Digital Revolution in Printing Inks

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Although inkjet printing may have permanently changed the printing ink sector, one consideration remains unchanged: dispersing is the decisive process step for an ink's stability, flow properties, and coloristic values. Two new dispersing additives now offer fresh possibilities for printing on textiles and ceramic tiles.

In the last 30 years, the printing ink market has been revolutionized by the meteoric progress in digital inkjet printing[1]). The technology – used in applications ranging from office printers to printed textiles, tiles, awnings and cell phone shells – offers boundless possibilities to the designer. Previously stagnating sectors are experiencing new momentum as, besides soaring sales, print process efficiency is increased with speeds of up to 75 m/min.

Unlike conventional printing processes, digital printing is non-contact, thus enabling printing on relief surfaces and, in principle, even on 3D structures. Picoliter-sized (10^{-9} ml) ink droplets are shot in microseconds through over one hundred µm nozzles in a print head onto the substrate generating images with a resolution of over 1000 dpi (dots per inch), so that the eye cannot distinguish the dots. Along with the quality and speed of digital print technology, demands on digital printing inks and thus raw materials have also greatly increased.

THE IMPORTANCE OF DISPERSING ADDITIVES. In the manufacture of inks, pigment dispersion is not only the most time-consuming and expensive stage, but it is also the decisive process step for the ink's stability, flow properties, and coloristic values[2]. The correct choice of dispersing additive is crucial for the control and optimization of this task. The dispersing process involves three consecutive steps: wetting, dispersion, and stabilization[3].

Today's dispersing additives are multi-functional and can affect both wetting and stabilization; i.e. anchor groups ensure strong adhesion to the colorant surface via, for example, aromatic rings. Other segments, which are water-compatible, enter the aqueous medium thus affecting stabilization[4].

FORMULATION GUIDELINES. Deciding on the choice and amount of dispersing additive for optimizing an ink formulation is a time-consuming challenge. Both parameters enormously impact the production efficiency and performance of the ink. Fig. 1 shows the effect of the additive concentration and the dye content on the viscosity.

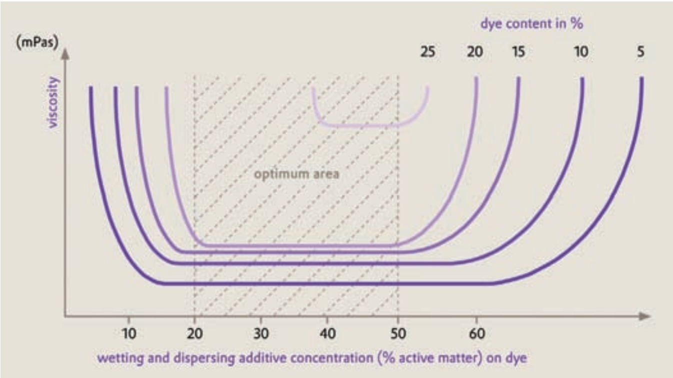

Fig 1: Influence of dye content and additive concentration on viscosity

First, dispersing additives lower viscosity and allow higher pigment loading. Second, the additive concentration plays a central role in achieving the lowest viscosity and shows an optimum area. At low additive concentrations, the particles still mutually attract and the viscosity is at a high level. The optimal additive concentration leads to complete coverage of the dye surface and its attraction forces, resulting in very low viscosities. On the other hand, too much dispersing additive causes high viscosity arising from the increasing layer of dispersing additive on the pigment particles and a possible thickening effect of the liquid phase.

CHANGE IN THE PRINTING INK INDUSTRY. The growing end-user trend towards customized products poses a challenge for inks for digital textile print and ceramics. The addition of high-performance wetting and dispersing additives imparts to such inks the required properties as shown in the investigations described below.

BEST PRACTICE FOR TEXTILE DIGITAL PRINT. For textile print, the colorant must be finely ground to the nm range. This prevents the nozzles from clogging and from missing dots during printing. Additionally, only the finest particles satisfy the high demands made on colour intensity and brilliance. Shear rates of up to 500,000 1/sec can occur during printing; therefore, high shear resistance, very low viscosities (in the range <10 mPas), and Newtonian flow characteristics are essential to ensure optimum printability. Digital printing on ceramic tiles requires application of a greater amount of material. Here, particle sizes should often be in the low µm range and viscosities should be a maximum of 25 mPas. Besides the dispersing additives, specialty defoaming additives ensure effective defoaming while humectants for pigment concentrates prevent drying out of the digital printing inks.

raw material	quantity	
	dye	pigment
dye	20.0	—
pigment	—	16.0
water	48.9	47.9
dispersant (40 % active)	25.0	20.0
TEGO® Humectant 7000	5.0	15.0
TEGO® Foamex 830	1.0	—
TEGO® Foamex 810	—	1.0
biocide	0.1	0.1
TOTAL	100	100

Table 1: Formulations for textille ink concentrates based on dyes and pigments

In the waterborne textile inkjet inks shown in Table 1, a high-performance, polymeric wetting and dispersing additive is tested against a standard additive. The subsequent tests focus on the core properties of viscosity, particle size, and stability after 2 weeks storage at 50 °C. The formulations with standard dyes Yellow 54, Brown 27, and Blue 360 were dispersed for 4 hours in a LAU Disperser with 3 parts w/w of glass beads Ø = 1-1.2 mm, with Pigment Red Ø = 2.5-2.8 mm, sieved and measured on the following day. For further optimization of the formulation, dispersing with 0.3-0.4 mm zirconium beads in a pearl mill is recommended to obtain the finest particles. Experience shows that results from the LAU Disperser screening process mirror those in practice.

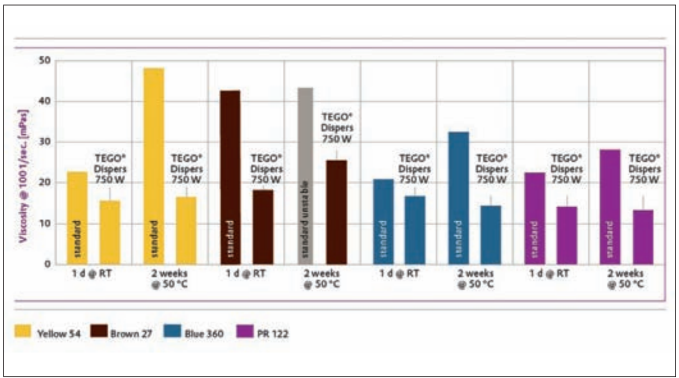

Fig.2: Viscosities determined according to DIN EN ISO 3219 using Anton Paar Model NCR 301, geometry CP50/2 at 23 °C and a shear ramp of 1 – 1000 1/sec.

The results in Fig. 2 show the superiority of the high-performance wetting and dispersing additives in all the test formulations: Their use achieves significantly lower printable viscosities with all the dyes and Pigment Red 122 as an example pigment. After two weeks in storage, the standard product shows a strong increase in viscosity and is therefore unusable. In the case of the dye Brown 27, particles were formed which could not be stirred and resulted in a hard sediment (see also Fig. 3). Inadequate anchoring and weak stabilization of the dispersing additive on the surface of the dye impair storage stability and lead to undesirable viscosities as well as an increase in particle sizes through re-agglomeration. This is why modern dispersing additives are designed to be multifunctional. The performance of dispersing additives is strongly determined by chain length, choice of monomer, and the arrangement of monomer units.

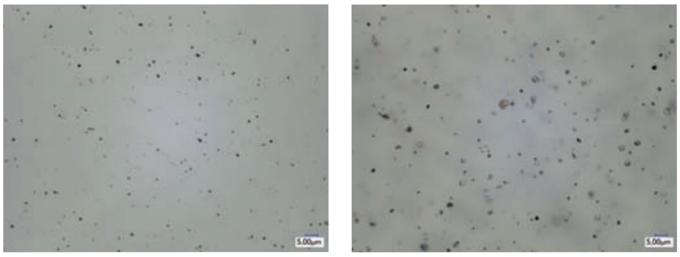

Fig. 3: KEYENCE VHX 5000 digital icroscopic images of rub-outs with Brown 27 after one day storage at room temperature. Left: fine, homogeneous particles with high-performance wetting and dispersing agent (d50 = 294 nm). Right: coarse agglomerates with standard additive (d50 = 547 nm)

For example, local densification of anchor and stabilization groups is advantageous. The schematic representation of one particular high performance wetting and dispersing additive in Fig. 4 shows numerous anchor groups in close proximity in the region of the main chain of the polymer additive. This enables quick and strong anchoring of the dispersing additive onto the dye surface. The extensive side chains serve to stabilize against re-agglomeration. The high-performance wetting and dispersing additive stabilizes by electric and steric repulsion mechanisms. Electric stabilization occurs through Coulombic repulsion of like charges, in this case, anions. In steric stabilization, side chains slide away from each other as a result of entropic effects and osmotic pressure.

The high-performance wetting and dispersing additive thus guarantees that, even after storage and shear, inks manufactured with the dyes commonly used for textile print will be stable, low viscosity, and exhibit the highest brilliance.

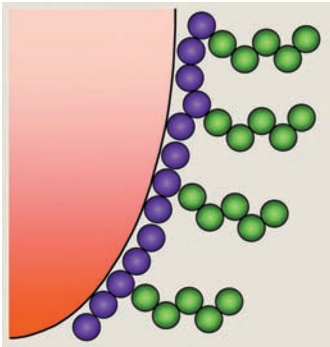

Fig. 4: Schematic representation of the anchoring of a graft copolymer on a colorant surface.

BEST PRACTICE FOR CERAMIC INKS. Close cooperation between the manufacturers of printing equipment, inks and tiles has resulted in digital print largely replacing the previously customary rotary screen printing process.
Modern dispersing additives have enabled the challenges in the formulation of and printing with ceramic inks and glazes with high solids content and high density, hard to disperse particles to be overcome. The described test series of waterborne ceramic inks

compares the desired core properties of low viscosity and simultaneous slight tendency to settle during accelerated storage. Fig. 5 shows that despite increased viscosity, the standard product is subject to sedimentation. The tested polymeric wetting and dispersing additive exhibits the highest performance through an impressive lowering of viscosity. Furthermore, the ceramic ink remains stable without sedimentation after 3 weeks storage at 50 °C. The unique performance of the polymeric wetting and dispersing additive makes printable, process-stable waterborne ceramic inks a reality.

Fig. 5: Storage samples after 3 weeks at 50 °C of ceramic inks based on PB 28 with 45% solids content. Left: no settling with polymer wetting/dispersing additive (η = 21 mPas at 1000 1 / sec.). Right: sediment with standard additive (η = 26 mPas at 1000 1 / sec.)

RESULTS FOR TEXTILE DIGITAL PRINT AND CERAMIC INKS. The authors showed that the use of standard additives in textile print results in low storage stability and excessive viscosities. In contrast, high-performance wetting and dispersing additives, such as TEGO® Dispers 750 W, meet the high technical demands in textile digital print as they achieve the lowest, easily printable viscosities and finest particle sizes for all dyes. This is also true for the difficult-to-stabilize Pigment Red 122. The special polymer design allows for the electrosteric stabilization of various colorants and ensures the lowest viscosities at outstanding shear stability and storage stability. This strong anchoring of pigments and dyes is particularly necessary in the textile sector. For the waterborne ceramic sector, it was shown that polymeric wetting and dispersing additives, such as TEGO® Dispers 752 W, achieve a significant lowering of viscosity and high stability. Thus, they make printable, process-stable waterborne ceramic inks a reality. ↙

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