Speed of Ink Absorption on Modified Paper Surfaces

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Abstract

In the last couple of years Inkjet printing speeds have increased dramatically. It can be expected that commercial inkjet printing with associated 'web-press' systems soon will meet or exceed the very high printing speeds of impact printing methods, such as offset. Microporous paper coatings used for modern photo inkjet paper are known for their extremely fast drying behavior and ink drop absorption, compared to standard paper. Fumed silica with its unique fractal structure is the key ingredient, hence creating pores and capillaries of the microporous coating. It can also be used on standard printing paper by applying very thin layers at the sizes press of the paper machine. The result is impressively improved print quality but also enhanced absorption speed of the ink drops. In this technical study, we used high speed cameras to measure the speed of absorption of water and a model ink at different modified paper surfaces.

Introduction

Fumed silica is commonly used in coating formulations to produce the high quality photo inkjet media that feature instant drying times, brilliant colors, uniform ink absorption, superb resolution and water fastness. The fractal structure of the aggregated particle is the basis which allows the microporous network to be developed within the coating at a finer scale than conventional pigments. This structure provides the essential capillary action needed to transport the ink vehicle quickly away from the media surface.

Recently we introduced a concept [1] that transfers the basic idea of this technology to plain paper. We have performed extensive trials on a pilot paper machine and carried out additional analytics, which we reported last year [2]. There were first indications, that even a very thin layer of fumed silica without an extended pore system like in inkjet photo paper can increase the imbibition speed of the ink drops dramatically. This paper will report first results of high speed camera measurements following single drops interacting with the paper surface.

Paper Sizing Concept

Paper sizing is a generally used technique applied to most office and printing papers. Adding fumed silica dispersions to the size press formulation offers an easy and affordable way to introduce nanostructured particles and a respective pore system to the surface. It effectively raises the print quality of the correspondingly treated papers to another quality class.

The process makes use of aqueous dispersions of fumed silica ("AEROSIL®"), which are available in both cationic and anionic variants. When used in combination with starch or PVA as binder or sizing agent respectively, they form the matrix for the formulation that is applied on the paper machine online with the aid of puddle-type or premetered size press. Our pilot tests carried out on a Kämmerer paper machine have proven the feasibility of the process on a simple puddle-type press and provided important discoveries. Even better results are expected on modern premetered size presses, as leading paper manufacturers have already impressively confirmed in operating tests.

The improvements in print quality are eye-striking. Especially ink coverage and homogeneity, but also optical density, print through and general print appearance show significant performance enhancements [2, 3, 4].

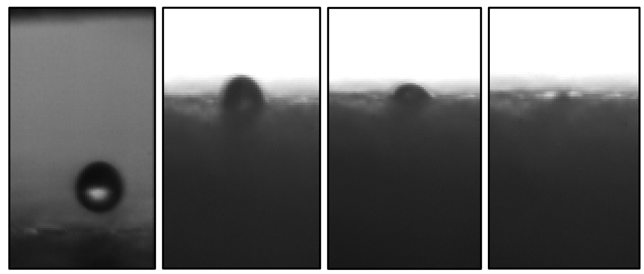

***Figure 1**. Following the drop by high speed camera. From left to right: 1) just before impingement, 2) just after spreading, 3) during imbibition, 4) just after complete imbibition.*

Need for Speed

Actual commercial inkjet web presses like the HP Inkjet Web Press or OCE's Jetstream series can print with linear speed of up to 3.3 m/s, which calculates to 2865 full color duplex A4 pages per minute [5]. Interestingly, this number is similar to the output of the first industrial impact printing machines at the end of the 19^{th} century. Assuming a length of three meters of the paper web from print head to rewinding, one ink drop has as little as one second to be absorbed by the substrate to avoid wetting the opposite side of the web. Furthermore, since multiple print heads are used in a row, the available drying time between two print heads is only a fraction of a second.

The manufacturers of commercial web presses emphasize that their speed can be scaled up linearly by the numbers of print heads used in a row. Therefore, in contrast to other competing digital printing technologies the web speed is not limited. This means that we are just at the beginning of high speed web press generations. One can doubt that classic printing paper is able to fulfill these new speed requirements and smart concepts to overcome this issue are necessary. Paper sizing with fumed silica is a possible solution.

Theory

For a single drop, inkjet printing on microporous media can be described as a three stage process: 1) spreading, where the respective surface energies and properties of the ink liquid and the microporous framework play a role, 2) absorption of the ink drop by capillary forces into the pores, and finally 3) drying or evaporation of the liquid. For the spreading phase Desie et al. [6, 7] could show that it is determined by the hydrodynamic properties and is very fast. The absorption phase can be well described by a capillary wicking process according to the theory of Davis-Hocking. Evaporation is the slowest process only being finalized after many seconds ore even minutes.

The kinematics of the interesting stage 2 can be described by the well-known Lucas-Washburn equation, giving the drop penetration depth d as a square root of time:

$$d(t) = \sqrt{\frac{r \cdot \sigma \cdot \cos(\theta) \cdot t}{2\eta}}$$

The boundary parameters are the surface tension of the liquid σ, the contact angle θ and the viscosity η. The most important parameter is the pore radius r, which is in the range of 5 to 40 nm for most relevant microporous systems. The smaller the pore, the deeper the liquid can penetrate into the media (capillarity). In contrast, large pores support fast transport and ensure enough absorption volume. Hornig et al. have proven the applicability on a series of different pore sizes using a modified Bristow wheel [8].

Experimental

Speed Measurements

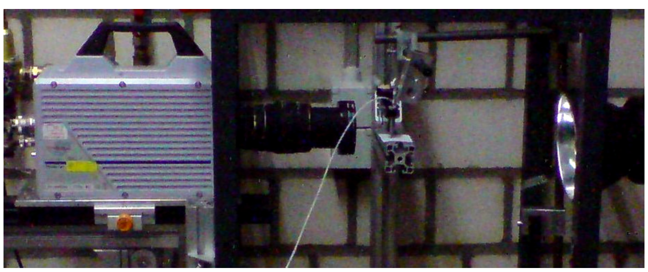

***Figure 2**. Experimental setup for high speed camera measurements*

In figure 2 the experimental setup for the high speed camera system is shown. A Microdrop(TM) piezo drop generator is used to generate droplets of 100 micrometer diameter at about 1 m/s. The droplets are impacted on the different paper samples underneath the generator. For the observation a Photron Fastcam SA1 was used with a long distance microscope. The frame rate was varied to achieve high temporal resolution for the measurement of the penetration process, but still capture the whole process. For illumination a Bowens Flashlight was used.

Materials Used

For the trials, the sizing solutions used were at 11 % solids. Either cationic starch or nonionic starch were dissolved in a jet cooker and held at a constant temperature of 60 °C before use. They were mixed with the fumed silica dispersions at different ratios. All results given in this paper were obtained with silica to starch ratios of 1:1 or 2:1 (solid/solid). The sizing applied by a simple puddle type size press has a weight of approx. 0.7 g/m^2 per side. Table 1 lists the physico-chemical properties of the fumed silica dispersions used.

More details of the paper sizing samples like paper composition etc. are given in [2]. In addition, samples of sizing trials on a commercial scale are shown. These papers have an estimated sizing weight of 2.5 g/m^2 using enzymatic starch.

Table 1: Properties of used fumed silica dispersions

Product name	AERODISP® WK7330	AERODISP® W7330N
Surface charge	cationic	anionic
pH	3	10
Stabilizing additive	cationic polymer	NaOH
Silica content	30 %	30 %
Aggregate size	120 nm	120 nm

Surface analysis

Looking at the paper surface at large magnification under an electron microscope (see Figure 3) provides an idea of the critical factor that determines good printing results and high speed properties: a very thin, porous coating acts like a tiny filter and covers the paper fibers.

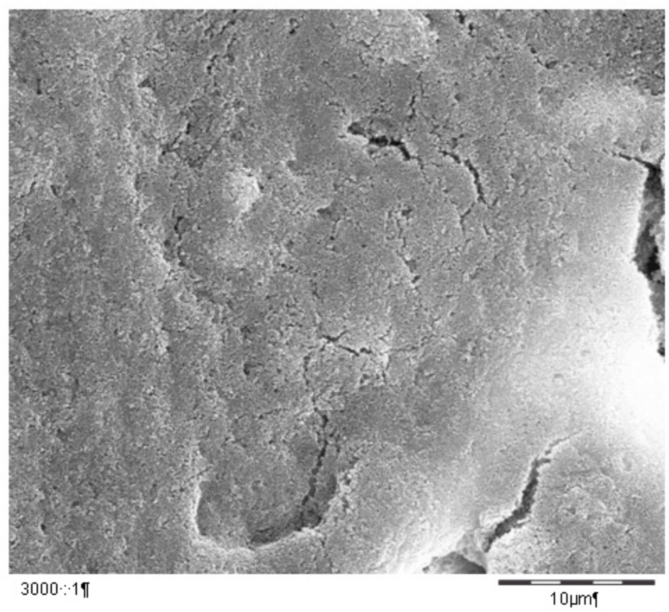

***Figure 3.** SEM micrograph of the paper surface sized with AERODISP® WK7330 + cationic starch (2:1)*

Results

Improved Print Performance

Extensive print evaluations were carried out with the surface sized paper samples. Details were published in [2]. Figure 4 shows the visible improvements of the concept and figure 5 summarizes the results. Especially high ink homogeneity and gamut are the most eye-striking benefits. But the subjective impression of sharpness is also improved because fuzziness and roughness decline, particularly in intercolor bleeding.

***Figure 4**. Inkjet printing results after surface sizing with cationic starch (left) and with AERODISP® WK7330 + cationic starch (2:1 with respect to solid, coating weight approx. 1 g/m^2).*

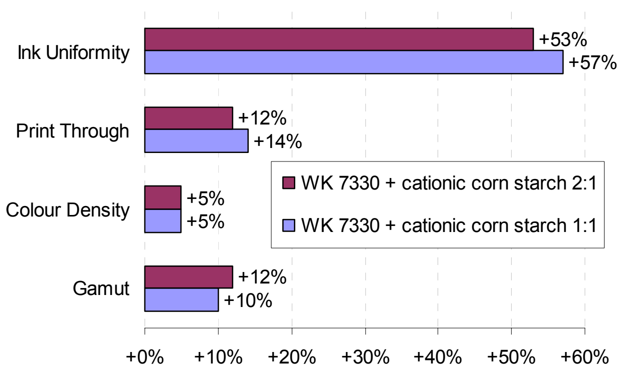

***Figure 5.** Relative print quality improvements using AERODISP®*

The paper can absorb the liquid in the inks unhindered, while dyes or color pigments attach to the surface of the silica particles, thereby enriching the visible surface. This leads to the pronounced optical ink densities that are observed. The paper surface also becomes visibly more homogeneous, which in turn has a favorable effect on the other properties mentioned.

Penetration behavior

For the concept presented here, dynamic penetration measurements made with ultrasound using the Emco DPM-33 show that water-based liquids have a distinctly faster penetration behavior. Figure 6 shows the respective transmission curves. Comparing the maximum of the curves indicates that the fumed silica based sizing is a factor 5 faster than the pure starch sizing.

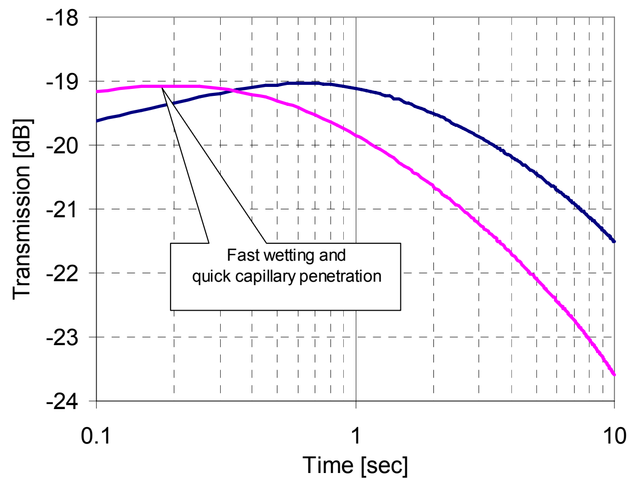

***Figure 6.** Penetration analysis with water using emco DPM-33. The marked curve (paper sized with WK7330, cationic corn starch 2:1) shows a much faster wetting and a quicker capillary penetration than the reference (paper sized with cationic starch only)*

While the Emco measurement is looking at the speed of a complete wetting of the paper sample, the high speed camera is following single drops, which of course is more realistic. However, the results confirm the trend. Standard papers treated with a pure starch sizing need up to 3 seconds to absorb a single drop of 100 µm diameter. The fumed silica containing paper surfaces are a magnitude faster:

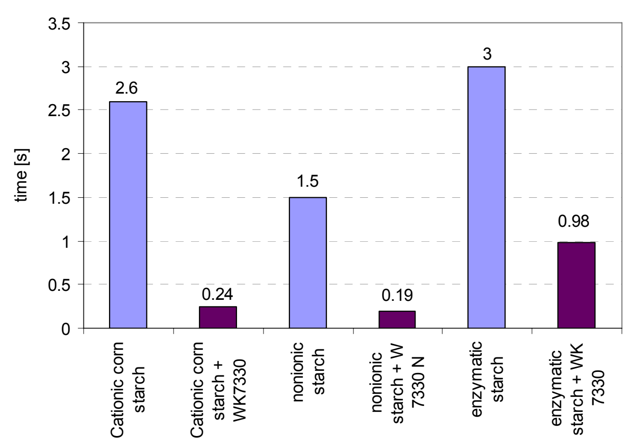

***Figure 7.** Results of high speed camera measurements. Times are given as differences between impact and complete disappearance of the drop.*

Beside these measurements with water as liquid, we have performed some experiments using a model ink liquid with a surface tension of approx. 40 mN/m (DI-water with 3% Dipropylene glycol, 6% 1,2-Propanediol, 5% 1-Methoxy-2-Propanol, 1.6% 1,2-Hexanediol). The speed of drop absorption for all papers decreased slightly as expected from the Lucas-Washburn equation.

One may object that 100 µm drop diameter is much bigger than the normal inkjet ink drop size of a few µm. In that sense our measurements can be regarded as a worst case scenario for multiple small ink drops hitting the same surface area simultaneously or just shortly after each other.

Summary

Beside the outstanding print performance with expanded gamut range and impressive ink homogeneity, plain paper sized with fumed silica based sizing formulations show extremely fast ink absorption, which no other means for increasing inkjet printability can offer.

Although the fumed silica layer is thin compared to the well known microporous RC-photo papers, the same mechanisms seem to work. Capillary forces of the approx. 20 to 100 nm wide pores of the silica-based coating suck in the ink drops and distribute the liquid to the paper layer beneath. Dyes and/or color pigments inside the inks stay on the silica surface as the resulting print properties impressively show. In addition to the capillary forces the silica increases the hydrophilicity of the paper surface and therefore supports the drop surface interaction.

The power of the concept is based on the special fractal structure of fumed particles. Mainly two products are recommended for this application, which are both easy to formulate and use: AERODISP® WK 7330 (30 % aqueous dispersion, cationic) and the anionic AERODISP® W 7330 N.

Today we see the first generation of commercial inkjet web presses entering the market. The linear speed of the web just fits to standard paper. Next generations will surely show increased speed and will have a need for special paper with tailored ink absorbing surfaces. Other approaches used for tailored inkjet papers like multi-valent salts or special cationic polymers increase print properties, too.[13]. However, none of them show also increased absorption speed like micro-porous coatings based on fumed silica does.

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Author Biography

Dr. Christoph Batz-Sohn studied chemistry and received his Ph.D. in organo-metallic chemistry at the University of Bielefeld (Germany) in 1996. In 1997, he joined Degussa (now Evonik) as a research chemist in the field of functional silanes. From 2000, he was the team leader for the development of tailor-made silica and alumina dispersions for different application areas including paper coatings. Since 2003 Christoph has been responsible for applied technology and technical service and is now the head of Evonik Industries' global applied technology labs for Non-Impact printing. He has filed for more than 50 patents and has published numerous papers and publications.