Improving Inkjet Print Performance of Plain Sized Paper with Nanostructured Pigments

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Abstract

Following the industry trends, it is clear that commercial inkjet printing will compete increasingly with traditional printing processes in the coming years. While special paper is already available for traditional impact printing processes, papers that meet the requirements of high speed inkjet printing are just in the infancy of their development. Standard papers, like those found in the office, still exhibit significant weaknesses in such important properties as optical density, gamut and water resistance.

A very thin layer of a fumed silica based coating (0.5-2.0 g/m²) applied to plain paper at the size press improves inkjet printing performance. The silica coating behaves as an inorganic sponge with a well defined void and channel structure to absorb ink rapidly for enhancing color qualities, print uniformity and image resolution. In the presentation we show results of a paper machine trial and compare nano-structured silica based pigments with traditional coating pigments, e.g. calcium carbonate. Comparisons are made to other approaches, such as the incorporation of multivalent metal ions into the paper.

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 micro-porous 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 paper surface.

Two years ago we introduced a concept [1] that transfers the basic idea of this technology to plain paper. In the meantime we have performed extensive trials on a pilot paper machine and carried out additional analytics, which we will report upon in this paper.

Concept

The concept offers paper manufacturers a solution for online use in puddle-type or metered size presses. In spite of its use of nanostructured particles, the new concept is affordable and effectively raises the printing quality of the correspondingly treated papers into another quality class. In addition it enables faster ink adsorption behavior needed for increased printing speed of web-to-web inkjet presses.

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

***Figure 1**. 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/m²).*

aid of puddle-type or metered 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 metered size presses, as leading paper manufacturers have already confirmed in operating tests.

Test conditions

For the online-sizing trials (Kämmerer machine) a standard chemical pulp consisting of birch and pine fibers was used (Hi-Cat starch, PCC filler, ASA sizing, Percol and Bentonite as microparticle retention aid, no optical brighteners). Fibers were beaten to a usual value of 25 °SR (Schopper-Riegler). A fixed standard chemical pulp formulation was utilized). Pulp stock conductivity and pH were adjusted to the same level for each of the trials. The paper machine was run at constant speed (1.8 m/min) and drying conditions during all trials. The only variable was the composition of the sizing solution. The coat weight on the top side of the paper was about 0.5 – 0.7 g/m².

Used Materials

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). Table 1 lists the physico-chemical properties of the used fumed silica dispersions.

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

Image quality measurements

The treated papers were printed on various inkjet printers, such as Hewlett Packard Deskjet 5652, Epson Stylus PHOTO R240, and Canon PIXMA iP6600D. These printers were selected for their distinctly different ink sets and printing mechanisms employed. The Epson inks typically contain higher concentrations of organic solvents which make them more discriminating with respect to the paper used. Results on additional printers such as Epson Stylus PHOTO R2400, Epson Stylus PHOTO R285, Epson Stylus PHOTO R800, HP Photosmart D7360 and Kodak Easyshare 5300 are available on request.

Print patterns were created with CorelDRAW® software, which contain the various elements needed for quantifying print attributes such as optical density, color gamut area, print mottle and grain, color-color bleed and dot circularity.

All data in this work were obtained with both the "Personal Image Analysis System" (PIAS) (QEA, Inc) and the SpectroEye Densitometer (GretagMacbeth RP imaging).

Color density and L*a*b* values were measured using the SpectroEye. The gamut area is calculated based on CIELAB a* and b* values for the different colored measuring areas.

For calculating the strike through the reflection at 460 nm of the backside (BS) of the printed area (black) and the unprinted paper is measured using the SpectroEye calculation for strike through: $\log(R_{BSunprinted}/R_{BSprinted})$.

In order to graphically illustrate the changes in print performance versus the corresponding paper sized with 100 % polymer, values measured for resolution, color density, gamut, mottling & graininess and strike through were converted into relative grades with the pigment-free reference at 1.0. Grades above 1.0 indicate a performance exceeding the performance of the reference. Differences of more than 0.05 are significant. It is safe to say that the values for each reference paper itself are always dependent on the printer used.

Results

Improved Print Performance

The improvement in printability of inkjet printers soon becomes clearly noticeable and measurable at the minimum coating weight of approx. 0.5 g/m^2. Although other non-impact printing processes such as laser printing do not benefit from the thin microporous layer, the papers nevertheless remain compatible and can be printed without any loss in quality.

In inkjet printing, however, it is the high ink homogeneity and gamut in particular that are the most eye-striking. But the subjective impression of sharpness is also improved because fuzziness and roughness decline, particularly in inter-color bleeding.

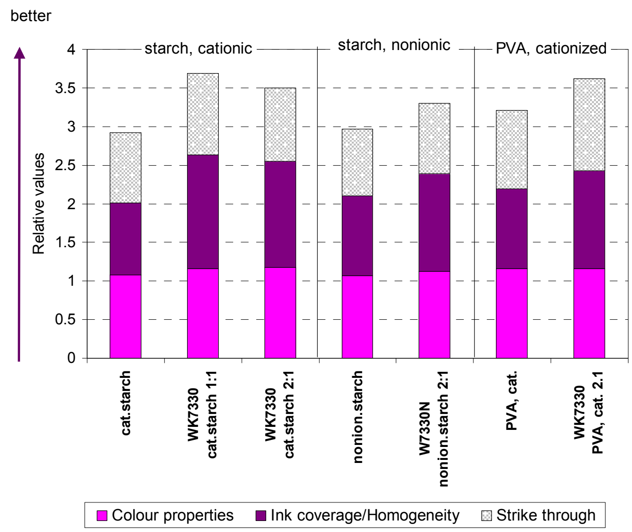

***Figure 2**. Selected printing results from pilot sizing trials (average of three printers). We also looked at other properties like resolution etc. which more or less remained unchanged*

Process Advantages

When we observe the process, it is striking that the viscosity predefined by the metered size press greatly increases the possible solids content of the silica-containing formulation: the formulation based on WK 7330 has twice the solids content (21 wt.%, 100 mPas, pigment/binder ratio 2:1) compared to pure cationic corn starch (11 wt.% at 100 mPas). This means lower energy expenditure during drying and, depending on the limitations of the paper machine, possibly also higher productivity.

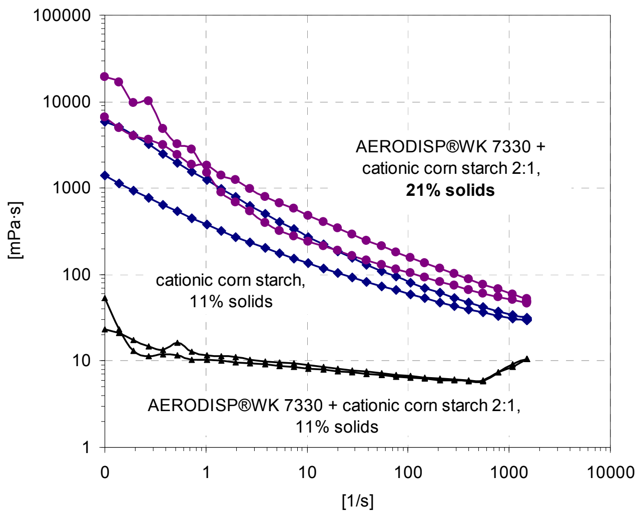

***Figure 3.** Flow curves (Parr Physica MCR300) of sizing formulations*

Surface analysis

Looking at the paper surface at large magnification under an electron microscope (see Figure 4) provides an idea of the critical factor that determines the good printing results: a very thin, porous coating, acts like a tiny filter and covers the paper fibers.

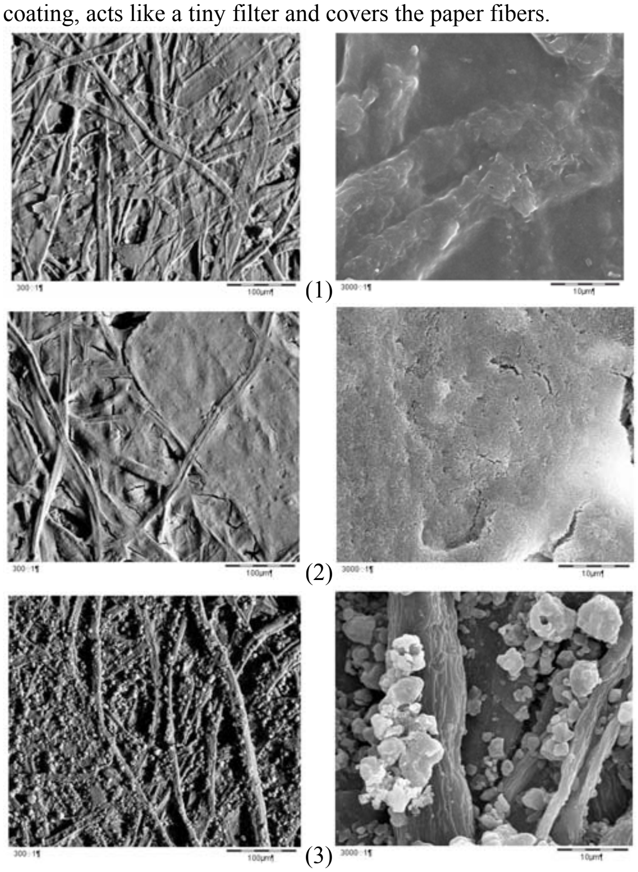

***Figure 4.** SEM micrographs of the paper surface at low (left) and high (right) magnification, respectively. (1) sized with cationic starch only; (2) sized with AERODISP® WK7330 + cationic starch (2:1); (3) sized with a micron-sized calcium carbonate pigment + cationic starch*

The paper can furthermore 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. Here, the capillary forces of the approx. 20 to 100 nm wide pores of the silica-based coating play a major role. The next generation of faster commercial inkjet printers will find great benefit from this property.

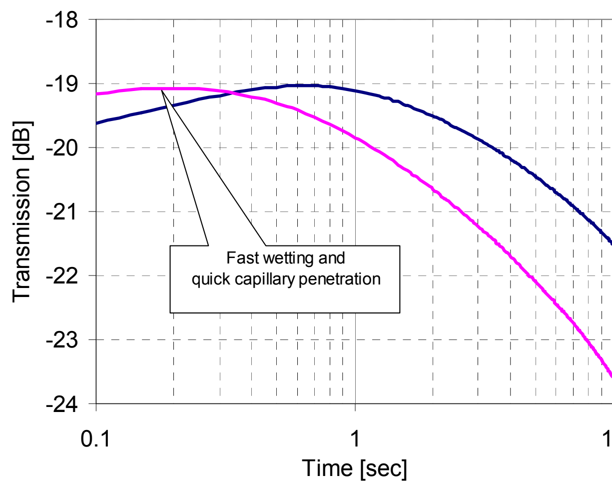

***Figure 5.** Penetration analysis with water using emco DPM-33. The marked curve (paper sized with WK7330, cationic corn starch 2:1) shows a much faster wetting and a quicker capillary penetration than the reference (paper sized with cationic starch only)*

Comparison with alternative pigments and concepts

In a comparative study we also looked at non-structured nano sized pigments (colloidal silica) and micron-sized coating pigments (calcium carbonate), the latter recommended for improving inkjet print properties.

Looking at the SEM images (Figure 4) the surface coverage with the calcium carbonate is very non-homogeneous. The large pigments provide some additional porosity for ink absorption; thus, a slight increase of the printing properties can be noticed. To obtain a closed paper surface comparable to the fumed silica concept, a coating weight of at least 4 g/m^2 is required.

Using colloidal silica consisting of non structured spherical nano-particles leads to no improvements in printability compared to pure starch sizing. For more details, see [6].

The incorporation of multivalent ions (mostly Ca^{2+}) into the paper surface, known for example as “ColorLok”, increases the optical densities of pigmented inks. The mode of action is based on the flocculation and destabilization of the pigments when the ink drop hits the paper surface. This does not work for the wide variety of dye based inks. Compared to the concept using nano-structured pigments, print and surface homogeneity are not affected. In addition, the penetration behavior and speed of the surface remains unchanged compare to standard paper. Therefore, those papers cannot be printed faster. A combination of multivalent ions and nano-structured silica is difficult, but seems to be possible.

Summary

The power of the concept is based on the special fractal structure of fumed particles which have been commercially produced via a flame process for over 60 years. Two main products are recommended, which are both easy to formulate and use: AERODISP® WK 7330 (30 % aqueous dispersion, cationic) and the anionic variant AERODISP® W 7330 N.

Besides processing advantages during the application at the size press, the improvements of printability are eye-striking:

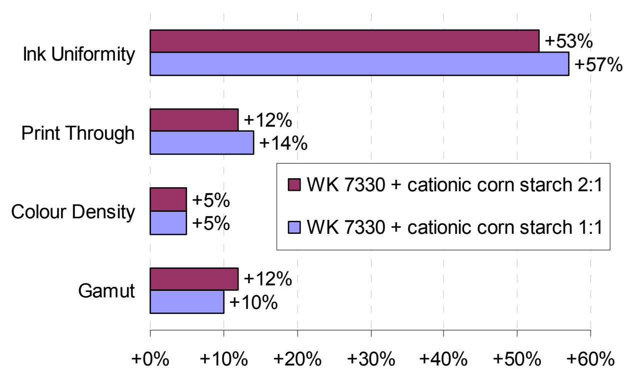

Figure 6. *Relative improvements using AERODISP®*

Today's home and office inkjet printers cannot make use of the faster penetration behavior of such papers. However, the upcoming generation of commercial inkjet presses will most likely need tailored ink-absorbing surfaces incorporating this type of technology.

References

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Author Biography

Dr. Christoph Batz-Sohn studied chemistry and received his Ph.D. in organometallic 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. Since 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 he 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 more than 50 patents and published numerous papers and publications.