Uniformity of liquid absorption by coatings - Technique and impact of coating composition

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**KEYWORDS:** Liquid absorption, Test Method, Flexographic printing, Coated Board.

**SUMMARY:** The interaction between a liquid and a paper surface is important for a number of paper treatment processes, where absorption is of special significance during printing. Many absorption measurement techniques use a large available volume of liquid to characterise absorption, when compared to the volume of the coating. The uniformity of the absorption is also seldom characterised.

We have developed a new technique, which is presented in this article, to study the uniformity of absorption of a small amount of liquid. This technique is based on the short-time absorption (tenth of a second) of a coloured liquid, the blotting of excess liquid and a characterisation of the pattern of the stain.

This method made it possible to detect differences among coating layers with different compositions. In many cases, the absorption non-uniformity could be linked to variations in the coating thickness and/or wettability. The thinner and thicker areas of the coating layers were interpreted as having different pore structures. Neither the coating thickness nor the wettability could provide a full explanation, which showed the need to develop a method to characterise absorption uniformity instead of only relying on measuring the total absorption potential.

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Print quality and ink transfer are very much determined by surface roughness (Aspler et al. 1998; Barros 2006; Woods et al. 2000). However, there are cases where roughness does not distinguish between samples with the potential for high print quality from ones that will result in poor quality. In such cases, absorption characteristics could be a key matter. However, absorption needs to be measured in a way that is relevant to printing. For water-based flexography, this means quite a rapid absorption of a small volume of liquid. When considering print quality parameters, such as variations in print density (mottle) or gloss, the total absorbed volume and the uniformity of the absorption would both be of importance.

We have developed a technique to study the uniformity of absorption of a small amount of liquid. This technique is based on the short-time absorption of a dyed liquid, the blotting of excess liquid and the characterisation of the stain pattern (Fig 1). Emphasis was placed on the absorption by coated boards of water-based flexographic inks. However, this technique can be used on a universal level.

Fig 1. Example a liquid stain obtained with the new technique. Reflectance variations indicate an uneven absorption.

**Wetting and Capillary Absorption**

The interaction between a liquid and a surface can be characterised in terms of the contact angle the liquid forms on the solid and, for porous bodies, also by the rate the solid absorbs the liquid. Contact angle, or the cosine of the contact angle, is often referred to as wetting of the solid. It depends on surface tension of the liquid and surface free energy of the solid, and is of significant importance for capillary absorption.

In absence of external pressure, absorption rate is mainly determined by the capillary pressure, liquid viscosity and density. The capillary pressure in turn depends on wettability, liquid surface tension and pore structure. For a single capillary tube the capillary pressure \( P \) 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 i.e.

\[
P = 2\gamma \cos \theta \over r \tag{1}
\]

The rate of a capillary flow can be described by the Lucas-Washburn Equation \((Eq 2)\), which includes Eq 1, the viscosity of the liquid \( (\eta) \) and the length of penetration \( (h) \):

\[
\begin{align*}
\frac{dh}{dt} &= \frac{r^2 \rho}{8\eta h} = \frac{r \gamma \cos \theta}{4\eta h} \\
\end{align*}
\]

Absorption at short timescales involves acceleration of the liquid and inertia becomes important. The Bosanquet absorption equation account for this and a solution for the equation at short timescales in absence of external pressure has been presented by Schoelkopf et al. (2000):

\[
h = t \sqrt{\frac{2\gamma \cos \theta}{\rho r} } \tag{3}
\]

where \( \rho \) is the density of the liquid and \( t \) is time.

Absorption of a liquid by a thin layer of a porous material that has a non-uniform pore structure, most likely take place according to both Eq 2 and 3.
Techniques to Measure Average Absorption

Many of the available absorption measurement techniques, e.g. the Cobb Test, give information about the volume of total absorption after quite a long period and for a large area (TAPPI 1998; Aspler et al. 1987; Elftonson, Ström 1995; Swerin et al. 2008). The time scale needs to be shortened to obtain the absorption characteristics that are relevant to printing (Skowronska et al. 2005; Borch et al. 2002). This can be achieved to some extent, when measuring the dynamic contact angle (TAPPI 1997) or penetration using the Bristow Test (Bristow 1967), for example.

In addition, there are more sophisticated approaches for obtaining information about absorption and wetting, such as the MicroDAT for analysing the absorption rate of very small drops (Svanholm 2007), the print mottle), are linked to unevenness in a substrate. Therefore the ability to characterise absorption uniformity is of major importance.

When it comes to offset printing, ink-stain tests using different oils, such as Croda red draw-down, K&N or Porometric (Bristow, Bergenblad 1982), can give an indication about uniformity in oil absorption. Shen et al. introduced a liquid bridge probe to measure uniformity using silicon oil (2004). The force from the liquid bridge between a small probe and the substrate is detected and then translated into local permeability. Variations are captured through multiple measurements distributed over the surface. There are also ultrasound techniques, where water can be used as the testing liquid. The transmission of ultrasound signals through a sample will change as liquid penetrates into the sample. As pointed out by Borch et al. (2002), the exact relationship between signal and liquid absorption is not defined, but the ultrasound techniques allow relative comparisons.

Skowronska et al. (2005) introduced a second generation of these instruments that can measure the evenness of the signal using a multi-sensor. Another option is to examine the evenness of stains in a Bristow Test. However, this includes an influence by the roughness, due to the filling of surface pores, (Bristow 1967) and not only reflects variations in penetration. The roughness contribution can be excluded mathematically, when evaluating the absorption rate in a Bristow Test, but it cannot be excluded from the physical stains. The new technique suggested here is based on the same principle, but includes the removal of excess liquid to minimise the impact of roughness. The excess liquid is removed with a blotting paper in a similar way as in the Cobb Test.

Materials and Methods

Absorption Uniformity Setup – Development of the Method

A sample is allowed to absorb dyed liquid during a brief, defined time-lapse, see Fig 2. This leaves a stain on the surface of the sample. The time for absorption is defined by the speed and distance between the liquid application and removal of non-absorbed liquid by a blotting paper. To minimise the effect from surface roughness it is important that there is an excess of liquid on top of the whole sample, until it is finally removed in the nip with the blotting paper. The removal is based on the same principle as in a Cobb Test. When the whole blotting paper gets “stained”, there has been excess liquid available on the whole sample.

The stain is smooth if the absorption is homogeneous over the surface, whereas local variations in absorption create reflectance disturbances in the stain. The uniformity of the stain is measured in the same way as print mottle (Johansson 1999).

Testing Liquid

Different dyes can be used and tests are still in progress. When using methylene blue, the dye separated from the water phase and stayed in the coating layer, whereas the colorant in an aqueous ink for inkjet printing accompanied the water phase and was used to estimate the depth of water penetration. The behaviour of the methylene blue was considered better for simulating the absorption of flexographic inks.

When evaluating the coated board samples, two different aqueous solutions containing 12 vol.-% of methylene blue were used. One was pure water and the other contained 8.6 wt.-% of n-propanol. The alcohol lowered the surface tension of the water, from approx. 72 to 38 mJ/m², which is comparable to the surface tension of flexographic inks. This ought to make the absorption pattern less sensitive to surface chemistry and more sensitive to the pore structure, since the wettability (cosθ) approaches 1.

IGT F1 Printability Tester

Fig 2. Illustration of the measurement set-up, including an example of how the full stain can look. A laboratory print tester was used to control the time of absorption (down to 0.1 second) and blotting pressure. Coated samples were tested at 0.5 m/s and 350 N / 50 mm width.
The intensity of illumination ($I_0$) will be reduced by a factor (reflectance of the board $R_B$) when reflected from the board. Adding a stain on the board will reduce the total reflectance further by a stain transmission factor $T$. In fact, $T$ is the combined effect of light passing twice through the stain, i.e. $T = \text{squared single-pass transparency.}$

$$I_0 R_{\text{STAIN}} = I_0 T R_B$$  \[4\]

According to Eq 4, the total reflectance of the stain ($R_{\text{STAIN}}$) is a product of the intensity of the illumination ($I_0$), reflectance of the board ($R_B$) and transparency of the stain ($T$). This means that the uniformity of the stain is dependent on both the white-top mottle and the absorption uniformity (corresponding to variations in the transparency). It may be possible to estimate the contribution by absorption (here referred to as CV\_TRANSPERENCY or “absorption mottle”), when measuring the uniformity of the stain ($C_V\_\text{STAIN}$) and the uniformity of the board reflectance ($C_V\_\text{WTM}$) separately. Assuming that the absorption mottle pattern is spatially independent of the white-top mottle pattern and using the rules for error propagation (Beers 1957), it holds that:

$$C_V^2 = (C_V^2 + C_V^2)$$  \[5\]

Observe that all mottle values are coefficients of variation in reflectance ($\text{CVR} = \text{std.dev} / \text{mean}$).

So far, we have not established whether the stain uniformity (total) or the absorption contribution was the most relevant measure. Thus, both have been considered at this stage.

### Materials

A set of liquid boards were prepared by pilot-coating one base board with the same pre-coat but using different top-coat formulas (Table 1).

The composition of the coating colours for the top coat was designed to produce coating layers with different porosities, pore sizes and wetting potentials. By using the same base board, the aim was to keep surface roughness as similar for all samples as possible (Table 2). Ten samples were included and divided into three series:

- **An increasing of the latex content:** 12.5, 15, 17.5 and 20 parts per hundred parts pigment (pph). The pigment was a mixture of 60 pph Hydrocarb 90 (referred to as B90 GCC) and 40 pph Setacarb HG (referred to as B98 GCC). Hydrocarb 90 has a broad particle size distribution with 90% of its mass having a particle size < 2 µm. Setacarb HG also has a broad particle size distribution but is a finer pigment where 98% of its mass has a particle size < 2 µm. The carbonates were supplied by Omya.

- **An increasing of the clay content** (Brazilian delaminated clay, Capim NP from Imerys) mixed with B90 GCC: 10, 20 and 40 pph clay. 15 pph of the vinyl acetate acrylate latex was used in all of these formulations.

- **Three different types of ground calcium carbonates** (100 pph of each): Two with a broad particle size distribution (B98 GCC, B90 GCC) and one with a narrow size distribution. The latter was Covercarb 75 from Omya (referred to as N75 GCC), with 75% of the particles < 1 µm and 95% < 2 µm. 15 pph of the vinyl acetate acrylate latex was used in all of these formulations.

The finest ground calcium carbonate (B98 GCC) was expected to create a coating with small pores, the B90 GCC a coating with larger pores but similar porosity, while the N75 GCC ought to form a coating with high porosity and large pores. The internal surface area of these pores would decrease when changing from B98 GCC to B90 GCC and then to N75 GCC.

### Characterisations of the Boards

- **Absorption Uniformity:** As described above.

- **White-top mottle:** Variations in reflectance of the coated boards were analysed with a scanner in the same way as print mottle.
Coat-weight variations: Characterised through burn-out treatment and then an analysis of the variations in reflectance was made in the same way as print mottle.

Wettability: calculated as the cosine value of the contact angle after 0.1s, measured with the Dynamic Contact Angle Tester from FIBRO System. The water and the alcohol solution were both analysed.

Pore structures: characterised by mercury porosimetry using a Micrometric Autopore III. The pre-coated board and the ten 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. The results presented in Fig 4 and Table 2 are from the pore radius interval between 25 and 100 nm. Pore volume is given as cm³ voids per m² board and the value of pore size is the Rₙ₉₅, which means that 50% of the void volume has finer pores and 50% has coarser pores. However, one needs to bear 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 this operation involves a fairly large uncertainty due to the subtraction of a large number from another large number. However, the calculations and the analysis of data show that the top coats obtained expected pore structures.

Surface roughness: topography variations in the spatial wavelength interval 0.06-0.25 mm. Calculated as the standard deviation of height. Profile measurements were made with the MicroProf instrument from Fries Research & Technology.

Table 2. Pore structures of the top-coating layers and surface roughness as height variations in topography profiles.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Pore volume [cm³/m²]</th>
<th>Pore size, Rₙ₉₅ [µm]</th>
<th>Roughness [µm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>12.5 latex</td>
<td>1.7</td>
<td>0.05</td>
<td>0.56</td>
</tr>
<tr>
<td>15 latex</td>
<td>1.8</td>
<td>0.06</td>
<td>0.57</td>
</tr>
<tr>
<td>17.5 latex</td>
<td>1.8</td>
<td>0.06</td>
<td>0.56</td>
</tr>
<tr>
<td>20 latex</td>
<td>1.2</td>
<td>0.06</td>
<td>0.58</td>
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<td>10 clay</td>
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</tr>
<tr>
<td>N75 GCC</td>
<td>2.0</td>
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Results

Pore Structure, Wettability and Surface Roughness

Mercury intrusion measurements confirmed that the expected pore structures of the top-coating layers were achieved. Further, it was possible to confirm that surface roughness was very similar on all samples. The results are given in Fig 4 and Table 2.

Fig 5 shows that increased content of clay improved wettability but it decreased with an increased latex content. The wettability of the alcohol solution was quite similar for all coatings, although small differences were observed.

Relevant Depth of Penetration during Absorption

After splitting the flexographic printed boards into thin layers, it showed that the ink pigments did not penetrate below the coating layer. This was comparable to the absorption stains, which showed a certain penetration but most of the dye had remained close to the coating layer. When the absorption time was reduced to a tenth of a second, the magenta dye stopped at the first fibre layer under the coating (2nd layer in the splitting sequence), as shown in Fig 6.

Absorption Uniformity

This new technique was utilised to characterise pilot-coated boards, and it was established that it captured how evenly the liquid had been absorbed. If the stain was expected pore structures of the top-coating layers were achieved. Further, it was possible to confirm that surface roughness was very similar on all samples. The results are given in Fig 4 and Table 2.

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Fig 5. The wettability based on measurements of the contact angle (0.1s). Error bars indicate a 95% confidence interval.

Fig 6. Coated boards split into thin layers to reveal the ink liquid penetration into the material. The three top layers are shown. The ink from printing stayed in or on top of the coating, and the stained liquid (deionised water) remained close to the coating layer.
Correlation between reflectance variations of the stain and the board itself. Stains were made with two different liquids. Higher mottle values of the stains than white-top mottle indicated an uneven absorption.

Variations in liquid absorption, calculated from stain mottle and white-top mottle according to Eq 5. Error bars indicate a 95% confidence interval.

perfectly homogeneous and only lowered the reflectance with a constant factor, the mottle value would have stayed the same as on the unstained boards, i.e. as white-top mottle. In fact, there was an effect from the variations in absorption on the stain patterns, which were observed as a higher level of mottle in the stains than the white-top mottle, see Fig 7.

The analysis of the pilot-coated boards showed that the composition of the coating colour had an effect on the uniformity of the stains, see Fig 8.

The trends were very similar when looking separately at the contribution by the absorption uniformity, according to Eq 5 (Fig 9).

The results indicate that finer calcium carbonate pigments and incorporation of delaminated clay improved the uniformity in absorption. Also a narrow particle size distribution of the calcium carbonate appeared to have a positive effect.

When increasing the latex content, the absorption became more uniform. There appears to be a maximum in variations at 15 parts of latex, but the rather large confidence interval of the sample with lowest latex content (12.5 parts) makes this a bit uncertain.

Link to variations in coating thickness
There was a strong correlation between absorption variations and the variations in coating thickness, here characterised as white-top mottle, since the base board contained an unbleached layer. There was not only a correlation with the stain pattern but also with the calculations of the absorption contribution, according to Eq 5 (Fig 10).

On a few of the samples, white-top mottle and stain patterns were compared locally, i.e. on the same marked area before and after making the stain. For these tests, it was possible to observe that the darker areas of the coating, i.e. thinner coating layers, had absorbed more water and obtained a darker stain.

Furthermore, burn-out treatments were done to study the uniformity of the coating layers. As expected, this confirmed that the white-top mottle reflected the variations in coat-weight, when there was an unbleached layer in the base board. However, the correlation was not perfect.
The impact from different ground calcium carbonate pigments showed a connection with the variations in thickness and white-top mottle. The coating that contained B90 GCC was not as evenly distributed as the others, see Fig 12. This further indicated that the pore structure was not as uniform in this layer and could explain the more uneven absorption by this coating.

When using the alcohol solution, the situation was quite different from when using water on the coatings that contained clay. For the alcohol solution, the uniformity improved with more clay in the coating, which seemed related to an improvement in white-top mottle (Fig 12) as well as a better wettability (Fig 5).

The positive impact on the absorption uniformity, when using the high amount of latex, did not seem related to the variations in coat-weight (Fig 12). If the latex was more evenly distributed with the high dosages, it could explain the more uniform absorption.

**Discussion**

With this method, we were able to detect differences in absorption variations. One can suspect that varying composition of the coating layers had an impact on the absorption uniformity, though it is not only the porosity and pore size that will have an impact, but also the variation in pore structure laterally. We have, however, not had the opportunity to characterise such pore-structure variations.

In many cases, the absorption uniformity could be linked to variations in the coat-weight and/or wettability, although this was not fully true in all cases. This demonstrated the importance of measuring the absorption uniformity, while not only focusing on the total absorption potential or variations in the coating thickness.

The correlation among absorption uniformity and variations in coat-weight (characterised as white-top mottle or with burn-out treatments) was interpreted as there being different pore structures in the thinner and thicker areas of the coating layer. Results, where thinner coating layers showed higher porosity, have been presented by other researchers and supports this theory (Laudone et al. 2003). Azimi and colleagues have shown that increasing the coat weight will result in a lower water uptake, which further supports the indications of brighter stains on the parts with thicker coating layer (Azimi et al. 2011). Thickness is likely to have an impact on the consolidation of the coating colour, which can create different pore-structures (pore size and porosity). Changes in pore size and porosity will affect the internal surface area of the pores. This could also have an effect on the measured reflectance of the stains.

Using the alcohol solution with a lower surface tension improved the wettability and ought to make the absorption pattern less sensitive to the surface chemistry and more sensitive to the pore structure. This showed as a low correlation between white-top mottle and absorption uniformity when using the pure water and greater correlation when using the alcohol solution. Nevertheless, if there is a nip pressure involved the system will change.

Even though white-top mottle had an optical effect on the measurements of the stain patterns, it was possible to calculate the contribution from an uneven absorption, i.e. variations in stain transparency.

**Conclusions**

This method measures absorption uniformity in a realistic way for water-based flexographic printing and it could identify differences among pilot-coated boards. It was possible to observe an impact on the absorption uniformity from the wettability and the variations in coating thickness. Thinner and thicker areas were interpreted as possessing different pore structures.

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**Literature**


