EFFECT OF MILLING AND DISPERSANT ADDITION ON THE PHYSICAL PROPERTIES, PRINTABILITY, AND DROP FORMATION OF INKJET INKS

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ABSTRACT

The formulation and development of inkjet inks based on ceramic materials entail control and adjustment of their physical properties, with a view to assuring printability in drop-on-demand (DOD) inkjet printheads.

The present paper seeks to provide basic, fundamental insight, in a real environment, into ceramic inkjet ink behaviour during the drop formation and printability stage, using industrial printheads, to understand the effect of milling and dispersant addition on the flight behaviour of the formulated inks.

For this, alumina-based ceramic inkjet inks were formulated and developed, analysing in detail the influence of their physico-chemical properties, measured under operating conditions, on the ease of ejection and flight behaviour of the drops generated during the printing stage. This study enables the behaviour resulting from new developments to be determined and predicted, in order to provide new and innovative tools for designing and formulating inkjet inks, with assurances of use in digital technology for adapting to industrial working conditions (line speed, jetting frequencies, etc.).

1. INTRODUCTION

1.1. CURRENT SITUATION AND TECHNOLOGICAL CONTEXT

The irruption of inkjet digital printing technology into the ceramic sector, which until a few years ago used screen printing, flexography, and rotogravure technology, has allowed ceramics manufacturers, among others, to reduce manufacturing costs, increase productivity, and expand their new product offer for the market. Therefore, nowadays, research into and development of processes in which digital technology is not found makes little sense, as the competitive advantages that digital technology provides are fully justified by the infinite demand for novel products, designs, functions, and applications that can be obtained on ceramic substrates.

In light of the above, ink is a key component because, thanks to the great variability in the materials to be used (inorganic pigments, frits, refractory solids, plastic raw materials, additives, solvents of different chemical nature, etc.) and the current technical proposals on the market, it is possible to raise the added value of ceramic products, in which quality and degree of personalisation prevail over such essential matters as the economic factor.

Although the number or rather the different types of commercial inks available on the market is quite notorious, it is necessary to understand the variables in the formulation and printing process that will deliver optimum levels of quality, without compromising final ceramic product finish at all.

In view of the above, an obvious question arises:

How can an ink be deemed optimum so that it will deliver high quality in the design printed on the work substrates?

Seeking to be objective and bearing in mind the dynamic mechanisms that occur in the ejection and drop formation stages in the printing process via an inkjet printhead, the answer appears clear. Indeed, the answer to the question lies in the high-speed generation of individual drops, without any interruption or alteration of their shape, mass, and directional movement from the injector plate to the substrate to be decorated. (See figure 1)

However, a further question emerges that requires clarification:

Why do printing problems therefore continue to exist, if it seems obvious that the only thing that needs to be done is to generate individual, unalterable drops?

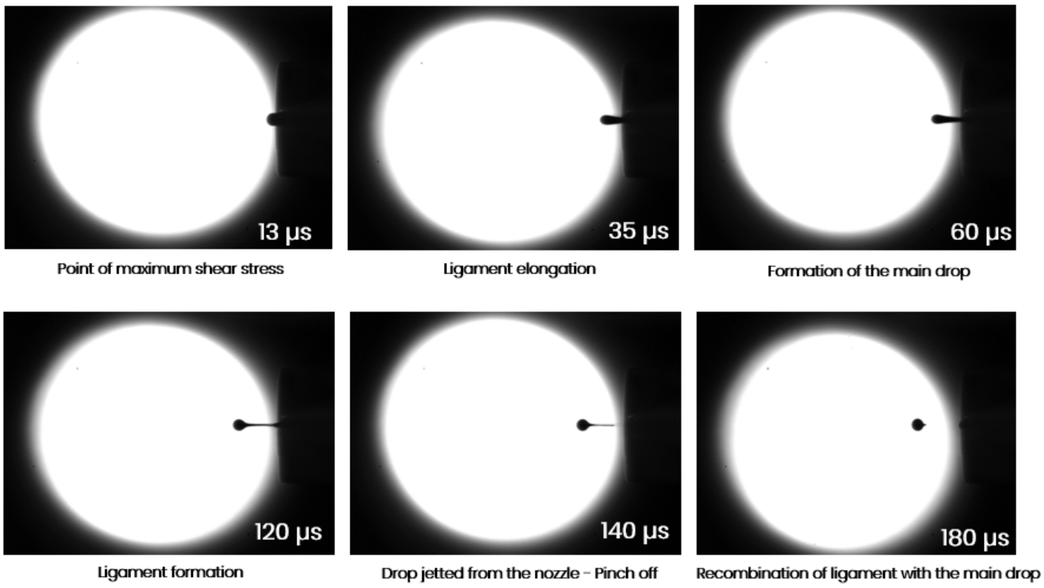

Figure 1. *Behaviour of a drop of ink in flight from a MicroFab inkjet injector.*

To answer this question it is necessary to resort to fluid dynamics. In this sense, in accordance with the simplified expression that describes the behaviour of a liquid through a small opening (Eq. 1), it can observed how the inertia forces (described by Bernoulli), the viscous forces (described by Poiseuille), and the capillarity forces resulting from the liquid's surface tension are going to define the minimum pressure (P) required to generate a continuous flow of ink through the opening considered. If these forces are not overcome, flow will obviously not be possible. [1],[2]

$$P = \frac{\rho \cdot v^2}{2} + \frac{32 \cdot \mu \cdot v \cdot l}{d^2} + \frac{2 \cdot \gamma}{d} \qquad (Eq. 1)$$

where:

l: Length of the opening or injector.
d: Diameter of the opening or injector.
ρ: Suspension density.
μ: Suspension viscosity.
γ: Suspension surface tension.
v: Suspension velocity.

In view of the above and returning to the question, the answer clearly appears to be related to the physical properties of the working inks, as well as to the geometric characteristics of the injector considered.

Therefore, as a result of the great number of physical and geometric parameters involved in inkjet drop formation and printability processes, different methodologies may be found in the state-of-the-art that allow the approximate, general behaviour of the inks inside a printing injector to be verified. In this sense, it is possible to determine the joint influence of the properties set out above, known as dimensionless modules (Reynolds Number, Weber Number, and Ohnesorge Number). [3],[4]

1.2. NEED FOR THE PROPOSED RESEARCH

A literature survey confirmed the existence, within the scientific community, of a widespread consensus and approval regarding the use of dimensionless modules (and their representation), as an easy, useful approach to inkjet ink formulation. [3],[4]

However, all the experimental development and theoretical work carried out to prepare this was performed using drop generators (Microfab and Solidscape), whose piezoelectric actuator exhibited a different tube geometry from that used in ceramic tile decoration, the inks used moreover being an idealised and very summary representation (ideal Newtonian behaviour, low or zero polymer content, etc.) of the suspensions currently used in the ceramic industry, which distances it from the real physical properties, as well as from the behaviour of actual inks in an inkjet printhead. [5],[6]

This thus highlights the unsuitability of the approach used, which makes it difficult to really apply it to ceramic suspensions, these being understood as complex systems of concentrated suspensions (often, multi-component) that can, in turn, generate non-linear behaviour during the ejection process, contributing to the formation of instabilities (ligaments and satellite drops) and, as a result, compromising key parameters such the velocity and volume of the generated drops. [5],[6],[7],[8]

New studies and major developments are therefore needed that will provide insight into the key characteristics and parameters in ceramic inkjet ink formulation with a view to assuring appropriate behaviour throughout the printing process. [5]

This study has analysed in detail the influence of inkjet ink milling conditions, as well as the addition of different percentages from a dispersant additive, in order to understand their effect on the physical properties of the formulated inks and on the behaviour in flight of the drops generated during the digital printing process. A number of empirical relationships were thus established that allow different printing process variables to be correlated with physical parameters such as prepared suspension density.

2. EXPERIMENTAL

2.1. MATERIALS USED

The materials used in formulating the test inkjet inks are detailed in Table 1.

Component	Description	Functionality
Solvent	100% Fatty acid ester	Milling and dilution solvent
Additive	Polymer dispersant	Synthetic polymer
Solid	Calcined alumina (99.89%)	Reactive alumina alpha phase, with low sodium and silica content. Specific surface area: 7 m^2/g (BET surface area); Particle size (d_{100}): 21.2 µm.

Table 1. *Constituents used in formulating the test inkjet inks.*

2.2. FORMULATION OF THE DEVELOPED INKJET INKS

The compositions of the inkjet inks developed with the previous methodology and the energy consumption in the milling stage are detailed in Table 2.

Ref. OIDL-Al	Solid (wt%)	Solvent (wt%)	Dispersant (wt%)	Consumption (kWh/kg solid)
001	56.60	37.70	5.70	0.93
002	55.70	37.10	7.20	0.93
003	54.70	36.50	8.80	0.93
011	57.60	38.40	4.00	1.23
013	57.60	38.40	4.00	0.93
014	58.60	39.10	2.30	0.93
015	57.60	38.40	4.00	0.69
016	57.60	38.40	4.00	1.47
017	59.40	39.60	1.00	0.93

Table 2. *Formulations of the test ceramic inkjet inks.*

Each of the above inks was diluted with the same milling solvent to final densities of 1.40, 1.35, 1.30, 1.25, 1.20 and 1.15 g/cm^3.

2.3. PHYSICAL CHARACTERISATION OF THE DEVELOPED INKS

The physical characterisations carried out on the developed inks to determine the technical feasibility of the developments in regard both to storage and behaviour inside an inkjet printhead were as follows:

- Viscosity by optical microfluidic rheometry using a Formulaction FLUIDICAM-RHEO rheometer. A channel (GAP) of 150 was used, reaching maximum shear rates of $1.5 \cdot 10^4$ s^{-1}, and operating at 40°C.
- Density using an Anton-Paar DMA 35 portable densimeter.
- Particle size distribution with a Malvern Mastersizer 3000 instrument.
- Colloidal stability after 10 days at 50ºC using the multiple light scattering (MLS) technique.
- Suspension destabilisation for 40 days, every 10 days consecutively alternating cycles of high temperature (50 ºC) exposure with cycles of low temperature (4ºC) exposure. After this time, redispersion and renewed determination of viscosity.
- Experimental printability/behaviour in flight at 40 °C with a Jetxpert stroboscopic system, coupled to a XAAR 1003 GS12C printhead. In all cases, the same "waveform" was used (6 kHz), only modifying the electric working voltage.

3. RESULTS

3.1. EFFECT OF DISPERSANT ADDITION ON THE PHYSICAL PROPERTIES OF THE FORMULATED INKS

Table 3 lists the physical properties of the developed inkjet inks using different dispersant additions (1.0%, 2.3%, 4.0%, 5.7%, 7.2%, and 8.8%, by weight) and an energy consumption of 0.93 kWh/kg solid.

As may be observed, generally, as additive content increased, suspension viscosity rose, the rise increasing with the added amount and with suspension density. See the addition values at 4.0% by weight and densities above 1.30 g/cm^3. (See Figure 1)

Dispersant (wt%)	OIDL-AI	Density (g/cm^3)	Viscosity 40ºC and 15,000 s^{-1} (mPa·s)	D_{100} (µm)	Sedimentation 50ºC (%) MLS	Agglomeration 50ºC (%) MLS
1.0	017-40	1.400	17.3	0.767	6.50	0.50
	017-35	1.350	15.5		6.50	0.55
	017-30	1.300	14.1		6.60	0.65
	017-25	1.250	13.1		6.50	0.55
	017-20	1.200	11.4		6.70	0.60
	017-15	1.150	10.4		6.80	0.65
2.3	014-40	1.400	17.5	0.766	6.00	0.55
	014-35	1.350	15.8		6.50	0.50
	014-30	1.300	14.1		6.60	0.65
	014-25	1.250	13.1		6.50	0.60
	014-20	1.200	11.5		6.60	0.65
	014-15	1.150	10.5		6.70	0.65
4.0	013-40	1.400	17.7	0.766	6.00	0.50
	013-35	1.350	15.8		6.30	0.50
	013-30	1.300	14.3		6.60	0.55
	013-25	1.250	13.2		6.50	0.55
	013-20	1.200	11.7		6.50	0.55
	013-15	1.150	10.8		6.60	0.60
5.7	001-40	1.400	23.7	0.760	6.00	0.50
	001-35	1.350	22.3		5.50	0.40
	001-30	1.300	18.5		5.60	0.40
	001-25	1.250	17.6		5.95	0.40
	001-20	1.200	15.8		6.10	0.45
	001-15	1.150	14.1		6.20	0.40
7.2	002-40	1.400	28.5	0.767	5.50	0.30
	002-35	1.350	24.6		5.40	0.45
	002-30	1.300	22.9		5.50	0.40
	002-25	1.250	20.7		5.50	0.40
	002-20	1.200	19.1		5.90	0.35
	002-15	1.150	18.3		6.10	0.30
8.8	003-40	1.400	35.6	0.767	4.20	0.25
	003-35	1.350	31.3		4.20	0.30
	003-30	1.300	28.1		4.50	0.30
	003-25	1.250	25.7		4.10	0.25
	003-20	1.200	23.8		5.00	0.25
	003-15	1.150	21.6		5.60	0.30

Table 3. *Physical characterisation of the formulated inks. Effect of dispersant addition (0.93 kWh/kg solid).*

In regard to particle size, the addition of larger amounts of dispersant did not appear to lead to variations in the final values.

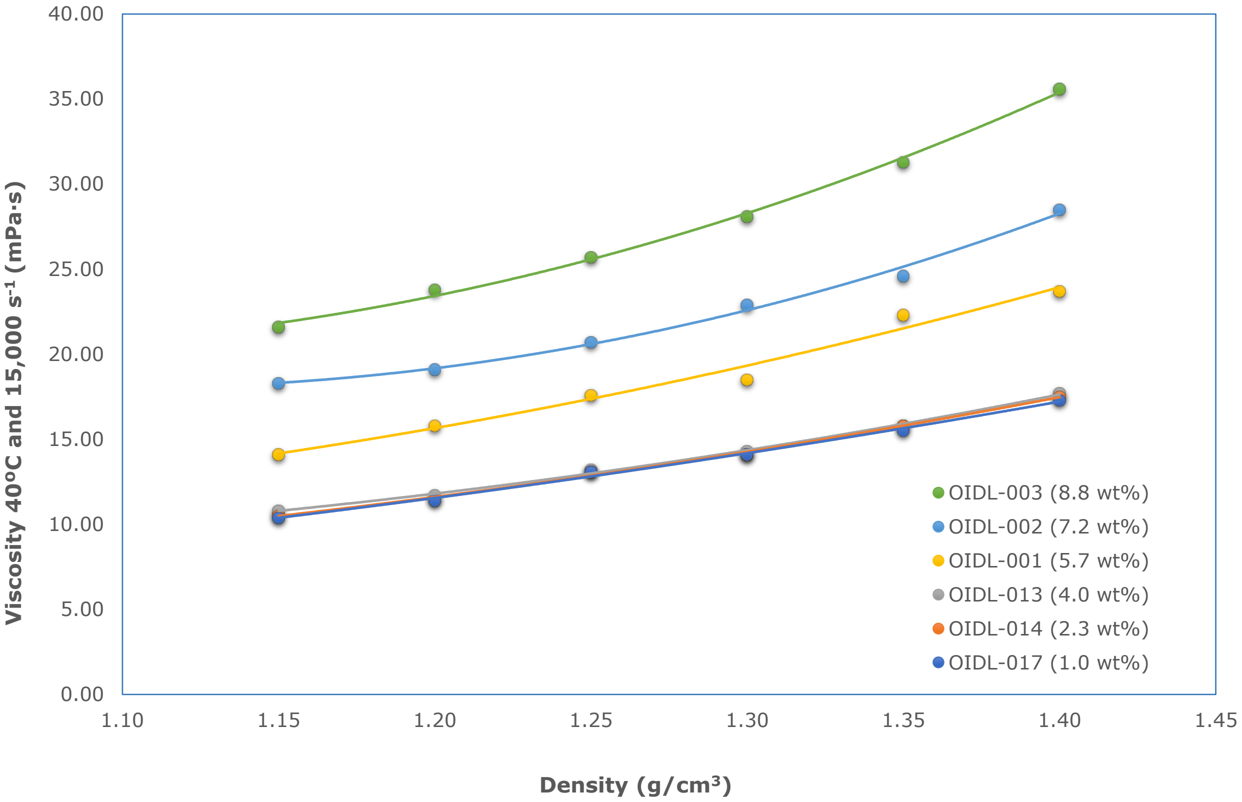

Figure 1. *Effect of dispersant addition on viscosity of the formulated inks at different densities and 0.93 kWh/kg solid.*

In relation to the colloidal stability of the developments using the MLS technique, as the dispersant addition increased, ink behaviour also improved in regard to particle sedimentation and agglomeration as a result of higher suspension viscosity.

Despite this trend, it would not appear logical to conclude that a greater amount of dispersant was the optimum and most efficient solution for improving the colloidal stability of the suspensions. Indeed, the results in Table 4 show that, after the destabilisation/accelerated weathering tests, the suspensions prepared at 1.0%, 2.3%, 5.7%, 7.2%, and 8.8% dispersant by weight, exhibited higher viscosity values than those initially obtained with the MLS technique, with the exception of the samples prepared at 4.0% by weight, which remained unchanged with exposure time and temperature. It thus appears certain that dispersant additions below 4.0% by weight sufficed to stabilise the particles in the suspension (causing the system to flocculate), whereas above this value there was surplus additive, which compromised the particle agglomeration and/or flocculation state in the prepared inks.

Dispersant (wt%)	OIDL-AI	Density (g/cm^3)	Viscosity 40ºC and 15,000 s^{-1} (mPa·s)	Viscosity 40ºC and 15.000 s^{-1} after 40-day aging (mPa·s)
1.0	017-40	1.400	17.3	20.5
	017-35	1.350	15.5	18.3
	017-30	1.300	14.1	16.6
	017-25	1.250	13.1	15.4
	017-20	1.200	11.4	14.9
	017-15	1.150	10.4	13.8
2.3	014-40	1.400	17.5	20.8
	014-35	1.350	15.8	18.5
	014-30	1.300	14.1	16.7
	014-25	1.250	13.1	15.6
	014-20	1.200	11.5	14.9
	014-15	1.150	10.5	13.9
4.0	013-40	1.400	17.7	17.6
	013-35	1.350	15.8	15.8
	013-30	1.300	14.3	14.2
	013-25	1.250	13.2	13.1
	013-20	1.200	11.7	11.7
	013-15	1.150	10.8	10.6
5.7	001-40	1.400	23.7	24.2
	001-35	1.350	22.3	23.0
	001-30	1.300	18.5	22.1
	001-25	1.250	17.6	21.8
	001-20	1.200	15.8	21.1
	001-15	1.150	14.1	20.7
7.2	002-40	1.400	28.5	30.6
	002-35	1.350	24.6	29.1
	002-30	1.300	22.9	28.5
	002-25	1.250	20.7	27.3
	002-20	1.200	19.1	26.9
	002-15	1.150	18.3	26.1
8.8	003-40	1.400	35.6	37.8
	003-35	1.350	31.3	36.5
	003-30	1.300	28.1	36.0
	003-25	1.250	25.7	35.3
	003-20	1.200	23.8	34.5
	003-15	1.150	21.6	33.8

Table 4. *Accelerated weathering of the formulated inks. Effect of the dispersant addition (0.93 kWh/kg solid).*

3.2. EFFECT OF DISPERSANT ADDITION ON THE EXPERIMENTAL PRINTABILITY AND BEHAVIOUR IN FLIGHT OF THE FORMULATED INKS

After the physical properties of the formulated inkjet inks had been determined, the behaviour of each ink inside the inkjet printhead was assessed. Thus, the velocity and volume of the drops generated were determined with a stroboscopic system operating at an electric voltage of 23 V. (See Figure 3).

It may be observed that, as working density decreased, at the same dispersant addition, suspension viscosity also dropped and, as a result, the velocity and volume of the ejected drops could also be increased. This effect became more pronounced as the amount of dispersant used (7.2% and 8.8% by weight) increased.

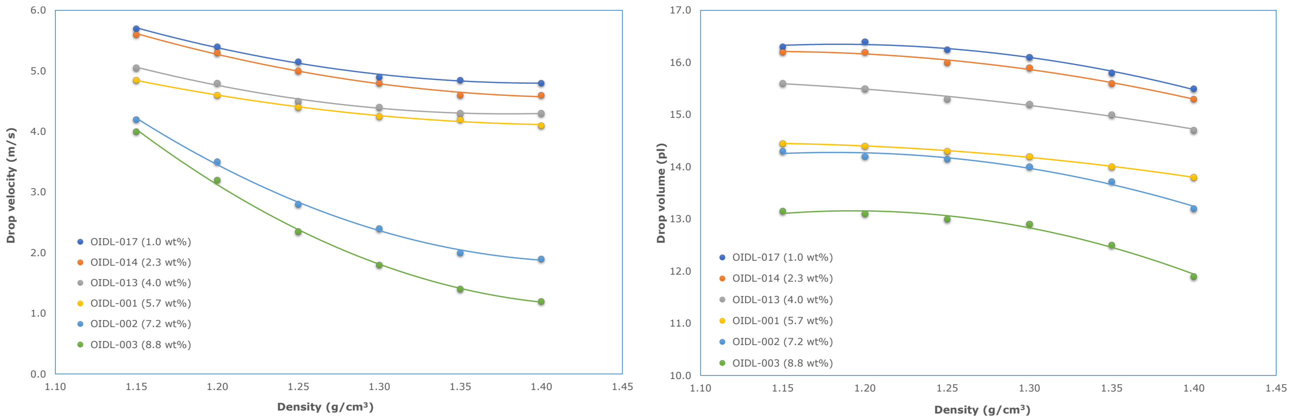

Figure 2. *Effect of dispersant addition on the velocity (left) and volume (right) of the drops of inks formulated at different working densities and 23 V operation. (0.93kWh/kg solid).*

3.3. EFFECT OF MILLING ON THE PHYSICAL PROPERTIES OF THE FORMULATED INKS

Table 5 details the physical properties of the developed inkjet inks, using different energy consumptions (0.69, 0.93, 1.23, and 1.47 kWh/kg solid) and a dispersant addition of 4.0% by weight.

It may be observed that, as energy consumption increased in the milling stage, the viscosity of the prepared inks also rose, owing to the increase in the number of particles present in the suspensions and in the number of interparticle contacts.

With regard to the resulting final particle size distribution, an increase in energy consumption allowed smaller particle sizes to be attained. However, this trend, whatever the working density, was only valid for energy consumptions equal to or smaller than 1.23 kWh/kg solid. For values of 1.47 kWh/kg solid, however, this trend reversed, leading to a rise in particle size.

This was because, on raising energy consumption, the resulting number of small-sized particles also increased, causing a greater proneness to particle agglomeration and flocculation. It therefore appears clear that a 4.0% by weight dispersant addition was not sufficient to stabilise suspensions undergoing highly energetic milling stages.

As occurred with the results corresponding to the effect of the dispersant (Table 3), the colloidal stability of the developments after 10 days' testing, understood as particle sedimentation and agglomeration, depended strongly on the viscosity values obtained. Only in the case of the inks milled at 1.47 kWh/kg solid, did the inks undergo an anomalous increase in the agglomeration values at 50ºC, a fact that confirmed the aforementioned flocculation phenomenon.

Comparison of these results with those obtained in the destabilisation/aging tests (see Table 6) reveals that the inks prepared at 0.69 kWh/kg solid, 1.23 kWh/kg solid, and 1.47 kWh/kg solid exhibited an important increase in viscosity. This fact could be associated with the difficulty of redispersing the particles present in the aged samples. However, for energy consumptions of 0.93 kWh/kg solid, the viscosity values remained unchanged with exposure time and temperature.

Consumption (kWh/kg solid)	**OIDL-AI**	**Density (g/cm^3)**	**Viscosity 40ºC and 15,000 s^{-1} (mPa·s)**	**D_{100} (µm)**	**Sedimentation 50ºC (%) MLS**	**Agglomeration 50ºC (%) MLS**
0.69	015-40	1.400	16.5	0.840	6.30	0.55
	015-35	1.350	14.6		6.30	0.55
	015-30	1.300	13.3		6.30	0.55
	015-25	1.250	12.1		6.50	0.60
	015-20	1.200	10.9		6.50	0.60
	015-15	1.150	9.7		6.60	0.65
0.93	013-40	1.400	17.7	0.766	6.00	0.50
	013-35	1.350	15.8		6.30	0.50
	013-30	1.300	14.3		6.60	0.55
	013-25	1.250	13.2		6.50	0.55
	013-20	1.200	11.7		6.50	0.55
	013-15	1.150	10.8		6.60	0.60
1.23	011-40	1.400	18.8	0.563	5.70	0.40
	011-35	1.350	17.2		5.70	0.40
	011-30	1.300	16.0		5.70	0.45
	011-25	1.250	15.1		5.80	0.45
	011-20	1.200	13.9		5.90	0.45
	011-15	1.150	13.0		6.00	0.50
1.47	016-40	1.400	22.4	0.963	4.10	1.10
	016-35	1.350	21.8		4.10	1.10
	016-30	1.300	21.1		4.20	1.15
	016-25	1.250	20.6		4.50	1.20
	016-20	1.200	20.1		4.80	1.20
	016-15	1.150	19.5		4.80	1.25

Table 5. *Characterisation of the formulated inks. Effect of milling (4.0 wt% dispersant).*

Figure 3 illustrates the effect of energy consumption on the viscosity of the inks prepared at different working densities.

Consumption (kWh/kg solid)	OIDL-Al	Density (g/cm³)	Viscosity 40ºC and 15,000 s⁻¹ (mPa·s)	Viscosity 40ºC and 15,000 s⁻¹ after 40-day aging (mPa·s)
0.69	015-40	1.400	16.5	21.5
	015-35	1.350	14.6	20.8
	015-30	1.300	13.3	20.1
	015-25	1.250	12.1	19.5
	015-20	1.200	10.9	18.7
	015-15	1.150	9.7	18.0
0.93	013-40	1.400	17.7	17.7
	013-35	1.350	15.8	15.7
	013-30	1.300	14.3	14.3
	013-25	1.250	13.2	13.2
	013-20	1.200	11.7	11.6
	013-15	1.150	10.8	10.8
1.23	011-40	1.400	18.8	25.6
	011-35	1.350	17.2	24.8
	011-30	1.300	16.0	24.1
	011-25	1.250	15.1	23.3
	011-20	1.200	13.9	22.7
	011-15	1.150	13.0	22.0
1.47	016-40	1.400	22.4	35.1
	016-35	1.350	21.8	34.3
	016-30	1.300	21.1	33.5
	016-25	1.250	20.6	32.6
	016-20	1.200	20.1	31.9
	016-15	1.150	19.5	31.1

Table 6. *Accelerated weathering of the formulated inks. Effect of milling (4.0 wt% dispersant).*

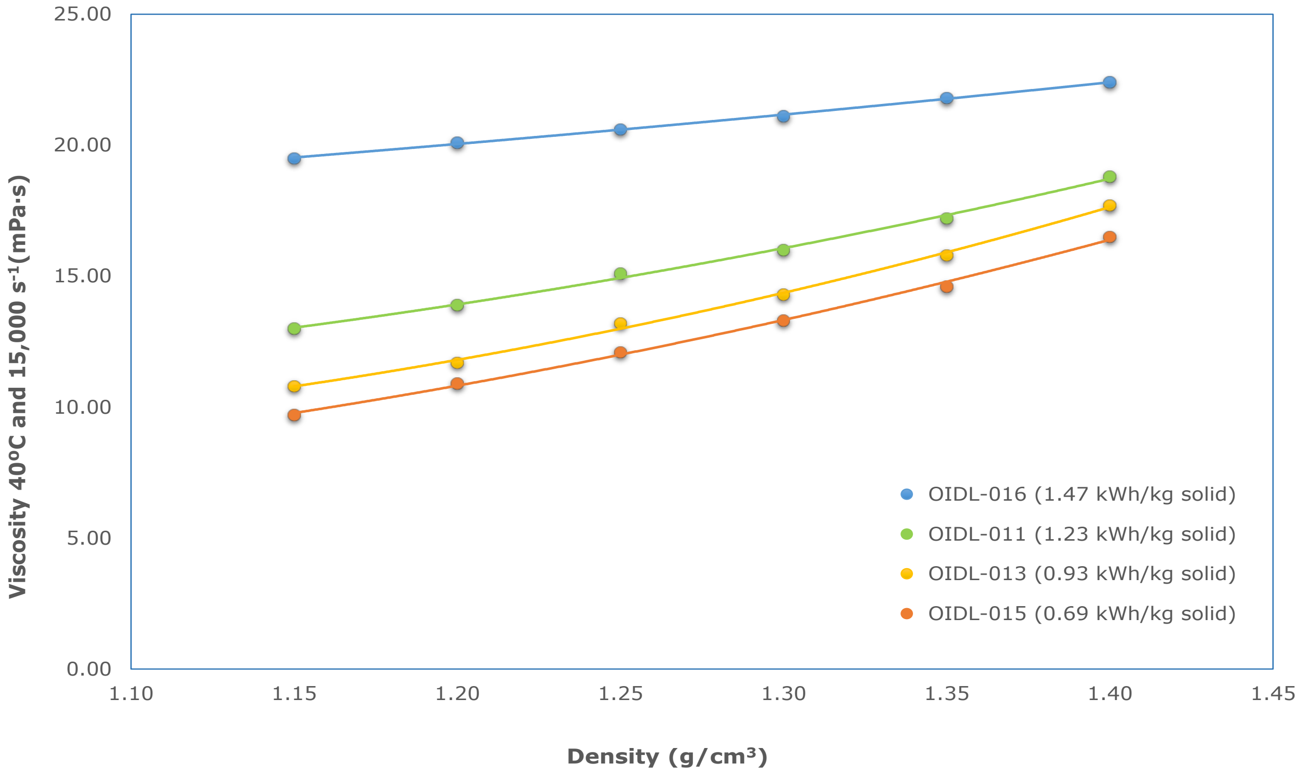

Figure 3. *Effect of milling on the viscosity of the inks formulated at different densities and 4.0 wt% dispersant.*

3.4. EFFECT OF MILLING ON EXPERIMENTAL PRINTABILITY AND BEHAVIOUR IN FLIGHT OF THE FORMULATED INKS

Figure 4 illustrates the effect of milling on the velocity and volume of the ejected drops during the experimental printability process of the inks formulated at different working densities. An operating voltage of 23 V was assumed in all cases.

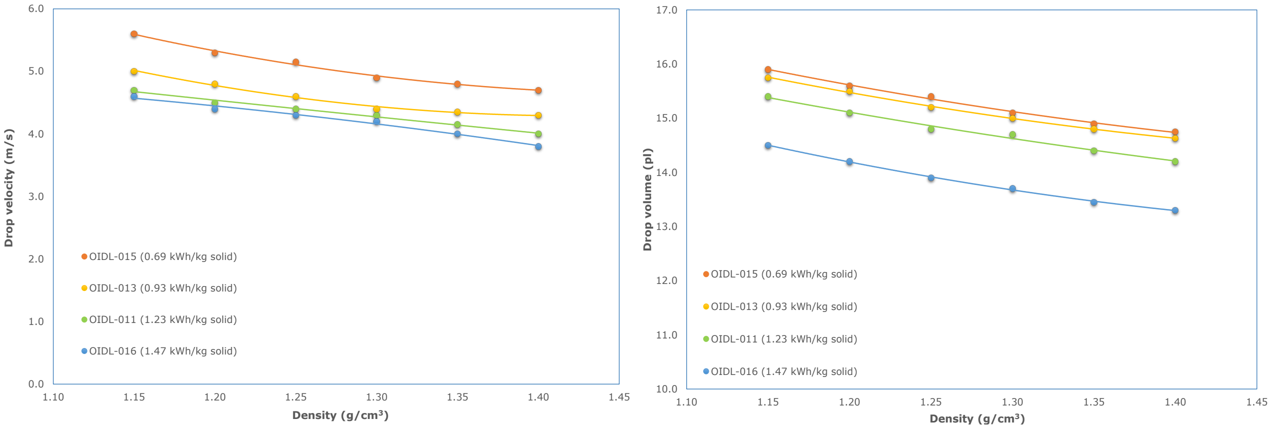

Figure 4. *Effect of milling on the velocity (left) and volume (right) of the drops of inks formulated at different working densities and 23 V operation. (4 wt% dispersant)*

As may be observed, the increase in energy consumption during the milling stage entailed an increase in viscosity of the developments owing to the rise in the number of particles generated, as well as in the increased interparticle contacts. This led to a decrease in the velocity and volume of the drops ejected during the inkjet digital printing stage. It may be noted that the insufficient amount of dispersant (4.0% by weight) added to the suspensions milled at an energy consumption of 1.47 kWh/kg solid adversely contributed to raising perhaps even further the viscosity values and, therefore, to compromising the printability of the developed inks.

4. CONCLUSIONS

The destabilization/accelerated aging tests allowed differences in the technical feasibility of the developments to be established. Values of 4% by weight dispersant content and energy consumption of 0.93 kWh/kg solid provided better behaviour, no changes in suspension viscosity being observed.

Furthermore, the influence of the dispersant addition to the inkjet ink composition, as well as the energy consumed during the milling stage in ink preparation, was studied on a laboratory scale. The results indicate that:

- The increase in dispersant content (1.0%, 2.3%, 4.0%, 5.7%, 7.2%, and 8.8%, by weight), keeping energy consumption constant at 0.93 kWh/kg solid, led to an increase in suspension viscosity, reducing the velocity and volume of the drops ejected during the experimental printability of the working inks.
- The increase in energy consumption associated with the milling stage (0.69 kWh/kg solid, 0.93 kWh/kg solid, 1.23 kWh/kg solid, and 1.47 kWh/kg solid), keeping the dispersant addition constant (4.0% by weight), entailed a rise in suspension viscosity. This reduced the velocity and volume of the drops generated during the inkjet application. At an energy consumption of 1.47 kWh/kg solid, in addition, the dispersant addition did not appear to be sufficient to keep the particles individualised and to palliate the agglomeration and flocculation phenomena observed, and consequently produce a "synergy" effect that adversely contributed to increasing, perhaps even further, the viscosity values of the working system.

Empirical correlations were obtained that allow the parameters of suspension viscosity, as well as of the velocity and volume of the generated drops to be determined and predicted as a function both of the density and of the voltage applied during the digital inkjet printing process of the test inks.

5. ACKNOWLEDGEMENTS

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