Absorption non-uniformity characterisation and its impact on flexographic ink distribution of coated packaging boards

Sofia Thorman
Absorption non-uniformity characterisation and its impact on flexographic ink distribution of coated packaging boards

Sofia Thorman
Absorption non-uniformity characterisation and its impact on flexographic ink distribution of coated packaging boards

Sofia Thorman

LICENTIATE THESIS

Karlstad University Studies  |  2015:7

urn:nbn:se:kau:diva-34910

ISSN 1403-8099


© The author

Distribution:
Karlstad University
Faculty of Health, Science and Technology
Department of Engineering and Chemical Sciences
SE-651 88 Karlstad, Sweden
+46 54 700 10 00

Print: Universitetstryckeriet, Karlstad 2015

WWW.KAU.SE
Abstract
For this licentiate thesis, focus was on the ability of coated boards to absorb liquid and (a) how the uniformity of liquid absorption can be measured and (b) to what extent absorption characteristics have an impact on print mottle when it comes to water-based flexographic printing. The liquid absorption and surface roughness of a substrate are believed to impact on flexographic print mottle, but their respective contributions are not well defined, since they co-exist and are independent. Hence, it is not easy to isolate the contribution from each source. Additionally, it is possible that non-uniform absorption creates more problem than when the average absorption is high or low (and uniform) when printing. However, in spite of this, there are only a few, if any, relevant ways of directly characterising aqueous absorption non-uniformity.

This thesis contributes to further knowledge by suggesting one characterisation tool and one quantification method. A staining technique was developed to characterise the non-uniformity of liquid absorption. This technique is unique in the sense that it measures how unevenly an aqueous solution is absorbed in a short period and without any impact from surface roughness. Moreover, the contributions of white-top mottle and absorption non-uniformity can be quantified simultaneously from one measurement.

A method to study independently the effects of absorption non-uniformity on print quality was established. This was achieved by introducing artificial absorption non-uniformities with well-controlled barrier patterns. These patterns modified not only the pore structure by closing the surface pores, but also the surface chemistry. By these means, it is possible to produce a substrate property-matrix; the absorption non-uniformity being compared to, for example, the surface roughness. The impact from either of the properties can be studied independently with the use of this matrix.

The concept of creating a property matrix successfully demonstrated that non-uniform absorption indeed will have a negative impact on print quality, both on smoother and rougher boards. Low absorption made print density decrease and uneven absorption caused print mottle. This was the case when other properties of the samples were kept within a narrow range; otherwise surface roughness appeared to determine print mottle ranking.
Papers included in this thesis


Sofia Thorman contributed with experimental design and set-up, data analysis and the majority of the writing in these three studies.
Acknowledgements

I would like to express my deep appreciation and gratitude to my advisors, Associate Professor Li Yang, Associate Professor Göran Ström and Professor Magnus Lestelius. Their scientific guidance and support throughout this process have been invaluable. Without the initiative from my manager, Associate Professor Anita Teleman, this journey would not have started. Thank you for starting it and making it possible to be finalised.

Among my very good colleagues at Inventia, three deserve special thanks. I am truly fortunate to have had Mrs Anni Hagberg, Mr Hans Christiansson and M.Sc. Hajer Kamal Alm by my side. Anni and I have faced many challenges in the laboratory, but the ups outweighed the downs and, without her work this thesis would be in short on many results. Hasse, apart from being my programming guru, our brainstorming and discussions got me back on track numerous times. My friend and colleague Hajer, who makes the same journey, kept my spirits up while being a source of inspiration.

Without moral support, scientific guidance and encouragements along the way, this thesis would not look the same as it does. Furthermore, without financial support and the VIPP (Values created in Fibre-based Processes and Products) industrial graduate school at Karlstad University, there would be no thesis at all. I therefore wish to gratefully acknowledge the following financing parties: Research Institutes of Sweden (RISE), the Knowledge Foundation, BillerudKorsnäs, Klabin, Mondi Kraft Paper, Stora Enso, Tetra Pak and Inventia AB. I would like to thank Mr Martin Taylor and Miss Eli Gaskin at Imerys for contributing with SEM and Reflectometry analyses.

To my family who believed in and supported me; I can never thank them enough. This milestone was reached, mainly thanks to the sacrifices made by my husband, Olle, in taking on more than his fair share of the parenting and household burdens.

I would like to dedicate this to Aston, my pride and joy.
# Table of contents

<table>
<thead>
<tr>
<th>Chapter</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Introduction</td>
<td>1</td>
</tr>
<tr>
<td>1.1</td>
<td>Need</td>
<td>1</td>
</tr>
<tr>
<td>1.2</td>
<td>Scope</td>
<td>2</td>
</tr>
<tr>
<td>1.3</td>
<td>Effect goal – the broader context</td>
<td>2</td>
</tr>
<tr>
<td>2</td>
<td>Background</td>
<td>5</td>
</tr>
<tr>
<td>2.1</td>
<td>Flexographic printing</td>
<td>5</td>
</tr>
<tr>
<td>2.2</td>
<td>Coated liquid packaging boards</td>
<td>7</td>
</tr>
<tr>
<td>2.3</td>
<td>Ink transfer, setting and drying</td>
<td>11</td>
</tr>
<tr>
<td>2.4</td>
<td>Fluid absorption and wetting</td>
<td>15</td>
</tr>
<tr>
<td>2.5</td>
<td>Characterisation of liquid absorption</td>
<td>28</td>
</tr>
<tr>
<td>2.6</td>
<td>Print quality and impact from substrate</td>
<td>32</td>
</tr>
<tr>
<td>3</td>
<td>Experimental approach</td>
<td>39</td>
</tr>
<tr>
<td>3.1</td>
<td>Board materials</td>
<td>39</td>
</tr>
<tr>
<td>3.2</td>
<td>Modifying the absorption non-uniformity of coated boards</td>
<td>41</td>
</tr>
<tr>
<td>3.3</td>
<td>Absorption and wetting</td>
<td>42</td>
</tr>
<tr>
<td>3.4</td>
<td>Coat-weight variations</td>
<td>45</td>
</tr>
<tr>
<td>3.5</td>
<td>Coating pore structure</td>
<td>45</td>
</tr>
<tr>
<td>3.6</td>
<td>Surface roughness</td>
<td>47</td>
</tr>
<tr>
<td>3.7</td>
<td>Printing and print quality evaluation</td>
<td>47</td>
</tr>
<tr>
<td>4</td>
<td>Results and discussions</td>
<td>49</td>
</tr>
<tr>
<td>4.1</td>
<td>Measuring absorption non-uniformity</td>
<td>49</td>
</tr>
<tr>
<td>4.2</td>
<td>Studying the impact of non-uniform absorption on print mottle of coated boards with barrier</td>
<td>54</td>
</tr>
<tr>
<td>5</td>
<td>Conclusions</td>
<td>60</td>
</tr>
<tr>
<td>6</td>
<td>Future work</td>
<td>61</td>
</tr>
<tr>
<td>7</td>
<td>References</td>
<td>62</td>
</tr>
</tbody>
</table>
1 Introduction
This licentiate thesis covers the first half of a doctoral project. The overall aim of whole doctoral project is to gain a better understanding of flexographic print quality and the impact resulting from the interaction among substrate, ink and printing press. Focus is placed on coated liquid packaging boards (a group of carton boards used to package liquid foodstuffs). The overall target is to identify how a substrate impacts on print quality. The licentiate thesis puts focus on absorption properties and their uniformity.

1.1 Need
When it comes to flexographic printing, the relative importance of surface smoothness, liquid absorption and wetting is a complex matter. Results in the literature diverge on which property it is that has the major impact on print quality. As suggested by Zang and Aspler (1995a) surface smoothness is often considered a necessity for high print quality, but this does not produce high print quality by default. As the samples become smooth or, at least, consistently rough, other parameters, such as the surface chemistry of the substrate, can start having an impact. It was also suggested that unfavourable absorbency and wetting do not cause print quality problems, unless being they are either very high or low (Aspler et al., 1998, Jensen, 1989, Zang and Aspler, 1995a), or when combined with a high level of surface roughness (Lagerstedt and Kolseth, 1995). One reason for the different results may be how hard it is to design experiments in such a way that the contribution from one parameter can be isolated from another. This means that the selection of samples is of utter importance to be able to obtain the answers required.

Additionally, non-uniform absorption is likely to be more troublesome, compared to when the absorption level is being either high or low, since compensations are difficult to make during the printing process. The aspect of absorption uniformity and its impact on flexographic print quality has not been deal with well in the literature. In fact, it is quite difficult to find a way of measuring it. Hence, there is a need for an improved knowledge on how to measure this property and its impact on print mottle. An experimental design is required, where the uniformity of absorption can be varied independently and in a controlled manner.
1.2 Scope

For this licentiate thesis, focus was put on the ability of boards to absorb liquid and (a) how the uniformity of liquid absorption can be measured and (b) to what degree absorption characteristics have an impact on print quality.

The first part was dedicated to the development of a new technique for the characterisation of absorption non-uniformity. It was important to define a measurement method relevant to the absorption of water-based flexographic inks, which meant that short absorption times and an aqueous testing liquid were utilised (Paper I). Furthermore, the technique was refined to include a simultaneous determination of absorption non-uniformity and white-top mottle from a single measurement and area (Paper II).

The second part focussed on investigating the way an uneven (laterally) absorption affects print quality and, specifically print mottle. One question asked was whether parts of the surface with a low absorption level would also produce a lower print density than those parts with a high absorption level? To tackle these issues, a controlled absorption pattern was added to coated liquid packaging boards and then they were subjected to printing (Paper III).

1.3 Effect goal – the broader context

Today, high demands are being made on print quality, and the quality needs to be at an adequate and consistent level in order to create packaging that is competitive. The aim of these studies was to provide packaging board manufacturers with the means to produce material that is consistent and produces the expected results in the print shop. This will increase value for the printer. When packaging boards behave consistently, printers can achieve the same quality each time and have a faster start-up for each printing job. This does not necessarily imply increased customer satisfaction, but the focus is rather on avoiding dissatisfaction, which can be even more important. Apart from maintaining a good relationship with customers (printers), the driving force behind this is being more cost effective and having efficient production. Basically, this could be translated into improved value proposition.

The packaging board material can contribute to high-value processes, if it is possible to predict and obtain a certain print surface quality during board production. This way, there will be less waste (both at board mills and print shops), products can be sold as intended (high-end products do not need to be shipped to less demanding operations), less claims and less unnecessary transportations of heavy reels. Even though the aim is not to achieve
sustainable development or to give improve service, explicitly, efforts made to become more cost effective and production efficient can also:

1. Increase the value and reduce dissatisfaction created in the print shop.
2. Lead to a better utilisation of resources, with less waste.
3. Make fibre-based packaging more competitive compared to plastic packaging.

1.3.1 More cost effective - less waste of resources
A production of packaging boards that does not reach the required level of quality is associated with the creation of less value and possibly a waste of resources and energy. The sooner a quality flaw can be identified, there will be improvements in customer relations and, in monetary and resource/energy wise aspects. If the parameters to control can be identified, they can be utilised in production to ensure the proper level of quality. An undesired scenario would be when quality problems show up when a packaging board has already been shipped and is being used in a printing press. Consequently, not has the resource and energy put into the production been in vain, but also the energy involved in the distribution. The whole production may end up as waste or it could, in some cases, be rescued at additional costs to the printer, e.g. using more ink and/or a slower press speed etc. An even worse scenario would be for a package to end up on a store shelf without being sold, due to consumers preferring more attractively printed packages. On the other hand, they might be sold and yet end up as waste, because the best-before date or other important information was not legible. Thus, this becomes a discussion not only about the value of the packaging being wasted but also about the product/food it contains. Food losses due to faulty or bad printing on packaging need to be avoided.

1.3.2 Is improved print quality necessary?
It may be questioned whether there is value for the consumer, society and the environment when print quality is improved. However, efforts to achieve consistent quality and “problem-free” printing (product efficiency) do not necessarily lead to improvements in print quality.

There is a general opinion that pretty and spectacular looking prints draw attention of the consumers. In spite of this, the consumers consider themselves (when asked) to be indifferent to attractive and nice looking printing on packages of consumer goods (Löfgren and Witell, 2005, Löfgren et al., 2011). However, in the same studies the communicative attributes (such as
information, aesthetics, branding and appearance), had an impact on the customer satisfaction. A consumer may not consider print quality as being important when asked directly, but the negative effects caused by inadequate (deteriorated communication) and inconsistent (trust issues being raised) print quality could still impact on that satisfaction. This does not necessarily cause dissatisfaction, but the consumer may well choose one of the more attractive packages instead at the point-of-purchase.
2 Background

2.1 Flexographic printing

In flexographic printing the ink is transferred from a flexible printing plate (also known as a cliché) to the substrate. The plate is usually made of photopolymer or rubber material with raised image areas, which means that the relief pattern on the plate determines where the ink will end-up on the paper or board. There are various types of plates available, often targeted at certain substrates and/or the printing of either solid tones or halftones. The material in the plate not only varies when it comes to hardness, thickness, surface chemistry and surface structure, but the plate making process can also give rise to characteristic relief profiles, such as the depth, the steepness from printing to non-printing and the shape of the dots for instance. Adhesive tape is used to mount a plate and it can consist of a different softness and thickness. The flexibility of the plates and/or the mounting tapes means that they conform to rather macro-rough surfaces. The down-side with a deformable image carrier is that an image can become distorted. (Kipphan, 2001, Leach and Pierce, 1993)

Contact between the ink and a paper depends on a large set of variables. In addition to variables in the plate, the printing pressure is very important for the contact and transfer of ink. In full-scale printing presses, the impression determines the pressure in the printing nip. This impression refers to the distance between the plate and impression cylinder, although it is not the actual distance, but rather how close the cylinders are brought together after the ink starts being transferred to the substrate (or the transfer of an acceptable image). The pressure involved in flexographic printing is normally considered to be low, Kipphan (2001) suggested a pressure of 0.3 MPa. Similarly, Lim et al. (1996) found the maximum pressures in steel elastomer nips to be around 0.1 MPa to 0.3 MPa (depending on speed for instance) and Bohan et al. (2002) numerically determined the maximum pressure to around 0.5 MPa. However, Johnson et al. (2004) measured the pressure pulse in the nip of a flexographic central impression cylinder (CI) press and found that the maximum pressure was significantly higher, 1 MPa to 2 MPa. This is supported by Mirle and Zettlemoyer (1988), where numerical (including the viscoelastic deformation of the plate) and experimental determinations indicated a maximum pressure in flexographic nips to be around 1.2 MPa - 1.4 MPa.
As described by for instance Taylor and Zettlemoyer (1958), Myers et al. (1959), Coyle (1988), and Yang (2013) the pressure-pulse in a nip can be divided into three regimes: (i) the nip pressure increases when approaching the centre of the nip (compression), (ii) after the narrowest gap the pressure decreases (decompression) and then (iii) there is even a negative force acting on the substrate during ink film splitting.

In each printing deck (unit), an engraved anilox roll feeds ink to the plate. In a simplified description, the cell volume controls the amount of ink applied to the plate. Actually, the transfer between an anilox and a plate can be influenced by many other variables, such as the cell geometry, the ink properties, the surface chemistry and the topography of the plate, as well as the pressure between the anilox and the plate. The inking unit may consist of different designs, where the anilox is basically filled from an ink tray and any excess ink is removed by means of a doctor blade, where an enclosed or chambered system with double doctor blades is commonly used (Leach and Pierce, 1993).

For roll-to-roll flexographic printing, there are at least three classes of presses, viz. a CI, an in-line and a stack type press. The classification refers to the location of the printing decks. In a CI press, all the printing decks are geared around a large common impression cylinder, whereas each deck has a separate impression cylinder in the other two types. An in-line press refers to the horizontal arrangement of the decks and a stack type press to a vertical arrangement of decks, in which the web often passes half of the decks on the way down and half on the way up. The register shifts from colour to colour are minimised in a CI press, due to the substrate being supported by the central impression cylinder between the decks (Leach and Pierce, 1993). Intermediate drying stations are usually used to dry the ink between the printing units. Wet-on-wet printing exists, but it is not so common in flexographic printing. (Kipphan, 2001)

There is also laboratory equipment available for flexographic printing, e.g. the F1 Printability tester (IGT Testing Systems), Flexiproof 100/UV (RK PrintCoat Instruments Ltd), Little Joe (Little Joe Industries), Perfect ProoferTM (Print Proof Solutions B.V.) and Printing Proofer (Biuged Laboratory Instruments (Guangzhou) Co, Ltd.). Although, there are some obvious differences when compared to full-scale printing, such as geometry, the inking unit and the press speed, Aspler (2004) saw a high correlation and visual similarities when comparing unbleached liner boards printed on a commercial web press and the
IGT F1. Pilot or full-scale printing trials are still needed, mainly due to the differences pointed out above and for the aspect of runnability.

*A water-based flexographic ink* consists of dispersed pigments and a vehicle with binder resins, a solvent (water) and various additives, such as defoamers, surfactants, waxes etc. The resins need to be soluble in the solvent and act as a carrier for the pigments during printing, thus binding them to the surface on drying. There are commonly two different types of binders, which are used separately or combined. They are dispersed resin and alkaline solutions. In the dispersed vehicle, there is an emulsion of fine particle resins, usually acrylic, vinyl or styrene butadiene polymers, suspended in water. As the emulsion, the particles coagulate or flow together to form a film. The alkaline solutions consist of alkali-soluble resins, such as carboxylated resins. Amines or ammonia is often used as a solubilizing agent, while the amino/ammonia groups react with the acid in the group of resins. When the amino or ammonia group evaporates, the ink is able to dry. The emulsion resins lead to a high solids content at a low viscosity and they dry quickly. However, they do not print so well and they quickly become insoluble in the press. On the other hand, the alkaline solutions offer a better press stability and printability, which is why the two are often mixed. Flexographic inks are normally diluted with water in the print shop to reach the required viscosity. (FTA, 1992) On press, viscosity is normally measured with an efflux flow cup, which is fast and easy, but it can give inadequate response if the ink is tixotropic (Leach and Pierce, 1993).

Ink surface tension, viscosity, tack and pH are important properties in ink transfer and trapping in the printing process (Steadman et al., 1993). More about the rheology of flexographic inks can be found in 2.4.6 Liquid rheology.

Uniform substrate is of high importance: The process of printing can be described in different ways but, in short, the ink has to be transferred to the substrate first and then it sets and dries. It is important to state that it might not be enough to just describe an average ink transfer or setting mechanisms. Uniformity can be as equally important and sometimes even more significant, since it is difficult to compensate for it during printing. An average print density can be corrected during printing by adjusting the press settings or the ink, whereas a non-uniform density is not as easily worked around laterally.

### 2.2 Coated liquid packaging boards

The term liquid packaging board refers to the material being used in packages for liquid foodstuffs. Together with e.g. folding boxboard, solid bleached and
unbleached boards, they create a specific group of paperboards that is referred to as carton boards. Liquid packaging boards are commonly constructed in multiple layers, i.e. multi-ply. The number and types of layers can differ with, for example, a bleached or unbleached middle layer and an uncoated or coated top layer. This study focused on what occurs when printing directly onto a coated board before applying any barrier. The focus was on how the final structure impacts ink penetration and print quality. However, a general discussion on the formation of the final structure has some relevance.

The fibre network of an uncoated base consists of pores of many different sizes. This is not optimal, when it comes to achieving uniform ink absorption and print quality. The application of one/multiple coating layers will create a more uniform pore structure with finer pores. (Dean, 1997)

In brief, a coating layer consists of particles of mineral pigments bound together with latex or a soluble binder, such as starch and air voids. The fluid absorbency and optical properties will largely be determined by the air filled voids (pores) and the interfaces between the air and the binder/pigment. (Lepoutre, 1989) Light-scattering is determined by the difference in the refractive indices of the pigment/binder and air, the size of the particles and pores as well as the number of interfaces (Alince and Lepoutre, 1980). This implies that there will be more scattering and, hence, a higher degree of opacity in a more porous coating, provided identical coat weight.

2.2.1 Coating process

When coating colour is applied, liquid starts to migrate into the base stock, causing some of the coating layer to immobilise. After this, a metering device removes any excess coating. After the metering takes place the coating layer levels and a smooth surface is formed. (Dean, 1997)

Immediately after applying the coating colour, the binder and pigment particles can move around freely in the wet coating. When the fluid phase is removed (dewatered) by means of drainage into the base stock or through evaporation, the mobility of the particles is greatly restricted (Watanabe and Lepoutre, 1982). When it comes to rapid dewatering and/or evaporation, there is no time for the particles to pack tightly together and a bulky and open structure becomes consolidated, whereas slower dewatering allows more time for pigment orientation to take place, resulting in there being more efficient packing and thereby finer pores (Al-Turaif et al., 2002, Lepoutre, 1978b). On the contrary, Ragnarsson et al. (2013) did not find that there was any effect on the mean
porosity or variations in porosity when the drying strategy was altered, i.e. changing the dewatering rate.

As the structure is consolidated large pigments are immobilised first, while the smaller particles, i.e. pigment fines and binders, can still move around. They follow the fluid phase causing what is referred to as migration. Over the years, it has been debated whether binders migrate towards the surface (Fujiwara et al., 1991) or the base (Al-Turaif et al., 2002, Lepoutre, 1978b). Regardless of an enrichment or a dilution of binders on the surface, any migration may cause a non-uniform distribution in the z-direction. Dahlström and Uesaka (2012) indicated that conflicting results may originate in the measuring depth of the analysis techniques used. In their study, latex enrichment was shown in the very thin (500 nm thick) outermost layers of the coating, both on the coating surface and in the interface between the coating and the base.

Dewatering can be slowed down with the aid of water-retention additives, less absorbent base stock, increased coating weight and/or changes in solids content in the coating colour (Larrondo and St-Amour, 1994, Laudone et al., 2006, Lepoutre, 1978b). It has been shown that a coating layer reaches a higher void fraction when being applied on a more absorbent base stock (Larrondo and St-Amour, 1994). The coating porosity has been linked to coat-weight, with thinner coatings being more porous and thereby having a higher degree of water-uptake. In thicker coatings, the pigments have more freedom to become rearranged and to pack tightly together, which is possibly due to a slower dewatering as a result of high resistance by the filtercake (Azimi et al., 2011, Endres and Tietz, 2007, Fujiwara et al., 1991, Laudone et al., 2003, Lepoutre, 1978b).

Apart from absorbance, the paperboard’s formation (fibre density variations) and its roughness will impact on the properties of the coating layer. Dahlström and Uesaka (2009) and Tomimasu et al. (1990) showed that small-scale variations in coating thickness depended on surface roughness, whereas larger scale variations were more dependent on base-sheet formation. With a thicker coating, the mass density of the base sheet was lower.

With blade coating, a smooth coating surface is created at the cost of a varying coating thickness. As the blade meters the coating, voids of the base are filled and peaks are left with a thinner coating colour (Dahlström and Uesaka, 2009). Contour coating techniques, such as curtain coating, create a uniform coating thickness but leave a rough surface profile (Endres and Tietz, 2007, Lee et al., 2012).
2.2.2 Coating colour

A coating colour is normally composed of pigments, binders, thickeners, water and various additives. The particle size, shape and particle size distribution (PSD) will have an impact on the packing and, therefore, the porous structure. With a wide PSD, the fine particles can fill the pores between the larger pigments, which means that the packing is tighter and the pores become smaller. (Dean, 1997, Preston et al., 2008)

Often in combination, clay (kaolin) and calcium carbonates are pigments that are commonly used in coatings for liquid packaging board. The calcium carbonates are normally divided into natural or ground (GCC) and precipitated calcium carbonates (PCC), where the latter is synthetically prepared and is of a more uniform size. The crystal forms of the pigments differ. Kaolin has a platy shape, whereas GCC is sometimes compared to a cauliflower shape. Furthermore, kaolin is not as bright as calcium particles. (Dean, 1997)

It is possible for finer pigments to create a smoother surface that is also glossier (Tyagi et al., 2010). However, the pigments have to be large enough to fill the roughness of the base board and not disappear into the surface pores. Alternatively, multiple coating layers are used where larger pigments are used in the pre-coating typically.

The properties of a coating layer are affected by the type of binder, its content and distribution. The higher the binder content, the more closed the structure will be, resulting in lower porosity and negative effects on the paper optics (Aspler and Lepoutre, 1991, Bohlin, 2013, Lepoutre et al., 1979, Preston et al., 2008). There have also been reports of latex accumulating in the small pores, which means that the pore-size distribution will change when a binder is added (Dahlström and Uesaka, 2012, Ström et al., 2010). It has been reported that the polymer stiffness (glass transition temperature, $T_g$) will have an impact on the shrinkage of the coating layer during drying (Laudone et al., 2006, Watanabe and Lepoutre, 1982). A severe shrinkage causes low porosity and greater surface roughness. With a stiffer polymer (a high $T_g$) there are more voids remaining after drying, resulting in a more porous and surface smooth structure (Olsson, 2007).

2.2.3 Coating uniformity

It cannot be expected that the pore-structure, the pigment or the binder distribution will be completely uniform laterally (Arai et al., 1988). An uneven coating coverage and coating mass distribution may give rise to uneven surface latex profiles (Fujiwara and Kaga, 1992, Fujiwara et al., 1990) and variations in
pore structure. Since porosity is affected by the average coat weight, a varying coat weight is likely to cause variations in the lateral porosity (Azimi et al., 2011, Endres and Tietz, 2007, Fujiwara et al., 1991, Laudone et al., 2003, Lepoutre, 1978b).

An uneven thickness of the coating layer and or an uneven pore structure will cause lateral variations in the optical properties, such as opacity, reflectance and brightness. A coating layer with uneven opacity on an unbleached base will give rise to what is called white-top mottle (uneven reflectance) (Pauler, 1999).

2.3 Ink transfer, setting and drying

During printing, firstly, ink is transferred to a substrate and the amount and evenness of this transfer will affect the appearance of the final printing. Secondly, the ink film sets and dries. Before the ink film has set, it can still redistribute and spread laterally over the surface to form a uniform ink layer, which is a process often referred to as ink levelling.

The mechanisms of ink transfer and ink setting will be described in the coming sections, but generally one can say that transfer can be affected in several ways by the substrate properties, such as its surface roughness, compressibility and absorbency. On the other hand, ink setting is mainly affected by absorbency. However, evaporation also comes into play as may formation of a filtercake or gel phase.

2.3.1 Mechanisms of ink transfer

Ink transfer is often divided into three general steps: (1) the contact and wetting between the ink and the substrate at the entrance to the nip, (2) immobilisation of part of the ink layer and (3) the still fluid ink splits, with some of it following the substrate and the rest remaining on the plate. One of the commonly used models, at least for offset printing, describing the ink transfer mechanisms were derived by Walker and Fetsko (Walker and Fetsko, 1955):

\[ y = (1 - e^{-kx})[b(1 - e^{-x/b}) + f(x - b(1 - e^{-x/b}))] \]  

[1]

Where \( y \) = amount of ink transferred per unit area to the substrate, \( k \) = a constant related to the smoothness of the substrate (regulating the degree of area contact between the ink and the substrate as the initial amount of ink increases), \( x \) = the initial amount of ink on the plate, \( f \) = split factor (the fraction of ink remaining on the paper) and \( b \) = amount of ink that can be immobilised during impression.
One criticism that can be raised against the Walker-Fetsko model is the fact that there is interdependence between the immobilisation ($b$) and the splitting ($f$) parameters (Aspler, 1993). As described by Zang (1993) the above equation has in many cases given ink transfer curves that do not agree with the published experimental data and/or unrealistic ink transfer parameters, such as negative splitting coefficients. Ink transfer in flexographic printing is most often characterised in terms of a total weight increase and, as far as this study is aware, it is not commonly divided into contact, immobilisation and splitting. Therefore it is hard to assess the relevance of the Walker and Fetsko equation for flexographic printing.

First of all, ink transfer is dependent on the ink film making physical contact with a substrate when entering a printing nip. Contact is more easily achieved when the nip gap is narrower and/or when the ink film is thicker. A hindering factor is the surface roughness of the substrate. To some extent, this can be overcome by the compressibility of the substrate, the nip pressure and the softness of the plate material (causing it to conform to the surface of the substrate). It is sometimes stated that the ink needs to wet the substrate in order to achieve contact and transfer (Aspler and Lepoutre, 1991). However, De Grace and Mangin (1983) showed that equal amounts of letterpress ink can be transferred onto plastics with varying surface energies. It was suggested that wetting resistance may be overcome by nip pressure. In De Grace and Mangin’s test on low energy Polytetrafluoroethylene (PTFE), the ink film formed beads after the nip.

While the ink is in contact with the substrate, some of it will start to immobilise by absorption and/or filling the micro-structure of the surface (De Grace and Mangin, 1983). Absorption is driven by the external nip pressure but it can also be governed by both wetting and adhesion, with addition of the capillary action. When it comes to offset printing it has sometimes been claimed that the immobilisation are more dependent on filling of micro-structures than absorbency (Isoard, 1983, Lepouitre et al., 1979, Zang and Aspler, 1995b).

As the ink film leaves the nip, the free ink-film (not immobilised) will be divided between the plate and substrate. Myers et al. (1959) showed that at high speeds, cavitation forms and expands when it approaches the role nip exit, leaving ink filaments attached to both the plate and the substrate. These filaments remain elongated until they break up. As suggested by Taylor and Zettlemoyer (1958) and, later, by De Grace and Mangin (1983) and De Grace and Mangin (1987) the split of offset inks is asymmetric and the ratio often in
favour of the plate. Taylor and Zettlemoyer proposed that cavitation was being initiated in the centre of the nip and then expanding most rapidly towards the paper, due to a drop in viscosity close to the substrate. A temperature increase and/or shear thinning of the ink will cause a drop in viscosity. On the other hand, De Grace and Mangin advocated that cavitation was being initiated on the substrate surface, due to micro-roughness and entrained air bubbles. They proposed that, when there is not enough time for the cavitation to travel to the centre of the ink film, the split becomes asymmetric.

It has also been suggested that the filtration resistance of the offset inks has an effect on the immobilisation and ink splitting. A lower resistance will allow for a higher pressure absorption in the nip and, consequently, the ink split moves away from the paper (Gros et al., 2002). Zang and Aspler (1995b) proposed that ink tack will rise close to the coating layer as a filtercake is formed, which also moves the location of the ink split away from the substrate.

A more recent study by Luu et al. (2010a) and Luu et al. (2010b) suggested that the filtercake resistance of flexographic inks affected the ink transfer and print density on uncoated papers and uncoated linerboards. An ink with high filtercake resistance will slow down the dewatering and thereby impact the ink film splitting. The studies by Luu et al., showed that ink transfer was less dependent on the substrate’s hydrophobicity when using a solution binder ink with a high filtercake resistance, compared to with an emulsion binder ink with less resistance to dewater. Due to the high filtration resistance of the solution binders, the ink by itself, limited the dewatering rate and made the hydrophobicity of the substrate irrelevant.

### 2.3.2 Mechanisms of ink setting and drying

When discussing flexographic as offset printing, the ink setting and drying are not as clearly disconnected. In the following description, ink is considered to have set when no further redistribution (levelling) can occur. Ink binder will film-form and polymerise during drying, which makes the dried ink water-insoluble.

When the fluid phase is removed, the ink pigments are consolidated and immobilised. The immobilisation process happens very quickly and before becoming immobilised the ink film is supposed to level and form a uniform ink layer on the substrate, as for example described for offset printing by Donigian (2006). Filaments formed during flexographic ink splitting can also cause a print density pattern that is visible in the dried print (often referred to as ink-splitting
pattern), when there is not sufficient time for levelling (Barros and Johansson, 2007).

The levelling process is governed by film thickness, viscosity and surface tension of the ink. As described by Kheshgi (1997), a capillary pressure and gravity will act to level and smooth irregularities in thin films. The surface tension of the liquid will act to minimise the surface area and create as flat boundary between ink and air as possible. Hence, liquid will be transported from convex to concave regions of the film. This action can create an uniform film thickness, when the solid surface is smooth, or an uneven film thickness, when the solid surface is rough, see Figure 1. On the smooth solid surface, a surface tension will transport liquid from thin to thick regions, which flattens the liquid surface and makes the film thickness uniform. On the rough solid surface, a surface tension will cause liquid to flow from the surface peaks, with thin coating, to surface depressions, with already thick coating. When the surface is horizontal, the gravity will promote the fluid motion and speed up the levelling. Viscoelastic effects may slow down the capillary levelling. Bousfield (1991) also suggested that the levelling can be counteracted by centrifugal forces when rotating at high speeds (for example in high speed laboratory coating in a CLC, SimuTech International, Inc.).

**Healing of irregularities**

![Figure 1. Illustration of the levelling effect by surface tension. The direction of fluid transport (top) and the final levelled film (bottom) is shown for a film on one solid that is smooth (left) and one solid that is rough (right).](image)

As the coating reaches high solids content, the levelling will stop. This means that thin liquid films, a quick removal of fluid phase through absorption or evaporation, high initial solids content and high viscosity will shorten the time
for levelling (Bousfield, 1991, Kheshgi, 1997). The results by Bousfield suggested that the water flux into the base sheet had stronger impact on the levelling than the evaporation rate. The larger the spatial wavelength of the irregularity, the longer it will take to level it (Kheshgi, 1997). Thereby long wavelength disturbances may not have time to heal before the film has dried, and only short wavelength disturbances can be smoothened when having a quick drying.

While the ink pigments are still mobile and tiny enough to fit into the pores, there is also a possibility that they will penetrate into the porous network of the substrate. On a coating layer, the possibility of ink pigments penetrating into the small pores is smaller (Xiang and Bousfield, 2003), compared to them penetrating into the much more open structure in uncoated papers and paperboards. Measurements by both Ström et al. (2001) and Preston et al. (2000) indicated that offset pigments stays within the ink layer, without penetrating into the pore structure of the substrate.

Print density can be assumed to decrease when the ink pigments penetrate into the pores, compared to staying on the coating surface. This is similar to what has been reported for uncoated papers by Pauler (1987). He showed that the light scattering coefficient changes when ink penetrates into papers. The deeper a given ink volume penetrates, the lower will print density become, since the light scattering in the mixed ink-paper layer is higher than in the pure ink layer. A slow ink setting is preferred to allow for ink levelling, with as little pigment penetration as possible, but without it being too slow, which can cause runnability issues. It is necessary that an ink film has set before reaching the next printing unit, where printing wet on dry takes place.

It is not fully understood how the fluid phase is removed. However, spontaneous absorption into the coating, which is driven by capillary forces, is often mentioned and usually occurs in combination with evaporation (Aspler and Lepoutre, 1991, Leach and Pierce, 1993).

### Fluid absorption and wetting

It is generally accepted that liquid absorption into porous networks can be dependent on wetting (the solid needs to be wet by a liquid before absorption occurs), liquid properties and the pore structure. The mechanism of absorption may be approximated by penetration into a single pore, a bundle of pores or simulations of penetration into entire pore networks. As described in the
previous section, absorption can be part of the ink transfer as well as the ink setting processes.

Many research and experimental tests have focused on offset printing and oil absorption. Since the liquid properties impact a lot on how absorption behaves, there may not be any point in carrying out oil absorption tests to predict the penetration behaviour of water-based inks. In a review by Aspler (1993), it was suggested, for example, that the sorption of water into newsprint is determined by surface chemistry, whereas the sorption of oil is mainly affected by the pore structure. Furthermore, Olsson et al. (2006a) showed that more polar fluids penetrated deeper into the coating layer.

There is a limitation in modelling and measuring the absorption of “pure” liquids in order to describe adequately the penetration of the fluid phase from a thin layer of pigmented ink (Aspler, 1993, Aspler and Lepoutre, 1991). When the fluid phase penetrates into the pores, the pigments follow the fluid phase and/or are deposited on the surface. Hence, a high degree of absorption could result in more ink being transferred to a substrate but also to a deeper level of penetration of the whole ink or just the fluid phase of the ink. To add to the difficulty of modelling and understanding ink absorption mechanisms, the ink changes as the fluid phase dewatered, which means that viscosities and the contact angles are not constant (Aspler, 1993). The following sections focus on how the coating layer controls aqueous absorption, in most cases, without specific consideration being given to ink pigments.

2.4.1 Driving forces for fluid penetration

Liquid can be dragged into a capillary or pore by the capillary pressure \( (P_c) \) and/or pushed into the capillary by an external pressure \( (P_e) \), such as nip pressure during the printing process. When it comes to a single capillary tube, the Young-Laplace\(^1\) pressure difference shows that the capillary pressure \( (P_c) \) is proportional to the product of the liquid surface tension \( (\gamma) \) and the cosine of the contact angle between the liquid and the solid \( (\theta) \) and inversely proportional to the radius \( (r) \) of the capillary:

\[
P_c = 2\gamma \frac{\cos \theta}{r}
\]

\[\text{[2]}\]

\(^1\) This equation is often used, e.g. Washburn (1921), Schoelkopf et al. (2000b) and Ridgway et al. (2001), but seldom given any citation. Finn (1999) described that Young (1805) and Laplace independently arrived at the same conclusions.
Salminen (1988) (also presented in Eklund and Salminen (1987)) stresses that the capillary pressure is more correctly described as a dynamic than a static pressure. Liquid vapour will precede the liquid phase and as the liquid molecules adsorbs to the pore wall, the contact angle will change. The dynamic contact angle will depend on the penetration velocity and possibly also on liquid viscosity.

Ma et al. (2007) described liquid imbibition thermodynamically, in terms of lowering the Gibbs free energy. The capillary pressure is the basic force driving the imbibition and, the higher the pressure, the greater the change in Gibbs free energy. During equilibrium imbibition, Ma et al. suggested to only account for the driving force, i.e. change in Gibbs free energy, since increasing this will increase the flow rate, regardless of the retarding forces. The change in Gibbs free energy ($\Delta G_i$) for a capillary of any given pore size ($i$), is defined as the volume ($V_i$) times the Young-Laplace pressure difference (Eq. 2):

$$\Delta G_i = -V_i \frac{4\gamma \cos \theta}{D_i} = -4A_i h_i \frac{\gamma \cos \theta}{D_i} = -\frac{\pi D_i^2 h_i}{4} \times \frac{4\gamma \cos \theta}{D_i} = -\pi D_i h_i \gamma \cos \theta \quad [3]$$

This means that, at given contact angle ($\theta$) and surface tension ($\gamma$), the change in Gibbs energy in the final stage (filled coating) is determined by the diameter of the pore ($D_i$) and its length ($h_i$). The negative sign accounts for the penetration of wetting liquids, with $\cos \theta > 0$ being spontaneous.

### 2.4.2 Resistive forces for fluid penetration

A number of factors can slow down absorption into a capillary. First of all there will be a resistive viscous drag, accounted for by the Hagen-Poiseuille flow. The pressure loss ($P_F$) is proportional to the liquid viscosity ($\eta$), capillary length ($h$) and volumetric flow rate ($Q = dV/dt$) and inversely proportional to the capillary radius ($r$) to the power of four:

$$P_F = \frac{8\eta h Q}{\pi r^4}, \quad Q = \frac{\pi D_i^4 P_F}{128\eta h} \quad \text{or} \quad Q = \frac{\pi r^4 P_F}{8\eta h} \quad [4]$$

As described by Sutera and Skalak (1993), Eq. 4 is commonly referred to as Poiseuille’s law, but this form was not derived by Poiseuille. In his equation $\pi/128\eta$ was denoted with $K''$, which is being a function of the temperature and the type of liquid.

Secondly, the liquid accelerates at the very beginning of absorption into a capillary. This means that inertia and the density of the liquid become important. There is also the possibility of a counter pressure caused by entrapped (or at least not easily flowing) air, as described by Salminen (1988).
A phenomenon called wetting delay may also retard absorption or rather postpone the initiation of absorption. Bristow (1967) presented experimental data indicating that absorption did not start immediately on some samples and it was suggested that this was related to the wetting of the solid. In the delay time, the contact angle was reduced below 90°. The concept of a wetting delay has been debated and, Salminen (1988) claimed the term to be misleading and that a paper surface is being wetted quicker than the shortest contact that is experimentally measureable. As pointed out by Aspler (1993), it might be more accurate to call it absorption delay.

Filtercake of ink pigments, can also affect the removal of fluid from inks (Aspler and Lepoutre, 1991, Gane and Ridgway, 2009, Ma et al., 2009, Xiang et al., 2004). However, Ström (2005) and Ström et al. (2001) suggested that the concentrated binder solution and the dispersed pigments form a gel phase on the coating surface. It was proposed that the concentration of the offset pigment was too low to form a filtercake.

When it comes to research on offset printing, it has been suggested that the filtercake reduces permeability and, thereby, impedes fluid drainage (Xiang and Bousfield, 2000, Xiang et al., 2004, Zang and Aspler, 1995b). The model suggested by Xiang et al. showed that the combined effect of the filtercake resistance and the pore-size distribution of a coating layer had an effect on the absorption rate. When the permeability of the filtercake was low, the absorption rate decreased with the pore size. With a more permeable filtercake, the absorption rate increased when the pore sizes were small whereas, when the pore sizes were larger, the absorption rate decreased.

In comparison, Gane and Ridgway (2009) found that the higher the filtercake resistance of a flexographic ink, the faster the absorption. They proposed that the filtercake actually traps the dissolved ink polymers inside the filtercake, instead of them clogging up the fine entry pores into the coating structure. This way an ink with a high filtercake resistance can maintain an ink flow without interruption, thus working as an “imbibition pump”. Ma et al. (2009) suggested that the filtercake could provide a possible explanation as to the reason why the tack increases while flexographic inks set.

2.4.3 Models of absorption

Liquid absorption can be described using the Navier-Stokes model. However, due to its complexity, various simplified forms are commonly used in the paper industry. Ridgway et al. (2002) made a summary of how imbibition has been analysed and modelled from Bell and Cameron in 1906 to the present day.
Ridgeway et al. concluded that the best known solution is the Lucas (Lucas, 1918) and Washburn (Washburn, 1921) equation (see Eq. 5), which does not account for inertia dependency during short time absorption, which the Bosanquet (Bosanquet, 1923) equation (see Eq. 8) does.

At the liquid front there is a balance between the driving pressure, i.e. capillary and external pressure, and the resistive pressure, i.e. the viscous flow: $P_E + P_C = P_F$ (Salminen, 1988). This assumes the capillaries to be open at both ends and therefore the atmospheric pressure can be neglected. In the Lucas-Washburn model, fully laminar flow is assumed and the penetration rate ($dh/dt$) is driven by the total effective pressure acting on the liquid ($\Sigma P$) and slowed down by the viscous flow ($P_F$). When setting the slip coefficient to zero, which is true when the liquid wets the pore walls (Washburn, 1921), the penetration rate is described by the following expression:

$$\frac{dh}{dt} = \frac{r^2 \Sigma P}{8\eta h}$$  \[5\]

Considering the case when penetration is driven by external and capillary pressure, the expression takes the form $\frac{dh}{dt} = \frac{r^2 (P_E + P_C)}{8\eta h}$ and when driven by capillary pressure alone it takes the form $\frac{dh}{dt} = \frac{\tau r \cos \theta}{4\eta h}$. In the latter case, the depth of liquid penetration can be explicitly expressed as:

$$h = \sqrt{\frac{\tau r \cos \theta}{2\eta}}$$  \[6\]

Whereas the combined effect of external and capillary pressure gives (Salminen, 1988):

$$h = \sqrt{\frac{2\tau r \cos \theta + r^2 P_E}{4\eta}}$$  \[7\]

The Bosanquet absorption force balance includes both spontaneous absorption (inertia of the accelerating fluid, viscosity drag, capillary forces) and forced absorption (external pressure) (Bosanquet, 1923):

$$\frac{d}{dt} \left( \pi r^2 \rho h \frac{dh}{dt} \right) + 8\pi h \frac{dh}{dt} = P_E \pi r^2 + 2\pi \gamma r \cos \theta$$  \[8\]

The first term on the left-hand side is the inertia of an accelerating fluid with a mass density ($\rho$), at the depth of a liquid column ($h$) in a capillary tube with a specific radius ($r$). The second term is the viscosity drag of the ink. On the right-hand side, the first term originates from the external pressure ($P_E$), such as the nip pressure in printing, which is usually a short time pulse. And the second
term corresponds to the capillary force. In absence of external pressure, a solution to the equation for short time-scales was presented by Schoelkopf et al. (2000b):

\[
h = t \sqrt{\frac{2y\cos \theta}{r\rho}} \left( \frac{8\eta}{r^2\rho} t \ll 1, P_E = 0 \right)
\]  

[9]

The Bosanquet model assumes that there is constant pressure, although the pressure exerted from two rotating cylinders is a time-dependent pressure pulse. To account for this, Yang (2013) changed the constant pressure in Eq. 8, \( P_E \), to a time dependent function, \( P_E(t) \). In describing the major characteristics of the ink penetration dynamics, the amplitude and duration of the pressure pulse were of vital importance, whereas the exact shape of the pulse was not as important.

There are some of important differences between the Lucas-Washburn model (Eq. 6) and the Bosanquet model (Eq. 9). According to the latter, the depth of liquid penetration is inversely proportional to the square root of the capillary radius, while the Lucas-Washburn model states the opposite. In other words, the Bosanquet model indicates that ink initially moves faster in smaller pores, since it is slowed down more by the liquid density in larger pores, after which liquid moves faster into the larger pores. Calculations based on the Bosanquet model, made by Ridgway et al. (2002), predict that a 100 \( \mu \)m capillary is filled faster than a 10 \( \mu \)m after \( t=0,00026s \). According to the Lucas-Washburn model, liquid penetrates faster in larger pores at all times. The depth of ink penetration is linearly proportional to time in the Bosanquet model, while the Lucas-Washburn model states that it is proportional to square root of contact time. Eklund and Salminen (1987) suggested the capillary driven penetration to be linearly proportional to time and when adding an external pressure it instead became linearly proportional to the square root of contact time.

As already described, Salminen (1988) concluded that the capillary penetration is complicated by e.g. molecular interactions ahead of the liquid front which gives a dynamic nature of the contact angle. When applying an external pressure, it was suggested that the impact from these factors diminished and hence the penetration being determined by the external pressure, a comparatively constant capillary pressure and the viscous flow.

2.4.3.1 Comments on mechanically forced penetration

The mechanisms of liquid penetration, forced by an external pressure, may be of relevance when considering printing. Salminen (1988) concluded that
pressure penetration into uncoated papers is a key factor in many industrial process. The external pressure only contributes during the nip-pressure pulse, whereas the capillary movements are active for a longer period. Yang (2013) illustrated that the maximum penetration depth is reached at the central point of a nip (when considering both nip pressure and capillary suction). Pressure penetration pushes the ink into the substrate when approaching the nip centre and then pulls it out again, in the regime between nip centre and exit. However, the capillary force holds a portion of the ink inside the pores until they leave the nip.

Applying an external pressure will change how the substrate and liquid interacts. The impact from pore structure increases in relation to a greater external pressure, while at the same time, the impact from surface tension and the substrates surface chemistry decreases (Rennes and Eklund, 1989, Salminen, 1988).

Researchers have also studied the pressure penetration and squeezing action in rolling nips, through numerical and/or analytical models, and for example connected this to dot gain (Bohan et al., 2000, Dubé et al., 2008, Megat Ahmed et al., 1997). The numerical models by Megat Ahmed showed that only a small portion of the ink in offset printed dots enters into the substrate. The comparatively large initial ink thickness, promotes spreading over penetrating into the porous structure. When the ink film becomes thinner, the spreading action decreases. As the pressure is increase, the ink transfer increase, especially through spreading into the substrate. Holmvall and Uesaka (2008) studied the impact from local pressure variations in corrugated board printing. Their study indicated that print density increased with higher local pressure and that it on a solid tone was connected to achieving a saturated density. The increased halftone density was instead related to ink spreading and dot gain.

2.4.3.2 Scaling from single capillary to porous network

The absorption models, e.g. Lucas-Washburn and Bosanquet, often deal with absorption into a single capillary tube, which needs to be scaled up to a porous coating layer consisting of many capillaries. There are different approaches to this and, in many cases, the capillaries have been treated as a bundle of separate pores of a single size and without any interconnection among the pores. This implies multiplying the volume absorbed in one capillary by the total number of pores. The volume absorbed per unit area \( V \) will depend on the number of capillaries \( N \), their radius \( r \) and the length of penetration as given by Eq. 6:
To approximate the actual distance the liquid has travelled, the porosity and tortuosity of the pore structure have often been used, as described by Gate and Windle (1973) and Lepoutre (1978a). The porosity ($\varepsilon$) is normally defined as the ratio of pore volume of coating (or paper) to total volume of the coating (or paper), and is expressed as a fraction or percentage (Murakami and Imamura, 1983). Lepoutre (1978a) described the porosity of the coating layer by the number of pores, their radii and lengths ($L$) divided by the coating thickness ($E$): $\varepsilon = \frac{N \pi r^2 L}{E}$. Further, the pores are normally not straight capillaries, but tortuous, with the tortuosity factor ($\tau$) being defined as $\tau = \frac{L}{E}$. Hence, the porosity can be written as $\varepsilon = N \pi r^2 \tau$. Using this in Eq. 10 will give the absorbed volume per unit area as a function of porosity and tortuosity:

$$V = \frac{\varepsilon}{\tau} \sqrt{\frac{tr \cos \theta}{2\eta}}$$  \hspace{1cm} [11]$$

Preston et al. (2002) suggested that an offset ink setting is mainly determined by the pore density (the number of pores/area of coating) and the pore size. It is often stated that small pores set ink faster than larger pores, when the coatings are compared at an equal pore volume. This suggestion comes from the idea that structures with finer pores also consist of a greater number of pores. However, when compared at an equal pore density, the larger pores displayed a faster ink setting. Ma et al. (2009) showed an inverse dependence between the flexographic ink setting time (time to reach maximum tack) and the pore-wall surface area ($\sum \pi D_i h$). This, in turn, was proportional to the combined effect of pore volume and pore size ($\sum V_i / D_i$).

Approximating a porous structure based on a bundle of separate capillaries with a certain size, is not always a satisfactory method. For example, Ma et al. (2005) concluded there should be a bigger difference in capillary forces among small pores than among larger pores. Hence it is of importance to consider the pore-size distribution and not only estimate the average pore size. There have been proposals to calculate the absorption as the sum of each pore size. Ma et al. (2007) summed up the Gibbs energies of each pore size and Xiang et al. (2004) calculated the absorbed volume as the sum of the absorption rates (multiplied by the absorption time) of each pore size. Schoelkopf et al. (2002) showed a divergence between the equivalent hydraulic radius calculated from
experimental volume uptake (using the Lucas-Washburn model) and the pore radius that was measured, based on mercury intrusion.

Adding a pore-size distribution to the bundle of capillaries may be an improvement, but this still ignores the fact that the pores in the coating layer are interconnected. Schoelkopf and co-workers have shed light on this fact by combining an experimental test with simulations that included the inertial effects (Schoelkopf et al., 2000a, Schoelkopf et al., 2000b). They came to the conclusion that liquid is selective in filling a pore network and that inertial preference controls the selectivity for both short and long periods, which created what they call a “preferred pathway”. Initially, liquid prefers fine pores and moves faster in them, whereas the larger pores are excluded. As penetration proceeds, the inertial effects decline and, instead, the absorption follows the Lucas-Washburn dynamics. However, it was suggested that inertial retardation also needs to be considered in the network after longer times, such as acceleration when the liquid enters different pore sizes. Even when the absorption follows the Lucas-Washburn dynamics, inertia will still be effective and exclude the very large pores. Consequently, only the preferred paths in the network will be filled, leaving other paths unfilled. (Schoelkopf et al., 2000a, Schoelkopf et al., 2000b) Additionally, Ridgway et al. (2002) have shown that not only the pore radius is important in the filling of individual elements, but also the aspect ratio of the capillaries (length divided by the radius).

Similar to the preferred pathway, Xiang and Bousfield (2003) showed experimentally that an offset ink mainly filled the small pores in a coating, whereas the larger pores were not affected during printing. However, the possibility of an ink vehicle initially filling the large pores was not excluded. The vehicle would then be drained from the large pores and instead be pulled by capillary pressure into the small pores after leaving the printing nip.

2.4.4 Absorption uniformity

As pointed out by McGratten (1990), ink can be adjusted for high and low absorbent substrates, but problems mainly arise when a range of boards with different kinds of absorbencies are used. This was a conclusion based on collective experience of the Linerboard/Corrugated Subcommittee of the Papermakers Committee. However, this may also apply to coated liquid packaging boards. It would probably be even more difficult to compensate for an absorption that is uneven laterally. For example, Preston et al. (2008) pointed out the fact that uniform spreading is of critical importance for avoiding print mottle, since this cannot easily be worked around in the print
shop. Any lateral heterogeneity in surface chemistry or pore structure, such as uneven binder distribution, can potentially cause non-uniform absorption.

### 2.4.5 Wetting and surface energy

When a solid, liquid and vapour interact, their interfacial energies will determine how the liquid spreads on the solid. There will be a balance of adhesive forces (between the liquid and the solid) and cohesive forces within the liquid. A drop will spread and wet the solid when the cohesive force is weaker and the adhesive force is stronger. The interaction can be characterised in terms of the contact angle that the liquid makes with the solid. Using Young’s equation, the contact angle ($\theta$) can be determined from the interfacial energies between the solid-vapour ($\gamma_{sv}$), the solid-liquid ($\gamma_{sl}$) and the liquid-vapour ($\gamma_{lv}$) (see Eq. 12 and the diagram in Figure 2). The spreading coefficient ($S$) is defined as the difference between the work of the adhesion ($W_A$) and the work of the cohesion ($W_C$) (see Eq. 13).

\[
\gamma_{sv} = \gamma_{sl} + \gamma_{lv} \cos \theta \quad [12]
\]

\[
S = W_A - W_C = \gamma_{sv} - \gamma_{lv} - \gamma_{sl} = \gamma_{lv} (\cos \theta - 1) \quad [13]
\]

![Figure 2. Diagram showing the interfacial energies and contact angle formed by a liquid drop, a solid and a vapour. Young's equation, Eq. 12, describes the interactions.](image)

Ideally, an equilibrium contact is formed between the solid/liquid interface and the liquid/vapour interface. This requires the solid to be non-porous, flat, chemically homogeneous, insoluble and non-reactive by the liquid. In reality, there is often a hysteresis between the advancing (maximum) contact angles and the receding (minimum) contact angles, meaning that the angle will not be the same when the liquid spreads out on the solid as when it recedes over the surface. As shown by Oliver and Mason (1973), the contact angle around a drop is not equal on a microscopic level. Surface heterogeneities and surface roughness cause local protrusions of liquid with a far lower contact angle than the rest of the drop and the macroscopic average. The initial penetration into porous materials will also impact on the contact angle measurement (Elftonson and Ström, 1995). The hysteresis, surface roughness and penetration into the
solid make it problematic to measure the true contact angle, so that what is detected is the apparent contact angle.

The total surface energy ($\gamma^{TOT}$) of a solid or liquid can be divided into apolar and polar components. According to van Oss et al. (1987), the apolar component is assigned to electrodynamic interactions, termed Lifshitz-van der Waals ($\gamma^{LW}$) and are comprised of London dispersion, Keesom dipole-dipole and Debye dipole-induced dipole forces. The polar component relates to acid-base interactions ($\gamma^{AB}$) and are comprised of hydrogen bond interactions (Brønsted acids and bases), Lewis acid and base interactions and dipole moment interactions. The basic behaviour ($\gamma^-$) is due to proton acceptor or electron donor functionality, whereas the acid behaviour ($\gamma^+$) is due to proton donor or electron acceptor functionality. Surfaces can have acidic and/or basic groups and functionalities. When both are present, it is termed bipolar, as opposed to a monopolar surface, where one of the functionalities is dominant (van Oss et al., 1987).

Furthermore, Owens and Wendt (1969) divided the surface energy into an apolar (dispersive) component and a polar component. Here, the dispersive component ($\gamma^d$) constitutes London dispersion forces only and the polarity ($\gamma^p$) is comprised of hydrogen bonds and dipole-dipole interactions. van Oss et al. (1987) suggested that the Keesom and Debye forces only make a small contribution to the surface and interfacial tensions, hence $\gamma^{LW}$ and $\gamma^d$ may be regarded as comparable.

The surface energy of a solid can be calculated and separated into its components based on the contact angle measurements, by using liquids with a known surface tension and from the polarity. It is common that one of the liquids is only able to make apolar interactions, e.g. diiodomethane, which makes the calculation of the apolar component simple to do. In the case of the Owens and Wendt approach, two liquids are required and the calculations take place using Eq. 14-15 (Owens and Wendt, 1969).

The Owens and Wendt model:

$$\gamma_1 (\cos \theta + 1) = 2 \sqrt{\gamma_s^d \gamma_L^d} + 2 \sqrt{\gamma_s^p \gamma_l^p}$$  \[14\]  
\[\gamma^{TOT} = \gamma^d + \gamma^p\]  \[15\]
The surface energy ($\gamma$) of the solid and liquid is separated by subscripts ($s$ and $l$, respectively). Superscript $d$ denotes the dispersive, $p$ the polar component and $TOT$ the total surface energy.

A determination of the bipolar nature of a solid in the van Oss approach requires contact angles from three liquids, Eq. 16-18 (van Oss et al., 1987):

$$\gamma_1 (\cos \theta + 1) = 2\sqrt{\gamma_s^{LW} \gamma_l^{LW} + 2\sqrt{\gamma_s^{+} \gamma_l^{+} + 2\sqrt{\gamma_s^{-} \gamma_l^{-}}}$$  \[16\]

$$\gamma_{x}^{ab} = 2\sqrt{\gamma_x^{-} \gamma_x^{+}} \quad (x = s, l)$$  \[17\]

$$\gamma_{x}^{TOT} = \gamma_x^{LW} + \gamma_{x}^{ab} \quad (x = s, l)$$  \[18\]

Superscript $(LW)$ denotes the apolar (Lifshitz van der Waals), $(ab)$ the polar component, $(+)$ the acidic character and $(-)$ the basic character.

2.4.6 Fluid rheology

The rheological aspects of an ink, will affect the flow properties and thereby the behaviour during the printing process, such as the transport through the press, but also the transport on or into the paper. As already mentioned, the ink viscosity will slow down capillary absorption.

The viscosity is defined as the resistance to deform (flow) when applying a shear stress, i.e. a force acting on the liquid. For Newtonian liquids that are sheared between two parallel plates, see Figure 3, the viscosity ($\eta$) is calculated as the shear stress ($\tau$) divided by shear rate ($\dot{\gamma}$) (Leach and Pierce, 1993):

$$\eta = \tau / \dot{\gamma}$$  \[19\]

The shear stress is defined as the force ($F$) per unit area ($A$), $\tau = F / A$, and the shear rate is the velocity gradient, $\dot{\gamma} = dv / dy$ (Leach and Pierce, 1993). Eq. 19 will give the apparent viscosity for non-Newtonian fluids.

Figure 3. Diagram showing the velocity gradient within a fluid that is sheared between one moving and one stationary plate. When a force ($F$) is applied to the moving plate, the velocity ($v(y)$) in the fluid will depend on the $y$-position between the plates.
Water for example is Newtonian, but a flexographic ink deviates from this behaviour and the flow response, to shear stress, is no longer linear. The particle association, chemical bonds and physical interactions during flow will change the linear relation between shear rate and shear stress (Leach and Pierce, 1993). Viscosity responses that are of interest when considering inks:

- **Shear thinning** *(pseudo-plastic)* means that the ink viscosity will decrease, with increasing shear rate.

- **Shear thickening** *(dilatant)* means that the viscosity will increase, with increasing shear rate. This can occur when particles packs and form rigid structures (Leach and Pierce, 1993).

- **Thixotropic** means that the viscosity will decrease during shearing (at a constant rate and stress). When the ink is at rest, a gel structure is formed and when being sheared this will progressively break down. The ink will recover back to the original gel structure when the shearing stops, but the recovery takes longer time than it takes to break down the structure (Leach and Pierce, 1993).

- **Yield value** refers to the minimum shear stress needed for the ink to start flow.

- **Visco-elastic** implies that the ink possess both viscous and elastic properties. There will be a deformation and flow when applying a stress and when the stress is removed the ink can recover to its original form. Leach and Pierce (1993) suggested that the visco-elastic property is important in printing processes. It will determine how the ink will flow in nips, but also how it will recover after separation which affects the ability to level.

A high yield value, high viscosity or excessive thixotropic behaviour will prevent the ink flow. A too low viscosity may on the other hand cause dot spreading (FTA, 1992). Olsson et al. (2007a) showed that the flexographic ink binder has a dominant impact on the viscosity curve, whereas it was not as affected by the pigment particle type. It was also concluded that the water retention, depended on the interactions of ink components and water, but also on the particle packing ability.

Flexographic inks usually have low viscosity and are shear thinning (Aspler and Lepoutre, 1991, Gane and Ridgway, 2009, Havlínová et al., 1999, Olsson et al., 2007a, Olsson et al., 2007b). The viscosity is also temperature dependent and when temperature increase the viscosity will decrease (Olsson et al., 2007a).
2.5 Characterisation of liquid absorption

The most commonly used techniques and a selection of the more advanced and/or not standardised methods are described briefly below.

2.5.1 Absorbed volume or rate

The total absorbed volume can be determined gravimetrically or volumetrically either by the increased weight of a sample or the decrease in weight in the liquid reservoir. The manual Cobb test is frequently used, especially to determine the amount of sizing, although it does not capture the initial absorption, which is relevant to printing (Lyne, 2002, Skowronski et al., 2005, Zang and Aspler, 1995a). An automated version, called Automatic Cobb Tester, that dynamically measures the liquid uptake was introduced by Fibro system AB. The water is fed through a porous membrane, which the sample is clamped against, and the absorbed amount is monitored continually, giving the absorption (g/m²) as a function of time, including the initial absorption (FIBRO, 2014).

Compared to the manual Cobb test, the time-scale can be shortened in the Bristow wheel technique. In this test, a stain is made from a defined amount of dyed liquid. The substrate passes beneath a liquid holder with a slit, where the liquid can be transferred. The liquid uptake is calculated from the length of the track, while being dependent on the surface roughness and absorptivity of the substrate. Several stains carried out with an increasing speed are needed to obtain an absorption curve (uptake per area as a function of time). The curve can be used to study the wetting delay, the roughness index (intersect with the y-axis) and the absorption coefficient (absorption rate). (Bristow, 1967)

There are other techniques based on the Bristow wheel, such as the Automatic Scanning Absorptometer (ASA) from KRK Kummagai. This is an automated version, where the testing of different speeds has been incorporated into a single measurement (KRK, 2005). It is much like a gramophone, where the liquid holder has replaced the stylus and the sample is mounted on the turntable. As the liquid holder moves outwards at an accelerating turntable speed, it leaves a spiral track. The liquid transfer is detected continuously, resulting in an absorption curve as a function of time in one measurement.

A Micro Drop Absorption Tester (MicroDAT) calculated the rate of absorption of water droplets into the paper substrate (Ström et al., 2008). Water droplets that are roughly 300 pl are formed using a piezoelectric dispenser and hit the surface at a velocity of approx. 1.5 m/s. This forces a certain amount of the volume of the drop into the substrate and flattens the drop into a half sphere.
The absorption and evaporation are captured dynamically as volume decrease at a frequency of 8 ms. The MicroDAT test is mainly used in research work and is suitable for coated grades, but not for rough and uncoated grades.

There are also various other gravimetric approaches for measuring absorption. Schoelkopf et al. (2000b) measured the imbibition into compacted pigment tablets. Similar tablet blocks were also used to measure pressurised liquid permeability (Schoelkopf et al., 2004).

### 2.5.2 Contact angle and Surface energy

There are various techniques for characterising the contact angle, surface energy and surface tension. There are instruments that measure the static apparent contact angle, whereas others capture the dynamic contact angle when the liquid and solid meet. It was suggested that the dynamics are important for understanding what takes place in a printing nip (Bassemir and Krishnan, 1990).

The surface energy of a solid can be calculated by using contact angle measurements involving two or three liquids, as discussed in 2.4.5 Wetting and surface energy.

Images of sessile droplet profiles are captured in goniometers. A droplet is often around 2 μl - 4 μl. To capture the effects of hysteresis, the plate holding the sample can be tilted to identify the maximal (downhill side) and minimal (uphill side) angle achievable without a drop starting to roll. Another option, to capture the hysteresis, is to add and remove liquid to the droplet, without changing the contact line. (ramé-hart instrument, 2014)

The Wilhelmy plate technique makes use of another approach, as compared to the sessile drops. The solid is lowered into and withdrawn from the liquid. The force acting on the solid is then measured. This technique is suitable when determining the surface tension of a liquid. Surface tension of a liquid can also be determined with the pendant drop technique. A drop is formed at a needle tip and the contour will be determined by the gravity and mass as well as the surface tension. The drop is commonly surrounded by air, but it is also possible to use other gasses or liquids.

### 2.5.3 Oil-based ink stain test

Various oil-based stain tests have been in existence for many years, such as K&N, Croda and Noiré Porometric. Although the testing oils differ, the working principle is the same for each test. Dyed viscous oil is absorbed for a given period before any excess is removed and the reflectance of a stain is used as an indicator of absorbency. (Bristow and Bergenblad, 1982). However, since
the reflectance of the stain depends on the oil pick-up, it changes with the ink distribution in the z-direction (Hattula and Oittinen, 1982). Over the years, some modifications to the tests have been explored, such as weighing the samples after different contact times have elapsed in order to obtain the absorption rate (Ranger, 1981) and calculating the void fraction of a coating (Larrondo and St-Amour, 1992).

2.5.4 Ultra sound attenuation

There are also ultrasound techniques, where various liquids can be used as testing liquid. The transmission of ultrasound signals through a sample will change as the liquid penetrates into the sample. The ultrasound techniques allow relative comparisons but, as pointed out by Borch et al. (2002), the exact relationship between a signal and liquid absorption has not been well defined.

Daun (2006) worked with the instrument called Mutec Penetration Dynamics Analyser and suggested that capillary suction into porous membranes was too quick to be measured by this device, where the first record was taken after 8 ms. As liquid penetrated into the membranes, air was trapped because of the reverse side being sealed by a tape. Consequently, Daun claimed that penetration of liquid into the pores was dependent on air diffusion into the liquid. For paper samples he had not enough information to give a quantitative description of the absorption.

Yang et al. (2013) worked with another ultrasound device, emtec Penetration Dynamics Analyser (PDA) module HVL (emtec Electronic GmbH). With a physical model, the transmittance values could be converted into penetration depth into uncoated papers. It would be more challenging to create a model for a multilayer coated board. Also Bergvall (2006) used and emtec device (emtec PDA.C modul) in his master thesis, and found that it was possible to determine the time it takes to penetrate through the coating layer. The time to reach maximum transmittance correlated with the ratio of Cobb45 to coating grammage.

2.5.5 Flexographic ink-tack test

Ma et al. (2009) introduced a “micro-tack” device to measure ink-tack curves for water-based flexographic inks. This device produces curves similar to what has been seen for offset inks. The ink setting is defined as the time needed to reach maximum tack. A 2 mm x 2 mm rubber blanket probe is covered with ink and then brought into contact with a paper. The force needed to pull the probe away from the paper is measured. As liquid volumes are larger than in printing,
the time-scale is also longer. It takes a couple of hundreds of seconds to reach
the maximum, implying that the ink may also penetrate through the coating
layer and into the base according to Ma et al.

2.5.6 Pressurised absorption
There are not many commercially available techniques that characterise forced
absorption. Different attempts at pressurising the Bristow technique have been
made, where at least one developed by KRK Kummagi is available today
(KRK, 2005). The traditional Bristow wheel was equipped with a pressurised
head-box (contact pressure = 0.1 to 0.5 MPa and liquid pressurisation = 0.003-
0.01 MPa).

The Clara Device is a measuring apparatus for research purposes (Lamminmaki
et al., 2010, Lamminmaki et al., 2011). It is based on the capacitance changes
during liquid absorption by paper. By adjusting the pressure inside a liquid
chamber, it is possible to study absorption under different external pressures,
ranging from -0.5 bar to 5 bar.

In the IGT print penetration test (W24), a lab printer is equipped with a syringe
containing red oil (Diethylhexyl adipate) (IGT, 2006, July). A 5.8 mg ±0.3 mg
oil droplet falls onto a print disc and is then squeezed in a nip between the disc
and sample, at an accelerating speed. The length of the stain is related to the
absorbency of the substrate, so that the faster the absorption occurs, the
shorter the stain is. This method (or a similar) has been considered one of the
better techniques when it comes to absorbency in flexographic printing. It was
used with diluted flexographic inks (Steadman et al., 1993) and with dyed water
(Wågberg and Wennerblom, 1992).

2.5.7 Absorption uniformity
Uniformity in absorption is seldom characterised, particularly not in relation to
water-based ink absorption. Variations may be roughly estimated using multiple
measurements with some of the other techniques, such as MicroDAT, contact
angles or the flexographic micro-tack device. Skowronski et al. (2005)
introduced a multi-sensor to the ultrasound technique. The evenness of the
signal is detected with an array of 32 sensors, 1 mm² each. As already
mentioned, it is challenging to convert an ultrasound signal to liquid
penetration. Another option is to examine the evenness of Bristow Test stains.
However, this includes an influence from the roughness, due to a filling of
surface pores, and does not only reflect variations in penetration and wettability
(Bristow, 1967). The contribution from roughness can be omitted
When it comes to offset printing, the oil-based staining techniques mentioned above can give an indication about uniformity in oil absorption. Shen et al. (2004) introduced a probe to measure uniformity using silicon oil. The capillary force from the liquid bridge between a small probe and the substrate is detected and subsequently translated into local permeability. Variations are captured by means of multiple measurements distributed across the surface.

### 2.6 Print quality and impact from substrate

Although there are several methods for measuring print quality, only a few are focused on in this thesis. Print mottle receives the main attention. However, print density and uncovered areas (UCA) are also of relevance. Non-uniformities in a solid tone or a halftone are often mentioned as having a big, or possibly the biggest, effect on print quality (Aspler and Lepoutre, 1991). This also goes for flexographic printing on both coated and uncoated substrates (Aspler, 2004, Aspler et al., 1998, Wågberg and Wennerblom, 1992).

**Optical print density** ($D_s$) characterises the darkness of the ink and is expressed as the logarithm of the ratio between the reflectance of an unprinted substrate ($R_\infty$) and the reflectance of the print ($R_s$): $D_s = \log_{10}(R_\infty/R_s)$. Print density readings are affected by the uniformity of an ink-film, where the average density can be far from the saturated density of the spots with full ink coverage (Lavelle et al., 1996, Tollenaar and Ernst, 1961).

Print density is sometimes used as an indicative measurement of ink transfer, which is not completely accurate, since optical density increases exponentially up to a certain limit of ink, there is then no further increase when applying more ink (Aspler et al., 1992, Tollenaar and Ernst, 1961). In spite of a high ink transfer, print density can still be low due to ink pigments penetrating further into a porous structure (Aspler et al., 2004). At a constant ink volume, print density is higher, when ink holdout is effective in keeping ink pigments on the surface. The penetration of ink pigments is dependent on the pore size on a surface (Aspler et al., 1992), which makes this less likely to be an issue when it comes to coated papers with finer pores than those on uncoated papers with larger pores.

**Print mottle** is here defined as print reflectance variations, which is proportional to print density standard deviation (Johansson, 1999). These variations are commonly divided into classes of spatial size, although neither the
nomenclature nor the size limits are completely consistent. Small-scale variations are sometimes referred to as speckle (MacGregor and Conners, 1987), ink-splitting pattern (Barros and Johansson, 2007), filament pattern (Bohlin et al., 2013), marbling (Quesne et al., 2013) or just as micro-mottle etc. and often appear in the sub-millimetre wavelengths. Large-scale variations are more commonly referred to as visual mottle (Barros and Johansson, 2007) or just simply as mottle. It has been suggested to be rather large-scale print non-uniformity that is relevant to the visual appearance: Johansson (1999) suggested that wavelengths of 1 mm - 8 mm and, Jensen (1989) suggested that wavelengths of 3 mm - 9 mm, provide relevant information with regard to perceived quality.

The extreme of print mottle is when the ink is completely missing in limited areas. These uncovered areas (UCA) are a characteristic defect in solid tone flexographic printing. Many small UCA spots also affect print mottle measurement and, hence, the two can be closely connected.

It is difficult to overcome or compensate for laterally non-uniform print during the printing process. Due to this, Preston et al. (2008) suggested that uneven ink-spreading is an important parameter, which causes lateral variations in dot gain and, therefore, mottle.

2.6.1 What paperboard property is decisive for print quality?

Results in the literature are sometimes conflicting as to the property that has the greatest effect on print quality. It seems that the most important property is related to the samples being studied, the press settings used during printing and the particular print quality involved. The samples can span a wide range when it comes to one property but not the other, the press can be run in a forgiving manner for one property but not the other and when studying a halftone compared to solid tone the results may differ.

As suggested by Zang and Aspler (1995a) it is often thought that surface smoothness is necessary for high print quality with low print mottle, however this does not, by default, result in high print quality. As the samples become smooth or at least equally rough, other parameters, such as surface chemistry of the substrate, can start having an effect. Lagerstedt and Kolseth (1995), on the contrary, suggested that the combination of two unfavourable properties (e.g. roughness and hydrophobicity) might be need to cause bad print quality. There are also reports that both roughness and surface chemistry correlate with print quality, when comparing very different samples but not when examining very similar samples. For example, more hydrophilic and surface smooth linerboards
gave increased printing efficiency (density per gram of ink) when including samples from different segments (e.g. white-top, brown and solid white liners, sized and not) in the comparison (Aspler et al., 1998, Zang and Aspler, 1995a). In line with this, it was suggested that surface energy and absorbency of the substrate have a negative impact on print mottle, when they are at extremely high or low levels (Aspler, 2004). Another example showed how pre-treatment made uncoated papers more hydrophilic, which had a positive effect on print mottle when the samples had low absorbency from the start (Johnson et al., 2005). A similar treatment had no impact on papers that were already highly absorbent (Johnson et al., 2008).

It was reported that ink binder type (Luu et al., 2010b, Olsson, 2007), press speed (Lagerstedt and Kolseth, 1995), plate hardness and nip pressure (Barros and Johansson, 2007) have all had an effect on the relative sensitivity to surface roughness and surface energy. In the latter study, higher print mottle was seen on coated substrates with higher surface energy, when combining a high or low nip pressure with a soft or hard plate, which showed that the surface energy did not make an impact on print mottle under less extreme conditions.

The impact from surface energy on ink spreading may not have equal impact on solids and halftones, as pointed out by Lagerstedt and Kolseth (1995) and Aspler (2004). The spreading may have a higher impact on halftones through dot gain. Ink-paper boundaries are formed around each dot (at least in lower tone values) and the spreading potential will impact the dot size. In the solid tones, ink spreading is more likely to have a levelling effect giving a more uniform density. Ink-paper boundaries are also formed where there are UCAs, and consequently spreading may reduce their size.

### 2.6.2 Surface roughness

When considering surface roughness or topography, the kind of characterisation technique has to be taken into account. The commonly used air-leak techniques may not be adequate for predicting print quality and, consequently, more sophisticated topographical analyses will be required. This was shown for coated substrates (Aspler, 2004, Barros et al., 2005) and uncoated samples (Steadman et al., 1993). All kinds of roughness are not important for print quality, but focus should be put on their relevant degree (Barros et al., 2005). The various air-leak techniques are sensitive when it comes to different ranges. It was reported that Bendtsen and Sheffield instruments capture long wave variations (2-5 mm), whereas Parker Print Surf (PPS) can
detect structures across the whole range but without very high correlation for any given band (Steadman et al., 1993, Wågberg and Wennerblom, 1992).

There are reports that, for uncoated papers, surface roughness negatively affects ink transfer and, as a result, print density and the perceived quality (Lagerstedt and Kolseth, 1995, Luu et al., 2010b, Wågberg and Wennerblom, 1992). Jensen (1989) showed that rough coated linerboards required larger print impression to achieve satisfying quality. The higher nip pressure resulted in larger point-spread and with the rough substrates the pressure was not distributed evenly, which gave low print evenness. Similarly, visual print mottle on coated boards has been linked to topography (Barros and Johansson, 2007). In this study it was suggested that ink was pressed away from areas due to greater local pressure and that it accumulated in the depressions. In fact this result was found on a set of very similar samples (representing natural fluctuations in a board machine), which contradicted the report by Aspler et al. (1998) that stated that roughness was only being able to separate samples that were largely different. Micro-mottle, on the other hand, has been linked to both topography and capillary absorption (Barros and Johansson, 2007, Wågberg and Wennerblom, 1992).

It was shown, by Barros et al. (2005) that UCA was correlated to surface cavities on coated and uncoated boards. The deeper the cavity, the more frequent the UCA, due to an incomplete transfer of ink. The authors concluded that it is very important to focus on the relevant structures, such as spatial size and depth. Large (wavelengths of >0.75 mm) or fine-scale (wavelengths of <150 μm) cavities were not considered critical (Barros and Johansson, 2006). The report stated that large cavities may have been flattened in the printing nip and that small depressions may have been bridged by the ink. In the study 2006, topography accounted for roughly 50% of the UCAs, whereas Bohlin (2013) found that about 30 % of the UCAs were connected to structural variations (from fibres near the surface) and that the rest may originate from poor wetting.

2.6.3 Absorbency

As already discussed, surface chemistry and pore structure impacts the absorption potential of a paperboard. Some researchers have studied the connection between print quality and surface energy, wetting or pore structures, whereas others instead have focussed on measuring the absorption, i.e. combined effect, and linking this to print quality. The following paragraph deals with the correlation between print quality and absorption measurements and
sections 2.6.3.1 and 2.6.3.2 deal with the impact from pore structure and surface chemistry respectively.

In the review by Aspler (1993), it is suggested that a high degree of absorbency may lead to worse ink hold-out and an increase in ink penetration, but also to higher degree of ink transfer. Hence, print density can go either way; it can increase or decrease according to the absorbency. Reports state that print density on uncoated boards increases with a lower level of absorbency (McGratten, 1990, Steadman et al., 1993, Wågberg and Wennerblom, 1992). At the same time, it has been shown that print mottle increases and it, consequently, deteriorates the perceptual print quality (Wågberg and Wennerblom, 1992). Jensen (1989) explained that a higher print mottle occurs when the ink setting is slowed down and gives more time for ink spreading. When absorbency is too low, it may also lead to drying problems.

2.6.3.1 Pore structure

With a more open coating structure, ink penetration is reported to increase and ink holdout decrease, which can lead to lower print density (Bohlin et al., 2013, Mesic et al., 2004, Preston et al., 2008). At the same time, the ink setting can go faster, which limits ink spreading and, hence, lowers dot gain. Using a similar reasoning, Zang and Aspler (1995a) concluded that an uneven porosity in a lateral direction, may lead to print mottle.

Ink holdout is largely dependent on the surface pore size, where finer pores are better at keeping pigments on the surface for any printing technique (Aspler and Lepoutre, 1991, Zang and Aspler, 1995b). Apart from maintaining ink solids and dye-stuffs on the surface due to size exclusion, they may also be retained as a result of a high adsorptive surface area, combined with low permeability in water-based flexographic printing, such as when the wetting front spends a long time close to the surface (Ridgway and Gane, 2002).

2.6.3.2 Surface chemistry

Wettability is potentially of greater significance when it comes to water-based flexographic printing as compared to offset printing (Zang and Aspler, 1995a). However, the external pressure in the printing nip, may overcome wetting problems (Lagerstedt and Kolseth, 1995).

According to Hou and Hui (1990), both the polar and dispersive components of the surface energy of substrates need to be at a low level in order to impede water-based ink absorption. The dispersive component, alone, needs to be at a low level in order to impede oil absorption. Concurrently, more polar coating
layers resulted in a higher print density (Olsson et al., 2006b) and more uniform print (Bassemir and Krishnan, 1991) in water-based flexography.

Increasing the surface energy and making paper or board more hydrophilic may increase ink transfer and print density (Aspler et al., 1998, Lagerstedt and Kolseth, 1995, Sheng et al., 2000). Ink spreading has been shown to decrease as the substrate becomes more hydrophobic (Lagerstedt and Kolseth, 1995).

### 2.6.4 Coat-weight distribution

Since the thickness of a coating layer can affect pore structure (Lepoutre, 1978b), an uneven coat-weight distribution may result in uneven porosity, absorbency and hence non-uniform print density (MacGregor and Conners, 1987, Zang and Aspler, 1995a). MacGregor and Conners identified a connection between print density speckles and wire marks on a web-offset printed light-weight coated paper. Areas with thicker coating corresponded to lower print density and were considered to possess lower absorptivity. Likewise, Engström et al. (1989), found a high correlation between offset print mottle and a variance in coating mass on fine papers. Similar effects can be expected to find in water-based flexography as well.

### 2.6.5 Impact from press settings on print quality

**Printing pressure:** Up to a limit, the contact between plate (ink) and substrate can be increased by using a bigger printing pressure. In this way, ink splitting patterns and UCA can be reduced with an increase in ink transfer. There may also be negative effects on print quality, worse visual print mottle, for instance, when increasing the nip pressure (Aspler et al., 1998, Barros and Johansson, 2007, Zang and Aspler, 1995a). As the plate is compressed, the dots become distorted and the print tends to be less precise (McGratten, 1990, Olsson et al., 2006b).

**Plate hardness:** It has been shown that using a softer plate increases print density and ink transfer, as well as reducing UCA (Barros and Johansson, 2007, Johnson et al., 2004). As suggested by Barros and Johansson, a softer plate is more compliant and, consequently, increases the contact area between the ink and substrate. The down-side of using a soft plate is that the dots are more distorted, thus causing a high level of dot gain (Aspler et al., 1998).

**Ink:** Various properties of an ink may affect print quality. A high degree of dynamic surface tension and polarity will have a negative impact on the transfer and spreading ability of the ink (Aspler et al., 2004). On the other hand, low polarity inks have shown a deeper ink penetration (Olsson et al., 2006a).
Decreasing the viscosity of an ink has resulted in an increase in the print density on coated substrates (Olsson et al., 2007b). The reverse was observed on non-absorbent polyethylene (Lavelle et al., 1996).

Olsson et al. (2007a) showed that the resistance of ink fluid to separate from the ink solid phase, depends on the interaction between ink components and water, together with the packing ability of the ink pigments. It has been termed filter-cake resistance (Luu et al., 2010a, Luu et al., 2010b) as well as the dewatering rate (Olsson et al., 2007a) of an ink (high dewatering means that the filter-cake resistance is low). Solution polymer based inks have shown a slower dewatering, which leads to a longer period for ink levelling and spreading, i.e. higher print gloss (Luu et al., 2010a, Luu et al., 2010b, Olsson et al., 2007a). In the studies by Luu et al., a fast dewatering of emulsion polymer inks made the print more sensitive to substrate properties. For example, the hydrophobicity of uncoated substrates had a negative effect on transfer and print density when using inks with the emulsion polymer binder.
3 Experimental approach

3.1 Board materials

The samples in this study were chosen from one group of commercial boards (coated liquid packaging boards for flexographic printing), provided by Stora Enso (Swede), BillerudKorsnäs (Sweden) and Tetra Pak (Sweden), and from one group of pilot-coated boards, see Table 1.

When developing the staining technique presented in Paper I, ten of the pilot-coated boards were used (20 latex A being excluded). In the round robin test presented in Paper II the six commercial boards A-F were included. When studying the effect on print quality as a result of uneven absorption in Paper III, four of the pilot-coated boards (15 Latex A, 20 Latex A, 20 Latex B and N75 GCC) and two of the commercial boards (Com. A and Com. B) were used together with a cast-coated offset grade as a super-smooth reference (Com. C).

Table 2 Formulation of pilot-coated samples.

<table>
<thead>
<tr>
<th>Four series of top-coating formulations (11.3-12.0 g/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(i) Three different types of ground calcium carbonates (100 parts per hundred parts pigment, pph, of each): Covercarb 75 (N75 GCC), with narrow PSD and 75% of the particles &lt; 1 μm and 95% &lt; 2 μm. Two pigments with broad PSD; Hydrocarb 90 (B90 GCC) with 90% of the particles &lt; 2 μm and Setacarb HG (B98 GCC) with 98% of the particles &lt; 2 μm. The carbonates were supplied by Omya International AG, Oftringen, Switzerland. 15 pph of latex A (see below).</td>
</tr>
<tr>
<td>(ii) An increasing of the latex (type A) content: 12.5, 15, 17.5 and 20 pph. Latex A was vinyl acetate acrylate latex (CHP 2635EP, CH Polymers Oy, Raisio, Finland), with Tg 15°C. Pigment. 60 pph B90 GCC and 40 pph B98 GCC.</td>
</tr>
<tr>
<td>(iii) Another type of latex (type B): 20 pph. Latex B was styrene butyl acrylate latex (Acronal S722, BASF, Ludwigshafen, Germany), with Tg 23°C. Pigment. 60 pph B90 GCC and 40 pph B98 GCC.</td>
</tr>
<tr>
<td>(iv) An increasing of the clay content (Brazilian delaminated clay, Capim NP, Imerys S.A, Paris, France) mixed with B90 GCC: 10, 20 and 40 pph clay. 15 pph of latex A.</td>
</tr>
</tbody>
</table>

In addition: 0.5 pph thickener (FinnFix 10, Noviant Oy, Finland) and 0.08 pph soda

Pre-coating: 11.8-12.5 g/m², 100 pph Hydrocarb® 60 (Omya International AG, Oftringen, Switzerland) with 60% of particles < 2 μm, 13 pph Latex A, 0.5 pph thickener (FinnFix 10) and 0.08 pph soda.

Base board: 200 g/m² duplex (Klabin S.A., Brazil)
Table 1  Boards included in the studies. Pilot-coated: 12.5 Latex A through N75 GCC
Commercial: Liquid Pack., A-F, Com. A and Com. B were all flexographic grades (coated
packaging boards) and Com C. was a coated offset grade.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Pore volume (top coating) [cm³/m²]</th>
<th>Pore size R₅₀ [µm]</th>
<th>Roughness, λ 0.06-1 mm [µm]</th>
<th>Contact Angle H₂O 0.1 s [°]</th>
</tr>
</thead>
<tbody>
<tr>
<td>12.5 latex A</td>
<td>1.7</td>
<td>0.05</td>
<td>0.80</td>
<td>71.2</td>
</tr>
<tr>
<td>15 latex A</td>
<td>1.8</td>
<td>0.06</td>
<td>0.85</td>
<td>75.2 78.3</td>
</tr>
<tr>
<td>17.5 latex A</td>
<td>1.8</td>
<td>0.06</td>
<td>0.86</td>
<td>80.7</td>
</tr>
<tr>
<td>20 latex A</td>
<td>1.2</td>
<td>0.06</td>
<td>0.86</td>
<td>81.5 77.3</td>
</tr>
<tr>
<td>20 latex B</td>
<td>1.2</td>
<td>0.04</td>
<td>0.83</td>
<td>88.1 85.8</td>
</tr>
<tr>
<td>10 clay</td>
<td>1.8</td>
<td>0.07</td>
<td>0.87</td>
<td>75.8</td>
</tr>
<tr>
<td>20 clay</td>
<td>2.7</td>
<td>0.07</td>
<td>0.82</td>
<td>73.3</td>
</tr>
<tr>
<td>40 clay</td>
<td>2.2</td>
<td>0.07</td>
<td>0.79</td>
<td>70.3</td>
</tr>
<tr>
<td>B98 GCC</td>
<td>1.9</td>
<td>0.05</td>
<td>0.83</td>
<td>72.6</td>
</tr>
<tr>
<td>B90 GCC</td>
<td>1.8</td>
<td>0.07</td>
<td>0.86</td>
<td>78.3</td>
</tr>
<tr>
<td>N75 GCC</td>
<td>2.0</td>
<td>0.08</td>
<td>0.83</td>
<td>73.4 75.4</td>
</tr>
<tr>
<td>Liquid Pack.</td>
<td>0.67</td>
<td>0.60</td>
<td></td>
<td></td>
</tr>
<tr>
<td>A</td>
<td></td>
<td></td>
<td>0.70</td>
<td></td>
</tr>
<tr>
<td>B</td>
<td></td>
<td></td>
<td>0.53</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td></td>
<td></td>
<td>0.75</td>
<td></td>
</tr>
<tr>
<td>D</td>
<td></td>
<td></td>
<td>1.05</td>
<td></td>
</tr>
<tr>
<td>E</td>
<td></td>
<td></td>
<td>0.77</td>
<td></td>
</tr>
<tr>
<td>F</td>
<td></td>
<td></td>
<td>0.64</td>
<td></td>
</tr>
<tr>
<td>Com. A</td>
<td></td>
<td></td>
<td>1.13</td>
<td>75.4</td>
</tr>
<tr>
<td>Com. B</td>
<td></td>
<td></td>
<td>0.82</td>
<td>82.6</td>
</tr>
<tr>
<td>Com. C</td>
<td></td>
<td></td>
<td>0.28</td>
<td>86.4</td>
</tr>
</tbody>
</table>


The top-coatings of the pilot-coated materials were designed to create different absorbency and hydrophobicity, while using the same base and pre-coat. The samples can be divided into four groups: different calcium carbonates, increasing amount of latex (type A), another type of latex (type B) and increasing of the clay content, see Table 2. The pilot-coating was performed in the machine at BillerudKorsnäs, Frövi, Sweden, using a Jagenberg bent ceramic blade (angle approx. 18°). Running speed was 600 m/min.
3.2 Modifying the absorption non-uniformity of coated boards

Paper III, proposed a method that has the aim of studying independently the effects of absorption non-uniformity on print mottle. This was achieved by introducing artificial absorption non-uniformity on coated boards using well controlled barrier patterns. The surfaces were modified with barrier patterns to induce non-uniform absorption without changing other properties of the coated boards. The objective was to create a property matrix involving a comparison of absorption non-uniformity with, for example, surface roughness.

A flexographic ink vehicle (without colorant) worked as a barrier. It was added during flexographic printing (F1 Printability tester, IGT Testing Systems, Amsterdam, Netherlands) as a very coarse halftone screen (31 lpc, lines per centimetre) with tone values between 2% and 14%. The nip pressure was 25 N in the printing and the anilox nip. The printing was made at a speed of 0.5 m/s, with an UVR 1.7 mm (MacDermid Printing Solutions Europe, France) plate and a 2.7 cm³/m² anilox (IGT Testing Systems, Amsterdam, Netherlands).

The absorption became uneven, as the barrier partly filled the porous structure and changed the surface chemistry. The non-uniformity, seen as uneven absorption, for instance, was primarily observed in the wavelength interval of 0.25 mm – 8 mm, peaking at 0.5 mm - 1 mm, see Figure 4. With higher tone values, absorption became more uneven.

![Figure 4](image-url)

Figure 4. Example of absorption non-uniformity divided into wavelength classes. The non-uniformity of four barrier patterns of different nominal tone values (2% - 14%) are shown in separate series. The peak around 0.5 mm - 1 mm is caused by the barrier pattern. The non-uniformity increased with the nominal tone-value.
3.3 Absorption and wetting

3.3.1 Spontaneous absorption non-uniformity through aqueous staining technique

A new staining technique, using coloured water, was proposed in Papers I and II and then carried out in Paper III. The staining technique is described here in the experimental section, whereas an analysis of the stains and a validation of the technique are described in the section 4 Results and discussions.

A sample is allowed to absorb dyed liquid during a brief, defined time-lapse, see Figure 5. This leaves a stain on the surface of the sample. The time for absorption is defined by the speed and distance between the positions of the liquid application and the removal of excess liquid using blotting paper. To minimise the effect from surface roughness it is vital that there is an excess of liquid on top of the entire sample until it is removed in a nip with the blotting paper.

A laboratory print tester, F1 Printability tester (IGT Testing Systems, Amsterdam, Netherlands), was used to control the absorption period and the blotting pressure. Samples were tested at 0.5 m/s running speed, 350 N nip pressure and 50 mm application width, with a soft backing around the “blotting” cylinder (2.39 mm thick SF950 cushioning material from Rogers Corporation, Evergem, Belgium) and with the Munktell BF3 blotting paper (330 gsm, with a capillary rise of 130 mm/10 min and a thickness of 0.76 mm from Munktell Filter ab, Falun, Sweden). The period for liquid absorption was about 0.15 s, which was the time lapse between the liquid application and the beginning of the removal of the liquid.

Figure 5. Illustration of the measurement set-up. (Thorman et al., 2012)
Various liquids were tested and in the three studies, with the colorant being methylene blue. In Papers I and II, water was mixed with a methylene blue solution containing some surfactant, whose specifications were not given by the producer. In Paper I, the test also included an addition of n-propanol. In the experimental work leading up to Paper III, different surfactants (commercially available surfactants for flexographic inks) and alcohols were evaluated for lowering the surface tension of pure water and for ensuring that the testing would be more stable. The best option for the liquid was a mixture of deionised water, 0.025 wt.-% of methylene blue (C.I. 52015, Merck KGaA, Darmstadt, Germany) and 0.007 wt.-% of Surfynol 2502 (Air Products Chemicals Europe BV, Utrecht, Netherlands).

The stains were uniform when the absorption was homogeneous over the surface, whereas local variations in absorption created reflectance disturbances. Due to the stains being semi-transparent, variations in the reflectance of the boards, such as white-top mottle, affected the stain reflectance. The uniformity of the semi-transparent stains were scanned (Epson Perfection V750 PRO, Seiko Epson Corp., Japan), after which the contribution from non-uniform absorption was calculated in two different ways (Papers I and II), which are described in the section 4.1.1 Analysis of stain.

The reproducibility of the test method was evaluated using a Round Robin test (Paper II). Three laboratories participated in the Round Robin (P1, P2, P3), two at board producers and one at Innventia AB, using their respective F1 Printability tester (IGT Testing Systems) equipment and operators. All laboratories used the same dyed water and the same board samples. To eliminate any influence from different image grabbing acquisition, all the stains were scanned and analysed by the same laboratory. Apart from the Round Robin test, the stability of the stain pattern, the effects from surface roughness and the accuracy of the white-top mottle predictions (from stain measurements) were also evaluated.

In Paper I, the effect from surface roughness on the aqueous stains was calculated. Before the stains were made, topography maps of three samples were captured using the OptiTopo (Innventia AB, Stockholm, Sweden) instrument. The grey level of the stain and the height of the surface were aligned and compared, pixel by pixel. Focus was placed on the wavelength intervals of 0.25 mm - 1 mm and 0.06 mm - 1 mm.

Additionally, the liquid availability before the nip was investigated with a Niko D200 camera (Nikon Europe B.V). Position 1, see Figure 6, was studied to
verify that there were liquid films covering the samples up to the blotting nip. A Speedlight SB-800 flash (Nikon Europe B.V.) was used. The images were only assessed visually. These results were partly presented in Paper II.

![Diagram](image)

**Figure 6.** Illustration of where the liquid film (position marked 1) was studied. The images were taken from above the sample. Position 1: For this test the liquid applicator was moved out of its normal position (temporarily), so that the liquid film on the samples could be studied 88 mm after liquid application. The centre of the images focus on the position where the blotting would take place normally.

### 3.3.2 Contact angle and surface energy

Contact angle measurements were made using a dynamic contact angle analyser, DAT (FIBRO system AB, Hägersten, Sweden). In Paper I, the contact angle of the water and the aqueous solution of water and the 8.6 wt.-% n-propanol were measured on the pilot coated boards.

In Paper III, the surface energy was calculated from the contact angle measurements involving three liquids. The calculations of the surface energy were carried out according to the Owens and Wendt method (Owens and Wendt, 1969). The contact angle readings were taken at 0.1 s for the deionised water (treated by reverse osmosis and deionisation at Innventia AB, Stockholm, Sweden) and 0.8 s for the Diiodomethane (for synthesis, Merck KGaA, Schuchardt, Germany). The drops had stabilised and the liquid volumes were quite steady around these times. However, it is worth noting that the water drops had spread (advancing angles) on the boards. However, they were about to shift from receding to advancing contact angles at 0.1 s on the barriers. It was considered that the solid tones of the barrier materials provided a general idea of how the surface energy was affected in the barrier dots, although the ink coverage was expected to differ between the solid and halftone.
3.4 Coat-weight variations

3.4.1 White-top mottle
White-top mottle comes from the unbleached base being unevenly covered with white top layers (bleached fibres and coating). Hence, coat-weight variations are often linked to white-top mottle. In Paper I, white-top mottle was measured based on grey-scale images and calculated as a coefficient of the variation in reflectance, using STFI Mottle software (Innventia AB, Stockholm, Sweden). In the Paper II, white-top mottle was calculated using the blue channel in RGB-images of the stains and boards, using the same software. To verify a successful separation, white-top mottle, calculated from the stains, was compared with white-top mottle without any stain.

3.4.2 Coat-weight variations through burn-out treatment
Another method of calculating coat-weight variations was by means of reflectance variations after a burn-out treatment on the pilot-coated boards. The pilot-coated boards underwent burn-out treatment by saturating the samples with an aqueous solution containing 25 g/l Ammonium Chloride (pure, probably Sigma Aldrich Co. LLC.) in 50%-wt. water (treated by reverse osmosis and deionisation at Innventia AB) and 50%-wt. Ethyl alcohol (absolute 99.5%, VWR International S.A.S.). The saturated samples were then kept at 200°C until the fibres turned black. An uneven coating coverage is clearly visible when the fibres turn black and the coating stays white. This was analysed as a standard deviation in reflectance from the grey-scale scanned images using STFI Mottle software (Innventia AB, Stockholm, Sweden). This treatment is valuable for comparisons of variations, but does not reveal the absolute value of coating thickness.

3.5 Coating pore structure

3.5.1 Mercury porosimetry
The coating pore structure of the pilot-coated boards was characterised with the aid of mercury porosimetry, using a Micrometric AutoPore IV (Micromeritics Instrument Corp., Norcross, USA). The pre-coated boards, which was the same for all top-coatings, and the fully coated boards were analysed. The structure of the top coat was obtained by subtracting the pores of the pre-coated board from the fully-coated board, using the pore radius interval of 25 nm to 100 nm. The pore volume was given as cm³ voids per m² of board and the value of pore size was the R50-value, which means that 50% of the void volume had finer pores and 50% had coarser pores. However, it must be
borne in mind that the volume of finer pores most often becomes over represented, due to the bottle-neck effect. Moreover, it is important to understand that subtracting the pore volumes measured on a pre-coated board (large volume) from that of a fully-coated board (large number), to estimate the pore volume of the top-coating alone (small number) involves quite an amount of uncertainty. If the porosity of e.g. the pre-coated base board deviates between the regions where the two pore volumes were determined, it can have a large impact when calculating values for the top-coating. However, the calculations and the analysis of data showed that the top coatings that were obtained contained pore structures that ranked samples as expected.

3.5.2 Local surface pore structure

The surface pore-structure of two selected barrier patterns (Paper III) was acquired by means of local measurements of the refractive indices, using the Surfoptic Imaging Reflectometry System (Data Systems Ltd, Bristol, United Kingdom). This technique uses plane polarised light and detects the intensity and angular distribution of reflected light. From this, the effective refractive index (RI), the micro-roughness, the macro-roughness and the gloss can be calculated. Using a high angle of incidence (75°) minimised the effects of light absorption into the substrate, which could otherwise make the effective RI deviate from the real RI. It was reported that this works well for surfaces with a real RI of approx. 1.5, which coating layers normally have (Elton and Preston, 2006b). The greater the air content in the surface, i.e. more porous, the lower the effective RI will be. It was shown that RI decreases with the pore diameter, but also with the pore density (the number of pores per area) (Elton and Preston, 2006a). This measurement detects RI in the top surface, less than 1 μm depth (Hiorns et al., 2005). Two barrier printed boards were analysed and an area of 50 mm x 50 mm was scanned in the mapping mode. The ink vehicle used as a barrier was expected to have similar refractive index as the coating solids. When the ink vehicle closes the surface pores, the RI is expected to increase.

A limited selection of the barrier patterns was analysed, using a scanning electron microscopy (SEM). Scanning electron microscopy (SEM) images were taken after the sputtering of a conductive mono-layer of gold/palladium (Au/Pd) alloy. The secondary electron emission from the surface of the samples was detected in a Jeol 6700 field emission SEM (JEOL Ltd., Tokyo, Japan), using a primary electron beam of 5.0 kV.
3.6 Surface roughness

A MicroProf® (MPR 1106 with sensor CWL, Fries Research & Technology GmbH, Bergisch Gladbach, Germany) and an OptiTopo (Innventia AB, Stockholm, Sweden) were used to capture the surface topography of the samples. The MicroProf uses chromatic aberration and the OptiTopo uses a photometric stereo technique to analyse a surface. In Paper III, the height was measured directly on the unmodified board materials. In addition, measurements were made on replicas of the coatings and 10% barrier tones that had been cast using a silicon rubber compound (RepliSet-GF1 from Struers A/S, Ballerup, Denmark).

Profiles were captured, using a MicroProf and x-y maps with OptiTopo:

- MicroProf: twenty profiles per sample were placed 3 mm apart, each having a length of 60 mm and a resolution of 5 μm in the cross direction (CD). (paper I)
- OptiTopo on unmodified boards: Paper I: For each sample one area of 13 mm x 13 mm was aligned and compared pixel by pixel with an image of the stain made in the same position. Paper II: An average of eight areas of 16 mm x 16 mm with a lateral resolution of 15.6 μm in both directions. Paper III: An average of eight areas of 13 mm x 13 mm with a lateral resolution of 12.7 μm in both directions.
- OptiTopo on replicas: one area of 16 mm x 16 mm with a lateral resolution of 15.6 μm in both directions. The height maps were inverted to represent the sample profile. Since the barrier material was transparent, it could not be properly detected without the intermediate replica step. (Paper III)

The surface roughness was calculated as a standard deviation of the height and divided into spatial wavelength intervals using one-dimensional FFT (Fast Fourier Transform). Focus was on the following wavelength intervals for the unmodified boards: 0.06-0.25 mm, 0.06-1 mm and 0.25-1 mm. The replicas were analysed with respect to height variance spectra but, more importantly, thresholds were set to identify the high areas of the surface and to compare these with the position of the barrier dots.

3.7 Printing and print quality evaluation

After creating the sample matrix with varying absorbencies in Paper III, a solid cyan print was applied to evaluate the impact from the absorption pattern on
printing. Printing was made in the F1 Printability tester (IGT Testing Systems), using the same, but complete, ink as when creating the barrier patterns (the barrier patterns were made with the colourless vehicle). The cyan ink was from Siegwerk and designed for printing at Tetra Pak, Lund, Sweden. The viscosity of the ink was 19 s (DIN cup 4 mm) and the surface tension was 38.6 ± 0.08 mJ/m, which was similar to the surface energies of the samples or slightly below. The nip pressures were 100 N and 75 N, in the printing and anilox nip respectively. The anilox, plate, and running speed were the same as when adding the barriers, see 3.2 Modifying the absorption non-uniformity of coated boards.

The inking of the plate was not uniform in the laboratory press, hence two strips were printed in opposite directions, going from 0% to 14% and vice versa, after which an average was calculated. The two strips deviated to some extent, and one was more heavily inked in the 0% area and the other in the 14% area. This will impact print mottle, and calculating an average helps to even out the effect. Due to this, the 95% confidence interval can be fairly large.

The uniformity of the solid cyan print was evaluated by means of print mottle analysis. Images of the print were captured with an Epson Perfection V750 PRO scanner (Seiko Epson Corp., Japan) at 1200 dpi and the print mottle was analysed using the STFI Mottle software from Innventia AB (Johansson, 1999). Grey-scale images were calibrated to reflectance and the variation was separated into spatial wavelength bands using a two-dimensional FFT. Emphasis was put on the standard deviation of the reflectance in the wavelengths between 0.5 mm and 8 mm. The measurement areas were 21.7 mm x 21.7 mm.

For certain samples, the printed areas were studied using a stereoscopic microscope (SMZ-U zoom 1:10, Nikon Corp.).
4 Results and discussions

4.1 Measuring absorption non-uniformity

When it comes to characterising the absorption uniformity of water-based liquids, there are hardly any available techniques. To fill this gap, the focus in Papers I and II, was to develop a test capable of characterising absorption non-uniformities. This is referred to in Paper II as absorption mottle. Focus was placed on characterising the spontaneous absorption, but that was not to state that mechanically forced absorption is of any lesser importance. However, a full understanding of the impact on flexographic printing may require characterisations of both spontaneous and mechanically forced absorption. The proposed technique, which is robust and repeatable, uses a relatively short absorption duration time.

4.1.1 Analysis of stain

In Paper I, the absorption non-uniformities were calculated using individual measurements of white-top mottle and stain mottle, which were both from grey-scale images. The absorption non-uniformity ($CV_{TRANSPARENCY}$) was then calculated as the difference between the stain mottle ($CV_{STAIN}$) and the white-top mottle ($CV_{WTM}$): $CV_{TRANSPARENCY}^2 = (CV_{STAIN})^2 - (CV_{WTM})^2$. The difference sometimes produced a negative result, which was therefore incorrect physically.

In Paper II, an improved approach was presented, which was more reliable and enabled the determination of absorption non-uniformity and white-top mottle from one measurement. From an RGB image, the red and the blue image channels were used separately to normalise the reflectance value of each individual pixel. The blue stain is almost transparent to blue light and absorptive to red light, see Figure 7-8. In other words, the non-uniformity in the blue channel is dominated by white-top mottle and the red channel is dominated by the non-uniform liquid absorption. However, there is also a contribution from white-top mottle in the red channel, which needs to be suppressed.
Figure 7. Illustration of the principle of the analysis method. The stain is digitalised by a scanner into RGB colour images. The blue channel is dominated by white-top mottle of the paper board, while the red channel image is dominated by the absorption non-uniformity. (Thorman et al., 2013)

Figure 8. Example of the reflectance spectra of the board (including the coating layer), the base board and the stain. There is a contribution from white-top mottle in all bands, whereas the stain mainly absorbs light in the red band.

To acquire the normalised reflectance related to absorption \( R_{\text{absorption}} \), the reflectance value of the stain \( R_{\text{red}} \) in each pixel was divided by the reflectance value of the board \( R_{\text{blue}} \) in the corresponding pixel and then multiplied by the average reflectance of the board \( \bar{R}_{\text{blue}} \), see Eq. 20. This was done for each pixel and a new absorption image was created.

\[
R_{\text{absorption}} = \frac{R_{\text{red}}}{R_{\text{blue}}} \times \bar{R}_{\text{blue}} \tag{20}
\]

The absorption non-uniformity was calculated as variations in the absorption image and divided into spatial size classes, using a FFT.

There is a risk of overcompensating for white-top mottle, when calculating the absorption non-uniformity, according to Eq. 20. There are two reasons for this. First, the measurements of white-top through the stain gave slightly higher values than when measured without any stain (see 4.1.5 Accuracy of white-top mottle prediction). Second, the brownish colour of the base, see Figure 8, is likely to be somewhat more visible in the blue channel than in the red channel. However,
the two channels rank mottle equally. Any difference in the white-top mottle between the red and blue channels was not accounted for in the normalisation procedure.

4.1.2 Aqueous liquid

Preferably, the liquid should be representative of the water-based flexographic ink. However, it was not considered desirable to include the complete ink in the test, since inks can vary a great deal among manufacturers and even between batches. Several ink properties can be of importance, to correctly mimic the inks behaviour, e.g. the surface tension, polarity, viscosity, pH and type of colorant. So far, focus was on keeping the liquid in an aqueous state, in order to maintain a polar nature and to lower the surface tension for keeping the wetting similar to the ink. It was not possible to increase the viscosity, due to runnability problems during the test. Yet, other aspects to investigate are pigment-based colorants and to examine the effect that the pH level has.

Methylene blue dye has a chromatographic effect and, hence, a certain amount of preferential adsorption. This has not been studied in detail, although the action of being deposited in the top layer when liquid was being absorbed into the coating structure was considered a positive aspect. This reduced the risk of highly absorbing pores dragging the dye deep down into the structure and, thereby, making the stain appear brighter.

4.1.3 Reproducibility of the absorption non-uniformity technique

The Round Robin test indicated that it was quite simple to reproduce the absorption uniformity test. The standard deviation between the three laboratories was 0.02 on average. The deviation for each sample is listed in Table 3. It would have been preferable for with samples chosen in this test to have covered a wider, since several of the samples did not produce a significant difference, Figure 9. Nevertheless, the coefficients of determination ($R^2$) among the measurements at the different laboratories were 0.68 - 0.75.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mottle 1 mm - 8 mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.46</td>
</tr>
<tr>
<td>B</td>
<td>0.56</td>
</tr>
<tr>
<td>C</td>
<td>0.50</td>
</tr>
<tr>
<td>D</td>
<td>0.44</td>
</tr>
<tr>
<td>E</td>
<td>0.53</td>
</tr>
<tr>
<td>F</td>
<td>0.42</td>
</tr>
<tr>
<td>Average</td>
<td>0.49</td>
</tr>
</tbody>
</table>

Table 3. Standard deviation among absorption non-uniformity measured at the three laboratories.
4.1.4 Stability of mottle pattern
Absorption patterns faded when they were left out in daylight but, when kept in the dark, the stains were found to be stable in both the longer (1 mm to 8 mm) and shorter (0.5 mm to 1 mm) ranges of wavelength (see Figure 10). The ranking of the samples was not affected and the absolute levels were almost constant, indicating that the mottle pattern did not change with time.

4.1.5 Accuracy of white-top mottle prediction
In Paper II, the white-top mottle of a board was characterised by measuring the reflectance variation of the stain in the blue channel of an RGB image. This was validated by means of comparing measurements made of the white-top mottle in the same area, before and after the stains were made. As shown in Figure 11,
the correlation was very high, indicating that it was definitely possible to measure white-top mottle through a stain, using the blue channel in an RGB image.

![Figure 11. Correlation between white-top mottle in the same area, before and after staining (both from the blue channel). Error bars indicate the 95% confidence interval.](image)

There is a slight offset from 1:1 line and, the values measured through the stain were probably higher because of the stain being slightly visible in the blue channel. This made the average reflectance decrease by 1-4 percentage points. The coefficient of variation (CV), i.e. white-top mottle, will increase when the average reflectance decrease, since the standard will be divided by a smaller number. The coefficient of variation will also increase if any stain variations are detectable in the blue channel.

### 4.1.6 Additional verifications of the method

The topography and stain grey levels were compared in the work leading up to Paper I. Before the stains were made, topography maps were captured. The grey level of the stain and the height of the surface were aligned and compared, pixel by pixel (wavelength intervals 0.25-1 mm and 0.06-1 mm).

There were no indications of the grey-level being related to the topography, i.e. liquid was not left in the cavities after being removed with the blotting paper. Their coefficients of determination ($R^2$), when making the comparison pixel by pixel (wavelength interval 0.25 mm - 1 mm), were only 0.01 and 0.05 for two commercial and 0.10 for one pilot-coated liquid packaging boards.

Additionally, it was important to ensure that liquid availability up to the blotting nip was not a limiting factor. An unbroken liquid film covered the sample.
surfaces up to the blotting nip, see example in Figure 12. The image is showing the position where the blotting nip would be normally.

![Image showing the position where blotting would occur normally](image)

Figure 12. Picture showing that the sample is covered by a liquid film, until reaching the blotting nip. The board strip is 50 mm wide.

### 4.2 Studying the impact of non-uniform absorption on print mottle of coated boards with barrier

To study the effect from uneven absorption on print mottle, the absorption uniformity needs to be altered in a controlled way. The absorption is uneven when the pore structure and/or wettability are uneven. This may be accomplished through an uneven dewatering and drying of the coating layer, an uneven binder distribution, an uneven coating thickness or calendaring, where the pressure distribution is non-uniform etc. However, creating any of these would in most cases imply that many other properties change as well, such as the base board, roughness or compressibility, which would make it difficult to study the impact from absorption non-uniformity separately. Another approach is suggested in Paper III, where artificial absorption non-uniformities were introduced through well-controlled barrier patterns.

#### 4.2.1 Verifying the absorption patterns

The barrier partly filled and blocked the surface pores in the dots and, as a result, lowered the surface porosity, see Figure 13. There was not a full coverage in the barrier dots and some pores remained open. In addition, the surface chemistry was altered and the barrier material was generally more easily wetted, due to their higher surface energy and polarity compared to the layers of “pure” coating. Hence, lower surface porosity suggested that less ink might be transferred to the barriers, but on the other hand ink hold-out might increase. Surface chemistry indicated that more ink might be transferred to the barriers.
Figure 13. Two SEM images of a 10% barrier dot on the very open coating structure of board N75 GCC. Image A has higher magnification than image B. The barrier does not completely cover the porous structure.

For the majority of the samples, the coating layers absorbed more liquid and obtained a darker stain than the barrier dots did. This can be attributed to the fact that the barrier material lowered the surface porosity (see Figure 13) and, therefore, hindered the absorption. Nevertheless, the barrier dots still obtained a slight bluish shade in the stain. This may be a consequence of the barriers having a favourable surface chemistry, which caused them to be wetted easily and thus allowed adsorption/deposition of the methylene blue dye to take place, due to polar interactions.

There were two exceptions, where the coatings did not turn darker than the barrier dots in the absorption stains. This might be explained as a combined effect, where the boards absorbed the aqueous liquid very slowly, while the barrier dots were more easily wetted than the coatings. On sample 20 Latex B, the stain was equally bright on the coating layer as on the barrier dots. This effect was even more pronounced on commercial sample C, where there was a brighter stain on the coating layer than on the barrier dots. When making the stain test manually to increase the contact time, the stains on these samples changed to brighter dots and darker coatings (as for the other samples), which may indicate that there was a delay in the absorption (e.g. wetting delay). However the manual testing can only be considered indicative, since it was not carried out under controlled conditions and hence not analysed. The absorption non-uniformity measured on commercial sample C may have detected how non-uniform the surface was in a correct way, but this did not translate directly to the print density, since the pattern was inversed.
Unlike the results from the absorption test, all the barrier dots appeared brighter in the printed samples, including sample 20 Latex B and commercial sample C. It is possible that the effects of surface chemistry that caused the absorption delay were overcome by the nip pressure when printing took place. The impact from pore structure appeared to have greater effect than that of the surface chemistry on the print uniformity.

It was essential that the patterns did not affect the topography. This was accomplished in most of the cases. There were some indications of the barrier dots creating surface peaks on three of the boards, but this was only considered to be a problem on one of them. Commercial sample C had a very closed pore structure, which probably enabled a good barrier hold-out and thereby kept barrier material on top of the surface. This sample was also very smooth and 93% of the barrier dots were higher than the rest of the sample, but only by 0.1 μm. This corresponded to 0.7 μm above the average height. The other two samples were rougher at the start and the barrier dots did not create any clear topography pattern. Only about 9% to 10% of the barrier dots tended to be higher than the rest of surfaces. There were actually many other sections that were equally as high. As much as 83% and 72% of the surface peaks, respectively, were not connected to the barrier dots.
4.2.2 Impact from uneven absorbency on print mottle

The barrier dots slowed down the absorption and lowered the print density, see Figure 14.

Figure 14. Images illustrating how absorption was slowed down by the 10% barrier tone on sample N75 GCC a) coloured water (absorption image from stain) and b) cyan ink (microscopy image). Six barrier dots are seen in each of the images. The absorption of the coloured water was calculated using Eq. 20, this image has then been altered to make the variations more visible (20% increase of brightness and contrast).

When studying the impact from non-uniform absorption separately, it was evident that the print mottle increased when inducing more heterogenic absorption in a sample, see Figure 15. For most of the samples, this relationship was linear, but not equally steep. Hence, it was thought that the print mottle was more sensitive to the non-uniform absorption on certain coated boards than it was on others. This tended to be on the boards that had uniform absorption originally, where the print mottle was affected the most by the changing barrier pattern. The pilot-coated sample N75 GCC, had larger pores, larger pore volume and were more easily wetted than the other two boards in Figure 15a. Consequently it was very sensitive to any increase in absorption non-uniformity. There was no significant difference in sensitivity to uneven absorption, between the two boards with 15 and 20 pph of Latex A, in spite of the more porous structure when having less latex.
Figure 15. Print mottle compared to absorption non-uniformity, both in a wavelength interval of 0.5 mm - 8 mm. Each series represents barrier patterns of 0% - 14% on one board. The seven samples were divided into three separate graphs, a-c. Error bars indicate the 95% confidence interval.
When inspecting the impact of native coating layers (no barrier patterns), the print mottle ranking appeared to be very much controlled by their surface roughness (see Figure 16a) and not at all by uneven absorption, with the latter having a coefficient of determination of 0.03. This indicated that ranking among these samples was mainly controlled by surface roughness, but the low correlation between print mottle and absorption non-uniformity did not say whether uniform absorption generally is of importance in achieving a high print quality or not. As already shown (Figure 15), an uneven absorption caused print mottle on all coated boards, more or less. The effect from non-uniform absorption was evidently less than that from the surface roughness, but it was nevertheless present. Since the samples were compared at a low and constant level of absorption non-uniformity, the effect from the surface roughness became even more pronounced, see Figure 16b. On the contrary, the correlation between print mottle and surface roughness disappeared, when the absorption became largely uneven.

Figure 16. Print mottle compared to surface roughness. In Graph (a), the liquid packaging boards without any barrier patterns are shown (native coatings) and in Graph (b) the print mottle data was normalised to three levels of absorption non-uniformity.
5 Conclusions
The main results of the work presented here is the tools for measuring liquid absorption non-uniformity and the experimental approach to studying its relative contribution on print mottle. The staining technique fills the gap in the methods that are relevant for water-based flexographic printing. It enables characterisation of how uniformly an aqueous solution is absorbed in short time spans and without being affected by surface roughness. The measurement technique can simultaneously quantify the contributions from white-top mottle and uneven absorption by image analysis. The reproducibility and reliability are promising, as suggested by results from the Round Robin tests.

Creating a property matrix, with artificially induced absorption non-uniformities, made it possible to study separately the impact from absorption. Additionally, it is also possible to compare the effect from surface roughness, for example, when absorption is maintained at a constant level. When adding a barrier pattern, it was shown that uneven absorption had a negative effect on print mottle. Absorption non-uniformity may result from an uneven pore structure or an uneven surface chemistry and the results suggested that the effects of surface chemistry, which caused local absorption delays, may be overcome by the nip pressure during the printing process.

When absorption in a sample became less uniform, it had a negative impact on print mottle, which is the reason why it is important to keep this factor under control during board production. However, it did not have as great an importance as surface roughness, when comparing the different samples. Removing the impact from absorption non-uniformity, by keeping it constant and low, revealed that there was an increase in the effect from the surface roughness. When the absorption level was highly uneven, the correlation between the print mottle and the surface roughness decreased and then disappeared completely.

Since sensitivity to uneven absorption differed among the samples, a general statement cannot be made about how uniform the absorption has to be. The limits of “acceptable” absorption non-uniformity will not be the same for all samples.
6 Future work

This report has studied the impact from the combined effect of non-uniform surface energy and porosity. It was suggested that surface chemistry was more important in the spontaneous absorption test, than during the printing process. Hence, it would be beneficial to verify this and evaluate separately to what extent surface energy variations can be overcome by nip pressure. For example, one proposal is to make a hydrophobic pattern without having an effect on the surface pore structure. Furthermore, different inks may react more or less strongly to changes in surface chemistry and porosity.

The barrier pattern caused a lower print density, locally. Since ink pigment penetration is likely to be impeded in these spots, it may be assumed that the lower print density is linked to a lower ink transfer, rather than ink pigments penetrating deep into the porous structure. The results indicated that, variations in the local print density level were impacted by the ink transfer to a greater extent than by the pigment penetration. This may be studied in greater detail using SEM or light microscopy, for example. If it would be possible to keep the ink transfer completely uniform, the impact from pigment penetration on print mottle could be studied separately.

Solid tone printing was the focus here. It can be assumed that other factors come into play when it comes to halftones, where the interface between the ink and the regions increases. For example, ink spreading compared to ink penetration in halftone dots may be studied.

When it comes to the technique to measure variations in absorption, it could be tested with a pigment colorant and the impact from pH level may be investigated. Furthermore, if finding other techniques that measures lateral variations in aqueous absorption, means that comparisons between the two can be made.
References


Absorption non-uniformity characterisation and its impact on flexographic ink distribution of coated packaging boards

Packaging is an important part of a product with the main purposes of protecting and providing information about the packaged goods. The information is most often printed and draws consumer’s attention and helps attaining their trust. Among other things, the print quality needs to be at a sufficiently high and consistent level to create legibility and a competitive packaging. To accomplish this, one needs to gain a thorough understanding of how the substrate interacts with the ink and impacts the print quality. This is essential to both runnability and print quality.

This thesis focuses on the ability of coated packaging boards to absorb liquid and particularly on a) how the uniformity of ink absorption can be measured in a relevant way and b) to what extent absorption characteristics contribute to print mottle in flexographic printing. The thesis encompasses the development of a staining and analysis technique for characterisation of ink absorption non-uniformity and establishment of a method for independent studies of the effects from non-uniform absorption on print quality.