Danbury, USA) in IMS for 120 s at 28 W in a 100 ml

Pyrex beaker. The Ag powder was then stirred into the mixture and ultrasonic disruption was carried out for another 360 s at 39 W. During mixing, the beaker was kept in an ice-water bath.

Gravitational sedimentation tests were used to determine the extent of particle flocculation by monitoring the evolution of the volumes of sediment, suspension and cloudy/clear liquid [31]. The test was performed over a period of $8.64 \times 10^5 \text{ s}$ (10 days) immediately after the ink was subjected to ultrasonic disruption. Three 10 ml samples of Ag ink were taken and transferred to Pyrex test tubes, which were pre-calibrated to an accuracy of $\pm 0.1 \text{ ml}$. The test tubes were stoppered, sealed and the inks were left undisturbed to settle throughout the period of study. The evolution of the volumes of sediment, suspension and cloudy/clear liquid was measured at regular intervals of 3600 s (1 hour) during the first eight hours of study and thereafter every $8.64 \times 10^4 \text{ s}$ (24 hours).

At time $t = 0$, $2.59 \times 10^5 \text{ s}$ (3rd day), $5.18 \times 10^5 \text{ s}$ (6th day) and $7.78 \times 10^5 \text{ s}$ (9th day), the viscosities of the inks undergoing sedimentation were measured, where $t = 0$ denotes the commencement of each sedimentation study. Viscosity measurements (repeated twice) were made at shear rates of 100, 500 and 1000 s^{-1} with a Haake RheoStress 150 rotational rheometer (Haake GmbH, Karlsruhe, Germany) using a C35/2 cone and plate sensor system (cone diameter = 35 mm, cone angle = 2°) at 20°C .

3. Results and discussion

3.1. Sedimentation behaviour

In this study, inks of 2 and 5 vol% of Ag were used. With the Ag concentration $> 1 \text{ vol}\%$, settling of particles is hindered by liquid moving upwards, hence Stokes law cannot be applied [26]. The sedimentation of the inks and hence their flocculation are influenced by a number of factors including particle size, particle-particle interaction, particle-solvent interaction, particle-solvent density difference and initial powder concentration [32].

A high sediment volume is an indication of increased flocculation. However, the determination of the final sediment volume is difficult as sedimentation can take a considerable time to reach equilibrium. The volume or height of the sediment normally varies asymptotically with time during sedimentation. The half-value time ($t_{1/2}$), which is the time at which the change in sediment volume has reached half its final value, may be used as a measure of the degree of flocculation in the dispersion [31].

The sedimentation behaviour of the Ag ink over a period of $8.64 \times 10^5 \text{ s}$ can be categorised into two basic modes as illustrated in Fig. 1. In Mode I, the sediment volume increased during sedimentation whereas it decreased in Mode II.

3.1.1. Mode I

At the beginning of sedimentation, only two layers were observed, corresponding to the sediment and the suspension. As sedimentation continued, the sediment volume increased (Fig. 1a) and a cloudy liquid containing

TABLE I Silver inks prepared using different dispersants

Dispersant	Silver (Vol%)	Dispersant/Ag weight ratio (%)
Atphos 3202	2	0.5, 1.5, 2.5, 5
Atphos 3202	5	0.5, 1.5, 2.5, 5
Atphos 3205E	5	0.5, 1.5, 2.5, 5
Zephyrym 7000	2	0.5, 1.5, 2.5, 5

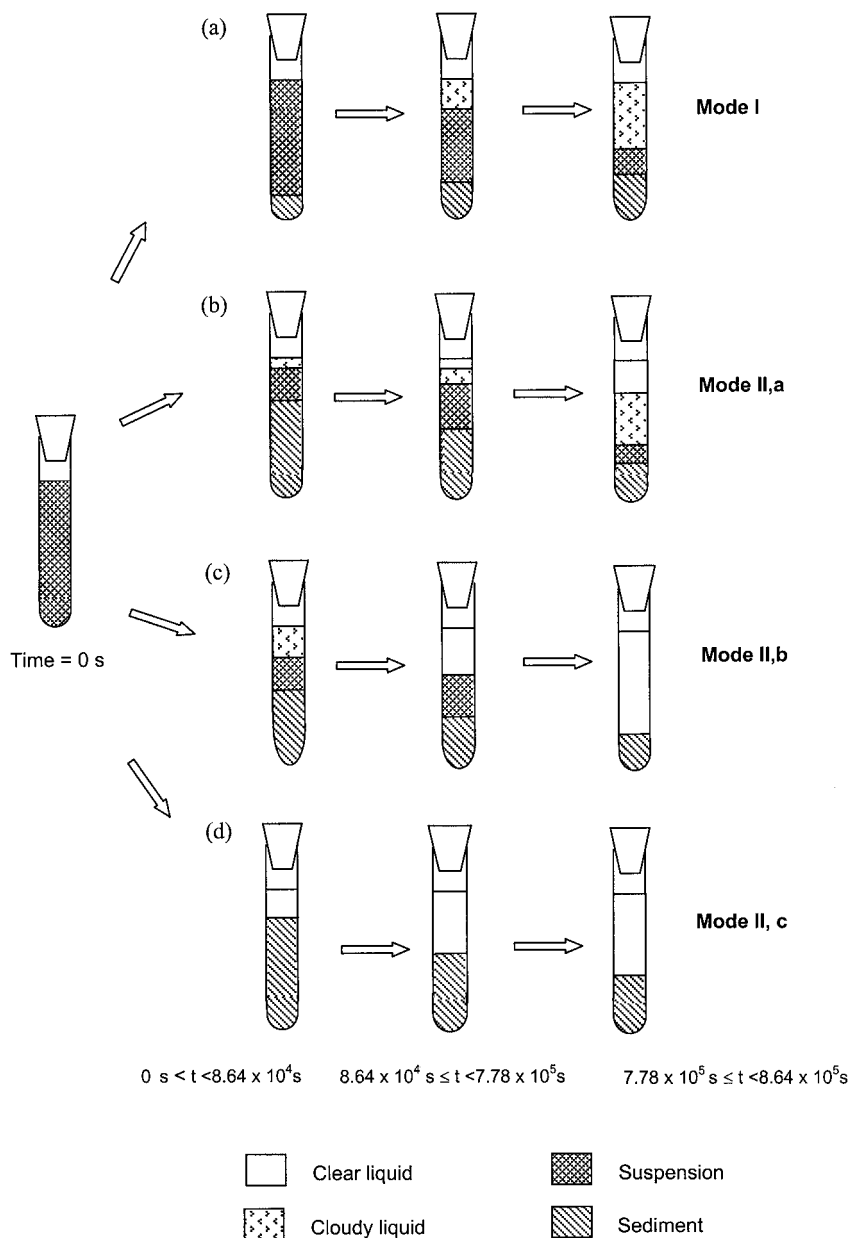


Figure 1 Classification of sedimentation behaviour of Ag inks: (a) Mode I, (b) Mode II, a, (c) Mode II, b and (d) Mode II, c.

Ag powder gradually separated from the suspension. At the end of the 10-day period, there were three zones in the test tube. Bell and Crowl [31] considered this type of sedimentation to be typical of a deflocculated dispersion.

3.1.2. Mode II

This mode, where the sediment volume decreased, is typical of a flocculated dispersion [31, 33]. Three patterns were noted. Mode (II, a) began with three layers: sediment, suspension and cloudy liquid (Fig. 1b). As sedimentation proceeded, a layer of clear liquid appeared at the top. At the same time, the volume of cloudy liquid increased at the expense of the suspension and became increasingly more dilute. At the end of the 10-day period, there was only a small amount of suspension existing between the sediment and the cloudy liquid.

As in Mode (II, a), Mode (II, b) also started with three layers (sediment, suspension and cloudy liquid) at the beginning of sedimentation. However, all the Ag

in the cloudy liquid zone gradually settled and this zone transformed to a layer of clear liquid above the suspension. The volume of suspension also decreased. By the end of the 10-day period, only the sediment and clear liquid remained in the test tube (Fig. 1c).

Mode (II, c) is typical of a completely flocculated dispersion (Fig. 1d). Once sedimentation started, most of the dispersed Ag powder settled immediately. This left a layer of clear liquid above the sediment within the first 8.64×10^4 s (24 hours).

The variation of the volumes of the sediment, suspension, cloudy liquid and clear liquid with time was recorded and an example is shown in Fig. 2. There was no clearly defined boundary between the cloudy liquid and clear liquid in the inks in which sedimentation proceeded according to Modes (II, a) and (II, b). As such, these two layers were considered as one zone in analysing the sedimentation curves. The behaviour of each ink is summarised in Table II.

Increasing the amount of dispersant in the ink increased flocculation, regardless of the type of dispersant

TABLE II Sedimentation behaviour and final sediment volume ($V_{s,10}$) of the inks

Dispersant	Ag loading (vol%)	$V_{s,10}$ at various WPD (ml)			
		0.5	1.5	2.5	5.0
Atphos 3202	2	0.9	2.0	2.9	2.4
		Mode (I)	Mode (I)	Mode (II, a)	Mode (II, c) ^a
Atphos 3202	5	3.3	4.2	3.3	4.4
		Mode (II, a)	Mode (II, b)	Mode (II, c) ^a	Mode (II, c) ^a
Atphos 3205E	5	2.8	3.1	3.2	3.3
		Mode (II, a)	Mode (II, a)	Mode (II, b)	Mode (II, c) ^a
Zephyrym PD7000	2	0.9	1.0	1.2	2.1
		Mode (I)	Mode (I)	Mode (I)	Mode (II, c) ^a

^aCompletely flocculated.

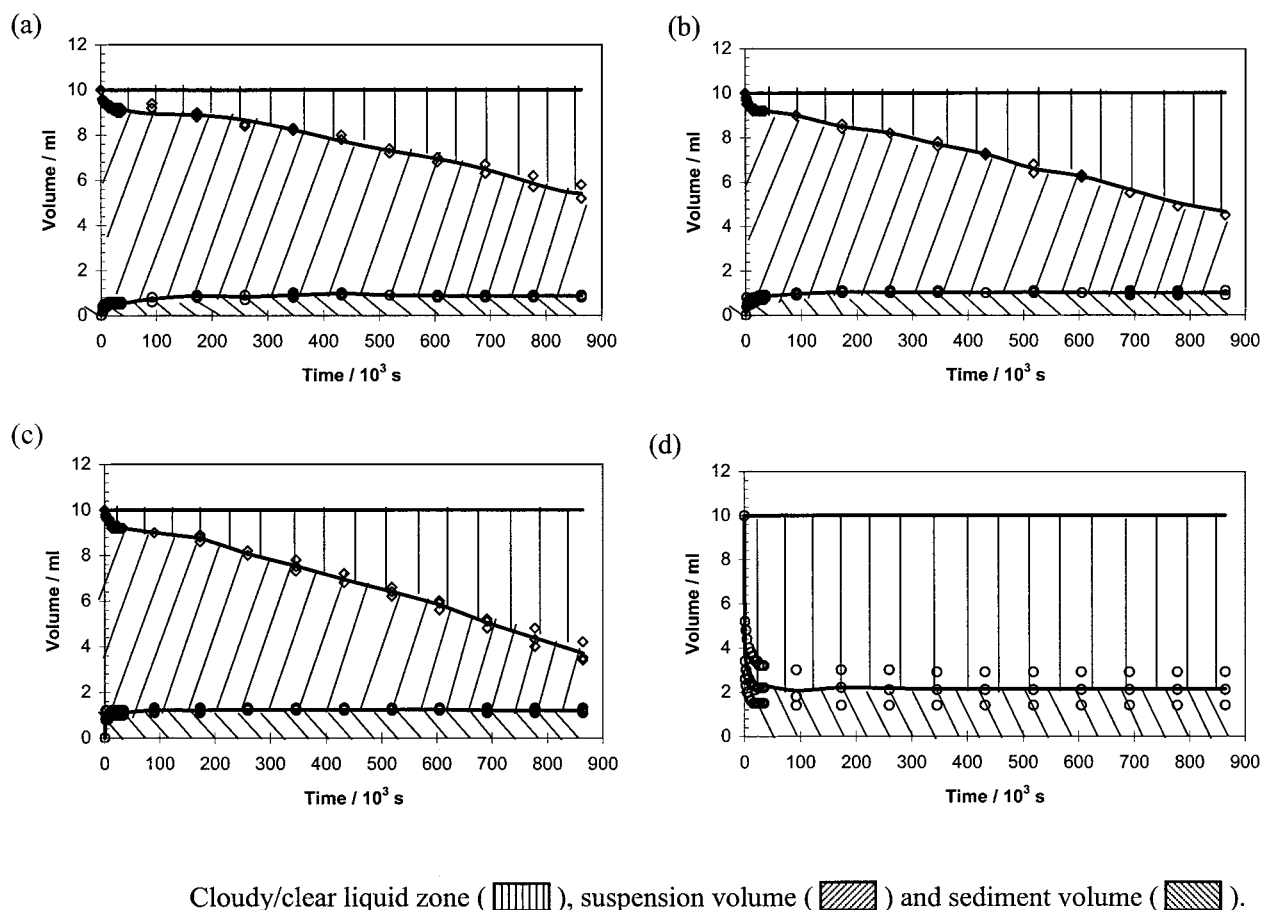


Figure 2 Example of typical sedimentation behaviour. In this instance, 2 vol% of Ag is dispersed in IMS and Zephyrym PD7000 with WPD values set at (a) 0.5, (b) 1.5, (c) 2.5 and (d) 5.

used and the vol% of Ag. At the highest WPD of 5, a completely flocculated ink was produced where most of the Ag powder settled within the first 8.64×10^4 s (24 hours) of sedimentation, leaving a layer of clear liquid above the sediment. The increased flocculation at higher WPD was also observed during the preparation of glass-based slurries [34] and may be attributed to the excess dispersant adsorbed on the monolayer of dispersant coating on the Ag particles. This can neutralise the effect of the monolayer, which provides optimum coverage of the particle, resulting in agglomeration [35]. With the stabilisation effect annihilated, the agitation force (by ultrasonic disruption), which was intended originally to disperse the powder, can cause agglomeration and lead to an increased volume of floc [34]. Hence, as shown in Table II, the sedimentation behaviour of the 2 vol% Ag inks that contained Atphos 3202 changed

from Mode (II, a) to Mode (II, c) as WPD was increased from 2.5 to 5. Similarly, sedimentation of inks containing Zephyrym PD7000 also digressed from Mode I to Mode (II, c) for the same increment in WPD.

When the amount of Ag powder in the ink was increased from 2 to 5 vol%, the inks became flocculated. This is illustrated in Table II, comparing the 2 and 5 vol% inks made using Atphos 3202. At 2 vol%, only two out of the four inks gave Mode II sedimentation, whereas all the four inks containing 5 vol% of Ag showed Mode II sedimentation. Irrespective of the amount of dispersant used, the sediment volume of the 5 vol% Ag ink dispersed using Atphos 3202 reached its final value within the first 8.64×10^4 s (24 hour). The final sediment volume at the end of the 10-day period was also more than that of the 2 vol% ink. Furthermore, flocculation was greater during the initial 8.64×10^5 s,

with the interface of the suspension-cloudy liquid moving downwards rapidly.

The increased flocculation in the 5 vol% ink might be due to insufficient ultrasonic disruption. The same level of energy (39W) used for the 2 vol% ink might not be insufficient to break down the agglomerates present in the 5 vol% ink and therefore, individual particles may not have been adequately coated with the dispersant. Although a higher level of ultrasonic energy may break down the agglomerates, it will inevitably increase the temperature. The effect of increased temperature on dispersion is rather complicated. It may lead to either an increase or decrease in adsorption on the particle surface, depending on the type of stabilisation mechanism and the dispersant-solvent interaction [30]. Furthermore, a higher level of ultrasonic energy will increase the mixing temperature close to the boiling point of the solvent, increasing volatility and thus changing the composition of the ink. Other high shear mixes such as twin or triple roll mill can be used to break down the agglomerates in the powder. However, processing aids such as plasticisers, binders and anti-oxidants are required to coat the powder surface to prevent its oxidation.

Comparing the two series of inks at 5 vol% of Ag, Atphos 3205E yielded a lower sediment volume than Atphos 3202. The former also promoted deflocculation. For example, it produced a partly flocculated ink at $WPD = 2.5$, but a completely flocculated ink was obtained with the same WPD of Atphos 3202. However, at both lowest (0.5) and highest (5) WPD levels, the same sedimentation modes were observed for these two series of ink. Overall, an increased amount of phosphoric acid (in Atphos 3202) did not improve the deflocculation of the Ag powder in IMS. This is probably due to the high ionic strength which compressed the double layer to such an extent that van der Waals attractions induced flocculation [23].

As shown in Table II, the use of Zephyrym PD7000 produced a series of deflocculated inks except when $WPD = 5$. The final sediment volume was less than that of ink made with Atphos 3202 at the same vol% Ag, except when $WPD = 0.5$. This indicates improved deflocculation with Zephyrym PD7000. When $WPD = 0.5$,

inks made with these two dispersants yielded the same final sediment volume. As in the case of the Atphos 3202, if the quantity of Zephyrym PD7000 was too high, a completely flocculated ink was obtained.

3.2. Degree of flocculation

The sediment volume (V_s), as a function of time, and $t_{1/2}$ were calculated using the following assumptions:

(i) In the case of Mode I sedimentation behaviour, V_s was approximated with a logarithmic law and at $t = 0$, $V_s = 0$.

(ii) In the case of Mode II sedimentation behaviour, V_s was approximated with a power law and at $t = 0$, $V_s = 10$ ml.

(iii) The sediment volume at equilibrium ($V_{s,eq}$) was taken to be approximately equal to that at the end of 10th day ($V_{s,10}$), i.e., $V_{s,eq} \approx V_{s,10}$.

Table III shows the $t_{1/2}$ values of the inks with the exclusion of those that were completely flocculated, i.e., exhibiting Mode (II, c) behaviour.

A smaller $t_{1/2}$ value indicates greater flocculation. Therefore, as shown in Table III, there was increased flocculation with increasing WPD in each series of ink. This agrees with the observations made during sedimentation tests (Table II). There was also a correlation between $t_{1/2}$ and $V_{s,eq}$, or $V_{s,10}$, in a series of ink, with $t_{1/2}$ inversely proportional to $V_{s,eq}$.

$t_{1/2}$ was used to further assess the degree of flocculation between different series of ink. With the largest $t_{1/2}$ value of 3.91×10^4 s, the 2 vol% ink made using Atphos 3202 with $WPD = 0.5$ was the least flocculated. Its $t_{1/2}$ value is about 4.5 times higher than that of a 2 vol% ink containing Zephyrym PD7000 at identical WPD . As a smaller $t_{1/2}$ is an indication of greater flocculation, the stabilisation provided by Atphos 3202 was more effective than that by Zephyrym PD7000. $t_{1/2}$ can also be used to compare two inks dispersed with different types and quantities of dispersant, such as the 5 vol% inks that are made using Atphos 3202 with $WPD = 0.5$ and Atphos 3205E with $WPD = 2.5$. For these inks, V_s offered no extra information as both inks gave approximately the same value. However, a higher $t_{1/2}$ in the

TABLE III $t_{1/2}$ of inks

Dispersant	Ag (vol%)	WPD	$V_{s,eq}$ (ml)	Equation fitted	$t_{1/2}$ (s)
Atphos 3202	2	0.5	0.9	$V_s = 0.15 \ln(t) + 0.09$	3.91×10^4
		1.5	2.0	$V_s = 0.41 \ln(t) - 0.21$	2.52×10^4
		2.5	2.9	$V_s = 3.35 t^{-0.04}$	7.20×10^{-4}
		5.0 ^a			
Atphos 3202	5	0.5	3.3	$V_s = 6.32 t^{-0.14}$	2.52×10^3
		1.5	4.2	$V_s = 6.10 t^{-0.9}$	6.12×10^2
		2.5 ^a			
		5.0 ^a			
Atphos 3205E	5	0.5	2.8	$V_s = 6.32 t^{-0.14}$	3.31×10^3
		1.5	3.1	$V_s = 6.17 t^{-0.15}$	2.38×10^3
		2.5	3.2	$V_s = 5.34 t^{-0.12}$	5.76×10^2
		5.0 ^a			
Zephyrym PD7000	2	0.5	0.9	$V_s = 0.11 \ln(t) + 0.36$	8.71×10^3
		1.5	1.0	$V_s = 0.09 \ln(t) - 0.58$	1.58×10^3
		2.5	1.2	$V_s = 0.05 \ln(t) + 0.99$	1.80×10^2
		5.0 ^a			

^aCompletely flocculated ink.

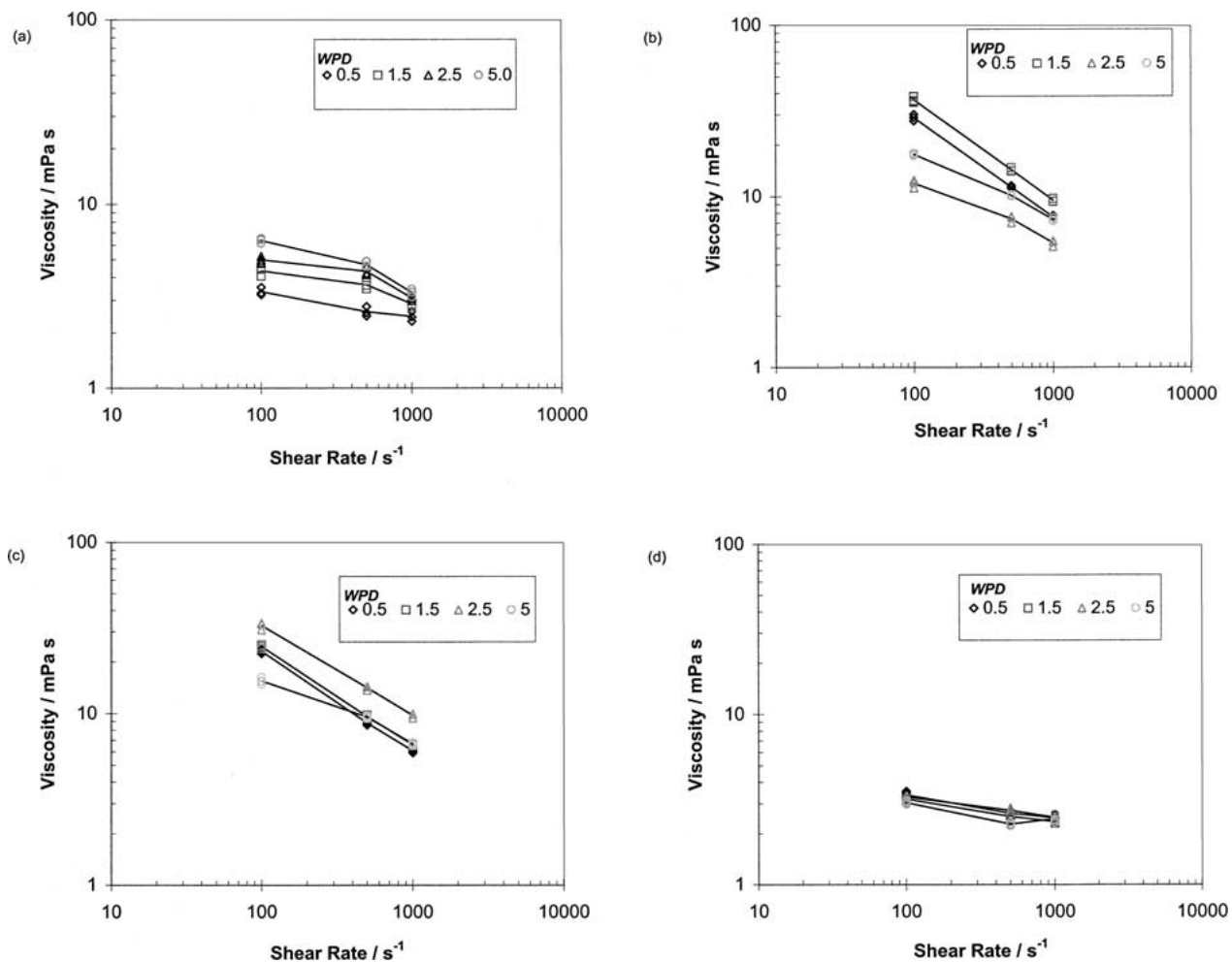


Figure 3 Variation of viscosity with shear rate in inks made using $WPD = 0.5, 1.5, 2.5$ and 5 at $t = 0$. (a) 2 vol% Ag and Atphos 3202, (b) 5 vol% Ag and Atphos 3202, (c) 5 vol% Ag and Atphos 3205E and (d) 2 vol% Ag and Zephyrym PD7000.

former indicates lesser flocculation. This also ties in with the qualitative descriptions of their sedimentation behaviour (Table II).

Increased flocculation with higher Ag content in the inks made using Atphos 3202 was also corroborated by $t_{1/2}$, which reduced drastically at 5 vol% Ag. The lower $t_{1/2}$ value of the inks made with Atphos 3202 compared with those prepared using Atphos 3205E also proves the detrimental effect of the higher ionic strength in the former which induces flocculation.

3.3. Rheological behaviour

The viscosities (at shear rate 1000 s^{-1}) of the dispersants were 684.5, 354.6 and 260.6 mPa s for Atphos 3202, Atphos 3205E and Zephyrym PD7000, respectively.

3.3.1. Effect of shear rate

Most of the inks displayed pseudoplastic flow behaviour within the range of shear rate investigated. The attraction between the Ag particles induced flocs in the ink, which caused solvent immobilisation [26]. Under the influence of a higher shear rate, the flocs broke down. This facilitated the mobility of solvent between the particles and gave a lower viscosity. The viscosity of the inks containing 2 vol% Ag were closer to

Newtonian (Fig. 3a and d) than those at 5 vol% (Fig. 3b and c). This was due to a lower Ag content, thereby giving reduced powder interaction and lesser flocs.

An exception to the pseudoplastic behaviour was the ink made with Zephyrym PD7000 and $WPD = 5$, which displayed dilatant behaviour (Fig. 3d). At the end of viscosity measurements of this ink, powder was found to segregate at the centre of the plate of the rheometer, circumscribed by a rim of solvent. The segregation was induced under the action of high shear rate and was probably due to the weak interaction between the solvent and Ag powder. This could have led to the 'apparent' increase in viscosity at 1000 s^{-1} . However, viscosity measurements made using cone and plate at high shear rates can be unreliable due to the outward movement of suspension.

3.3.2. Effect of WPD

No general trend could be derived between the viscosity of the inks and the amount of dispersant. This appears to be dependent on the mode of stabilisation (electrostatic or steric), powder loading and the state of dispersion in the ink (flocculated or deflocculated). For the 2 vol% inks containing Atphos 3202, a higher WPD can result in a greater number of flocs or bigger flocs [34] and either of these cause viscosity to increase as shown in Fig. 3a.

At a higher powder loading of 5 vol% (Fig. 3b), the completely flocculated inks ($WPD=2.5$ and 5) appeared to be less viscous than the partly flocculated inks ($WPD=0.5$ and 1.5). Within each “subset” of ink, the viscosity increased with WPD . In the “subset” of inks that was completely flocculated, the flocs could be touching each other. For flow to start, sufficient stress or strain must be applied to overcome the bonds between the individual flocs [26]. Thus, the increase in viscosities observed could be attributed to an increased number of flocs, bigger flocs and the free dispersant molecules that remained in the solvent [34].

The same observation was made in the series of ink dispersed with Atphos 3205E (Fig. 3c). For inks with $WPD < 5$, which were not completely flocculated, the viscosity increased with WPD . Ink with $WPD = 5$ was completely flocculated and behaved in a similar manner to the flocculated inks containing Atphos 3202. The ink appeared to be less viscous than those with $WPD < 5$.

There was little variation in the inks dispersed with Zephyrym PD7000 as WPD was increased (Fig. 3d). This correlates well with the small changes in sediment volume with WPD (Table II). The near-Newtonian behaviour also indicates that the interaction between the powder particles in the ink was weak and hence lesser flocculation resulted.

3.3.3. Aging

In the present study, viscosity was measured every 2.59×10^5 s (3 days) to investigate ink stability. Viscosity of the 2 vol% Ag inks dispersed with various WPD of Atphos 3202 at $t = 0, 2.59 \times 10^5$ s, 5.18×10^5 s and 7.78×10^5 s are shown in Fig. 4a–d. Similar results for Zephyrym PD7000 are presented in Fig. 5a–d. As for the 5 vol% inks, the viscosity measurements made at $t = 2.59 \times 10^5$ s, 5.18×10^5 s and 7.78×10^5 s were mostly < 2 mPa s, which is the lower measurement limit of the rheometer. Hence, they are not reported here. In these inks, the flocculation was so rapid that most of the Ag powder settle in 5.18×10^5 s (6 days), leaving a dilute ink of low viscosity that comprised mainly of solvent.

At $WPD = 0.5$, the ink made using 2 vol% and Atphos 3202 exhibited pseudoplastic behaviour at $t = 0, 2.59 \times 10^5$ s, 5.18×10^5 s, and 7.78×10^5 s (Fig. 4a). From 2.59×10^5 s (day 3) onwards, the ink showed a stable viscosity value. From 0 to 2.59×10^5 s, there was an 18% reduction in viscosity at a shear rate 1000 s^{-1} , whereas only a 2% variation was detected between 2.59×10^5 – 7.78×10^5 s. This agrees well with the time taken for the sediment volume to achieve its constant value.

Reduced stabilisation at higher WPD values of 1.5 and 2.5 was also noted in inks made using

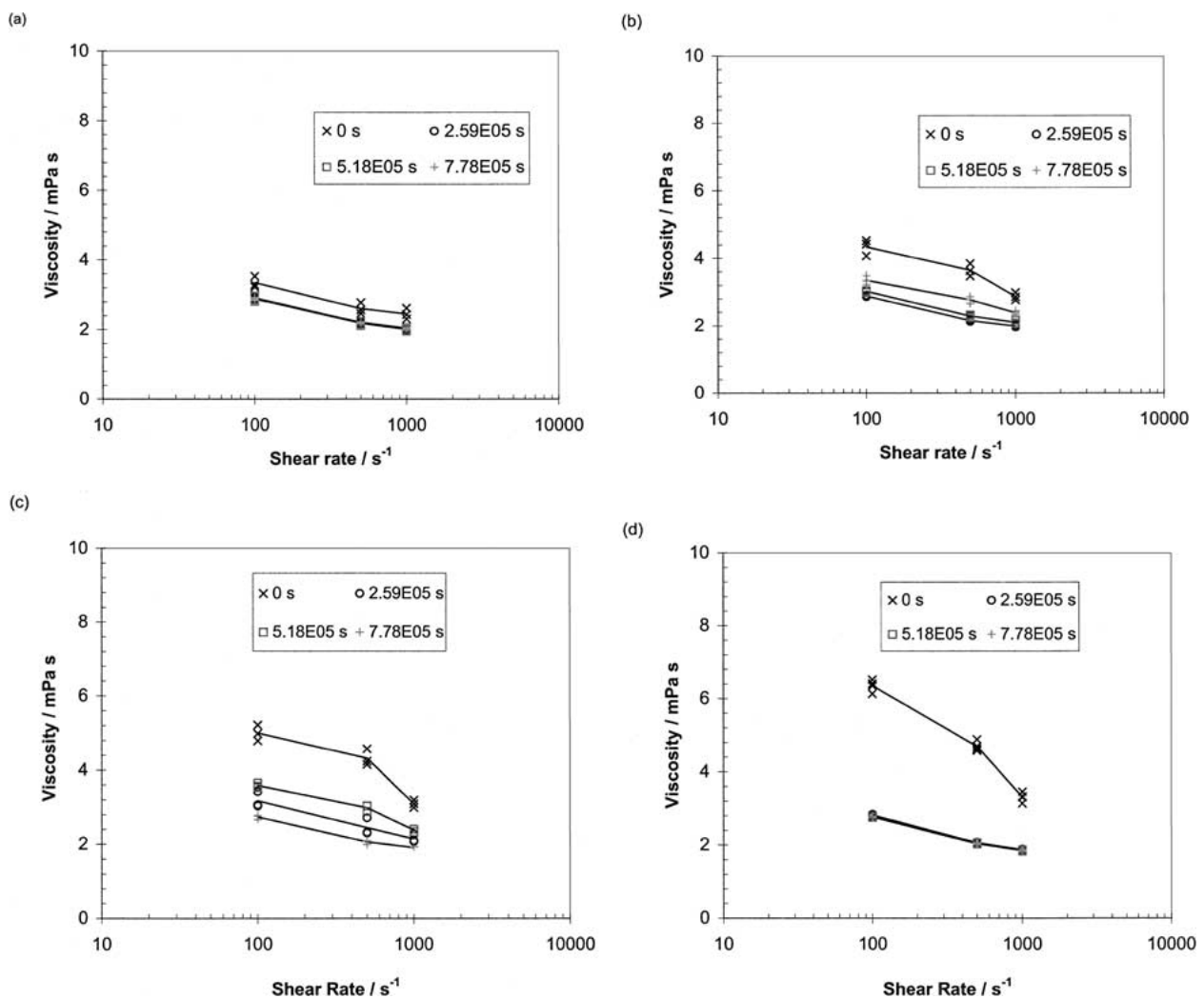


Figure 4 Viscosity-shear rate graphs of 2 vol% Ag inks made using Atphos 3202 and different WPD values: (a) 0.5, (b) 1.5, (c) 2.5 and (d) 5.

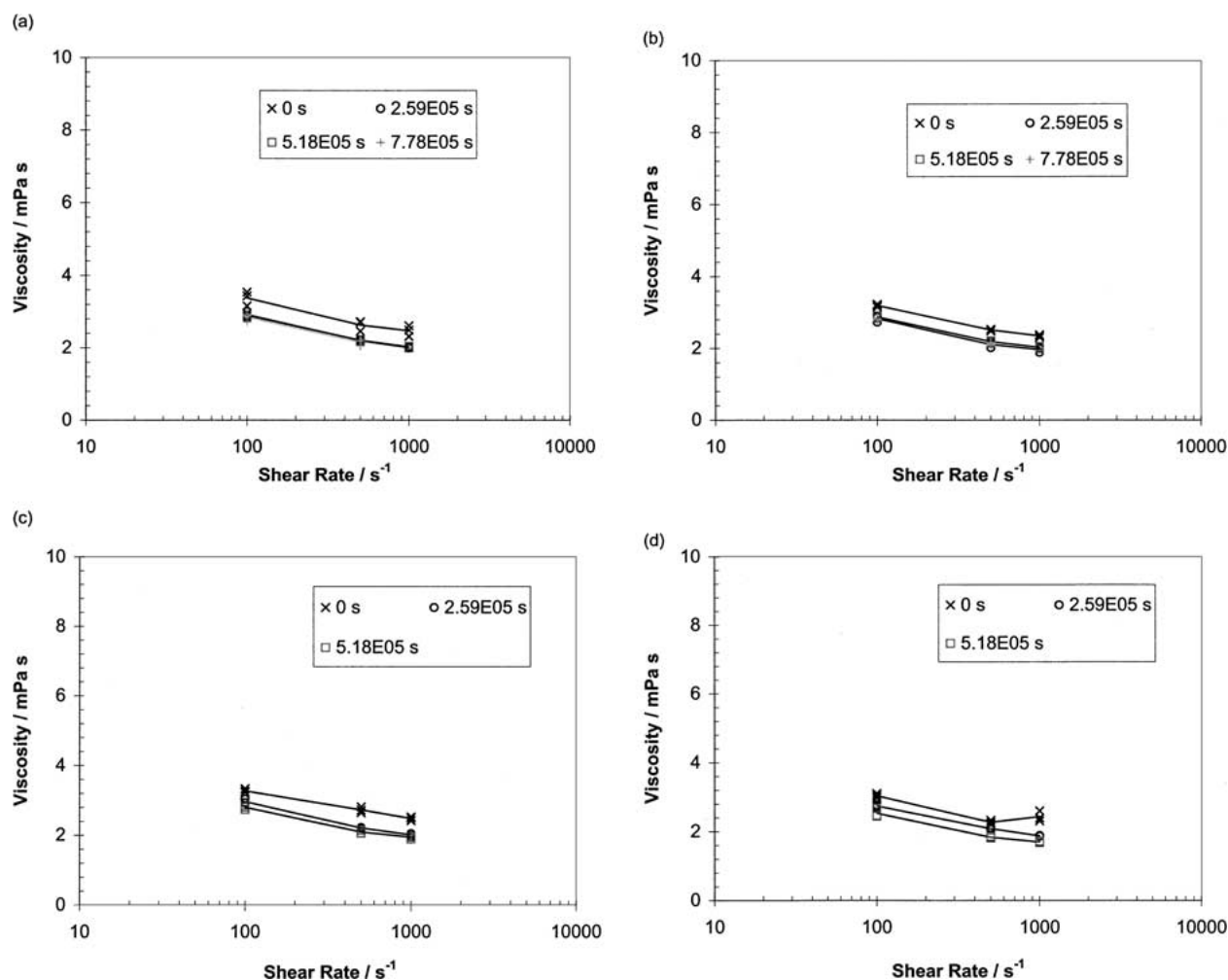


Figure 5 Viscosity-shear rate graphs of 2 vol% Ag inks made using Zephyrym PD7000 and different WPD values: (a) 0.5, (b) 1.5, (c) 2.5 and (d) 5.

2 vol% Ag and Atphos 3202, with the viscosity values fluctuating appreciably between $t = 2.59 \times 10^5$ s and $t = 7.78 \times 10^5$ s. Moreover, the reduction in viscosity between $t = 0$ to $t = 2.59 \times 10^5$ s (Fig. 4b and c) was significant. It amounted to 31% at 1000 s^{-1} for both inks, compared to only 18% at $WPD = 0.5$. These two inks also have smaller $t_{1/2}$ values than the ink with $WPD = 0.5$ (Table III), indicating greater flocculation which induced faster settling of the Ag powder. Furthermore, the flow behaviour of these two inks was increasingly Newtonian after $t = 2.59 \times 10^5$ s. For example, at $WPD = 2.5$, the percentage drop in viscosity on increasing the shear rate from 500 to 1000 s^{-1} was only 7.5, 8 and 13% for measurements taken at $t = 2.59 \times 10^5$ s, 5.18×10^5 s and 7.78×10^5 s, respectively; but this was 21% at $t = 0$.

From $t = 2.59 \times 10^5$ s to $t = 7.78 \times 10^5$ s, the ink containing 2 vol% Ag and Atphos 3202 with $WPD = 5$ contained a large proportion of the solvent, from which the Ag powder separated and flocculated to form the sediment. There was thus little changes in the viscosities measured during this period, as shown in Fig. 4d.

Most of the inks made using 2 vol% Ag and Zephyrym PD7000 displayed pseudoplastic behaviour. In these inks with $WPD < 5$, the percentage reduction viscosity from $t = 0$ to $t = 2.59 \times 10^5$ s was 10–19%. However, this was <5% from $t = 2.59 \times 10^5$ s to $t = 5.18 \times 10^5$ s and $t = 2.59 \times 10^5$ s to $t = 7.78 \times 10^5$ s. This small

variation in viscosity indicates that the inks were stable by $t = 2.59 \times 10^5$ s.

4. Conclusions

(i) Three dispersants, Atphos 3202, Atphos 3205E and Zephyrym PD7000, were used to disperse 2 and 5 vol% of Ag powder in industrial methylated spirit. Deflocculated and flocculated inks were produced. Generally, 2 vol% inks made with low dispersant contents ($\sim 0.5 \text{ wt}\%$) were deflocculated. Regardless of the type of dispersant used and the vol% of Ag, increasing the amount of dispersant beyond 0.5 wt% increased flocculation in the inks.

(ii) The half-value time ($t_{1/2}$) was used successfully to assess the degree of flocculation in the Ag inks. A larger $t_{1/2}$ value is an indication of lesser flocculation and ties in well with the sedimentation results of the inks and their final sediment volumes. The 2 vol% ink made with 0.5 wt% of Atphos 3202 had the highest $t_{1/2}$ value of 3.91×10^4 s. This ink also yielded the lowest sediment volume. Varying amount of Atphos 3202 was also used to prepare Ag inks at 2 and 5 vol%. With the same ultrasonic disruption energy input during preparation of the inks, it was found that flocculation was more significant in the 5 vol% ink.

(iii) 5 vol% Ag inks made using a less acidic dispersant such as Atphos 3205E (compared with Atphos 3202), gave a lower final sediment volume and larger

$t_{1/2}$ values. These inks were less flocculated. It is thus possible to alter the state of flocculation in the Ag ink by adjusting the pH of the inks.

(iv) As prepared, most of the inks displayed pseudo-plastic flow behaviour. The variation of their viscosities with respect to the amount of dispersant used was found to depend on the powder loading and the state of dispersion in the ink. Two Ag inks at 2 vol% prepared with 0.5 wt% of Atpfos 3202 and Zephyrym PD7000 gave stable sediment volumes after 8.64×10^4 s (1 day) and stable viscosities after 2.59×10^5 s (3 days).

(v) Based on the their $t_{1/2}$ values, inks prepared with Atpfos 3202 were less flocculated than those with Zephyrym PD7000. The $t_{1/2}$ value of the former was 4.5 times higher than that of the latter.

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