Faculty of Technology and Science
Chemical Engineering

Erik Svanholm

Printability and Ink-Coating Interactions in Inkjet Printing

DISSERTATION
Karlstad University Studies
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Abstract

Inkjet is a digital printing process where the ink is ejected directly onto a substrate from a jet device driven by an electronic signal. Most inkjet inks have a low viscosity and a low surface tension, which put high demands on the coating layer's porosity and absorbency characteristics.

The aim of this study has been to gain an increased knowledge of the mechanisms that control the sorption and fixation of inkjet inks on coated papers. The focus has been on printability aspects of high print quality (although not photographic quality) laboratory-coated inkjet papers for printers using aqueous-based inks.

Papers coated solely with polyvinyl alcohol (PVOH) and starch presented excellent gamut values and good print sharpness over the uncoated substrate, due to good film-forming characteristics observed by light microscopy and ESCA. ESEM analyses showed the complexity and variation of PVOH surface structures, which has probably explained the wide scatter in the colour-to-colour bleed results. Pure PVOH coatings also gave a surface with high gloss variations (2-8 times greater than that of commercial inkjet papers), prolonged ink drying time, and cracked prints when using pigmented inks. When an amorphous silica gel pigment (with broad pore size distribution) was used in combination with binder, a new structure was formed with large pores in and between the pigments and a macro-roughness generated by the large particles. The inkjet ink droplets could quickly penetrate into the large pores and the time for surface wicking was reduced, which was beneficial for the blurriness. However, the macro-roughness promoted bulk spreading in the coarse surface structure, and this tended to increase the line width. Finally, when the ink ends up within the coating, the colourant is partly shielded by the particles, and this reduced the gamut area to some extent. The binder demand of the silica pigments was strongly related to their pore size distributions. Silica gel required two to three times the amount of binder compared to novel surfactant-templated mesoporous silica pigments (with small pores and narrow pore size distribution). This finding was attributed to the significant penetration of PVOH binder into the pores in the silica gel, thereby, increasing its binder demand. Furthermore, this binder penetration reduced the effective internal pore volume available for rapid drainage of the ink vehicle. Consequently, the surfactant-templated pigments required significantly lower amounts of binder, and gave improvements in print quality relative to the commercial pigment.

Keywords: coating, inkjet, print quality, printability, pigment, silica, polyvinyl alcohol, colourant, ink absorption.

List of Papers

This Doctoral thesis consists of the following papers:

Paper I *Inkjet Print Quality Measurements - Correlation Between Instrumental and Perceptual Assessments*
E. Svanholm and K. Almgren, 2006.

Paper II *Influence of Polyvinyl Alcohol on Inkjet Printability*
E. Svanholm and G. Ström.
- An earlier version is available in the preprints of the 2004 TAPPI International Printing and Graphic Arts Conference.

Paper III *Surfactant-Templated Mesoporous Silica as a Pigment in Inkjet Paper Coatings*
P. Wedin, E. Svanholm, P.C.A. Alberius and A. Fogden.
- *Journal of Pulp and Paper Science 32(1), 2006.*

Paper IV *Colourant Migration in Mesoporous Inkjet-receptive Coatings*
E. Svanholm, P. Wedin, G. Ström, and A. Fogden.
- 2006 TAPPI Advanced Coating Fundamentals Symposium.

Paper V *Using the Micro Drop Absorption Tester (MicroDAT) to Study Droplet Imbibition and its Effect on Inkjet Print Quality*
E. Svanholm and G. Ström, 2006.

Table of Contents

1. Introduction

Inkjet is a digital printing process where the ink is ejected directly onto a substrate from a jet device driven by an electronic signal. The majority of printers used for colour printing in offices and homes today are inkjet printers. Due to its ability to print on a wide variety of substrates, inkjet technology is also increasingly being used in industrial printing and in the package printing industry. Together with laser printing, inkjet printing is the fastest growing area of the printing industry [1].

Most inkjet inks have a low viscosity and a low surface tension, which put high demands on the coating layer's porosity and absorbency characteristics. Today, silica-based coatings constitute the main alternative for inkjet-optimised paper coatings. The silica-based coating colours are highly viscous and have low coating solids content. Furthermore, they are much more expensive than ordinary paper coatings for offset printing, which are calcium-carbonate and/or clay-based. The inkjet coatings also incorporate a binder that swells when the ink carrier liquid is absorbed. Thus, an important task is to find alternative coating formulations that fulfil the dye-fixation requirements and have the drainage capacity needed for inkjet inks, but that are less expensive and have good runnability in a coating machine. The knowledge available concerning paper-coating-ink interactions in inkjet printing is limited. As a first step towards finding alternatives to the existing coating colours, the aim of this study has been to gain a deeper understanding of the mechanisms that control the absorption and fixation of inkjet droplets on coated papers. The focus of the research has been on printability aspects of high quality (although not photographic quality) laboratory coated inkjet papers for printers using aqueous-based inks.

The investigation addressed the following topics: a general overview of the printability of coatings consisting of the most commonly used commercial inkjet coating chemicals; an investigation on how well instrumental print quality measures correlate with the subjective print quality perceived by a panel of human observers (Paper I); a more in-depth look at the printability aspects of polyvinyl alcohol coated sheets (Paper II); a study of the influence of pigment structure on the formulation and printability of inkjet paper coatings (Paper III); a study of colourant migration in inkjet receptive coatings (Paper IV); and finally a study of droplet imbibition and its effect on print quality (Paper V).

2. Background

2.1 Inkjet Technology

2.1.1 Technology Overview and Printhead Design

The foundations for what would later become the inkjet printing technology were laid over a century ago. In 1856, the Belgian physicist J.A.F. Plateau wrote *On the recent theories of the constitution of jet liquid issuing from circular orifices* [2]. More than 20 years later, the English physicist Lord Raleigh started to publish a series of papers which became the theoretical foundation for liquid jets. However, the application of the physical principles of liquid jets was still to come.

Before the introduction of computers, analogue measurements and electronic instruments were often accompanied by a pen-base chart recorder. The ink pens were electromagnetically deflected to record the amplitude of the voltage waveform. Higher sensitivity recording of higher frequency signals could be achieved by reducing pen drag and mass. For this purpose, Rune Elmqvist at Siemens-Elema AB in Stockholm (Sweden) configured a fine capillary nozzle *inkjet* in 1949 [3]. In 1952 Siemens-Elema introduced a voltage recorder based on the invention called *Minograf* (Figure 1), which was primarily used with medical instrumentation. The *Minograf* did not have a synchronised jet break-up, and individual ink drops could not be printed at selected positions.

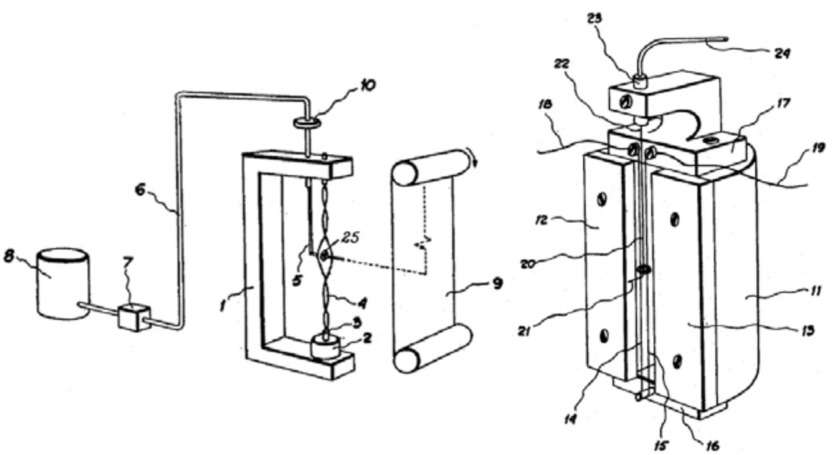


Figure 1. The Siemens-Elema Minograf. The device utilizes a liquid jet of ink deposited by a fine capillary mounted to a galvanometer [3].

In the late 1940's, Clarence Hansell at Radio Corporation of America (RCA) in New York (USA) invented a device that ejected droplets only when they were required for imaging on the substrate (this technology later came to be known as *drop-on-demand*, abbreviated DoD) [4]. Hansell's concept, illustrated in Figure 2, used a disc of a piezoelectric material to convert electrical energy into mechanical energy. When an acoustic frequency signal pulse was applied to the disc, it pressed an ink-filled conical nozzle and a spray of ink droplets was ejected. The device was never developed into a product.

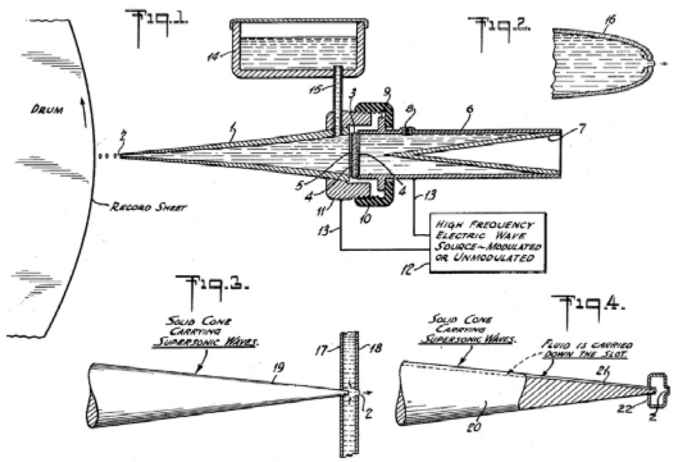


Figure 2. The earliest piezoelectrically activated DoD configuration [4].

In 1962, Mark Naiman at Sperry Rand Corporation in New York (USA) invented *sudden steam printing* [5]. This approach, illustrated in Figure 3, used a large array of nozzles. The ink was held in chambers having a nozzle exit and two electrodes in contact with the ink. A voltage pulse caused the electrodes to violently steam the ink, ejecting it from the nozzle. Sperry Rand did not develop the sudden steam printing into a commercial product, and the concept was not taken up until almost 20 years later, this time by Canon and Hewlett Packard.

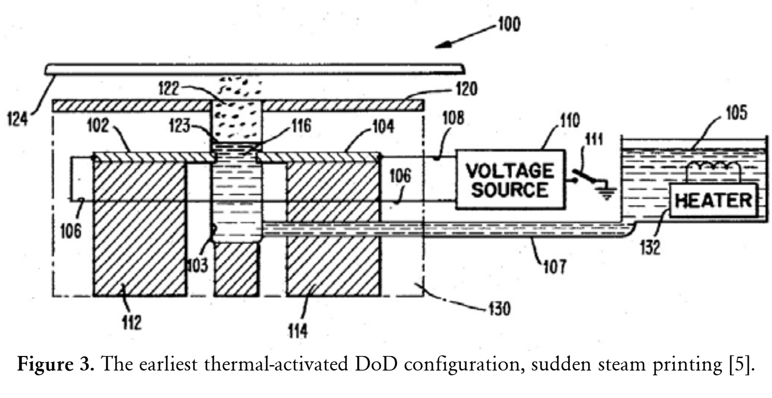


Figure 3. The earliest thermal-activated DoD configuration, sudden steam printing [5].

In 1963, Richard Sweet at Stanford University in Palo Alto (USA) experimented with a version of the Minograf. Sweet managed to apply a pressure wave pattern to an orifice; thus breaking the ink stream into droplets of uniform size and spacing. This allowed control of individual drop-charging and drop deflection. When passed through an electric field, charged drops were deflected into recirculation gutter and uncharged drops impacted with the printing media. Sweet's work was the beginning for most *continuous* inkjet printing systems. His inkjet oscillograph [6] is illustrated in Figure 4.

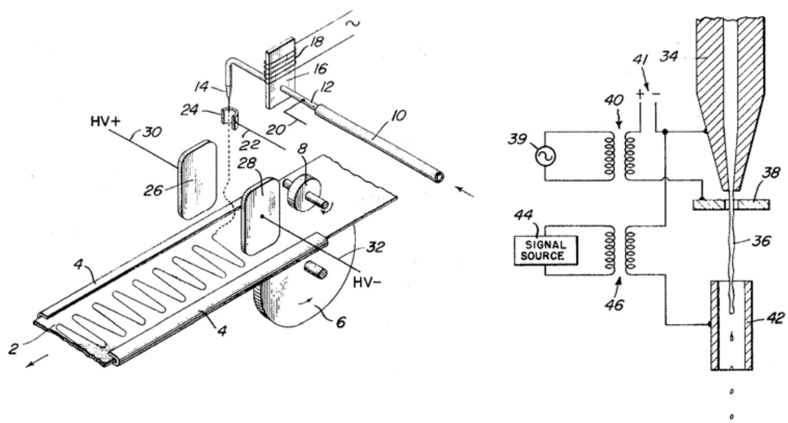


Figure 4. Richard Sweet's synchronised, continuous inkjet voltage signal recorded [6].

During the late 1960's and 1970's, significant developmental efforts were primarily made of the continuous method. During this time, the first actual practical inkjet printing devices appeared. Sweet's printer used a *binary deflection system* where individual drops were either charged or uncharged. Development of this method lead to *multiple-deflection system*, which charged and deflected drops at various levels. This allowed a single nozzle to print a small image swath [7, 8]. The electrostatic pull was a continuous method using conductive ink pulled out through the nozzle by a high voltage pulse [9, 10]. In 1977, Burlington (USA)-based company Applicon introduced the first colour inkjet printer, based on the pioneer work done in the 1950's by Carl H. Hertz of the Lund Institute of Technology in Lund (Sweden) [11]. Although not successful, it can be seen as the forerunner of many high resolution printers, such as the IRIS Graphics colour proofers introduced in the 1980's.

The real commercial breakthrough for inkjet technology came in the early 1980's, largely because of the introduction of IBM's personal computer (PC). The IMB PC's architecture was open, making it possible for all clones to use the same software. This strategic decision encouraged competition, which resulted in the beginning of the explosive growth of PC's shown in Table I.

Alongside the development of personal computers came the development of graphics software and hardware paraphernalia, such as digital cameras and scanners, which all benefited inkjet printer sales and development.

Table I. Number of Computers in Use (www.c-i-a.com).

Year	Millions of computers installed (world wide)
1982	2
1986	20
1990	137
1995	257
2000	575
2005	660

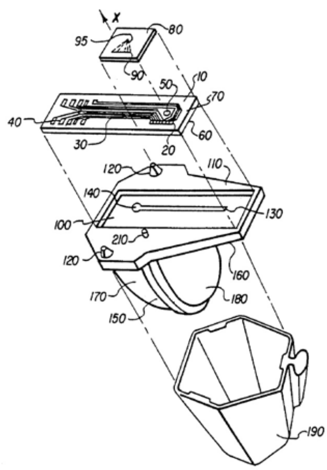


Figure 5. The first successful, low-cost inkjet print cartridge – the Hewlett-Packard's ThinkJet [12].

The 1980's saw further developments by Canon and Hewlett Packard, such as the thermal printers (e.g. Bubble-Jet [13, 14] and ThinkJet [12] printers), building on the principles of the sudden steam printing. The simple design of the printheads, together with the semiconductor-compatible manufacturing process, made it possible to produce printers at a low cost and with a large number of nozzles. In 1984, Hewlett Packard launched their first line of low-cost printers with disposable inkjet print heads (Figure 5), which reduced the costs even further [12, 15]. In the beginning of the 1980's, technological advances had made inkjet a technology that was more reliable and more affordable, making it a strong potential candidate for desktop printer applications. There were, nevertheless, still some remaining difficulties associated with the early inkjet devices in the late 1970's and early 1980's: poor reliability, low resolution, nozzle clogging, start-up and shut-down problems, mismatches between ink and paper, limited number of nozzles, low speed, and high cost.

By the mid-1990's and onward, the image quality, reliability, and cost effectiveness had improved to a point where it was realistic for inkjet to compete with conventional small-scale printing. At this point, the so-called photo printers were introduced and started to compete with traditional silver halide photography. The low resolution was improved from approximately 100 x 100 dots per inch (dpi) in the early 1980's to above 9600 x 2400 dpi in 2006. The reliability of inkjet devices was also improved with the introduction of disposable ink cartridges that included the nozzle arrays and with advances in ink, media, software and microprocessors. During 1982-1984, a DoD printer cost € 750-€ 4500. In 2007, a desktop inkjet printer can be purchased for as little as € 40 (due largely to the fact that several of the manufacturers sell printers at a loss, relying on supplies to provide the profit).

The physics of drop generation and, to a certain extent the subsystem hardware/software, is quite different in continuous and DoD printing. The choice of printhead depends on a long list of considerations, such as: image resolution, media type, number of throughputs, ink chemistry, drying time, maintenance, cost, and reliability, etc. The use of DoD printers is somewhat limited due to the slow speed determined by the systems physics. Consequently, DoD printers are mainly used for office and home printing applications. Continuous inkjet printers print at much higher speeds than their DoD counterparts because the drop generation rate is 10-100 times higher. However, these machines are also much more complicated, expensive, and the equipment is not compact enough to meet small-scale printing requirements. Therefore, this makes them more suitable for industrial applications, such as the printing of packages, labels, and direct mail [16]. At the end of the 1980's, continuous inkjet work for office applications virtually ended. In 2002, more than 95% of the colour desktop printers in the world were DoD units [17].

2.1.2 Ink Design

The most important part of the inkjet printer is the ink that is used in the cartridge. The quality of printing is directly affected by the quality, type, and amount of ink. Inkjet inks are designed for use in specific printers or print heads. There are three major groups of inkjet ink: aqueous, non-aqueous, and hot melt. Table II shows the drying processes of the various inks.

Table II. The Ink Drying Process [15].

Type of ink	Drying controlled by...
Aqueous	Absorption and evaporation
Solvent-based	Evaporation and absorption
Oil-based	Absorption
UV-curable	Absorption and the time available before cure
Hot-melt/phase change	Freezing

The ink undergoes multiple processes and stages of use; it is made in bulk, held in the printer/printhead, processed into droplets, absorbed (or adsorbed) by the substrate, fixed to the substrate and finally, used as an image resistant to environmental exposure and mechanical handling. The numerous phases and the fact that the ink composition changes over time requires a versatile ink, which normally comprises of a complex mixture of numerous components. For a desktop printer, ink can contain in the region of 20 different chemicals, which play an important role both individually and in combination with others in creating the final print [18]. For a typical narrow-format (home/office) inkjet printer (using aqueous-based ink), the ink consists of: 2-5 weight-% colourant (dye or pigment), 2-5% surfactants and additives, 30% humectant (ethylene glycol or diethanolamine), and 65% water. The viscosity is 2-5 cp and the surface tension 30-40 dyne/cm [19]. In solid ink technology, the ink is solid at room temperature. The operating ink temperature is higher than 100 $^{\circ}$C, the viscosity is 10-30 cp, and the surface tension is 25-40 dyne/cm [18].

The colourants in an inkjet ink are either dye based or pigment based: a dye is a colourant that is fully dissolved in the carrier fluid; a pigment is a fine powder of solid colourants particles dispersed in the carrier fluid (Figure 6).

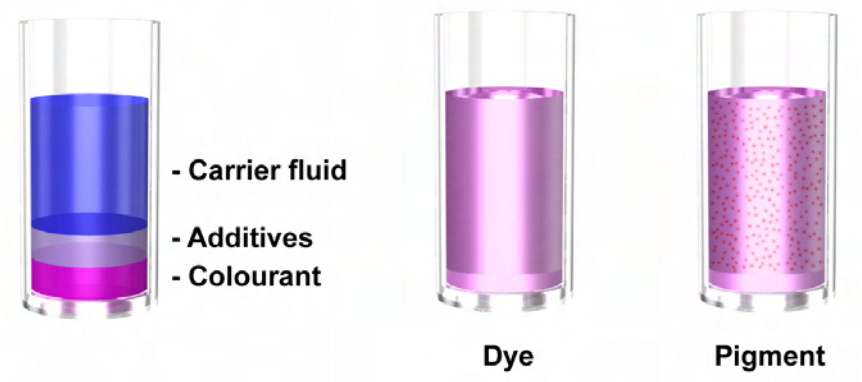


Figure 6. Inkjet ink colourants.

Dyes can provide highly saturated colour; they are able to refract or scatter very little light. They do, however, fade quicker, are very sensitive to water and humidity, and more vulnerable to environmental gasses, such as ozone. Pigmented colourants are made of a combination of a thousand molecules and are much larger than their dye counterparts, usually less than 100 nm in size [20, 21]. This gives the pigment-based inks the advantage of being more stable, more lightfast (particularly for outdoor exposure), and less affected by environmental factors [22]. The downside to these inks is that particles in a dried pigment ink have a very rough surface [23, 24], so the light reflected off the print tends to scatter (Figure 7), thus, producing less saturated and duller colours [25]. However, recent advances in pigment preparation technologies have improved colour quality by grinding pigments to even smaller sizes, and by using resins to coat the particles, which smoothes out their rough surface [26].

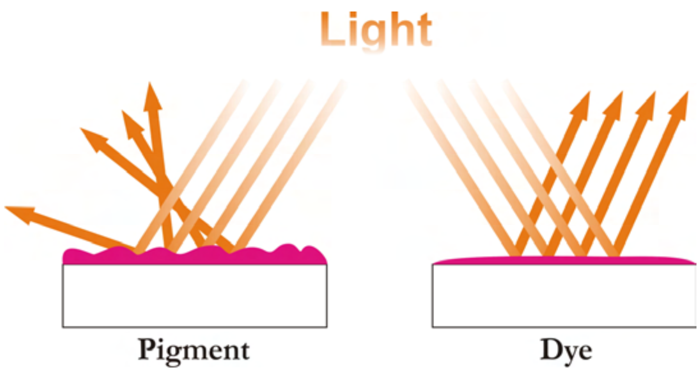


Figure 7. Light reflection off printed surfaces.

2.1.2.1 Aqueous and Solvent-Based Inks

Aqueous and solvent-based ink formulation consists mainly of a carrier fluid that keeps the ink in a liquid state, acting as a "carrier" for the colourant. A co-carrier - usually glycol or glycerine - is often used to control the ink's drying time, as well as its viscosity during manufacturing. Small amounts of other additives are also present in most inks. These additives help control such factors as: dot gain, drop formation, print head corrosion, pH level, fade resistance, and colour brilliance [26]. The main components of an aqueous/solvent based inkjet ink and their purposes are presented in Table III. Many components, however, have a dual function; for example, a single component may act as both humectant and viscosity modifier.

Table III. Main Components of an Aqueous/Solvent Based Inkjet Ink [18].

Ink component	Purpose	wt-% *
Colourant	Gives the ink its primary function – absorbing light of a particular wavelength band	2-8
Carrier fluid	Dissolves or suspends the colourant	35-80
Surfactant	Lowers the surface tension of the ink to promote wetting	0.1-2.0
Humectant	Inhibits evaporation (miscible with the carrier fluid)	10-30
Penetrant	Promotes penetration of the ink into the paper structure for the purpose of accelerating ambient drying	1-5
Dye solubilizer	Promotes dye solubility in the primary carrier fluid	2-5
Anticockle additive	Reduces the interaction with paper fibres which otherwise leads to paper cockle and curl	20-50

* Percentage of the total ink per weight

2.1.2.1.1 Aqueous-Based Inks

Aqueous-based inks were the first to be used in inkjet printing, and are still common today. They have no volatile organic compounds, and have low toxicity. Aqueous-based inks have a relatively slow drying rate (on uncoated media) and the prints have a low water fastness; hence they are mainly printed onto coated media for indoor use. Outdoor graphics can be produced by applying a protective laminate; however, but that adds considerably to the cost of the final product.

2.1.2.1.2 Solvent-Based Inks

The term "solvent" is often described in encyclopaedias as "a substance having the power of dissolving other substances". This could describe most liquids, including water. However, in the inkjet industry, "solvent" is used generically to describe any ink with a carrier fluid that is not water-based. Solvent-based inks are largely made up of: a solvent (often containing glycol ester or glycol ether ester), a pigmented colourant, a resin, and a "glossing" agent [26]. When the solvent evaporates, the pigmented particles are "glued" to the media by the resin. Solvent-based inks are usually used for commercial printing, such as the coding and marking on cans and bottles. These inks dry faster that aqueous-based inks, but emit volatile organic compounds.

2.1.2.2 Oil-Based Inks

Oil-based inks use a very slow drying carrier fluid (such as Isopar) that is usually derived from a mineral oil source, hence, the term "oil-based." The benefit of this approach is that the printer is very easy to use and maintain as the print head jets are unlikely to clog with dried ink. Oil-based inks are used for card printing, packaging, labels, and boxes where ink is fully absorbed. As the droplets can be formed with very small quantities, they can be used for high-resolution printing. There are many oil-based inkjet printers in use, although there are few machine manufacturers introducing new models [26].

2.1.2.3 Hot Melt Inks/Phase Change Inks

Hot melt inks are gel-like at room temperature. When heated, they melt; in the melted condition, they are jetted to the substrate where they immediately cool down again. Due to the change in state of the ink (solid - liquid - solid), these inks are also called phase-change inks. Hot melt inks have been emerging in the inkjet printing industry since the early 1990's. In phase change inks, low viscosity waxes are the vehicle for the colourants; the inks have polymer-like properties in the solid phase while maintaining a very low viscosity in the melt. One of the main advantages of these inks is that final print quality is relatively independent of substrate type or quality. The hot melt inks give a distinct topography that may be subject to wear and abrasion, or cracking with flexible substrates [27]. The inks are predominantly used in industrial marking and in labelling [28].

2.1.2.4 UV-Curable Ink

UV inkjet inks are inks that are cured with the use of an ultraviolet light. UV inks were introduced in the 1990's and have mainly been used in wide-format printing of rigid substrates: corrugated plastics, glass, metal, and ceramic tile are a few examples. UV inks have the main advantage of instant drying that leaves the print completely cured; as a result, no solvents penetrate the substrate once it comes of the printer. Due to the rapid drying, there is less substrate dependence, and there is a diminishing need post-print processes. Recently, opaque white ink has been introduced in UV-printing. These inks can be used as an undercoat, allowing colour-correct printing on non-white or transparent substrates. It can also be used to create additional highlights to printed images [29]. The drawbacks of UV inks are the relatively high cost and health and safety-related issues. The high cost is due to the specialty raw materials used in the formulations. UV inks can be up to two to three times more expensive than conventional inks [27]. The exposure to UV materials can result in chronic health effects on the skin, eye, and immune system. The UV-lamps generate ozone, and that must be vented or neutralized. The printers also generate a small amount of mist that has to be removed from the printer enclosure.

2.2 Inkjet Receptive Media

As inkjet is a versatile technology and as the range of inks is vast, virtually any surface can be printed; however, paper has proven to be the most commonly used media in the graphic industry. Most inkjet inks are highly surface active and penetrative. The quality of the print is highly dependent on droplet spreading, which is controlled by both ink properties (surface tension and viscosity) and to a great extent by media absorption properties (surface tension, roughness, and porosity) [19].

Most inkjet inks are anionic, as is the surface of an uncoated paper. There is, therefore, hardly any attraction between the ink and paper, and this can lead to technological difficulties in the printing process such as curl, cockle, and slow drying. The ink colourant needs to be immobilised quickly on the surface of the paper, and to be separated from the ink carrier [30, 31]. If the ink is absorbed into the sheet too rapidly, it can lead to poor optical density and, thus, strike-through in the print. On the other hand, if the ink is not absorbed quickly enough, it may spread laterally, resulting in colour-to-colour bleed, edge raggedness, and line broadening. These requirements are contradictory, and an appropriative trade-off between these two effects is needed. This is achieved by manipulating the sheet's porosity and absorbency characteristics, by either sizing or coating [32, 33].

An ideal paper for inkjet printing should possess the following properties:

- Sufficient hold out of ink dye on the surface to provide high optical print density
- Quick absorption of ink carrier liquid for fast drying, to prevent feathering and bleeding
- Low colour-to-colour bleed (well-defined diffusion of the ink)
- Low strike-through
- Water- and light-fastness

Unlike most printing methods, the smoothness of the substrate is not of major importance for inkjet printing. Undesired quality differences in inkjet prints have been shown to be the effect of differences in density of the paper (and the corresponding differences in adsorption ability), rather than of differences in smoothness [34].

There are four main categories of paper used in inkjet printing: bond paper, inkjet paper, fine art papers, and coated papers. Bond paper is the plain multi-purpose paper used in laser printers and office copiers. They are usually made of wood pulp, sized with resin. Inkjet papers, which have a slightly better quality than bond paper, have improved surface sizings such as starches, polymers, and pigments. These sizes make the surface of the paper whiter and more receptive to inkjet printing. Fine art papers have been used for watercolours, drawings, and traditional printmaking. The papers are made from 100% cotton rag (alpha-cellulose), and there is no resin sizing or lignin. The fine art papers are usually combined with dye-based inks [25]. Coated inkjet papers are papers that have a receptor coating to aid in receiving the inks. These coatings create a higher colour range, greater brightness and print sharpness. Coatings may include materials such as silica, alumina forms, titanium dioxide, calcium carbonate, and various polymers. These coatings can be categorized as swellable or microporous. Swellable coatings are nonporous, made with organic polymers that expands and encapsulates the ink after it strikes the paper. The coating increases brightness by keeping the colourants from spreading, while protecting the image from atmospheric pollutants. These papers are best used with dye-based inks [35]. Microporous coatings were developed for rapid ink uptake since swellable papers have the disadvantage of slow ink drying, loss of gloss, and curling after printing. Microporous coatings contain small inorganic particles dispersed in a synthetic binder such as polyvinyl acetate or polyvinyl alcohol [36] that create holes in the coating. The ink is absorbed into these holes, which results in faster drying, and prevents the ink from smearing. These papers offer good image quality and can have a glossy or matte finish. They are best used with pigment-based inks [35].

Most inkjet papers sold today are of the multi-purpose type. Typical cost of these range from € 0.008 to € 0.02 per sheet. At the other end of the scale are the coated inkjet papers, which cost € 0.25 to € 1.20. The market is seeking improved performance over basic uncoated grades. These papers would fill the gap between expensive silica-coated papers and the surface sized papers (Figure 8), giving improved quality at an affordable cost [1].

Figure 8. Quality cost matrix for inkjet printing paper.

2.2.1 Surface Sizing

Papers with a low degree of sizing (such as newsprint) absorb ink very quickly; this leads to fibre swelling, which in turn leads to low print quality as well as cockle and curl. A paper with too high a degree of sizing, on the other hand, gives a low penetration of the carrier liquid into the sheet. As a result, the carrier liquid stays on the surface of the sheet, creating drying problems and uncontrolled XY-spreading of the colourant [37]. A highly sized and treated paper (with a Hercules Size Test (HST) value greater than 200 seconds), will perform best for inkjet printing [38-40]. Common surface-sizing agents are starch and polyvinyl alcohol (PVOH). However, sizing does not present a suitable foundation for high quality prints. To reach these levels, a coating is needed.

2.2.2 Inkjet Receptive Coatings

In 1985, when inkjet coating technology was still in its early stage of development, Lyne & Aspler [41] stated that: "Paper made for ink jet printing should have a hydrophilic, high-porosity surface with no macroscopic structure if it is to absorb ink jet droplets quickly and with little spreading, wicking or dye penetration. Papers made with silica coating appear to best satisfy the image quality requirements for ink jet printing with water-based inks. Shortcuts, such as size-press application of thin hydrophilic coatings and/or the use of surfactants, result in markedly poorer print quality". The inkjet receptive coatings used today still build on these fundamental assertions. Conventional coating pigments, such as kaolin, calcium carbonate, and titanium dioxide are not commonly used for inkjet papers, primarily because of the small void fraction available for liquid uptake and the narrow pore diameters for fluid flow [19]. The conventional pigments also require calandering to obtain gloss and smoothness properties, and this reduces the void fraction available for liquid uptake. The three primary ingredients used in most coated inkjet papers today are: mesoporous pigment, polymeric binder, and a cationic additive.

2.2.2.1 Pigments

Silica (SiO_2) is formed from the most common elements in the earth's crust: silicon and oxygen. Silica is a common mineral, existing in range of crystalline and non-crystalline forms. Synthetic silicas have been used in the paper industry since the 1960's due to its positive effects on brightness, opacity, and print quality [42]. In later years specialty silicas (Table IV) have been adopted by manufacturers of inkjet papers.

Table IV. Specialty Silicas Defined [43, 44].

Type of silica:	Description:
Colloidal silica	Finely divided (7-100 nm), non-porous particles of amorphous silica
Fumed silica	Finely divided (5-40 nm), non-porous particles of amorphous silica
Fused silica	Consistent chemistry, high resistance to thermal shock and low thermal conductivity
Silica gel	A porous, amorphous form of silica known for its high degree of internal surface area. Pure and composed of virtually 100% silicon dioxide
High-purity ground silica	Produced from silica sand or soft, friable rocks and is often referred to as amorphous silica
Precipitated silica	A porous, amorphous form of silica composed of >98% silicon dioxide. Forms distinct agglomerates based on primary particles; range in size from 50-100 µm

The types of specialty silica pigment differ mainly in terms of pore volume, pore distribution, and pore diameter. In general, silica has a high internal porosity (providing a large volume for liquid uptake) and a large surface area (in the range of 50 to 1000 m^2/g, available for ink adhesion) [45, 46]. Silica gel and precipitated silica are predominantly used in coated matte finish paper; and fumed silica and colloidal silica are predominantly used in coated gloss finish paper [44, 47, 48].

The coating solids level is a major limiting factor when silica pigment is used due to the viscosity and water absorption problems involved. Silica slurries alone do not flow very well at solids levels above 15% to 20%. Also, silica has a great affinity for water because of its high pore volume, so it forms a paste when water is added until all the voids are filled. Only then does it become sufficiently fluid to be used in coating formulations [49]. As a result of the absorbed water, silica requires a large amount of energy in the drying process. Another drawback of the silica pigments is their high price. Specialty silica pigments sell for € 100 to nearly € 6000 per ton [1, 43].

As alternative to silica the major pigment suppliers have developed specialty engineered pigments. These can be defined as: “a pigment whose particle size, shape, and surface properties have been deliberately and uniquely modified by mechanical, chemical, mechanochemical, thermal or other means to enhance single- or multiple-performance attributes” [1]. The specialty pigments are designed to replace, in total or in part, other more expensive pigments and additives.

The strategy for coatings consisting of these pigments usually follows one or more of the following criteria:

- Pigment that cost less than silica
- Lower binder demand
- Capability to use lower cost co-binder with PVOH
- Lower dependence on cationic additives
- Improved coating solids and rheology
- Capability to coat on-machine at high speed

Examples of specialty modified pigments designed to replace silica are; clays [50-52], calcium carbonates [49, 50, 53-56], precipitated calcium carbonates [57, 58] and zeolite pigment [1]. None have gained widespread commercial acceptance, as of yet [1].

2.2.2.2 Binders

Silica pigments have a very low strength due to their high internal porosity, therefore they require a substantial amount of binder. Typical binders, such as latex or starch, are either too weak in their binding strength, which creates dusting problems, or they interfere with the ink absorption during printing, which results in poor print quality [59, 60]. In coating colours containing silica pigment, PVOH has been found to be the most efficient binder [61-63]. PVOH is believed to form a strong film and to enhance printability. PVOH is primarily characterized by its molecular mass and degree of hydrolysis (the degree to which polyvinyl acetate is converted to polyvinyl alcohol) [64]. The molecular mass determines the coating rheology and the binding power for pigment adhesion, whereas printability and optical density are controlled by the degree of hydrolysis. The degree of hydrolysis also affects the colour rheology and binding power; however, it is less important than the molecular weight [63]. Alternative binders that have been introduced over the last years are cationic starches [65-68] and specialty PVOH [69].

2.2.2.3 Additives

Common additives in inkjet coatings include optical brightening agents (OBA) and dye fixatives: OBAs help to boost the brightness of the coating; dye fixatives, such as poly-DADMAC, ethyleneimine or polyvinylamine, help to attach the anionic dyes in the ink to the coating surface [67, 68, 70]. The cations attract the anionic dye molecules to the very large surface area of the silica pigment. The fixatives are used in small parts (1 to 3 parts per 100 parts dry pigment). The cationic nature of the coating or pigmented surface of an inkjet paper provides charge neutralization between the surface and the anionic dyes. This gives the paper water-fastness properties and it may also enhance optical density and print quality, making it particularly suitable for colour printing.

2.2.3 Coating Methods

The combination of silica pigment, polyvinyl alcohol binder, and cationic dye fixative works quite well for inkjet printing, once the paper is successfully coated. However, the coatings have a relatively poor rheology and very low solids content, which explains why low-speed, off-machine coating lines are usually used for coating inkjet paper. Air knife or roller coaters are the most commonly used methods [65].

2.2.4 Coating Layer Structure of Inkjet Media

The coating structure of an inkjet receptive media ranges from a simple single-layer coating to more complex multi-layered structures, examples are given in Figure 9. Figure 9A illustrates a typical single-coated inkjet paper [71, 72]. A photographic quality inkjet paper is illustrated in Figure 9B. Figure 9C illustrates a transparent inkjet medium [73].

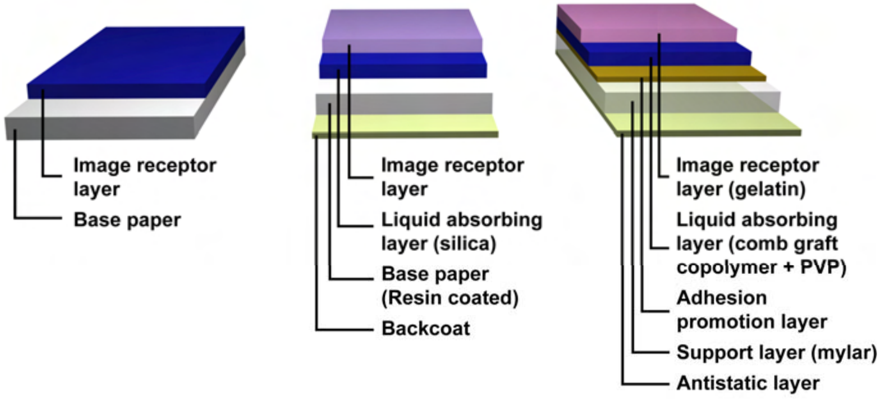


Figure 9. Coating layer structure of different inkjet media.

3. Materials and Methods

3.1 Base Substrate

A pre-coated fine paper with a grammage of 90 g/m^2 was used as the main substrate for the coatings. As a non-absorptive substrate a polymer film was used (Melinex 752, DuPont, 35μm).

3.2 Coating Formulations and Coating

Coating colours were made using a wide range of commercial as well as non-commercial coating chemicals. Pigments used were silica from the Syloid product range (Grace Davison), silica from the Sipernat product range (Degusssa) and specialty carbonates from Omya and Specialty Minerals. The binders used were polyvinyl alcohol from the Mowiol product range (Clariant), polyvinyl acetate from the Mowilith product range (Clariant) and starches from Lyckeby (oxidised potato starch) and Cerestar (modified cationic cereal starch). Various cationic dye fixatives (BASF and Rhom & Haas) and polyvinyl pyrrolidone (PVP) (AWL Scandinavia AB) were also used.

The aqueous polymer solutions contained either 15% PVOH or 30% starch. Coating colours with binder/pigment had a final solids content of 20-25%. Higher solids content are accompanied by viscosities, which are too high for good runnability. The Brookfield viscosities varied from 400 to 2000 mPa·s. The pH was adjusted to pH 8-8.5 higher for coatings containing specialty carbonates. Coating colours were prepared and applied at ambient temperature and humidity. The coating colours were applied to the pre-coated fine paper using a bench-top coater (K Control Coater, RK Coat Instruments Ltd.) with wire-wound rods, marked 0, 2, 3, 4, 5, and 6. At least three coat weights in the interval between 3 and 10 g/m^2 were prepared for each coating colour. The coated sheets were dried for 1 minute in a hot air oven at a temperature of 105 °C followed by conditioning at 23 °C and 50% relative humidity. During the 24 hours prior to printing, the coated sheets were kept under a light pressure in order to counteract the curl that tended to develop due to the one-sided coating. The conditioned and pressed sheets were weighed to determine the coat weight (using the conditioned base paper as reference).

3.3 Printers and Ink

3.3.1 Printers and Printing Considerations

There is a veritable "jungle" of printers, inks, and substrates available on the market; and, each printer has numerous paper and quality settings. Studies have shown that a single printer may produce prints on various grades of paper with a 20-40% difference in print quality (colour density). These differences are so substantial that quality variations are easily detected even by an untrained observer [34]. Other studies have shown that a significantly higher print quality can be achieved using a good printer on plain paper rather than with a poor printer on photographic quality paper [74].

In initial trials, the following printers were evaluated: Canon S520, Epson Stylus Photo 890, Epson Stylus C82, Hewlett Packard 870 Cxi, Hewlett Packard 930 C, Hewlett Packard 970 Cxi, and Lexmark Z5. The same OS and graphics software were used throughout. The primary consideration was print quality, but printing speed, ink drying and water-fastness were also considered.

Figure 10 shows the colour gamut areas obtained with two of the printers, using five different papers and two different paper settings in the printer driver (plain paper and inkjet paper). The figure indicates that there is a benefit in using a combination of paper and printer by the same brand. There can, however, be a considerable difference in print quality when a printer is used with a variety of printer settings.

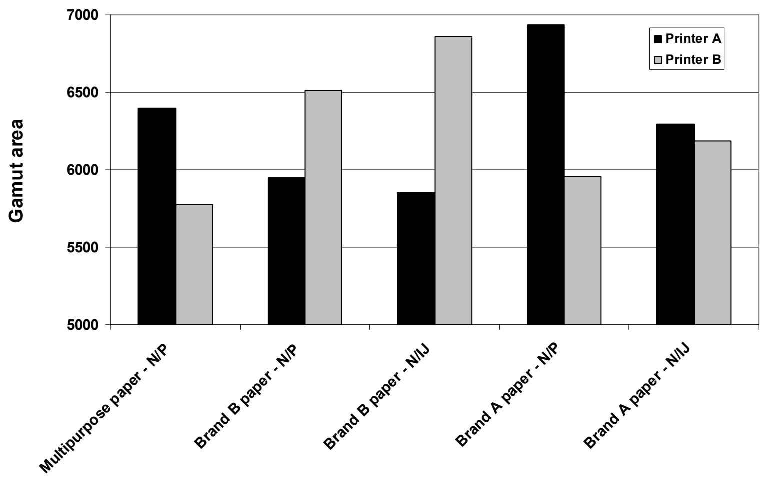
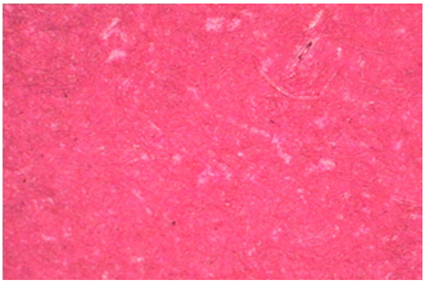
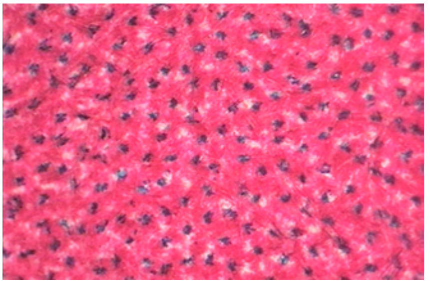


Figure 10. Multi-purpose and pigmented inkjet papers (A and B) printed with Printer A (using dye colours) and printer B (using pigmented colours). (N = normal print quality setting, P = plain paper setting and IJ = inkjet paper setting).

Figure 11 shows another difficulty of controlling the final print. Here a patch of solid magenta (100% M) was defined in the graphics software. As can be seen, Printer A produces a solid magenta print, whereas Printer B produces a magenta print with a raster of blue dots.

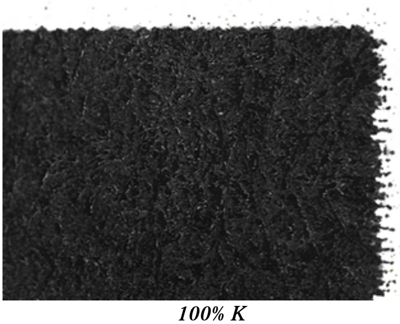




Printer A ***Printer C***

Figure 11. Colour definition of two different printers using dye-based colours (print patches 2 x 3 mm).

Further examples of difficulties in print control are presented in Figure 12, where a black print patch was defined in two ways in the graphics software: 100% K and 300% CMY. However, printer A, using dye-based colours and a pigmented black, produced two prints with 100% pigmented black. Figure 12 also shows another important feature worth considering when designing test forms for print evaluation; since the printhead traverses the paper from left to right in the figure, there is a much rougher edge on the right-hand side of the printed patch than on the top of it.



100% K ***300% CMY***

Figure 12. Colour definition of Printer A (print patches 2.2 x 3 mm).

Although these observations do not necessarily imply a print with lower quality, they nevertheless show that WYSIWYG is not really applicable in inkjet printing. Thus, it is important to be aware of unexpected alterations in the printer drivers when setting up a print evaluation method. The final choice for main printers to be used in the tests fell upon the Hewlett Packard 970 Cxi thermal printer (using dye-based colours (C6578) and pigmented black (51645) and the Epson Stylus C82 piezoelectric printer (using all pigment-based inks (T0321 and T0422-T0424)). These printers showed compatibility with a wide range of papers, and prints produced were in agreement with the graphics software. Furthermore, these printers enable both dye-based and pigmented inks to be evaluated.

3.3.2 Printing Conditions

It can be concluded that there are many factors which influence the final print quality. The relative importance of these is difficult to predict and the full series of coated sheets (presented in Paper I-V) has therefore been printed using the same PC-OS (Windows 2000 Professional), graphics software (MicrograFX Designer version 7.1), printers (HP 970 Cxi and Epson Stylus C82), printer drivers (the former being version 4.3 and the latter being version 5.41), and printer settings (plain paper quality and normal print quality). The printing was carried out at 23 °C and 50% relative humidity.

3.4 Evaluation

What largely defines the applicability of a coating layer is the print quality of the text and/or graphics printed on it. The coated sheets were primarily evaluated in terms of print density, colour gamut, and various measurements of bleeding, such as line width and blurriness. Microscopy analyses were carried out in order to study the coated substrate (both the surface and cross sections). Coating coverage was analysed using Electron Spectroscopy for Chemical Analysis. Micro drop absorption tester was used to study liquid absorption.

3.4.1 Instrumental Measurements of Print Quality

Colour gamut measurements (the range of colours that can be produced by a given colour reproduction system) and various measurements of bleeding, such as line width (the uniform spreading of a printed line) and blurriness (the non-uniform spreading of a printed line) were carried out on prints on coated sheets. The test form used is shown in Figure 13.

Colour densities and L^*, a^*, b^* values were measured on the 7 blocks (25 x 25 mm) printed with 100% cyan, magenta, and yellow, 400% black and 200% red, green and blue, using an X-Rite 938 spectrodensitometer. The gamut value was obtained from the a^* and b^* values of the 100% C, M, and Y blocks together with those for the secondary (200%) red, green and blue (R, G and B) blocks, and was calculated as the area of the (a^*, b^*)-hexagon. This definition of gamut (the gamut area) represents a simplified top-projection of the full 3-dimensional gamut volume in (L^*, a^*, b^*) space obtained by taking into consideration the corresponding L^* values (Figure 14).

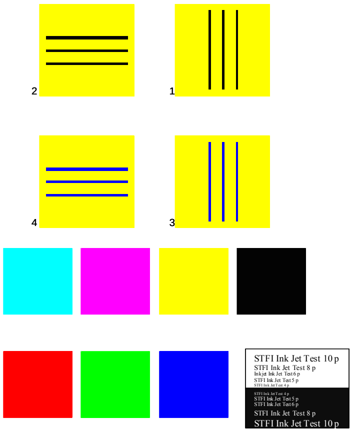


Figure 13. The print test form.

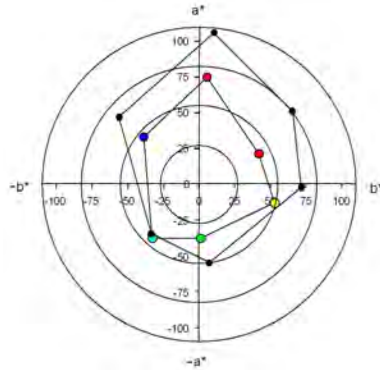


Figure 14. Gamuts on a multipurpose paper (large circles) and an inkjet photo paper (small black circles).

The colour-to-colour bleed was measured on both 400% black and 200% blue lines on a 100% yellow background (labelled 1-4 in Figure 13) using a high resolution scanner (Agfa Duoscan T2500 with a resolution of 2500 dpi) followed by image analysis using Matlab and suitable data-processing to give a measure of sharpness (*STFI InkJet Test*). The image analysis process converts scanned images to grey scale values (GSV), calculates a histogram for each line/background combination, automatically assigns threshold GSV's from these, thresholds the GSV image to a binary image, and finally calculates the various geometrical measures of this bounding contour.

Line width (in mm) is defined as being the sum of the intended width of the line and the extra contribution, due to its uniform spreading to the threshold GSV value. Blurriness (in µm) is the mean separation distance of the sub-contours corresponding to 25% and 75% decrease in GSV from its line interior to the threshold value. Blurriness thus characterises the distinctness of the transition from line to background. In both cases, a smaller value indicates greater sharpness. For ease of presentation, the final results of bleeding are condensed by averaging over the 2 colours and 2 orientations. Measurement data for the three coat weights of each sample were interpolated (linearly) to a coat weight equal to 8.5 g/m^2.

3.4.2 Perceptual Print Quality

Print quality is an individual experience. The instrumental measurements must relate to the subjective perceptual impressions in order to be meaningful. Details of the perceptual studies are presented in Paper I. There is a strong correlation between the two. The smallest difference in print quality that visually could be discerned was approximately 350 units in gamut area, 1.6 μm in blurriness, and 0.002 mm in line width.

3.4.3 Optical Microscopy

A light microscope has been used to enable photomicrographs of cross sections of coated and printed substrates to be obtained. Dry samples were infiltrated with epoxy resin, and mounted into a mold which was left to cure in 70 ºC for 8 hours. As the inkjet inks are water soluble, the cutting had to be performed under dry conditions with a cutting speed of 1 mm/s. The cutting thickness was 1-2 μm. Images has been obtained using a Zeiss Axioplan 2.

3.4.4 Environmental Scanning Electron Microscopy (ESEM)

ESEM was used to show the surface structure of the (non-printed) coatings. Electronmicrographs were obtained using an ElectroScan 2020.

3.4.5 Electron Spectroscopy for Chemical Analysis (ESCA)

ESCA was used to detect PVOH coating coverage. The samples were analysed using an Al X-ray source for the high-resolution carbon spectra and an Mg X-ray source for wide and detail spectra. The analysis area was less than approximately 1 mm^2. ESCA spectra were recorded using a Kratos AXIS HS X-ray photoelectron spectrometer.

3.4.6 MicroGloss

The STFI-Packforsk MicroGloss test was used to quantify disturbing gloss variations on the coated sheets. The instrument uses a 20º/20º degree setup for camera and illumination when acquiring images. These are subsequently frequency analysed to give gloss variations at small, mid and large scales [75].

3.4.7 Micro Drop Absorption Test (MicroDAT)

MicroDAT was used to study ink-coating interactions. The instrument is described in detail in Paper V.

4. Effect of Coating Formulation on Inkjet Printability

As an initial practical approach toward identifying the important properties of coating components that govern printability, coatings consisting of silica, polyvinyl alcohol (PVOH), and dye-fixation agents was studied. The ambition was to clarify the role of different paper coating components such as pigments, binders, and additives, as well as the importance of structure and specific surface area. The focus is on high quality mineral-coated papers, however, not photographic quality, in combination with aqueous-based inks.

4.1 Coating Structure of Printing Papers

A number of different commercial inkjet papers i.e. multi-purpose (universal office), improved inkjet, synthetic silica-coated, and photographic quality papers were evaluated with respect to gamut area, blurriness, and line width. The pre-coated fine paper, top-coated with various laboratory coatings, was also included for comparison. Results for a selection of papers are shown in Figure 15. High print quality is represented by the upper left-hand corner (i.e. high colour gamut and low blurriness), while low quality is represented by the lower right-hand corner. Photographic quality inkjet papers and inkjet papers coated with special coatings (normally synthetic silicates and polyvinyl alcohol) are found in the high quality region; whereas, the offset papers present the poorest print quality.

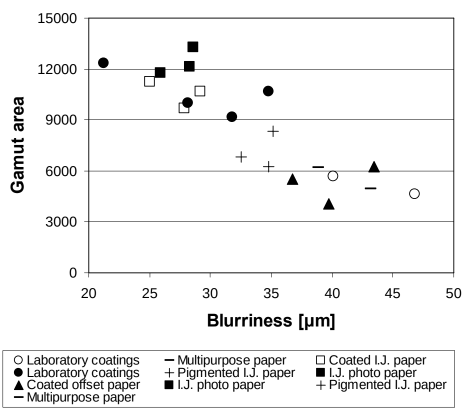


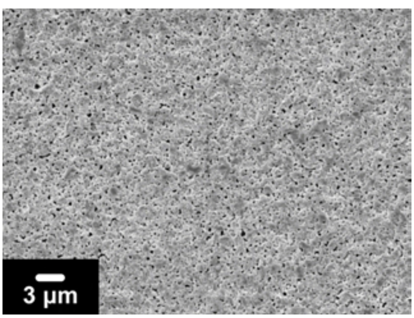
Figure 15. Gamut area and blurriness for commercial and laboratory-coated papers. Filled circles represent laboratory coatings with PVOH, unfilled without.

A great spread in print quality is expected, since a vide range of coating pigments are used (Table V); consequently, the coating structures of the various papers differ greatly, as can be seen in Figure 16.

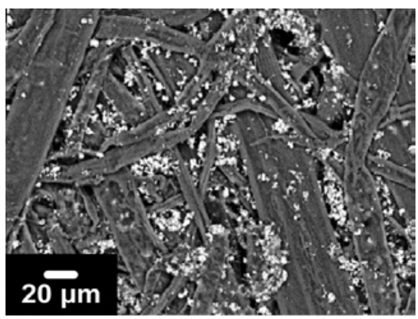
Table V. Characteristics of Pigments Used in Paper Coatings [76].

Pigment	Refractive index	Particle density [g/cm^3]	Surface area [m^2/g]	Pore volume [cm^3/g]
Clay	1.57	2.6	16	
GCC	1.55	2.7	11	
PCC	1.55	2.9	25	
Titanium dioxide	2.72	4	30	
Calcined clay	1.57	2.6	19	
Precipitated silica	1.46	0.5	400	1.5
Silica gels, med. PV	1.46	0.6	400	1.2
Silica gels, high PV	1.46	0.4	300	2
Fumed silica	1.46	2	300	
Colloidal silica, small	1.46	2	400	
Colloidal silica, large	1.46	2	50	

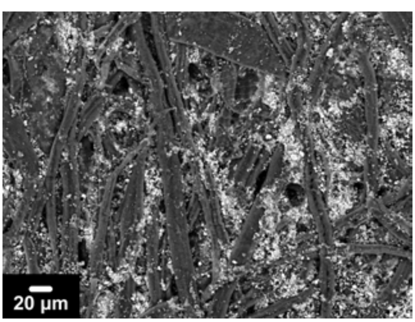
The pigments used for coated offset papers are mainly calcium carbonates and clay. They are small (predominantly less than 2 µm in diameter) and non-porous (Figure 16A). Fully coated inkjet papers, however, have larger pigments (~5-10 µm in diameter) and are porous (~1-2 ml/g). The SEM image shown in Figure 16D clearly shows that the inkjet coated paper has a much more open structure with very large pores and large pigments. The inkjet paper coating actually has a bi-modal pore size distribution with large pores between the pigment particles and fine pores within the pigment particles. This is an interesting structural feature of the synthetic silicas; they have a very large internal surface area that originates from micro-pores within the particle.



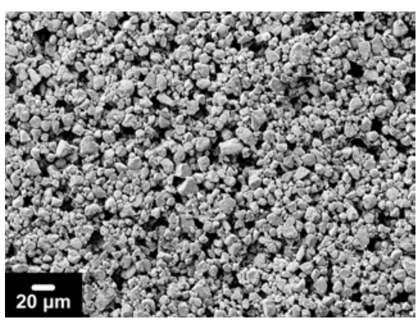
A) Coated paper for offset printing.



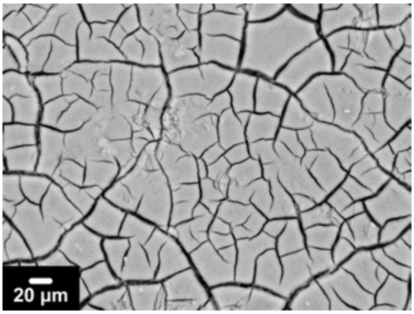
B) Multipurpose (universal office paper).



C) Pigmented inkjet paper.



D) Fully coated inkjet paper.



E) Photographic quality inkjet paper.

Figure 16. SEM micrographs of various printing papers.

Photographic quality paper normally has a top coating consisting of an emulsion polymer that develops "micro-cracks" (Figure 16E), which may enhance ink/coating interaction. The low blurriness of the coated inkjet papers is probably due to the fast ink absorption, which is in turn due to the large pores in the structure. Once the liquid is located in these large pores, it starts to be absorbed by the small pores of the individual particles. This is a slow process. The high colour gamut of the coated inkjet papers may be due to at least two factors: an efficient separation of colourant close to the surface and the low refractive index of the silicate pigment. Silicate has a refractive index of 1.46-1.48 [77], while calcium carbonate and clay have refractive indices of 1.55 and 1.57, respectively. Thus, colourant will be shielded much more efficiently by the minerals used in offset papers than by silicates [46].

In order to gain an overview of the effect of various components in the paper coating, laboratory coatings were prepared and evaluated according to the procedure described in *Materials and Methods*.

4.2 Binders in Inkjet Receptive Coatings

Binders are used primarily to bind coating pigments together, and to anchor the coating to the substrate. However, the binders used in inkjet coatings also contribute highly to the coating's print quality [59, 63, 78]. The most commonly used binders in inkjet receptive coatings are PVOH and (cationic) starch, both with a good binding strength and a proven high impact on the colour gamut [62, 66, 79].

It has been shown [8] with light microscopy, that the dye which makes up only a small percent of the total inkjet ink, poorly penetrates a PVOH or starch film. Instead, the dye is concentrated in the top region of the binder film. This is shown in Figures 17 and 18. The drawbacks with the PVOH coating are their high gloss variation and prolonged ink drying time.

However, the polymer film formed by PVOH or starch may be regarded not only as a binder but also as a gamut enhancer.

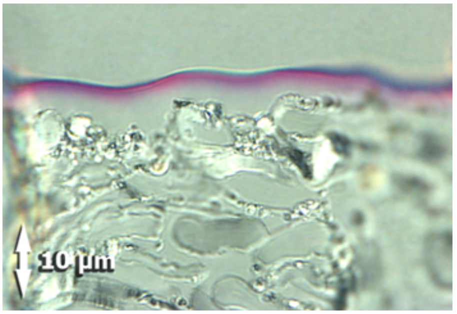


Figure 17. Photomicrograph of a cross-section of a PVOH coated paper after printing.

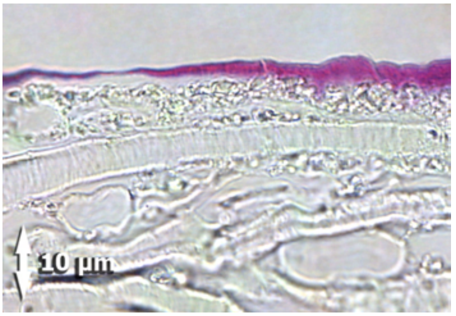


Figure 18. Photomicrograph of a cross-section of a starch coated paper after printing.

4.3 Pigments in Inkjet Receptive Coatings

The general effect when silica is introduced into a coating with PVOH or starch is a reduction in gamut area and an improvement in the sharpness (this is illustrated in Figure 19). The reason for the decrease in gamut is obvious: the dye is incorporated into a layer with the pigment. The decrease is moderate due to the low refractive index of the pigment. The reason for the improvement in sharpness is probably due to the coating structure and absorption rate. The droplet will be quickly absorbed into the large pores between the silica particles; this will reduce lateral spreading and surface wicking.

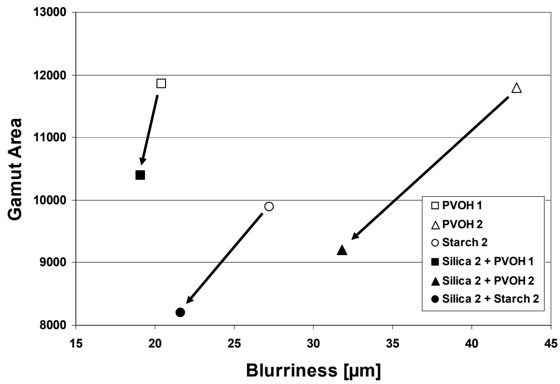


Figure 19. Gamut area and blurriness on PVOH and starch coatings with and without silica pigments.

Coatings with two different silicates and two different PVOH's were studied. The main difference between the two silicates was the mean particle size. Silica 1 had a particle size of 5.3-6.3 µm, while silica 2 had 7.6-9.2 µm. The PVOH's were chosen to represent good and poor sharpness, as indicated by earlier work with pure PVOH coatings [79]. The data obtained on pure coatings are given in Table VI along with chemical properties of the products.

Table VI. Data for PVOH's Included in the Study.

Properties	**PVOH 1**	**PVOH 2**
Viscosity [mPa·s]	26	28
Degree of hydrolysis [%]	88	99
M_w [kg/mol]	160	145
Print quality on pure coatings		
Gamut area	11852	11802
Blurriness [µm]	20.4	42.8
Line width [mm]	1.115	1.225
Water contact angle [°]	58	38

The main difference between the two polymers was the degree of hydrolysis. PVOH 2 was almost fully hydrolysed and, thus, quite hydrophilic. It also showed poor sharpness [79].

The print quality of coatings with a binder content of 40 to 100 parts is given in Figures 20-22 (where ∞ shows the pure PVOH coatings). As expected, the gamut area increased with an increasing amount of PVOH. Furthermore, there is a tendency for the pigment with larger particle size to give higher gamut.

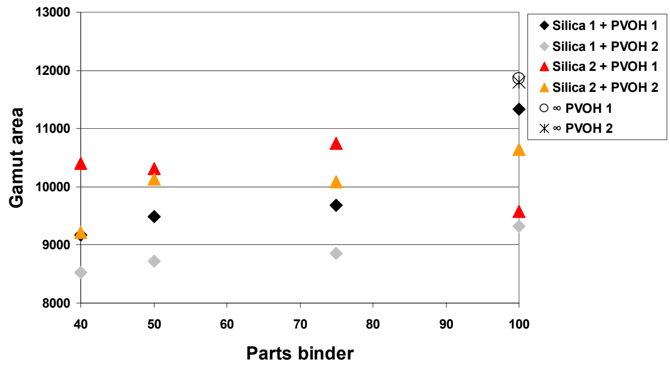


Figure 20. Gamut area on PVOH-silica coatings.

The lower gamut area obtained with the finer particles is probably associated with the larger number of available pores per coating area, which gives the ink a greater possibility of sinking into the coating. At a binder level of 100 pph, the difference in results could be explained by the fact that the large surface area of the silica pigments is no longer available to interact with the ink if the PVOH coverage dominates the coating surface.

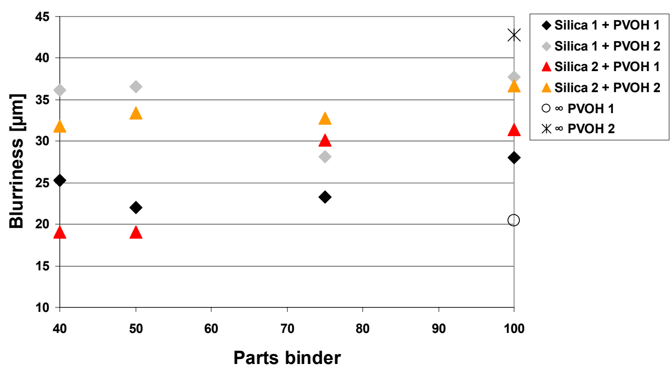


Figure 21. Blurriness on PVOH-silica coatings.

The two pure PVOH coatings showed extreme blurriness values: 20.4 µm for PVOH 1 and 42.8 µm for PVOH 2. Figure 21 clearly shows that a PVOH, which tends to give high blurriness as pure coatings (∞), also gives silicate coatings with a high blurriness although to a somewhat lower extent. In the same way, a PVOH that gives low blurriness as a pure coating tends to give silica coatings with low blurriness, but the low blurriness is only maintained at a low PVOH content. At a high content, the blurriness increases, although not to a very high value. The reasonable explanation for these observations is that a low blurriness of the pure PVOH film is inherited by the silicate coating, but that the structure formed by the coating also has a strong impact.

Results similar to those for blurriness were obtained for the line width measurements (Figure 22). The PVOH with a high line width also gave silicate coatings with a high line width, although it was slightly lower than that of the pure PVOH coating.

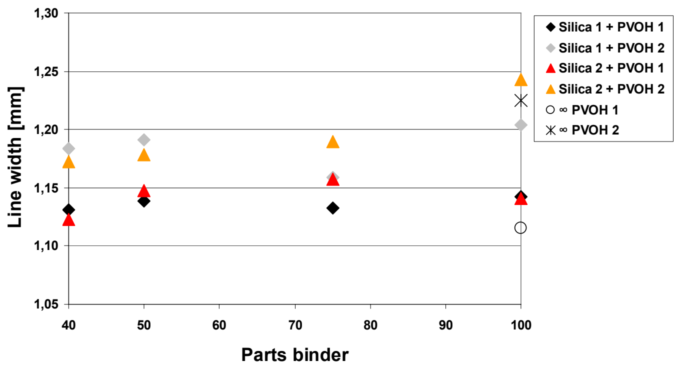


Figure 22. Line width on PVOH-silica coatings.

In general, there are no printability benefits associated with the use of more than 40 pph binder. The improvements in gamut gained from an increase in the amount of binder are secondary to the loss of sharpness. It can be concluded that the best print quality was observed for silica in combination with PVOH 1. As this had the lower degree of hydrolysis (i.e. less hydroxyl-groups attached to the hydro-carbon chain of the PVOH), it also tended to give a coating colour with a lower viscosity. Consequently, this formulation was chosen for further studies of possible printability improvements.

4.4 Cationic Additives in Inkjet Receptive Coatings

Cationic poyelectrolytes are often included in the formulation of coating colours for inkjet papers. In literature, they are often referred to as *fixation agents*. Since dye molecules have a negative net charge; one may expect that the anchoring of these molecules to the coating will be enhanced by an electrostatic interaction with the cationic fixation agent and ionic bonds may be formed. The fixation agents may promote gamut area, sharpness, and water-fastness [67, 70] by electrostatic interaction. They also affect the structure of the coating, since cationic polyelectrolytes are efficient flocculants; this may, in turn, affect the print quality. It has been reported [80] that coated surfaces containing a cationic additive (poly-DADMAC) show surface irregularities. However, this is not known to reduce ink bleed. In [80] ink bleed is presented as the non-uniform spreading of a printed dot, resembling the measurement of line width used in this report. Figures 23-25 show the effect of an addition of 2 pph cationic additive on gamut area, blurriness, and line width. The effect on gamut area is quite moderate. The value increases or decreases in general with 200-500 units. It was not possible to determine whether or not this cationic additive enhances the retention of dye molecules in the top layer of the coating. The small effect was more likely to be because of a change in the coating structure, due to the flocculation power of the polyelectrolyte.

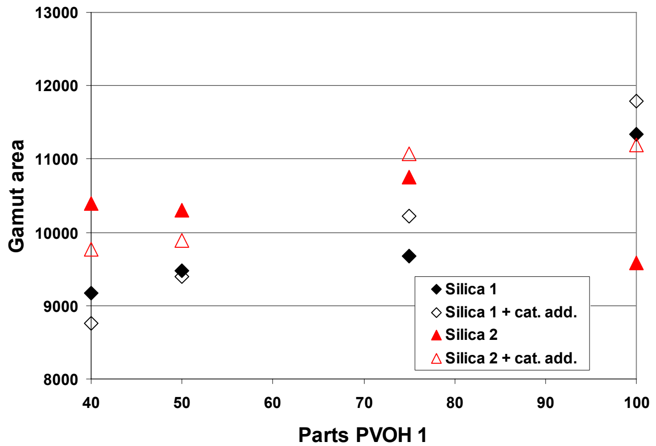


Figure 23. Gamut area on PVOH-silica coatings with and without cationic additive.

The effect on blurriness and line width was somewhat greater for most of the coatings; however, there was no clear trend. The cationic additive may increase or decrease the sharpness depending on the amount of PVOH. This again suggests that the effect of the cationic polyelectrolyte is due to a change in coating structure, and not to any electrostatic interaction. It is not logical that an increased amount of cationic charges would reduce sharpness if the electrostatic interaction were important.

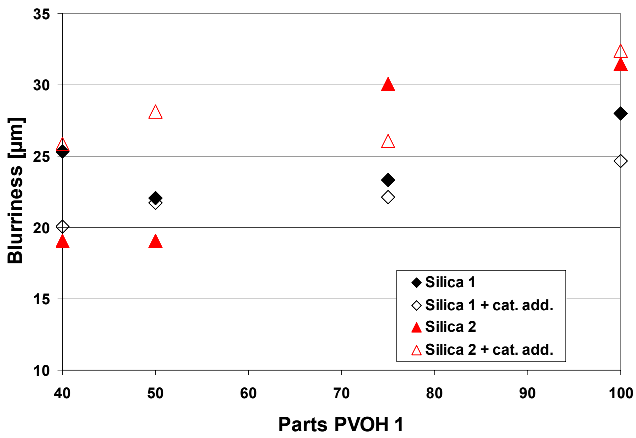


Figure 24. Blurriness on PVOH-silica coatings with and without cationic additive.

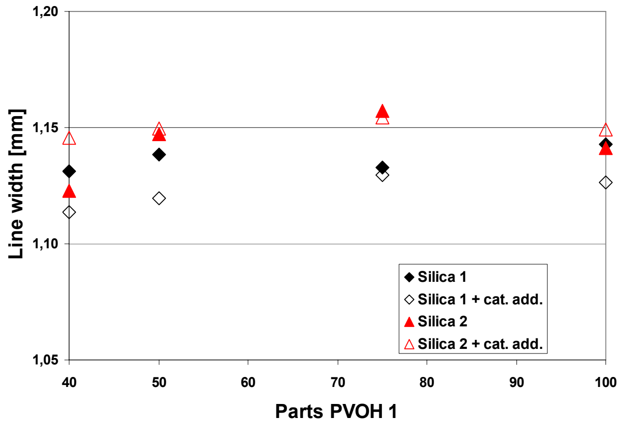


Figure 25. Line width on PVOH-silica coatings with and without cationic additive.

To further investigate the printability of a PVOH-silica coating, a series of additives used to improve the dye-binding capacity were examined. To aid dye retention at the surface, two types of cationic additives and two types of polyvinyl pyrrolidone (PVP) were used. As with the cationic additives, the PVP's have good dye-binding capacities and contribute to improved water-fastness of the coatings. Moreover, PVP also has good film forming abilities [81]. PVP 1 had a cationic charge, whereas PVP 2 was nonionic. Silica 1 with 100 pph PVOH 1 was used as a base coating, as this coating gave the best combination of high gamut area and high print sharpness.

Figure 26 shows the results of the gamut area measurements. The base coating gave a gamut area of 11333 (which is a similar value to those of high quality inkjet papers). However, some further improvements were still achieved with an increased gamut for all but one of the coatings. For the cationic additives, there was no benefit in using two parts rather than one. For the PVP 2, there was a decrease in gamut area, probably due to the lack of cationic charge.

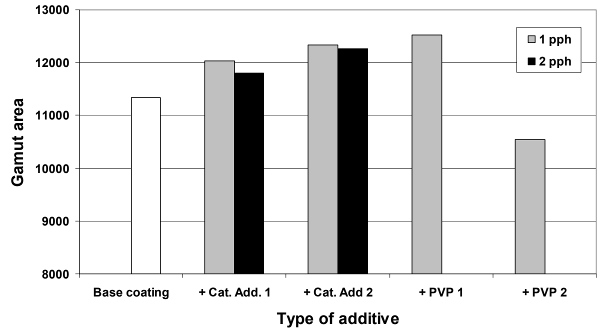


Figure 26. Gamut area on PVOH-silica coatings with additives.

Blurriness is shown in Figure 27. As observed with regard to the gamut, there was no benefit in using more than one part of cationic additive. The coating with two parts of cationic additive 2 and the cationic PVP (PVP 1) gave a higher blurriness than the base; whereas, the nonionic PVP (PVP 2) gave the lowest blurriness. It was, therefore, concluded that blurriness is probably not affected by the charge of the coating.

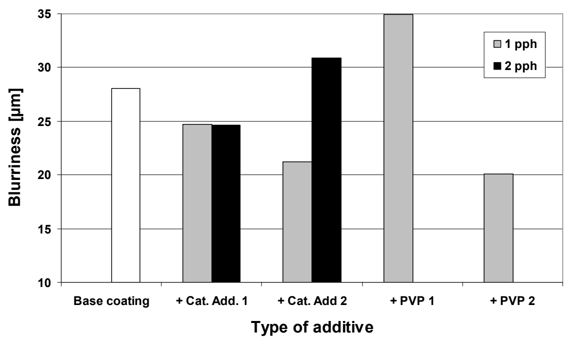


Figure 27. Blurriness on PVOH-silica coatings with additives.

The line width measurements are shown in Figure 28; here, there is an improvement in print sharpness for all the coatings. Cationic additives were, once again, most effective at the lower addition levels. For the PVP's the conditions were inverse of the blurriness measurements, with PVP 1 showing lowest line width and PVP 2 the greatest.

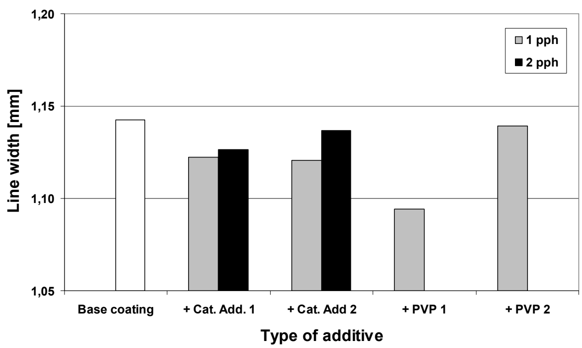


Figure 28. Line width on PVOH-silica coatings with additives.

4.5 Summary

PVOH-coated samples all presented an excellent colour gamut, which is likely as a result of good film-forming capabilities. The sharpness was also good; however, the coatings suffered from high gloss variation and slow ink drying. With the addition of pigment, a new structure is formed with large pores in and between the pigments, and a macro-roughness generated by the large particles. The inkjet droplets can quickly penetrate into the large pores, and the time for surface wicking is reduced, which is beneficial for the blurriness. However, the macro-roughness promotes bulk spreading in the coarse surface structure; this tends to increase the line width. Finally, the ink ends up within the coating and the colourant is partly shielded by the particles; this reduces the gamut area to some extent. Additives such as cationic polymers and PVP can further improve the print quality. The addition of a cationic additive showed an overall positive effect of gamut area. However, it did not always prevent lateral ink spreading. It is suggested that blurriness is a surface wicking that is greatly determined by the micro-structure of the substrate [82], while line width is a bulk spreading that is promoted by a hydrophilic substrate and perhaps also by a slow absorption by the underlying substrate and/or ink.

5. Summary of Appended Papers

5.1 Inkjet Print Quality Measurements - Correlation Between Instrumental and Perceptual Assessments (Paper I)

Inkjet print quality can be quantified in various ways, the most important ones being colour reproduction and print sharpness. The aim of this study was to investigate how well these instrumental print quality measures correlate with the subjective print quality perceived by a panel of human observers.

The first phase of the study consisted of instrumental measurements with STFI InkJet Test on 38 different types of paper. The second phase consisted of a perceptional study where inkjet prints on a selected range of papers were evaluated visually by a test panel. The results show that there are strong correlations between both the colour gamut and print sharpness measurements, and the visual experience. The smallest difference in print quality that could be visually discerned was approximately 350 units in gamut area, 1.6 µm in blurriness and 0.002 mm in line width.

5.2 Influence of Polyvinyl Alcohol on Inkjet Printability (Paper II)

In this paper, the inkjet printability effects associated with PVOH in a coating layer were investigated using 10 different PVOH (with varying degrees of hydrolysis and molecular masses). The sheets coated solely with PVOH displayed excellent gamut values, and the majority also showed a better print sharpness than the uncoated substrate (pre-coated fine paper). A significant increase in colour gamut was observed even at low coat weights, as can be seen in Figure 29.

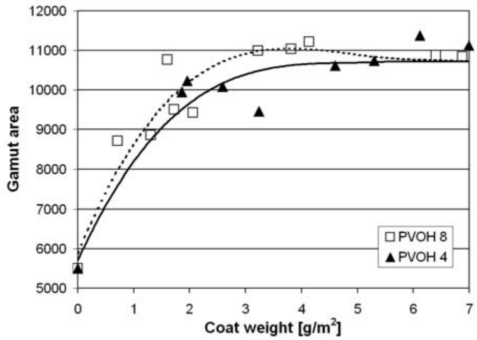
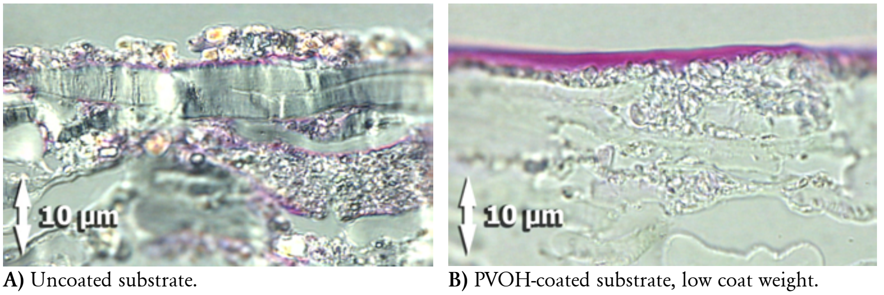


Figure 29. Gamut area as a function of coat weight for two different PVOH grades.

The excellent gamut values were due to the good film-forming characteristics of the PVOH, which was shown by ESCA and light microscopy (Figure 30). The PVOH layer acts as a membrane that separates the dye from the ink carrier liquid. ESEM analyses showed the complexity and variation of PVOH surface structures, which probably explains the fact there was a wide scatter in the colour-to-colour bleed results.



A) Uncoated substrate. **B)** PVOH-coated substrate, low coat weight.

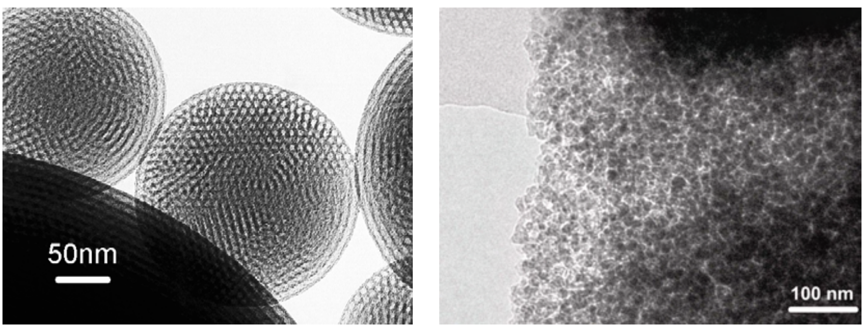
Figure 30. Photomicrographs of cross-sections of coating layers printed with water-soluble magenta ink.

The drawbacks of using PVOH as the sole coating agent are the high gloss variation (2-8 times greater than that of commercial inkjet papers), the prolonged ink-drying time, and the fact that the pigmented ink in large solid printed areas tended to flocculate, resulting in a cracked print with low optical density.

5.3 Surfactant-Templated Mesoporous Silica as a Pigment in Inkjet Paper Coatings (Paper III)

In this paper, two surfactant-templated mesoporous silica pigments were studied with respect to coating colour rheology, coated paper structure, and binder demand, and inkjet printability.

Two types of novel surfactant-templated mesoporous silica pigments with small pores (2.6 and 5.6 nm, respectively) and narrow pore size distributions were investigated, and were compared to a typical commercial silica gel with larger pores (~15 nm) and a broader size distribution. The silicas were used in combination with two PVOH's, having two different degrees of hydrolysis (partial and full) and at two levels of addition (30 and 80 pph). The silica gel pore structures are more randomised than those of the surfactant templated silicas. This is apparent from the sponge-like appearance of open interconnected cells as shown in Figure 31.



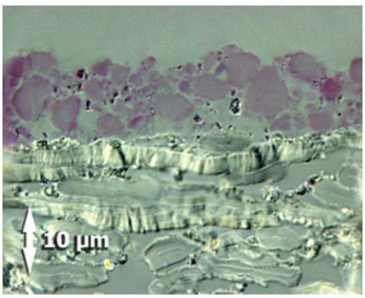
A) Templated mesoporous silica. **B)** Silica gel.

Figure 31. TEM-micrographs showing the internal pore structure of silicas.

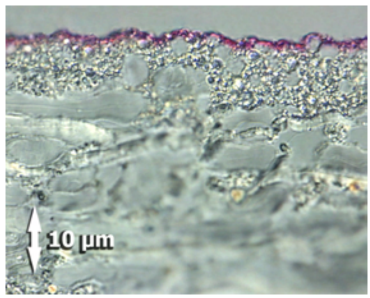
The binder demands of the various mesoporous silica pigments were strongly related to their pore size distributions. The silica gel with large pores required two to three times the amount of binder required by the surfactant-templated silica pigments with small and monodisperse pores. This finding is attributed to the significant penetration of PVOH binder into the larger pores in the silica gel. This binder penetration also reduced the effective internal pore volume available for rapid drainage of the ink vehicle. Thus, it is necessary to consider not only the internal pore volume of the pigment, but also the relationship between the pigment's pore size distribution and the properties of the binder in order to formulate an inkjet paper coating. The novel surfactant-templated mesoporous silica pigments allowed a more efficient use of binder, in terms of both surface strength and inkjet print quality.

5.4 Colourant Migration in Mesoporous Inkjet-Receptive Coatings (Paper IV)

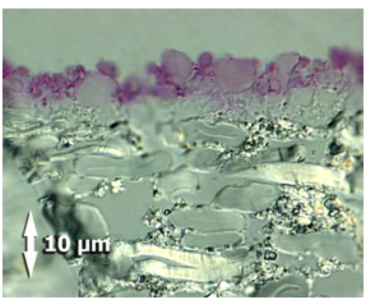
The focus of this study was on inkjet colourant migration in mesoporous coatings, and its relation to print quality. The influence of factors such as coating pigment type, binder concentration, and ink composition on printability were assessed by microscopy and optical print quality measurements. The results obtained indicate that pigments with large pores required more binder than pigments with smaller pores, and that this reduces the internal pore volume for ink carrier liquid uptake, which also reduces gamut area. For the small-pore silica, 30 pph binder was adequate for ink holdout, whereas the silica gel with a larger pore size required two to three times more binder (Figure 32).



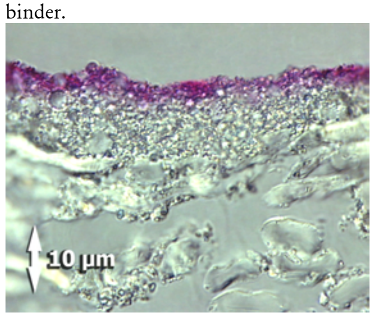
A) Silica gel with 30 pph binder.



B) Surfactant-templated silica with 30 pph binder.



C) Silica gel with 80 pph binder.



D) Surfactant-templated silica with 80 pph binder.

Figure 32. Photomicrographs of cross-sections of inkjet-printed coating layers. The cross sections display samples printed with (water-soluble, dye-based) magenta ink.

With all pigment types, a partially hydrolysed PVOH gave the best print quality, and also sufficient binding strength. The print quality was also influenced by the choice of ink. In general, a dye-based ink gave the largest gamut area, while a pigment-based ink gave the best print sharpness. Cross-section micrographs showed that both types of ink penetrate the inter-particle voids in the coating. The dye-based inks also penetrate the pores of the silica, whereas pigment-based ones reside on the surface.

5.5 Using the Micro Drop Absorption Tester (MicroDAT) to Study Droplet Imbibition and its Effect on Inkjet Print Quality (Paper V)

In this study, a laboratory scale microscopic drop absorption test equipment (MicroDAT) was developed (shown schematically in Figure 33).

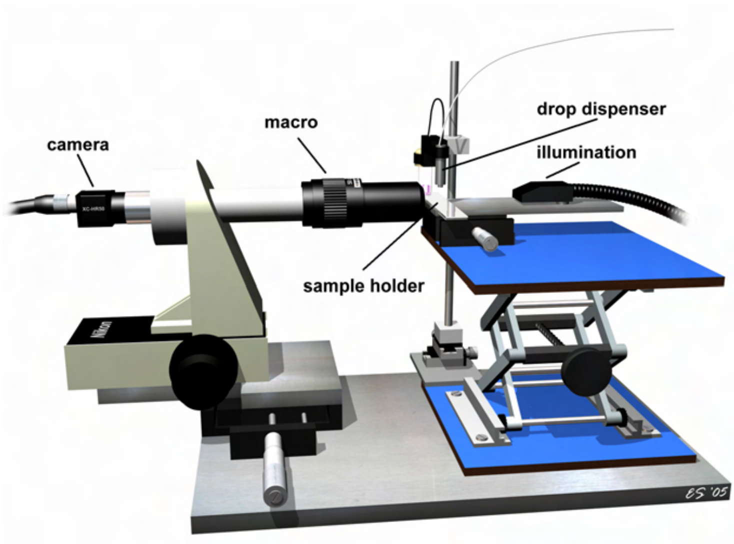


Figure 33. Schematic view of the MicroDAT instrumental set-up.

Unlike many existing droplet absorption measurement devices, the MicroDAT has working conditions similar to those in an inkjet system; it can dispense a wide range of liquids with high velocities and droplet sizes down to 35 pl. The impact and spreading of droplets can be observed; the equipment measures droplet contact angle, height, and diameter for a duration of up to 8 seconds.

The droplet absorption rate was studied for porous and non-porous recipients. Initial results indicated that the MicroDAT is a useful tool for predicting print quality. The conditions preferable for dye-based inks were found not to be valid for pigment-based inks where a high carrier liquid absorption rate gave the highest optical density, but the lowest print sharpness.

6. Conclusions

The main results from this study can be summarised as follows:

- What largely defines the applicability of an inkjet receptive coating is the print quality of the text and/or graphics printed on it. Among the most important inkjet print quality factors are colour reproduction and print sharpness. Print quality is an individual experience. The instrumental measurements must relate to the subjective perceptual impressions in order to be meaningful. Studies showed a clear correlation between the two. Just noticeable differences for various print quality measurements were obtained.

- Papers coated solely with binders used in inkjet receptive coatings (PVOH or starch) presented excellent gamut values and a better print sharpness than the uncoated substrate. The significant increase in colour gamut for the PVOH was observed even at low coat weights (3-4 g/m^2), due to the good film-forming characteristics observed by light microscopy and ESCA analysis. ESEM analyses showed the complexity and variation of PVOH surface structures, and this probably explains the wide spread in the colour-to-colour bleed results. Pure PVOH coatings produced a surface with high gloss variations (2-8 times greater than that of commercial inkjet papers), prolonged drying time, and cracked prints when using pigmented inks.

- When an amorphous silica gel pigments (with large pores and broad pore size distribution) was used in combination with binder, a new structure is formed: with large pores in and between the pigments, and a macro-roughness generated by the large particles. The inkjet droplets can quickly penetrate into the large pores and the time for surface wicking is reduced, which is beneficial for the blurriness. However, the macro-roughness promotes bulk spreading in the coarse surface structure, and this tends to increase the line width. Finally, the ink ends up within the coating and the colourant is partly shielded by the particles; this reduces the gamut area to some extent. Additives such as cationic polymers and PVP can further improve the print quality. The addition of a cationic additive saw an overall positive effect of gamut area. However, it did not always prevent lateral ink spreading.

- The binder demand of silica pigments was strongly related to their pore size distributions. Silica gel (with large pores and a broad pore size distribution) required two to three times the amount of binder required by novel surfactant-templated mesoporous silica pigments (with small pores and narrow pore size distributions). These findings were attributed to the significant penetration of PVOH binder into the larger pores in the silica gel. This binder penetration also reduced the effective internal pore volume available for rapid drainage of the ink vehicle so the surfactant-templated pigments not only required significantly lower amounts of binder, but they also gave a better print quality than the commercial pigment.

- Print quality of inkjet receptive coatings is influenced by the choice of ink colourant. In general, a dye-based ink gave the largest gamut area, whereas a pigment-based ink gave the best print sharpness. Cross-section micrographs showed that both types of ink penetrate the inter-particle voids in the coating. The dye-based inks also penetrate the pores of the silica, while pigment-based ones reside on the surface.

- In order to be able to study ink-coating interactions in inkjet printing-like conditions, a laboratory scale microscopic drop absorption test equipment (MicroDAT) was developed. This can dispense a wide range of liquids with high velocities and small droplet sizes. The impact and spreading of droplets can be observed, and the equipment measures droplet contact angle, height, and diameter for a duration of up to 8 seconds. Droplet absorption rate was studied for porous and non-porous receivers. Initial results indicated that the MicroDAT is a useful tool in predicting print quality.

7. Suggestions for Future Work

The aim of this study was to gain an increased knowledge of the mechanisms that control the absorption and the fixation of inkjet droplets on coated papers. Coatings consisting primarily of silica and polymeric binder together with cationic additives were studied.

The results have given reason to believe that line width (uniform ink spreading) is governed by surface energetics, whereas blurriness (non-uniform ink spreading) is governed more by the surface micro-roughness. Further analysis of the coating layer structures, such as microscale roughness and surface energy, might provide information of these hypotheses. Further investigation on coating pigment properties, such as pore size, pore shape, and surface area, could be of interest in printability and rheology aspects, as well.

Although developed, the MicroDAT technology still holds room for further improvements. A mechanisation of the sample holder would increase the accuracy in droplet placement, and making a larger sample area possible. A faster image acquiring rate would provide more information of droplet flight and impact phase. A flexible arrangement of the light source(s) could assist the recording process and aid in the segmentation of the droplet from the background in the image analysis. Improvements in the software that can be of interest is an automated catalogisation of acquired images, and a more efficient handling and averaging of large series of droplet absorption data.
Using the MicroDAT might shed light on other topics of research in ink-coating interactions. It is believed that the initial ink spreading phase takes only a few microseconds, whereas the absorption phase takes tens of milliseconds. More in-depth studies of the ink absorption process could clarify the influence of time and substrate surface characteristics on printability measures (e.g. gamut and colour-to-colour bleed). The studies within this thesis have mostly included commercial inkjet inks (in other words, the composition of the ink is unknown). It would, therefore, be of interest to study fluids and model inks with a controlled content in order to study the effects of a systematic variation of composition on printability, in combination with different coating components.

The correlation between instrumental and perceptual print quality was scrutinised in this work. More in-depth studies would lead to more accurate JND, which could aid in the creation of acceptance levels for inkjet print quality. This could, in turn, benefit the design of coating colour formulations.

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The author

9. References

1. Rooks, A., "New Technology for New Markets", *Solutions!*, (July), 28-30 (2004).

2. Plateau, J.A.F., "On the Recent Theories of the Constitution of Jet Liquid Issuing from Circular Orifices", *Phil. Mag*, (286), 12 (1856).

3. Elmqvist, R., "Measuring Instrument of the Recording Type", U.S. Patent 2566443 (1951).

4. Hansell, H.W., "Jet Sprayer Actuated by Supersonic Waves", U.S. Patent 2512743 (1946).

5. Naiman, M., "Sudden Steam Printing", U.S. Patent 3179042 (1965).

6. Sweet, R.G., "Fluid Droplet Recorder", U.S. Patent 3596275 (1971).

7. Anon, "IBM 6640", *IBM Journal of Research and Development*, (January), (1977).

8. Heard, R.S., and Philips, D.W., "Raster Slant Control in an Ink Jet Printer", U.S. Patent 4167741 (1979).

9. Ascoli, E., "Method of and a Machine for Writing", U.S. Patent 3136594 (1964).

10. Ascoli, A., Pidoux, P., and Perdrix, M., "Process and Device for Writing by Ink Jet", U.S. Patent 3893126 (1975).

11. Hertz, C.H., and Simonsson, S-I., "Ink Jet Recorder", U.S. Patent US3416153 (1968).

12. Buck, R.T., Cloutier, F.L., Erni, R.E., and Low, R.N., "Disposable Ink Jet Head", U.S. Patent 4500895 (1985).

13. Kobayashi, H., Noboru, M., and Ohno, S., "Liquid Recording Medium", U.S. Patent 4243994 (1981).

14. Hara, T., Sato, Y., Takatori, Y., and Shirato, Y., "Ink Jet Recording Device Using Thermal Propulsion And Mechanical Pressure Changes", U.S. Patent 4296421 (1981).

15. Le, H.P., "Progress and Trends in Ink-Jet Printing Technology", *Journal of Imaging Science and Technology*, 42(1), 49-62 (1998).

16. Hutchin, C., "Ink Requirements for Continuous Ink-Jet Printers", Proceedings from PITA Coating Conference, Edinburgh, UK, pp. 139-141 (2003).

17. Gaynor, J., "Predicted and Unpredicted Changes in Non-Impact Printing: 1981-2001", *Journal of Imaging Science and Technology*, 46(4), 292-299 (2002).

18. Pond, S.F., "Inkjet Technology and Product Development Strategies", Carlsbad: Torrey Pines Research (2000).

19. Lee, H.-K., Joyce, M.K., Fleming, P.D., and Cameron, J.H., "Production of a Single Coated Glossy Inkjet Paper Using Conventional Coating and Calendering Methods", Proceedings from TAPPI Coating and Graphic Arts Conference and Trade Fair, Orlando, FL, USA, pp. 24 (2002).

20. Ohya, H., Kida, S., and Abe, T., "A Study of New Pigment Precursor for Inkjet Applications", *http://konicaminolta.com*, (2004).

21. Yu, Y., and Von Gottberg, F., "Surface Modified Color Pigments for Inkjet Applications", Proceedings from NIP 16: International Conference on Digital Printing Technologies, Vancouver, BC, Canada, pp. 512-515 (2002).

22. Chovancova, V., Fleming, P.D., Howell, P., and Rasmusson, A., "Color and Lightfastness Performance of Different Epson Ink Sets", *Journal of Imaging Science and Technology*, 49(6), 652-659 (2005).

23. Desie, G., Deroover, G., De Voegt, F., and Soucemarianadin, A., "Printing of Dye and Pigment-Based Aqueous Inks onto Porous Substrates", *Journal of Imaging Science and Technology*, 48(5), 389-397 (2004).

24. Desie, G., Allaman, S., Lievens, O., Anthonissen, K., and Soucemarianadin, A., "Influence of Substrate Properties in Drop on Demand Printing", Proceedings from NIP18: International Conference on Digital Printing Technologies, San Diego, CA, USA, pp. 360-365 (2002).

25. Fischer, M.C., "Creating Long-lasting Inkjet Prints", *www.nedcc.org*, (2005).

26. Martin, T., "Navigating the Digital Ink Jungle", *SGIA Journal*, (3), 5-11 (2005).

27. LeClaire, J., "UV-Curable Technology", *Signindustry.com*, 4 (2006).

28. Titterington, D.R., "A Preview Of Phase Change Inkjet Technology", Proceedings from New Printing Technologies Symposium, Atlatna, GA, USA, pp. 153-154 (1996).

29. Marx, D., "UV-Inkjet Printing for Commercial Graphics: Markets and Applications": Radtech (2004).

30. McManus, P.A., Jaeger, W., Le, H.P., and Titterington, D.R., "Paper Requirements for Color Imaging with Ink-Jets", *Tappi Journal*, 66(7), 81-85 (1983).

31. Jaffe, A.B., Luttman, E. W., and Crooks, W., "Colour Inkjet Printing: Materials Parameters", in Colloids and Surfaces in Reprographic Technology. pp. 530-541 (1982).

32. Oliver, J.F., D'souze, E., and Hayes, R. E., "Application of Ultrasonic and Porometric Techniques to Measure Liquid Penetration in Digital Papers", Proceedings from NIP18: International Conference on Digital Printing Technologies, San Diego, CA, USA, pp. 505-508 (2002).

33. Bares, S.J., "Handbook Of Imaging Materials", In the series: Papers and Films for Ink Jet Printing. 546-562 (1991).

34. Babinsky, V., "Ink Jet Paper Development", Proceedings from Intertech Conferences: Specialty & Technical Papers 98, San Fransisco, CA, USA, pp. 12 (1998).

35. Johnson, H., "Mastering Digital Printing", ed. 2: Course Technology PTR (2004).

36. Kasahara, K., "A New Quick-Drying, High-Water-Resistant Glossy Inkjet Paper", Proceedings from NIP 14: International Conference on Digital Printing Technology, Toronto, ON, Canada, pp. 150-152 (1998).

37. Tsai, Y.-G., Inoue, M., and Colasurdo, T., "The Effect of Sizing Materials on the Ink Absorption in Paper", Proceedings from TAPPI 99 Preparing for the Next Millenium, Atlanta, GA, USA, pp. 111-122 (1999).

38. Rahman, L., "Factors Affecting the Performance of Inkjet Papers", Proceedings from Spring Technical Conference & Trade Fair, Chicago, IL, USA, pp. 19 (2003).

39. Bares, S.J., and Rennels, K. D., "Papers Compability With Next Generation Ink-Jet Printers", *TAPPI Journal*, 73(1), 123-125 (1990).

40. Bares, S.J., "Printing on Plain Paper with a Thermal Ink-Jet Printer", *Hewlett-Packard Journal*, (1988).

41. Lyne, M.B., and Aspler, J.S., "Paper for Ink Jet Printing", *TAPPI Journal*, 68(5), 106-110 (1985).

42. Perry, C.L., and Dulin, C.E., "Amorphous Silicas and Silicates", in Pigments for Paper (1984).

43. Dumont, M., "Silica", Canadian Minerals Yearbook (2000).

44. Harris, T., "Treading Carefully - Specialty Silicas Market Cools Down", *IM*, 52-55 (2003).

45. Morea-Swift, G., and Jones, H., "The Use of Synthetic Silicas in Coated Media for Ink-Jet Printing", Proceedings from Coating Conference, Washington, DC, USA, pp. 317-328 (2000).

46. McFadden, M.G., and Donigian, D., "Effects of Coating Structure and Optics on Inkjet Printability", Proceedings from Coating Conference, Toronto, ON, Canada, pp. 169-177 (1999).

47. Dunlop-Jones, N., Murase, N., Jonckheree, E., and Mabire, F., "A Novel Approach for Producing Glossy Photographic Quality Inkjet Papers", Proceedings from Coating and Graphic Arts Conference and Trade Fair, Orlando, FL, USA, pp. 9 (2002).

48. Chapman, D.M., and Michos, D., "Novel Silica Gels for Glossy, Ink-Receptive Coatings", *Journal of Image Science and Technology*, 44(5), 418-422 (2000).

49. Londo, M., "On-Machine Coating of Inkjet Paper Possible with Modified Kaolin", *Pulp & Paper Journal*, 74(5), 37-43 (2000).

50. Cody, H.M., "Consolidation, Competition Changing Printing Paper and Pigment Markets", *Pulp & Paper Journal*, 73(9), 46-50 (1999).

51. Prakash, B., and Devisetti, S., "Novel Kaolin Pigment for High Solids Inkjet Coating", *Pulp & Paper Journal*, 79(4), 49-54 (2005).

52. Cawthorne, J.E., Joyce, M., and Fleming, D., "Use of a Chemically Modified Clay as a Replacement for Silica in Matte Coated Inkjet Papers", *Journal of Coatings Technology*, 75(973), 75-81 (2003).

53. Ivutin, D., Enomae, T., and Isogai, A., "Ink Dot Fornation in Coating Layer of Inkjet Paper with Modified Calcium Carbonate", Proceedings from NIP 21 International Conference on Digital Technologies, Baltimore, MD, USA, pp. 448-452 (2005).

54. Mori, Y., Enomae, T., and Isogai, A., "Application of Spherical Calcium Carbonate to Paper", Proceedings from 73rd Pulp and Paper Research Conference, Tokyo, Japan, pp. 172-173 (2006).

55. Gane, P.A.C., "Mineral Pigments for Paper: Structure, Function and Development Potential (Part II)", *Wochenblatt Für Papierfabrikation*, 129(4), 176-179 (2001).

56. Gane, P.A.C., "Mineral Pigments for Paper: Structure, Function and Development Potential (Part I)", *Wochenblatt Für Papierfabrikation*, 129(3), 110-116 (2001).

57. Pelto, M., "PCC: The Coating Pigment of the Future", *Wochenblatt Für Papierfabrikation*, 134(9), 510-511 (2006).

58. Donigian, D.W., "Precipitated Calcium Carbonate: New Coating Products", Proceedings from Coating Conference and Exhibit, Toronto, ON, Canada, pp. 1 (2005).

59. Boisvert, J.-P., Persello, J., and Guyard, A., "On th Use Of Nanoporous Silica Products as Ink Holder Agents for Ink-Jet Printing", Proceedings from 89th Annual Meeting, Montreal, QUE, Canada, pp. 6 (2003).

60. Hladnik, A., and Muck, T., "Characterization of Pigments in Coating Formulations for High-End Ink-Jet Papers", *Dyes and Pigments*, 54(3), 253-263 (2002).

61. Hentzschel, P., and Pelzer, R., "Improving the Printability of Inkjet Papers by use of Polyvinyl Alcohol and other Components", *Wochenblatt Für Papierfabrikation*, 124(18), 795-801 (1996).

62. Boylan, J.R., "Using Polyvinyl Alcohol in Inkjet Printing Paper", *Tappi Journal*, 80(1), 68-70 (1997).

63. Hentzschel, P., "Polyvinyl Alcohol", in Papermaking Science and Technology: Pigment Coating and Surface Sizing of Paper, TAPPI Press. pp. 277-287 (2000).

64. Schuman, T., "Poly(vinyl alcohol)-Coated Papers - Effects of Surface Characteristics of the Substrate", Licentiate thesis, Department of Materials Science and Engineering, Chalmers University, Gothenburg, Sweden (2002).

65. Lunde, D.I., "Rapidly Changing Market Drives New Developments in Coated Papers", *Pulp and Paper Journal*, 73(5), 41-47 (1999).

66. Glittenberg, D., and Becker, A., "Cationic Starches for Surface Sizing: The Better Solution", *Paperi Ja Puu*, 79(4), 240-243 (1997).

67. Hladnik, A., Muck, T., and Kosmelj, K, "Influence of Coating Colour Ingredients on Paper and Printing Properties of Inkjet Paper", Proceedings from 30th International IARIGAI Research Conference: Advances in Printing Science and Technology, Dubrovnik-Cavtat, Croatia, pp. 91-97 (2003).

68. Khoultchaev, K., and Graczyk, T., "Influence of Polymer-Polymer Interactions on Properties of Ink Jet Coatings", *Journal of Imaging Science and Technology*, 48(1), 16-23 (2001).

69. Hara, K., "Specialty PVOH in Inkjet Coating Formulations", Proceedings from PITA Coating Conference, Barcelona, Spain, pp. 77-80 (2005).

70. Muck, T., "The Investigation of Interaction at Ink-Jet Print", *Papir*, 31(1-2), 44-52 (2003).

71. Chao, H.-T., "Coating for Inkjet Recording", U.S. Patent 5851651 (1998).

72. Schröder, H., and Shupp, G., "Recording Paper for Ink Jet Recording Processes", U.S. Patent 4474847 (1984).

73. Lubar, M.J., "Ink Jet Recording Medium", U.S. Patent 5888629 (1999).

74. Lindqvist, U., and Heilmann, J., "The Paper Dependence of the Print Quality in Drop-on-Demand Ink Jet Printing", Proceedings from IARIGAI 26th International Research Conference, Advances in Digital Printing, Munich, Germany, pp. 10 (1999).

75. Christiansson, H., and Johansson, P.Å. "MicroGloss by STFI Packforsk - A Way of Measuring Gloss Quality as We Perceive It": STFI-Packforsk AB Product Sheet (2005).

76. Storbeck, W., "Silica Pigments in Ink-Receptive Coatings": OH-Presentation (2002).

77. Chapman, D.M., "Coating Structure Effects on Ink-Jet Print Quality", Proceedings from TAPPI Coating Conference, Philadelphia, PA, USA, pp. 73-78 (1997).

78. Glittenberg, D., Voight, A., and Becker, A., "Available Options For Mass Production of High-Grade Ink-Jet Papers", Proceedings from TAPPI Metered Size Press Forum, Atlanta, GA, USA, pp. 229-233 (2002).

79. Svanholm, E., Ström, G., "Influence of Polyvinyl Alcohol on Inkjet Printability", Proceedings from International Printing and Graphic Arts Conference, Vancouver, BC, Canada, pp. 187-198 (2004).

80. Ryu, R.Y., Gilbert, R.D., and Khan, S.A., "Influence of Cationic Additives on the Rheological, Optical and Printing Properties of Ink-Jet Coatings", *Tappi Journal*, 82(11), 128-134 (1999).

81. Jopson, R.N., "Binder Modification for Blade-coated Inkjet Papers, Applications of PVP Copolymers or: What to do to Offset Coated Grades to Make Them Inkjet Printable", Proceedings from Coating and graphic arts conference and trade fair, San Diego, CA, USA, pp. 163-182 (2001).

82. Gerdes, S., Cazabat, A-M., and Ström, G., "The Spreading of Silicone Oil Droplets on a Surface with Parallel V-shaped Grooves", *The ACS Journal of Surface and Colloids*, 26(13), 7258-7264 (1997).

Printability and Ink-Coating Interactions in Inkjet Printing

Inkjet is a digital printing process where the ink is ejected directly onto a substrate from a jet device driven by an electronic signal. Most inkjet inks have a low viscosity and a low surface tension, which put high demands on the coating layer's porosity and absorbency characteristics.

The purpose of this work has been to gain an increased knowledge of the mechanisms that control the absorption and the fixation of inkjet droplets on coated papers. The focus has been on printability aspects of high quality (although not photographic quality) laboratory coated inkjet papers for printers using aqueous-based inks. Coating colours, made from a wide range of commercial, as well as non-commercial coating chemicals, have been evaluated mainly in terms of inkjet printability and runnability. Print quality aspects, such as line expansion, blurriness, and colour gamut were analysed and correlated to structural features of the coating layer, as well as to ink composition. It was determined that coatings with pure polymer binders gave an excellent colour gamut and that, with an addition of mesoporous pigments, the print sharpness improved. Moreover, it was also determined that the printability and the binder demand were affected by the pore size, as well as pore size distribution of the pigments.

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