An Attempt to Reduce Dampening Water Absorption Using Hydrophobic Plasma Coatings

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Abstract

Hydrophobic plasma coatings were deposited on pigment coated paper and their influence on sheetfed offset printability was studied. Three plasma chemistries, fluorocarbon, organosilicone and hydrocarbon, were used to adjust the hydrophobicity of paper surface. The plasma coatings reduced, and in some cases prevented the dampening water absorption into pigment coated paper in both laboratory- and pilot-scale trials. Ink transfer, mottle and ink setting changed due to the presence of the plasma coatings, whereas porosity and surface strength of the pigment coated papers were not affected. Based on the results, the preferred way to improve the print quality with both mineral and linseed oil-based inks is to use plasma chemistry that modifies the paper surface to be hydrophobic and oleophilic.

1. Introduction

Plasma surface modification has raised interest in recent years, because atmospheric non-thermal plasma processing provides a possibility to develop new dry surface modification methods based on roll-to-roll processing. Atmospheric plasma processing does not demand batch processing and costly vacuum equipment such as the conventional low pressure plasma processes.

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Plasma is a state of ionized gas, consisting of excited atomic, ionic, molecular, and free-radical species. Plasma-solid interaction can be divided into three sub-categories (d'Agostino et al., 2005): in etching or ablation, the material is removed from the solid surface, in plasma activation, the surface may be chemically and/or physically modified by species present in the plasma, and thirdly, in plasma coating, the material is deposited as a form of molecular monolayer thin film on the surface, a process also known as plasma polymerization or plasma (-enhanced) chemical vapour deposition (P(E)CVD). The PCVD plasma coatings can be divided into five categories according to starting materials; hydrocarbons, hydrocarbons with polar groups, organosilicones, halocarbons (e.g., fluorocarbons) and organometallics (d'Agostino, 1990; Roth, 2001). Hydrocarbon, organosilicone and halocarbon plasma coatings have been used to introduce hydrophobic character on the paper surfaces (e.g., Tu et al., 1994; Tan et al., 2001; Vaswani, 2006), but its influence on printability has not been investigated.

With pigment coated paper, offset ink vehicle penetrates through the concentrating ink layer into the coating. The penetration is driven by capillary sorption of the liquid into the coating pores, and diffusive interaction between the ink solvent and coating binder (Aspler, 2006; Rousu, 2002). In addition, Rousu (2002) has demonstrated that ink setting rate is increased by the ratio surface tension to viscosity of ink oils. In ink setting, ink pigments and binders form a film on the surface and vehicle mineral and/or polar vegetable oils penetrate into the coating structure (Ström, 2005).

In sheetfed offset printing, ink drying continues over many hours through polymerization of resins and drying oils initiated by oxygen (Ström and Gustafsson, 2006). Even if the ink transfer occurs in a nip under high pressure, it is known that the separation and absorption of the low viscous fluids of the ink occurs after the printing nip (Oittinen, 1976; Rousu et al., 2001). The time frame in ink setting is between one to ten minutes, whereas the chemical curing may start ling after ink transfer, sometimes after several days. Ones started the curing is completed within in few hours (Ström and Gustafsson, 2006).

Dampening water is used to help separate image and non-image areas on the offset printing plate. According to Aspler (2006), the water transfer from the non-image areas to paper can be from 0.1 g/m^2 to 0.2 g/m^2 per colour per side for coated papers. It is known also that the ink may contain high levels (15%–30 %) of emulsified dampening water during the printing operation (Aspler, 2006), which penetrates into paper due to de-emulsification under the nip pressure (Liu et al., 2008). Therefore, both ink and water absorption properties are crucial in offset printing.

Dampening water penetration into a coating or even into base paper may cause fibre rising resulting in disruption to the coating layer, and uneven dampening

water absorption may cause mottling (Aspler, 2006). It has been shown that increasing hydrophobicity of the coating by changing binder properties decreases the water sorption rate (Rennes and Eklund, 1989). However, changes in coating component properties, usually brings along changes in the coating structure. Therefore, it has been challenging to investigate the effects of surface chemistry alone on offset printability.

The aim of the present work was to reduce dampening water absorption into pigment coated paper using hydrophobic plasma coatings, and to understand how the plasma coatings influence the sheetfed offset printability.

2. Experimental

Plasma coatings and printing trials were performed first in the laboratory-scale and then in pilot-scale. A ground calcium carbonate (GCC) and kaolin containing pigment coated paper with latex binder (Lumiflex 90 g/m^2, Stora Enso) was used as substrate. According to manufacturer the paper gloss (75º) is 62% and PPS roughness 1.10 µm.

2.2 Plasma Coating

The laboratory-scale plasma deposition experiments were performed at the Institute for Surface Chemistry (YKI), Stockholm. The plasma reactor used was an in house-constructed reactor consisting of a glass vessel connected to a double-stage rotary vacuum pump (Leybold-Heraeus D 65 B). Two externally wrapped, capacitively coupled copper electrode bands were powered by either a low radio-frequency (125–375 kHz) power generator (ENI, Model HPG-2) or by a 13.56 MHz radio-frequency power generator (ENI, Model ACG-3) connected to an automatic matching network (ENI, Model MW-5D). The A4 paper sheets were mounted in the lower part of the chamber. The chamber was evacuated down to a base pressure below 10 mTorr before introducing the precursor (monomer) from the top of the reactor. Ethylene was used as monomer for the hydrocarbon coating, hexamethyldisiloxane (HMDSO, >98.5%) for the organosilicone coating and perfluorohexane (C_6F_{14}, 98%) for the fluorocarbon coating.

The pilot-scale plasma depositions were performed at VITO, using a PlasmaZone® parallel plates dielectric barrier discharge (DBD), operating at atmospheric pressure. The DBD was produced between two parallel stainless steel electrodes, both covered with an insulating glass plate of 3 mm thickness. The gap between the electrodes was 2 mm. Plasma discharges can be generated at variable frequency comprised between 1 and 100 kHz, and a dissipated power varying between 0.5 and 5.0 W/cm^2. On the pilot-scale installation, speed up to 200 m/min can be reached. HMDSO was used as precursor for the organosilicone coating and acetylene for the hydrocarbon coating. Nitrogen was

used as carrier gas in all experiments. The plasma parameters for each type of plasma coating are presented in Table 1.

Table 1. *Plasma parameters for laboratory- and pilot-scale experiments.*

	Laboratory scale			Pilot scale	
Monomer	HMDSO	Ethylene	C_6F_{14}	HMDSO	Acetylene
Frequency	13.56 MHz	135 kHz	13.56 MHz	1.5 kHz	1.5 kHz
Discharge power, W	30	20	40	400	400
Pressure during treatment, mTorr	~25	~49	~140	atmospheric	atmospheric
Flow rate precursor	~5 cc/min	10 cc/min	out of range	3.8 L/min	0.35 L/min
Flow rate of carrier gas (N_2)	–	–	–	20 L/min (1.5% O_2)	20 L/min
Treatment time/ line speed	2 min	2 min	1 min	4 m/min	6 m/min

2.3 Surface Characterization

The porosity of the uncoated and plasma-coated samples was measured using mercury porosimeter PASCAL 140/440 (ThermoElectron).

The plasma-coated samples produced at laboratory-scale at YKI were characterized by XPS (X-ray Photoelectron Spectroscopy), using a Kratos AXIS Ultra^{DLD} x-ray photoelectron spectrometer (Kratos Analytical, Manchester, UK). The samples were analyzed using a monochromatic Al x-ray source and wide (low-resolution) spectra were run to detect elements present in the surface layer. The relative surface compositions were obtained from quantification of detail spectra (low-resolution) run for each element. Two different spots were measured in each sample. The plasma-coated samples produced at pilot-scale at VITO were characterized by XPS using a Physical Electronics Quantum 2000 ESCA instrument, equipped with a monochromatic Al Kα X-ray source and operated at a power of 25 W. Three different spots were measured in each sample. The pass energy for the survey spectra was 184 eV, and the measurement time was five minutes.

Contact angle measurements were performed using a DAT 1100 (Fibro System AB) contact angle meter applying the following liquids: water, mineral and linseed ink oils. A minimum of six parallel measurements were carried out on each sample. The properties of the test liquids are presented in Tables 2 and 3. The viscosity of the oils was measured with a Gemini-Advanced Rheometer (Bohlin Instruments) and the surface tension was determined using the ring method (KSV Sigma70).

Table 2. *Total surface tension (γ^{tot}) and its non-polar (dispersion or Lifshitz-van der Waals forces, γ^{LW}) and polar (acid-base, γ^{AB}) components of the water.*

Liquid	γ^{tot} (mN/m)	γ^{LW} (mN/m)	γ^{AB} (mN/m)
Water	72.8	21.8	51.0

Table 3. *Density and surface tension of oils used in inks and in contact angle measurements.*

	Density, g/cm ^{3}		Surface tension, mN/m		Viscosity, mPas	
		Std.		Std.		Std.
Mineral oil	0.8312	0.0105	28.000	0.004	11.3	0.5
Linseed oil	0.8981	0.0326	33.652	0.015	51.8	0.8

The pilot-scale plasma coatings have been analyzed using a WYKO NT3300 surface profiler in phase-shifting (PSI, resolution: 3Å) or vertical scanning (VSI, resolution: 3 nm) on glass plates. The precision is 0.1 µm in X and Y directions and 0.01 nm in Z direction. The thickness measurements have been performed using the peak-to-peak method, where a calculation of surface statistics for separated regions is realised. The step height is measured at 2 different places on a glass plate substrate containing a mask and coated according to the experimental conditions.

Dampening water absorption was studied using Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) cross section images. Samples were damped using solution containing 25 wt. % cesium iodide (CsI 99.5%, Fluka) and 10 wt. % of isopropyl alcohol (IPA) in water. Dampening was performed by a gravure wheel with cell volume of 0.5 g/m^2 on the Ink Surface Interaction Tester (ISIT) unit at a speed of 0.5 m/s and nip force was 400 N. Air dried samples were embedded in epoxy resin and sectioned using ultramicrotome. The ToF-SIMS cross section images were carried out using a model PHI TRIFT II spectrometer with positive ion mode. The molecular mass range of 2–2000 Da was acquired using gallium primary source on a raster size of 200 µm x 200 µm with applied voltage of 25 kV and a primary ion current of 600 pA. The acquisition time was 10 min. At least three different spots were analyzed on each sample.

2.4 Offset Printability

Laboratory-scale printing was performed with an ISIT unit with pre-dampening using 10 wt.% of IPA in water. Samples were printed at a speed of 0.5 m/s and nip force was 400 N. Two constant ink amounts on the roller with two parallel measurements were performed for each sample. Laboratory-scale printing was performed with five sheetfed offset model inks, where the proportion of the

mineral and linseed oils was changed, as shown in Table 4. In addition, a commercial ink; SiegWerk Tempo Max Soft, containing both ink oils was used.

Table 4. *Model ink properties.*

	Ink1	Ink 2	Ink 3	Ink 4	Ink 5
Portion of the mineral oil	100	75	50	25	0
Portion of the linseed oil	0	25	50	75	100
Viscosity [Pas]	160	186	195	156	180
Tack [N]	115	171	207	215	242

Pilot-scale printing was performed on a sheetfed offset press (Heidelberg Speedmaster CD 74) at Forest Pilot Center Oy, Finland. Printing was performed both with contact process parameters and run to constant density. Mineral oil-dominated SiegWerk Tempo Max Soft and linseed oil-based Tempo Perfect were used as inks.

Print density (Densitometer R410e, Techkon), print gloss (ZGM 1022 Glossmeter 20º/70º, Zehntner GmbH Testing Instruments) and mottle were measured. Mottle was analyzed using STFI-Mottling software, and reflectance variation from 1 to 8 mm. Ink on paper tack was measured with the ISIT unit, in which three parallel measurements were analyzed on each sample with each ink. The effect of plasma activation on surface strength of the coated paper was studied with respect to dry pick strength (SCAN-P 63:90) using accelerated speed 1 m/s and nip force of 345 N. Wet pick resistance and wet repellence was measured according to the IGT standard (IGT AIC2-5T2000) using printing speed of 2 m/s and nip force of 625 N.

3. Results and Discussion

Below, the laboratory- and pilot-scale results are presented in separate paragraphs.

3.1 Surface Characterization of Laboratory-Scale Plasma-Coated Samples

According to the mercury porosimetry results, the plasma-deposited coatings had no effect on the porosity of the paper, implying that plasma coatings had an influence only on the chemistry of the paper surface. This result is in agreement with previous research from Tan et al. (2001), who stated that organosilicone plasma deposition is an efficient method for making a paper surface hydrophobic, while maintaining its porous structure.

The relative surface composition of untreated and plasma-coated samples, as determined by XPS, is displayed in Table 5. It can be seen that pigment coated paper contains kaolin (Al, Si) and calcium carbonate (Ca) pigments, and also that each type of plasma coating has its own characteristic surface chemistry.

Weak signals from the pigment coatings were detected on the hydrocarbon and organosilicone plasma-coated surfaces (Table 5), indicating that the coating coverage was not complete or the plasma coatings were thinner than 10 nanometers, which is the escape depth of the XPS photoelectrons. The fluorocarbon plasma coating provided total coverage.

Table 5. *Relative surface composition in atomic % measured by XPS for untreated and laboratory-scale plasma-coated papers.*

			Laboratory scale plasma coated					
	Untreated		**CH plasma**		**HMDSO plasma**		**CF plasma**	
	Average, at.%	Std.	Average, at.%	Std.	Average, at.%	Std.	Average, at.%	Std.
C	43.7	0.2	89.8	*)	56.3	0.2	35.4	0.9
O	41.7	0.1	8.1	*)	24.0	0.1	1.3	0.3
Si	5.0	0.1	0.7	*)	17.4	0.0	n.d.	n.d.
Al	4.8	0.1	0.7	*)	1.6	0.1	n.d.	n.d.
Ca	3.2	0.0	0.4	*)	0.8	0.1	n.d.	n.d.
Na	1.4	0.0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
N	n.d.	n.d.	0.3	*)	n.d.	n.d.	0.2	0.0
F	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	63.0	0.4

n.d. not detected – detection limit 0.1 at.%
**) Only one measurement from two parallel measurements was taken into account.*

The fluorocarbon plasma-coated sample obtained the highest water contact angle. The value was close to 140º, as can be seen in Figure 1. The water contact angle of the organosilicone plasma-coated sample was above 130º and the hydrocarbon plasma coating obtained a contact angle higher than 110º. Thus, the coatings can be classified as hydrophobic. The different values of contact angles on are due to the plasma coating chemistry, coverage level and/or coating thickness. Water contact angles on untreated and hydrocarbon plasma-coated samples had the same initial value, however the angle decreased significantly (~30º) on the untreated one due to time-depended lateral spreading of droplet and absorption into the coating. The untreated coating may thus be regarded as less hydrophobic than the other three. The standard deviation of the contact angles were between 2 and 4 degrees.

The mineral and linseed oil contact angle results showed that the fluorocarbon- and organosilicone-based plasma coatings were (beside hydrophobic) oleophobic since they obtained high contact angles for oils, whereas the untreated and hydrocarbon plasma coating were oleophilic with the CH plasma coating being the most oleophilic of all samples. The contact angles of linseed and mineral oils are given in Figures 2 and 3. With the hydrocarbon and organosilicone plasma coatings the changes in contact angle values were minor for mineral than for linseed oil. However, fluorocarbon plasma coating increased more mineral oil contact angles compared to linseed oil.

The pre-assumption in the current work was that the hydrophobic-oleophilic character would be beneficial in offset printing, because it would allow the ink

oil penetration into a pigment coating, but simultaneously reduce the dampening water absorption.

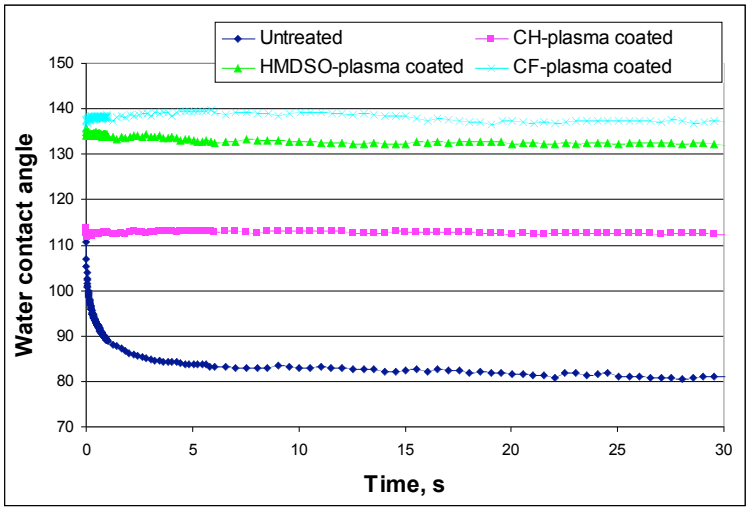

Figure 1. *Change of water contact angles (°) on untreated and laboratory-scale plasma-coated paper samples with time.*

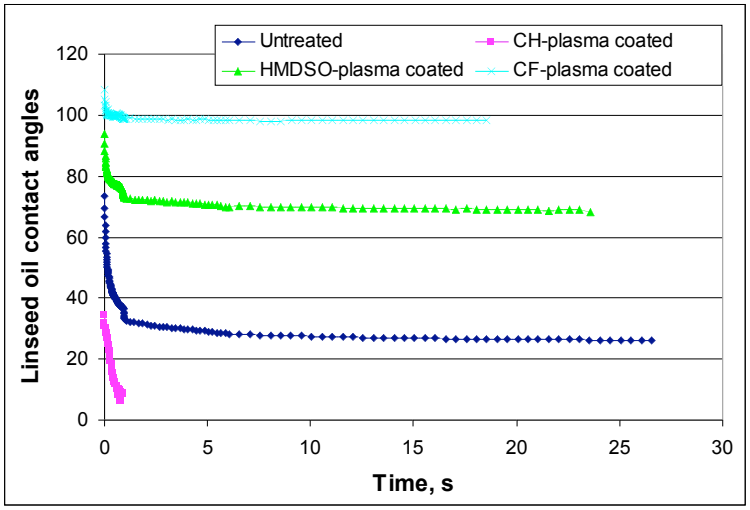

Figure 2. *Change of linseed oil contact angles (°) on untreated and laboratory-scale plasma-coated paper samples with time.*

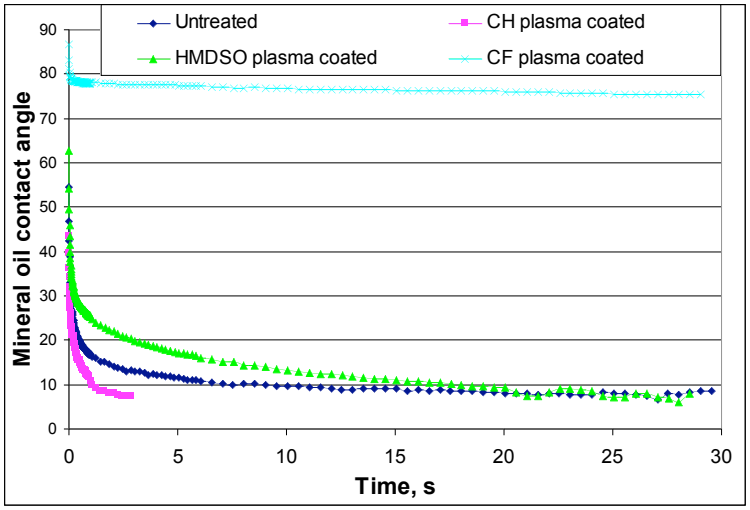

Figure 3. *Change of mineral oil contact angles (º) on untreated and laboratory-scale plasma-coated paper samples with time.*

ToF-SIMS cross section images (Figure 4) show the depth of the dampening water absorption. Cesium was added as a trace material to enable detection of the dampening water. It is shown that the water is absorbed into the pigment coating in the untreated and hydrocarbon plasma-coated samples. Some dampening water was detected on the top of the pigment coating in the organosilicone plasma-coated sample but it did not cover the whole surface. No dampening water was detected in the fluorocarbon plasma-coated sample, which indicates that no dampening water absorbed into the pigment coating.

The relative concentration of the cesium measured by XPS on damped surfaces was 0.7 at.% for untreated paper, 0.2 at.% for the hydrocarbon plasma-coated paper, less than 0.1 at.% for organosilicone plasma-coated and 0 at.% (no signal) in the fluorocarbon plasma-coated paper sample.

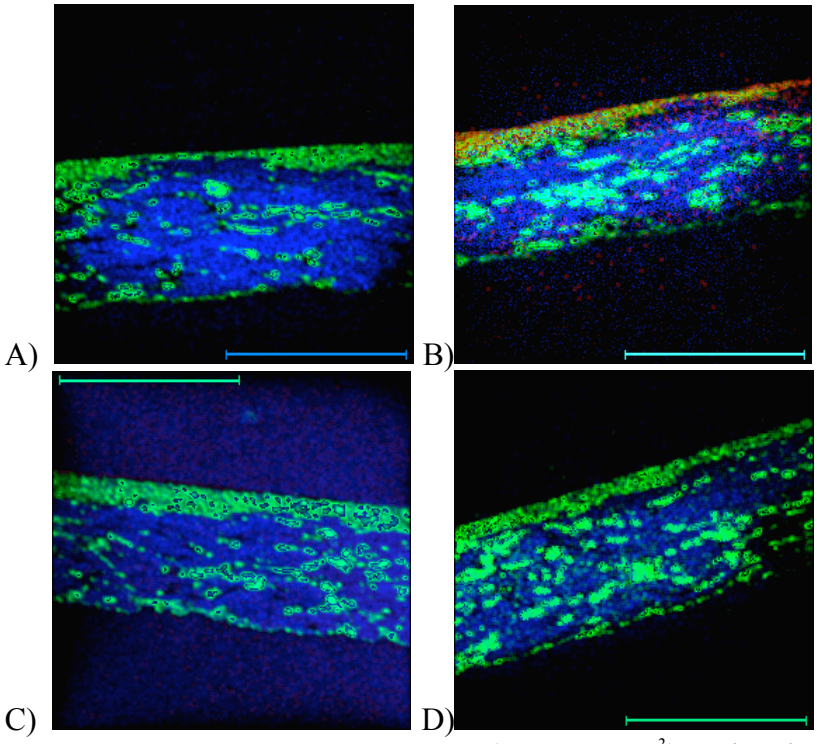

Figure 4. *ToF-SIMS cross section images (200 x 200 μm^2) to show level of dampening water absorption in laboratory-scale plasma-coated samples. A: untreated, B: CH plasma-coated, C: HMDSO plasma-coated and D: CF plasma-coated. Cesium is marked with red, calcium with green, and hydrocarbons (here C_3H_7) with blue.*

3.2 Offset Printability of Laboratory-Scale Plasma-Coated Samples

Table 6 shows that the hydrophobic and oleophilic hydrocarbon plasma coating increased the amount of transferred ink from the ink roll on the paper (higher print density) with all the inks, whereas in the hydrophobic and oleophobic fluorocarbon and organosilicone plasma-coated samples, the change in ink transfer depended on the ink oil type: the transferred ink amount decreased with mineral oil-based inks and increased with linseed oil-based inks.

Print gloss did not correlate with print density: the print gloss decreased with linseed oil based inks, and increased with mineral oil based inks in the fluorocarbon plasma-coated samples. The organosilicone and hydrocarbon plasma coatings showed no clear trends in print gloss. The gloss of the paper was slightly increased due to the presence of the different plasma coatings. The gloss was 54% in the untreated sample, 57% in the hydrocarbon plasma-coated

sample, 59% in the organosilicone plasma-coated sample, and 60% in the fluorocarbon plasma-coated sample. Print uniformity was also improved by all the plasma coatings, which indicates that the plasma coating coverage was sufficient and the chemistry was homogeneous, resulting in uniform dampening water absorption into the pigment coating.

Table 6. *Print density, gloss and mottle values for laboratory-scale plasma-coated samples.*

Sample		Print density -120		Print density -80		Print gloss, % -120		Print gloss, % - 80		Mottle	Mottle
		Average	Std.	Average	Std.	Average	Std.	Average	Std.	–120	–80
Ink 1	Untreated	1.12	0.06	0.88	0.05	43.2	1.1	47.3	0.8	5	5
	CH plasma	1.50	0.05	1.25	0.04	39.6	1.5	45.5	2.4	2	4
	HMDSO plasma	0.73	0.07	0.50	0.02	37.7	1.8	45.1	4.7	4	4
	CF plasma	0.20	0.04	0.13	0.02	51.5	2.7	56.6	0.8	3	2
Ink 2	Untreated	0.94	0.04	0.66	0.03	49.0	1.0	55.7	0.9	4	5
	CH plasma	1.47	0.05	1.24	0.03	50.5	0.5	54.4	2.2	1	1
	HMDSO plasma	0.81	0.07	–	–	48.8	3.7	–	–	3	–
	CF plasma	0.43	0.03	0.31	0.02	48.1	2.3	57.1	1.5	2	2
Ink 3	Untreated	1.04	0.02	0.76	0.03	55.9	1.7	59.1	1.7	3	3
	CH plasma	1.53	0.01	1.25	0.03	55.8	1.2	62.6	1.3	1	1
	HMDSO plasma	1.26	0.07	–	–	56.8	2.7	–	–	1	–
	CF plasma	1.10	0.06	0.84	0.07	49.5	1.9	54.1	0.6	2	2
Ink 4	Untreated	1.07	0.03	0.78	0.02	55.9	1.0	60.0	0.2	3	3
	CH plasma	1.56	0.02	1.27	0.05	58.0	0.6	60.0	1.1	1	1
	HMDSO plasma	1.35	0.06	1.01	0.07	57.5	2.2	55.7	1.3	1	1
	CF plasma	0.87	0.08	0.82	0.09	32.9	2.3	47.5	2.9	2	2
Ink 5	Untreated	0.68	0.05	0.58	0.03	55.0	0.8	57.5	1.0	4	4
	CH plasma	1.35	0.05	1.09	0.07	50.4	1.6	52.1	1.9	3	4
	HMDSO plasma	1.18	0.08	1.00	0.04	43.4	3.3	51.4	5.2	2	2
	CF plasma	1.07	0.08	0.90	0.07	37.5	6.2	43.7	8.5	2	2
Commercial ink	Untreated	1.67	0.09	1.34	0.04	65.4	1.7	64.6	1.1	2	2
	CH plasma	1.91	0.04	1.63	0.02	62.5	0.9	62.0	1.4	2	1
	HMDSO plasma	1.82	0.05	1.43	0.04	67.1	1.0	64.0	2.6	1	1
	CF plasma	1.18	0.09	1.00	0.08	44.9	2.8	47.7	3.1	2	2

The influence of the plasma coatings on ink setting depended also on the ink oil type as can be seen in the ISIT paper-tack curves in Figures 5 and 6. No changes could be detected with ink 1, since the ink was already set before the tack measurement started. The fluorocarbon-based plasma coating accelerated the ink setting or decreased ink-coating adhesion, and no ink tack development could be seen with any of the inks. The organosilicone-based plasma coating also decreased the tack force. The hydrocarbon-based plasma coating increased the tack force and slowed down ink setting rate when using mineral oil based inks (ink 2 and commercial ink). However, when the linseed oil based ink (ink 5) was used, the hydrocarbon-based plasma coating also caused a decrease in tack force, as did the other plasma coatings. As shown in Figure 6, the tack force correlates well with the water contact angles. One should also take in consideration that the plasma coatings could have influenced ink transfer. The ISIT paper tack curves reflect not only the ink setting, but also ink-coating adhesion. A reduced ink transfer decreases ink tack. In our previous study (Pykönen et al., 2008), oxidation of pigment coated paper by plasma activation accelerated ink setting and decreased the tack force when the ink was mineral oil-based. Influence of plasma activation on ink setting was the opposite when the ink was based on linseed oil. Therefore, it seems that hydrophilic surfaces accelerate ink setting and decrease tack force when mineral oil-based inks are

used, and slow down ink setting when using linseed oil-based ink. On the contrary, hydrophobic-oleophilic surfaces slow down ink setting and increase ink tack force with mineral oil-based inks and decrease tack force in combination with linseed oil-based inks. Hydrophobic-oleophobic surfaces seem to decrease tack force using both mineral and linseed oil-based inks. It has to be emphasized that ink setting results can not be directly compared to print quality results, since no pre-dampening was used in the ink setting measurements.

Typically, high print density leads to high print gloss, since the thick ink film fills up the microstructure of the coating. However, it has been shown that the print gloss decreases when the ink film thickness reaches the level where the size of the ink filaments is too large to level out, which results in macro roughness. It is also well known that fast ink setting reduces print gloss due to poor ink filament leveling (Ström, 2005). In this study, the print density and print gloss did not correlate, probably because print gloss was also affected by ink setting changes caused by the plasma coatings.

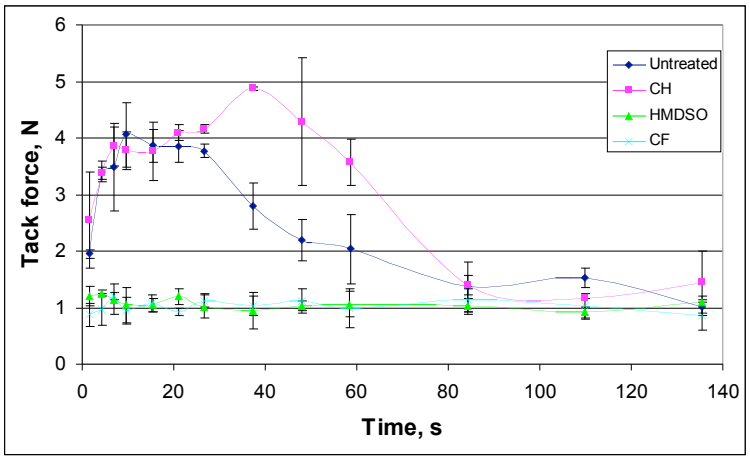

Figure 5. *ISIT curves for ink 2.*

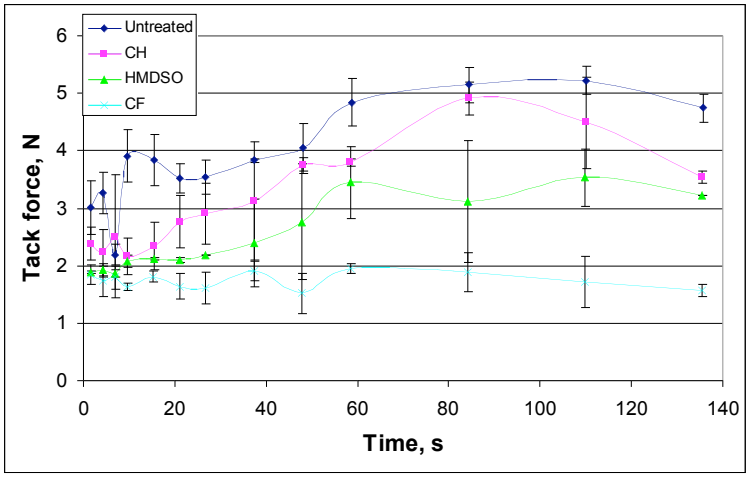

Figure 6. *ISIT curves for ink 5.*

According to the dry pick measurements, the plasma coatings had no influence on the surface strength of the pigment coated paper. Wet pick/wet repellence test was performed according to the IGT standard, but it seems that the result interpretation is complicated by the ink repellence caused by the plasma coatings. Calculating the wet pick and wet repellence values according to standard, the results indicate that the wet repellence is reduced and wet pick increased, even if this is in conflict with the visual evaluation, the water contact angle results, and the ToF-SIMS dampening water absorption images.

In wet pick/wet repellence tests, the hydrocarbon- and organosilicone-based plasma coatings increased the print density when pre-dampening was used. However, the hydrophobic and oleophobic organosilicone- and fluorocarbon-based coatings reduced print density (Table 7), when pre-dampening was not used. This result indicates that the oleophobic coatings caused ink repellence. Even if the fluorocarbon-coated surface was hydrophobic and oleophobic and had no chemical affinity to the oil-based ink, some of the ink was transferred onto the paper, which indicates that mechanical aspects in ink transfer are important, causing forced wetting by the ink.

Table 7. *Wet pick and wet repellence results. Presented figures are print density values, and wet pick and wet repellence values are calculated from results according to IGT standard.*

First print	Test paper - not damped		Test paper - damped		Wet repellence + wet pick	
	Average	Std.	Average	Std.		
Untreated	1.9	0.1	0.7	0.1	62.7	
CH plasma	1.9	0.1	1.8	0.1	8.9	
HMDSO plasma	1.6	0.1	1.7	0.1	-0.8	
CF plasma	1.0	0.2	1.0	0.2	-2.7	
Second print	**Standard paper - not damped**		**Standard paper - not damped**		**Wet pick**	**Wet repellence**
	Average	Std.	Average	Std.		
Untreated	1.6	0.2	1.8	0.2	-13.8	76.5
CH plasma	1.6	0.1	1.6	0.1	-5.0	13.9
HMDSO plasma	1.6	0.1	1.7	0.2	-5.7	4.9
CF plasma	1.6	0.2	1.7	0.2	-8.0	5.3

Since the results in the laboratory-scale tests were promising, the work was continued in a pilot-scale plasma apparatus, using hydrocarbon and organosilicone-based plasma coatings.

3.3 Surface Characterization of Pilot-Scale Plasma-Coated Samples

The plasma coatings deposited in the pilot-scale equipment did not have any influence on the substrate porosity, as was also the case in the laboratory-scale tests. Since the plasma coatings were deposited under atmospheric conditions, both hydrocarbon- and organosilicone-based plasma coatings contained twice as much oxygen compared to the laboratory-scale vacuum plasma-coated samples (Table 8). The higher amount of oxygen is due to fact that in atmospheric pressure treatments always contains small amount of oxygen in the system, but also the type of chemical reactions occurring in the plasma and the process parameters are great importance on the Si/O ratio. Both coatings also contained some nitrogen, since it was used as a carrier gas in the pilot-scale treatments. It must be emphasized the fact that no real correlation can be expected between experiments carried out at low-pressure and at atmospheric pressure. As in the laboratory-scale tests, the plasma coating coverage in the pilot-scale tests was not complete, as some signals from the pigment coating could be detected by XPS. The thickness of organosilicone-based plasma coating was 50 nm and hydrocarbon-based 25 nm.

Table 8. *Relative surface composition in atomic % measured by XPS for untreated and pilot-scale plasma-coated papers.*

	Untreated		**CH plasma**		**HMDSO plasma**	
	Average, at.%	Std.	Average, at.%	Std.	Average, at.%	Std.
C	42.7	1.4	78.2	1.4	29.7	0.2
O	43.2	0.9	16.0	0.5	48.1	0.8
Si	5.6	0.6	n.d.	n.d.	17.8	0.6
Al	4.1	0.3	0.7	*)	1.3	0.1
Ca	2.8	0.2	n.d.	n.d.	0.9	0.3
Na	1.5	0.5	0.1	*)	1.0	0.1
N	n.d.	n.d.	5.4	0.9	1.7	0.2

n.d. not detected – detection limit 0.1 at.%
**) Only one measurement from three parallel measurements showed the presence of Al and Na.*

The pilot-scale coatings did not provide as high water contact angles as the laboratory-scale coatings, which can be explained by the higher amount of polar oxygen groups on the surface (Figure 7). The organosilicone-based plasma coating was again hydrophobic and oleophobic, whereas the hydrocarbon-based plasma coating was hydrophobic and oleophilic compared to the untreated sample (Figures 8 and 9).

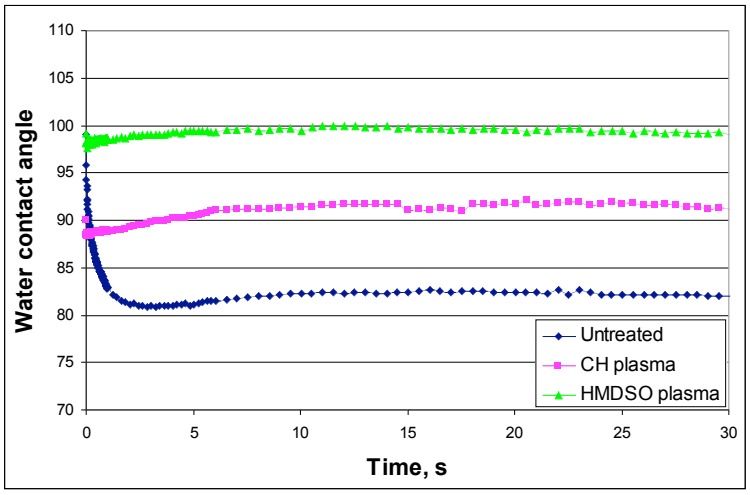

Figure 7. *Change of water contact angles (°) on untreated and pilot-scale plasma-coated paper samples with time.*

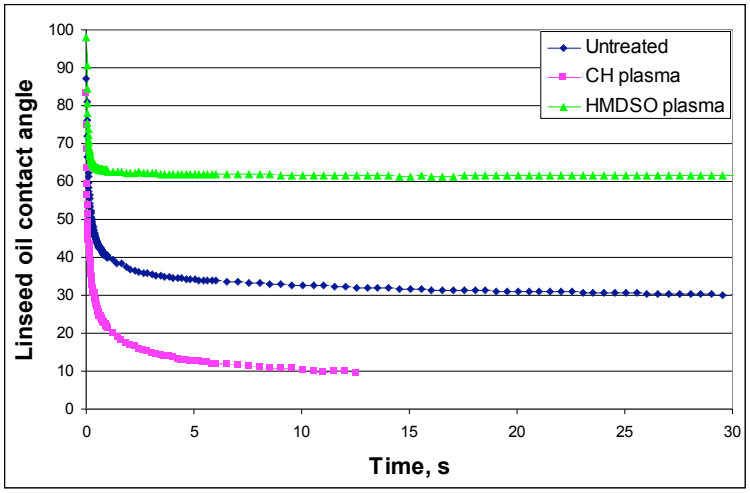

Figure 8. *Change of linseed oil contact angles (º) on untreated and pilot-scale plasma-coated paper samples with time.*

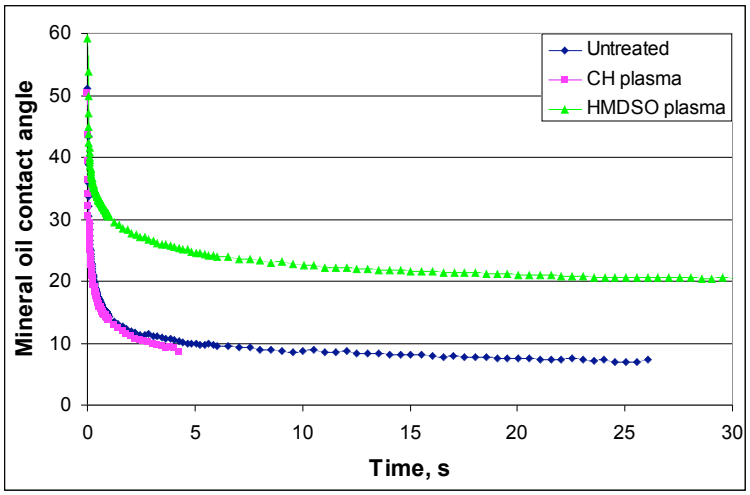

Figure 9. *Change of mineral oil contact angles (º) on untreated and pilot-scale plasma-coated paper samples with time.*

ToF-SIMS cross section images (not presented) showed also in pilot-scale that dampening water was absorbed into the pigment coating with the untreated and hydrocarbon plasma treated samples. In the presence of the organosilicone-based plasma coating, the dampening water was not transferred evenly onto the paper, and some remainder of dampening water was detected on the pigment coating surface. The relative concentration of cesium measured by XPS on the

damped surface was 0.9 at.% in the untreated sample, 0.3 at.% in the hydrocarbon plasma-coated sample and 0 at.% (no signal) in the organosilicone plasma-coated sample. This indicated that the hydrocarbon-based plasma coating deposited at atmospheric pressure in the pilot-scale equipment reduced the dampening water absorption into the pigment coating in the same way as did by the vacuum-deposited plasma coating in the laboratory-scale test.

3.4 Offset Printability of Pilot-Scale Plasma-Coated Samples

In pilot-scale printing trials using the two commercial inks, the amount of the transferred ink increased with both inks. However, the mineral oil-dominated ink gave a more significant change. One should note that since the inks were of commercial grade, ink components other than the oils may have been different as well. The differences between the inks cannot with certainty be regarded to depend on the oil type only. The print gloss was not affected by the pilot-scale-produced plasma coatings and the mottling seemed to increase. This suggests that the pilot-scale-deposited plasma coatings were not uniform, and may have caused uneven dampening water absorption.

Table 9. *Print density, gloss and mottle values for pilot-scale plasma-coated samples.*

Sample		Print density		Print gloss, %		Mottle
		Average	Std.	Average	Std.	
Mineral oil dominated ink	Untreated	1.07	0.05	72.5	2.1	5
	HMDSO plasma	1.16	0.11	67.8	3.7	9
	CH plasma	1.42	0.09	74.7	1.3	7
Linseed oil based ink	Untreated	1.15	0.04	77.9	2.2	4
	HMDSO plasma	1.28	0.09	75.9	1.1	6
	CH plasma	1.23	0.05	78.6	2.3	5

The organosilicone- and hydrocarbon-based plasma coatings decreased the ink tack when the mineral oil-based ink was used, and slowed down the ink setting when using the linseed oil-based ink. In Figure 11, the tack curve correlates with contact angle results; the organosilicone-based plasma coating slowed down and the hydrocarbon-based plasma coating accelerated the linseed oil penetration.

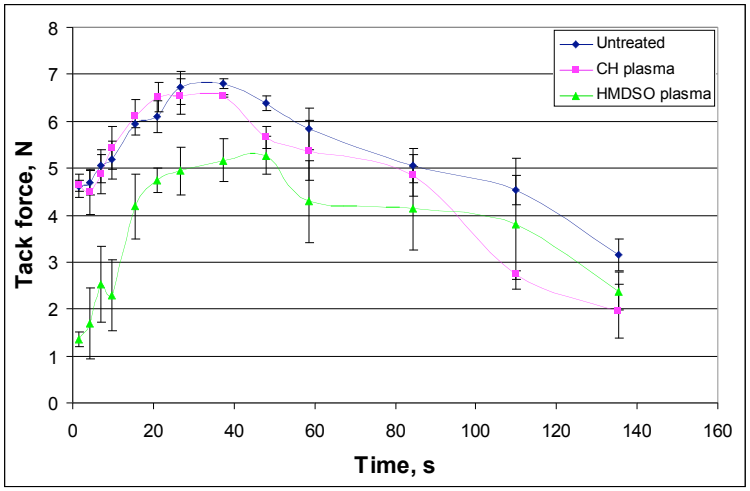

Figure 10. *ISIT curves for mineral-oil dominated ink.*

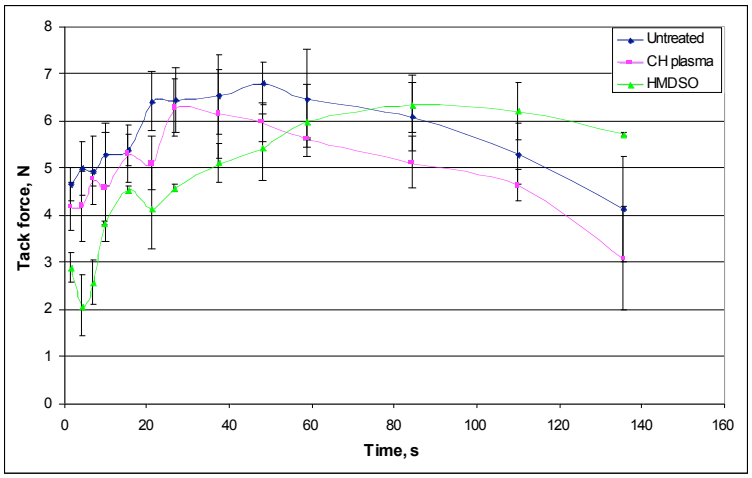

Figure 11. *ISIT curves for linseed oil based ink.*

Regarding the surface strength of the pigment coating, the pilot-scale plasma-deposited coatings behaved similarly to the laboratory-scale; no strength loss was observed. The wet pick/wet repellence results were similar to laboratory-scale results, as can be seen in Table 10.

Table 10. *Wet pick and wet repellence results. Presented figures are print density values, and wet pick and wet repellence values are calculated from results according to IGT standard.*

First print	Test paper - not damped		Test paper - damped		Wet repellence + wet pick	
	Average	Std.	Average	Std.		
Untreated	1.86	0.01	0.68	0.03	63.4	
CH plasma	1.95	0.00	1.71	0.02	12.2	
HMDSO plasma	1.71	0.02	1.79	0.03	-4.6	
Second print	**Standard paper - not damped**		**Standard paper - not damped**		**Wet pick**	**Wet repellence**
	Average	Std.	Average	Std.		
Untreated	1.54	0.06	1.76	0.04	-14.6	78.0
CH plasma	1.57	0.03	1.59	0.03	-1.6	13.8
HMDSO plasma	1.68	0.01	1.70	0.00	-0.7	-3.9

4. Conclusions

The present study showed that the hydrophobic plasma coatings were able to reduce or even completely prevent dampening water absorption into the pigment coating. Hydrophobic plasma coatings had an influence on ink transfer, mottling and ink setting, but not on the porosity or surface strength of the pigment coated paper. The hydrophobic and oleophilic hydrocarbon-based plasma coating increased the ink transfer with all the inks in both the laboratory- and pilot-scale trials. The results indicated that the hydrophobic coating should also have some oleophilic character in order to work with both mineral and linseed oil-based inks. The ToF-SIMS cross section images showed that the hydrocarbon-based plasma coating allowed the dampening water penetration into the pigment coating. However, the cesium amount measured by XPS indicated that the amount of absorbed dampening water was less compared to the in the untreated sample. The results showed that higher print densities could be achieved using a hydrophobic coating which only reduced the dampening water absorption (such as the hydrocarbon-based plasma coating) but did not prevent it completely, as did the organosilicone- and fluorocarbon-based plasma coatings. Comparison of mottle results in the laboratory and pilot-scale tests showed that if the coating coverage and uniformity of the plasma coatings were high enough, the mottling could be decreased, whereas poor coverage and nonuniformity increased the mottling. Wet pick/wet repellence results showed that the hydrophobic and oleophobic organosilicone- and fluorocarbon-based plasma coatings caused ink repellence, when pre-dampening was not used. On the other hand, ink transfer was increased when substrates were pre-damped. Therefore, it seems as if the improvements in the print quality are related to dampening water absorption changes, even if the ink setting was also influenced by the plasma coatings. It is known that the presence of the dampening water influences both ink transfer and ink penetration (Liu et al., 2008). Therefore, the ISIT results obtained without pre-dampening are not completely comparable with printing results where dampening was used.

In general we conclude that an increased hydrophobic character of the coating will result in less absorption (and consumption) of dampening water and if the

hydrophobicity is uniform it will lead to an improved print quality in terms of higher print density and lower print mottle.

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