NEW TRENDS IN DIGITAL INKJET INKS AND DIGITAL INKJET GLAZES FOR THE CERAMIC FIELD. FORMULATIONS OF AQUEOUS DIGITAL INKJET INKS AND GLAZES.

Niklas Kircher [(1)], Roger Escámez [(2)]

[(1)] **Byk Chemie GmbH, Alemania**

[(2)] **Comindex S.A., España**

1. ABSTRACT

Digital inkjet printing has been implemented within the last years in the ceramic field covering nowadays the majority of designs currently available in the market of ceramic tile decoration.

With the help of the latest high resolution digital scanners, modern printheads and image processing software of digital inkjet printers, it is possible nowadays to print any conceivable design in high definition.

Digital inkjet printing inks have been upgraded within the last years towards using more environmentally friendly and sustainable solvents. It is the time now to develop new aqueous inks and aqueous glazes and the most impressive designs by applying special effects with the help of digital inkjet printing, leading to an infinite world of designs.

Water-based systems are generally more difficult to formulate than solvent-based systems. Water has a surface tension value of 73 $mN.m^{-1}$, much higher than the solvents used in solvent-based digital inkjet printing inks. Consequently the adjustment of aqueous digital inkjet printing inks and glazes requires a bigger surface tension reduction than solvent-based digital inkjet printing inks. This leads to the use of surface tension reducing agents, which implies a higher probability of printing defects and the need to use other additives to avoid them. Furthermore, the specific requirements of digital inkjet printheads and the severe application conditions in regards to temperature and humidity make the formulation of these inks and glazes much more difficult.

Therefore, Byk-Chemie GmbH, works together with digital printing inks and glazes manufacturers in order to achieve the highest quality standards in their products.

This lecture presents developments in the different types of additives used in formulations of aqueous digital inkjet printing inks and aqueous digital glazes:

- Wetting and dispersing additives.
- Static and dynamic surface tension reducing agents.
- Defoamer additives.

2. INTRODUCTION

The new digital inkjet printing technology has been a revolution in the field of ceramic tile decoration replacing almost entirely the traditional Rotocolor[1] technology within the last years: only a few designs with residual volumes are made nowadays by the traditional technology.

Solvent-based inkjet inks have been already implemented into the market and have already moved towards the use of more environmentally and sustainable solvents. It is the time now to start the transition to aqueous digital inkjet inks and glazes. The possibility of applying special effects combined with high resolution designs printed by digital inkjet technology opens up an infinite world of design possibilities that is really fascinating.

The peculiarities of aqueous systems compared to solvent-based systems require the development of new additives able to overcome the difficulties of the transition towards new aqueous systems.

3. PECULIARITIES OF AQUEOUS SYSTEMS VERSUS SOLVENT-BASED SYSTEMS

Aqueous systems have some peculiarities that complicate the formulation of these products compared to solvent-based systems. Surface tension values of different solvent media are shown in **Table 1**.

Solvent	Surface Tension (mN·m)
Glycols	26-38
Esters	26-32
Oils	27-35
Paraffins	26
Water	73

***Table 1**. Surface tension values of different solvent media.*

As shown in Table 1, water has a surface tension value of 73 $mN.m^{-1}$, which is much higher than other solvent media. So adjusting aqueous digital inkjet inks and glazes requires a greater reduction of surface tension than solvent-based digital inkjet inks. This requires the use of surface tension reducers, which:

- Increase the probability of appearing printing defects as foaming or air.
- Require the use of other additives to correct such defects.

4. NEW WETTING AND DISPERSING ADDITIVES FOR AQUEOUS DIGITAL INKJET INKS AND GLAZES

The need for a drastic reduction of surface tension in aqueous digital inkjet inks and glazes, the specific requirements of inkjet printheads and the harsh application conditions in regards to temperature and humidity make very difficult to formulate these products. Therefore a close collaboration between manufacturers of additives and manufacturers of digital inkjet inks and glazes is required to develop new additives in order to achieve maximum product quality.

Wetting and dispersing additives play an important role to stabilize pigment dispersions in general and particularly inkjet inks and glazes. New Controlled Radical Polymerisation Technologies[2], CPT, are useful in the development process of digital inkjet inks and glazes in general and particularly the aqueous versions. **Figure 1** shows the comparison between polymers obtained by using new Controlled Radical Polymerisation Technologies, CPT, and polymers obtained by using Traditional Free-Radical Polymerisation Technologies, FRP.

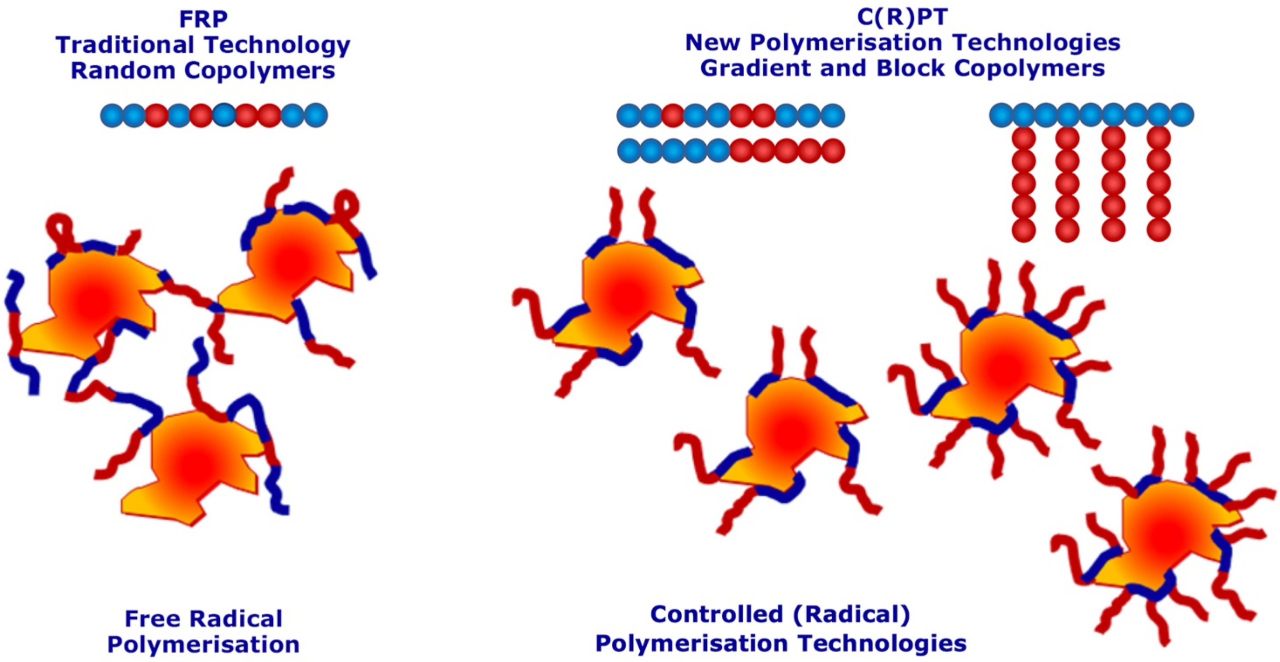


Figure 1. *Controlled Radical Polymerisation Technologies versus Traditional Free-Radical Polymerisation Technologies.*

Using New Controlled Radical Polymerisation Technologies:

- Random distribution of monomer is avoided therefore a tailored design of final copolymer is reached[2], as, for example:
    - Gradient copolymer.
    - Block distribution copolymer.
- A narrower molecular size distribution is achieved[2] as shown in **Figure 2**.

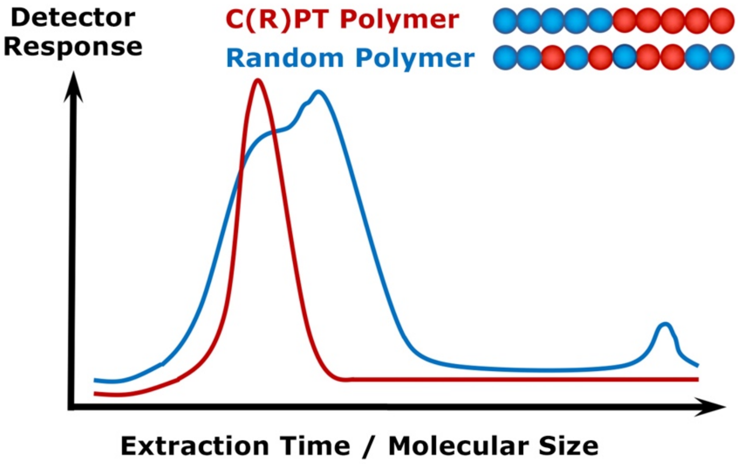


Figure 2. *Molecular size distributions of random polymers versus C(R)PT polymers.*

This narrower molecular size distribution allows designing wetting and dispersing additives showing a closer correspondence with the characteristics of the pigments[2].

Therefore, by using polymers designed by the new Controlled Radical Polymerisation Technologies:

- Wetting and dispersing additives show higher effectiveness.
- Stability of digital inkjet inks and glazes[3,4] is improved.
- Filterability of digital inkjet inks and glazes is improved, as shown in **Figure 3**.

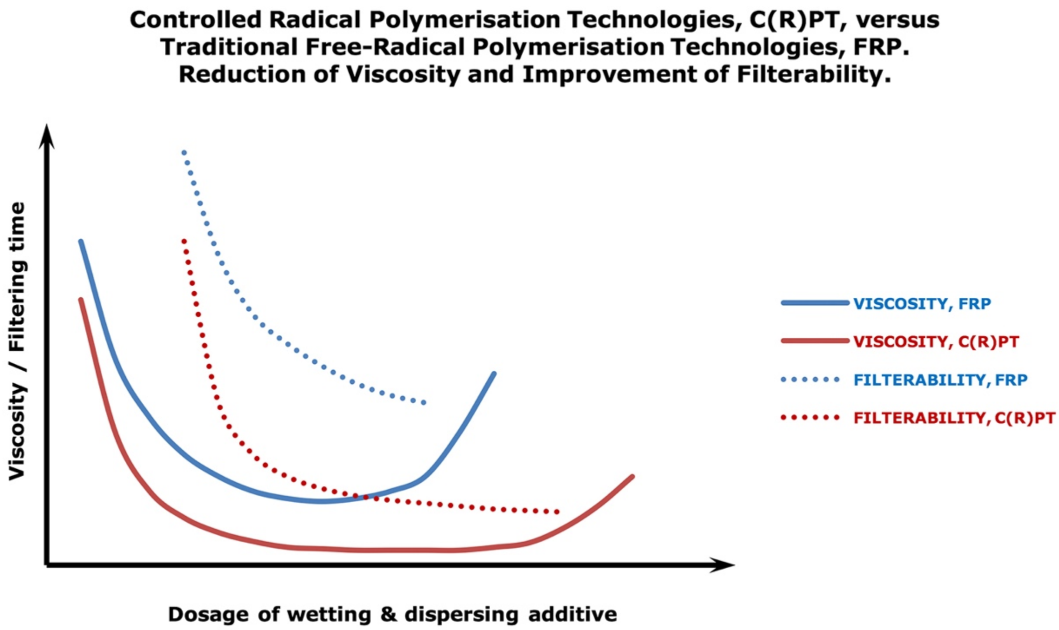


Figure 3. *Improved Filterability by using C(R)PT polymer based additives.*

As shown in **Figure 3**, the viscosity of ink or glaze is reduced and the filtering time of ink or glaze is also reduced, that is, filterability is improved, by increasing the dosage of wetting and dispersing additive. This is due to the reduction of interactions between pigment particles that usually limit both properties[2]. Viscosity tends to increase from a certain value of dosage of wetting and dispersing additive. This is caused by either an accumulation of fine pigment particles or an accumulation of electrical charge on the surface of pigment particles which promote interaction between particles[2], therefore agglomeration. It is also shown in **Figure 3** that the use of wetting and dispersing additives based on Controlled (Radical) Polymerisation Technologies, CPT, leads to a greater reduction of viscosity and greater reduction of filtering time, that is, improvement of filterability, compared to the use of wetting and dispersing additives based on Traditional Free-Radical Polymerisation Technologies, FRP.

It has been found that milling processes carried out in two phases, a first phase at high pigment concentration followed by a final transformation by adding the remaining liquid carrier, also improves the filterability of digital inkjet inks and glazes. Accumulation of fine pigment particles, that usually make filterability of inkjet inks and glazes much more difficult, is reduced if the processes are carried out in two phases.

5. SURFACE TENSION REDUCERS

Aqueous digital inkjet inks and glazes require a drastic reduction in surface tension due to the very high surface tension of water. Thus, the control of static surface tension and dynamic surface tension is a key point in digital inkjet printing processes.

Static surface tension is associated to extension and penetration processes of ink into the substrate, as shown in **Figure 4**.

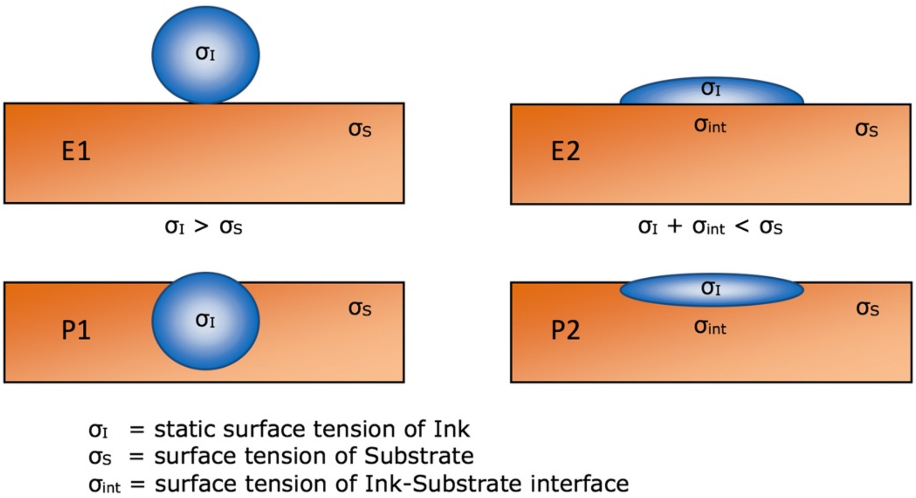


Figure 4. *Static surface tension: extension and penetration.*

As shown in **Figure 4**:

- E1: if the static surface tension of ink, σ_I, is higher than the surface tension of substrate, σ_S, the ink does not extend onto the surface of substrate.
- E2: if the sum of the static surface tension of ink, σ_I, and the surface tension of ink-substrate interface, σ_{int}, is lower than the surface tension of substrate,

σ_S, the ink and the ink-substrate interface extend onto the surface of substrate.

- The static surface tension of ink, σ_I, can be modified by using Liquid-Air surface tension reducers. The surface tension of ink-substrate interface, σ_{int}, can be modified by using Liquid-Solid surface tension reducers, i.e., wetting and dispersing additives.
- P1 and P2: if the ink contains Liquid-Solid surface tension reducers, σ_{int}, i.e., wetting and dispersing additives, the ink showing higher static surface tension, σ_I, therefore showing lower extension, P1, penetrates more in depth into porous substrates than the ink showing lower static surface tension, σ_I, P2.

Surface tension values associated to the formation of ink-substrate interface, σ_{int}, are usually very low, in fact negligible, compared to the values of static surface tension of ink, σ_I, and surface tension of substrate, σ_S.

Figure 5 shows the association of Dynamic surface tension with drop formation process[4].

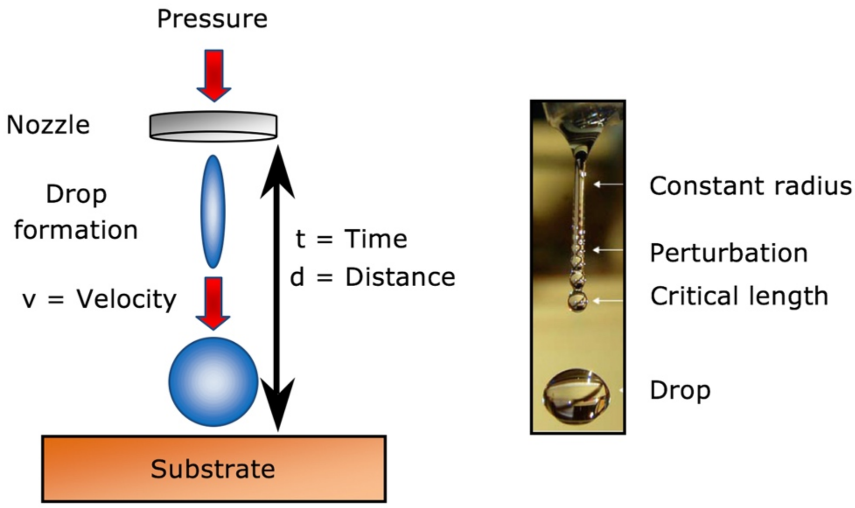


Figure 5. *Dynamic surface tension.*

Drops of ink must be completely formed in a reproducible manner within the short period of time between pulsation at the printhead and the deposition at the substrate. Otherwise, satellites[3,4] will appear and the desired design will not be properly reproduced.

So static and dynamic surface tension values are associated to different and independent processes, but it is well-known by experience that there is some interaction level between both properties because the modification of one of these values affects the other one.

6. DEFOAMER ADDITIVES

The drastic surface tension reduction required in aqueous products involves the appearance of defects such as foam or air into the inks or glazes. This leads to the use of defoamer additives in order to prevent and/or destroy the foam or the air eventually introduced into the ink or glaze. Some thermodynamic aspects of the action mechanism of defoamer additives are shown in **Figure 6**.

Extension Coefficient

$S = \sigma_I - \sigma_{int} - \sigma_D$

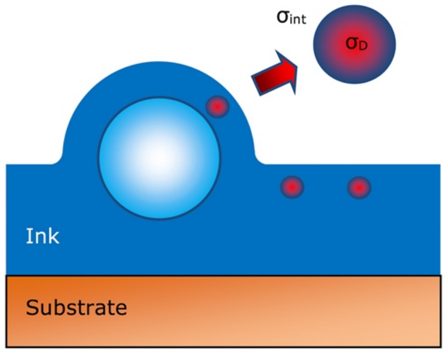
Penetration Coefficient

$E = \sigma_I + \sigma_{int} - \sigma_D$

A defoamer additive must show:

$S > 0 \qquad \sigma_I > \sigma_{int} + \sigma_D$

$E > 0 \qquad \sigma_I + \sigma_{int} > \sigma_D$



σ_I = surface tension of the Ink
σ_D = surface tension of the Defoamer
σ_{int} = surface tension of the la interface Ink/Defoamer → Incompatibility

Figure 6. *Thermodynamic aspects of the action mechanism of defoamer additives.*

A defoamer additive must show:

- Positive Extension Coefficient, S: the defoamer additive extends all over the ink.
- Positive Penetration Coefficient, E: the defoamer additive penetrates into the ink/foam interface, onwards lamella, thus it can be destroyed.

The defoamer additive must migrate into the lamella: this means that it must be slightly insoluble or incompatible with the ink otherwise it would remain stable/solved within the ink.

Milling processes of ceramic pigments are very aggressive so the micelles of defoamer additive are degraded during milling process, reducing its size in a major way. This fact determines the defoamer additive to be used as shown in **Figure 7**.

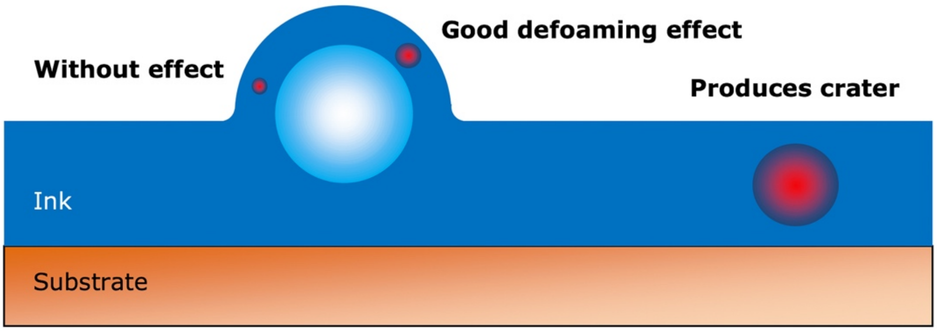


Figure 7. *Degradation of micelles of defoamer additive during milling process.*

As shown in **Figure 7**:

- If micelles of defoamer additive are degraded during milling process to a too small size, they will not be able to separate and break the double electrical layer of the lamella, then the lamella will not be destroyed.
- If micelles of defoamer additive are not sufficiently degraded during milling process, their size will be too big and some craters will appear.

Therefore, an appropriate balance must be found as shown in **Figure 8**.

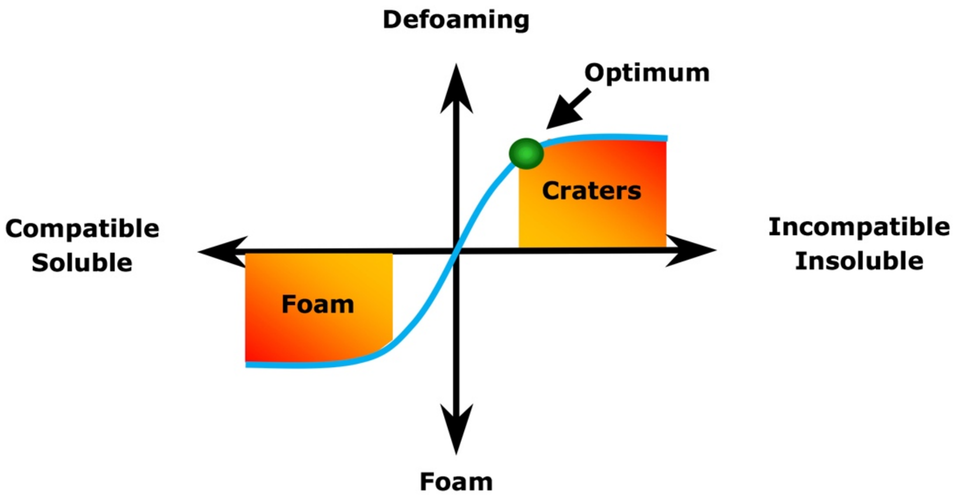


Figure 8. *Balance of incompatibility of a defoamer additive.*

The defoamer additive must show certain level of insolubility or incompatibility with the ink to show a positive penetration coefficient into the lamella but it must be neither too insoluble nor too incompatible since this involves the appearance of defects as craters.

By other hand, if the manufacturing process of the ink involves different shear levels, i.e., by some transformation stage after milling which could introduce air or foam into the ink, the use of a second defoamer additive showing lower incompatibility or smaller micelle size than the defoamer additive used during milling process should be considered, since the shear conditions during the transformation stage could be not higher enough to degrade the defoamer additive, producing craters.

7. FORMULATIONS OF AQUEOUS DIGITAL INKJET INKS AND GLAZES

Starting formulations of aqueous digital inkjet inks and glazes are shown in **Table 2** and **Table 3**.

Stage / raw material:	%
Milling:	
Water	37,0
Defoamer	0,2
Wetting and dispersing additive 1 (100%) *	4,5
Wetting and dispersing additive 2 (100%) *	1,5
Ceramic pigment **	40,0
Transformation (optional):	
Glycol	15,8
Biocide	0,1
Transformation:	
Static surface tension reducer	0,1
Dynamic surface tension reducer	0,8
	100,0

* w&d additive on solids: dosage depending on pigment type
** pigment contents: 30-40% depending on pigment type

Table 2. *Starting formulation of an aqueous digital inkjet ink.*

Stage / raw material:	%
Milling:	
Water	56,1
Defoamer	0,2
Wetting and dispersing additive (100%) *	2,5
Glaze **	25,0
Transformation (optional):	
Glycol	15,0
Biocide	0,1
Transformation:	
Static surface tension reducer	0,1
Dynamic surface tension reducer	1,0
	100,0

* w&d additive on solids: dosage depending on glaze type
** glaze contents: 15-25% depending on glaze type

Table 3. *Starting formulation of an aqueous digital inkjet glaze.*

Within these formulations:

- The use of wetting and dispersing additives is required to ensure the stability of the ink or glaze, that is, to prevent increase of viscosity and/or flocculation after production and/or during storage.
- The type and the dosage of the wetting and dispersing additive depend on the type of pigment or glaze.
- Some pigments require the use of two wetting and dispersing additives to ensure the stability of the ink. It is said that the additive at major dosage minimizes interactions between pigment particles and the additive at minor dosage performs as a synergistic additive and/or minimizes interactions with liquid media.
- Pigment dispersion is carried out in aqueous phase, without glycol. This allows a better evaluation and better performance of the defoamer additive as, with the presence of glycol, some partition between aqueous phase and organic phase would happen. Glycol can be added at milling stage if required by production requirements.
- The use of at least one defoamer additive during milling process is required. The use of a second defoamer additive showing lower incompatibility or smaller micelle size than the defoamer additive used during milling process should be considered in post-milling stages which could introduce air or foam into the ink or glaze, since the shear conditions during post-milling stages are not higher enough to degrade the defoamer additive used during milling process, then craters would appear.
- Two surface tension reducers are used, one of them to reduce mainly static surface tension and the other one to reduce mainly dynamic surface tension. Surface tension reducers based on hydrocarbons usually migrate faster to the surface of the drop therefore act mainly as dynamic surface tension reducers whereas surface tension reducers based on silicones act mainly as static surface tension reducers.
- Surface tension reducers can show certain affinity for the particles of pigment or glaze therefore can compete with wetting and dispersing additives if added simultaneously. Therefore, the addition of surface tension reducers after grinding process is recommended.

8. CONCLUSIONS

Aqueous products, as solvent-based products, require the use of wetting and dispersing additives to stabilize pigments. New Controlled Radical Polymerization Technologies, CPT, provide a development platform of additives to develop digital inkjet inks and glazes.

The need of a drastic reduction in surface tension in aqueous products requires the use of static and dynamic surface tension reducers as well as defoamer additives.

Therefore, the formulation of aqueous digital inkjet inks and glazes is much more difficult than solvent-based products.

BIBLIOGRAPHY

[1] System-Ceramics. www.system-ceramics.com

raunhofer Institute Manufacturing Engineering and Automation, Stuttgart, Germany, www.ipa.fraunhofer.de

[2] Stabilisation of pigments in digital inkjet printing inks by wetting and dispersing additives based on new polymerisation technologies.

Qualicer Congress 2014. Markus Roessner, Byk-Chemie GmbH, Germany. Roger Escámez, Comindex S.A., Spain

[3] Physics of Piezoelectric Shear Model Inkjet Actuators, Jürgen Brünahl, Stockholm, Sweden. 2003. ISBN: 978-981-281-821-8.

Turbiscan® application paper on ink. 2009. www.formulaction.com

[4] Fraunhofer Institute Manufacturing Engineering and Automation, Stuttgart, Germany, www.ipa.fraunhofer.de

The chemistry of inkjet inks. Ceramic inks. Stefan Güttler, Fraunhofer Institute Manufacturing Engineering and Automation, Stuttgart, Germany. Andreas Gier, Inomat GmbH, Neunkirchen, Germany. 2009. ISBN 91-628-5675-8.