



INFLUENCE OF PLASMA MODIFICATION ON SURFACE PROPERTIES AND OFFSET PRINTABILITY OF COATED PAPER

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Influence of Plasma Modification on Surface Properties and Offset Printability of Coated Paper

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ABSTRACT

Influence of Plasma Modification on Surface Properties and Offset Printability of Coated paper

The properties of the paper surface play a crucial role in ensuring suitable quality and runnability in various converting and finishing operations, such as printing. Plasma surface modification makes it possible to modify the surface chemistry of paper without altering the bulk material properties. This also makes it possible to investigate the role of the surface chemistry alone on printability without influencing the porous structure of the pigment-coated paper. Since the porous structure of a pigment coating controls both ink setting and optical properties, surface chemical changes created by a plasma modification have a potential to decouple these two effects and to permit a better optimization of them both.

The aim of this work was to understand the effects of plasma surface modification on paper properties, and how it influences printability in the sheet-fed offset process. The objective was to broaden the fundamental understanding of the role of surface chemistry on offset printing. The effects of changing the hydrophilicity/ hydrophobicity and the surface chemical composition by plasma activation and plasma coatings on the properties of coated paper and on ink-paper interactions as well as on sheet-fed offset print quality were investigated. In addition, the durability of the plasma surface modification was studied. Nowadays, a typical sheet-fed offset press also contains units for surface finishing, for example UV-varnishing. The role of the surface chemistry on the UV-varnish absorption into highly permeable and porous pigment-coated paper was also investigated.

With plasma activation it was possible to increase the surface energy and hydrophilicity of paper. Both polar and dispersion interactions were found to increase, although the change was greater in the polar interactions due to induced oxygen molecular groups. The results indicated that plasma activation takes place particularly in high molecular weight components such as the dispersion chemicals used to stabilize the pigment and latex particles. Surface composition, such as pigment and binder type, was found to influence the response to the plasma activation. The general trend was that pilot-scale treatment modified the surface chemistry without altering the physical coating structure, whereas excessive laboratory-scale treatment increased the surface roughness and reduced the surface strength, which led to micro-picking in printing. It was shown that pilot-scale plasma activation in combination with appropriate ink oils makes it possible to adjust the ink-setting rate. The ink-setting rate decreased with linseed-oil-based inks, probably due to increased acid-base interactions between the polar groups in the oil and the plasma-treated paper surface. With mineral-oil-based inks, the ink setting accelerated due to plasma activation. Hydrophobic plasma coatings were able to reduce or even prevent the absorption of dampening water into pigment-coated paper, even when the dampening water was applied under the influence of nip pressure. A uniform hydrophobic plasma coating with sufficient chemical affinity with ink gave an improved print quality in terms of higher print density and lower print mottle. It was also shown that a fluorocarbon plasma coating reduced the free wetting of the UV-varnish into the highly permeable and porous pigment coating. However, when the UV-varnish was applied under the influence of nip pressure, which leads to forced wetting, the role of the surface chemical composition seems to be much less.

A decay in surface energy and wettability occurred during the first weeks of storage after plasma activation, after which it leveled off. However, the oxygen/carbon elemental ratio did not decrease as a function of time, indicating that ageing could be caused by a re-orientation of polar groups or by a contamination of the surface. The plasma coatings appeared to be more stable when the hydrophobicity was higher, probably due to fewer interactions with oxygen and water vapor in the air.

Keywords: *plasma, surface modification, pigment-coated paper, sheet-fed offset printing, ink-paper interactions, surface chemistry.*

ABSTRAKT

Inverkan av plasmabehandling på ytegenskaper och offsettryckbarhet hos bestruket papper

Papperets ytegenskaper spelar en viktig roll kvaliteten och körbarheten vid olika konverterings- och ytbehandlingsoperationer, till exempel tryckning. Plasmabehandling erbjuder en möjlighet att modifiera papperets ytkemiska egenskaper utan att påverka dess bulkegenskaper. Detta gör det även möjligt att enskilt studera den inverkan som de ytkemiska egenskaperna har på tryckbarheten, utan att man påverkar det pigmentbestrukna papperets porositet. Eftersom porositeten påverkar både tryckfärgens sättning och de optiska egenskaperna, erbjuder de ytkemiska förändringar som plasmabehandlingen ger upphov till en möjlighet att frångå dessa två effekter från varandra. Detta gör att man kan uppnå en bättre optimering av bådaderna.

Målsättningen med denna avhandling var att förstå plasma-ytmodifieringens inverkan på papperets egenskaper, samt hur den inverkar på tryckbarheten i arkoffsetprocessen. Målet var att utvidga den fundamentala förståelsen för ytkemins betydelse i offsettryckprocessen. Effekterna av plasma-aktivering och plasmabestrykning på hydrofilicitet, hydrofobicitet samt ytkemisk sammansättning undersöktes. Vidare studerades dessa faktorer inverkan på det bestrukna papperets egenskaper, på interaktionen mellan tryckfärg och papper och på kvalitetsegenskaperna hos produkter tryckta genom arkoffset. Dessutom undersöktes plasma-ytmodifieringens beständighet. Nuförtiden innehåller en typisk arkoffsettryckpress även ytbehandlingsenheter, till exempel för applicering av UV-lack. Även ytkemins betydelse för UV-lackens absorption in i högermeabla och porösa pigmentbestrukna papper undersöktes.

Det visade sig vara möjligt att öka papperets ytenergi och hydrofilicitet genom plasmabehandling. Både de polära interaktionerna och dispersionsinteraktionerna ökade, även om förändringen var större hos de polära interaktionerna. Detta berodde troligen på ett ökat antal syremolekylgrupper på pappersytan. Resultaten indikerade att plasmaaktivering i synnerhet sker i kemikalier med höga molekylvikter, till exempel de dispersionskemikalier som används för att stabilisera pigment- och latexpartiklar. Papperets ytsammansättning, till exempel pigment- och bindemedelstyp, hade inverkan på plasmabehandlingens effekt. En allmän trend var att plasmabehandlingarna i pilotskala modifierade de ytkemiska egenskaperna utan att påverka bestrykningsskiktets fysikaliska struktur. En kraftig behandling i laboratorieskala ledde däremot till ökad ytråhet och reducerad ystyrka. Detta resulterade i sk. mikro-picking under tryckningen. Plasma-aktivering i pilotskala, i kombination med passande tryckfärgsoljor, visade sig möjliggöra en justering av tryckfärgens sättningshastighet. Sättningshastigheten minskade hos tryckfärg baserad på linolja, troligen på grund av ökade syra-bas interaktioner mellan de polära grupperna i oljan och de plasmabehandlede papperen. Hos tryckfärg baserad på mineralolja blev tryckfärgens sättningshastighet däremot högre. Hydrofoba plasmabestrykningsskikt minskade eller förhindrade absorption av fuktvattnet in i det pigmentbestrukna papperet, trots att fuktningstvattnet applicerades under inflytande av tryck i nypet. En homogen, hydrofob plasmabestrykning med tillräcklig kemisk affinitet gav förbättrad tryckkvalitet i form av högre tryckdensitet och lägre flammighet. Resultaten visade att en kolfluorplasmabestrykning kunde reducera UV-lackens fria vätning i starkt permeabla och porösa pigmentskikt. När UV-lacken applicerades under inverkan av nyptryck, vilket ledde till påtvingad vätning, var inflytandet av den ytkemiska sammansättningen minimal.

Ytenergin och vätbarheten avtog under de första veckorna efter plasmaaktiveringen, varefter förändringen planade ut. Syre/kol-elementförhållandet minskade inte som en funktion av tiden, vilket indikerar att åldrandet troligen sker till följd av reorientering av de polära grupperna samt av återkontamination av ytan. Plasmabestrykningens stabilitet förefaller vara bättre vid högre hydrofobicitetsnivåer, vilket antagligen beror på färre interaktioner med luftens syre och vattenånga.

Nyckelord: *plasma, ytmodifiering, pigmentbestrukta papper, arkoffsettryckning, tryckfärg-pappersinteraktioner, ytkemi.*

PREFACE

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- I Pykönen, M., Sundqvist, H., Järnström, J., Kaukoniemi, O.-V., Tuominen, M., Lahti, J., Peltonen, J., Fardim, P. and Toivakka, M., *Effects of Atmospheric Plasma Activation on Surface Properties of Pigment-Coated and Surface-Sized Papers*, Applied Surface Science 255 (2008), 3217–3229.
- II Pykönen, M., Sundqvist, H., Kaukoniemi, O.-V., Tuominen, M., Lahti, J., Fardim, P. and Toivakka, M., *Ageing Effect in Atmospheric Plasma Activation of Paper Substrates*, Surface & Coatings Technology 202 (2008), 3777–3786.
- III Pykönen, M., Sundqvist, H., Tuominen, M., Lahti, J., Preston, J., Fardim, P. and Toivakka, M., *Influence of Atmospheric Plasma Activation on Sheet-Fed Offset Print Quality*, Nordic Pulp and Paper Research Journal 23 (2008), 181–188.
- IV Pykönen, M., Silvaani, H., Preston, J., Fardim, P. and Toivakka, M., *Influence of Plasma Activation on Absorption of Offset Ink Components into Pigment-Coated Paper*, Nordic Pulp and Paper Research Journal 25 (2010), 95–101.
- V Pykönen, M., Silvaani, H., Preston, J., Fardim, P. and Toivakka, M., *Plasma Activation Induced Changes in Surface Chemistry of Pigment Coating Components*, Colloids and Surfaces A: Physicochem. Eng. Aspects 352 (2009), 103–112.
- VI Pykönen, M., Johansson, K., Dubreuil, M., Vangeneugden, D., Ström, G., Fardim, P. and Toivakka, M., *Evaluation of Plasma-Deposited Hydrophobic Coatings on Pigment-Coated Paper for Reduced Dampening Water Absorption*, Journal of Adhesion Science and Technology 24 (2010), 511–537.
- VII Pykönen, M., Johansson, K., Bollström, R., Fardim, P. and Toivakka, M., *Influence of Surface Chemical Composition on UV-Varnish Absorption on Permeable Pigment-Coated Paper*, Industrial and Engineering Chemical Research Journal 49 (2010), 2169–2175.

Author's contribution

- I The author defined the research plan together with the co-authors, performed the experimental work related to surface chemical measurements (XPS and ToF-SIMS) and laboratory scale plasma modification, participated in pilot-scale plasma trials, analyzed the corresponding results and wrote the manuscript with the exception of the results relating to surface energy and AFM measurements.
- II The author defined the research plan together with the co-authors, performed the experimental work related to surface chemistry measurements (XPS) and laboratory-scale plasma modification, participated in pilot-scale plasma trials, analyzed the corresponding results and wrote the manuscript with the exception of the results relating to surface energy.
- III The author defined the research plan together with the co-authors, performed the experimental work related to surface chemical characterization (XPS),

offset printability and laboratory-scale plasma modification, participated in pilot-scale plasma trials and printing trials, analyzed the corresponding results and wrote the manuscript.

- IV The author defined the research plan together with the co-authors, performed part of the experimental work related to model ink preparation, surface chemical characterization (XPS) and offset printability (ISIT), participated in plasma modifications, analyzed the corresponding results and wrote the manuscript.
- V The author defined the research plan together with the co-authors, performed part of the experimental work related to surface chemical characterization (XPS and ToF-SIMS), participated in plasma modifications and printing trials, analyzed corresponding results and wrote the manuscript.
- VI The author defined the research plan together with the co-authors, performed the experimental work related to plasma modification, surface chemical characterization (contact angle measurements, XPS and ToF-SIMS), offset printability, analyzed the results and wrote the manuscript.
- VII The author defined the research plan together with the co-authors, performed the experimental work related to plasma modification and surface chemical characterization (contact angle measurements, XPS and ToF-SIMS), analyzed the results and wrote the manuscript.

Related Publications

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Pykönen, M., Johansson, K., Larsson, J., Fardim, P. and Toivakka, M., *Improved Flexographic Printing through Atmospheric Pressure Plasma Treatment*, In proceedings: 24th PTS Coating Symposium 2009, Baden-Baden, Germany.

NOMENCLATURE

Abbreviations

AC	alternating current
AFM	atomic force microscopy
AKD	alkyl ketene dimer
ATR	attenuated total reflectance
BTC	back-trap mottling
DBD	dielectric barrier discharge
DCSBD	diffuse coplanar surface barrier discharge
DIM	diiodomethane
DRIFT	diffuse reflectance infrared fourier transform
EDS	energy dispersive spectroscopy
ESCA	electron spectroscopy for chemical analysis
FIB	focused ion beam
FTIR	fourier transform infrared
FTMS	fluorotrimethylsilane
GCC	ground calcium carbonate
HMDSO	hexamethyldisiloxane
IGT	Institut for Graphische Technik
IPA	isopropyl alcohol
ISIT	ink-surface-interaction-tester
PAS	photoacoustic
PCC	precipitated calcium carbonate
PCVD	plasma chemical vapour deposition
PFC	perfluoro-compound
RMS	root-mean-square
S_{dr}	surface area ratio
S_q	root-mean-square roughness
SB	styrene-butadiene
SA	styrene-acrylate
SEM	scanning electron microscopy
TEOS	tetraethyl orthosilicate
ToF-SIMS	time-of-flight secondary ion mass spectroscopy
UV	ultraviolet
WIM	water interference mottling
XPS	x-ray photoelectron spectroscopy

Symbols

b	immobilization parameter related to paper porosity
E_B	binding energy of electrons
f_∞	limiting value of the splitting
h	penetration depth
$h\nu$	energy of the x-ray source
k	contact parameter related to the paper smoothness
KE	kinetic energy of emitted photoelectrons

p_E	external pressure
r	pore radius
t	time
T_g	glass transition temperature
W_a	work of adhesion
x	ink on the printing plate
y	ink transferred to the paper
η	viscosity
θ	contact angle
γ_{SG}	surface energy of the solid in equilibrium with the gas
γ_{SL}	interfacial tension between solid and liquid
γ_{LG}	surface tension of the liquid in equilibrium with the gas

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1. INTRODUCTION

Paper is a versatile material widely used for various purposes. Coated paper and board grades are typically used in the production of books, magazines, brochures and packages, where control of surface properties is crucial. Paper coating with an aqueous mineral pigment suspension or sizing for example with starch improves its compatibility with various converting and finishing operations, such as printing. These coatings provide enhanced smoothness, surface strength, optical and absorption properties. However, special functional properties, such as hydrophilicity or hydrophobicity, are still required for a variety of current and future applications in order to satisfy runnability and quality demands. Examples include wetting and adhesion improvement in various coating applications, such as between paper and polymer in the extrusion and lamination process, enhancement of printability, and barrier properties in packaging materials. Rising costs, limited market growth and expansion of electronic media have led the paper industry to develop new innovative fiber-based products, such as printed electronics and biologically active papers, where the control of surface properties plays an important role. Therefore, it can be said that surface modification plays an important role in transforming inexpensive paper materials into value-added finished products.

Plasma, “the fourth state of matter”, is an ionized gas consisting of reactive species, such as electrons, ions and radicals. The worldwide sale of plasma sources and systems was estimated to be USD 35 billion in 2005. USA, Germany, Japan and Korea are pioneer countries which strongly support plasma-related scientific research and technological development. For example, in Germany, 70 to 80 thousand workplaces can be directly associated with plasma technology and approximately 500 thousand workplaces are estimated to be related to plasma technology, with an estimated annual growth rate of 10 % [1]. In Finland, plasma technology is still a young technology. It has been studied and developed since the late 1990s mainly in different publicly funded research projects with a focus on applications in the textile and paper industries. Plasma surface modification has increased interest in recent years, because atmospheric non-thermal plasma processing makes it possible to develop new dry surface modification methods based on on-line processing.

Plasma surface modification is an effective way to control the surface energy and chemical properties of substrates without affecting the bulk material. Plasma-solid interactions can be divided roughly into three sub-categories [1]: (i) etching or ablation, where material is removed from the solid surface, (ii) plasma activation, where the surface may be chemically and/or physically modified by species present in the plasma, and (iii) plasma coating, where material is deposited in the form of a thin film on the surface. This work has concentrated on the latter two modification methods. One kind of atmospheric plasma activation, so-called industrial corona treatment, has already been used for decades in the paper industry for example to improve adhesion between paper and polymers in extrusion processes. However, the drawbacks of corona treatment, such as low treatment uniformity and pinholing due to a tendency to form streamers, reverse-side treatment of the substrate, and ageing effects have encouraged the development of new plasma activation equipment with better treatment controllability, greater uniformity and higher efficiency [2]. The plasma coating process yields more versatile surface energy and chemistry effects than plasma activation, but it has been traditionally performed under low-pressure conditions. The first industrial utilization of plasma coatings did not come until the late 1960s, when the microelectronic industry noted the potential of the process for circuit fabrication. Nowadays, it has been realized that atmospheric plasma coatings have advantages in various applications [2,3] by providing completely new

possibilities in material processing. Being a dry process, plasma-deposited coatings are considered more environment-friendly than conventional coatings produced by wet-chemical processes, since they produce hardly any waste or by-products and do not demand energy-consuming drying. In addition, plasma deposition enables surface modification with a nano-scale thin coating, without altering desired bulk material properties. Therefore, the development of the atmospheric plasma deposition processes has been very active in recent years.

In the present work, the effects of plasma surface modification on paper surface properties and sheet-fed offset printability have been investigated. Offset technology has spread markedly since 1970 and it is today the major printing technology [4]. Typical products in sheet-fed offset printing are high quality products with a wide range of print volumes, such as catalogues, books, and magazines. The increased speed of sheet-fed offset presses demands a fundamental understanding of ink-paper interactions to enable an optimisation of quality and runnability [5]. Extensive research has been conducted to study the impact of the surface properties of coated paper, such as uniformity, smoothness and porosity, on printability. It is commonly believed that a high nip pressure during printing and a high viscosity of the offset ink decrease the influence of the surface chemistry [6], which may be a reason why the role of the surface chemistry is not fully understood today. In fact, surface analytical methods are quite new tools in the paper and printing industries [7]. In the beginning of this work, there were no specific commercial reasons for using plasma surface modification on coated grades. However, plasma surface modification made it possible to study the impact of surface chemistry alone on offset printability, which has been challenging since changes in coating component properties usually lead to changes in the coating structure. Since the porous structure of a pigment coating controls both the ink setting and optical properties, surface chemical changes created by plasma modification have a potential to decouple these two effects and to allow a better optimization of them both.

The aim of this work was to understand the effects of plasma surface modification on paper properties, and how it influences sheet-fed offset printability. In addition, the objective was to broaden the fundamental understanding of the role of surface chemistry in offset printing, particularly on ink-coating interactions. The influence of atmospheric plasma activation on different types of coated paper and its impact on ink setting and print quality were investigated. Experimental pilot-scale plasma equipment was compared to conventional corona treatment, and the impact of excessive plasma activation was demonstrated with laboratory-scale plasma equipment. With plasma coatings, two separate case studies were investigated. In the first study, hydrophobic plasma coatings were evaluated to reduce the absorption of dampening water into pigment-coated paper, and its influence on print quality was studied. In the second study, the aim was to understand the role surface chemistry on UV-varnish absorption into a highly permeable and porous pigment-coated paper. In addition, the stability of the plasma modification on paper was investigated.

2. INTERACTIONS BETWEEN OFFSET INK AND PIGMENT-COATED PAPER

This chapter contains basic background information about the offset printing process and describes typical paper, ink and dampening water used. In the second part of this chapter, ink-paper interactions, including ink transfer, setting and final drying, are discussed.

2.1 Offset Printing Process

Offset is an indirect lithographic printing method, where the printing area is first created on a printing plate, then transferred to a rubber blanket, and finally transferred from the blanket to the printing substrate (Figure 1). The printing plate consists of oleophilic-hydrophobic image areas and hydrophilic-oleophobic non-image areas in the same plane. First, a dampening solution is applied to the plate as a thin film, and then an oil-based ink. The dampening water functions as a weak boundary layer preventing the ink from adhering to the non-image areas. When ink is applied, splitting occurs in the dampening water layer in the non-image areas due to the lower cohesion forces in water than in ink. In the image areas, where the water cannot form a complete film, the ink is able to adhere due to strong chemical affinity, and the splitting occurs in the ink phase leaving an ink layer on the plate. A detailed review about the ink transfer mechanism in offset lithography is given by Shen et al [8].

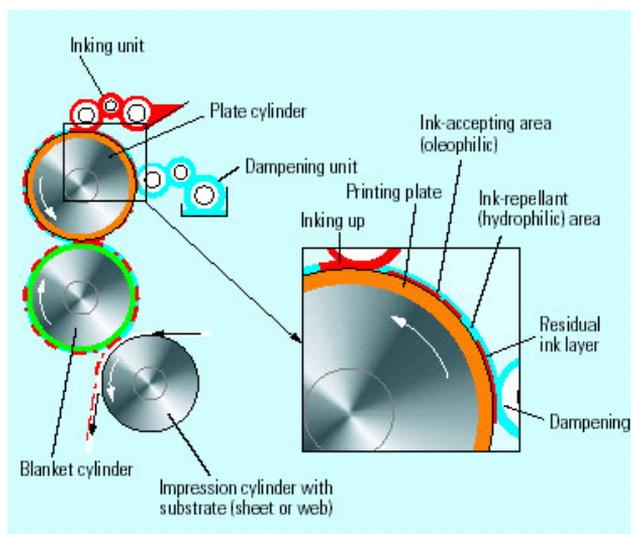


Figure 1. Schematic illustration of offset printing [4].

In sheet-fed offset printing, ink-paper interactions include phenomena such as ink transfer from the blanket to the paper, ink setting, i.e. ink component absorption and thickening of the ink film and final drying through polymerization. These interactions play an important role in print production, since they influence both print quality and press runnability [5]. The amount of ink transferred to a coated paper surface has been found to be the key factor that determines the final print density; one of the most important criteria in the evaluation of print quality [9]. Many printing problems are also related to ink-paper interactions. For example, piling (i.e., deposits on the blanket) or low print gloss may be a result of a too fast ink setting. In addition,

too fast a tack build-up in the ink film, combined with low surface strength of the paper may cause picking, where small particles from the paper surface are pulled off and cause light areas in the print. If the ink setting and drying are too slow, problems such as smearing and scuffing can occur [10]. Non-uniform print appearance, i.e., mottling is also related to problems in ink-paper-water interactions. Back-trap mottling (BTM) is found in the multicolor process. In normal press operations, a printed ink layer will trap back onto the blanket in subsequent printing. If the back-trapping is non-uniform, it causes non-uniform ink coverage, and thus back-trap mottling. A non-uniform binder distribution on the paper surface or a non-uniform pore distribution have been suggested to be the main reasons for BTM [11]. Water interference mottling (WIM) is often related to non-uniform or poor dampening water absorption [6]. Non-absorbed dampening water from a previous printing unit may prevent ink transfer. It has been also shown that a surface which has absorbed dampening water is less favorable for the spreading and adhesion of oil-based inks [12].

2.2 Paper, Ink and Dampening Water

Paper

The primary paper requirement in offset printing is a smooth surface, which has a sufficiently high surface strength to bear a high nip pressure and tacky ink. In addition, suitable absorption properties are important, because ink dries partly through ink oil absorption and the paper should be able to absorb some water. Sheet-fed offset printing is widely used for high quality production, and coated fine paper and board are therefore the most typical substrates, although uncoated grades are also used. Coated fine papers have typically a base paper of wood-free pulp filled with mineral pigment. The coat weight is normally from 12–15 g/m² to 35–40 g/m² per side. Silk-coated fine papers are calendered in a soft nip, whereas gloss-coated papers are calendered with hard nips [5].

The main components in a pigment coating are the mineral pigment and a polymer binder. The most commonly used pigments are calcium carbonate and kaolin, while talc and calcium sulphate are also utilized. To achieve good runnability at a high solid content, dispersants such as sodium polyacrylate are used. The standard coating colour formulation for graphic papers is 70–100 parts of calcium carbonate and up to 30 parts of clay, 10–12 parts of latex binder, 0.5–1 part thickener, and other additives such as biocides, optical brightening agents, lubricants and surfactants [5]. As a result of the various components of the coating color, the coated paper surface is chemically heterogeneous, and the top surface consists mainly of dispersants covering the pigment and latex particles and other surface active chemicals, rather than the particles themselves.

The coating color provides a smooth, porous layer on the paper, which enhances its optical properties and its compatibility in printing. The coating layer is characterized by its pore volume, pore size distribution, pore shape and tortuosity. The pores in the coating layer are typically 0.02–1 µm in size with different shapes and connectivities. A typical pore volume of a pigment coating is 10–30 % [13]. The pore structure is known to be one of the main factors influencing the ink-paper interactions [5], and it can be controlled by the coating formulation and calendering.

Ink

Offset inks are highly viscous (dynamic viscosity 40–100 Pas) multi-phase dispersions. The ink has to be structured in such way that it has suitable ink flow properties for the inking unit

and for ink transfer. The ink should be able to hold a certain portion of the dampening water, and form a solid ink film (0.5–1.5 μm) on the substrate [4]. The sheet-fed offset ink consists of colorant, resins, ink oils and additives such as catalytic dryers, antioxidants and wax particles [5]. The typical colorant is an organic pigment with a particle size of 0.01–0.5 μm . In addition to providing color for the ink, the pigments have to possess suitable strength, rheology and dispersibility properties [14]. The resins, such as alkyd and hard resins, bind the ink pigments together and to the paper surface. They also influence the rheology of the ink, and affect the gloss and strength properties of the final print [14,15]. The ink oils can be classified into mineral and vegetable oils. The mineral oil is a mixture of hydrocarbons from petroleum distillates, whereas vegetable oils are typically glycerides or triglycerides of fatty acids [5,13]. The hydrocarbon mineral oils are non-polar liquids, whereas vegetable oils are typically referred to as being slightly polar [15]. The trend has been to increase the use of environment-friendly vegetable oils. Based on their ability to solidify through oxygen-induced polymerization during drying, the vegetable oils can be classified as drying, semi-drying and non-drying oils. The drying oils polymerize at room temperature, semi-drying oils require heat, and non-drying oils do not polymerize at all. The most common vegetable oil used in offset inks, linseed oil, is a triglyceride containing linolenic and linoleic acids, and it is referred to as a drying oil [14,16].

Dampening Water

Dampening water, also known as fountain solution, is used to help to separate image and non-image areas on the offset printing plate, and to cleanse ink and other contaminants on the non-image areas during printing. Typically, the dampening water consists of water, iso-propyl alcohol (IPA, ~ 10 parts), and additives such as surfactants. The IPA is used to decrease the surface tension of water, but it also increases the viscosity. Typical surface tension of dampening water is between 30–50 mN/m [14]. The pH and hardness of the solution is usually adjusted to between 4.8–5.5 and 8–12° dH, respectively [4]. Since the trend has been to expand the use of environment-friendly materials, the replacement of IPA by surfactants has become common, especially in presses in the United States.

In the printing process, a significant fraction of the added dampening water evaporates by heat from various rollers and printing plates. A portion of the dampening water is transferred to the paper, while the rest is emulsified into the ink [17]. The dampening water thus plays a crucial role in ink-paper interactions. The transfer of water 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 so that, after a four-colour press, the amount of water can be as much as 0.8–1.6 g/m^2 [6]. It is also known that the ink may contain high levels (15–30%) of emulsified water during the printing operation [6], and this penetrates into the paper due to de-emulsification under the influence of nip pressure [18].

2.3 Ink Transfer

During ink transfer, when the ink and paper meet under the influence of a high nip pressure, the nip dwell time is approximately 1–2 ms [4,6]. During this time, part of the ink layer is immobilized on the paper surface and the ink layer splits between the blanket and the paper. When the ink emerges from the nip, a sudden decrease in the pressure and tensile forces on the ink film due to receding cylinders results in cavitation [19]. The cavitation bubbles expand and form ink filaments (Figure 2), and the leveling tendency of the filaments has a crucial impact on the print gloss [5]. Gloss dynamic investigations have shown that fast ink setting leads to a rapid increase in ink viscosity, which opposes the leveling and formation of a smooth ink surface. Therefore, fast ink setting typically results in slow leveling and low print gloss [16].

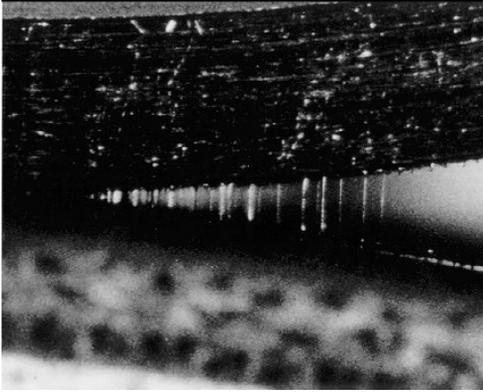


Figure 2. Formation of ink filaments in ink transfer [6].

The Walker-Fetsko equation (Equation 1) or its modifications are the most commonly-used ink transfer model [6, 20, 21]. It considers the ink transfer in three steps: In the first step, plate and paper come into *contact*, in the second, ink is *immobilized* on the paper surface and in the third, *free ink film splitting* occurs.

$$y = \underbrace{(1 - e^{-kx})}_{\text{Contact}} \underbrace{\left(b(1 - e^{-x/b}) \right)}_{\text{Immobilization}} + \underbrace{\left[f_{\infty} + (0.5 - f_{\infty})e^{-2f_{\infty}x} \right]}_{\text{Free ink film split}} \underbrace{\left[x - b(1 - e^{-x/b}) \right]}_{\text{Immobilization}} \quad (1)$$

In this equation, y is the ink transferred to the paper, x the ink on the printing plate, k the contact parameter related to the paper smoothness, b the immobilization parameter related to paper porosity and f_{∞} the limiting value of the splitting [6]. Walker and Fetsko [22] studied the influence of pressure and press speed on these parameters, and found that k and b increased with increasing pressure, and decreased with increasing press speed. The f_{∞} parameter decreased as the printing speed was increased and as the amount of immobilized ink (b) increased, but remained unchanged when the pressure was increased.

Ink tack and rheological properties are also important factors influencing the ink transfer [6]. Tack in the nip increases with increasing ink film thickness. With the same initial amount of ink in the nip, the tack is known to depend on the paper. In multi-color printing, the ink tack is critical to the transfer of ink layer onto the fresh ink layers already on the paper and also to ink setting. The tack of the freshly printed ink film has to be greater than the tack of the ink in the subsequent printing unit. Recent studies have demonstrated the importance of ink-paper interactions and the ink setting rate in determining the amount of ink transferred to the paper, especially in multi-color printing [23]. Xiang and Bousfield [23] found that a paper with a faster ink setting rate yields a higher print density than a paper with slower ink setting rate. In addition, a non-uniform ink setting rate on the surface was found to create a non-uniform ink film in multi-color printing because of back-trapping in the subsequent printing nips. These authors suggested a new ink transfer model for multi-color printing, where the final ink amount on the surface depends not only on the amount of ink on the plate but also on the ink-paper interactions and ink setting rate.

The ink transfer phenomenon has also been investigated from a thermodynamic wetting and adhesion point of view. The ink transfer has been predicted by comparing the work of adhesion

between the ink and printing plate image area, and the work of cohesion of the printing fluids [24, 25]. Thermodynamic approaches have been criticized because they are valid only under equilibrium conditions, and may offer incorrect explanations of the wetting process under dynamic conditions, such as in ink transfer [25]. It has been shown that offset ink can even be transferred to Teflon, although the work of cohesion of an ink is always greater than the work of adhesion between ink and Teflon [25,26]. DeGrace and Mangin [19] compared ink transfer to non-porous polyester, polyethylene, and Teflon surfaces. They found that ink transfer was not significantly affected by the substrate despite the large differences in surface energies. However, a close examination of the printed area showed non-wetting, because the ink appeared as droplets on the surface. The ink transfer to the films of polyester and polypropylene and Teflon was explained by the pressure impact on surface energy, which suggests that the surface tension of the ink decreases dramatically under the influence of nip pressure so that it matches that of the low surface energy substrates [25, 26]. Liu and Shen [25] continued to investigate ink transfer to Teflon, and found that it was insensitive to pressure. Thus, they suggested a new approach, where the adhesion strength and the liquid film splitting force are used to predict the ink transfer. When the work of adhesion between Teflon and ink was divided by a typical intermolecular distance of 1 nm, an adhesion strength of 4200 N/cm² was obtained. In practical situations, the macroscopic adhesion strength might be much lower than the calculated ideal adhesion strength due to flaws and other irregularities in the surface. Even if only 10 % of the macroscopic areas were considered, the actual adhesion strength was shown to be greater than a typical ink splitting force of 6.9–13.7 N/cm².

2.4 Ink Drying

In sheet-fed offset printing, ink drying can be divided into two phases: The first is a separation of the low viscosity components from the ink film by absorption into the paper, which can be referred to as ink setting and leads to a touch-proof ink layer. The second phase is a chemical drying through polymerization [5]. Even if the ink transfer occurs in a nip under the influence of high pressure, it is known that the separation and absorption of the low viscosity fluids of the ink occur after the printing nip without any influence of the external pressure [15,27]. The time frame of ink setting is from one to ten minutes, whereas the final drying may start a long time after ink transfer, sometimes after several days. Once started, the curing is completed within a few hours [16].

Immediately after the ink transfer, the porous pigment coating starts to absorb the low viscosity components of the ink. These include the oils in the ink and emulsified dampening water. It has been shown that both alkyd and hard resins act as binders for the ink pigments and are not absorbed with the ink oils into the coating [28–30]. The drying oil (e.g. linseed oil) may also act as a binder, although most of it is absorbed into the coating [29]. Figure 3 (right) shows how the ink layer composition changes during drying. The oil penetration by capillary forces and diffusive interactions between coating binder and ink oil seem to be identified as the two major mechanisms for ink setting (Figure 3, left). The main coating layer factors contributing to the absorption are given as pore structure, pore size distribution, and surface chemistry [5,6,15]. Ink-setting rate has been shown to increase when the ratio of surface tension to viscosity for the ink oils increases [31]. The binder amount and type in the coating layer have also been shown to affect the ink-setting rate [5], and these factors will be discussed in more detail in section 2.5. Ink setting into a pigment-coated paper is a highly complex phenomenon due to its dynamic nature and simultaneously occurring chemical and physical phenomena. In addition, the heterogeneous and multi-component character of both the substrate and the ink complicate our understanding of the process. During the last two decades, extensive research

has been conducted in this area. More details about the influence of the surface chemical composition of coating and the ink are given in section 2.5, and the current theories of ink absorption into a pigment-coated paper will be presented in section 2.6.

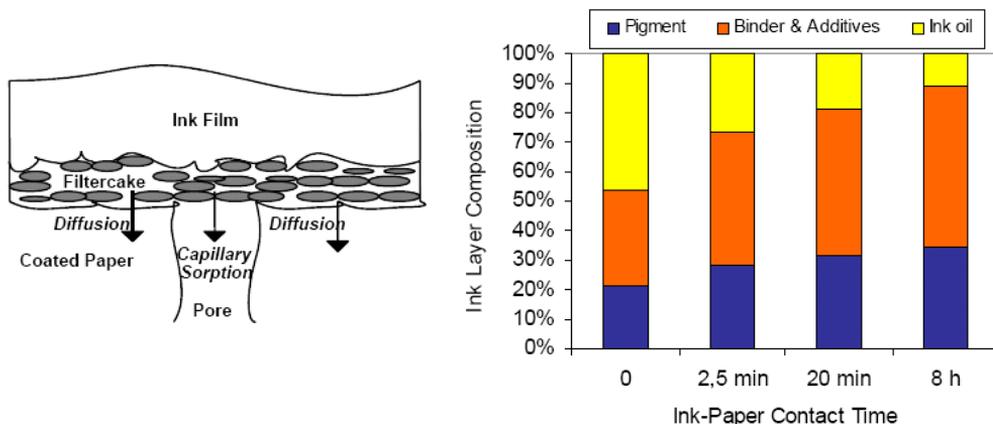


Figure 3. The figure on the left illustrates the main ink-setting mechanisms; capillary sorption and diffusive interactions, into pigment-coated paper [6]. The figure on the right illustrates the ink layer composition at different times after printing [5].

The chemical drying occurs through the oxygen-initiated polymerization of drying oils and alkyd resin. The active parts in the molecules are double bonds and methylene groups located close to the double bonds. In auto-oxidation, hydroperoxides are formed and a rearrangement of the double bonds occurs, after which the hydroperoxides decompose into a various radicals leading to the formation of cross-links [31]. Ström et al. [31,32] have shown that ink additives such as antioxidants and catalytic dryers strongly affect the time needed for chemical drying. A higher temperature and greater access to oxygen increased the drying rate, whereas an increase in the amount of absorbed water increased the time needed for chemical drying. Ström and Gustafsson [32] have also shown that paper properties may influence the time needed for chemical drying. With matt paper grades, the chemical drying was faster than in glossy grades.

2.5 Influence of Composition of Coating and Ink

Composition of Pigment Coating

The effects of substrate surface energy and chemical composition on ink setting have been investigated in several studies. However, changes in coating component properties are usually accompanied by changes in the coating structure. Therefore, it has been challenging to investigate the effects of surface chemistry alone on offset printability.

Already almost 40 years ago, Kelly et al. [33] showed that ink setting is highly influenced by the diffusive interactions between ink oils and latex. In general, it can be said that an increase in latex content results in a slower setting [34,35], but for a given latex content, increased latex-oil interactions result in faster ink setting [36]. An increase in the butadiene content in styrene-butadiene (SB) latex has been shown to increase the ink setting rate [15,35], and an increase in the polarity of the latex has been found to decrease the ink setting rate [37–41]. Van Gilder and Purfeest [37] found that a high surface energy and high polarity of the latex polymer led to significantly less interactivity with the ink, resulting in a slower rate of ink-tack build-up

and thus a greater resistance to coating pick. They studied the latex-oil interactions by determining the solubility parameter for the latex and ink oils, and found a correlation between the interaction and the ink setting. Polymer solubility is known to depend on the physical state of the polymer (linear or crosslinked), and its chemical structure (surface energy/polarity). Rousu [15] has shown that the glass transition temperature (T_g) of latex has a strong contribution to latex-oil interactions. Decreasing T_g was seen to increase the interactions. In a comparison of styrene-butadiene and styrene-acrylate (SA) latices with similar T_g , styrene-butadiene was found to be more interactive with oil than styrene-acrylate [15,39]. An increase in the degree of crosslinking (gel content) has been shown to decrease the ink setting rate [15,35].

The influence of the pigment and its dispersants has also been investigated. Sandås and Salminen [42] showed that the importance of the surface chemistry of pigments diminished with increasing external pressure. Rousu et al. [43] compared dispersed and undispersed carbonate pigments in order to evaluate the influence of surface energy on ink oil separation and wetting rate. Ink oil separation was clearly greater with the dispersed system, which had a higher polar surface energy due to the polyacrylate dispersant. Although the particle size distribution was the same, the pore size distribution differed significantly because of flocculation of the undispersed system. Therefore, the results showed not only the effect of surface energy on ink oil separation, but also the effect of the pore size distribution. Ridgway and Gane [44] compared the absorption rates of water (polar) and hexadecane (non-polar) on polyacrylate-dispersed ground calcium carbonate (GCC) pigment tablets. They found that both surface chemistry and pore structure influenced the rate of absorption: The non-polar liquid had a faster initial absorption, whereas on longer time scales the polar liquid absorbed faster. According to Heanen [45], increasing the polar fraction of the coated paper surface energy by additives reduced the sensitivity for back-trap mottling through improved adhesion between paper and ink. Miettinen and Tammi [46] have shown that by adjusting the surface energy of the pigment coating using different types of binders (e.g. carbonate-reactive latices) it was possible to influence water and oil absorption, ink setting, dot gain, printed gloss and printed unevenness in heatset offset printing.

Chemical Composition of Ink

Several studies have shown the separation of different ink components during ink setting on coated paper [15,29,30,47,48]. Ström et al. [29] showed that the initial ink oil absorption was faster with mineral oil than with vegetable oil. In addition, non-drying vegetable oils (i.e., mono-esters) were found to absorb faster than drying vegetable oils (i.e., triglycerides). Rousu [15] showed that chromatographic separation of the ink oils takes place. The vegetable oil had a lower separation tendency than the mineral oil, and the absorption of the latter into paper was also faster. This, in combination with the low viscosity of mineral oil, usually leads to a faster ink setting than with high viscosity oils, such as linseed oil. The acid-base interactions between polar vegetable oil and ink film are stronger than the dispersion forces between non-polar mineral oil and ink film. Rousu [15] showed that hydrophilic dispersed coating pigment surfaces act as sites for adsorption, thereby slowing down the absorption of polar vegetable oils and allowing the non-polar mineral oils to absorb further. Polarity is claimed to be the main property of ink contributing to oil separation, because molecular size and viscosity difference are not factors when considering species in a miscible dissolved state [49]. Higher solubility and greater compatibility of linseed oil with resins also results in an increased retention of the oil in the ink, which is an additional factor slowing down the absorption of linseed oil [50]. It has also been demonstrated that vegetable oils are more prone to oil-latex diffusion than non-polar mineral oils [15].

Most of the previous work has been conducted with undamped surfaces and dry inks, which does not correspond to the situation in a multi-colour press. Since it is well-known that a large amount of dampening water is emulsified in the ink during the process [6], its impact on ink-paper interaction has been investigated. It has been found that an increase in the amount of emulsified water lowers the tack force and accelerates the ink setting rate compared to that of pure dry ink [51, 52]. Xiang and Bousfield [51] also showed that water emulsified in ink results in lower print density and lower print gloss than printing with pure dry ink.

2.6 Current Theories of Ink Absorption

Fluid absorption into paper has been typically described by the Lucas-Washburn equation [53,54], in which the Laplace relation is incorporated into the Hagen-Poiseuille equation of laminar flow.

$$\frac{h^2}{t} = \frac{r\gamma_{LG} \cos \theta + p_E r^2}{2\eta} \quad (2)$$

where h is the depth of penetration and t is the time. The equation shows that the penetration rate increases with increasing pore radius (r), surface tension of the fluid (γ_{LG}), cosine of the contact angle between the liquid and the substrate (θ) and external pressure (p_E), and with decreasing fluid viscosity (η). Since the separation and absorption of the low viscous fluids of the ink occur after the printing nip, the external pressure gradient is zero and the capillary forces are considered to be the only driving force. The Lucas-Washburn equation assumes that all the pores are uniform and cylindrical, and that fluid continuously fills the pores in the pore network under equilibrium conditions.

Gate and Windle [55] have shown that ink oil absorption into porous coating can be described by the Lucas-Washburn equation, but that the separation of ink oil from the ink layer complicates the issue [29]. Preston [13] investigated the influence of pore structure on the rate of ink setting over a wide range of pore sizes, pore volumes and pore number densities, and found that larger pores have a faster ink setting than smaller pores when normalized on a pore number basis. Preston [13] also showed that the ink setting behavior does not follow the Lucas-Washburn equation. It has also been demonstrated that small pores result in faster ink setting due to higher capillary forces than large pores [56], which is in conflict with the Lucas-Washburn equation. These findings led to the development of new theories, especially concerning ink setting.

Xiang et al. [57,58] developed a mathematical model for ink setting based on the Lucas-Washburn equation and Darcy's law [59], in which the formation of an ink filter cake explains the faster filling of small pores. The capillary pressure is reduced by the filter cake formation, and it has been considered with the Darcy coefficient (filter cake permeability). Ström et al [29] stated that the ink oil absorption is not proportional to the square root of time, as the Lucas-Washburn equation suggests, and they proposed another mechanism based on capillary absorption counteracted by molecular diffusion due to an osmotic pressure generated in the ink film during oil separation. According to Ström et al. [29], the coating acts not only as a source of capillary pressure but also as a semipermeable membrane which separates the oil mixture from the concentrated ink film. The oil molecules have a lower chemical potential in the ink film, and this promotes a transport of the oil molecules back to the ink film. In the Lucas-Washburn equation, oil absorption is considered as continuous steady flow, whereas in real

situation, absorption proceeds stepwise with acceleration and retardation [5]. Schoelkopf et al. [60] applied the absorption model of Bosanquet [61], which suggests that the inertia exerted on a mass of fluid at each capillary entry is greater in larger capillaries, which leads to preferential filling of small pores on a short time-scale rather than the large pores. This approach suggests that large pores will be by-passed and left partially unfilled. Ma et al. [62] suggested a Gibbs free energy approach, which is directly related to capillary size and volume taking into account surface interactions but being independent of the time-dependence of these processes. They showed that the Gibbs energy correlates well with the rate of imbibition of ink as characterized by the development of ink tack. The Gibbs energy approach can also be used to distinguish the influence of surface interactions and the influence of structural properties on capillary absorption [63,64]. Rousu et al. [43] considered the aspect of multi-component transport into porous media pointing out that models derived for a single-component fluid system do not fully apply in more complicated systems like ink-coating interactions. Recently, Donigian [65] has proposed a multiphase hypothesis for initial ink-gloss development based on the assumption that ink oils and resins are distributed into different phases having differed rates of absorption.

3. PLASMA SURFACE MODIFICATION

Plasma is an ionized gas and is often referred as “the fourth state of matter” after solid, liquid and gas. When energy is introduced into a solid, the relative motion among atoms and molecules increases resulting in a transition to a liquid state and then to a gas. If we introduce still more energy into the system, some of the atoms and molecules will break apart and form equal number densities of charged sub-particles, electrons and ions [1]. Due to collisions, other reactive particles are also generated, such as radicals and excited state species. Even if the majority of the matter in the universe is in the plasma state, plasma is seen in the Earth’s atmosphere only under unusual conditions, such as lightning and the Aurora Borealis. Plasmas can be also created in the laboratory or in an industrial environment by applying a high voltage to a gas. Depending on the conditions in which the plasma is created, plasmas can be categorized into low-pressure or atmospheric plasmas, and into equilibrium thermal or non-equilibrium non-thermal (cold) plasmas. In the surface modification of an organic material, thermal plasma is not of particular interest, because the total temperature may reach 30 000–100 000 K. In the non-thermal plasma, the molecules and ions can be kept close to ambient temperature, while the electrons can be of a very high temperature, well above 20 000 K [66]. The energy of the reactive particles in the plasma is higher than or at least comparable with most of the molecule bond energies. Therefore, plasma enables surface modification at low temperatures, which would not otherwise be possible [67]. Through the choice of different plasma parameters, such as power, frequency, reactor geometry and selection of gases, it is possible to optimize the conditions for wide range of applications.

This chapter first gives an overview of the plasma-solid interactions concentrating on plasma activation and plasma coating. The second part of the chapter reviews previous studies relating to the use of these modification methods on paper substrates. The durability of plasma activation and plasma coatings is discussed in the last part of the chapter.

3.1 Plasma-Solid Interactions

Plasma-solid interactions can be roughly divided into three sub-categories [1]: (i) etching or ablation, where material is removed from the solid surface, (ii) plasma activation, where the surface may be chemically and/or physically modified by species present in the plasma, and (iii) plasma coating, where material is deposited in the form of a thin film on the surface (Figure 4). This section concentrates on plasma activation and plasma coating, because these are the modification techniques used in this thesis.

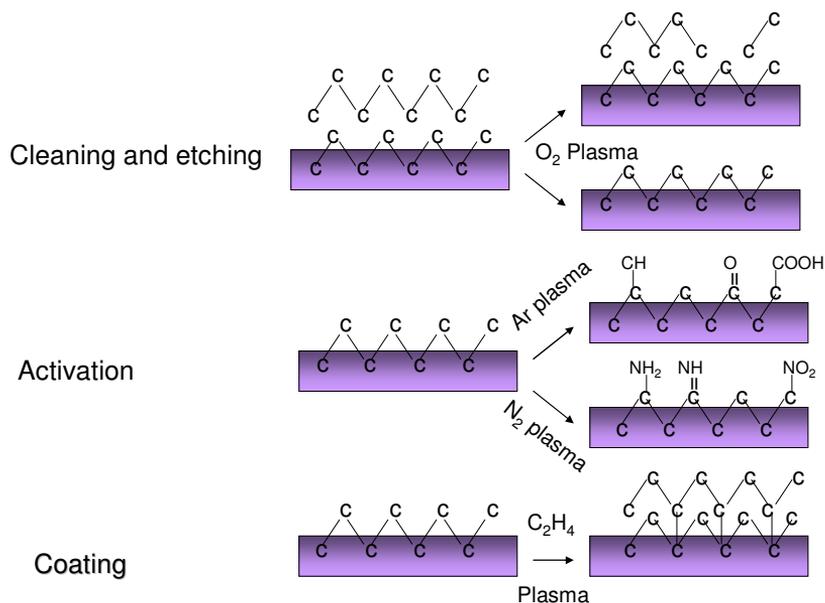


Figure 4. Examples of plasma-solid interactions including etching, activation and coating.

Plasma Activation

Atmospheric plasma activation in the form of industrial corona treatment has been utilized for many decades for the surface treatment of low surface energy plastic films and other polymer materials to improve adhesion in various applications, for instance between paper and extrusion coated polymer, electrophotographic toner and polymers [68] and water-based inks and polymers [69]. When the substrate passes through the plasma state, various chemical reactions occur due to exposure of the substrate to the reactive particles, and this increases the surface energy, and changes the chemical structure of the surface molecules [67]. It is well-known that atmospheric pressure plasma activation in air creates polar oxygen molecular groups on the surface, and thus increases the surface energy. Changes in the topography and electrostatic properties have also been reported [68].

In typical industrial corona equipment, the plasma state is generated between two metal electrodes in air, and at least one is covered with an insulating dielectric layer. The other electrode is usually a grounded metal roll, and the substrate moves between the electrodes. Although the atmospheric dielectric barrier discharges (DBD) are often marketed as corona [1,2,67,70,71], the industrial corona treatment should not be confused with a true corona source. The definition of the dielectric barrier discharge plasma is that plasma is created in the space between the two electrodes, in which at least one is covered by insulating dielectric material. A true corona is generated in a strong electric field near sharp points or fine wires [67].

Atmospheric DBD typically exhibits a filamentary mode, where the plasma is generated through a succession of microdischarges rather than homogeneously in the volume between the electrodes [2, 66,71]. At atmospheric pressure, high voltages are required for gas breakdown to ignite the plasma. Once streamers, thin ionized channels between electrodes, are formed, the current may be significantly increased to form a spark [71]. One major drawback of industrial corona treatment is its non-uniformity due to the non-uniform character of the filamentary plasma and easily occurring streamers. It has been shown that the streamers may create pin holes in the dispersion coatings lowering the barrier properties [72]. Furthermore, the reverse-

side treatment of the substrate is not desirable in every application. An additional drawback of industrial corona treatment is the ageing of the modified surface [2]. Due to these drawbacks, new types of atmospheric DBD's have been developed. The term atmospheric plasma activation or plasma treatment instead of industrial corona treatment is often used when the electrode configuration has been enhanced and treatment gases are used to produce a treatment with greater uniformity and higher efficiency [2]. In plasma activation, non-polymerizable gases can be used to achieve more uniform plasma and/or controlled chemistry on the surface. Chemically inert plasma is produced using noble gases such as helium and argon, whereas chemically reactive plasmas is produced using for example nitrogen or oxygen. Currently, extensive research has been conducted relating to DBD plasmas which can be operated in a homogeneous or so-called glow or diffusive mode avoiding streamers [67,71,73]. One example of the new type of DBD, called a diffuse coplanar surface barrier discharge (DCSBD), was developed by Czech and Slovakian university teams. It generates a thin plasma layer with a high power density, and the surface of the substrate is treated in close contact with plasma. The advantage of the DCSBD is that homogeneity of the plasma increases as a function of power, which is contrary to typical atmospheric pressure discharge sources [2,74].

Plasma Coating

Plasma modification with polymerizable starting materials makes possible thin film formation on the substrate surface. Plasma coating deposition is also referred to as plasma polymerization or more accurately as plasma (-enhanced) chemical vapour deposition (P(E)CVD). Typically, plasma coatings are operated at low pressure, but recently they have also been successfully operated under atmospheric pressure [3]. This advance will make wider applications possible, because currently plasma coatings have been used only to add value for already high-value products that can justify the costs of the vacuum and batch processing. Plasma coating also provides some advantages over conventional surface modification techniques. As a dry technology, it is regarded as being more environment-friendly than conventional wet-chemical processes, since it produces little waste or by-products and does not demand energy-consuming drying. In addition, plasma coatings enable surface modification with a nano-scale thin coating, when only very small amounts of starting material are needed [75,76].

In the plasma polymerization process, reactions between plasma species, between plasma and surface species, and between surface species occur [3]. Plasma polymerization differs from conventional polymerization, and the process does not follow the pattern of initiation, propagation and termination steps. It is typical that no repeated units are recognisable in the structure of the plasma-polymerized thin film [77]. Plasma polymer chains are typically short, randomly branched and terminated with a high degree of crosslinking [3]. Usually a free radical mechanism is considered [3]. However, the exact mechanism is still under discussion, even though the kinetics and mechanisms of plasma polymerization have been extensively studied [78]. It has been shown that the structure, composition, and physical and chemical properties of the plasma polymer are influenced by many parameters for a given starting material. Typical parameters for controlling the process are discharge frequency, discharge power, flow rate of the precursors and working gas pressure. In addition, the type of reactor and electrodes, and its geometrical configurations, substrate temperature, size and position are also known to have an influence, and therefore experiments done in different environments are rarely comparable [3]. The plasma parameters must be optimised in each case. Otherwise, it is possible, for example, ablation rather than polymerization starts to dominate the process. In addition, oily films may result, when the molecular weight of the formed polymer is relatively low. In contrast, powder or dust may form if the molecular weight is too high [67]. The plasma polymer film formed should be uniform and solid, so that it adheres to the substrate with the desired functional properties. In addition, typical films are transparent, amorphous, pinhole-

free, and cross-linked insoluble films [67,77]. However, the properties are greatly influenced by the monomer used and by the process. It is possible to form, for example, permeable [67] or hard plasma polymers [3], and a yellow tone has been reported for instance with hexafluoropropylene films [79]. The thickness of the polymerized film is limited by the internal stress caused by the bulk material [67]. It is commonly believed that plasma affects only the outermost surface [e.g. 75,80], although it has been reported for porous surfaces that plasma modification extends along the pores in the bulk material [81,82]. It has been shown that depth of the permeation of the plasma coating can be controlled by various process parameters including the choice of the starting materials [81].

Plasma coatings can be used to deposit functional layers such as hydrocarbons, hydrocarbons with polar groups, organosilicons, halocarbons (e.g. fluorocarbons) and organometallics [67]. This thesis concentrates on hydrocarbon, fluorocarbon and organosilicon plasma coatings. *Hydrocarbon plasma polymers* contain hydrogen and carbon with different structures, and, for example, ethane, methane and cyclohexane are typical gases. Starting materials can be divided into three sub-groups according to deposition rate; triple-bond-containing structures, double-bonded and/or cyclic structures and saturated monomers [77]. The hydrocarbons are the most commonly used starting material in industrial production [67], for example as protective garments, water repellent textiles, corrosion prevention, barrier coatings in biomedical systems etc. With *the fluorocarbon plasma polymers*, the starting material contains hydrocarbons with double or triple bonds or a cyclic structure, in which hydrogen atoms are replaced by fluorine. These films have been widely studied for several reasons. The fluorocarbon films produce biocompatible and hydrophobic films, which have good chemical and mechanical resistance, low friction and dielectric constant, and thermal stability [83]. With *the organosilicon plasma polymers* starting materials are typically chemically complex. The feedstock is dominated by three (H+C+Si) or more elements (e.g. H+C+Si+N), while the hydro- and fluorocarbons elements are typically formed by two pairs (H+C) and (F+C). Commonly used feed gases include various linear and cyclic siloxanes and silazanes, as well as silanes. These films can be obtained alone or in combination with the carrier gas, such as O₂, N₂, H₂, Ar and He. They are used as a coating material due to their hardness, optical transparency, adhesion and barrier properties [84]. Organosilicon thin films also have a low surface energy, and relatively large dispersion component comparing to polar component. The polar component can be increased, if highly polar NH-groups are incorporated into the structure. The successful deposition of organosilicon plasma polymers at atmospheric pressure has been reported in several studies, e.g. using tetraethyl orthosilicate, hexamethyldisilazane, and silane with N₂O or N₂ [e.g. 2,84-88].

3.2 Paper as Substrate for Plasma Modification

Plasma Activation

Only few studies have reported the atmospheric plasma activation of paper. Cernakova et al. [2] have demonstrated that a new type of DBD plasma, referred as the Diffuse Coplanar Surface Barrier Discharge, reduces the contact angle of water on paper sized with Alkyl Ketene Dimer (AKD) from 120° to less than 55°, leaving the hydrophobic properties of the reverse side of the paper unchanged (Figure 5).

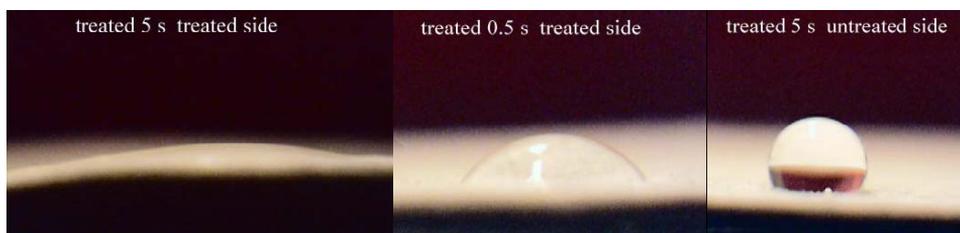


Figure 5. Wettability of hydrophobic AKD-sized paper after plasma activation [2].

Schuman et al. [72] have shown that the industrial corona and atmospheric plasma activation increases the oxygen to carbon (O/C) ratio, surface energy and polarity of a dispersion-coated paperboard surface. Industrial corona treatment was found to lead to deterioration in the barrier properties against the water, whereas plasma treatment had no influence on the barrier properties. Plasma-activated samples also had a higher O/C ratio than industrial corona treated samples. The increase in surface energy made flexographic printing with water-based inks possible. Several studies have reported the effects of low-pressure plasma activation on paper properties [76,89-94]. Carlsson [90] studied the effects of low-pressure cold plasma treatment on different types of pulp and cellulose filter paper. With cellulose filter paper, hydrogen plasma reduced the hydroxyl groups and wettability, whereas oxygen plasma oxidized the surface and increased the wettability. Deslandes et al. [91] chose nitrogen as a treatment gas for cellulose filter paper samples, since it was considered to be more efficient in achieving chemical changes and promoting adhesion than other gases (O_2 , H_2 , NH_3). It was found that N_2 -plasma treatment rendered the surface more hydrophobic and increased the amount of nitrogen-containing molecular groups. However, the increased hydrophobicity was shown to be caused by the vacuum pumping of the sample. Hua et al. [92] illustrated that both argon and oxygen low-pressure plasma activation created oxygen molecule groups on the cellulose filter paper, and the power and pressure of the treatment had a significant influence on the types of molecule group created. Denes et al. [93] investigated the effects of low-pressure oxygen plasma on unsized and sized security papers. Oxygen plasma was found to form oxygen-containing molecular groups, such as carbonyl functionalities, which led to a decrease in the water contact angle. Mahlberg et al. [94] have shown that low pressure oxygen plasma treatment may cause morphological changes on filter paper by the formation of a nodular surface structure.

Plasma Coating

Hydrocarbon, organosilicon and fluorocarbon plasma coatings have been used to introduce a hydrophobic character onto the paper surfaces. Kim et al. [76] reported the atmospheric plasma deposition of hydrocarbon (CH_4) on metallic and insulating materials, using both flat (Cu foil, Si wafer and glass slide) and rough surfaces (cotton and paper). The level of the coating hydrophobicity clearly depended on the surface roughness. With flat surfaces, contact angles were about 90° , whereas on rough surfaces, angles up to 150° were achieved. The effect of roughness on water contact angles has been a well-known since the publications of Wenzel [95] and Cassie and Baxter [96]. Tu et al. [82] used cyclohexane vacuum plasma deposition on filter paper to improve its adhesion to polypropylene film. The O/C ratio of the filter paper decreased from 0.68 to 0.08, which indicated that the hydrocarbon polymer film covered the filter paper surface. The water contact angle increased from 16° to 94° as a result of the treatment. However, the cyclohexane coating did not significantly improve the adhesion. Organosilicon plasma coatings on paper have been reported under both atmospheric and low-pressure conditions. For example, Cernakova et al. [2] deposited a layer of hexamethyldisiloxane (HMDSO) on cellulose-based filter paper under atmospheric pressure plasma in a nitrogen atmosphere. The Si-O-Si bonds introduced through such a treatment create a silicone-like

structure, and the remaining CH₃-groups induced hydrophobicity. Hänsel and Kleebau [97] also reported that organosilicon plasma deposition under atmospheric pressure generated a barrier layer on coated and uncoated paper surfaces. Organosilicon plasma coating was found to reduce water absorption. Tan et al. [98] deposited organosilicon coatings based on HMDSO on filter paper under low-pressure conditions leading to a hydrophobic surface, while maintaining its porous structure. Several articles concerning fluorocarbon plasma coatings on paper have been published [75,80,81,83,93,99]. For example, Vaswani et al. [83] used pentafluoroethane (C₂F₅H) and octafluorocyclobutane (C₄F₈) with argon as carrier gas to deposit fluorocarbon films on copy paper and a cellulose sheet to improve the barrier properties. The octafluorocyclobutane film gave higher F/C ratio and lower moisture uptake than pentafluoroethane. However, both coatings gave a highly hydrophobic character to the substrates. A thickness of 70–90 nm was sufficient to give uniform film coverage over the cellulose sheet. There has been great interest in using fluorocarbon films as a barrier layer in paper packages. The amount of fluorine is limited by the Food and Drug Administration and very thin plasma coatings may therefore enable the use of fluorochemicals. In addition, paper treated with plasma fluorochemicals can be recycled, whereas extrusion coated polymer and waxes must be separated before the recycling process [83,99]. The use of fluorocarbons has been criticized for their negative impact on the environment [100]. The long-lived perfluorocompounds (PFCs), such as SF₆, NF₃, CF₄, C₂F₆ and C₃F₈, are typically used in fluorocarbon polymerization, and they act as greenhouse gases. The contribution of the PFCs is still only a fraction of that of other pollutants, such as CO₂ and NO_x. In addition, the amounts emitted into the atmosphere due to plasma polymerization are very low compared to other sources.

3.3 Durability of Plasma Modification

Plasma Activation

It is a well-known that the surface energy decays after the treatment, and this behavior is referred as ageing or hydrophobic recovery. According to Roth [67], there are three models which may explain the ageing. The first is *the polar group attachment model*, which states that wettability changes due to plasma activation are permanent if an electrophilic atom (e.g. O or N) or molecular fragment (e.g. OH or CO) is chemically bonded to the hydrocarbon or polymer chain. According to *the polar group rotation model*, already existing polar groups may rotate on the surface by a plasma-related process. These groups may rotate back due to the thermodynamically driven tendency of the surface to lower its surface energy. However, it has been found that plasma treatment is not durable either with non-polar surfaces, such as metals. This has been explained by the third model; *the plasma cleaning model*, which states that a few monolayers of oils and other contaminants on the surface can be removed by the plasma species. Surface cleaning would be then one reason for the increase in surface energy and wettability. The decay in surface energy occurs through the contamination, which takes from hours to weeks [66]. Carlsson [90] studied the ageing of oxygen-plasma-treated pulp. The surface energy reduction was suggested to originate from the migration of the hydrophobic low molecular weight material to the surface of the fibres. Lahti [68] investigated the ageing of industrial corona-treated extrusion-coated papers over several months. The decrease in surface energy was fastest immediately after the treatment and then slowed down. The long-term surface energy level still remained higher than that of the samples without corona treatment. Guimond and Wertheimer [101] compared the ageing of air corona treatment and atmospheric nitrogen plasma activation on polymer films. The surface energy stabilized at a higher level after nitrogen plasma activation than after corona treatment. The observed ageing was suggested to result from the thermodynamically driven reorientations of polymer chains

reducing the surface energy by burying polar groups. Pykönen et al. [102] also compared the stability of air- and nitrogen-plasma activation, and found that nitrogen plasma produced a more stable surface energy change on dispersion-coated paper board than air plasma.

Plasma Coating

Plasma deposited polymers contain irregularities in the structure originating for example from impurities in the starting materials or side-reactions during polymerization. The weak bonds in these irregular polymer structures are often the starting point of the ageing process. In addition, a large number of free radicals can be trapped within the polymer network and react with oxygen and water vapor resulting in oxygen-containing molecular groups, which render the surface more hydrophilic [3].

It has been shown that plasma polymers undergo structural changes on different time scales, but, due to the complex structure of these polymers, the degradation mechanisms are difficult to investigate and it is difficult to generalize the findings [3]. The chemical structure of the starting material seems to play an important role in ageing. For example, oxygen-containing polymers are usually less stable than pure hydrocarbon polymers. The dissociation energy of the C-O bond is lower than that of most C-H bonds. In addition, the polarity of the C-O bond opens new reaction paths through acid/base reactions. For the hydrocarbon plasma coating, ageing in air can be caused by reactions with oxygen and water vapor at carbon-centered radicals. The monomer structure has been shown to influence the trapped radical concentration. The monomers with triple bonds yield the highest radical concentration, whereas radical formation was lowest with saturated monomers. The incorporation of oxygen has been shown to be very fast within the first few hours, and then to gradually slow down. The ageing of organosilicons is also highly dependent on the starting material. Gegenbauch and Griesser [103] studied the ageing of HMDSO, and found that the plasma polymer showed no measurable oxygen uptake, and that long-term storage lead to only minor structural changes. In contrast, the structure of disilazane (Si-N-Si) is known to be very unstable [104], and for example hexamethyldisilane plasma polymer appears to stabilize after 1-2 yeas resulting in a structure similar to that of HMDSO-based plasma polymers. With fluoroaromatic plasma polymers, a fast change from hydrophobic to hydrophilic character has been observed on exposure to air. This has been explained by a hydrolysis reaction, in which water molecules attack the aromatic ring in the presence of nitrogen atoms [3].

4. SURFACE CHARACTERIZATION OF PLASMA MODIFIED PAPER

A paper surface is an interface between two phases; air and solid paper. Typically, the surface is understood to be the few top most atomic layers (one atomic layer is about 2–3 Ångströms, i.e. 0.2-0.3 nm) [105]. Plasma modification is known to be very surface-specific, and thus the properties of the plasma-modified surface should be determined at least by the first few tens of nanometers of the surface [67]. This sets a high demand on the surface sensitivity of the instrument. Typical measured properties are surface energy by contact angle, surface chemical composition by spectroscopic methods, topographical and tribological properties (e.g. hardness, wear resistance and friction coefficient), chemical and mechanical resistance, and adhesion. There are a variety of suitable analysis methods for the plasma-modified paper, and function, simplicity, reliability, availability and expenses have to be considered when making a selection [105]. This chapter includes the main surface-characterization techniques used in this thesis.

4.1 Surface Chemical Characterization

Contact Angle Measurement

Since many applications of plasma surface modifications are intended to modify the wettability or adhesion properties, contact angle measurement is a useful technique for quantifying interfacial intermolecular forces. Intermolecular interactions can be divided into acid/base (polar) and Lifshitz-van der Waals forces. The Lifshitz-van der Waals forces include randomly oriented dipole-dipole (orientation) interactions described by Keesom, randomly orienting dipole-induced dipole (induction) interactions described by Debye and fluctuation dipole-induced dipole (dispersion) interactions described by London [106, 107]. The orientation and induction interactions depend on the molecules that have permanent dipole movements, but the dispersion interaction is universal and present also in atom-atom interactions. The dispersion interactions are commonly considered to be the most relevant of these three interaction types [106,107], and they are therefore often called just dispersion forces as in this thesis. The polar forces originate from permanent dipoles caused by asymmetry of molecule structure and electronegativity, and hydrogen bonding is an example of this. Since the polar interactions result in electron acceptor and electron donor interactions, they can be further divided into acid and base interactions according to Lewis acid-base theory [108,109]. By measuring the contact angles of liquids having different properties, the intermolecular interaction can be quantified. Dispersion interactions are determined using non-polar probe liquid with no acid-base properties, such as diiodomethane and α -bromonaphthalene. As a (partly) polar probe liquid, water or ethylene glycol is used. Water is a bifunctional liquid acting as both an acid and a base but, for example, chloroform (acid) and pyridine (base) act as monofunctional liquids. Acidity or basicity can also be estimated by a contact angle titration, where the pH of water is changed [108]. In practice, the surface is unwettable by the liquid if the contact angle is over 90°. On the other hand, a liquid is considered to wet a solid only if the contact angle is zero [106].

The surface energy of a solid can be determined by measuring the equilibrium contact angle, θ , which is related to interfacial forces in three-phase boundary between liquid, substrate surface and surrounding environment described by Young's equation [110]:

$$\cos \theta = \frac{\gamma_{SG} - \gamma_{SL}}{\gamma_{LG}} \quad (3)$$

where γ_{SG} is the surface energy of the solid in equilibrium with the gas (typically air), γ_{SL} the interfacial tension between solid and liquid, and γ_{LG} the surface tension of the liquid in equilibrium with the gas. Combining Young's equation with the concept of work of adhesion (W_a) described by Dupré [111], we obtain the Young-Dupré equation.

$$W_a = \gamma_{LG}(1 + \cos \theta) \quad (4)$$

Equation 4 is the basis for the development of several surface energy models, which have been reviewed by many authors [106,108,112,113]. In these models, surface energy is divided into polar and dispersion components. In some models, the polar component is further divided into acid and base components according to Lewis acid-base theory [107]. However, the division of the polar component must be viewed with some caution. For example, the theory for dividing the polar component introduced by van Oss, Chaudhury and Good has been criticized for overestimating the Lewis basicity [108].

In Young's equation, it is assumed that the substrate surface is ideally smooth, chemically homogeneous, and independent of drop volume. A rough and chemically heterogeneous paper with absorptive porous structure is far from the ideal. Both absorption and the spreading of the droplet occur simultaneously and this makes it impossible to determine the thermodynamic equilibrium contact angle for paper [114,115]. Shen et al. [116] have shown that the topographical and chemical heterogeneity of the surface lead to poor contact between liquid and sized paper. The actual interface area between water and a sized sheet is much smaller than the apparent contact area. To gain a better understanding of the effect of topographical heterogeneity on a water-repellent sized paper, they corrected the apparent contact angle values according to the equation proposed by Cassie and Baxter [96]. The work of adhesion values increased as a result of correction. Tåg et al. [117] have also shown that the surface roughness of a pigment-coated paper has a significant effect on wetting and, using the equation proposed by Wenzel [95], the work of adhesion value decreased when the contact angle was corrected for the roughness.

Despite these drawbacks, some authors have determined the surface energy for plasma-modified paper by contact angle measurements [72,93], and many of them have used only water contact angle to show wettability changes [75,76,80,81,83,98]. Since in a practical process, such as coating, the conditions are usually dynamic rather than static, the dynamic contact angles are also often measured.

XPS

X-ray Photoelectron Spectroscopy (XPS), also referred to as Electron Spectroscopy for Chemical Analysis (ESCA), is perhaps the most frequently applied technique to probe the surface chemical composition of a plasma-modified surface. XPS is based on the photoelectric effect explained by Einstein in 1905 and for which he received the Nobel Prize in 1921. The history of XPS started in 1914 when Robinson and Rawlinson published the first photoemission spectrum. Kai Siegbahn developed the theory and instrumentation of the XPS in the 1950's and 1960's, and he received the Nobel Prize in physics in 1981 [105].

The sample surface is irradiated by photons originating from a x-ray source, and the photons transfer their energy to electrons within an atom and the electrons emit the energy to the analyzer. Each element can be characterized by a specific binding energy of electrons, E_B . When the kinetic energy of the emitted photoelectrons (KE), and the energy of the x-ray ($h\nu$) are known, E_B can be determined according to:

$$E_B = h\nu - KE \quad (5)$$

The binding energy of electrons also varies according to the chemical environment. These changes in binding energy are referred to as chemical shifts, and they provide information about the chemical states of the elements [105]. In addition to qualitative and semiquantitative information about the elemental composition (except H and He) and chemical states, the XPS provides information about the chemical composition by depth, and spatially using imaging [109]. Surface sensitivity of the XPS is 5-10 nm, and the lateral resolution is 5–10 μm .

XPS has been widely used to analyze the chemical composition of plasma-modified paper [72,75,76,80-83,91–93,98]. For example, Vaswani et al. [83] used XPS to obtain the chemical composition and bonding structure of polymerized fluorocarbon films on paper. The F/C ratio of the films deposited from octafluorocyclobutane was slightly higher than that of pentafluoroethane films. High resolution C1s spectra were deconvoluted into five Gaussian peaks (CF_3 , CF_2 , CF , C-CF_x and C-C/ C-H), and the relative concentrations of these chemical groups were determined.

ToF-SIMS

In time-of-flight secondary ion mass spectroscopy (ToF-SIMS), the substrate surface is irradiated by a pulsed ion beam and, due to billiard-ball-type collisions, over 95 % of the ejected particles come from the top two atomic layers of the solid surface, as illustrated in Figure 6 [105]. The surface sensitivity of this technique is therefore very high (~1-2 nm).

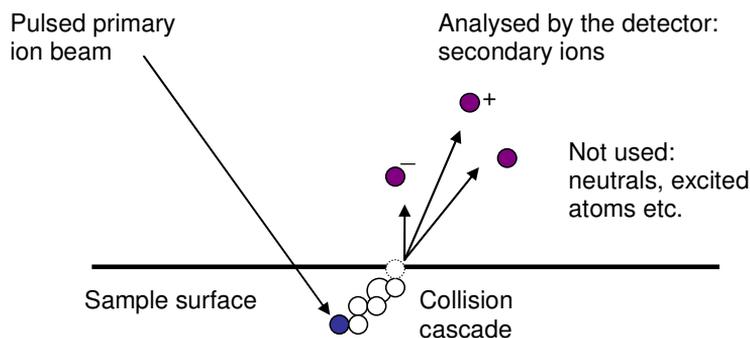


Figure 6. Sputtering process in ToF-SIMS.

The ToF-SIMS analysis is based on ejected secondary ions. The emission of secondary ions from a surface was noticed in 1910 by J.J Thompson, and the first static SIMS was developed in the early 1970's by Benninghoven. The main components of the ToF-SIMS are the primary beam, the mass spectrometer and a time-of-flight mass analyzer. The analyzer measures the flight times of all emitted ions, which depend on the length of the flight path, the mass-to-charge ratio of ions and the potential [105].

Qualitative information from all elements, isotopes and molecular fragments can be obtained from either positive or negative spectra of SIMS. In the positive spectra, only the ejected positive ions are analyzed, and in the negative spectra, only the negative ions. The ion ratios have been used for some quantification [118], but standard use of the quantitative analysis requires an even clearer understanding of the process [105]. One of the major advantages of ToF-SIMS is imaging, due its comparatively high lateral resolution (~200 nm). The

topographic and contamination effects due to high surface sensitivity are the greatest drawbacks of the ToF-SIMS, as in XPS [7].

Despite the high surface sensitivity, ToF-SIMS is not used as widely as XPS in the surface characterization of plasma-modified surfaces. Deslandes et al. [91] treated pure cellulose paper samples with vacuum plasma with nitrogen gas, and studied the surface chemical changes with XPS and ToF-SIMS. Both the instruments showed the formation of nitrogen-containing fragments on the surface. ToF-SIMS was more sensitive than XPS for detecting very subtle changes even after a very brief plasma exposure.

FTIR

Fourier Transform InfraRed (FTIR) spectroscopy is a widely used chemical analysis technique, the success of which is based on its versatility, simplicity and low cost. It is applicable to almost any surface and operates under both high- and low-pressure conditions. Infrared spectroscopy provides information about molecular vibration, and permits the identification of functional groups [114]. A molecule can absorb energy from an infrared light quantum to reach the first vibrationally excited state. Different forms of vibrations arise from different binding forces and angles of atoms in the molecule. The absorption bands are expressed in wave numbers, and the IR can detect radiation in the range of 400–4000 cm^{-1} .

Many commercial FTIR equipments are available with different accessories, including attenuated total reflection (ATR), diffuse reflectance infrared fourier transform (DRIFT), photoacoustic (PAS), transmission and reflection-absorption IR spectrometers. The challenge in FTIR techniques for plasma-modified surface is often the low surface sensitivity, which depends on the type of the equipment. For instance, in the case of ATR, the surface sensitivity is typically approximately 1 μm , which is relatively poor for the characterization of plasma-modified surfaces. The FTIR technique is however commonly used to analyze the chemical functionalities from the plasma-modified paper surface [e.g.75,80,82,92,98]. For example, Hua et al. [87] used ATR analysis for Ar- and O_2 -plasma activated cellulose samples. ATR data supported the XPS data, and showed more intense in-plane -OH vibrations, and the presence of a weak unsaturation absorption in plasma-treated samples. Sahin et al. [75] used ATR together with XPS to study chemical changes on a paper surface caused by a fluorocarbon plasma coating. ATR was used to identify the chemical linkages and to support the XPS results: CF_x functionalities were seen as a function of plasma treatment time. Kim et al. [76] used polarization modulation reflection-absorption IR spectroscopy to investigate the nature of the hydrocarbon plasma coating deposited on a clean gold substrate. The intensity of the peaks was shown to increase in proportion to the number of plasma deposition cycles.

4.2 Morphological and Structural Characterization

SEM

Scanning electron microscopy (SEM) was developed at the University of Cambridge in the early 1950s, and it has been used for many decades as a standard way to image paper surfaces and cross-sections [114,119]. The substrate surface is irradiated by an electron gun under vacuum conditions causing the ejection of secondary and back-scattered electrons. SEM provides two-dimensional black and white images of the surface [109], but with subsequent image analysis quantitative information is also available [119]. The development of the SEM technology has led to different instrument variations. For example, a field-emission SEM allows imaging in higher magnifications, and cryogenic SEM enables the imaging of freeze-dried samples [114]. SEM has been commonly used to investigate the morphology of plasma-

modified paper surfaces. Vaswani et al. [83] used SEM to study the influence of plasma-deposited fluorocarbon films on paper morphology. They saw no difference between the SEM images on plasma-coated and uncoated paper, suggesting that there was no change in surface morphology as a result of fluorocarbon film deposition. Tan et al. [98] investigated the morphological changes in an organosilicon plasma coating on filter paper using SEM. They found that the porosity of the paper was not affected by the plasma deposition.

Interaction of the primary beam with surface atoms also results in the emission of x-rays and this makes it possible to obtain information about the chemical composition through energy dispersive spectroscopy (EDS). However, EDS is not commonly used for plasma-modified surfaces due to its low surface sensitivity (1-2 μm).

AFM

Atomic force microscopy (AFM) was invented in 1986, and it is the most surface-sensitive method for visualizing the topographical features of the surface on a nanometer scale [67]. AFM is able to produce three-dimensional images of the surface and numerical roughness parameters by measuring the deflection of a laser beam in the cantilever due to forces between tip and sample surface. Sample preparation is not required, and measurements can be performed at atmospheric pressure. AFM can also provide information about surface forces and nanomechanical properties [109].

AFM has been widely used to analyze the effects of plasma modification on paper surfaces. Mahlberg et al. [94] compared the suitability of AFM and SEM for analyzing the oxygen-plasma-treated polypropylene and lignocellulosics. SEM seemed to damage the surface, and did not provide information at the nanometer level, which would make it possible to see the changes due to modification. AFM showed a nodular surface structure exposed by plasma activation. Sahin et al. [75] also used both AFM and SEM to study the topography of CF_4 plasma-coated paper. AFM analysis showed that the paper roughness increased as a result of fluorocarbon plasma deposition, whereas with SEM they had to trust a visual evaluation of the images. Navarro et al. [80] also used both AFM and SEM to study effects of fluorotrimethylsilane (FTMS) plasma polymerization on the paper morphology. AFM images showed that the microfibrillar paper surface was covered by a fine grain-type morphology of the uniform FTMS plasma coating. SEM images illustrated a smoother surface with a continuous layer of polymer-like material for plasma-coated surface compared to the untreated sample.

AFM can be also used to determine the thickness of the plasma coating [120]. A polymer mask is used to cover part of the substrate during plasma deposition, after which the height can be measured after removing the mask. However, other instruments have also been used for thickness determination, such as interferometry [Paper VI] or ellipsometry [83,76].

Mercury Porosimetry

Mercury porosimetry was developed in 1945, and it is the most common technique used to characterize the pore structure of coated paper. During the measurement, non-wetting mercury is forced by an external pressure into a porous network. The volume of the intruded mercury is measured as a function of the external pressure, and pore radius can be determined by the Laplace equation [106]. The practical range of external pressure corresponds to pore sizes between approximately 10 μm and 3 nm [15, 114]. It is known, however, that the pore structure and geometry can be altered by the external pressure, since paper is a compressible material. The other issue is that the mercury may not fill all the pores, because they are not connected to each other or some other way may not be accessible to intrusion mercury [14]. Models, such as

Pore-Comp [121], have been developed to overcome these issues by correcting the measured data.

In the literature, no previous studies exist where the influence of plasma surface modification on paper pore structure has been studied by mercury porosimetry. It is rather unlikely that plasma activation would influence the coating pore structure, but the impact of a nanometer scale thin plasma-deposited polymer coating should be considered. Mukhopadhyay et al. [81] showed by measuring surface composition and contact angle for water on five layered porous filter papers that a fluorocarbon plasma coating may extend along the pores in the bulk material. In addition, Tan et al. [98] showed by SEM images that the porous structure of a filter paper was not altered by an organosilicon plasma coating. As already mentioned in section 2.2, the pores in the pigment coating layer are typically 0.02–1 μm in size. The limitation of mercury porosimetry is approximately 3 nm, and mercury porosimetry should therefore cover the influence of plasma modification at the most relevant pore size, apart from the finest pores. Blocking of small pores on the pigment-coating surface by a plasma coating cannot be ruled out, since the volume of these would be smaller than the detection limit of mercury porosimeter.

5. EXPERIMENTAL

This chapter describes the materials, plasma modification equipment and analyses used in this work. Detailed descriptions of the materials and methods used are given in Papers I–VII.

5.1 Materials

Substrates

Both sides of the Lumiflex-paper (90 g/m², Stora Enso Oyj) were used as substrates in Papers I-III. One side of the paper had a typical commercial pigment-coating for offset printing containing calcium carbonate, kaolin and latex. The other side was surface-sized and pigmented. In Paper I, surface-sized copy paper (Berga Form Laser, 90 g/m², Stora Enso Oyj) was also amongst the substrates, and its inkjet printability was investigated in the related publication [122]. In order to gain a better understanding how plasma activation affects the various pigment coating components, four different pigment-coated papers were prepared using minipilot-scale roll-to-roll blade coater (Papers IV and V).

The pigment-coated side of the Lumiflex-paper was also used as a substrate in Paper VI. For Paper VII, a highly permeable pigment-coated paper was prepared using aragonite-shaped precipitated calcium carbonate (PCC) pigment with a narrow particle size distribution.

Inks and UV-Varnishes

In Paper III, printing was performed with a commercial sheet-fed offset ink (ArrowStar 8030 Process set, Flint Group Inc.). Model inks were prepared for Paper IV to obtain a better understanding of the effects of plasma activation on the absorption of different ink components. The model inks were manufactured at the Siegwark laboratory using different portions of slightly polar linseed and non-polar mineral oils. The amounts of the model inks were not sufficient for pilot-scale printing trials, and a commercial ink (Tempo Max Soft, Siegwark Inc.), containing the same linseed and mineral oils, was therefore also used.

In Paper VI, the same model inks and the commercial Tempo Max Soft were used for laboratory-scale printing. In the pilot-scale printing, 100 % linseed-oil-based ink Tempo Perfect (Siegwerk Inc.) was used in addition to Tempo Max Soft.

Two high-gloss UV-varnishes with different viscosities (Ultra King Overprint Varnish, Flint Group Inc.) were used in Paper VII.

5.2 Plasma Equipment

Plasma Activation

In Papers I–V, the pilot-scale experimental plasma equipment based on dielectric barrier discharges was compared to industrial corona treatment (Corona-Plus system, alternating current (AC)-excited, Vetaphone A/S). Due to the continuous development of the experimental pilot-scale plasma equipment, the treatments in Papers I-III can not be directly compared with those in Papers IV and V. By a unique electrode design, suitable power supply, impedance matching and controlled gas flow, the aim of the development was to minimize or eliminate the filamentary discharges which are typical of industrial corona treatment. Figure 7 shows the

equipments used in laboratory-scale and pilot-scale plasma activation. Figure 8 illustrates the experimental plasma equipment used in Papers IV and V. The power supply of the experimental pilot scale equipment was supplied by Vetaphone, Corona Plus System (AC-excited). A modified version of the Plasmatreat atmospheric plasma unit (rotating plasma nozzle RD1004 and plasma generator FG1002S) was used to investigate effects of excessive plasma activation. All the treatment parameters are given in Papers I–V.

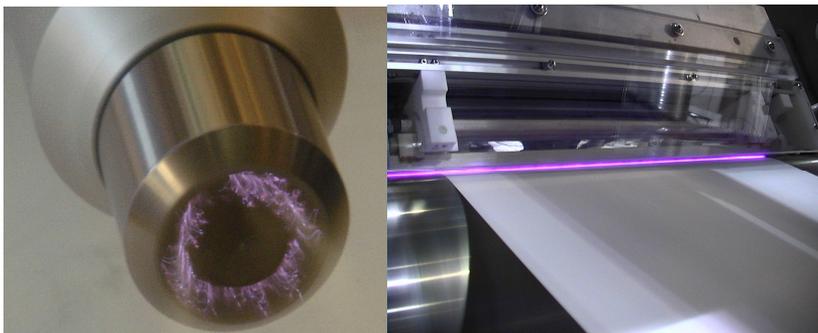


Figure 7. Laboratory-scale and pilot-scale plasma activation equipment.

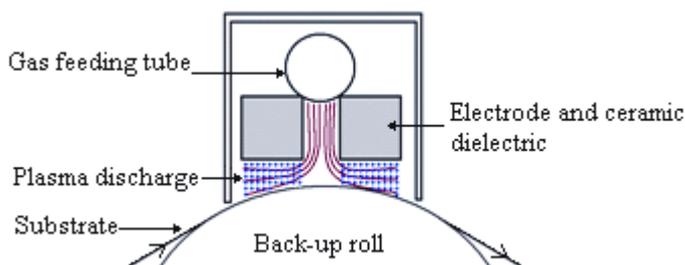


Figure 8. Illustration of the pilot-scale experimental plasma equipment used in Papers IV and V. The discharge is generated between the two dielectric electrodes and a backup roll. A treatment gas is fed between the two electrodes into a discharge, where the treatment gas breaks down due to the high voltage electric field, resulting in non-equilibrium plasma.

Plasma Coating

The in-house-constructed vacuum plasma reactor at the Institute for Surface Chemistry (YKI) was used to deposit plasma coatings in Papers VI and VII (Figure 9). Since the vacuum plasma deposition is a batch process and the maximum sample size was an A4 sheet, it was not possible to obtain sufficient material for pilot-scale printing trials with this method. Therefore, the plasma coatings for the pilot-scale printing trials in Paper VI were made with an on-line atmospheric plasma deposition installation (Figure 10). All the treatment parameters are given in Papers VI–VII.

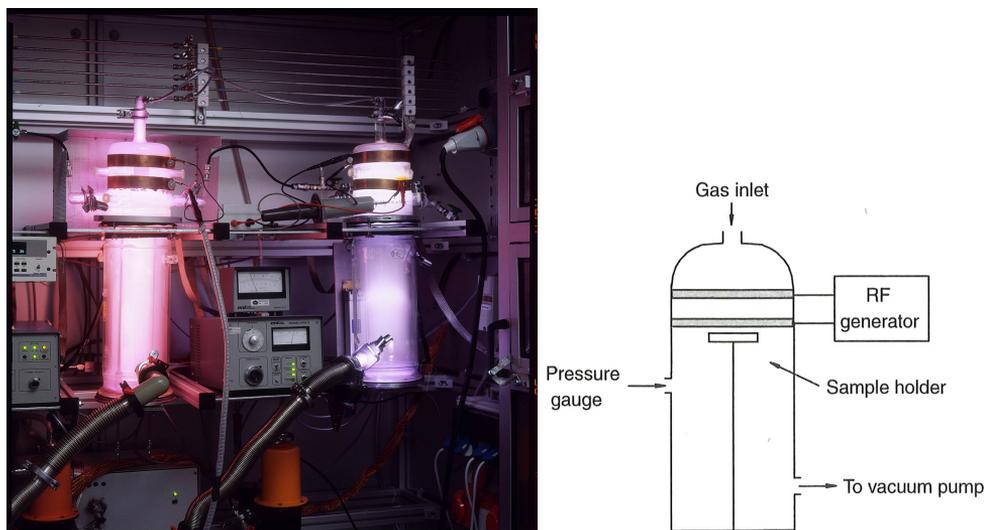


Figure 9. The laboratory-scale low-pressure plasma reactor (Institute for Surface Chemistry, YKI) contains two externally wrapped capacitively coupled copper electrode bands on a glass vessel connected to a vacuum pump. The electrodes were powered either by a low radio-frequency (125–375 kHz) or by 13.56 MHz radio-frequency power generator.

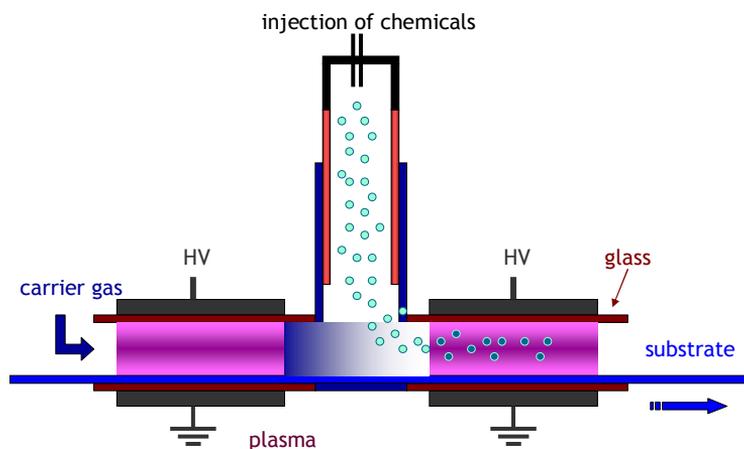


Figure 10. Illustration of the atmospheric plasma deposition equipment (PlasmaZone®, VITO Flemish Institute for Technological Research). The DBD is produced between two parallel stainless steel electrodes covered with an insulating glass plate.

5.3 Analyses

Surface Characterization

Highly surface-sensitive spectroscopic methods, XPS and ToF-SIMS, were used to examine the surface chemical composition of samples throughout the work. In addition, FTIR measurements were performed, ATR for plasma-activated samples and transmission FTIR for plasma coatings. The results were not, however, published since they did not provide any new relevant information in addition to the XPS and ToF-SIMS results. ToF-SIMS images were utilized to study the uniformity of the plasma modification (Papers I and VII), and ToF-SIMS

cross-section images were used to show the depth of penetration of the dampening water (Paper VI). The intermolecular forces and wettability were evaluated by contact angle measurements and surface energy determination (Papers I-VII). The morphological characterization was performed by AFM and SEM, and the coating pore structure was studied by mercury porosimetry.

Printability

To characterize the influence of plasma modification on the sheet-fed offset printability, both laboratory-scale and pilot-scale printing trials were performed. The laboratory-scale printing was conducted using an IGT (Papers III and IV) or ink surface interaction tester (ISIT) unit (Paper VI). The pilot-scale printing trials were conducted at Forest Pilot Center Oy (Turku, Finland) using a Heidelberg Speedmaster CD 74 (Papers III, IV, V, VI). More detailed descriptions of the printing set-ups in each case are given in Papers III, IV and VI. Print quality was evaluated through print density, print gloss and mottling measurements. Ink setting and drying were investigated by measuring print tack, set-off and rub-off. The influence of plasma surface modification on the surface strength of the paper was studied with pick tests.

In Paper VII, the UV-varnish was applied with a home-built roll-to-roll minipilot-scale printer using flexography method. The influence of changes in the surface chemical composition by plasma coating on the free wetting of UV-varnish was evaluated by contact angle measurements, and the depth of the UV-varnish absorption was investigated by measuring the gloss of the sample. A slower absorption of the UV-varnish should lead to a higher gloss due to a thicker layer of the cured UV-varnish on the surface rather than penetrated into permeable pigment coating.

6. RESULTS AND DISCUSSION

This chapter contains a summary of the main results from Papers I–VII. In section 6.1, the effects of plasma activation on paper surface properties and printability are discussed. In addition, the results relating to the durability of the plasma activation are considered. Section 6.2 describes the influence of a hydrophobic plasma coating on offset printability. The impact of surface chemistry changes created by plasma coatings on UV-varnish absorption and the stability of the plasma coatings are also discussed.

6.1 Plasma activation

In Papers I–V, the influence of plasma activation on paper surface properties and on sheet-fed offset printability was studied. Paper II concentrated on the durability of the plasma activation.

6.1.1 Influence on Paper Surface Properties

It is well-known that plasma activation increases a substrate's surface energy and wettability, as was also shown in this thesis. In Figure 11, it can be seen that the wettability increased for both polar (e.g. water) and non-polar (diiodomethane (DIM)) probe liquids, indicating that both the polar and dispersion interactions increase due to plasma activation. However, the change in contact angle was larger with the polar liquid, which can be explained by the induced polar oxygen-containing molecular groups shown by XPS (Figure 12). The reason for the increased dispersion interactions is unknown. It is possible that when the surface reactions result in the incorporation of oxygen, there is also some cleavage of the C-C bonds, e.g. in the polymer chains, and other chemical rearrangements thus increase the dispersion interactions.

In an earlier study [122], surface energy determination by the van Oss et al. [107] approach indicated an increase in base character. However, it is well-known that this approach may over-estimate the value of the base component [108]. In Paper IV, contact angle titration was used to clarify the nature of the polarity. The pH had no significant influence on the contact angle, suggesting that there are no strong acidic or basic groups on the surface.

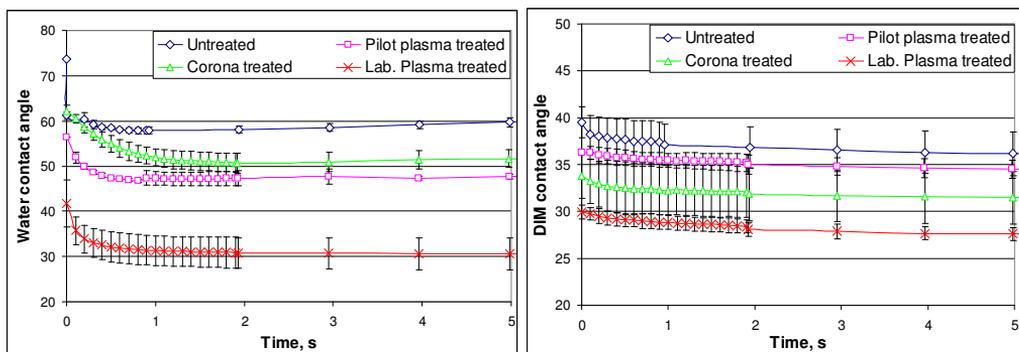


Figure 11. The change in contact angle (°) with time for a partly polar water (left) and non-polar DIM (right) on a kaolin/ GCC/ latex -containing pigment-coated paper. The error bars indicate the standard deviation minimum of four parallel measurements. These results are presented in more detail in Paper V.

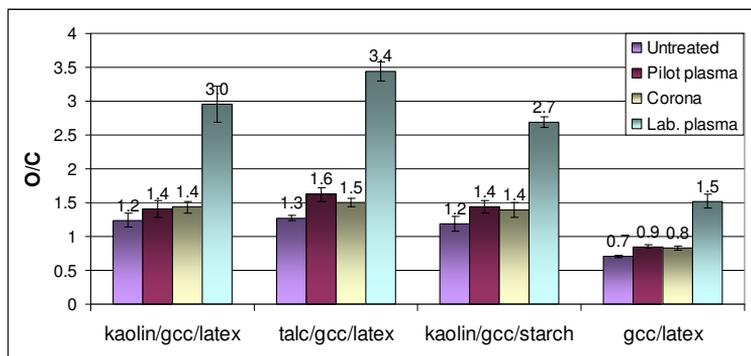


Figure 12. O/C ratio determined by XPS on untreated and plasma-activated model pigment-coated papers. The error bars indicate the standard deviation of three parallel measurements. These results are presented in more detail in Paper V.

ToF-SIMS spectra were used to provide detailed chemical information to see where the plasma activation takes place. The interpretations indicated that the plasma activation influenced especially the long-chain polymer chains on the surface of the paper, because the changes occurred mainly between 200 and 700 Daltons in the positive spectra (Papers I and V). Since the ion bombardment causes fragmentation, we were able to detect only indicative fragments of the polymers, not the whole polymer. The actual polymers have high molecular weights, which are outside the detection limit of the ToF-SIMS. In Paper V, using model pigment coatings and measuring also the spectra of the coating components, the ToF-SIMS interpretations made it possible to see that the plasma treatment influenced especially the high molecular weight dispersion chemicals of both the pigment and latex particles. However, it was not possible to identify the exact chemical nature of these chemicals from the spectra. For example, Figure 13 shows how peaks from the talc and latex spectra could be identified in the spectra of the talc, GCC and latex-containing pigment-coated paper. As a result of plasma activation, some peaks were missing or new peaks appeared in the spectrum. For instance, with kaolin, GCC and latex-containing paper, the peaks belonging to dispersed GCC were missing after the pilot-scale plasma activation. Figure 14 shows how the peaks belonging to dispersed GCC disappear from the pigment-coated paper spectra as a result of laboratory-scale plasma activation.

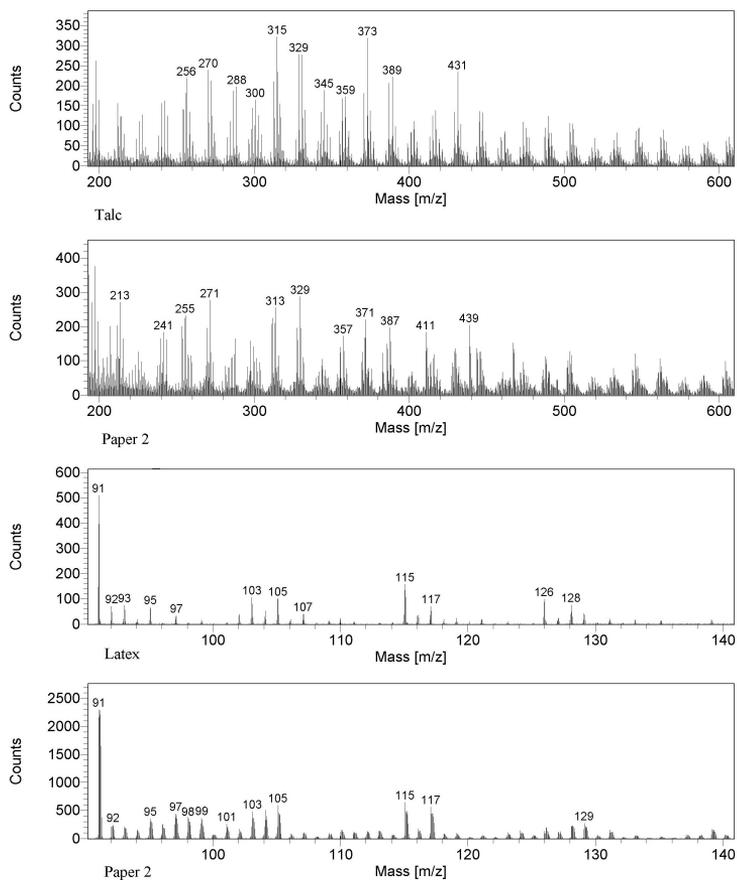


Figure 13. The ToF-SIMS spectra of dispersed talc and of talc/GCC/latex-containing pigment-coated paper (paper 2) contain similar peak groups between 200–600 Da. In addition, typical peaks of latex were found in the talc/GCC/latex-containing pigment-coated paper spectrum. These results are presented in more detail in Paper V.

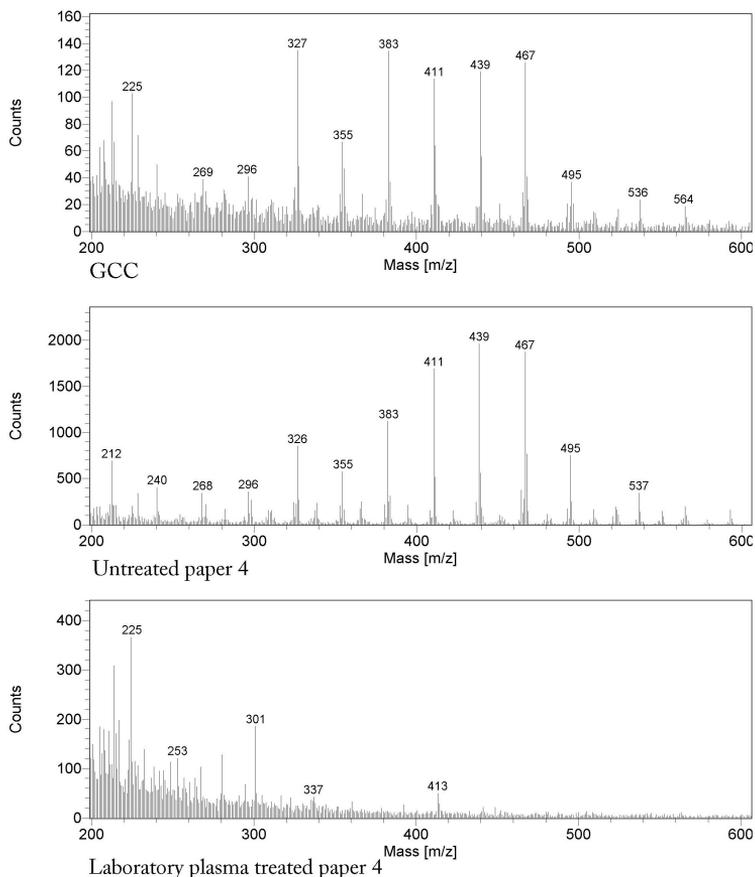


Figure 14. Spectra of dispersed GCC pigment, untreated and laboratory-plasma-treated GCC/latex-containing pigment-coated papers (paper 4). These results are presented in more detail in Paper V.

Impact of Surface Composition

The results in Paper I suggest that the chemical composition has an influence on the response of the plasma activation. For example, the increase in oxidation level was more pronounced on pigment-coated paper and surface-sized/pigmented paper than on the surface-sized copy paper. With the model pigment coatings (Paper V), it was shown how typical pigments and binders respond to plasma activation. The decrease in the contact angle of water was greater on kaolin-containing papers than on papers containing GCC or talc. In contrast, DIM contact angles decreased more on talc- or GCC-containing papers. It thus seems that on kaolin-containing papers the treatment increases the polarity more than on papers containing other pigments. The paper with 100% GCC pigment had the lowest O/C ratio after the treatments, whereas the talc-containing paper surprisingly showed the largest change in the O/C ratio (Figure 12). The addition of starch had no significant influence on the response with the pilot-scale-treated samples, but in the laboratory-scale-treated samples, the addition of starch seemed to reduce the increase in wettability and oxidation.

In our later tests, the influence of latex chemistry was investigated. Styrene-acrylate(SA)-latex- and styrene-butadiene(SB)-latex-containing pigment-coated papers and the coating components were treated with laboratory-scale plasma, and its influence was studied by contact

angle and XPS measurements. As can be seen in the Appendix A (Figures A and B), plasma treatment significantly decreased (20°) more the contact angles of water with SB-latex than was the case with the SA-latex. However, the amount of induced oxygen groups does not explain the difference, since the changes in the O/C ratio were similar for the two papers. With the GCC pigment, the increase in the O/C ratio was very small (0.05) compared to that with the latices (0.36–0.39), indicating that the modification is more pronounced on latex than on the GCC pigment.

The reason for the different responses to the plasma activation likely originates from different dispersion systems and the amount of dispersion chemicals, since the ToF-SIMS analyses indicated that plasma treatment caused changes mainly in respect to the dispersion chemicals of pigment and latex particles. For most kaolin and calcium carbonate pigments, the dispersants are based on sodium polyacrylates, but inorganic polyphosphates are sometimes also used [123]. Therefore, it is probable that the dispersant type does not solely explain the difference between kaolin and GCC pigments. Also the amount of latex on the top surface may differ according to pigment type. It is probable that the response to the plasma activation is also influenced by coating additives such as rheology modifiers and optical brighteners, but these were outside the scope of this work.

Comparison of Used Plasma Equipment

The previous installation (Papers I–III) of the experimental pilot-scale plasma equipment seemed to have slightly less impact on the surface properties than corona treatment. However, with the later installation used in Papers IV and V, the experimental plasma led to larger changes in the contact angles of water indicating a greater influence on the polar interactions, even though the power was only approximately half that of the corona. The corona treatment led to a larger change in DIM contact angle indicating a greater influence on the dispersion interactions (Figure 11). The experimental plasma and corona treatments seemed to lead to approximately the same increase in O/C ratio. The O/C ratio was also measured on the reverse side of the paper, because a reverse side treatment of the substrate is not desired in every application. The experimental plasma treatment led to a lower O/C ratio on the reverse side of the paper than corona treatment.

The intense laboratory plasma treatment led to the highest change in wettability and O/C ratio throughout the work. However, it was shown in Paper I that even if the oxidation level increased with longer treatment time with the laboratory-scale plasma, the surface energy did not continue to increase linearly. The XPS high-resolution carbon spectra showed that the longer treatment time of the laboratory-scale plasma led to a reduction both the C1 peak (C-C, C-H, C=C) and the C2 peak (C-O, C-OH, C-O-C) and increased especially the C4 peak (O-C=O), as can be seen in Figure 15. With pilot-scale treated pigment-coated papers, the C2-C4 peaks increased, although with surface-sized grades the increase was greater with C3-C4 peaks. In Paper V, the elemental ratios for the pigments (Si/C and Al/C for kaolin, Si/C and Mg/C for talc, and Ca/C for calcium carbonate) increased as a result of the laboratory-scale plasma activation, suggesting that the strong plasma treatment had exposed the pure pigment surface under the dispersion chemicals. The pilot-scale treatments did not influence the elemental ratios. In the literature [66], it has been shown that an intense atmospheric plasma treatment may be used for cleaning or etching. However, in our additional tests (Appendix A), it was shown that the Ca/C ratio increased much more in the sample containing both dispersed GCC pigment and latex than in the sample containing only dispersed GCC pigment (Figure B), which suggests that plasma activation may also expose pigment surfaces under the latex which binds the pigments together in the coating.

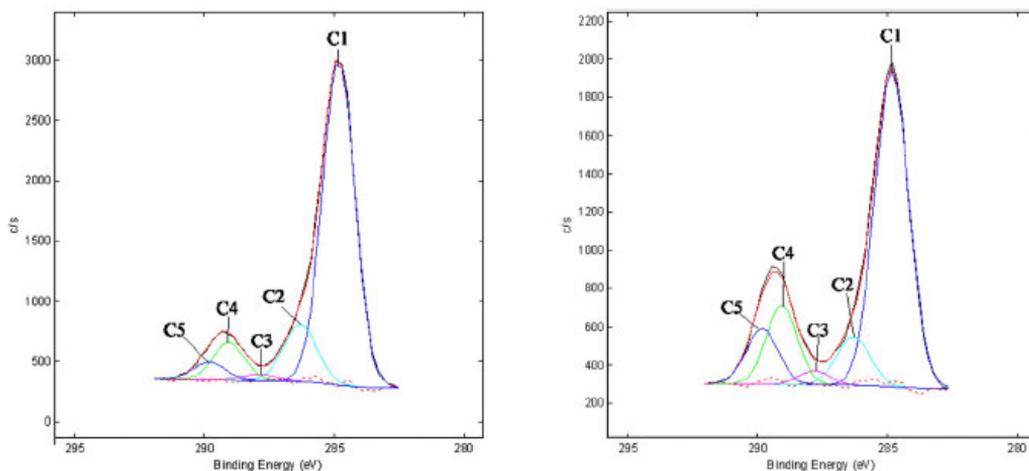


Figure 15. Examples of the XPS high resolution carbon (C1s) spectra and their deconvolution for untreated (left) and laboratory-scale plasma-treated (right) pigment-coated paper.

In Paper I, the distribution maps of CO⁺ fragments imaged by ToF-SIMS suggested that the pilot-scale treatments led to a more uneven treatment than the laboratory-scale plasma. However, this might be due to the longer treatment time with the laboratory-scale plasma, when the whole surface had time to oxidize. It should also be emphasized that ToF-SIMS provides only qualitative information. The printing results show that the laboratory-scale plasma treatment leads to an uneven treatment on the surface, which is perhaps related to morphological rather than chemical changes on the surface.

Impact on Roughness and Surface Strength

In Paper I, the influence of plasma activation on the nano-scale roughness of pigment-coated and surface-sized/pigmented papers was investigated by AFM. With the pigment-coated paper, the pilot-scale treatments led to a fairly small increase in roughness and the changes were almost within the experimental error. The change in roughness was more pronounced on the strong laboratory-scale plasma-treated samples, as can be seen in Figure 16. For the surface-sized/pigmented paper a difference between the laboratory-scale plasma-treated samples and the other samples was observed in the AFM phase contrast images. The laboratory plasma treatment induced a nodular structure between the paper pigments. These nodules were similar to those reported by Mahlberg et al. [94]. The surface roughness has been also investigated by SEM with different magnifications, but no changes have been detected as a result of plasma activation. In Papers IV and V, simple gloss measurement was used to study the effect on surface roughness. However, it is likely that the gloss measurements indicate the roughness changes on a larger scale than the AFM. The general trend was that the pilot-scale treatments, which utilized lower effective power, had no an influence on the gloss (excluding the talc-containing paper). The strong laboratory-scale plasma activation decreased the gloss of all the papers, indicating an increase in roughness as shown in Figure 17. This result was in good agreement with previous results achieved with AFM.

The impact of the plasma activation on the surface strength of the pigment coating which is an important property in offset printing was determined by a pick test (Figure 17). The results showed that the strong laboratory-scale plasma treatment decreased the surface strength, with the exception of the talc-containing paper. The surface strength results correlated well with the surface roughness evaluations performed by AFM and gloss measurements. The reason for the

reduction in surface strength is unknown, but it can be speculated that, since the laboratory-scale plasma activation seems to expose the pigments under the dispersion chemicals, this could reduce the pigment-binder interfacial bonding, or the plasma species such as radicals may cause a stiffening of the styrene-butadiene binder through cross-linking of the double bonds. In our later additional tests (Appendix A), where the influence of latex chemistry was investigated, it was shown that the latex chemistry does not affect the loss of surface strength. However, when the surface hardness and elastic modulus were measured with a nanoindentation tester (CSM Instruments) on the pure latex films treated with laboratory-scale plasma, the results suggested that some stiffening occurs with SB-latex but not with the SA-latex. The surface hardness increased and the elastic modulus decreased in the SB-latex film, whereas plasma treatment had no influence on the hardness of the SA-latex film and the elastic modulus seemed even to increase due to the treatment. The different behavior of the talc-containing paper can be due to its different dispersion system compared to the kaolin and calcium carbonate pigments.

The Young contact angle applies to an ideally smooth and homogeneous surface, which is far from a rough, porous and chemically heterogeneous paper surface. According to the Wenzel equation [95], an increase in roughness on a hydrophilic surface leads to a decrease in contact angle suggesting a higher wettability than a smooth surface. In Paper I, the surface energy was also calculated using roughness-corrected contact angle values. It was shown that the increase in roughness demonstrated a roughness-induced increase in the surface energy. The results showed, however, that the increase in the surface energy as a result of the plasma treatment cannot be explained solely by the surface roughening. Only a part of the wettability change in the strong laboratory plasma-treated samples is probably due to morphological changes in addition to chemical modification.

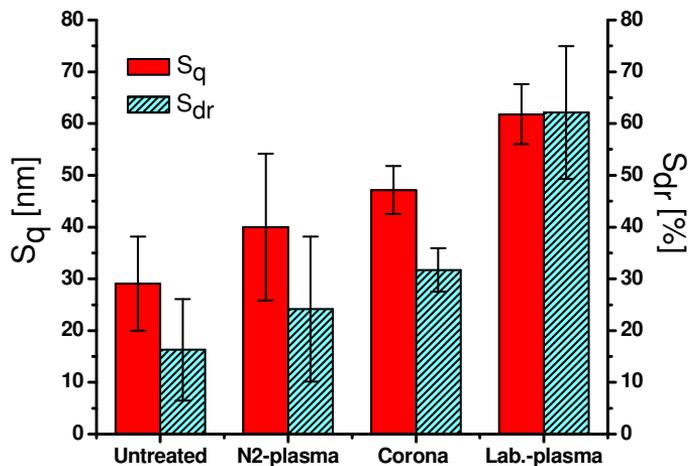


Figure 16. Root-mean-square (RMS) roughness (S_q) and surface area ratio (S_{dr}) determined by AFM for the pigment-coated paper. A measure of the percentage difference between the real surface area and the projected area is given by the S_{dr} parameter, which was used to calculate roughness-corrected contact angle values. The error bars indicate the standard deviation of the six parallel measurements. These results are presented in more detail in Paper I.

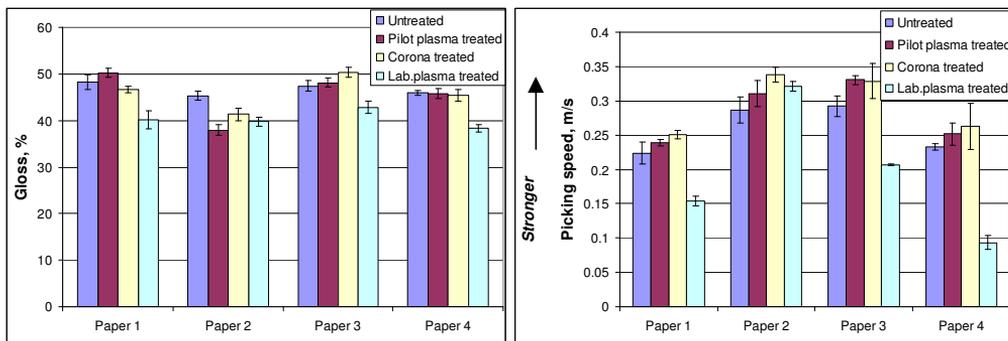


Figure 17. Gloss (75°) and surface strength of the untreated and plasma-activated model pigment-coated papers containing the following coating components: Paper 1 (kaolin/ GCC/ latex), Paper 2 (talc/ GCC/ latex), Paper 3 (kaolin/ GCC/ latex and starch) and Paper 4 (GCC/ latex). The error bars in the left-hand figure indicate the standard deviation of the five parallel measurements and in right-hand figure the minimum of three parallel measurements. These results are presented in more detail in Paper V.

6.1.2 Influence on Sheet-Fed Offset Printability

The surface characterization suggested that the pilot-scale treatment affected only the surface chemical properties, whereas the strong laboratory-scale plasma treatment also increased the roughness and decreased the surface strength of the paper. Therefore, the influence of the pilot-scale and laboratory-scale treatments on printability is presented here separately.

Pilot-Scale Plasma Activation

In Paper III, the ink tack measurements with pigment-coated paper indicated that plasma activation increased the speed of ink setting. In Paper IV, model inks with different portions of non-polar mineral and slightly polar linseed oils were prepared to achieve a better understanding of how different ink components react to surface chemistry and energy changes as created by plasma activation. The results showed that plasma activation had an influence on the ink setting, but that the response depended on the type of ink oil. The ink setting slowed down with slightly polar linseed-oil-dominated inks, and accelerated with non-polar mineral-oil-dominated inks. The influence of plasma activation on the setting of model on a kaolin/GCC/latex -containing paper is illustrated in Figure 18. A similar behavior was seen with all the model pigment-coated papers, as can be seen in Appendix B. The slower setting with linseed-oil-dominated inks is explained by the increased polar interactions between the polar molecule groups in the ink oil and plasma-treated coating, but no certain explanation of the changes with mineral-oil-based ink can be given. Since plasma treatment increases polar interactions more than the dispersion ones, it is possible that the relative portion of the dispersion interactions decreased. Therefore, the interactions of treated surface and non-polar mineral oil may have been reduced, thus allowing mineral oil to absorb faster. In previous studies [37, 39], the increased polarity of the latex has also been shown to slow down the ink setting, thus resulting in a greater resistance to coating pick. Van Gilder and Smith [38] have stated that the reduced rate of increase of the ink-splitting force with increasing latex polarity was associated with a greater resistance to both mineral and linseed oil diluents. The experimental plasma treatment seemed to have a greater influence on ink setting than corona treatment, as with the water contact angles.

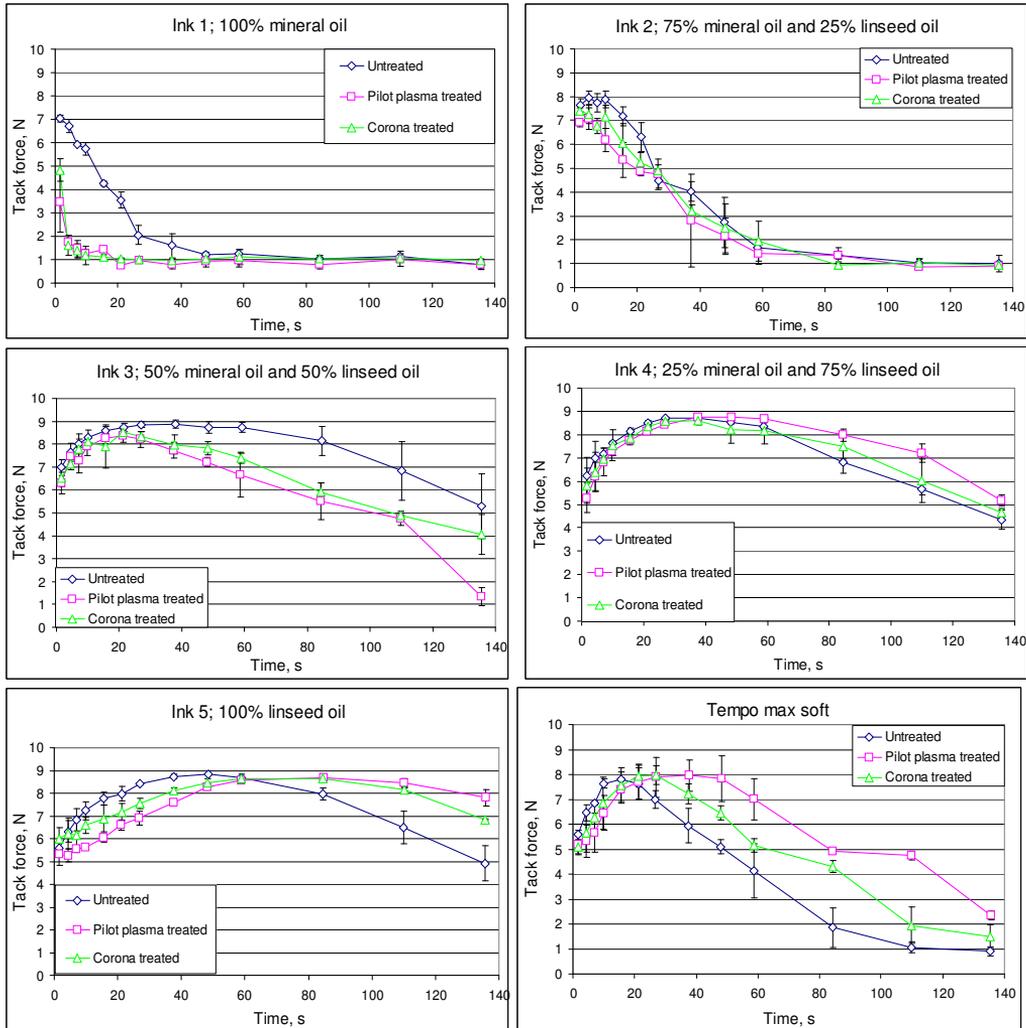


Figure 18. Influence of plasma activation on ink tack development with time on a kaolin/ GCC/ latex -containing pigment-coated paper. Measurements were performed with five different model inks and with commercial Tempo max soft –ink containing both linseed and mineral oils. Mineral and linseed oil portions for ink 1 were 100/0, for ink 2 75/25, for ink 3 50/50, for ink 4 25/75 and for ink 5 0/100. The error bars indicate the standard deviation of three parallel measurements. These results are presented in more detail in Paper IV.

In the case of the pigment-coated papers, the surface chemistry changes as a result of the pilot-scale plasma activation did not influence the offset print quality. The ink composition had a clear impact on both ink setting and print quality. The ink setting rate was slower with a higher amount of linseed oil and this resulted in a higher increased print gloss. This is in agreement with the literature [5], where it has been shown that vegetable oils reduce the ink setting rate compared to mineral oils, and that slower ink setting leads to greater ink leveling and thus higher print gloss [124].

In Paper III, a surface-sized and pigmented paper was also used as a substrate. The evaluation of the laboratory-scale printing samples suggests that the plasma treatment may have caused some ink rejection due to changed water absorption properties. Print density and print gloss

decreased and mottling increased in the pre-dampened areas, whereas no changes occurred in the areas printed without pre-dampening. Since the plasma activation increased the hydrophilicity of the surface, it was suggested that the water probably spread on the surface rather than penetrating into pores, causing ink rejection. Layer of water on paper surface reduces ink transfer on paper in the splitting event. It is still possible that also water penetration, in addition to spreading, increased due to plasma treatment. The effect of plasma activation was evaluated with contact angle measurements, which quantifies wettability including both spreading and absorption. The increased penetration would have decreased the affinity between paper and oil-based ink, which may also reduce ink transfer. It has been demonstrated previously [6] that when the surface hydrophilicity increases, spreading and absorption of oil-based ink become less favorable. However, the conclusion is that increased hydrophilicity and wettability resulted formation of water layer on paper and/or more water absorption and thus less ink was transferred to the paper. In the pilot-scale printing trials, print density was not affected, but the plasma activation decreased water interference mottle probably through more even absorption of dampening water. Both the laboratory- and pilot-scale printing showed that the plasma activation had an effect, but the impact on print quality differed. It seems that increased hydrophilicity has an indirect influence on offset print quality via changed water absorption properties. The difference between laboratory and pilot-scale results can be due to different amounts of dampening water or different process conditions. In addition, in the laboratory-scale printing pure water was used, whereas in the pilot-scale printing the dampening water contained e.g. IPA and surfactants. These additives are used to reduce surface tension of water (72.8 mN/m). Surface tension of the used dampening water was 45 mN/m. It is also generally accepted that laboratory- and pilot-scale printability tests do not always have a good agreement.

Laboratory-Scale Plasma Activation

The laboratory-scale plasma activation also had an influence on ink tack force development, but it was probably related more to roughness changes than to surface chemistry changes. The decrease in maximum tack force may be due to a reduced contact between the print and the tack disc, which occurs due to increased roughness.

The laboratory-scale plasma treatment had a significant effect on print density (Figure 19 in left), which was not seen with pilot-scale treated samples. Firstly, according to the results in Paper III, it seemed that the strong plasma treatment led to ink rejection, since the print density was lower in the spots where the treatment had the strongest influence and a visual evaluation showed no picking. In Paper V, the focused ion beam (FIB) and optical microscopy cross-section images (Figure 20) showed that the lower print density on the laboratory plasma-treated samples was probably caused by micro-picking, whereby only the top layer of the coating fails, and not the whole coating as is more commonly seen, leaving small areas unprinted. The effect of plasma treatment only on the top coating layer was not an unexpected result, because it is well-known that plasma treatment is extremely surface sensitive, as already mentioned in section 4. Nevertheless, with plasma coatings it has been shown that plasma modification may extend along the pores into the bulk material [81]. The lower surface strength results and surface roughening, shown in Figures 16 and 17, supported this conclusion and the speculation that the excessive laboratory-scale plasma activation may reduce the pigment-binder interfacial bonding due to dispersion chemical modification. The talc-containing paper suffered the least from the laboratory-scale plasma activation, when examining surface strength, roughness and print density results. This result can be explained by talc's different dispersion system compared to the kaolin and calcium carbonate pigments. Donigian et al. [125] have also reported that some printing defects that look like back-trap mottle may actually be micro-picking.

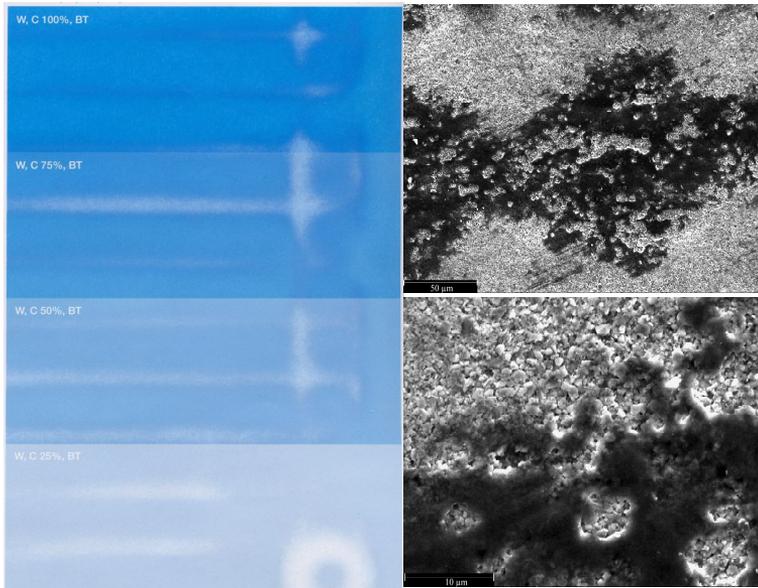


Figure 19. On the left, the print density variation on laboratory-scale plasma-treated and pilot-scale printed pigment-coated paper is shown. The SEM images on the right were taken at 500x and 3000x magnifications on the spots where the print density was decreased as a result of plasma activation. These results are presented in more detail in Paper III.

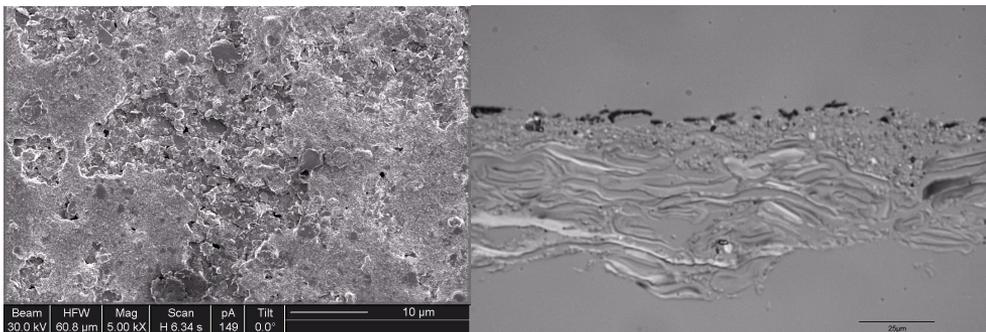


Figure 20. The FIB (left) and optical microscopy (right) images of the printed laboratory scale plasma-treated pigment-coated paper showing that micro-picking is a probable explanation of the density variation. These results are presented in more detail in Paper V.

6.1.3 Durability of the Plasma Activation

It is well-known that the effect of plasma activation on surface energy and wettability decays with time [67] as reviewed in section 3.3. In Paper II, the surface energy decay and surface chemical composition changes were studied over a period of twelve weeks with pigment-coated and surface-sized papers. As expected according to previous studies [68,90], the surface energy decayed as a function of time. With both papers, the decay in surface energy was faster during the first weeks of storage, and the surface energy then leveled off (Figure 21). After twelve weeks, the surface energy level was still higher than that of the untreated samples. The decay in surface energy was mainly due to a reduction in the polar component. However, it was found that the O/C ratio remained stable during the twelve weeks, as can be seen in Figure 22. Carlsson [90] investigated the ageing of different types of pulp after plasma activation and

observed a decrease in the O/C ratio. The initial increase in the O/C ratio due to plasma activation suggests that new polar oxygen groups are formed on the surface as a result of the treatment. According to the polar attachment model [67], these chemically bonded polar groups should cause a permanent change in wettability. However, the already existing polar groups may have rotated on the surface by a plasma-related process, increasing the surface energy. It is probable that these polar groups may rotate back with time through a thermodynamically driven reorientation, when the surface energy is reduced. A part of the decay was also suggested to be caused by re-contamination, since the active species in the plasma may remove the contaminants on the surface and thus increase the surface energy. However, re-contamination takes place with time, and this may reduce the surface energy. The surface sensitivity of the XPS is approximately 10 nm. Therefore, it is possible that the instrument does not recognize the changes occurring in the air-paper interphase as the contact angle measurement does.

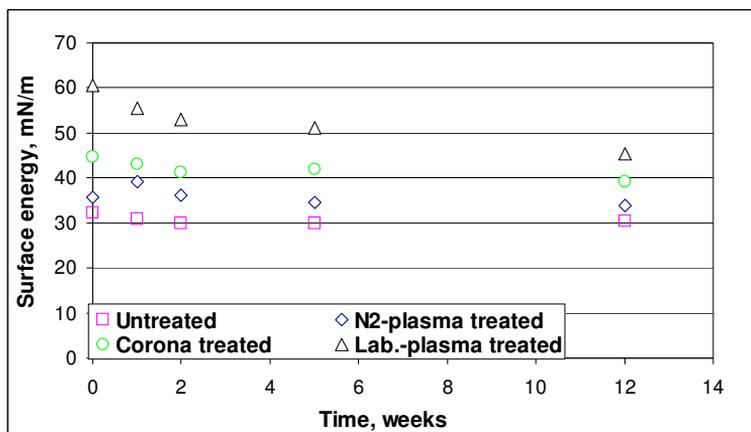


Figure 21. Surface energy of untreated and plasma-activated surface-sized paper measured over a period of twelve weeks.

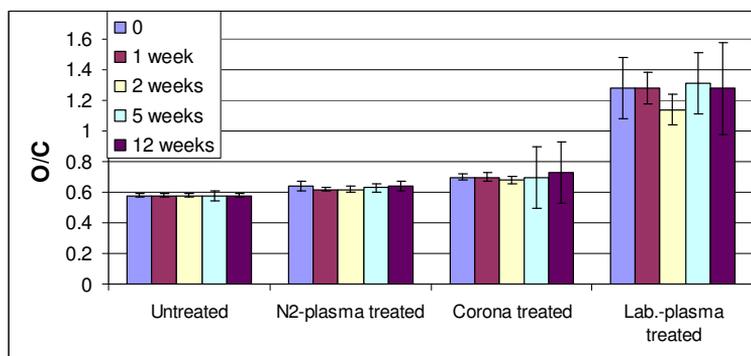


Figure 22. The O/C ratio determined by XPS for untreated and plasma-activated surface-sized paper measured during twelve weeks. The error bars indicate the standard deviation of three measurements.

6.2 Plasma coating

In Paper VI the effects of hydrophobic plasma coatings on pigment-coated paper in reducing dampening water absorption and print quality were evaluated. Paper VII focused on an investigating of the influence of plasma coatings on UV-varnish absorption into a permeable pigment-coated paper. In this section the stability of the plasma coatings is also discussed.

6.2.1 Reduced Dampening Water Absorption and Influence on Print Quality

In Paper VI, an attempt was made to reduce dampening water absorption by using hydrophobic hydrocarbon, organosilicon and fluorocarbon plasma coatings, and their impact on sheet-fed offset printability was studied. As reviewed in section 2.2, a significant amount of dampening water can penetrate into a coating or even into a base paper during the printing process, and this may cause swelling, debonding and rising of fibers, resulting in disruption of the coating layer and a roughening of the printed surface [6,126]. It has also been shown that such pigment coating structures, which retain the dampening water on the surface instead of letting it absorb into a coating layer, suffer less from a reduction in surface strength of the coated paper, thus reducing picking problems [127]. A uniform plasma coating layer could provide uniform dampening water penetration in a chemically heterogeneous paper surface and thus be beneficial in terms of reducing water interference mottling.

According to the mercury porosimetry results presented in Figure 23, the plasma coatings had only a negligible effect on the porosity of the paper. Table 1 shows that there was no change in the air permeability of the papers as a result of plasma coating. These results are in agreement with the previous research of Tan et al. [98], who stated that organosilicon plasma deposition was an efficient method for making a paper surface hydrophobic while maintaining its porous structure. This conclusion was based on surface characterization by SEM. The thicknesses of the pilot-scale deposited organosilicon and hydrocarbon plasma coatings were 50 nm and 25 nm, respectively. It seems that a thin plasma coating covers the surface, adapting the surface and pores without closing them. It is possible that the instrument used did not show the influence on the smallest pores. However, these results imply that the plasma coatings influence only the chemistry of the paper surface, and thus allow the investigation of the effects of surface chemistry alone on offset printing without inducing changes in the pore structure.

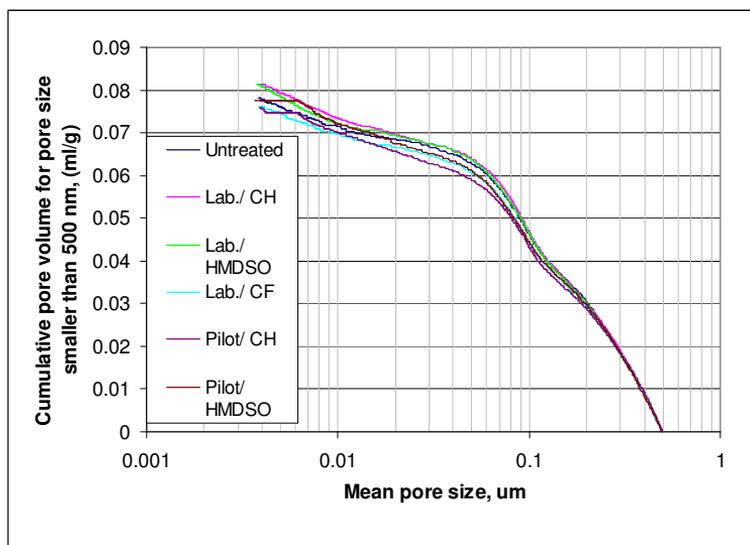


Figure 23. Pore size distribution determined by mercury porosimetry for untreated and plasma-coated samples for pore sizes smaller than 0.5 μm , which are relevant to the pigment-coating layer. The differences are within the experimental error.

Table 1. Bendtsen permeability for pilot-scale plasma-coated samples.

	Permeability, ml/min	
	Average	Std.
Untreated	4.7	0.4
CH plasma coated	4.5	0.2
HMDSO plasma coated	4.5	0.2

It is commonly believed that plasma surface modification does not alter bulk material properties [76,83]. In this work, the CIELab-values were measured to show possible changes in lightness and color of the paper due to plasma coating, and dry pick test to assess the surface strength. Table 2 shows that plasma coatings had no significant influence on the CIELab-values. Only the pilot-scale hydrocarbon plasma coating slightly increased b-value and decreased a-value changing the hue of the paper towards yellowish and greenish. However, the change in the Euclidean color difference, ΔE , is clearly below 3 units with all the samples, which is typically considered as a significant change. A ΔE of one or less is typically defined as a smallest color shift that can be visually detected. Navarro et al. [80] have also shown that fluorimethylsilane plasma coating does not influence on brightness of paper. Sufficient surface strength is one of the primary paper requirements in the offset printing process. Based on the dry pick measurements, the plasma coatings had no influence on the surface strength of the pigment-coated paper.

Table 2. CIELab-values of untreated and plasma-coated Lumiflex-paper. Measurements were performed by spectro-densitometer (SpectroDens A504017 Premium, Techkon GmbH) using absolute white as a reference.

Sample	L		a		b		ΔE Average	
	Average	Std.	Average	Std.	Average	Std.		
Untreated	95.9	0.2	-0.2	0.0	1.2	0.1	0.0	
Lab.-scale plasma-coated	CH	95.8	0.1	-0.3	0.1	1.6	0.3	0.5
	HMDSO	95.9	0.2	-0.2	0.0	1.2	0.1	0.0
	CF	95.8	0.1	-0.3	0.1	1.6	0.1	0.4
Pilot-scale plasma-coated	CH	95.7	0.2	-0.4	0.1	2.5	0.3	1.4
	HMDSO	96.1	0.1	-0.2	0.0	1.1	0.1	0.2

The surface chemical composition and changes in it created by plasma coating were determined by XPS. The laboratory-scale plasma-coated hydrocarbon, organosilicon and fluorocarbon samples had elemental ratios of 0.1 (O/C), 0.3 (Si/C) and 1.8 (F/C), respectively. Since the pilot-scale-produced plasma coatings were deposited under atmospheric pressure using nitrogen as a carrier gas, the O/C ratio increased and the coatings contained some nitrogen. In addition, the types of chemical reactions occurring in the plasma and the process parameters greatly affect the Si/O ratio. With vacuum-plasma-coated samples, the Si/C ratio was 0.3, whereas with atmospheric plasma-coated sample it increased to 0.6. Weak signals from the pigment coating were detected on the laboratory- and pilot-scale hydrocarbon and organosilicon plasma-coated surfaces, indicating that coating coverage was not complete, or that the plasma coatings were thinner than 10 nanometers, which is the escape depth of the XPS photoelectrons. The fluorocarbon plasma coating provided full coverage.

Contact angle measurements for water and ink oils were used to characterize the hydrophilicity and oleophilicity of the plasma coatings, because our assumption was that the hydrophobic-oleophilic character of the plasma coating would be beneficial in offset printing to reduce dampening water absorption (polar liquid) but still allow ink oil penetration (non-polar or slightly polar). The plasma parameters in laboratory- and pilot-scale installations were optimized to provide as high a water contact angle as possible on the paper. The contact angles for water on laboratory-scale-produced hydrocarbon, organosilicon and fluorocarbon plasma-coated samples were approximately 110°, 130° and 140° (Figure 24), respectively. The surface roughness of the pigment-coated paper together with the plasma coatings produced higher contact angles than those given in the literature e.g. for water on a flat polypropylene film (contact angle 93°) [76]. The higher amount of oxygen and nitrogen in the pilot-scale-produced plasma coatings explained the lower water contact angles. However, all the coatings can be classified as hydrophobic ($\theta > 90^\circ$). As shown in Figure 24, only the hydrocarbon plasma coating resulted in the preferred surface chemical character (hydrophobic-oleophilic) for offset printing, whereas hydrophobic-oleophobic organosilicon and fluorocarbon plasma coatings may also reduce ink oil absorption.

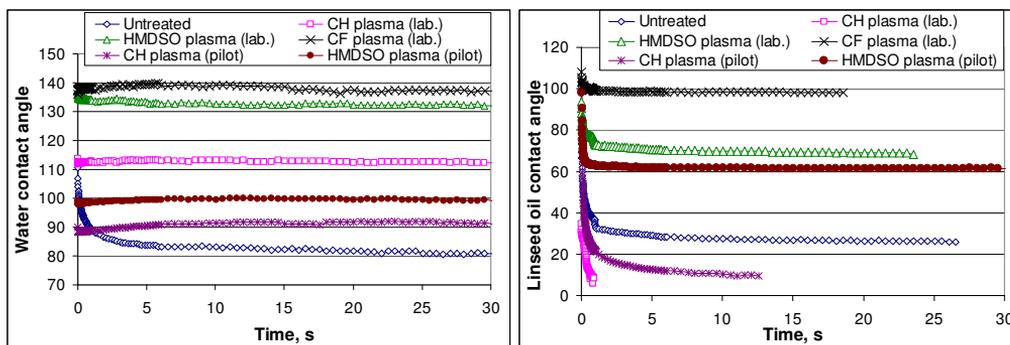


Figure 24. Change in contact angle ($^{\circ}$) with time for water (left) and linseed oil (right) on untreated and plasma-coated samples.

In Figure 25, the ToF-SIMS cross-section images illustrate the ability of the hydrophobic plasma coatings to reduce absorption of dampening water into a pigment-coated paper. Cesium was added as a trace element to enable dampening water to be detected. It is shown that the water is absorbed into the pigment coating of both the untreated and the hydrocarbon-plasma-coated samples. Some dampening water was detected on the top of the pigment coating in the organosilicon plasma-coated sample, but it did not cover the whole surface. With the pilot-scale-produced organosilicon-plasma coating, dampening water was absorbed in some areas (Figure 25F), which indicates that the coating coverage was not uniform. Cesium could not be detected in the fluorocarbon-plasma-coated sample, which indicates that no dampening water was absorbed into the pigment coating.

XPS showed the amount of cesium to a depth of approximately 10 nanometers, which seems to correlate with the hydrophobicity level: In laboratory-scale-produced samples, the relative concentration of cesium on the dampened surfaces was 0.7 at.% for untreated paper, 0.2 at.% for the hydrocarbon plasma-coated paper, less than 0.1 at.% (detection limit) for organosilicon-plasma-coated and 0 at.% (no signal) in the fluorocarbon-plasma-coated sample. In pilot-scale-produced samples, the amount of cesium was 0.9 at.% for untreated sample, 0.3 at.% for the hydrocarbon-plasma-coated sample and 0 at.% (no signal) for the organosilicon-plasma-coated sample. Although the ToF-SIMS images showed dampening water absorption into the hydrocarbon-plasma-coated sample, the XPS results suggest that a hydrocarbon-plasma coating nevertheless reduced the amount of dampening water absorbed.

SEM images showed that the hydrophobic plasma coatings cannot totally prevent the dampening water transfer onto the paper. The plasma coatings were not expected to prevent transfer under the influence of nip pressure. For example, De Grace and Mangin [23] have shown that ink is transferred to a Teflon film despite its low surface energy. However, after transfer, the ink appeared as droplets on the Teflon surface, revealing the non-wetting behaviour.

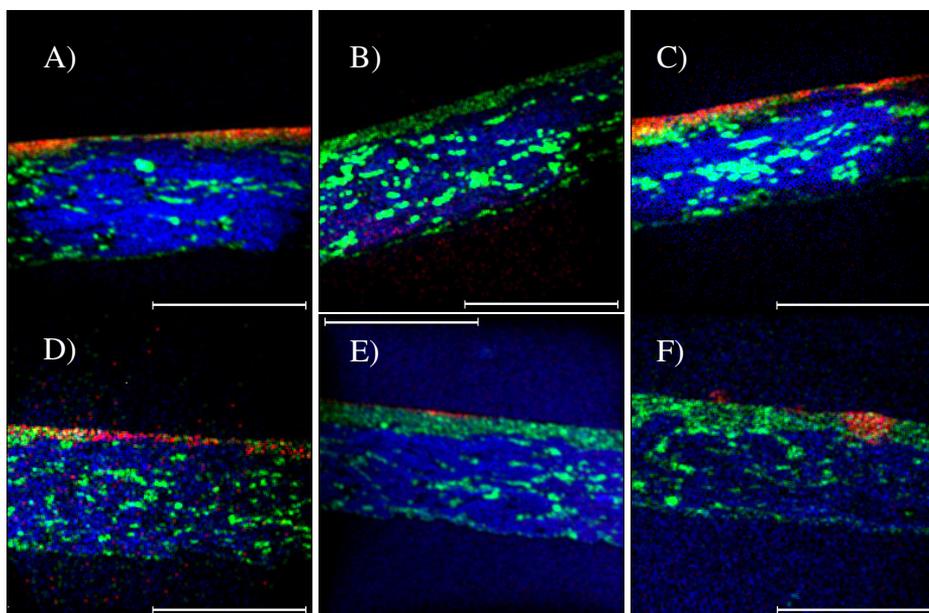


Figure 25. ToF-SIMS cross-section images ($200 \times 200 \mu\text{m}^2$) showing the level of dampening water absorption in the laboratory-scale and pilot-scale plasma-coated samples. Sample A was untreated, B laboratory-scale fluorocarbon-plasma-coated, C laboratory-scale hydrocarbon-plasma-coated, D pilot-scale hydrocarbon-plasma-coated, E laboratory-scale organosilicon-plasma-coated, and F pilot-scale organosilicon-plasma-coated. Cesium is marked with red, calcium with green, and hydrocarbons (here C_3H_7) with blue.

According to the print density results, an example shown in Figure 26, the oleophilic hydrocarbon plasma coating increased the amounts of all the inks transferred to the paper, in both the laboratory-scale and pilot-scale trials. Although the dampening water was shown to transfer to the paper surface, it is probable that it does not form a uniform film on the surface (water contact angle $> 90^\circ$), and thus more ink is transferred. Therefore, it can be said that the influence of plasma coatings on ink transfer seems to be mainly indirect, occurring through changes in dampening water absorption. As the hydrocarbon coating with a lower hydrophobicity gave a higher print density than the organosilicon and fluorocarbon coatings, it appeared that the affinity between ink and surface (oleophilicity/ oleophobicity) was also an important factor influencing the amount of transferred ink. The change in ink transfer depended on the type of ink oil in the case of the oleophobic fluorocarbon and organosilicon coatings, as can be seen in Figure 26. The amount of ink transferred was lower with mineral-oil-based inks and higher with linseed-oil-based ink. In addition to the different chemistries of the mineral and linseed oils, the ink tack increased with increasing amount of the linseed oil. This may partly explain why organosilicon and fluorocarbon samples behaved differently with mineral- and linseed-oil-based inks. As reviewed in section 2.3, tack in the nip increases with increasing ink film thickness, and, with a given initial amount of ink in the nip, the tack is known to depend on the paper. Low ink tack combined with a low affinity between ink and paper resulted a lower print density, whereas a high ink tack combined with a low affinity led to higher print density. In the case of the hydrocarbon plasma coating, greater affinity led to higher print density regardless of ink tack. One possible explanation, for why the ink transfer depended on the ink oil type in the case of the oleophobic fluorocarbon and organosilicon plasma-coated samples, could be formation of a weak boundary layer (WBL) by mineral oil. In this study it has been shown that the mineral oil has lower viscosity and it separates faster from ink film than linseed oil. Therefore, it could be possible that the oleophobic plasma-coated

samples do not absorb mineral oil fast enough, and thus the mineral oil forms a weak boundary layer on surface, which prefers the splitting in oil-rich positions.

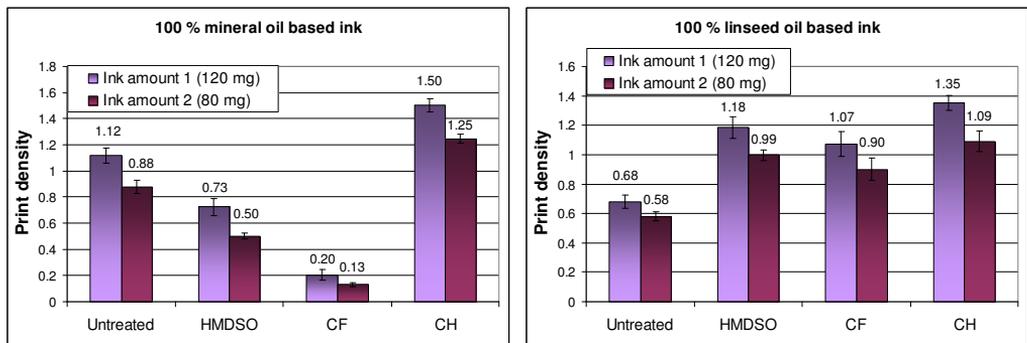


Figure 26. Influence of plasma coatings on print density on pigment-coated paper printed with model inks containing 100 parts of mineral (left) or linseed (right) oils. The printing with pre-dampening was performed with two constant ink amounts on the print cylinder with two parallel experiments for each sample. The error bars indicate the standard deviation of print density measured at ten different spots on the samples.

Using an IGT method and inks to test wet pick/ wet repellence, the printing was carried out both with and without pre-dampening. When the samples were pre-damped, the print density was higher for all the plasma-coated samples than the untreated sample (Table 3) similarly to the laboratory-scale printing when using model linseed oil-based ink (Figure 26). With the untreated sample, the pre-dampening significantly reduced the amount of ink transferred. With the plasma-coated samples, the change was clearly much less. These results support the conclusion that the influence of plasma coatings on ink transfer is mainly indirect by preventing the water from forming a film on the surface so that more ink is transferred to the paper. With highly hydrophobic organosilicon- and fluorocarbon-plasma-coated samples the pre-dampening had no significant influence on print density showing that water did not form any weak boundary layer on the surface. With the hydrocarbon-plasma coating, pre-dampening slightly decreased print density showing a small effect of WBL. Without pre-dampening, an oleophilic hydrocarbon-plasma coating gave a slightly higher print density, whereas the oleophobic organosilicon- and fluorocarbon-coatings decreased it when compared to untreated sample. In this case, the lower print density can not be explained by the formation of ink oil WBL, since we do not see this type of behavior with the pre-damped samples. Therefore, these results highlight the importance of having also chemical affinity between the ink and paper surface. The wet pick test strips are scanned in Appendix C.

Table 3. Print densities of the test samples printed with and without pre-dampening.

Sample		Print Density			
		Without pre-dampening		With pre-dampening	
		Average	Std.	Average	Std.
Laboratory-scale	Untreated	1.90	0.11	0.71	0.12
	CH plasma	1.92	0.09	1.75	0.11
	HMDSO plasma	1.64	0.13	1.66	0.15
	CF plasma	1.00	0.23	1.03	0.16
Pilot-scale	Untreated	1.86	0.01	0.68	0.03
	CH plasma	1.95	0.00	1.71	0.02
	HMDSO plasma	1.71	0.02	1.79	0.03

Visually evaluated, the laboratory-scale-produced plasma coatings provided a more uniform print appearance despite differences in the print densities observed. This indicates that the plasma coating coverage was sufficient and that the chemistry was homogeneous, resulting in a more uniform absorption of dampening water into the pigment coating. However, since the mottle evaluations should be done at similar print densities, the results should be considered with caution. With the pilot-scale-produced plasma coatings, the print uniformity seemed to decrease. This may be due to a poor water receptivity of the hydrophobic coating, which may lead to a thin water film on the surface and then prevent ink transfer in the subsequent printing station. However, this is contradicted by the fact that the hydrophobic plasma coatings gave a higher print density. The increased mottling may also indicate that the pilot-scale-produced plasma coatings were non-uniform, causing uneven dampening water absorption. The difference in mottle between the laboratory-scale and pilot-scale printing trials may be partly caused by differences in the printing conditions. For example, in the laboratory-scale printing the amount of water applied is probably higher, and the used dampening water contained only water and IPA without any additives or surfactants.

Typically, a high print density is associated with a high print gloss, since a thick ink film fills up the microstructure of the coating. However, in this work, print gloss did not correlate with print density. In the laboratory-scale trial, the print gloss was lower with linseed-oil-based inks, and higher with mineral-oil-based inks on the fluorocarbon-plasma-coated samples. The organosilicon- and hydrocarbon-plasma coatings showed no clear trends in print gloss. In the pilot-scale trial, neither the print nor the paper gloss was affected by the plasma coatings. The gloss of the paper was slightly increased by the presence of the laboratory-scale-produced plasma coatings. The gloss was 54 % on the untreated sample, 57 % on the hydrocarbon-plasma-coated sample, 59 % on the organosilicon-plasma-coated sample, and 60 % on the fluorocarbon-plasma-coated sample. It is possible that the print density and print gloss were not correlated, because the print gloss was also affected by changes in ink setting caused by the plasma coatings. It is well-known that fast ink setting reduces print gloss due to poor ink filament leveling [5].

The influence of the laboratory-scale-produced plasma coatings on ink tack development determined by ISIT also depended on the type of ink oil, as it was shown in Paper VI. However, the result interpretation was not as straightforward as usual, since the plasma coatings had such a significant influence on ink transfer. A decrease in ink transfer decreases the ink tack. Therefore, the ISIT paper-tack curves reflect not only the ink setting, but also the ink-coating adhesion. With the fluorocarbon-based plasma coating no ink tack development could be seen with any of the inks. This is probably because less ink was transferred on paper. The organosilicon plasma coating reduced the tack force, and with some inks (e.g. ink 5) ink-coating adhesion seems to be low and no tack development was achieved as was the case with the fluorocarbon-coated samples. The hydrocarbon plasma coating increased the tack force and slowed down the ink setting rate for mineral-oil-based inks. However, when the linseed-oil-based ink was used, the hydrocarbon plasma coating led to a decrease in tack force.

In Paper IV, it was shown that oxidation of pigment-coated paper by plasma activation accelerated the ink setting and decreased the tack force when the ink was mineral-oil-based, but the influence of plasma activation on ink setting was the opposite when the ink was based on linseed oil. Therefore, it seems that a hydrophilic surface accelerates ink setting and decreases the tack force when mineral-oil-based inks are used, and retards ink setting when a linseed-oil-based ink is used. In contrast, hydrophobic-oleophilic surfaces slow down ink setting and increase the ink tack force with mineral-oil-based inks and decrease the tack force with linseed-oil-based inks. Hydrophobic-oleophobic surfaces seem to decrease the tack force

with both mineral- and linseed-oil-based inks. In case of oleophobic plasma coatings the influence on ink transfer should be also considered. It should be emphasized that ink setting results from ISIT measurements cannot be directly compared to print quality results, since no pre-dampening was used in the former case.

In general, it can be concluded that an increase in the hydrophobic character of the coating leads to the absorption of less dampening water, and if the hydrophobicity is uniform it will lead to an improved print quality in terms of a higher print density and a lower print mottle. The results showed also that it is clearly possible to influence the ink-setting and printability by surface chemical changes alone.

6.2.2 UV-Varnish Absorption into Permeable Pigment-Coated Paper

In sheet-fed offset printing, the units for surface finishing, such as UV-varnishing, have become increasingly important for many print products. UV-varnishing adds value to the print by enhancing and protecting the printed product. Typical products which are varnished are the covers of magazines, annual reports, brochures, catalogues, wine labels and packages [4]. UV-curing inks and varnishes were introduced in the 1960s, and gained popularity during the 1970s [128]. Nowadays, the use of UV-technology in the printing industry is expected to expand [129]. UV-varnishes are based on acrylate chemistry consist of prepolymers, monomers and photo-initiators. The prepolymers act as a vehicle for the system and give brilliance, mechanical and chemical resistance. The monomers are used to adjust the end properties of the varnish, and they act as diluents to adjust viscosity, but also affect the surface chemistry and cross-linking. The photo-initiators are selective to light of a specific wavelength and initiate the curing. A UV-varnish absorbs photons of high energy ultraviolet light, and undergoes chemical polymerization, which converts the varnish from a liquid to a solid state [14].

In Paper VII, the aim was to understand the role of surface chemistry in the absorption of UV-varnish with highly porous and permeable pigment-coated paper. The hydrocarbon-, organosilicon- and fluorocarbon-plasma coatings were deposited on the pigment-coated paper in order to modify their surface chemical composition. Although the permeable, high porosity coatings provide excellent opacity and brightness to paper, due to high light scattering, the high permeability may lead to problems in printing related to too fast a penetration of printing liquids. For example, in the case of UV-varnishing, too fast an absorption may decrease the gloss and also result in an uneven gloss appearance [129]. In addition, uncured UV-varnish ingredients are undesirable, especially in food packaging applications, since unreacted monomers and photoinitiators may cause odor, taste, or toxicity in the end product [130].

According to the mercury porosimetry results, the plasma coatings had no measurable influence on the porous structure in the range of 3–500 nm. This is in agreement with previous studies [Paper VI, 98].

The surface chemical composition and changes in it created by plasma coatings were determined by XPS. Survey spectra for the untreated sample gave typical peaks for pigment-coated paper containing calcium carbonate and styrene-butadiene latex. The laboratory-scale-produced hydrocarbon-, organosilicon- and fluorocarbon-plasma-coated samples had elemental ratios of 0.25 (O/C), 0.3 (Si/C) and 1.73 (F/C), respectively. As in the previous study presented in section 6.2.1, for the hydrocarbon- and organosilicon- plasma-coated samples, the calcium signal indicated that the plasma coatings did not cover the whole surface, or that the plasma coatings were thinner than 10 nm, which is the escape depth of the XPS photoelectrons. With

the fluorocarbon-plasma-coated sample, no signals from the pigment coating were detected, suggesting that coating coverage was complete.

The uniformity and coverage of the plasma coatings were studied using ToF-SIMS chemical mapping of calcium which originates from the pigment coating. Figure 27 also implies that the plasma coating coverage was not complete in the cases of the hydrocarbon- and organosilicon-plasma-coated samples, but it seems that the calcium signals were evenly distributed across the surface. With the fluorocarbon sample, only a few signals from calcium could be detected.

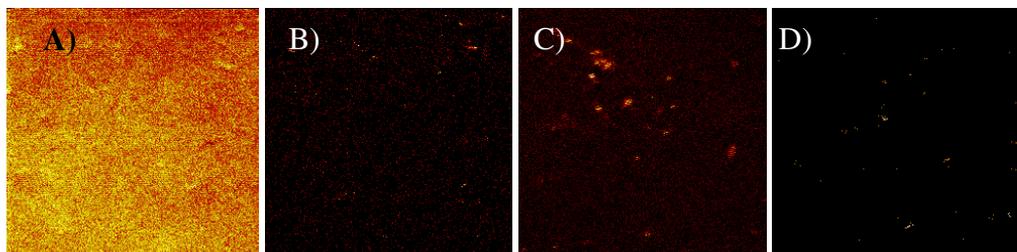


Figure 27. ToF-SIMS images; distribution (2.5 mm x 2.5 mm) of the calcium on untreated (A), hydrocarbon (B), organosilicon (C) and fluorocarbon (D) plasma-coated samples.

Contact angle measurement was used to study the impact of the plasma coatings on the wetting of UV-varnishes with two different viscosities. It should be emphasized however that the UV-varnish is typically applied under the influence of a nip pressure as forced wetting, and the results are not therefore directly comparable to the UV-varnish process. The fluorocarbon-plasma coating resulted in the greatest increase in UV-varnish contact angles, as can be seen in Figure 28. The organosilicon-plasma coating also increased the UV-varnish contact angle, but the change was much smaller. The hydrocarbon-plasma coating resulted in an unchanged or slightly reduced UV-varnish contact angle. The results indicate that the organosilicon-plasma coating had clearly more interactions with the UV-varnishes than the fluorocarbon-plasma coating, however the polar interactions cannot explain that, since fluorocarbon- and organosilicon-plasma coatings had similar water contact angles. One explanation could be the amount of hydrocarbons; the fluorocarbon plasma coating contained no any hydrocarbon groups, whereas an organosilicon-plasma coating contained at least methyl groups. UV-varnishes are based on polyacrylate chemistry, containing a hydrocarbon chain with vinyl and ester bonds. Figure 28 also shows that the high-viscosity UV-varnish gives a higher contact angle than the low viscosity UV-varnish. This is in agreement, for instance, with the surface tension to viscosity ratio and the Lucas-Washburn equation, as reviewed in section 2.6.

In addition to the contact angle, the drop volume and drop base diameter were investigated to show the influence of plasma coatings on sorption (drop volume) and spreading (drop base). The results suggest that the fluorocarbon-plasma coating reduced both the spreading and the sorption of the UV-varnish droplet.

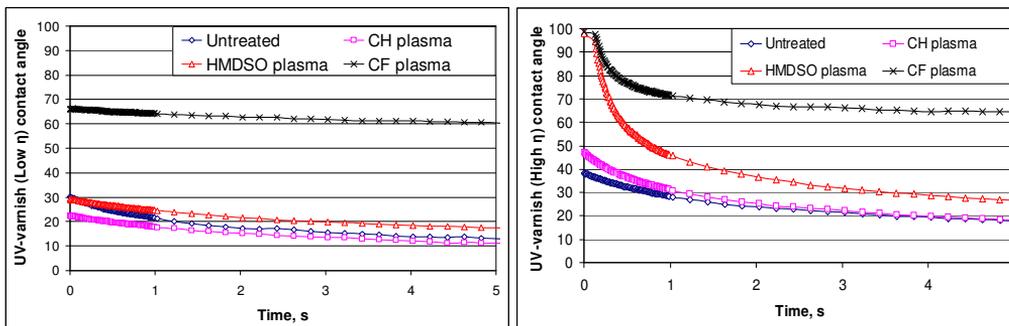


Figure 28. Change of low (left) and high (right) UV-varnish contact angles (°) with time on untreated and plasma-coated samples.

Too fast a penetration of the UV varnish into highly a permeable pigment-coated paper typically leads to low gloss and an uneven gloss appearance. A slower absorption of the high gloss UV-varnishes should give a higher gloss, since a thicker layer of UV-varnish would be cured on the surface rather than being absorbed into the coating.

When the UV-varnishes were applied with a roll-to-roll flexographic unit, the paper gloss was only slightly increased (Table 4) and the gloss appearance was visually equally uneven for all the samples. However, the fluorocarbon- and organosilicon-plasma coatings had no influence on the gloss of the roll-to-roll UV-varnished samples. It seems therefore that, with a highly permeable pigment-coated paper, the chemical interactions between fluid and substrate surface would have no or little influence on the absorption rate when an external pressure is applied. In addition, the results suggest that forced wetting cannot be well-described by contact angle measurements. However, Paper VI presented in section 6.2.1, the similar plasma coatings reduced the absorption of dampening water into pigment-coated paper under the influence of nip pressure. The hydrophobicity level determined by contact angle measurements correlated well with the amount of dampening water absorbed. The pigment coating in the previous study was a typical coating used in commercial offset printing papers, containing ground calcium carbonate (GCC) and kaolin. For this type of coating, the permeability is known to be lower than that of the 100% uncalendered PCC coating studied here. Considering also the results from Paper VI, it seems that, without external pressure, the surface chemical composition has a significant impact on absorption rate apart from the degree of permeability or porosity. When an external pressure is applied, however, the role of surface chemical composition seems to diminish in the case of a highly permeable pigment coating. With the less permeable GCC- and kaolin-containing pigment coating, the surface chemical composition had a significant impact on the rate of fluid absorption. A direct comparison of these studies is hampered, however, since the type of fluid, fluid amount and application method differed. It is possible that the amount of fluid is also crucial. Schoelkopf et al. [131] have stated that the absorption of high quantities of liquid, as in the case of varnishes, is associated more with permeability than with porosity. In this study, the high-viscosity varnish gave a higher gloss than the low-viscosity varnish, which indicates that the increase in viscosity reduces the absorption rate, even when the external pressure is present.

Table 4. Gloss of the untreated and plasma-coated samples with and without UV-varnish coatings.

	Without UV-varnish		UV-varnish, low η		UV-varnish, high η	
	Average, %	Std.	Average, %	Std.	Average, %	Std.
Untreated	38.6	0.2	41.6	1.1	48.1	0.5
CH plasma-coated	38.4	1.3	40.9	1.7	47.0	1.5
HMDSO plasma-coated	39.1	0.8	44.8	2.5	46.9	0.7
CF plasma-coated	38.2	0.5	40.9	2.0	47.4	0.7

In the application nip, the penetration of the UV-varnish occurs under the influence of an external pressure, and then from the nip to the UV lamp without any external pressure. The plate cylinder diameter was 7 cm, and the estimated nip length was 1 mm and the dwell time in the nip 15 ms. Since the UV-lamp was 2 cm from the printing nip and the printer was running at 4 m/min, it took 0.3 seconds to reach the UV-lamp. Table 5 presents the results of some calculations according to the Lucas-Washburn equation. The calculations suggest that the amount of UV-varnish applied (2g/m^2) was so small and that such a long time was available for absorption that all the varnish was absorbed into the paper before UV-curing, and this may also have been one reason why no differences could be seen.

Table 5. Penetration depth (h) and capacity for UV-varnish absorption (g/m^2) calculated according to the Lucas-Washburn equation, with a pore volume of 14 % and nip pressure of 0.5 MPa. Two different speeds are compared; 4 m/min (used in this study) and 100 m/min.

Sample			h [μm]	Capacity for UV-varnish absorption [g/m^2]	
Low η varnish	With nip pressure (0.5 Mpa, 0.015 s)	Untreated	19.9	2.7	
		CF plasma treated	17.9	2.4	
	Without nip pressure (0.3 s)	Untreated	53.2	7.3	
		CF plasma treated	36.5	5.0	
	Speed 4 m/min	Without nip pressure (0.012 s)	Untreated	10.6	1.5
		Speed 100 m/min	CF plasma treated	7.3	1.0
High η varnish	With nip pressure (0.5 Mpa, 0.015 s)	Untreated	13.8	1.9	
		CF plasma treated	12.2	1.7	
	Without nip pressure (0.3 s)	Untreated	36.4	5.0	
		CF plasma treated	22.0	3.1	
	Speed 4 m/min	Without nip pressure (0.012 s)	Untreated	7.3	1.0
		Speed 100 m/min	CF plasma treated	4.4	0.6

6.2.3 Stability of Plasma Coatings

The stability of the laboratory-scale-produced plasma coatings on a Lumiflex pigment-coated paper were followed by measuring the contact angles of water on a weekly basis for five weeks. The fluorocarbon- and organosilicon-coatings with the higher hydrophobicity had a better stability than the hydrocarbon plasma coating, as can be seen in Figures 29–31. This is probably because the more hydrophobic coatings react less with the oxygen and water vapor in the air. As reviewed in section 3.3, a large number of free radicals can be trapped within the polymer network and react with oxygen and water vapor resulting in oxygen-containing molecular groups, which render the surface more hydrophilic [3]. Especially with the hydrocarbon-plasma coating, it seems that the ageing slows down with time. This is in agreement with the literature [3], where it has been shown that oxygen incorporation is very fast within the first few hours, and then gradually slows down. The standard deviation of the contact angles in Figures 29–31 was between 2 and 4 degrees for all the samples.

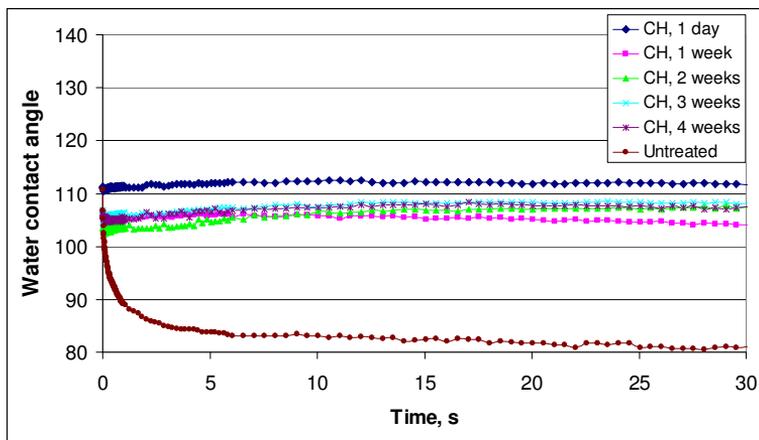


Figure 29. Water contact angle ($^{\circ}$) as a function of time on hydrocarbon-plasma-coated paper.

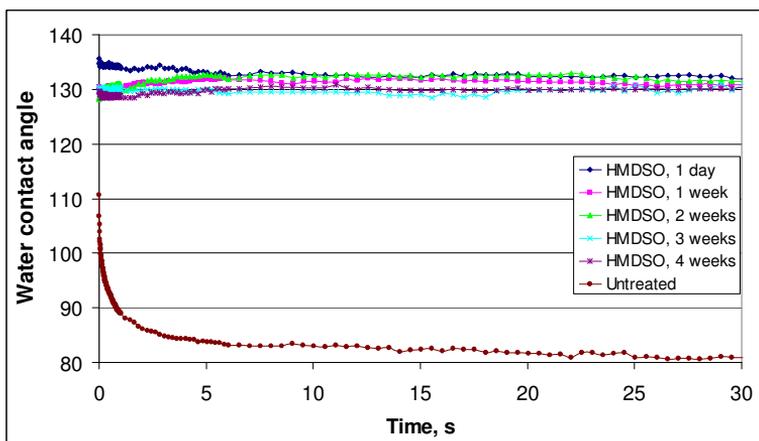


Figure 30. Water contact angle ($^{\circ}$) as a function of time on organosilicon-plasma-coated paper.

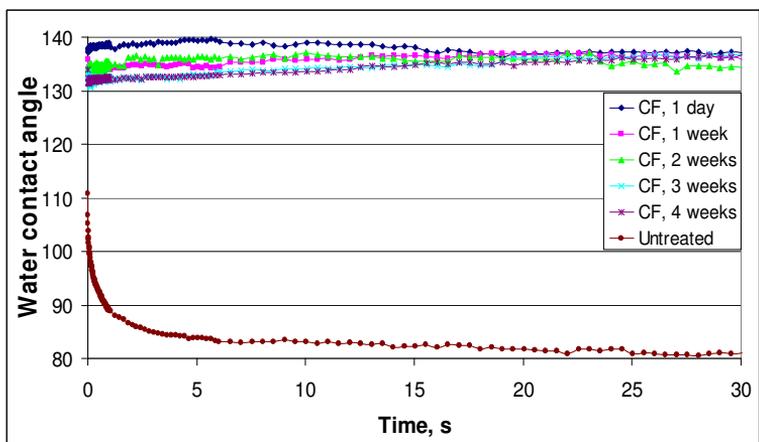


Figure 31. Water contact angle ($^{\circ}$) as a function of time on fluorocarbon-plasma-coated paper.

7. CONCLUDING REMARKS

Plasma surface modification was found to be an effective way to influence the paper surface energy and chemical composition. Plasma activation increased the surface energy and wettability of paper, as expected according to the previous studies reviewed in section 3.2. The wettability increased for both polar and non-polar probe liquids, indicating that both polar and dispersion interactions increased due to plasma activation. However, the change in contact angle was larger with the polar liquid, which can be explained by the polar oxygen-containing molecular groups induced. ToF-SIMS analyses indicated that the modification occurs especially in the long-chain polymer chains, such as the dispersion chemicals of the pigment and latex particles. Therefore, different dispersion systems and the amount of dispersion chemicals on these particles are likely to influence the response to the plasma activation. With the model pigment coatings, it was shown that, for example, kaolin-containing paper experienced a greater change in the contact angle of water than papers containing GCC or talc. With the GCC pigment, the change in water contact angle and O/C ratio was the smallest. It was also shown that the O/C ratio increased more in the latex than in the dispersed GCC pigment, when the coating ingredients were plasma-treated separately. The SB-latex-containing paper experienced a greater change in water contact angle than the SA-latex-containing paper. Starch addition reduced the change in wettability and oxidation, when compared laboratory-scale plasma-treated samples.

Hydrocarbon-, organosilicon- and fluorocarbon-plasma coatings gave the pigment-coated paper a hydrophobic character. The hydrocarbon coating was shown to lead to an oleophilic character, whereas organosilicon- and fluorocarbon-plasma coatings were oleophobic. The plasma coatings produced at atmospheric pressure in an on-line installation using nitrogen carrier gas induced more oxygen and nitrogen into the plasma coating, and thus yielded a lower hydrophobicity level than the coatings produced by low pressure plasma. Mercury porosimetry and air permeability measurements showed no evidence that the plasma coatings had any influence on the pore structure of the pigment-coated paper, which is in agreement with previous work by Tan et al.[98].

This work has increased the fundamental understanding of the role of surface chemistry on the sheet-fed offset printability of pigment-coated paper. The effects of substrate surface energy and chemical composition on ink-paper interactions have been evaluated previously in the literature as reviewed in section 2.5. Changes in coating component properties however usually lead to changes in coating structure. The advantage of the pilot-scale plasma activation and the plasma coatings was that they made it possible to study the influence of surface chemistry alone, without influencing the porous structure of the pigment-coated paper. Therefore, plasma surface modification made it possible the possibility to decouple the effects of porous structure and surface chemistry on printability, and thus permit a better optimization of both.

It was shown that with pilot-scale plasma activation, the ink setting rate could be adjusted without influencing the print quality. Van Gilder and Purfeest [37] have also found that a higher surface energy and polarity of the latex polymer led to a slower rate of ink tack build-up and thus gave greater resistance to coating pick. However, in the present work using the model inks, it was revealed that the response to the surface energy and chemistry change depended on the type of ink oil. The ink setting slowed down with slightly polar linseed-oil-dominated inks and accelerated with non-polar mineral-oil-dominated inks. The slower setting with linseed-oil-dominated inks is explained by the increased polar interactions between the polar molecule groups in the ink oil and the plasma-treated coating. The increased hydrophilicity due to pilot-

scale plasma activation did not influence the print quality of pigment-coated paper. However, with the surface-sized paper the increased hydrophilicity had an indirect influence on the print quality via changed water absorption properties.

It was shown that the hydrophobic plasma coatings were able to reduce or even prevent the absorption of dampening water into pigment-coated paper, even if the dampening water was applied under the influence of nip pressure. It was also evident that the plasma coatings influenced ink transfer. The main mechanism induced by changes in surface chemistry was found to be indirect by formation of weak boundary layer of water on the surface and thus allowing more ink to be transferred. However, the results also suggest that the affinity between an ink and the surface (oleophilicity/oleophobicity) is an important factor influencing the amount of ink transferred, since the hydrocarbon coating with a lower hydrophobicity gave a higher print density than the organosilicon or fluorocarbon coatings. In addition, without pre-dampening oleophobic coatings decreased print density, whereas oleophilic coating slightly increased it.

The fluorocarbon plasma coating was found to reduce the free wetting of UV-varnish on a highly permeable and porous pigment-coated paper. The amount of hydrocarbon groups in the plasma coatings seemed to have a strong influence on the wetting of the UV-varnish, since hydrocarbon plasma coating had no influence on wetting or even slightly increased it. When the UV-varnish was applied with a flexography unit with a nip pressure, the role of the changed surface chemical composition became minimal. The results suggest that the UV-varnish absorption under the influence of printing nip pressure, which leads to a forced wetting, cannot be well described by the contact angle. Taking into consideration the results from our previous study (Paper VI), it can be said that the influence of surface chemical composition may diminish in the case of highly permeable and porous pigment coatings. Calculations according to the Lucas-Washburn equation also suggested that the applied amount of UV-varnish was so small and that such a long time was available for absorption that all the varnish was absorbed into the paper before UV-curing, and this may have been the reason why no differences could be seen.

In addition to chemical modification, the excessive laboratory-scale plasma activation increased the roughness and reduced the surface strength of the pigment-coated paper. These changes resulted in print density variations which were probably due to micro-picking, where the top layers of the coating fail and leave small areas unprinted. It was suggested that the laboratory-scale plasma activation etches or modifies the dispersion chemicals in such a way that the interfacial bonding between pigment and latex particles decreases and reduces the surface strength. It was also shown that laboratory-scale plasma activation is able to stiffen the styrene-butadiene binder surface, possibly through cross-linking initiated by plasma species such as radicals.

The increase in surface energy and wettability due to plasma activation decayed with time, whereas the O/C ratio was shown to remain stable over the period of twelve weeks. The decay in surface energy was faster during the first weeks of storage, after which the decline in surface energy leveled off. After twelve weeks, the surface energy level was still higher than that of the untreated samples. According to the polar attachment model [67], the permanent change in wettability is caused by induced oxygen-containing molecular groups. The reason for the surface energy decay was suggested to be a thermodynamically driven reorientation of the polar groups and recontamination. In the literature, it has been shown [101,102] that durability of the plasma activation can be improved by providing more controlled chemistry, for example by inducing nitrogen groups onto the surface. This and other improvements may lead to the use

of new types of atmospheric DBD instead of industrial corona treatment. For example it was shown in the present work that the latest installation of the experimental pilot scale plasma activation provided greater change in water contact angle and ink setting than conventional corona treatment, even when the power used was only half that of the corona. In addition, the O/C ratio on the reverse side of the paper was smaller than with a corona treatment.

Hydrophobic plasma coatings were shown to be relatively stable with time. It seems that the stability was improved with higher hydrophobicity, when the coating interacted less with water vapor and oxygen in the air. These interactions may result in the incorporation of the oxygen-containing molecular groups, and thus increase the hydrophilicity. Atmospheric on-line plasma coating onto a paper substrate was demonstrated with promising results, but the speed and coating uniformity may be future challenges in the development work. If these challenges can be overcome, plasma-coating technology might provide completely new material processing possibilities for the paper and printing industry. In addition, the fact that it is a dry process, and thus more environment-friendly, is a significant advantage compared to conventional wet-chemical processes. Plasma-deposited coatings also provide the possibility of generating extremely thin coatings without changing the bulk properties of the material. In these days, when rising costs and limited market growth cause challenges for the paper and printing industries, quality improvements are not perhaps the key questions for bulk paper products. However, I am convinced that the versatile plasma surface-modification technology has a potential to provide solutions for more value-added fiber-based products, such as printed electronics and biologically active papers.

As usual in research work, various new questions surfaced during the process and some of these were left unanswered. These unanswered questions can be considered as shortcomings of this work, but also as recommendations for future research. Even if the surface components of coated paper, such as different pigment and binder types, were shown to respond differently to the plasma activation, more research could have been conducted, for example, to investigate how different coating additives respond to the activation. Thus, a more detailed understanding could have been achieved on what type of molecule groups and surface chemistry make the surface sensitive and responsive to plasma activation. Different types of plasma activation equipment were compared in this work, and some improvements in the effectiveness of experimental pilot-scale plasma when compared to conventional corona treatment were shown. However, studies on the influence of different plasma parameters such as power, line speed and different treatment gases were left outside of this work. The definite answer for the decreased paper surface strength and increased roughness due to excessive plasma activation was not found, but speculation of possible reasons is given in section 6.1.1. In addition, there is some uncertainty for the reasons causing the accelerated ink setting with mineral oil-based inks due to plasma activation (section 6.1.2).

The research relating to plasma coatings was conducted as two practical case studies. In these studies the effects of plasma coatings on surface chemistry were investigated widely. However, the impact of plasma coatings on surface roughness and its influence on wetting was outside the scope of this thesis. Related also to the previous issue, the results in Paper VI show that the detailed understanding of the plasma coatings' impact on paper gloss, especially on print gloss and ink setting would still need some further research. Afterwards, it is clear that the experimental approach in the study relating to the UV-varnishing (section 6.2.2) could have been performed better to show the differences. Originally, both the plasma coatings and UV-varnishing were intended to be carried out in pilot-scale. However, the pilot-scale plasma polymerization did not succeed on this particular highly permeable and porous paper. Therefore, the trials had to be conducted in laboratory-scale. The calculations according to

Lucas-Washburn equation showed that the small amount of UV-varnish and relatively low line speeds of the laboratory-scale trial may be the reasons why differences were not seen.

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APPENDIX

Appendix A: Additional Test Results

A pre-coated fine paper was coated with two coating colors containing 100 parts of GCC pigment (Hydrocarb 90, Omya) and 10 parts of either SB-latex (DL966, Dow) or SA-latex (XZ 95085.01 Experimental latex, Dow). The coat weight was 13 g/m². Laboratory-scale plasma treatment was performed as in Papers IV and V. The surface characterization was performed by water contact angle measurements (CAM200, KSV Ltd.) and XPS (Physical Electronics). The influence of latex type on the surface strength was evaluated by a pick test (SCAN-P 63:90). In addition, surface hardness and elastic modulus were determined by a nanoindentation tester (CSM Instruments).

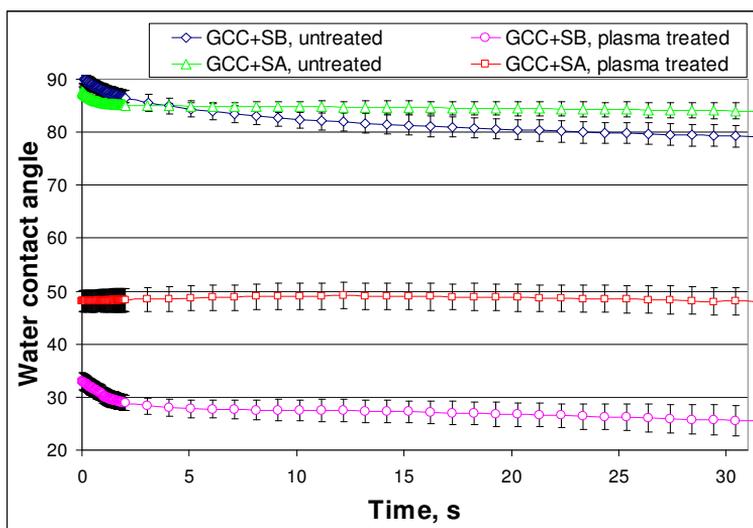


Figure A. Change in water contact angle (°) with time on untreated and laboratory-scale plasma-activated GCC paper containing either SB- or SA-latex. The error bars indicate the standard deviation of six parallel measurements.

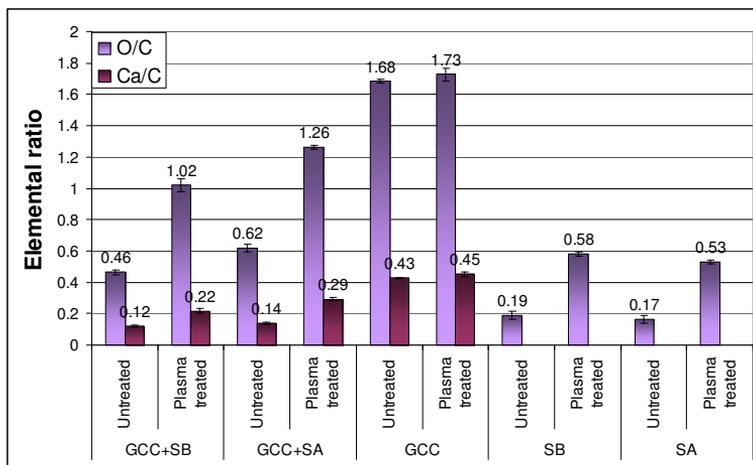


Figure B. O/C and Ca/C ratios determined by XPS for a paper coated with GCC pigment containing either SB- or SA-latex. The elemental ratios have also been measured for the separate coating components. The error bars indicate the standard deviation of three parallel measurements.

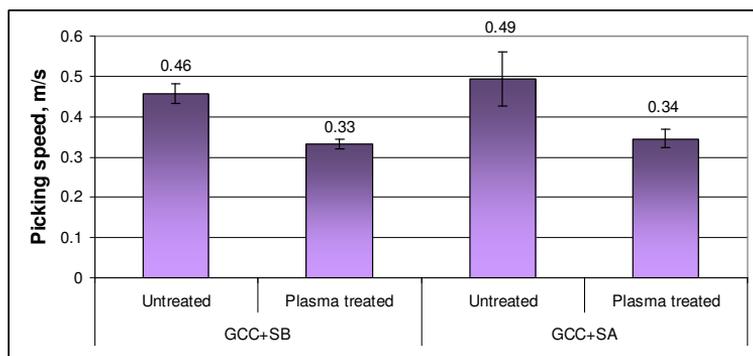


Figure C. Pick test results. A higher picking speed means a higher surface strength of the pigment-coated paper. The error bars indicate the standard deviation of three parallel measurements.

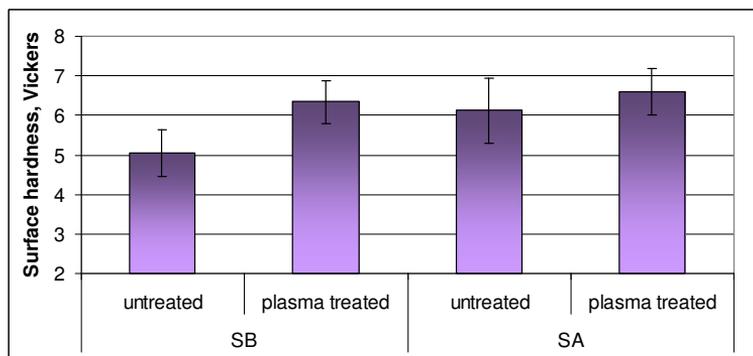


Figure D. Surface hardness of the untreated and laboratory-scale plasma-treated SB- and SA-latexes determined by the nanoindentation tester. The error bars indicate the standard deviation of six parallel measurements.

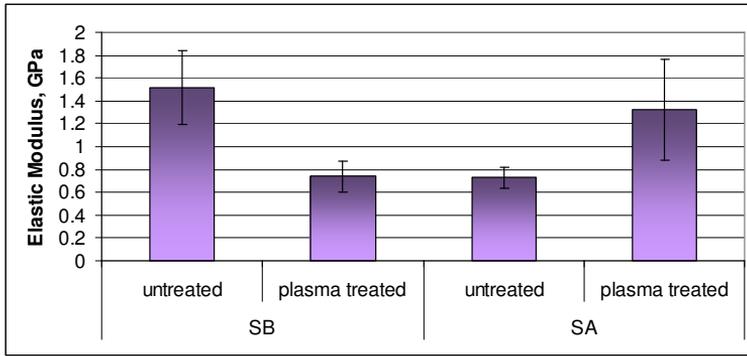


Figure E. Elastic modulus of the untreated and laboratory-scale plasma-treated SB- and SA lattices determined by the nanoindentation tester (CSM Instruments). The error bars indicate the standard deviation a minimum of five parallel measurements.

Appendix B: Influence of Plasma Activation on Ink Setting

The development of ink tack with time was determined with the ISIT (SeGan Ltd.) tester for all the model pigment-coated papers presented in Paper IV. The ISIT-results with kaolin/GCC/latex-containing paper (paper 1) were presented in Figure 18 and in Paper V. The results with papers 2–4 are presented here.

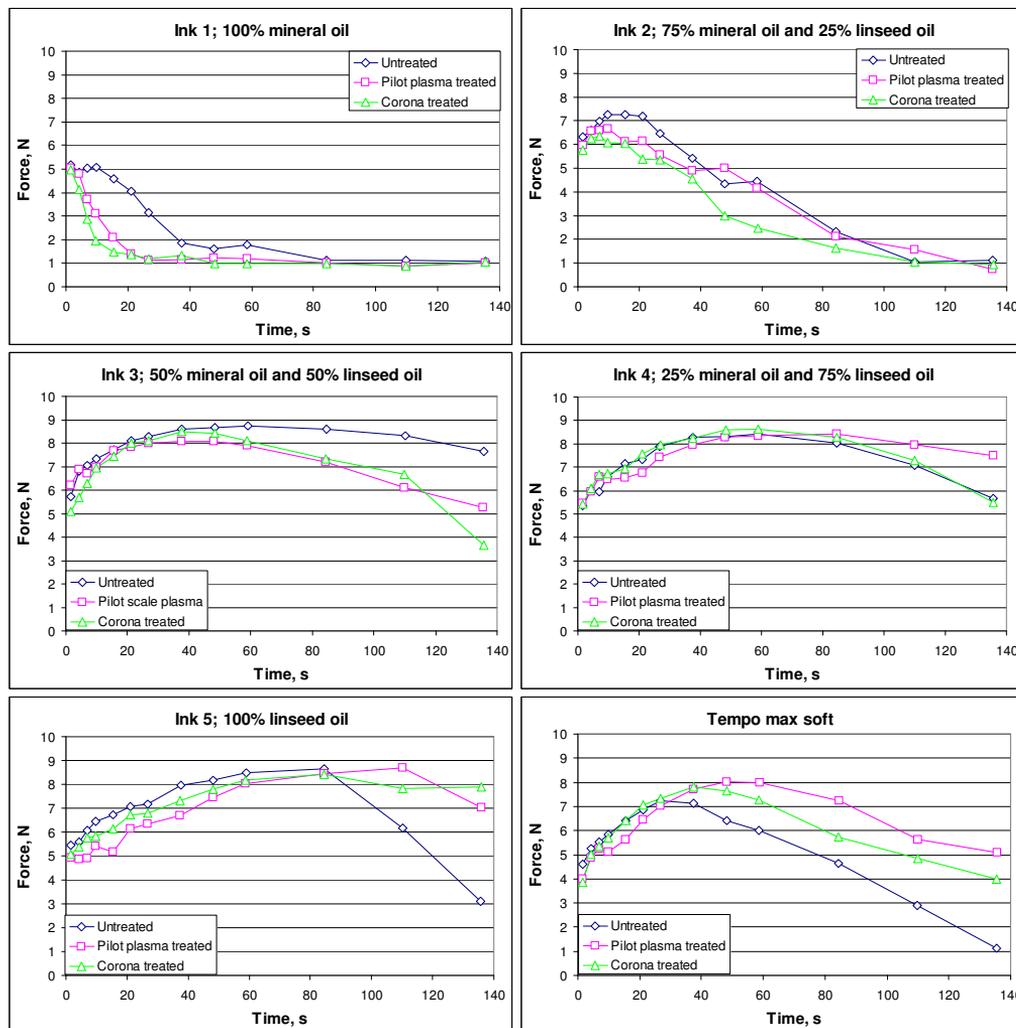


Figure F. Influence of plasma activation on the development of ink tack with time with talc/GCC/latex -containing paper (paper 2). Measurements were performed with five different model inks and with a commercial Tempo max soft –ink containing both linseed and mineral oils. Mineral and linseed oil portions for ink 1 were 100/0, for ink 2 75/25, for ink 3 50/50, for ink 4 25/75 and for ink 5 0/100. The error bars indicate the standard deviation of three measurements.

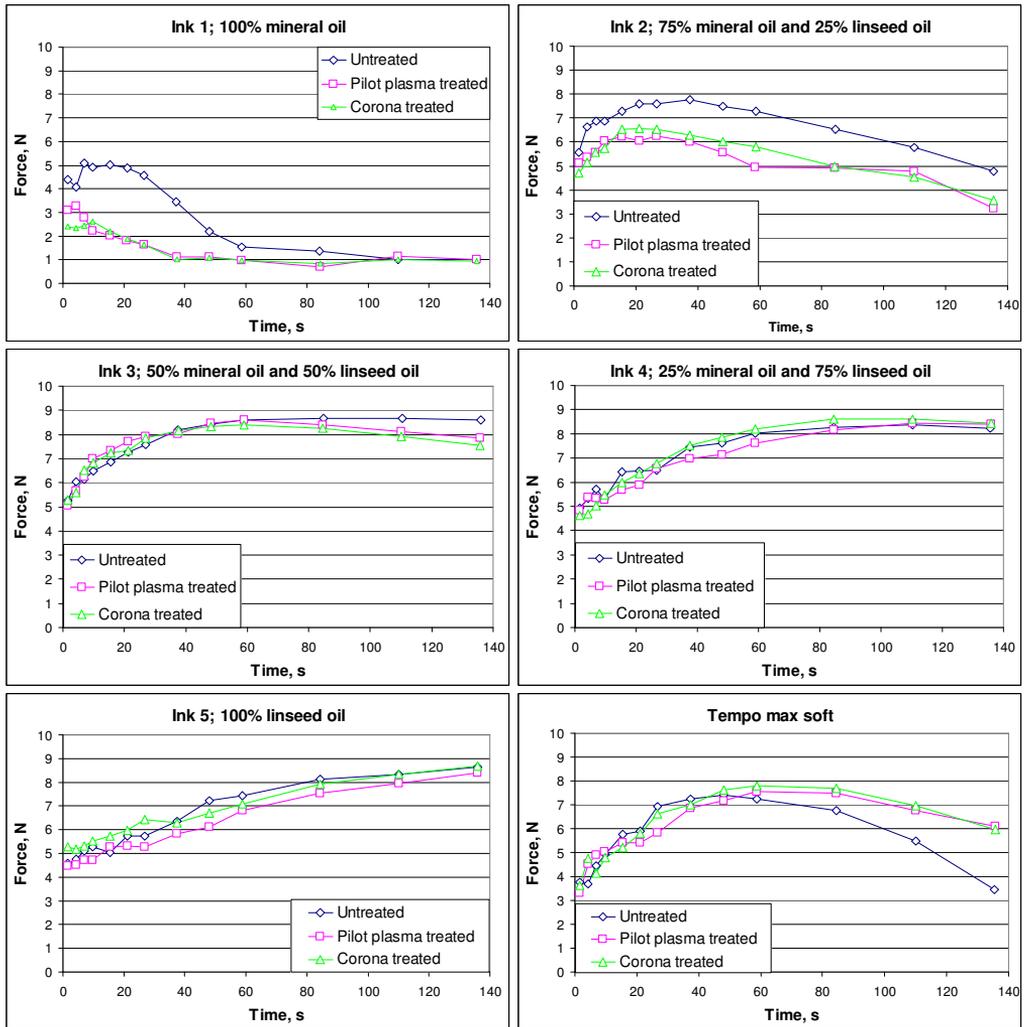


Figure G. Influence of plasma activation on the development of ink tack with time with kaolin/GCC/latex and starch -containing paper (paper 3). Measurements were performed with five different model inks and with commercial Tempo max soft –ink containing both linseed and mineral oils. Mineral and linseed oil portions for ink 1 were 100/0, for ink 2 75/25, for ink 3 50/50, for ink 4 25/75 and for ink 5 0/100. The error bars indicate the standard deviation of three measurements.

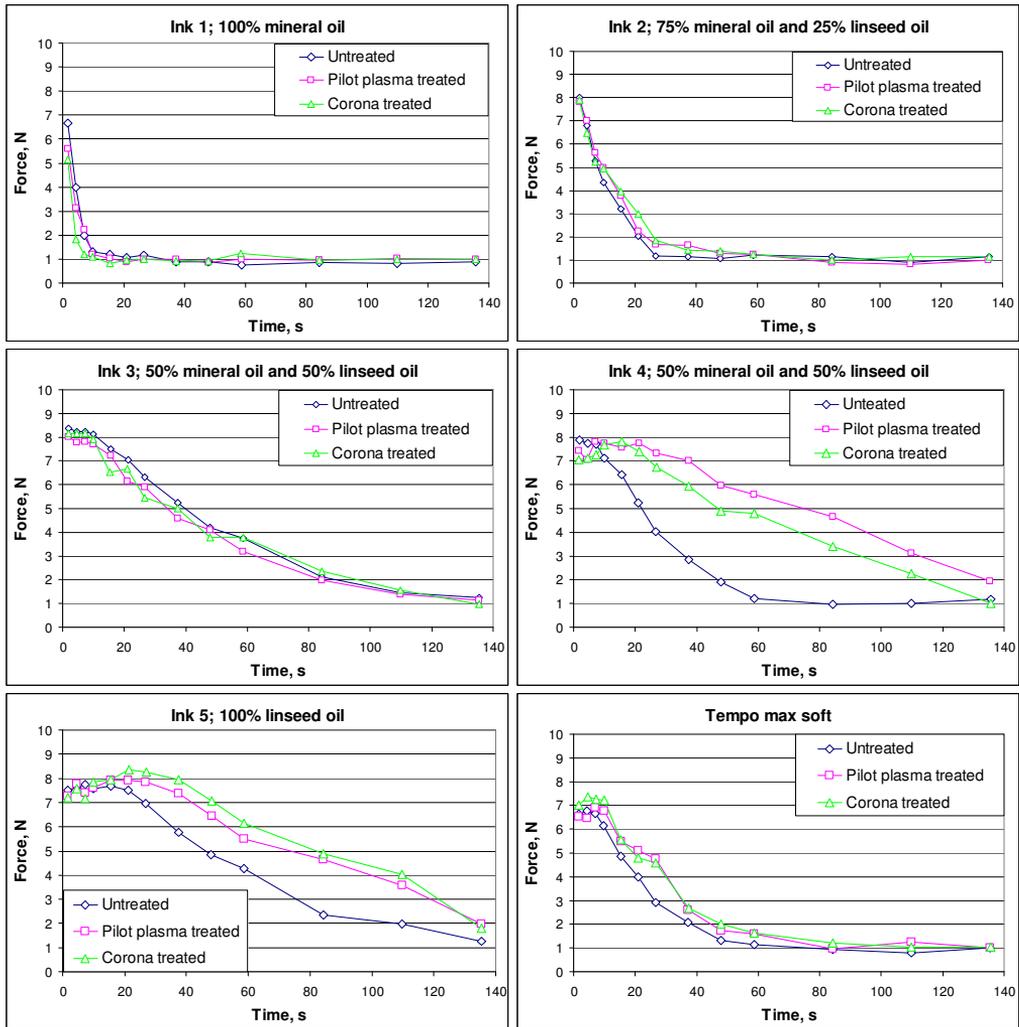


Figure H. Influence of plasma activation on the development of ink tack with time with GCC/latex-containing paper (paper 4). Measurements were performed with five different model inks and with commercial Tempo max soft –ink containing both linseed and mineral oils. Mineral and linseed oil portions for ink 1 were 100/0, for ink 2 75/25, for ink 3 50/50, for ink 4 25/75 and for ink 5 0/100. The error bars indicate the standard deviation of three measurements.

Appendix C: Wet Pick Test Samples

In Paper VI, the wet pick/wet repellence test was performed according to the IGT test method (IGT AIC2-5T2000). The examples of untreated and laboratory-scale plasma-coated Lumiflex-paper test strips reproduced in Figure I show the influence of plasma coatings on the print density, as discussed in section 6.2.1. The upper areas of the strips were pre-dampened before printing, whereas the lower areas were printed without pre-dampening.



Figure I. Examples of untreated and laboratory-scale plasma-coated wet pick test samples.

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