DEVELOPMENT OF NEW DISPERSANTS FOR CERAMIC INKJET INKS. ANALYSIS OF INFLUENCE ON THE FINAL PROPERTIES OF INK

F. Rodríguez(1), R. Pallarés(1), L. Carrals(1), M.S. Palmer(1), V. Sanz(2), A. Belda(2), J. Castellano(2)

(1) UBE Corporation Europe, S.A.U. Castellón. Spain.

(2) Instituto de Tecnología Cerámica (ITC). Universitat Jaume I. Castellón. Spain.

1. ABSTRACT

Ceramic inks must have a series of properties in order to be used in digital inkjet printheads. Many of these properties depend on the dispersants used.

Dispersants are additives whose basic function is to prevent agglomeration of suspended particles and prevent sedimentation, thus facilitating creation of stable inks. By designing functional chemical groups, along with the degree of polymerization of organic molecules and compatibility with solvents, dispersants that satisfy the different requirements of ceramic inks for inkjet technology may be synthesized.

This paper analyses the properties of ceramic inkjet inks as a function of the dispersant used and its percentage in the composition. The properties analysed were rheological behaviour, filterability, stability against sedimentation and ageing with time and temperature.

Inks were prepared with a yellow pigment, fatty acid ester and specially formulated UBEDISP dispersants. The remaining variables were kept constant, in particular the degree of grinding, while rigorously analysing the influence of the dispersant on ink final properties.

It may be noted that some properties were interrelated. In this sense, for example, stability was strongly conditioned by viscosity at low shear rates while filterability depended to a large extent on particle size and suspension viscosity. By analysing the properties together, it was possible to determine the suitability of the dispersant for the entire system. The use of spider charts enabled visual evaluation of the different properties as a function of the dispersant used in the formulation of the ceramic ink.

It was thus possible to assess the effects of the dispersant, select the most appropriate dispersant in terms of targeted ink properties and optimize the dispersant percentage in the composition.

Understanding dispersant operating mechanisms and the corresponding influence on properties facilitates formulation and customisation of new UBEDISP additives for the different digital decoration systems currently used in the ceramic sector.

2. INTRODUCTION

Ceramic inkjet inks are stable suspensions of ceramic pigments in a liquid medium or vehicle, usually of an organic nature. The pigments and vehicles employed may vary greatly, which requires the use of appropriate additives for each system to achieve the requirements for the inks[1].

Additives have a critical effect on the manufacture, stability and physical-chemical properties of inks.

The manufacturing process for ceramic inks consists of the grinding and dispersion of ceramic pigments, starting from a micrometric particle size until reaching stable dispersions with a particle size distribution below 1 µm. In the preparation of the dispersion, three clearly differentiated processes may be distinguished: wetting, grinding and stabilization[2], all highly dependent on the additives used.

1. The wetting of ceramic pigments consists of displacing the air occluded at the surface by the grinding vehicle. The wetting additives facilitate this process by decreasing liquid surface tension while reducing the interfacial tension between pigment and liquid. The most basic type of wetting agents used are surfactants, which consist of molecules composed of one part that has an affinity to the liquid and another to the solid.

2. In the grinding process, the size of the pigment particles and aggregates is reduced until the desired size is reached. The energy consumed in this process is very high and it is used both in the generation of new surfaces and in the generation of heat due to ink flow and grinding media friction. The efficiency of this process is very sensitive to the viscosity of the ink, and therefore also to the additives used.

3. The stabilization process consists of generating the appropriate inter-particle repulsive forces in order to keep the particles individualized or stable from a colloidal point of view. In organic media, these forces are mainly steric and are achieved through the use of additives[3].

The stability of the inks in terms of sedimentation facilitates appropriate marketing and use[1]. Ceramic inks are relatively concentrated suspensions, so that pigment sedimentation may be estimated using the modified Stokes equation with the physical parameters of the suspension instead of those of the liquid. Thus, for a pigment of constant size, the higher the viscosity of the ink, the lower is the sedimentation rate. However, if the ink is not colloidally stabilized, the pigment particles will aggregate over time, progressively increasing in size and settling, which again highlights the importance of the additives used.

Dispersants adsorb at the pigment surface and prevent flocculation by counteracting and/or minimizing inter-particle attractive forces. In organic media, the steric repulsion mechanism is usually the most efficient. Polymeric dispersants contain segments with groups that display affinity to the surface of the pigment to be dispersed and other segments highly soluble with the vehicle[4]. For proper functioning of these dispersants, it is necessary for the polymer to interact strongly with the pigment surface and for the vehicle-compatible parts to be completely solvated.

When two dispersant-coated particles approach one another, the compatible parts of the polymer interact, generating two types of repulsive force[5]. On the one hand, occupation of the same space conditions polymer mobility and three-dimensional structure, which causes an elastic reaction. On the other hand, the increased local concentration of polymer generates osmotic pressure, which also tends to impede particle aggregation. This set of forces is commonly referred to as a steric repulsion mechanism.

In general, dispersant additives usually act as wetting agents and are usually directly responsible for certain final chemical-physical properties of the inks. A good dispersant should stabilize dispersion, keep viscosity constant and as low as possible, minimize energy consumption during grinding, prevent particle aggregation and minimize the particle sedimentation rate.

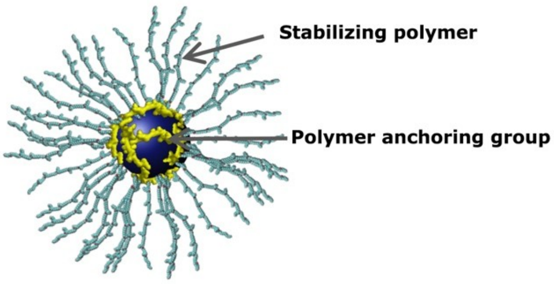
3. EXPERIMENTAL PROCEDUREdrgtretret

3.1. DISPERSANT SELECTION AND SYNTHESIS

Various polymeric dispersant additives were prepared in order to study the influence of their characteristics on the properties of the ceramic inks obtained with them. The UBEDISP additives used were customizable graft copolymers based on two types of polymer chains with clearly differentiated functionalities:

1) Anchoring polymer: This is a functionalized polymer chain with different functional groups that strongly interact with the surface of the particle to be dispersed through non-covalent interactions (hydrogen bonds and/or electrostatic interactions). The interaction between this polymer and the particle surface must be intense enough to assure dispersion stability.
2) Stabilizing polymer: The nature of the stabilizing polymer chain (polarity, length, flexibility, degree of branching) is key to achieving optimal performance of polymeric dispersants. Stabilizing polymers must be perfectly solvated in the dispersion medium used to achieve optimal steric repulsion.
3) Dispersion factor: This is a synthetic parameter that enables polymeric dispersant properties to be balanced.

Figure 1 shows the basic design of this type of dispersant with its corresponding nomenclature, in which N2 indicates a non-hazardous dispersant.



UBEDISPXyYZ-N2

X → **Length of polymer anchoring group**

yY → **Polarity and length of stabilizing polymer**

Z → **Dispersion factor**

Figure 1. *Schematic illustration of a particle coated with UBEDISP dispersant and nomenclature used.*

This paper describes the effect of modifying anchoring polymer molecular weight, stabilizing polymer polarity and the dispersion factor.

Prior to the synthesis of the polymeric dispersants, a selection of functional groups with possible affinity to the nature of the ceramic pigments was carried out. To this end, the experimental procedure detailed in the bibliography[6] was used for sequential testing of functional groups such as carboxylic acid, succinic acid, sulfonic acid, anhydride, amine, amide, and trichlorosilane, with each of the generic ceramic pigments that could be used in the development of ceramic pigment inks, selecting those functional groups that were able to disperse the largest number of pigments. These functional groups were introduced into the anchoring polymers in different positions and proportions until obtaining an optimal formulation.

Similarly, the minimum length of the stabilizing polymer was previously optimized to achieve steric stabilization, which must be about 10 nm[7].

In order to study the effect of each variable individually, the properties of the inks formulated with different dispersants were compared. Table 1 details the dispersants used according to the variable analysed.

Variables	**Dispersants**
Amount of dispersant in the formulation	1b65-N2
Molecular weight of the anchoring polymer	**1**b63-N2 vs **6**b63-N2
Stabilizing polymer polarity	1**b6**5-N2 vs 1**c7**5-N2
Dispersion factor	1b6**1**-N2 vs 1b6**3**-N2 vs 1b6**5**-N2

Table 1. *Dispersants prepared as a function of the variable studied*

3.2. PREPARATION AND CHARACTERISATION OF CERAMIC INKS

The following materials were used:

- Praseodymium yellow pigment with Pr-doped zircon structure. It was previously verified that no additional crystalline phases were present, neither by being slightly reacted nor as a result of preparation by mixing, and that it had an appropriate particle size.
- Vehicle: 2-ethylhexyl laurate fatty acid ester (viscosity 6.3 cP at 25°C).
- Different UBEDISP dispersant additives.

Inkjet inks with a solids content of 45% by weight were prepared by mixing, dispersion and grinding of the above components in a Netzsch LabStar laboratory mill using zirconia micro beads with a diameter of 0.3 mm. The working conditions used were: 3300 rpm rotor rotational speed and variable grinding times (65 - 70 minutes) until obtaining inks with the same particle sizes ($d_{50} \approx 0.45 \pm 0.02$ µm and $d_{90} < 0.90$ µm).

In order to clearly detect the effects of the dispersant on the final ink, a single low-viscosity vehicle was used and a single final particle size was set. Although in many cases the viscosity of the inks obtained in this study did not lie within the desired range, filtration problems associated with aggregation could be detected more easily and the differences between the inks were minimized on not having to adjust the viscosity with a second vehicle of higher viscosity.

The inks obtained were filtered at 2 µm and characterised, determining the following properties:

- Particle size: Measured using a Malvern Mastersizer 2000 laser diffraction instrument.
- Viscosity and rheological behaviour: A Bohlin CVO-120 rheometer with a double-gap measurement system was used; the force required to maintain a certain shear rate on the sample was measured. Measurements were carried out at 25ºC. Although the inkjet inks were applied at higher temperatures, it was verified that the tendencies were the same and for comparative purposes the same results were achieved. The complete viscosity versus shear rate curves were thus obtained.
- Filterability: A filtration test was carried out using a Kitasato-filter connected to a vacuum pump at an approximate relative pressure of -900 mbar. The time it took for 15 mL of sample to pass through a Whatman glass microfibre filter of 47 mm in diameter and 1 µm pore size was measured. This process was repeated several times, using the same filter sequentially, in order to detect clogging problems. If, in any case, the sample had not filtered after 30 minutes, the test was stopped and a time equal to 1800 s was considered. In this study, the filtering time in the second repetition (t2) is shown as the characteristic time.
- Stability against sedimentation: This was determined using a LUMiFuge analyser consisting of an analytical centrifuge that measured light transmitted through the length of the sample. The instrument enables determination of a speed relating to sedimentation, so that stability is

greater at lower speeds. Testing was carried out at 50°C and 4000 rpm, equivalent to 2000 g in the analyser, for 4 hours.

- Degradation: An analysis of property degradation, with time and temperature, was carried out. In the analysis, the properties were determined after storing the inks at 110°C for 1 week and at 50°C for 2 weeks. After thermal degradation, the inks were subjected to rigorous agitation to re-disperse the settled part of the ink. The variations of ink properties enabled the degree of degradation to be established.

4. RESULTS OBTAINED AND DISCUSSION

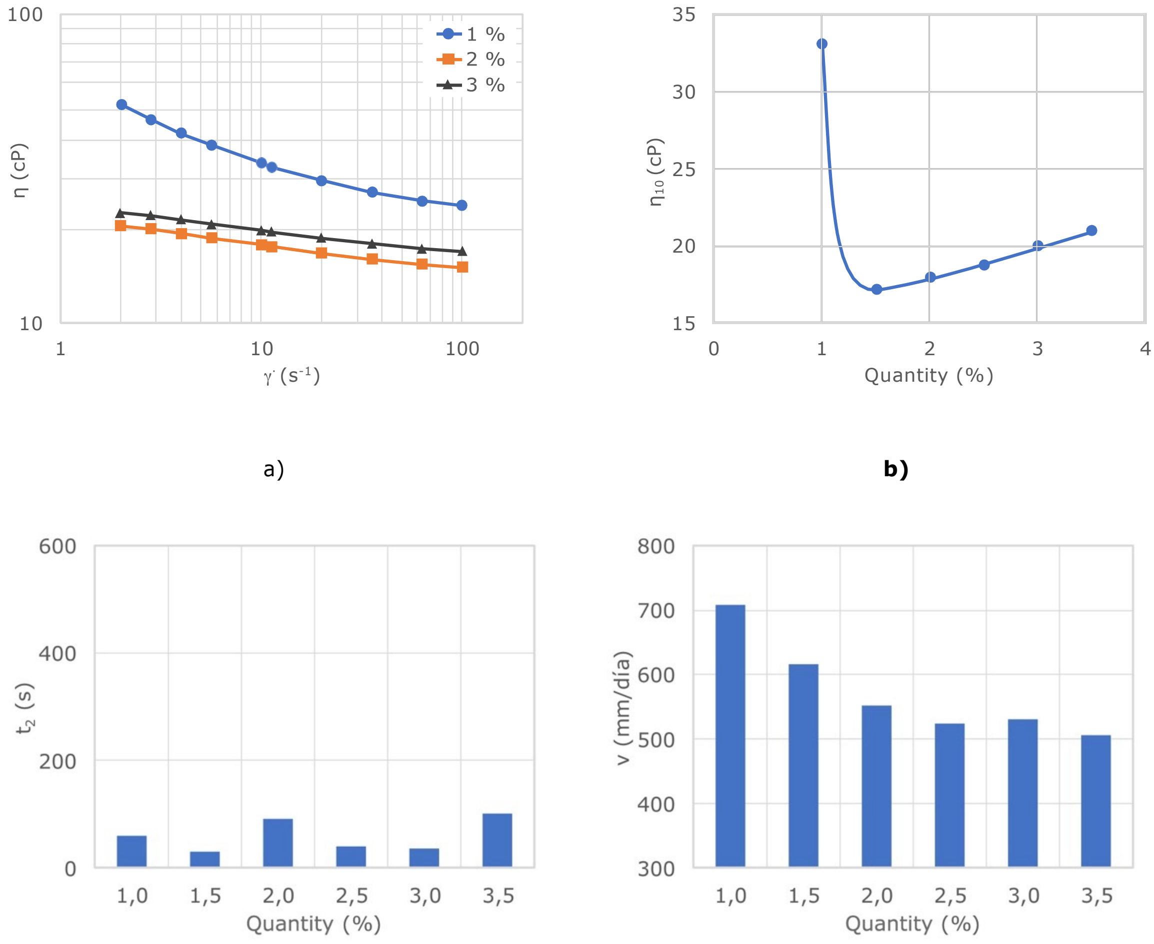
4.1. INFLUENCE OF THE AMOUNT OF DISPERSANT

The influence of the amount of dispersant on the properties of the inkjet inks was evaluated and, by way of example, the results are shown in the range of variation between 1 and 3.5% for dispersant 1b65-N2.

The rheological properties that defined the behaviour of the inks are shown in Figure 2. Figure 2a shows the rheological curves as a function of the dispersant percentage. Viscosity values are plotted against shear rates on a logarithmic scale, covering a range between 2 and 100 s^{-1}. It is observed that the inks showed slight shear thinning behaviour, which was slightly accentuated at very low additive percentages.

Graph 2b was constructed from these curves. Viscosity at a shear rate equal to 10 s^{-1} (η_{10}) was considered a representative value. At low percentages, viscosity decreased to a minimum and then increased slowly with the increased amount of dispersant. Inks were not prepared at lower percentages due to flocculation detected in previous tests using an agate mill. The optimal dispersant percentage for obtaining an ink with the lowest possible viscosity was about 1.5%. As this percentage increased, ink viscosity increased because the additive was not incorporated into the surface of the pigment to be dispersed but remained in solution. As viscous products (8000 - 10000 cP at 40ºC) were involved, increasing the amount of polymer in solution resulted in increased viscosity.

Figure 2c shows that filtration times were adequate and below two minutes, indicating the absence of significant particle aggregation even when the percentage of dispersant was low. Additionally, no direct relationship was established between the amount of dispersant added and filtration times.



a) **b)**

c) **d)**

Figure 2. *a) Rheological curves on a logarithmic scale versus amount of dispersant; b) Viscosity at 10 s-1 versus percentage of dispersant; c) Filterability results and d) Sedimentation rates at 2000 g and 50°C (Dispersant 1b65-N2).*

The stability of the inks obtained was studied and the results are shown in Figure 2d. As the percentage of dispersant increased, the sedimentation rate decreased. This decrease was particularly considerable in the range below 2%, while subsequent improvements in stability appeared to be directly associated with increased ink viscosity. This may be seen clearly in Figure 3a, where the sedimentation rate is plotted versus ink viscosity. Thus, although the ink with the lowest viscosity was formulated with 1.5% dispersant, it seems logical to work with concentrations higher than 2% in order to obtain sufficiently stable inks without flocculation problems during grinding.

In relation to thermal degradation studies at 50ºC for two weeks, no significant variations were detected in any of the studied properties (viscosity, sedimentation rate and filterability) in the inks formulated with UBEDISP dispersants in the range 2 to 3.5%. This result suggests that interactions between the anchoring polymer and the pigment were strong enough to withstand the typical working conditions of a ceramic inkjet ink.

Regarding degradation at 110°C for one week, significant variations in stability were observed. By way of example, the effect of degradation on ink sedimentation stability, expressed as a percentage of variation between initial and final sedimentation rate (Δv), is shown in Figure 3b for compositions with 2 and 3.5% dispersant.

It may be seen that the inks containing a greater percentage of dispersant were able to maintain their properties better with temperature. The study of degradation at 110ºC facilitated identification of inks that had greater resistance to thermal degradation. The results obtained suggest that excess dispersant in the ink would be necessary to be able to withstand strong thermal treatments, while at 50ºC this excess would not seem necessary.

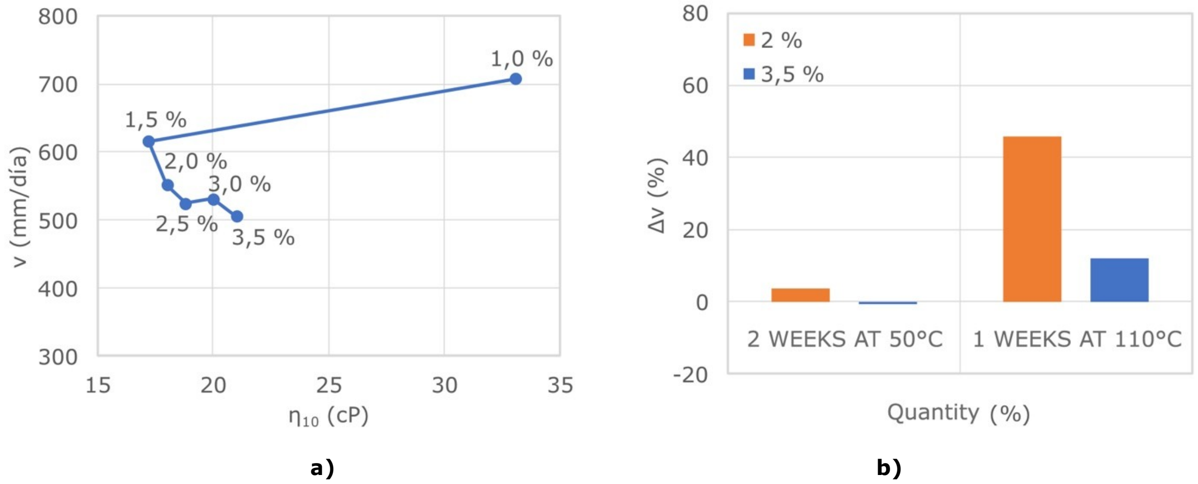


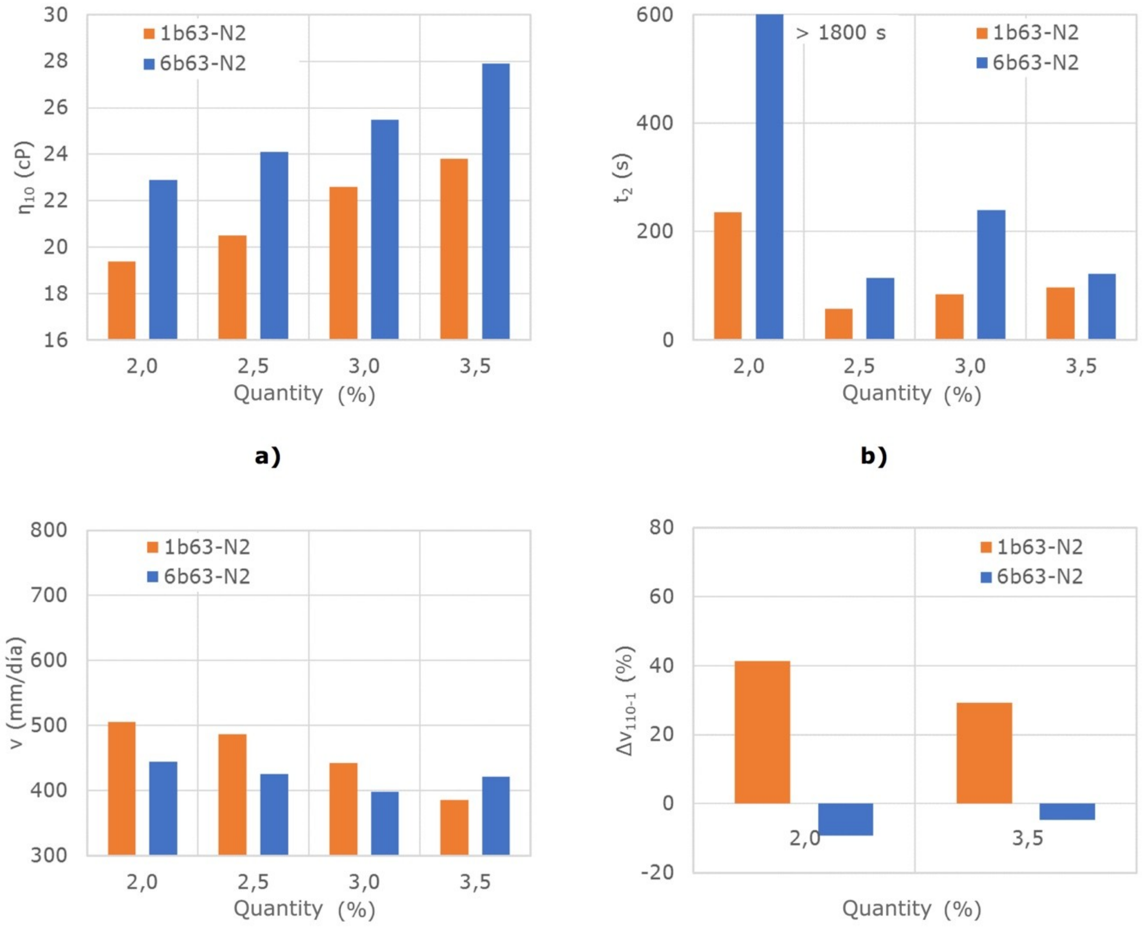
Figure 3. *a) Plot of the sedimentation rate at 2000 g at 50ºC versus viscosity obtained. b) Variations in the sedimentation rate after thermal degradation (dispersant 1b65-N2).*

4.2. EFFECT OF MOLECULAR WEIGHT OF THE ANCHORING POLYMER

In a second study, the effect caused by variation of the molecular weight of the dispersant anchoring polymer on the final properties of the ink was evaluated. Dispersant **1**b63-N2 was compared with dispersant **6**b63-N2, which had been designed with an anchoring polymer of higher molecular weight, but with the same composition and concentration of functional groups.

In Figure 4, plots are shown of viscosity at a shear rate of 10 s^{-1}, and filtration time t_2 and sedimentation rate versus the percentage in the composition for each dispersant analysed. Also included is the effect of degradation, expressed as the percentage of variation in sedimentation rate after storing the ink at a temperature of 110°C for one week (Δv_{110-1}). In the last case, only the inks with the lowest and highest percentages of dispersants were tested.

It is observed that varying the length of the anchoring polymer changed viscosity and stability. Both properties also depended on the percentage of dispersant in the composition. Formulations containing dispersant 6b63-N2 generated higher viscosity inks, which were therefore characterised by a lower sedimentation rate.



a) **b)**

c) **d)**

Figure 4. *Influence of polymer anchoring group on viscosity (a), filterability (b), stability (c) and degradation (d).*

The inks formulated with 6b63-N2 displayed reduced variations after being subjected to degradation, suggesting that stability did not worsen with temperature. The length of the anchoring polymer was therefore a characteristic to be considered for optimizing resistance to degradation. These results may be related to the greater number of functional groups in dispersant 6b63-N2.

Finally, it should be noted that, in the formulations with a low concentration of dispersant 6b63-N2 (formulation at 2%), filtration problems were detected that did not appear in the case of 1b63-N2.

4.3. EFFECT OF STABILIZING POLYMER POLARITY

Complete solvation of stabilizing polymers is essential to achieve maximum dispersion capacity. In order to study this effect, two dispersants with stabilizing polymers of different polarities were prepared.

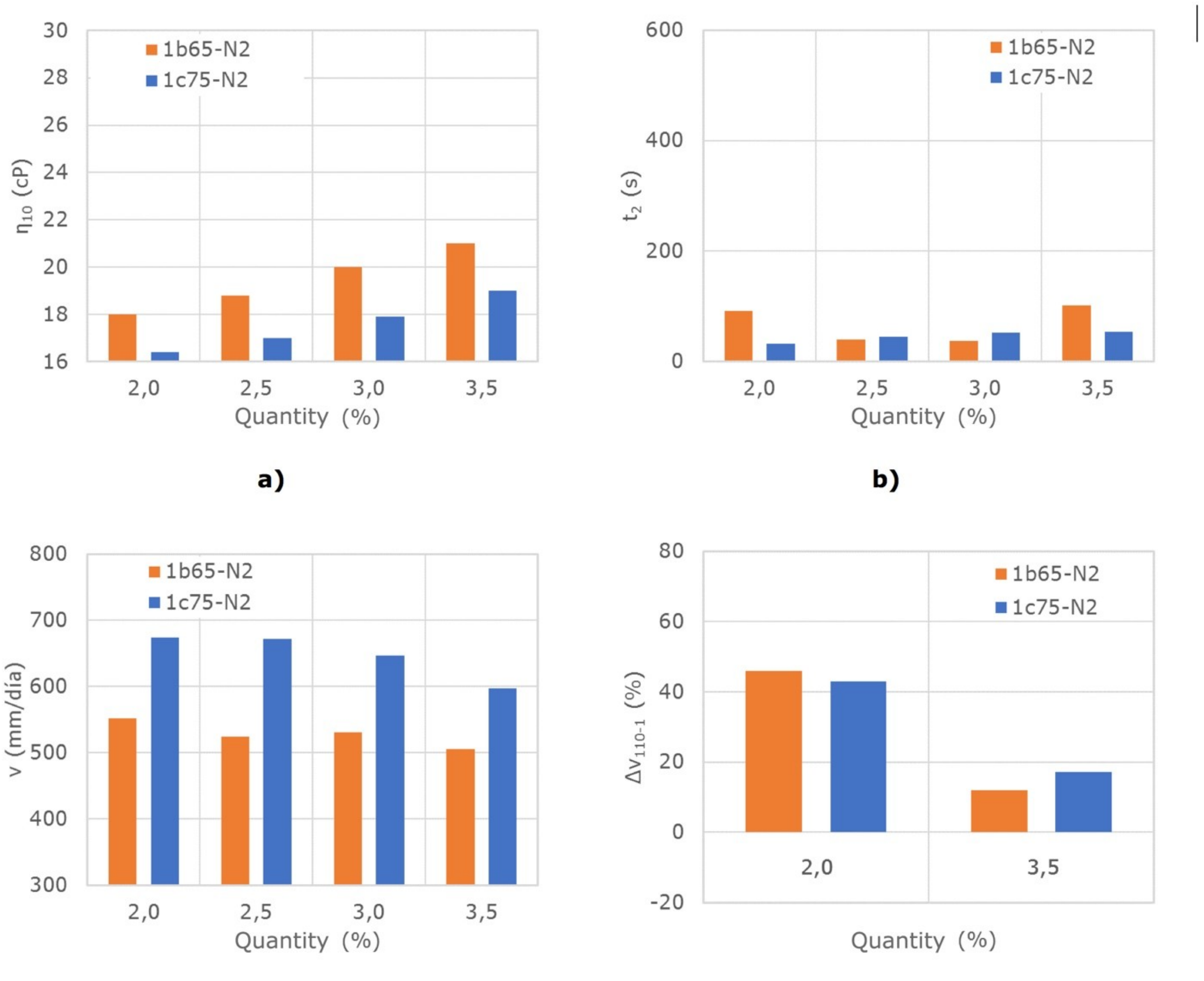
Dispersant 1**c7**5-N2 was designed with stabilizing polymer "c7", which had greater polarity than polymer "b6" of 1**b6**5-N2. The polarity of these polymers was adjusted by introducing different percentages of polar monomers into the formulation.

Figure 5a shows that the inks formulated with dispersant 1c75-N2 had lower viscosity than those obtained with 1b65-N2.

This result may be directly related to the greater compatibility between stabilizing polymer "c7" and the grinding medium used. Polymer "c7" was better solvated by the vehicle used, enabling maximization of steric repulsion between particles in the ink with the entailing decrease in system viscosity. Figure 2c shows that the lower viscosity obtained in the inks prepared with 1c75-N2 had a negative effect on the sedimentation rate, as was to be expected according to Stokes' Law.

On the other hand, no significant differences were detected in terms of filterability of the inks within the dispersant concentration ranges studied.

Using both dispersants, it is observed that stability with regard to thermal degradation improved considerably on increasing the percentage of dispersant used in the formulation. No significant differences were found regarding resistance to thermal degradation between both dispersants.



a) **b)**

c) **d)**

Figure 5. *Influence of the stabilization chain on viscosity (a), filterability (b), stability (c) and degradation (d).*

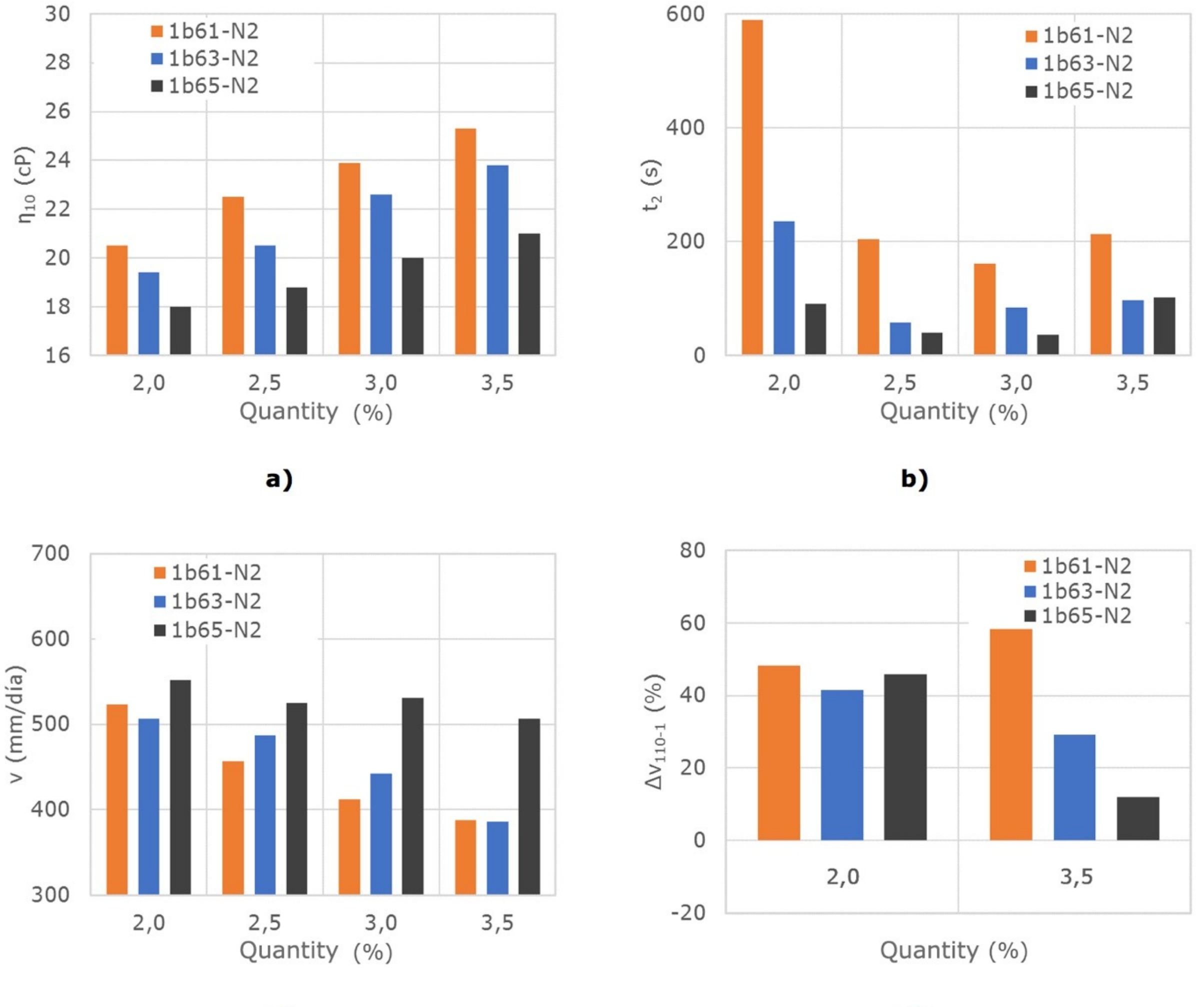
4.4. INFLUENCE OF THE DISPERSION FACTOR

6 shows the characterisation results of inks prepared using dispersants with different dispersion factors. This factor in the synthetic process enables adjustment of different dispersant properties. As in previous studies, increasing the percentage of dispersant in the formulation resulted in increased viscosity after exceeding the optimum level. This increased viscosity resulted in increased stability regarding sedimentation (6c).

When the dispersion factor decreased, viscosity increased, consequently decreasing the sedimentation rate. This improvement was observed on going from dispersant 1b6**5**-N2 to 1b6**3**-N2.

Inks with higher viscosities were obtained with dispersant 1b6**1**-N2. However, their stabilities were not an improvement over those of 1b6**3**-N2, indicating worse behaviour in terms of sedimentation. Additionally, it was found that inks formulated with 1b6**1**-N2 had longer filtration times with lower resistance to thermal degradation.

It may be concluded that adjustment of the dispersion factor in the design of polymeric dispersants enabled control of viscosity properties in the final inks, but had significant adverse effects on other related properties.



a) **b)**

c) **d)**

Figure 6*. Influence of the dispersion factor on viscosity (a), filterability (b), stability (c) and degradation (d).*

4.5. COMPARISON OF DISPERSANTS

In order to complete the analysis and compare the dispersants, additional graphics or plots were needed. The objective was to quantify the effect of each dispersant on the different properties. Radial or spider charts are useful in this regard.

A characteristic value was established for each property as a function of the dispersant used, viscosity (η_{10}), filterability (t_2), stability (v) and degradation (Δv_{110-1}). Each value was obtained as an average of the values at the different percentages. Next, the standardized "Z" score was used to compare the results from the arithmetic mean (μ) and standard deviation (σ). The "Z" score enabled calculation of the values (x) as standard deviation units according to equation (1):

$$z=\frac{x-\mu}{\sigma} \qquad (1)$$

Plotting the resulting values on a chart yielded Figure 7. This distinguishes the effect of each dispersant on the properties analysed. The sign was adjusted so that the lowest value of a property was in the centre and the highest value was at the corresponding end.

The chart shows the relationship between viscosity and stability, with non-intersecting lines that, at times, maintained a certain parallelism. The dispersant with the greatest anchoring polymer length exhibited lower degradation effects but had lower filterability. The dispersant with a different stabilization chain had the lowest viscosity and stability.

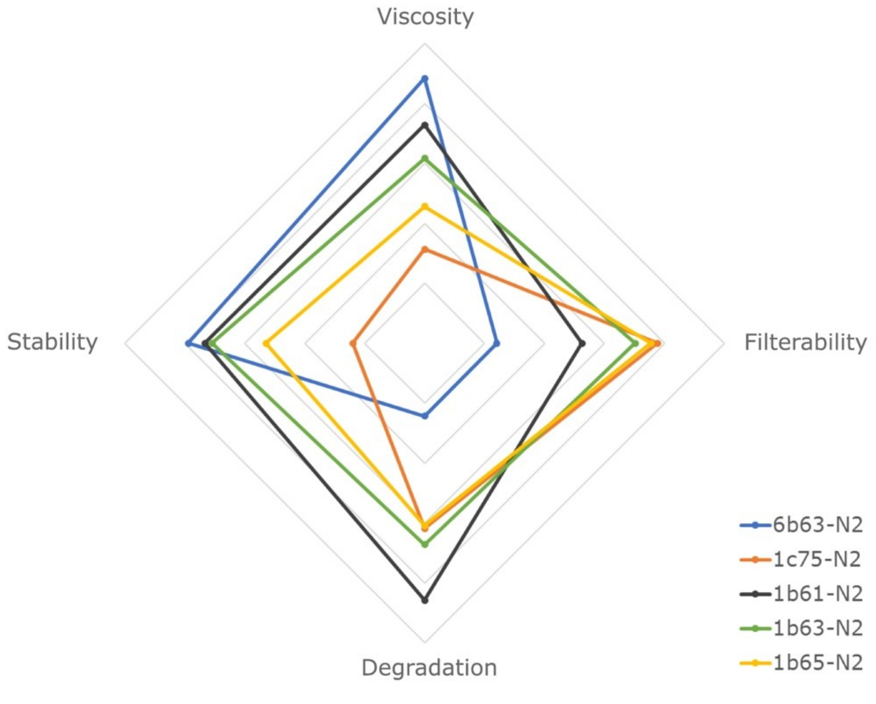


Figure 7. *Comparative graph of properties as a function of the dispersant.*

5. CONCLUSIONS

A systematic study was carried out of the effect that the design of UBEDISP dispersants had on ink final properties. The results obtained show how specific dispersant designs enabled production of ceramic inks with the desired properties.

It was verified that pigment inks with 45% solids content could be obtained using percentages of about 1.5 - 2% dispersant. The inks obtained under these conditions were stable at 50°C for long periods of time and had good filterability.

Resistance to degradation due to temperature could be increased using excess dispersant. In addition, more viscous formulations, which minimized the sedimentation rate, were obtained. Furthermore, ink final viscosity could be controlled by modifying the dispersion factor in the formulation.

Resistance to thermal degradation could also be adjusted by increasing the molecular weight of the anchoring polymer, given that it was anchored to the pigment surface at a greater number of points.

The steric repulsion mechanism could be optimised through the polarity of the stabilizing polymer for optimal solvation by the vehicle. It was thus possible to obtain very low viscosity inks.

In short, it may be concluded that it is possible to design polymeric dispersants for use in the preparation of ceramic inkjet inks that contain different inorganic fillers, including ceramic pigments, with vehicles of different polarities. Customisation of dispersants facilitates modification of the final properties of ceramic inks in a clear, simple and effective way, providing a powerful tool for the development of new formulations.

6. REFERENCES

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