

# A Novel Method to Study the Effect of Corona Treatment on Ink Wetting and Sorption Behavior

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## Abstract

A novel absorption test method was developed based on a modification of the Bristow Absorption Apparatus. The proposed method combines corona treatment (CT) with short contact time absorption behavior to study particularly ink wetting and sorption on substrates in-line. The method makes it possible to study e.g. the coagulation of pigment inks induced by deposited charges i.e. electrocoagulation, the effect of short contact times on liquid/substrate interactions, and problems related to charge decay such as whiskering. In-line measurement with a short delay time minimizes the effect of ambient conditions (heat, moisture) on charge decay, and thus simulates the conditions in commercial digital printing processes.

The functionality of the method was evaluated by testing paper samples with and without polymer coatings. Uncoated samples were used to study absorption properties. It was found that in some cases the CT changes both the wetting and absorption of ink and that in other cases the main changes are in the absorption behavior. Four CT levels (0, -100, -450, and -900 W\*min/m<sup>2</sup>) were studied and it was found that the highest treatment level increased the absorption of the applied inkjet ink the most. As expected, the contact time between liquid and substrate was found to be an important variable affecting the absorption. Print density and mottle were determined on coated samples with the CT levels of 0, -160, and +160 W\*min/m<sup>2</sup>. CT improved print density significantly, whether the treatment was positive or negative, and also reduced the mottling tendency.

## Introduction

Corona surface treatment (CT) is widely used to improve the surface functionality of polymers, wood and paper substrates. CT increases the surface energy and thus changes the surface wetting properties and improves printability, adhesion and friction. During corona treatment, the surface is affected by high energy ions O<sup>+</sup>, CO<sub>3</sub><sup>+</sup>, O<sub>3</sub><sup>+</sup> etc. [1] and species with high polarity are formed, which increase the surface energy. The surface energy does not, however, alone determine how the liquid behaves at the interface since the behavior depends also on the surface tension of the liquid [2]. The wettability is increased whether the liquid is polar or non-polar [3], but polar interactions are increased more than dispersion effects. The effect of CT on the contact angle on coated paper is substantial [4] and lengthy, but the charge decay half time is usually expressible in seconds, due to the instability of formed species with high polarity.

Water sorption into fiber-based substrates can be described by the Lucas-Washburn equation (Eq. 1), which considers a paper surface as a bundle of parallel capillaries having a certain radius  $r$  and gives the penetration depth  $x$  during time  $t$  for a liquid whose surface tension  $\gamma_{LV}$ , viscosity  $\eta$  and contact angle  $\theta$  on the substrate are known.

$$x^2 = \left( \frac{rt}{2\eta} \right) \gamma_{LV} \cos \theta \quad (1)$$

Lucas-Washburn equation is not scalable with pore size. The problem becomes emphasized with coated papers. On a short time scale, a large number of small pores results in faster wetting than large pores due to the larger number of possible pathways for the liquid to penetrate. The reason for accelerated absorption is inertial forces that take place shortly after the liquid is applied. [5] Bosanquet originally balanced the inertial and viscous forces with the capillary force [6]. By using the short time scale solution of the Bosanquet equation (Eq. 2), the effect of inertia can be studied, giving a more realistic description of the wetting behavior. In inertial flow, the liquid viscosity becomes insignificant but the travelled distance is inversely proportional to the square root of the fluid density  $\rho$ . [5]

$$x = t \sqrt{\frac{2\gamma_{LV} \cos \theta}{r\rho}} \quad (2)$$

Digital printing applications in particular might require optimization in corona charging. In inkjet printing, wet ink becomes immobilized in a few milliseconds or less; the pigment particles remain ideally on the surface and the liquid penetrates into the substrate. The surface tension of the ink and the contact angle determined for the substrate provide limited information about the actual short-time ink wetting and spreading behavior after CT. High energy ions can penetrate into paper pores and change the capillary effects, but they also cause changes on the submicron roughness level. This may lead to further changes in wetting time and specific or selective colorant and solvent interactions, which may affect the behavior of ink on the substrate. Secondary corona discharges may also occur in these pores, leading to changes in the surface of pore walls.

Bristow wheel can be used for studying e.g. liquid-substrate interactions on a time-scale of milliseconds [7]. Traditional uses for the Bristow Absorption Apparatus are related to wettability in

coating [8] and printing [9] processes and testing glueability of paperboard in the production of corrugated paperboard [10]. There are also few works that demonstrate the applicability of the Bristow wheel for studying ink-jet papers [11, 12]. A roughness index and an absorption coefficient are both calculable from the length of the produced ink track.

Since short time intervals in wetting and corona treatment studies are important, we added a corona wire to Bristow wheel in order to minimize charge decay between charging and ink application and the destruction of unstable species. Charge decay may cause print quality problems such as whiskering, so combining CT with an absorption test is beneficial and the modified instrument enables true printing or varnishing conditions to be simulated where the printing machine is equipped with a corona unit. The configuration also makes it possible to study the wetting properties of corona-treated paper as a function of time, because the corona unit and the Bristow wheel can be used separately. CT may also change the surface roughness [13], which can be studied either directly with Bristow wheel or with an AFM, profilometer or similar instrument. We believe that this method is a useful tool for testing paper and predicting print quality, making it possible to solve problems related to electrostatic printing assist in rotogravure, to optimize print quality in other printing processes using corona, and to gain more information about other possible print-related properties affected by corona such as rub resistance [14].

## Methodology

A commercial Bristow wheel was equipped with a special corona charger (Fig. 1–2). Paper is fastened on the wheel, the corona charge is switched on and while the wheel rotates, the paper is subjected to a negative or positive charge. Thus, there is no discontinuity between the CT and the ink application. It is also possible to use of AC corona, i.e. plasma treatment. No difference between negative, positive or AC corona treatment was detected. The CT level, which depends on the corona voltage and wheel rotation speed, is expressed as the corona current energy flow through the paper in  $W \cdot \text{min}/\text{m}^2$ . After treatment, ink wetting and absorption are tested using standard procedure immediately after the corona discharge is stopped.

Three types of substrate were used: a commercial fine paper with a grammage of  $80 \text{ g}/\text{m}^2$ , a pilot paper made from never-dried birch kraft pulp (Stora Enso Oyj, Imatra Mills, Imatra, Finland) with a grammage of  $180 \text{ g}/\text{m}^2$ , and a pilot paper made from xylanase-treated, hemicellulose-poor never-dried birch kraft pulp with a grammage of  $180 \text{ g}/\text{m}^2$ . The pilot papers were made on a pilot paper machine (Stora Enso Oyj, Imatra Research Centre). Both pilot samples were machine-calendered (nip pressure  $20 \text{ kN}/\text{m}$ ).

The commercial fine paper was surface sized in a pilot surface size unit (Stora Enso Oyj, Imatra Research Centre). The surface sizes applied were anionic sodium carboxymethyl cellulose (Finnfix 30, CP Kelco Oy) and cationic polydiallyldimethylammonium (poly-DADMAC, Catiofast BP, BASF GmbH). The joint effect of anionic-fumed silica (Aerodisp W 7330 N, Evonik Industries AG) and poly-DADMAC was also tested, the mixing ratio being 1:1. Four different sizing treatment were tested: i.) an unsized sample, ii.) a single poly-DADMAC

layer (C), iii.) a sample treated with five alternating layers of cationic and anionic polyelectrolytes (CACAC), and iv.) a single poly-DADMAC/silica layer (CS). The coat weight of a single coating layer was adjusted to  $1 \text{ g}/\text{m}^2$ .

Cobb tests were conducted according to standard SCAN P 12:64. AFM images were taken with a Bruker Multimode 8 scanning probe microscope (Bruker Corp., USA), using probes with a spring constant of  $42 \text{ N}/\text{m}$ . Contact angles were measured with an Attension Theta Optical Tensiometer (Biolin Scientific Ab, Sweden). The contact angle value after 1.0s was recorded. Ink density was determined with a Gretag D19C densitometer (Gretag-Macbeth AG, Switzerland). Print mottle was determined by the Intel IAS program, which is based on the ISO/IEC 13660:2001 standard.

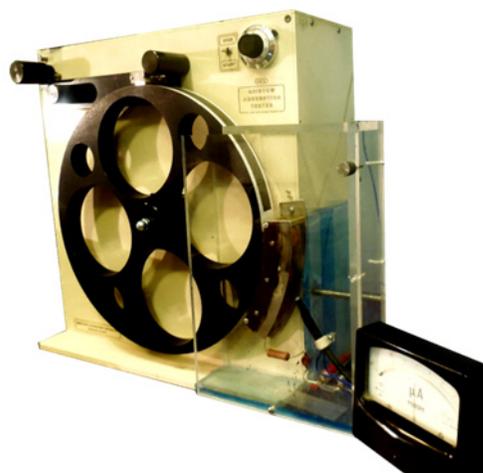


Figure 1. Modified Bristow wheel.

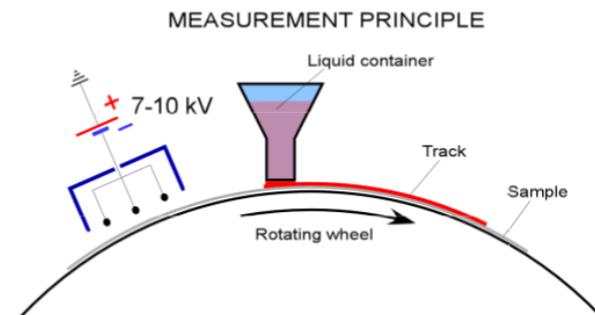


Figure 2. Treatment system.

## Results

### Properties of Deposited Ink Layers

The evenness of the ink layer deposited with Bristow wheel on the commercial surface-treated paper samples after CT was evaluated by print mottle and density measurements (Table 1). As expected, the CT increased the density of deposited ink layer substantially, regardless of the sign of the electric charge. In the case of the blend of cationic polymer and anionic silica (test points 10–12), CT improved the print density less than in the case of the

samples whose uppermost coating layer was cationic (test points 4–6 and 7–9).

Coating the paper increased the print mottle in the samples that were not treated with corona, but CT reduced the print mottle in all cases. A very high upgrade in print quality was detected in the multi-layer coated sample, where the print density increased and the print mottle was greatly reduced. The results indicate not only that multi-layer coating is an effective way of improving the ink hold-out of inkjet substrates but also that the new test method is suitable for testing the effects of corona treatment on print quality and gives new insight into the role of surface charging on substrate-ink interactions.

**Table 1. Print density and mottle of samples.**

Test point	Coating	Corona dose, [W*min/m <sup>2</sup> ]	Print density	Print mottle
1	-	0	1.17	0.91
2	-	-160	1.48	0.64
3	-	+160	1.41	0.70
4	C	0	1.22	0.90
5	C	-160	1.65	0.58
6	C	+160	1.63	0.61
7	CACAC	0	0.95	2.20
8	CACAC	-160	1.50	0.77
9	CACAC	+160	1.56	0.73
10	CS	0	1.18	0.94
11	CS	-160	1.37	0.67
12	CS	+160	1.37	0.61

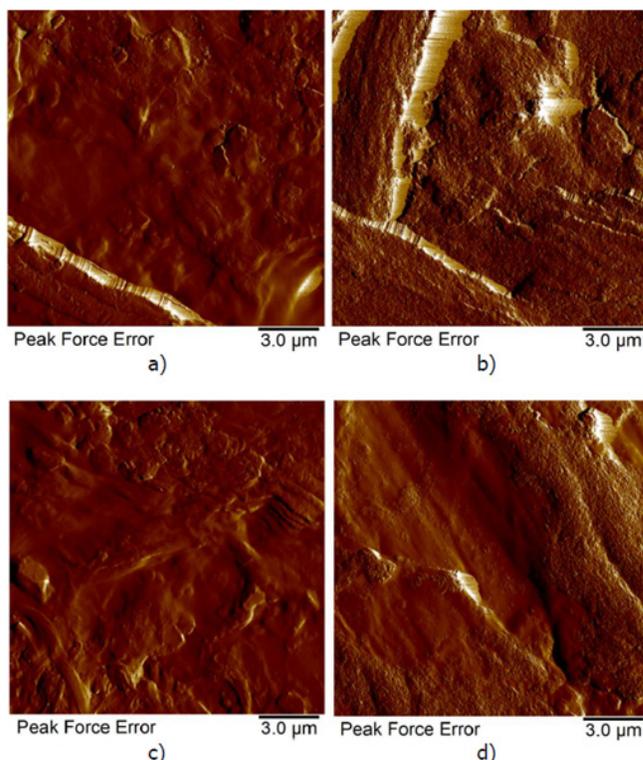
### AFM Imaging

Atomic force micrographs revealed very small differences between the ink-free multilayer coated samples with and without CT (Fig. 2a and 2c). However, as the print mottle values suggested, CT increased the evenness of spreading of the ink (Fig. 2b) compared to that on the untreated sample (Fig. 2d), the treatment level being -160 W\*min/m<sup>2</sup>.

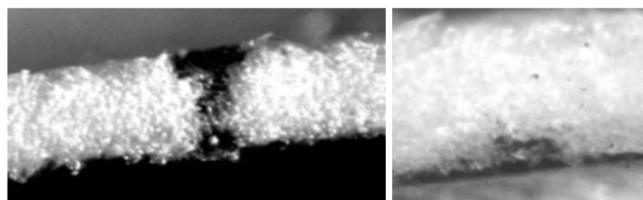
It is known that CT changes the pores of porous materials. The surfaces of the multilayered samples were relatively smooth according to the AFM images, but RMS roughness values revealed an increase in RMS from 360 nm to 560 nm as a result of CT, which agrees well with the results of a previous study of pigment-coated samples [15]. The RMS roughness of the printed and corona-treated area was 730 nm.

### Strike through of Ink

It was observed that, in the case of heavily treated low grammage paper, ink strikes through the paper partly as a result of the charge, resulting in “breakdown” (Fig. 4 left) which, in turn, makes ink visible on the back of the paper. The probability of the occurrence of strike through increased when the CT was intensive and long. However, ink did not penetrate through untreated or softly treated paper (Fig 4 right).



**Figure 3.** AFM images of multilayered CACAC sample with (a. unprinted area; b. printed area) and without (c. unprinted area; d. mottled printed area) corona treatment.



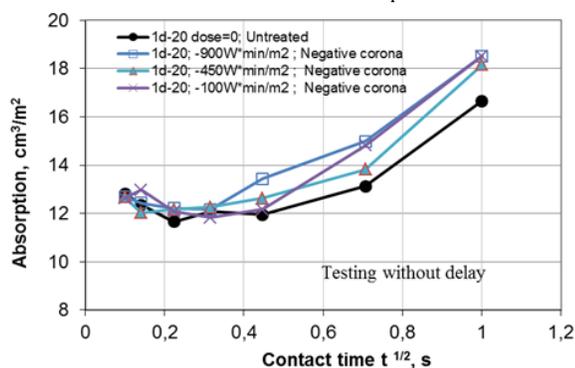
**Figure 4.** Cross section of paper coated with ink: left – strike through, right – surface coverage.

### Absorption and Wetting Behavior

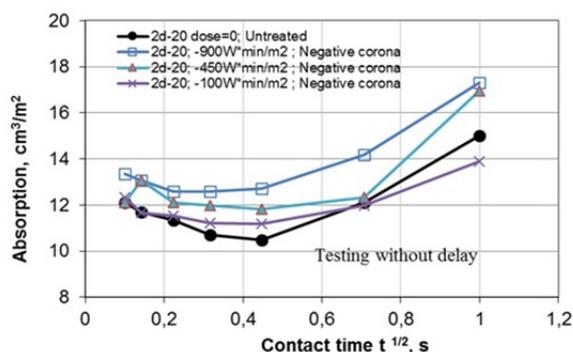
The pilot samples were used to study the absorption and wetting behavior of corona-treated substrates. Extraction of hemicelluloses did not affect the Cobb value which was 23.7 g/m<sup>2</sup> for paper made from untreated pulp and 23.4 g/m<sup>2</sup> for paper with low hemicellulose content, indicating that the difference in initial hydrophobicity of the samples was small. The strongest treatment with negative CT reduced the contact angle of water on substrate made from enzymatically treated pulp from 112°±3 to 103°±1, which is ascribed to an increase in the content of hydrophilic carboxyl groups on the cellulose surface [16], and this confirms that the newly developed method is suitable for studying the effects of CT on fiber chemistry.

The contact time clearly affected the liquid absorption (Fig. 5–6). Absorption increased with increasing CT particularly for the sample made from hemicellulose-poor pulp. The sample made from untreated pulp was able to absorb more water than the

hemicellulose-poor sample. A corona discharge increased the absorption further, although the treatment level had a greater proportional influence in the case of the hemicellulose-poor sample. Hence, the CT also affected the wetting kinetics, the effect being smaller in the case of the paper made from untreated pulp. Although it has been observed that the one minute Cobb value does not correlate with the absorption coefficient determined by the Bristow method [7], the measured absorption rates suggested that a larger Cobb value may indicate a greater absorbency per unit area in the case of the corona-treated samples.



**Figure 5.** Ink absorption dependence on the square root of the contact time for paper made from unextracted pulp.



**Figure 6.** Ink absorption dependence on the square root of the contact time for paper made from extracted pulp.

## Summary

Ink absorption and wetting trials were conducted using a novel test method based on a Bristow Absorption Apparatus equipped with a corona charger. The suitability of the method for use on paper and paperboard samples was tested successfully. The method was developed particularly with regard to inkjet printing and coating, in which its potential has been demonstrated, but other possible uses were also suggested. We find several valuable features from the modified Bristow wheel, such as i.) the possibility of focusing on short timescale sorption phenomena typical of inkjet printing, ii.) minimized delay between corona discharge and ink feeding, simulating the process conditions of modern commercial inkjet printers and iii.) the possibility of examining the effect of corona treatment on the substrate roughness. The trials also showed that the method enables the effects of corona discharge on print quality to be studied. However, strike-through as a result of the corona discharge may occur in the

case of low-grammage substrates, indicating that the maximum for each paper grade should be sought separately.

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## Author Biography

*Sami-Seppo Ovaska received his MS in chemical engineering from Lappeenranta University of Technology (2010). He began his doctoral studies in 2011, the topic being "Spreading of Complex Liquids on Barrier-Coated Boards". Earlier he worked with fiber-based nursing products. As a part of his studies, he works in a research group whose main tasks are related to renewable barrier and packaging materials. He is a member of the International Doctoral Programme in Bioproducts Technology (PaPSaT).*