STABILISATION OF PIGMENTS IN DIGITAL INKJET PRINTING INKS BY WETTING AND DISPERSING ADDITIVES BASED ON NEW POLYMERISATION TECHNOLOGIES

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ABSTRACT

Digital inkjet printing techniques are strongly introduced in the market of ceramic tile decoration and are continuously under development. Changes in piezoelectric printheads and the surface properties of the pigments used are only a few examples pushing to this continuous development. This is why Byk-Chemie is working together with inkjet inks manufacturers in order to achieve the highest quality standards in their products.

Wetting, dispersing, grinding and stabilisation processes play an important role in the manufacture of inkjet inks. Byk-Chemie has developed wetting and dispersing additives based on new polymerisation technologies with the aim of adapting to the new technical challenges in this market.

The surface properties of the pigment are the key to the selection of the suitable wetting and dispersing additive. Nevertheless the wetting and dispersing additive must be compatible with the dispersion vehicle used, so its polarity will be another important factor to take into account.

Steric hindrance is the main pigment stabilisation mechanism due to the intrinsic characteristics of inkjet inks. Only agglomerate-free dispersions will give excellent colour strength and avoid undesired effects in the printheads. The demanding quality standards and the new decoration requirements can only be reached using wetting and dispersing additives specifically designed for inkjet inks. High molecular weight wetting and dispersing additives or additives based on new Controlled Radical Polymerisation Technologies are examples of the newest developments in this market.

In this complex printing technique, special attention must be paid to the ink behaviour under the flow conditions at the printhead. The drop formation process, satellites formation and sensitivity to moisture, which is present during the printing process, determine the ink formulation. The viscosity of the ink, related to the pigment stabilisation process, and the surface tension play also a key role in this part.

1. INTRODUCTION

Within the last years a real technological revolution has happened in the world of ceramic decoration with the introduction of digital printing technology. There are, among others, some advantages over the traditional decoration technologies like Rotocolor technology[1]:

- A better definition of the design: it is possible to decorate ceramic substrates with any design, such as imitations of natural materials, reproductions of artistic works, historical designs and pictures.
- It is possible to decorate concave or convex surfaces as there is no contact between the printhead and the substrate.
- Production batches can be adjusted to each single order, without having to store overproduction items.
- Strong reduction of production downtime between batches of different designs, as there is no need to stop the machine for the next set-up.
- Better colour consistency between different production batches.

In this new technology, the formulation of the inks must fulfil the singularities of the ceramic pigments and the extreme application conditions

2. CHARACTERISTICS OF INKJET INKS

Inkjet inks for ceramic decoration must fulfil, among others, the following characteristics[2]:

- Pigment particle size between 300 and 800 nanometres.
- Pigment particles must be deflocculated and stabilised to prevent the presence of agglomerates.
- Viscosity.
- Surface tension.
- Application conditions.
- Drop formation, extension and penetration.

3. WETTING, DISPERSION AND STABILISATION PROCESSES OF CERAMIC PIGMENTS

There are 3 phases in the grinding process of a ceramic pigment during the production of an inkjet ink:

- **Phase 1.- Pigment wetting by the liquid vehicle**

Pigments are surrounded by air before they are added into the ink. At this stage, the liquid must displace the air surrounding the pigment. The surface tensions of the air γ_A, the pigment γ_P, and the liquid vehicle γ_L, play an important role as shown in Figure 1.

$\gamma_A < \gamma_P < {}_L$
Air around the pigment
Liquid does not wet the pigment

$\gamma_A < \gamma_L < {}_P$
Liquid wets the pigment

$\gamma_L < \gamma_A$
Liquid around air: foam

Figure 1. Surface tension in the pigment grinding process.

The surface tension of the liquid vehicle γ_L must be at the same time:

- Lower than the surface tension of the pigment γ_P so that the liquid vehicle spreads over the pigment.
- Higher than the surface tension of the air γ_A to avoid the formation of foam.

The basic or general structure of a wetting and dispersing additive is shown in Figure 2.

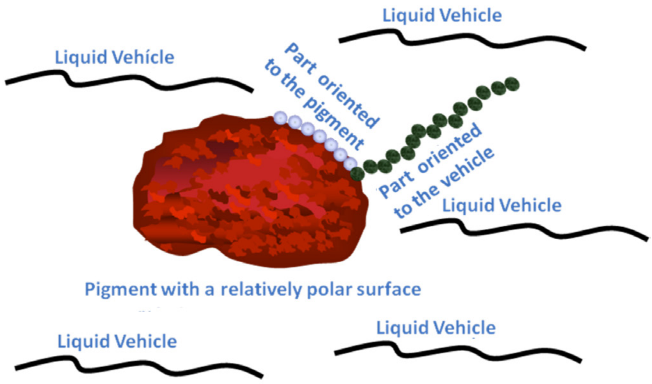

Figure 2. Basic or general structure of a wetting and dispersing additive.

A wetting and dispersing additive has different parts within its structure:

- Parts which are oriented towards the surface of the pigment and force the liquid vehicle to surround the pigment, i.e. the pigment is wetted.

- Parts which are oriented towards the vehicle, giving compatibility to the whole system.

- **Phase 2.- Pigment dispersion and grinding**.

Interactions between solid particles release higher energy than interactions between particles at any other state of matter. Therefore, solid particles show a tendency to agglomerate, e.g. flocculate, as this is a lower energy state of matter. Therefore, during pigment dispersion and grinding, enough energy is introduced into the system in order to:

- Separate pigment particles into their individual particles.

- Break down individual particles into finer particle size suitable to be used in the inkjet printing process.

The wetting and dispersing additive dosage depends on:

- The type of pigment.

- The pigment particle size.

- The type of vehicle.

Figure 3 shows the influence of the dosage of the wetting and dispersing additive on the viscosity of the inkjet ink.

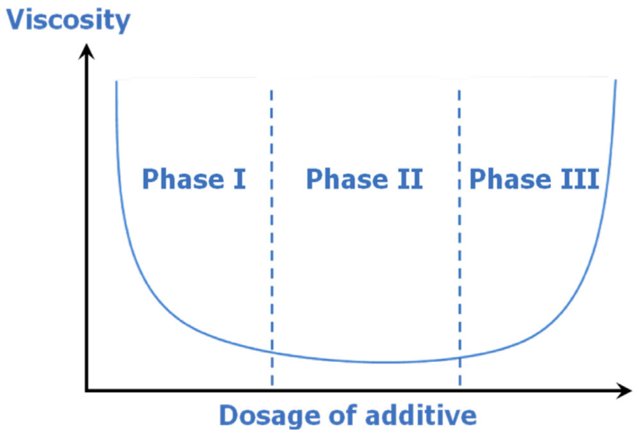

Figure 3. Viscosity of the inkjet ink versus dosage of wetting and dispersing additive.

3 PHASES ARE DIFFERENTIATED:

- Phase I: the wetting and dispersing additive wets the pigment particles and progressively reduces interactions between them with the consequent reduction of the inkjet ink viscosity while increasing the dosage of the additive.

- Phase II: from a certain dosage of wetting and dispersing additive, the pigment is completely surrounded by the additive and the excess of additive stays free in the liquid without interacting with the pigment, thus no substantial modification of the inkjet ink viscosity is shown.

- Phase III: from a certain dosage of wetting and dispersing additive, an increase of viscosity is shown due to, among other reasons:

    - Very fine pigment particle size. Figure 4 shows the influence of the particle size on the viscosity and the dosage of wetting and dispersing additive.

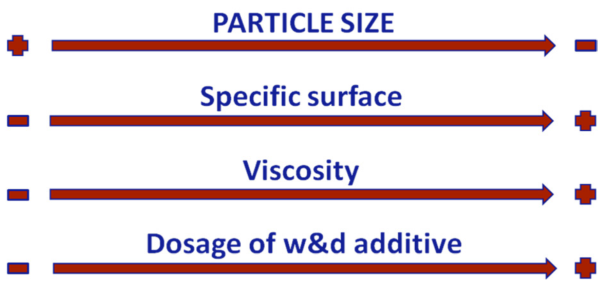

Figure 4. Influence of particle size on the viscosityand the dosage of wetting and dispersing additive.

The smaller the particle size is, the greater the specific surface is, which leads to:

- An increase of interactions between pigment particles that causes an increase of viscosity.

- A higher dosage of wetting and dispersing additive to completely surround pigment particles, avoid interactions between them and reduce viscosity.

- Accumulation of electrical charge on the surface of the pigment particles which leads to flocculation due to the electrostatic interactions between them, leading to an increase of viscosity.

Dispersion and grinding equipments with the help of grinding elements are used at this stage.

- **Phase 3.- Pigment stabilisation**.

Solid particles show a natural tendency to agglomerate, e.g. flocculate. Therefore, once the right particle size during the grinding process is reached, the pigment must be stabilised to avoid the natural process of agglomeration.

The main stabilisation mechanism for solvent inkjet inks is the steric hindrance mechanism which is shown in Figure 5.

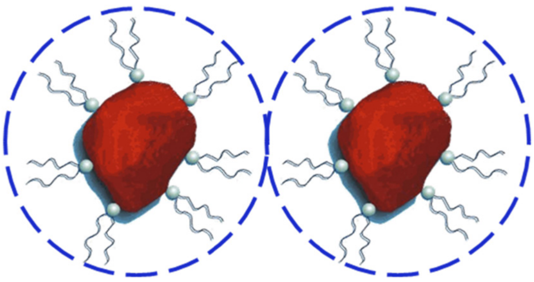

Figure 5. Stabilisation mechanism by steric hindrance.

The wetting and dispersing additive surrounds the pigment particles and builds a crown creating a certain volume around them which prevents the particles from approaching each other. This results in:

- Prevention of pigment flocculation.

- Prevention of viscosity increase.

This is especially important for:

- The transport and storage of inkjet inks.

- The printing process. Solid particles in the bosom of fluids in motion are under the action of Magnus[3,4] hydrodynamic forces. These forces explain the special trajectories of movement of balls in various sports. The Magnus hydrodynamic forces lead to the approach of solid particles under high shear forces developed at the printhead during the process of inkjet printing, between 10^4 and 10^6 s^{-1}, as shown in Figure 6.

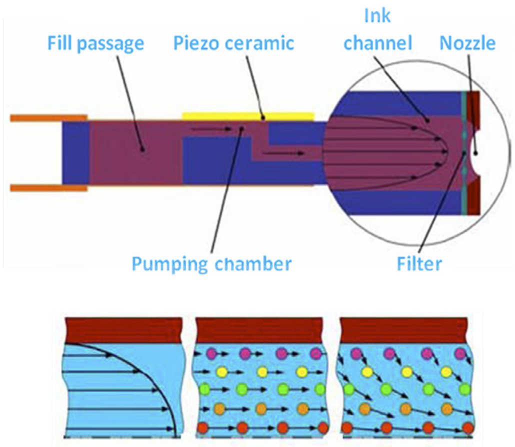

Figure 6. Magnus hydrodynamic forces developed at an inkjet printhead.

The ink goes through the ink channel up to the nozzle. The high shear forces developed at the printhead magnify the Magnus hydrodynamic forces that produce the approach of the pigment particles. This leads to:

- Increase of viscosity that influences / limits the drop formation.

- Increased risk of pigment flocculation.

4. TRADITIONAL TECHNOLOGIES OF WETTING AND DISPERSING ADDITIVES

There are several traditional technologies of wetting and dispersing additives based on different chemistries which include the ones shown in Figure 7.

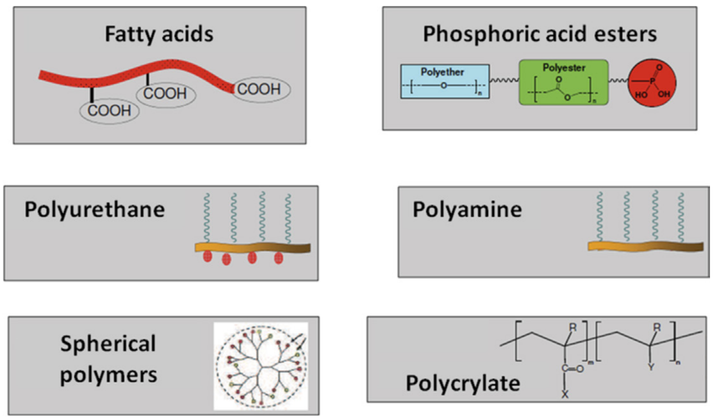

Figure 7. Traditional technologies of wetting and dispersing additives.

The choice of the type of the wetting and dispersing additive depends on the surface characteristics of the pigment and the type of liquid vehicle used.

5. THE NEW CONTROLLED RADICAL POLYMERISATION TECHNOLOGIES, CPT

The new Controlled Radical Polymerisation Technologies C(R)PT are a new option to improve the characteristics of inkjet inks. Figure 8 compares the traditional polymerisation technologies with the new technologies based on controlled radical polymerisation.

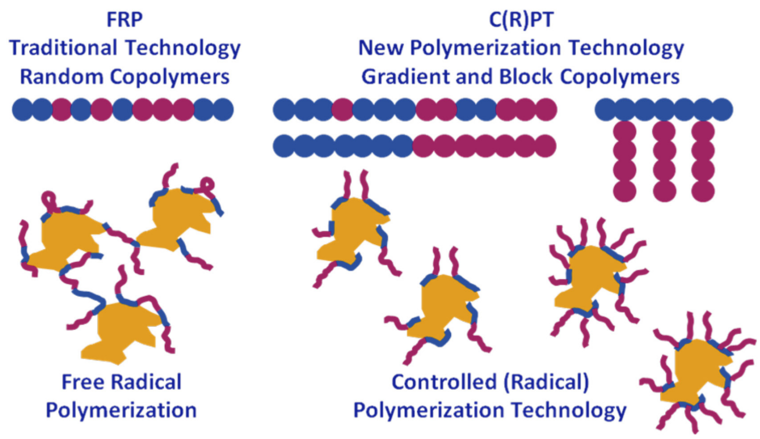

Figure 8. Traditional free-radical polymerisation technologies versus Controlled Radical Polymerisation Technologies.

As shown in Figure 8:

- Using traditional polymerisation technologies via free radicals:
  - Monomers are randomly distributed within the structure of the final copolymer.
  - Some of the structures are folded on themselves with the consequent reduction of the dispersing efficiency of the final copolymer.
- Using the New Controlled Radical Polymerisation Technologies:
  - Random distribution of monomers is avoided and therefore a tailored design of final copolymer is reached:
    - Gradient distribution copolymer.
    - Block distribution copolymer.

Figure 9 compares the molecular size distribution of polymers obtained by using traditional polymerisation technologies via free radicals with those obtained by using the new Controlled Radical Polymerisation Technologies.

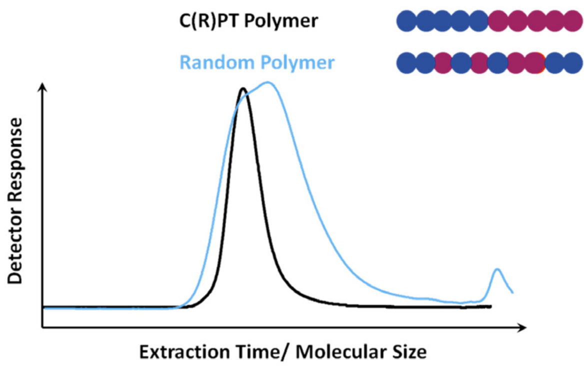

Figure 9. Molecular size distributions of random polymers versus C(R)PT polymers.

As shown in Figure 9:

- Traditional polymerisation technologies via free radicals provide polymers with a relatively wide molecular size distribution as collateral or chain reactions among free radicals are relatively difficult to be controlled / limited.
- The new Controlled Radical Polymerisation Technologies provide polymers with a more uniform and specific structure and a narrow molecular size distribution showing a greater correspondence with the characteristics of the pigment.

Therefore, polymers designed by the new Controlled Radical Polymerisation Technologies show a greater dispersing efficiency. Thus, the stability of inkjet inks during transport and storage is improved. This better dispersing efficiency improves stability of inkjet inks during the printing process as it reduces the effect of the Magnum hydrodynamic forces developed under the high shear suffered by the inkjet inks at the printhead which influence or limit the drop formation.

6. DROP FORMATION

Drop formation is crucial in inkjet printing processes. Figure 10 shows the process of drop formation by looking at the sequence of printhead shots through a stroboscope[5]: undesired formation of satellite drops reducing definition of the printed design is shown.

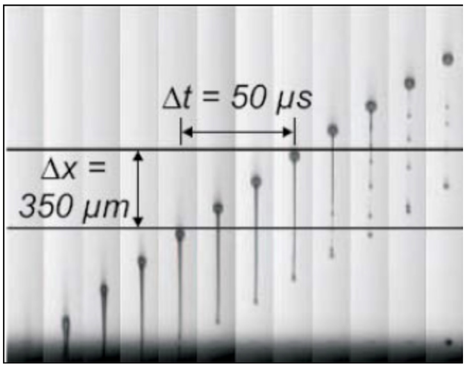

Figure 10. Drop formation by looking at the sequence of shots of a printhead through a stroboscope.

Inks must fulfil certain requirements related to drop formation:

- Viscosity around 25 mPa·s at room temperature and 10-15 mPa·s at printing temperature around 40-60°C. Higher viscosity is related to the undesired formation of satellite drops accompanying the main drop.

- Surface tension:

    - Static surface tension around 25-30 mNm^{-1}.

        - Higher static surface tension is related to the undesired formation of satellite drops accompanying the main drop.

        - Lower static surface tension can produce the extension of the drop on the exterior surface of the printhead, which causes drop shape deterioration, undesired drop fall by gravity and air entrapment inside the printhead.

· Lower dynamic surface tension can reduce drop formation speed then printing speed.

- High shear forces developed at the printhead during the printing process, between 10^4 y 10^6 s^{-1}.
- Diameter of nozzle around 20-70 microns (5-200 picolitres).
- Distance printhead-substrate around 1 millimetre or higher.

Inks must also withstand application conditions:

- Application temperature. Tiles are printed just after a drying process. Temperature is around 40-60 ° C when tiles pass under the printheads.
- Humidity during application. Tiles emit moisture in counterflow to the dosage of the ink.

Figure 11 shows the relation between surface tension, drop size, drop extension and drop penetration.

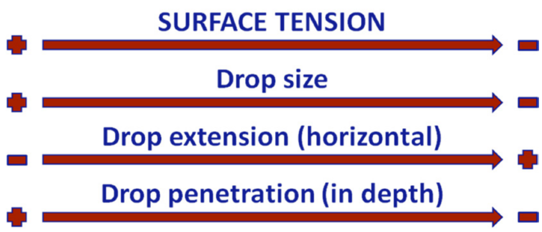

Figure 11. Relationship between surface tension, drop size, drop extension and drop penetration.

The lower the surface tension is, the lower the drop size is, and the lower the drop penetration is. The use of surface tension reducers is useful to improve drop formation.

7. DISPERSION STABILITY CONTROL

It is common practice to measure the pigment particle size to test the stability of inkjet inks:

- Just after the production of the inkjet ink, as an indicator of production control.
- Regular monitoring of the inkjet ink, as an indicator of time stability / shelf-life.

The most common used methods are filtering with the help of a syringe, laser diffraction and Turbiscan®[6], whose principle is shown in Figure 12.

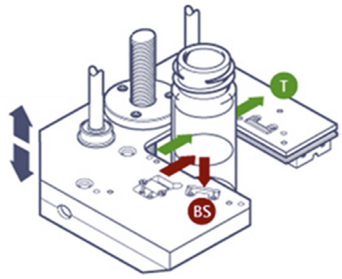

Figure 12. Principle of Turbiscan®.

Measurement of transmitted light (T) and backscattered light (BS) at different heights of the sample of the inkjet ink is carried out. Monitoring the measurement of backscattered light at different times gives graphics that characterise the state of the inkjet[6] inks as shown in Figure 13.

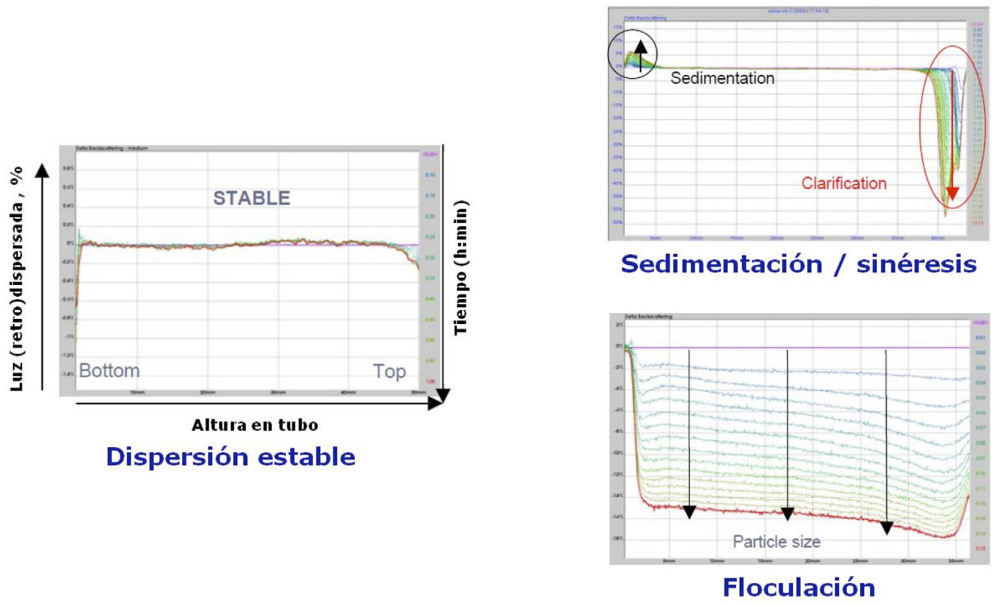

Figure 13. Characterisation of inkjet inks by Turbiscan®.

- The first measurement series give a baseline or reference.
- A stable base at different times, e.g. overlapped lines, indicates that the pigment is properly stabilised with a uniform distribution within the sample.
- A progressive increase of the backscattered light at the lower area of the sample indicates that the pigment has settled down.
- A progressive reduction of backscattered light line at the upper area of the sample indicates that the sample shows syneresis.
- A progressive decrease of backscattered light line at any height of the sample indicates that the pigment is flocculated, so that the stabilisation of the pigment is poor.

8. CONCLUSIONS

The specific requirements of inkjet printing systems for ceramic decoration and the constant evolution of ceramic pigments require constant development of wetting and dispersing additives, among other additives.

The new Controlled Radical Polymerisation Technologies provide a new platform to design wetting and dispersing additives that contribute to improve the stability of inkjet inks for ceramic decoration:

- During transport and storage.
- During the printing process.

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