QUANTITATIVE MICROSCOPY OF COATING UNIFORMITY

Christina Dahlström

Supervisors:
Professor Tetsu Uesaka
Professor Magnus Norgren

FSCN - Fibre Science and Communication Network
Department of Natural Sciences, Engineering and Mathematics
Mid Sweden University, SE-851 70 Sundsvall, Sweden

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Christina Dahlström

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FSCN - Fibre Science and Communication Network
Department of Natural Sciences, Engineering and Mathematics
Mid Sweden University, SE-851 70 Sundsvall
Sweden

Telephone: +46 (0)771-975 000

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ABSTRACT

Print quality demands for coated papers are steadily growing, and achieving coating uniformity is crucial for high image sharpness, colour fidelity, and print uniformity. Coating uniformity may be divided into two scales: coating thickness uniformity and coating microstructure uniformity, the latter of which includes pigment, pore and binder distributions within the coating layer. This thesis concerns the investigation of both types of coating uniformity by using an approach of quantitative microscopy.

First, coating thickness uniformity was analysed by using scanning electron microscope (SEM) images of paper cross sections, and the relationships between local coating thickness variations and the variations of underlying base sheet structures were determined. Special attention was given to the effect of length scales on the coating thickness vs. base sheet structure relationships.

The experimental results showed that coating thickness had a strong correlation with surface height (profile) of base sheet at a small length scale. However, at a large length scale, it was mass density of base sheet (formation) that had the strongest correlation with coating thickness. This result explains well the discrepancies found in the literature for the relationship between coating thickness variation and base sheet structure variations. The total variance of coating thickness, however, was dominated by the surface height variation in the small scale, which explained around 50% of the variation. Autocorrelation analyses were further performed for the same data set. The autocorrelation functions showed a close resemblance of the one for a random shot process with a correlation length in the order of fibre width. All these results suggest that coating thickness variations are the result of random deposition of particles with the correlation length determined by the base sheet surface textures, such as fibre width.

In order to obtain fundamental understandings of the random deposition processes on a rough surface, such as in paper, a generic particle deposition model was developed, and systematic analyses were performed for the effects of particle size, coat weight (average number of particles), levelling, and system size on coating thickness variation. The results showed that coating thickness variation
grows with coat weight, but beyond a certain coat weight, it reaches a plateau value. A scaling analysis yielded a universal relationship between coating thickness variation and the above mentioned variables. The correlation length of coating thickness was found to be determined by average coat weight and the state of underlying surfaces. For a rough surface at relatively low coat weight, the correlation length was typically in the range of fibre width, as was also observed experimentally.

Non-uniformities within the coating layer, such as porosity variations and binder distributions, are investigated by using a newly developed method: field emission scanning electron microscopy (FESEM) in combination with argon ion beam milling technique. The combination of these two techniques produced extremely high quality images with very few artefacts, which are particularly suited for quantitative analyses of coating structures. A new evaluation method was also developed by using marker-controlled watershed segmentation (MCWS) of the secondary electron images (SEI).

The high resolution imaging revealed that binder enrichment, a long disputed subject in the area, is present in a thin layer of a 500 nm thickness both at the coating surface and at the base sheet/coating interface. It was also found that the binders almost exclusively fill up the small pores, whereas the larger pores are mainly empty or depleted of binder.

**Keywords:** Coating uniformity, coating microstructure uniformity, base sheet effects, argon ion beam milling, scanning electron microscopy, image analysis, binder distributions, autocorrelation analysis, random deposition process, simulation
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LIST OF PAPERS

This thesis is based on the following six papers, herein referred to by their Roman numerals:

Paper I  

Paper II  

Paper III  

Paper IV  

Paper V  
**Surface Evolution of Pigment Coating**, Christina Dahlström and Tetsu Uesaka, to be submitted to *Chemical Engineering Science*, 2012.

Paper VI  

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1. INTRODUCTION

Paper is a porous fibre network, and is often coated with various materials to enhance surface smoothness, optical properties, print performance, and to add various functionalities, e.g. barrier properties. The base sheet is usually made from chemical and mechanical pulp fibres, and the coating is composed of mineral particles, mainly clay and calcium carbonate, and binder. The coated sheet is calendered, i.e. compressed, by two rolls to further enhance surface characteristics for high quality printing paper. Print quality demands for coated papers are steadily growing, and achieving coating uniformity is crucial for high image sharpness, colour fidelity, and print uniformity [1, 2].

Because of the original non-uniformities of base sheet structure, coating uniformity is probably one of the most important characteristics that affect end-use performance. Coating uniformity may be divided into coating thickness uniformity and coating microstructure uniformity, such as pigment, pore and binder distributions. Although this distinction may seem trivial, it becomes important when one investigates the basic mechanisms of coating uniformity.

Coating thickness variation is believed to cause non-uniform ink setting and absorption by many researchers, causing print defects [1, 3-7]. The coating thickness uniformity is generally governed by e.g., the coating methods, base sheet properties, coating rheology and the drying methods [8, 9]. In this thesis, the relationships between the base sheet and coating uniformity were investigated by focusing on the length scale effects.

The internal coating microstructures are important for ink transfer behaviour, for example, a non-uniform coating porosity is suspected to cause poor print quality and printing defects [10]. The coating microstructures play an equally important role for packaging paper and board where barrier properties are essential for oil, grease, oxygen and water vapour. It is, therefore, essential to quantify the coating layer microstructures, such as porosity distributions and binder distributions, as well as underlying structures of base sheet in order to identify what causes the coating microstructure non-uniformity.

1.1. Coating thickness uniformity

Figure 1 shows a coated paper cross section obtained by using a scanning electron microscope (SEM). The coating layer appears as bright material and it is obvious that the coating thickness varies considerably.

Base sheet structures, such as surface roughness and mass density distribution (formation), have been known to affect coating uniformity. However, a close
examination of the literature shows that the direct data supporting the above statement is surprisingly scarce and sometimes inconsistent.

Figure 1. This image visualises the coating thickness non-uniformities, where the coating layer appears as bright material. The image was obtained using a scanning electron microscope (SEM), with the magnification 250x.

Huang and Lepoutre used the burnout test to evaluate the coating uniformity using two base sheets with different formation [11]. The burnout test is a practical method to evaluate coating thickness uniformity at a glance, particularly at a large scale [12]. The sheets with worse formation showed greater coat weight variations at a coat weight of 12 g/m², whereas at the lower coat weight of 8 g/m² there was no clear effect of formation. Huang and Lepoutre also compared smooth, dense base sheets with rough, porous base sheets, both of which were blade-coated with approximately 8 g/m² coat weight [13]. Coat weight distributions were again measured by using the burnout test at length scales larger than 500 µm. It was found that coating uniformity was superior for smooth and dense sheets.

Tomimasu et al. used an electrograph method, in which electrons transmitted through the paper sample are detected on an electron microscope film, and also used a surface profilometer to examine the effects of base sheet structures on coat weight distribution [14]. Four commercial newsprints made on different formers were coated, and electrographs were taken before and after coating. Local coat weight correlated to local basis weight of the base sheet at large length scales (a resolution of 800 µm). At small length scales (a resolution of 100 µm), however, it was the base sheet roughness that correlated with coat weight distribution. Matsubayashi and co-workers used spectrophotometer equipped with a scanning X-Y stage to study the relationship between base paper formation and coat weight distribution (resolution > 1 mm) [15]. The method enabled measurements of coat weight distribution and sheet formation at the same area. High coat weight appeared to occur in areas of low basis weight (correlation ~50%). Gane et al. introduced Walsh analysis, using profilometer and optical imaging data, as a tool to investigate how the base sheet surface profile affects coating thickness.
distribution [16]. The total sampling length used to perform Walsh analysis was 128 µm, but can easily be extended for larger length scale analyses.

Normally the relationships between coating uniformity and base sheet structure are investigated by comparing some kinds of “spatial average” of the corresponding parameters of coating and base sheet. However, Zou et al. used SEM, combined with image analysis, to perform one-to-one local mapping of coating thickness and base sheet structures (e.g., mass density, surface height and porosity) [17]. Among the measured base sheet structure parameters, the local coating thickness showed the strongest correlation with the base sheet surface profile. A typical plot of coating thickness vs. surface height (base sheet surface profile) is shown in Fig. 2. The coating layer is thicker in the valleys and thinner on the peaks. The formation and porosity, however, had much weaker correlation with coating thickness than the surface height. (In this analysis the base sheet surface profile was measured using a reference line defined for each SEM-image of 300 µm in length. Therefore, variations greater than 300 µm were not captured.) However, the surface height variations explained only about 50% of the coating thickness variations, and the rest was attributed to non base sheet effects, such as caused by random depositions of coating colour, coating process dynamics, etc.

\[
y = -0.56x + 9.02
\]

\[
R^2 = 0.48
\]

Figure 2. The coating thickness is plotted against surface height for a blade-coated LWC with coat weight 12 g/m².

Wiltsche and co-workers extended a similar cross-section-analysis concept into 3D by using an automated serial sectioning method in combination with light microscopy [18]. They found that the blade-coated sample showed an almost ideal level-coating behaviour. However, in that study the samples chosen were
calendered, and the base sheet surface profile and the coating thickness variations may have been altered in the calendering process.

One important aspect of the coating thickness and base sheet variations is that they generally consist of a wide spectrum of variations of different length scales, i.e., quickly varying, fibre-width-scale variations and slowly varying, macro-scale variations. The literature clearly suggests that, depending on the measurement methods and length scales captured, the conclusions are different. The burnout test, for example, is not a direct measurement of coating thickness but a reflectance measurement, which is influenced by the optical properties of the coating layer, such as coat weight and scattering coefficient, and of underlying charred base sheets. In addition it cannot detect small scale variations, e.g., less than 500 µm where most of the coating thickness variations occur [14, 17]. On the other hand, the SEM/image analysis technique directly determines the coating thickness variations, together with other structural variables of the base sheet, with much less than 1 µm resolution. It is, however, time-consuming to determine the large length scale variations of more than, say 6 mm, even with an automated image analysis system. This limitation may be regarded as critical, if end-use performance, such as print mottle, is controlled by only the large scale coating uniformity. Engström et al. showed a good correlation between the coefficient of variation of coating mass measured by a soft X-ray technique and print mottle in the 2-4 mm range [9]. The comprehensive reviews of coating uniformity and base sheet effects and the measurement methods are given by Engström [8, 19].

Although the literature is pointing toward base sheet surface roughness as one of the controlling factors of coating uniformity, the results for the effects of formation are not consistent and need to be examined in a systematic manner. In this thesis, the relationships between the base sheet and coating uniformity were investigated, by focusing on the length scale effects, and then attempt to deduce the basic mechanisms that create coating non-uniformity from the point of base sheet structures.

1.2. Coating microstructure uniformity

Figure 3 shows a SEM image of a coated paper cross section. In this example, the pigment was clay and its platy morphology is clearly seen in the image. The binder appears as the bright material surrounding the pigments. Ink absorption and barrier properties are affected by the distributions and orientations of pigments and binders, and thus by the distributions of pores.

Extensive surface observations using scanning electron microscopy (SEM) were made by Xiang et al., Kim-Habermehl et al., and Chinga and Helle to distinguish
less porous (closed) and porous (open) areas, and they all found certain correlations with print mottle [20-22]. Micro-probes for measuring local liquid absorption have been used by Shen et al. and Xiang et al., and again the correlations with print mottle were found [23, 24]. These studies clearly suggest the presence of some types of non-uniform coating structures underneath the coated paper surface, including coating thickness and microstructure non-uniformities. Coating thickness variations were first suspected as a cause of non-uniform ink setting and absorption by many researchers [1, 3-7]. Indeed general correlations with print mottle were observed, and the result were discussed in terms of in-plane variations of total pore volume in coating, as well as pore size/porosity variations that may be coupled with coating thickness variations. Another important source of variations is the distribution of binder within the coating, particularly binder migration toward the coated paper surface. Binder migration has been long suspected and indirect experimental evidences have been accumulated by various methods [1, 25-29].

Figure 3. This image shows the internal coating microstructure, where the clay pigments are platy, the pores are dark/black and the binder appears as the bright material.

It is, therefore, important to quantify the coating layer microstructures, such as porosity distributions and binder distributions, as well as underlying structures of base sheet in order to identify what causes the coating microstructure non-uniformity. The microstructure variations within the coating are still being debated and speculated, because of the lack of appropriate experimental techniques. There have been a number of attempts to evaluate different aspects of coating microstructures.

Mercury intrusion is the most popular technique that determines the pore volume fraction and (effective) pore size distribution in the coating. It is, however, well-known that the interpretation of the results is not straightforward because of the complex mechanisms of mercury intrusion in the interconnected pore system [30, 31].
Atomic force microscopy (AFM) has high resolution at the nanometre scale and is well suited for coating topography analyses. Binder and pigments can be differentiated, and when applied to the cross sections of paper coating, the details of pore structures can be obtained [32]. However, according to Kugge, it is not possible to get a good quantitative determination of the binder content due to the influence of topographic properties [33]. In addition, the observation areas are too small to capture the typical length scales of coating non-uniformity.

Transmission electron microscopy (TEM) provides sub-nanometre resolution of the coating structure, though sample preparation is time-consuming, requiring ultra-thin sections. Despite the difficulties, some researchers have managed to analyse the pore size distribution using TEM and image analysis [34, 35]. Again the sample size was limited and it was not possible to obtain information on the base sheet structures underneath the coating.

Ozaki et al. used confocal laser scanning microscopy (CLSM) with fluorescence staining technique to study the three dimensional structure of the coating layer [36]. It is mainly the latex binder that adsorbs the dye, and thus this method is suitable for characterising binder distribution. However, the pigments and base paper are not easily detected since they were only slightly stained or not at all. Also, the resolution is too low to analyse the coating porosity.

SEM and digital image analysis have been widely used to assess the structure of the coating layer and base sheet properties [4, 37-39]. Further, field emission SEM (FESEM) provides higher resolution of paper cross sections than conventional SEM, and it is possible to detect the coating microstructure, such as pores, binder and pigments [40]. To detect the binder and enhance contrast, the paper is stained with OsO₄ before embedding with resin [37]. A drawback is that the embedding procedure might introduce artefacts, such as e.g., the removal of pigment particle during polishing, resulting in poor image quality. Porosity measurements are usually done by image analysis of the SEM backscattered electron image (BEI), but due to the signal depth of the backscattered electrons, the porosity might be overestimated. The literature is surprisingly scarce on z-directional distributions of the coating layer microstructures using FESEM and image analysis.

Other techniques, such as X-ray microtomography [41], serial grinding in combination with SEM [42] and automatic serial sectioning in combination with light microscopy [18], have been used for the characterisation of paper structures. Three-dimensional reconstructions were obtained where local information, such as the coating thickness, coating topography and base sheet topography, is provided over a relatively large area. It is, however, not possible to detect and quantify the pore structure of the coating layer because of their still limited resolution. Laser induced plasma emission spectroscopy (LIPS) is a technique that provides surface chemical information of the coated paper, and also depth profiling by ablating the surface layers [43]. However, the porosity cannot be obtained by this method, and the coating microstructure is not feasible to assess due to the low resolution. The
comprehensive reviews of recent technologies for analysing the multi-scale structures of paper are given in [44, 45].

In summary, in order to investigate coating microstructure non-uniformity and its origin, it is important to have an appropriate resolution to distinguish pigments, binders and pores. At the same time it is important to have a sufficiently large view that allows one to observe the underlying base sheet structures. In this sense, FESEM is a good candidate for looking at these two different scales (i.e., pigments/binders/pores vs. fibres). One of the outstanding challenges for coating structure characterisation using FESEM is the use of conventional sample preparation procedures, such as resin-embedding, microtoming and/or polishing. These procedures are not only time consuming, but also may introduce artefacts.

The focused ion beam (FIB) technique [46, 47] did overcome some of these problems. However, this method is often used in-situ in the electron microscope and is limited to the production of very small sections (e.g., production of ultrathin sections for TEM). Recently the argon ion beam milling technique, based on a de-focused broader beam, was suggested as a potential alternative to the FIB technique [48]. Although no measurement data were presented from its images, Robinson et al. showed very impressive pictures of coating cross sections that could be used for quantitative analyses [49]. The broad argon ion beam milling technique produces high quality cross sections similar to FIB, and larger cross sections are obtained.

In this work, the argon-ion beam milling technique was further developed to make it suitable for coating microstructure characterisation in combination with FESEM. The aim was to develop a method that could quantify the coating microstructures and to investigate binder distributions within the coating.

### 1.3. Outline of thesis

The main objective of this work was to investigate what controls coating uniformity, both the coating thickness uniformity and the coating microstructure uniformity. This was done by using SEM and FESEM in combination with image analysis and Chapter 2 describes all experimental work and the material used. The base sheet effect on coating thickness uniformity and the effects of length scale are described in Chapter 3. The coating thickness variations were also analysed using autocorrelation analysis and the results are presented in Chapter 3. In Chapter 4, a model for random deposition of pigment particles is made to further understand the experimental results obtained earlier. In Chapter 5 the results on binder distributions are presented. Finally, Chapter 6 concludes the results presented in the thesis.
2. MATERIALS AND METHODS

2.1. Characterisations of coating thickness variations and base sheet structures (Papers I, II and V)

2.1.1. Samples

The base sheet furnish used in this study was obtained from a light weight coated (LWC) paper mill and consisted of 40% kraft and 60% groundwood (GWD), with a basis weight of 40 g/m². The base sheet was coated on only one side (felt side) with a GCC coating colour using a cylindrical laboratory coater (CLC-6000) at a speed of 800 m/min. The coating formulation was made of 100% GCC (96 wt. % < 2 µm) and 8 pph SBR latex (Dow CP-692 NA). Solids content of the coating colour was 60% and the coat weights (cw) were 12 g/m² and 22 g/m². The same coating formulation was used for both coat weights, only the blade pressure was varied to get different coat weights. Two cross sections were prepared for the analyses of each paper sample coated with coat weight 12 g/m² and 22 g/m². As coat weight increases (blade coating), its standard deviation increases up to 13-15 g/m² and then it becomes constant [50]. Therefore, a coat weight of 22 g/m² is expected to show the maximum variation.

2.1.2. Sample preparation

Paper samples for cross section analysis were cut in 1 x 2 cm² pieces at random positions from the original sheet. The paper samples were placed vertically in string holders and put in a mould. The samples were embedded with a low viscosity resin and cured over night in an oven at 68-70 °C. The cured block was dry-ground by hand with 320, 500, 1200 and 4000 grit SiC-paper and then etched for 15 s with an etching solution to smoothen the surface for image analysis [51, 52]. The block was finally carbon coated to obtain an electrically conducting surface.

2.1.3. Scanning electron microscopy and image analysis

Digital images of the paper cross sections were obtained using the scanning electron microscope (SEM) LEO 1450EP. Backscattered electron images (BEI) were generated using 10 kV accelerating voltage and 8 mm working distance. A number
of images were taken in a sequence giving a total length of approximately 6 mm for each sample, as shown in Table I. The digital images were stitched together using ImageJ software (National Institutes of Health, U.S.A.). The results presented are averages of the two images for each coat weight. The local structure parameters measured were coating thickness, coating surface profile, base sheet thickness, surface height (base sheet profile), mass length (a measure of fibre mass density) and pore length according to the method developed by Allem [4]. This method was later extended and further developed by other researchers [37, 53, 54].

Table I. Image properties of the analysed paper samples.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Image length (mm)</th>
<th>Data points (pixels)</th>
<th>Resolution (µm/pixel)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LWC, cw 12 g/m², sample 1</td>
<td>6.1</td>
<td>39200</td>
<td>0.16</td>
</tr>
<tr>
<td>LWC, cw 12 g/m², sample 2</td>
<td>6.8</td>
<td>42400</td>
<td>0.16</td>
</tr>
<tr>
<td>LWC, cw 22 g/m², sample 1</td>
<td>6.2</td>
<td>39689</td>
<td>0.16</td>
</tr>
<tr>
<td>LWC, cw 22 g/m², sample 2</td>
<td>6.1</td>
<td>39500</td>
<td>0.16</td>
</tr>
</tbody>
</table>

Figure 4 is a schematic image to illustrate the local structure parameters measured and that the measurements were done point-wise in the x-axis direction. Figure 5 shows a BEI of the coated paper cross-section and binary images of the coating, mass and pores.

One deviation in the procedure from the previous worker [4] is that, to distinguish the coating thickness, the pixels with value 0 (black) are added at every position on the x-axis, see Fig. 6. The first pixel with value 255 (white), i.e. the base sheet, adjacent to the coating determines the interface between the coating layer and the base sheet. Another deviation is that the measurements were done point-
wise at every pixel giving approximately 40,000 data points for each sample. A typical plot of the coating thickness obtained from image analysis is displayed in Fig. 7.

**Figure 5.** From left to right, BEI of the coated paper cross section, binary image of the coating, binary image of the mass, and binary image of the pores.

**Figure 6.** The coating thickness is measured by adding every black pixel at every position on the x-axis.

**Figure 7.** Local coating thickness measured at every pixel of the binary image.
2.2. Characterisation of coating microstructures (Papers III, IV and VI)

2.2.1. Samples

The paper samples used in this study were coated on one side with 10 g/m² of coating, using a cylindrical laboratory coater (CLC-6000, SimuTech International Inc., U.S.A.) at FPInnovations at a speed of 1000 m/min. The coating was made from GCC (Hydrocarb 90), clay (Capim DG), starch (Penford Gum) and SBR latex (Dow CP-692 NA) in different formulations. The base paper was made from kraft and groundwood (GWD) pulps. The coated paper was calendered using one pass soft-nip calendering at 100 m/min. The coating formulation and calendering conditions are presented in Table II.

<table>
<thead>
<tr>
<th>Formulation</th>
<th>Clay/GCC Ratio</th>
<th>Latex/Starch Ratio</th>
<th>Binder Volume (pph)*</th>
<th>Calendering Pressure (kN/m)</th>
<th>Calendering Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Clay/GCC**</td>
<td>70/30</td>
<td>75/25</td>
<td>8</td>
<td>300</td>
<td>130</td>
</tr>
<tr>
<td>Clay, mild †</td>
<td>100/0</td>
<td>75/25</td>
<td>16</td>
<td>65</td>
<td>50</td>
</tr>
<tr>
<td>Clay, hard †</td>
<td>100/0</td>
<td>75/25</td>
<td>16</td>
<td>300</td>
<td>130</td>
</tr>
</tbody>
</table>

* Binder volume: Volume (ml) of binder per 100 g of pigment
** Both calendered and uncalendered samples were analysed for this formulation.
† Mild and hard refer to calendering conditions

2.2.2. Sample preparation

The paper samples were cut in 2x2 cm² pieces, where the side of interest was cut with a new razor blade. The samples were attached to a frame in such a way that most of the sample area is exposed to the surrounding air. The sample device was placed in a staining chamber along with liquid OsO4, and was exposed to OsO4 vapours overnight. Caution must be taken when working with OsO4 because of its highly toxic nature. After the staining process, the samples were left in the fume hood for at least another 2 hours. The starch is, however, not stained by this procedure. The moisture in the sealed chamber might cause some roughening of the base sheet in a macro scale, but the coating layer micro-roughness and pore details remains unaffected [55].

The stained paper samples were gold sputtered on both sides to create a thin gold layer, which makes the paper surfaces easy to detect. Note that this thin layer was subtracted by image analysis before measuring the binder content.

The paper sample was placed between two pieces of copper tape for argon ion beam milling, as shown in Fig. 8. The copper acts as a heat sink to protect the
sample during ion milling and it also supports the sample. The positioning of the sample is a critical step in the sample preparation and is therefore done using a light microscope. It is important that the paper sample is well aligned along the upper copper tape and just visible in front of the tape (Fig. 8). The ion milling is usually set to etch around 75 µm from the outer edge of the sample, and a paper that is positioned slightly offset will not get milled. The lower copper tape is placed on top of the stub, along one side. The sample is then attached onto the sample stub, 1-2 mm from the side.

A Hitachi E-3500 Ion Milling System (Hitachi High-Technologies Corporation, Japan) was used to prepare the cross sections. The argon ion beam is uniform in energy and direction, and atoms are sputtered from the sample surface.

<table>
<thead>
<tr>
<th>Table III. Process parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Accelerating voltage</td>
</tr>
<tr>
<td>Discharging voltage</td>
</tr>
<tr>
<td>Stage control</td>
</tr>
<tr>
<td>Time</td>
</tr>
</tbody>
</table>

Before milling, the sample stub was placed in a sample holder, and then put in a microscope beside the cross section polisher to align the straight edge masking plate and set the etching position. The masking plate shields the sample from part of the ion beam (Fig. 8). The milling process parameters are shown in Table III. The gas flow was adjusted to optimise the ion beam current. The obtained cross sections were around 2 mm length and the time needed was around 8 hours per section. One cross section was milled for each sample. It is important to rock the sample during milling and to choose the milling time long enough to avoid striations.

![Figure 8. The sample stub with the paper sample sandwiched between copper tapes (left), and schematic image of the milling procedure (right).](image-url)
2.2.3. Field emission scanning electron microscopy

Digital images were obtained using a field emission scanning electron microscope, FESEM Hitachi SU-70 (Hitachi High-Technologies Corporation, Japan). Before image acquisition, the samples were carbon-coated (Gatan Inc., CA, U.S.A.) to obtain an electrically conducting surface. The backscattered electron images (BEI) and secondary electron images (SEI) were generated using 7 kV accelerating voltage and around 7-8 mm working distance. Figure 9 shows an example of a BEI and a SEI taken of the same coating area. A low accelerating voltage was used to minimise the signal depth. Two different magnifications were used: 5000x for porosity and binder measurements, and 1000x for characterising the underlying base sheet structures in the area where the porosity measurements were performed. The image size was 2560x1960 pixels and the pixel size was 9.9 nm (magnification 5000x) and 49.6 nm (magnification 1000x).

![Images showing BEI and SEI with scale bars](image)

**Figure 9.** The left image is a BEI and the right image is a SEI of the same coating cross section area. White bar show a 5 µm scale.

BEI, SEI and low magnification images were taken at the position of interest of the paper cross sections. The electron beam might cause minor surface damage, which occurs as slight variations in the image contrast. These variations are particularly visible in the SEI and therefore, they were acquired first to overcome this problem. The image contrast in the BEI images originates more from the bulk of the sample. Thirty of the above mentioned types of images were taken for all paper samples. In the literature the number of images that are needed, at these magnifications, to obtain a statistically significant value of porosity was found to be 30 [40].

2.2.4. Image analyses

**Pore size distribution**

The SEI obtained with this new etching technique in combination with FESEM, shows very clearly the coating porosity as well as the edges of the pores. However,
it is not feasible to directly use greyscale thresholding on these images since dark areas of the same grey level appear in the pigments as well as in the pores, and vice versa (Fig. 9). In the literature, the BEI has been used for porosity measurements using greyscale histogram thresholding [37].

In this study, a method based on marker-controlled watershed segmentation (MCWS) was developed in Matlab (The MathWorks, MA, U.S.A.) to measure the coating layer porosity [56]. The relatively well-defined pores in the SEI make it possible to use this segmentation method. The watershed algorithm uses an edge image, representing the gradient of the spatial intensity level in the picture (Fig. 10). However, using watershed segmentation directly on the edge image might lead to over-segmentation due to irregularities in the local gradient. A way to solve this problem is to use markers. Internal markers are associated with the objects of interest, the pores in this case, and external markers are associated with the background, the surrounding pigment and binder structure, see Fig. 10. The external markers effectively partition the coating layer into regions where every region contains a single internal marker (representing one pore) and part of the background. Figure 10 shows an example of the MCWS, where a single pore in the coating layer is used for illustration.

![Figure 10. Example of the marker-controlled watershed segmentation (MCWS). (a) Original SEI of one pore in the coating structure. (b) Gradient image – showing the pore edge. (c) Internal marker – a mark within the pore. (d) External marker – marks the background area between each pore. (e) Watershed lines. (f) Segmented pore superimposed on the original image.](image)

One drawback with the MCWS is that some of the smallest pores are not detected, but this problem was reduced by introducing internal markers from the BEI. Before segmentation, some pre-processing steps were done. Image registration of the BEI and SEI was performed to make sure that no displacement occurred between the images. The registration was done automatically by comparing the intensity values in the SEI and BEI gradient images, and the position with minimum difference was selected.

The coating layer surface and the base sheet-coating interface were outlined manually using ImageJ software (National Institutes of Health, U.S.A.). Also, some
manual “cleaning” of the SEI was performed from, e.g., striations and dust if any. The function `regionprops` was used to obtain the pore properties, such as pore size, orientation and aspect ratio. Pore size is the actual number of pixels in the object.

A comparison was made between the usual method, i.e. greyscale histogram thresholding of BEI, and the new evaluation method where the SEI was segmented using MCWS. Chinga and co-worker showed the importance of automatic greyscale histogram thresholding to avoid large variations of manual segmentation [37]. Therefore, the greyscale histogram thresholding was made automatic using Matlab. As a thresholding function Otsu’s method was used, in which the threshold is determined to maximize the between-class variance of the intensity values of their pixels [56].

![Figure 11](image.png)

**Figure 11.** The pore area measured on 30 images of the calendered sample is displayed. The greyscale thresholding method detected 15 600 pores and the MCWS method found 14 900 pores.

Figure 11 shows the result of porosity measurements using the two different methods, performed on the same 30 images of the calendered sample. The cumulative sum of the pore area is shown as a function of the pore area. There is a clear difference between the two methods, where greyscale thresholding results in 20% higher pore area. The porosity tends to be overestimated due to the fact that the backscattered electrons come from a deeper position in the coating than the secondary electrons. The greyscale thresholding method detected 15 600 pores whereas the MCWS method found 14 900 pores. Approximately 5% more pores are found for the greyscale thresholding method, probably because this method has problem in recognising a large shallow pore as one large pore. Signals are coming from pigments in the shallow pore, resulting in many small artificial pores. Also, if
dark areas appear on pigments, it will be registered as a pore since the method is using greyscale histogram thresholding to segment the image. The MCWS method, however, also has some problems in finding the small pores, but the BEI was used to minimise this problem by adding internal markers.

**Binder distributions**

The binder distribution was obtained by segmenting the BEI according to greyscale histogram thresholding, using Matlab. To improve the segmentation, some steps of contrast enhancement between the binder and the pigments were necessary. Also, the bright thin gold layer was subtracted using image analysis from the image before measurements.

The z-directional distribution of binder was obtained by dividing the coating layer into 20 layers of equal thickness in the thickness-direction.

![Figure 12](image-url)

**Figure 12.** Binary images of the coating layer that correspond to (a) the pores, (b) the binder and (c) to both pores and binder, giving the total pore areas.

To quantify the latex amount in each pore, the total amount of pores was needed. Therefore, the binary pore image (obtained from the MCWS-method) and
the binary binder image were added to obtain an image that corresponds to the total pore area (Fig. 12). For clarification, the binder fills up void space that was originally empty, and the binder is therefore counted as a pore or part of a pore in this specific image. Figure 13 shows a simplified image of the total pore area and how the binder fills up some parts of the pores. The clay coated sample, calendered under hard conditions were analysed in this way and for each pore, we obtained the percentage of binder.

Figure 13. Schematic image of the total pore area and how the binder fills up some parts of the pores.
3. EFFECT OF BASE SHEET STRUCTURES ON COATING THICKNESS UNIFORMITY

3.1. Correlations between coating thickness variation and base sheet structures

As discussed earlier, the literature results vary and are sometimes inconsistent in regards to the effects of base sheet structures on coating thickness uniformity. Two of the important differences in the experiments reported in the literature are (1) the sample length of the measurements, and (2) the spatial resolution for determining coating thickness variations and base sheet structure variations. Both factors influence the correlations between coating thickness and base sheet structure variations.

![Graphs showing correlations between coating thickness and base sheet structure variations](image)

**Figure 14.** The correlations between coating thickness and base sheet structure variations are plotted as a function of the cut-off wavelength of the high-pass filter. The left plot represents the paper sample with coat weight 12 g/m² and the right plot corresponds to 22 g/m². The legend applies for both plots. The pore (or mass) length is defined as the total length of the base sheet pores (or fibres) that is measured at every position on the x-axis, as described in Sec. 2.1.3.

In order to examine the effects of sample size, high-pass filters were used to eliminate longer wavelength components from the coating thickness and base sheet variations. This procedure corresponds to removing the “waviness” components (e.g., removing “cockles” from the base sheet surface profile), or to reducing the sample size. In this investigation, different cut-off wavelengths were used to examine the effect of sample size. In Fig. 14 the high-pass-filtered, coating thickness variations are correlated with the corresponding base sheet structures.
and $R^2$ values are plotted against different cut-off wavelengths for the two coat weights. As the cut-off wavelength decreases (i.e., as shorter and shorter wavelength components are removed), the correlations increased between the (filtered) coating thickness variations and the corresponding base sheet parameters. All correlation coefficients reported in Figs. 14 and 15 are negative, e.g., the higher the base sheet parameter, the thinner the coating thickness.

particularly the surface profile of the base sheet shows an extremely high correlation at shorter cut-off wavelengths. This result is considered to be a manifestation of the levelling/surface filling effect. However, as the cut-off wavelength increases (i.e., as the sample length becomes larger so that increasingly longer wavelength components are included in the measurements), the correlation between the base sheet surface profile and coating thickness variations decreased progressively.

**Figure 15.** The correlations between coating thickness and base sheet structure variations are plotted as a function of the cut-off wavelength of the low-pass filter. The left plot represents the paper sample with coat weight 12 g/m$^2$ and the right corresponds to coat weight 22 g/m$^2$. The legend applies for both plots.

Figure 15 shows the results from the correlation analysis using a low-pass filter, instead of a high-pass filter. Low-pass filters eliminate the smaller length scale components. Therefore, low-pass filtering emulates the measurements with limited resolution (e.g., the burnout method). Interestingly, as the cut-off wavelength increases (i.e., as the resolution of the measurements decreases), the mass length and base sheet thickness emerged as the key parameters controlling the coating thickness variations, particularly at the lower coat weight 12 g/m$^2$. At the higher coat weight of 22 g/m$^2$, however, the correlation is rather modest, as will be discussed later. Since the correlation is negative, the result indicates, again, the levelling effect: the lower the mass density, the higher the coating thickness.
The results obtained for low- and high-pass filtration, respectively, explain very well the seemingly contradictory results reported in the literature for different measurement methods. For example, using the SEM-method with limited image size (say 300 µm) [17], it was found that the base sheet surface profile has the highest correlation with coating thickness variation, whereas formation showed very little correlation. However, using the burnout test with limited resolution (length scales larger than around 500 µm) [13], the formation appeared to be the most important base sheet structure parameter. Therefore, it is evident that the resolution of the measurements and the sample size has a significant effect on the correlations observed. Although the results in Figs. 14 and 15 consistently explain the different experimental results in the literature, there is one important point to be noted: the correlations shown in Figs. 14 and 15 are between the “filtered” data. In other words, although the correlation between the mass and coating thickness variations was very high ($R^2 \sim 1$) at more than 1 mm cut-off wavelength (Fig. 15), the variance of “filtered” coating thickness makes up only a small proportion of the “total” variance of original coating thickness. This situation is illustrated in a typical power spectrum of coating thickness variations, as shown in Figure 16. It is seen that most of the coating thickness variations exist at the length scales smaller than around 400 µm; as the wavelength increases, the variance diminishes. (Note that bin size is increased as wavelength increases in Fig. 16.)

![Figure 16. A typical power spectrum of the coating thickness variations. The two data series correspond to the paper sample with coat weight 22 g/m².](image)

In order to see the overall contribution of the filtered component of each base sheet structure parameter to the total coating thickness variations, $R^2$ was multiplied by the relative share of the filtered coating thickness variance, i.e., filtered coating thickness variance ($\sigma_{CT, \text{filt}}^2$) divided by total coating thickness
variance ($\sigma^2_{CT, tot}$). Figure 17 shows the results at a cut-off wavelength of 300 µm for both coat weights. For small scale variations (high-pass), the base sheet surface profile explained more than 50% of the total coating thickness variations. At length scales larger than 300 µm (low-pass) the base sheet structures contribute very little to the total coating thickness variations. This is the case even for the formation parameter (mass length). Although formation certainly affects coating thickness variation, its contribution to the total variance is small. It is especially so at a high coat weight (Fig. 17, right).

![Figure 17](image)

**Figure 17.** The relative contributions of the filtered base sheet structures parameters to the total coating thickness variation. The cut-off wavelength was 300 µm. The left plot represents the paper sample with coat weight 12 g/m² and the right corresponds to 22 g/m².

### 3.2. Spatial correlation of coating thickness variations

The variations of many of the paper structures are often random, rather than periodic. Therefore, it may be appropriate to characterise the variations by autocorrelation analysis. Different classes of random processes show unique signatures in the autocorrelation function. Figure 18 shows an example of autocorrelation function of the shot noise process, whose signal is the accumulation of shot noises that occur randomly on the time axis [57].

![Figure 18](image)

**Figure 18.** The left plot shows the shot noise process, i.e. random deposition process, and the right plot its corresponding autocorrelation function.
As will be discussed later, this example is particularly interesting from the point of coating. Coating may be regarded as the random deposition of coating colour (pigments) and the subsequent re-deposition of the particles toward the lower height area, i.e. “levelling”. The mountain-shape response function of each shot noise in Fig. 18 represents the probability of re-deposition [57]. Suppose an “imaginary particle” randomly deposits with the average frequency \( \lambda \) (the number of deposition per length) and the levelling takes place with an equal probability within the distance \( \omega \) and the height \( h_0 \), the autocorrelation function is given by Eqs. (1-2) [57].

\[
R(\xi) = h_0^2 \lambda^2 \omega^2 + h_0^2 \lambda (\omega - |\xi|) \quad |\xi| \leq \omega \quad (1)
\]
\[
R(\xi) = h_0^2 \lambda^2 \omega^2 \quad |\xi| > \omega \quad (2)
\]

Figure 19 shows an example of the autocorrelation function of a shot noise process, where the response function is assumed to have a box shape.

![Figure 19](image.png)

Figure 19. An example of the autocorrelation function of a shot noise process, where the response function is assumed to have a box shape.

Figure 20 shows a typical autocorrelation function for coating thickness variations of the LWC paper sample of coat weight 12 g/m². Comparing this autocorrelation function with that of Fig. 19, we find that the coating process closely resembles the shot noise process, i.e. a random deposition process. Further, a close examination of the peak (the right plot of Fig. 20) reveals that there is a finite correlation length, which can be easily resolved by the present method. Suppose we approximate the peak shape as a triangle, we can estimate the parameters, \( \omega \), \( h_0 \) and \( \lambda \) in Eq. (2) from Fig. 20. The results are listed in Table IV.

First, the estimated correlation lengths \( \omega \) (21.4 µm and 27.9 µm) are in the order of fibre width. This is understandable because most of the levelling of coating
suspensions, i.e., lateral flow from the peaks down to the valleys during the consolidation, occurs in this length scale. For the higher coat weight (22 g/m²) $\omega$ was wider and $h_0$ was lower. This result may be explained by the fact that for the higher coat weight there is more time available for levelling before consolidation. This will be further discussed in the next section. The average number of deposition, $\lambda$, increased with coat weight, as expected.

![Figure 20](image)

**Figure 20.** The autocorrelation function for the LWC paper sample with coat weight 12 g/m² (left) and the magnified view in the neighbourhood of $\xi=0$ (right).

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\lambda$ (m⁻¹)</th>
<th>$\omega$ (µm)</th>
<th>$h_0$ (µm)</th>
<th>$h_0\omega\lambda$ (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LWC, coat weight 12 g/m²</td>
<td>92 000</td>
<td>21.4</td>
<td>2.76</td>
<td>5.43</td>
</tr>
<tr>
<td>LWC, coat weight 22 g/m²</td>
<td>224 000</td>
<td>27.9</td>
<td>1.91</td>
<td>11.9</td>
</tr>
</tbody>
</table>

Kartovaara [50] determined the coat weight variations by $\beta$-radiography (a resolution of 1 mm), and noted that the standard deviation of coat weight increases with average coat weight, but reaches a plateau at around coat weight 13-15 g/m². This observation is interesting from the view of the fundamental properties of the random deposition process with local levelling. For example, Barabási and Stanley showed that random deposition on a flat surface with “surface relaxation” (or re-deposition, i.e., levelling) yields a plateau value of the standard deviation of the thickness variation as the total number of deposited particles increases [58]. This will be further analysed in the next section.

The autocorrelation functions were also determined for the base sheet structure parameters. The mass length variations (i.e., the so called formation) were found to follow the similar shot noise type process, as may be expected from the basic
mechanism of paper making (random deposition of fibres). The base sheet thickness and pore length also had the same stochastic property, i.e. random deposition process, as the mass length.

![Graph showing autocorrelation function](image)

**Figure 21.** The autocorrelation function is shown for the base sheet surface profile, LWC paper sample with coat weight 12 g/m².

The surface profile of the base sheet, on the other hand, gave a different functional form, as shown in Fig. 21. It is characterised by a signature from a large scale periodic variation (~3 mm wavelength) and a peak near $\xi=0$ with the correlation length of the same length scale of a typical fibre width (~30 µm). Visual inspection of the sample showed that the former originated from macroscopic paper distortions (called “cockling”) and the latter was related to micro-scale roughness caused by individual fibres.

In summary, coating thickness variations closely resembled the process of random deposition, with a levelling effect. Therefore, if there is any effect of base sheet structures, it should be through this effect of levelling on the “rough” surfaces.

In the next section, a generic, random deposition model with this levelling effect was constructed in order to investigate the universal properties of coating thickness variations.
4. SURFACE EVOLUTION OF THE COATING LAYER

As observed experimentally, if the coating process is essentially described as a random deposition process, it may be interesting to ask whether there is any universal statistical property in coating thickness variation. In order to answer this question, it might be worth to look at particle-level modelling approaches. Particle simulations have been used frequently to study particle motion and coating structure development.

Various models have been proposed, and Vidal and Bertrand made an extensive review on this subject [59]. The numerical models are often divided into two classes, phenomenological and deterministic deposition models. The phenomenological models, including steepest descent deposition [60] and Monte Carlo deposition [61], often rely on probabilistic rules and tend to be computationally more efficient than the other. The deterministic deposition models, such as Stokesian dynamics and discrete element method [62-66], on the other hand, are based on Newton’s second law, and are more faithful to first principles but computationally costly. Both methods have been mainly targeting to predict phenomena in relatively small length scales because of the computational demands.

In this work, a generic, random deposition model was constructed, but with volume exclusion effect and surface relaxation effect (so called, levelling in paper coating). This deposition model is applied both on a flat surface as well as on a rough surface, where the latter was taken from a light-weight coated paper (LWC). Although this model is far from realistic paper coating systems in terms of particle shapes and micro particle dynamics, the intention is to capture universal properties of coating thickness variation, which are present in a much larger length scale (e.g., a few millimetres) than those investigated in the particle models in the literature.

4.1. Modelling Coating Particle Deposition (Paper V)

In this model, coating was created by depositing particles, one by one, randomly in discrete points (in grids or lattices) in a two-dimensional square surface. Each particle has a simple box shape with sides of equal length. This deposition model very much follows the one used by Barabási and Stanley [58]. The number of particles deposited was varied to obtain different coating thicknesses. During the simulation, coating thickness and surface roughness were measured, and the surface roughness was defined by the rms of height variation,
w(L,t) = \sqrt{\frac{1}{L} \sum_{i=1}^{L} [h(i,t) - \bar{h}(t)]^2} \quad (3)

where $w(L,t)$ is the roughness, often called the interface width [58], $L$ is the system size (the side length of the square surface), $h(i,t)$ is the height of column $i$ at time $t$, and $\bar{h}(t)$ is the mean height of the coating surface. Since the deposition rate was constant, time $t$ may be exchanged to the average number of particles deposited on the surface $n$, 

$$n = \frac{Ns^2}{L^2} \quad (4)$$

where $N$ is the total number of deposited particles and $s$ is the particle size (side length of box). The number $n$ will be interchangeably called time and the average number of particles.

![Figure 22. Schematics of random deposition (left) and random deposition with levelling (right).](image)

In this study we investigated three cases: (1) random deposition on a flat surface, (2) random deposition on a flat surface with levelling, and (3) random deposition on a rough surface with levelling. In the first case, the particles simply follow a straight vertical trajectory until it reached the surface, as shown in Fig. 22 (left). In the second case, the particles are allowed to move along the surface if there is any site of the lower height in the nearest neighbours. This movement continues until the particle finds no site of lower height (Fig. 22, right). This levelling effect is alternatively called surface relaxation [58]. Surface relaxation is a representation of the surface tension effect, which minimizes the surface areas of high curvature and thus tends to flatten the surface. A continuum representation of this random deposition with surface relaxation is given by Edward-Wilkinson equation [58]

$$\frac{\partial h(x,t)}{\partial t} = v\nabla^2 h + \eta(x,t) \quad (5)$$
where $\gamma$ is surface tension, and $\eta(x,t)$ is the random deposition term. The same effect was analyzed by Bousfield on a macroscopic scale for levelling of surface undulations of coating during consolidation process [67]. In this study we try to capture the surface tension effect with this discrete model. However, this model is still a gross simplification of the actual coating consolidation process.

In the third case, particles are deposited on a rough surface. As an example of the rough surface, a base sheet of a real LWC paper [39] was used in the experimental study. As seen in Fig. 23, the base sheet surface consists of a wide range of variation of different length scales. The surface profile of the LWC base sheet was obtained from an optical surface measurement with the resolution of $1 \, \mu m/\text{pixel}$, giving a surface of total area $2000 \times 2000 \, \mu m^2$.

![Surface height image of the LWC base sheet, size 2 000 x 2 000 \, \mu m^2.](image)

One deviation from the typical deposition models in the literature [58] is that finer grids than the particle size were used (see Fig. 24). For example, if the particle size is equal to the grid size, there is no pore created in the deposition process, whereas with finer grids that allow more deposition sites, we can represent volume exclusion effects between particles, and thus create pores in the structure. The effect is similar to, so called, ballistic deposition [58], but the particle size effect is represented in a more intuitive manner. In our numerical tests, by using the grid resolution of a factor of 10 or higher at a given particle size, pore structures could be obtained that was independent of the grid resolution. To avoid the grid effect of the LWC base sheet, the resolution was increased by a factor of 10, resulting in a
matrix with 20 000 x 20 000 pixels and resolution 0.1 µm/pixel. To resize the base sheet surface image, linear interpolation was used between the pixel values in the original image.

![Image](image.png)

**Figure 24.** The left image shows that by increasing the resolution, each particle has more possible deposition sites, creating a porous network as illustrated in the right image.

### 4.2. Random deposition on a flat surface

In order to depict basic statistical properties of this discrete model, we start from the simplest case, random deposition without levelling on a flat surface. Figure 25 shows a log-log plot of the roughness versus average number of particles, where the size of the particles is varied between 1 and 4 µm and the system size is 100 µm. The surface roughness gradually increases during deposition, and eventually it saturates. Obviously, the surface roughness is dependent on the size of the deposited particles. When the particle size is increased, correlations develop between the points in the grid due to the volume exclusion effects between the particles. A larger particle interacts more frequently with other particles, creating a form of aggregated structure. The result is similar to a ballistic deposition where the deposited particles form a cluster or an aggregate [58], except that the present model does not follow the nearest-neighbour sticking rule.

Figure 26 shows the log-log plot of roughness versus average number of particles for various system sizes, 50 to 200 µm (particle size was 2 µm). All three curves almost fell onto the same curve and there was no clear effect of the system size. This result differs from the literature where the roughness was dependent of the system size [58]. This is partly because we already plotted the data against \( n \), which is scaled with the system size by \( L^2 \).

By using the method by Barabási and Stanley, 1995, we can collapse the curves in Figs. 25 and 26 into one, such as shown in Fig. 27, where the roughness was
divided by the saturated roughness \( w_{\text{sat}} \), and the average number of particles by
the cross-over time \( n_c \), as defined in Fig. 28.

**Figure 25.** Log-log plot of the surface roughness versus the average number particles. The
particle size varied between 1 and 4 µm, and the linear size of the square lattice was \( L = 100 \) µm.

**Figure 26.** Log-log plot of the surface roughness versus the average number particles. The
system size was varied between 50 and 200 µm, and the particle size was 2 µm.
Barabási and Stanley found that the ballistic process generally consists of two different roughness regions, separated by the cross-over time $n_x$ [58]. The first region increases with time raised to the $\beta$-th power, where $\beta$ is called growth exponent (Fig. 28). Beyond $n_x$ there is a plateau region where the roughness becomes saturated, $w_{sat}$. It has also been shown that at initial stage of deposition, simple Poisson growth dominates giving $\beta$ equal to 0.5 [58, 68].
As seen in Figs. 25 and 26, both \( w_{\text{sat}} \) and \( n_x \) are functions of \( s \) and \( L \). Using least-square fitting the following functional dependence was obtained:

\[
\frac{w(n)}{w_{\text{sat}}} \propto \left( \frac{n}{n_x} \right)^{0.74} \quad n << n_x, \quad (6)
\]

\[
w_{\text{sat}}(s,L,n) = 4.85s^{0.82}L^{0.16} \quad n >> n_x, \quad \text{and} \quad (7)
\]

\[
n_x(s,L) = 2.18s^{-0.30}L^{0.25} \quad (8)
\]

The growth rate \( \beta = 0.74 \) is significantly higher than 0.5 for the simple Poisson growth, because of the volume exclusion effect, similar to the ballistic deposition process. Other components will be compared in the subsequent sections.

### 4.3. Random deposition on a flat surface with levelling

Figure 29 shows a log-log plot of the surface roughness versus the average number of particles for the random deposition process on a flat surface with levelling. The roughness increases with particle size, and saturates in the similar manner as in the previous result in section 4.2. It is clear that the roughness is dependent on particle size in this case as well.

![Figure 29](image)

**Figure 29.** Log-log plot of the surface roughness versus average number of particles. The particle size was varied between 1 and 4 \( \mu m \), the linear size of the square lattice was \( L = 100 \mu m \).
Figure 30 shows the log-log plot of roughness versus average number of particles for various system sizes, 50 to 200 µm (particle size was 2 µm). This time there was a slight difference in the saturated roughness, depending on the system size.

![Log-log plot of roughness versus average number of particles](image)

**Figure 30.** Log-log plot of the surface roughness versus average number of particles. The particle size was 2 µm and the linear size of the square lattice was varied, 50 ≤ L ≤ 200 µm.

The curves were scaled according to the procedure used in Sec. 4.2. Figure 31 showed that all data points in Figs. 29 and 30 were collapsed onto the same single curve. The growth exponent was 0.45 which is lower than 0.5 of the simple Poisson growth case. This is obviously due to levelling. The maximum surface roughness, i.e., the saturated roughness, was lower as well with levelling.

Following the same procedure as in the previous section, we obtained the following functional dependence:

\[
\frac{w(n)}{w_{sat}} \propto \left( \frac{n}{n_x} \right)^{0.45} \quad n << n_x, \quad (9)
\]

\[
w_{sat}(s, L, n) = 10.0s^{0.87}L^{-0.32} \quad n >> n_x, \quad \text{and} \quad (10)
\]

\[
n_x(s, L) = 61.7s^{1.59}L^{-0.59}. \quad (11)
\]

As seen in Fig. 29, \(w_{sat}\) increases with increasing particle size \(s\), and the cross-over time \(n_x\) increases as well (more time to saturate).
Figure 31. The simulation data in Figs. 29 and 30 are rescaled, resulting in all curves falling on one single curve.

Figure 32 shows autocorrelation function for the random deposition (RD) cases with and without levelling. As expected, the total variance went down drastically by levelling. The case with levelling shows a typical random-shot type process, with correlation length 2 µm, the same as the particle size.

Figure 32. The plot shows the autocorrelation functions for the two models, random deposition (RD) with and without levelling. Particle size was 2 µm, system size was 100 x 100 µm² and the number of particles deposited was 50 000.
Figure 33. The top image corresponds to a magnified view of the autocorrelation function for random deposition and the bottom represents the autocorrelation function for the random deposition with levelling.

Figure 33 shows autocorrelation functions for both without (top image) and with levelling (bottom image) in a different magnification, for different $n$. When the total number of particles is small ($n < n_x$), the autocorrelation function has the correlation length approximately equal to the particle size for both cases, i.e. the surface is almost uncorrelated. With increasing total number of particles, the total variance of the coating thickness, i.e. $R(0)$, ceases to increase, as expected from the saturation behaviour in Figs. 27 and 31. The correlation length, however, continued to increase with the total number of deposition for both cases, reaching a limiting value. In the case of Fig. 33 where the system size was 100 µm, the limiting length was 25 µm. For other system sizes, the limiting length was found to be around one
fourth of the system size. The correlation length clearly depends on both the total number of particle deposition and the system size.

Figure 34 visualises surface features for the two different cases and confirms that the case without levelling exhibits more pronounced floc-like features, whereas the case with levelling clearly shows a smoother, finer surface texture.

**Figure 34.** The surface images correspond to random deposition without levelling (left) and with levelling (right). The grey level represents different surface heights.

### 4.4. Random deposition on a rough surface with levelling

In this section, the results when particles are deposited on a rough substrate will be discussed. The surface data was taken from a commercial LWC sample with a measurement resolution of 1 µm. Therefore we chose the particle sizes of 2 and 3 µm to represent the volume exclusion effect. The maximum system size was set to be 2 mm this time.

**Figure 35.** Log-log plot of the surface roughness versus the average number of particles. The particle size was 2 and 3 µm and the surface size was 2 000 x 2 000 µm.
Figure 35 shows the surface roughness as a function of the average number of particles for the particle size 2 and 3 µm. (It should be noted that in this case the roughness is actually the rms of coating thickness variation. For flat surface, the rms of both parameters is of course the same.) The roughness depends on the particle size in this case as well. In Fig. 36, the surface roughness is plotted against the average number of particles for different system sizes. There is a clear effect of the system size.

Figure 36. Log-log plot of the surface roughness versus the average number of particles. The particle size was 2 µm and the system size was varied between 100 and 2 000 µm.

Figure 37. The simulation data in Figs. 35 and 36 are rescaled, resulting in all curves falling on one single curve.
All curves in Figs. 35 and 36 were collapsed onto a single curve in the same manner as before (Fig. 37).

By using linear least square fitting the following functional dependence was obtained:

\[
\frac{w(n)}{w_{\text{sat}}} \propto \left( \frac{n}{n_s} \right)^{0.46} \quad n << n_s, \quad (12)
\]

\[
w_{\text{sat}}(s, L, n) = 8.67 s^{0.82} L^{-0.16} \quad n >> n_s, \quad \text{and} \quad (13)
\]

\[
n_s(s, L) = 81.8 s^{0.31} L^{-0.46}. \quad (14)
\]

The growth exponent was 0.46 which was similar to the roughness exponent for random deposition with levelling on a flat surface. It is also interesting to note that the exponent that represents the particle-size dependence of \( w_{\text{sat}} \) is almost the same for the three different cases: (1) on a flat surface (0.82), (2) on a flat surface with levelling (0.87), and (3) on a rough surface with levelling (0.82).

Figure 38 shows the autocorrelation functions for random deposition with levelling on a rough surface with two different system sizes, 100 µm (top) and 2000 µm (bottom). When increasing the “coat weight”, i.e., the total number of particles, the total variance \( R(0) \) increased up to the saturated surface roughness. Similar to the previous cases, the correlation length also shows the dependency on the system size and particle size: the correlation length starts from the particle size, and then grows with increasing coat weight (the total number of particles). An important difference is that, in the case of 100 µm system size, the correlation length showed a (seemingly) limiting value of 20 µm, which is different from a quarter of the system size (25 µm) that was observed in the previous two cases. In the case of the system size of 2 mm, the correlation length still continued to grow within the range tested, but it does not appear to reach a quarter of the system size, 500 µm but approached to about 50-60 µm. This result may be understood by considering the surface texture of the real base sheet surface. It contains a very fine feature, corresponding to fiber width (20-50 µm), and larger features like wire marks, press felt marks, micro flocs, etc. Therefore, it is not surprising to see that with increasing the system size, the analysis picks up larger and larger features of the paper surface, and thus correlation length increases. Obviously, at a lower coat weight, smaller features are detected, and thus the correlation length of fiber width scales is not a coincident.

Figure 39 shows actual experimental data for LWC paper. Comparing Figs. 38 and 39, similarity is striking. It is also important to note that, in the case of actual coated paper, the roughness \( R(0) \) (the total variance of coating thickness) has not reached the saturation range, but is still growing as seen from the coat weight
dependence of $R(0)$ (Fig. 39, bottom). In other words, surface is still evolving in a real coated paper.

Figure 38. The autocorrelation functions are shown for the random deposition with levelling for different "coat weight" on a rough surface, where the system size was 100 µm (top image) and 2,000 µm (bottom image). The particle size was 2 µm.
Figure 39. Autocorrelation functions for the samples with coat weight 12 and 22 g/m². The right image is a magnified view of the left image.
5. **BINDER DISTRIBUTIONS (PAPER IV AND VI)**

The non-uniform binder distribution in the coating layer is often considered to be a source of poor print quality [25], and it is therefore of interest to determine the binder distribution throughout the coating layer.

Figure 40 clearly shows an example of the distributions of the binder, pigments and the pores of the coating layer in the calendered sheet. The binder appears as the bright spots (since it is stained with OsO₄), with the thin gold layer on the coating surface. The pores are black or dark grey and the pigments have different shades of grey. Clay is a platy pigment while the ground calcium carbonate has a blocky shape. Agglomeration of pigments and non-uniform distribution of binder are clearly seen. The base sheet fibres can also be seen, supporting the coating on the bottom side.

![Figure 40](image)

**Figure 40.** This BEI shows a cross section of a stained coating layer (calendered sample), where the latex is visible as the bright material, the pigments are different shades of grey and the pores are black or dark grey. The base sheet fibres can be seen, surrounding the coating on the bottom side.

5.1. **Binder distribution in thickness direction**

The spatial distribution of binder, particularly the migration of binder toward the coating surface has been debated over the years. Pöhler et al. and Kenttä et al. used FESEM cross sections to determine binder distribution through the coating...
layer. The coating layer was divided into five layers from the coated surface, each 1 µm thick [40, 69]. They found no binder migration toward the coating surface. Arai et al. used electron spectroscopy for chemical analysis (ESCA) in combination with razor blade scraping for depth profiling, where every scraping removed 0.5-0.8 µm of thickness [70]. They found a higher binder content near the coating surface. Ozaki et al. used confocal laser scanning microscopy (CLSM) to study binder distribution [1], with the typical resolution of around 0.2-0.7 µm [45]. Vyörykkä et al. used confocal Raman microscopy to investigate the binder distribution with lateral resolution 2.5 µm and depth resolution 4 µm [29]. In both cases, no clear evidence of binder migration was found. In the literature, surface measurement techniques, such as UV-absorption, ESCA or X-Ray Photoelectron Spectroscopy (XPS), and energy-dispersive spectroscopy (EDS), were used to detect the amount of binder at the surface [25-28, 70]. These surface measurements seem to be pointing toward some migration of binders, but the details of the internal distributions are obviously not known.

The binders typically have a diameter around 100 nm, which requires ultra-high resolution for the measurements and thus special demands on sample preparation. The argon ion beam milling technique produces smooth cross sections free from artefacts and thus, in combination with FESEM, it is ideal for this type of direct observation [71].

Figure 41. BEI of the clay coated sample (hard calendered).

Figure 41 shows the binder distribution for the hard-calendered, clay coated sample. The binders seem to be richer on the coating surface and at the interface with the base sheet. The image analysis reveals more clear trends.
The binder distribution in the thickness direction was determined by dividing the local coating thickness, i.e. the coating thickness measured at each position (every pixel point) in the x-direction of the image, into 20 layers at each position and by calculating latex amount for each layer by using the same technique used for analysing the porosity distributions [37]. Figure 42 shows the binder distribution through the coating layer, from the coated surface down to the base sheet. The coating layer thickness is on average about 6 µm, which means that every measured layer is approximately 300 nm thick. It is interesting to note that binder enrichment was found both at the surface of the coating and also at the interface with the base sheet. However, the clay coating calendered under mild conditions, does not have an enriched layer of binder at the coated surface. It should also be noted that the binder enrichment is only in the outermost areas, corresponding to less than 500 nm. This may explain why some of the measurements were unable to detect this binder distribution. Although the exact mechanism of the binder distribution is still in question, this study has, at least, confirmed a special pattern of binder distribution.

![Binder distribution through the coating layer](image)

**Figure 42.** The figure show how the binder amount is distributed from the coated surface down to the base sheet.

### 5.2. Binder distribution within the coating structure

Figure 43 shows another interesting feature of the binder distribution. The small pores are almost completely filled with the binders, whereas the large pores are
mostly empty, depleted of the binder. Ström et al. observed similar results, suggesting that a substantial part of the binders are associated with fine pigments [72]. Di Risio and Yan also suggested that the binder distribution is related to the pigment size distribution, where coarse pigments increase the variation of binder distribution [73].

Figure 43. This image shows a magnified view of Fig. 40. The larger pores tend to be depleted with binders, whereas many of the smaller pores are filled with binders.

In order to quantify this type of binder distributions, we measured the amount of binder in each pore, to directly relate pore size and binder content. Image analysis showed that about 70% of the total amount of pores in numbers is completely filled with binder, and that 94% of them are located in pores smaller...
than 0.2 µm. Figure 44 shows the cumulative distribution functions of the number of pores of a certain size. The black curve corresponds to the total number of pores (including both pores and “binder pores”), whereas the grey dashed curve represents the pores that are completely filled with binder. It is obvious that the small pores are almost exclusively filled with binders. At the same time, there are very few large pores that contain binder. One explanation can be that the binder is attracted to smaller pores with high surface curvature by capillary forces during the consolidation process.

The implication of this non-uniform binder distribution is significant: relatively few, but large pore regions between pigments could become weak links in the coating layer, leading to coat chipping and delamination.
6. CONCLUSIONS

The results obtained for the length scale effect explain very well some of the controversies in the literature regarding the main factors controlling coating thickness variations. For lower resolution (or larger sample size measurements), formation (mass distributions) and base sheet thickness variations appear as the key properties controlling coating thickness variations. For higher resolution (or smaller sample size measurements), however, the surface profile of the base sheet becomes a prominent parameter that controls coating thickness variations. Both were observed in the literature. These are originated from the unique statistical properties of coating thickness variations, rather than measurement errors or artefacts. The power spectrum of the coating thickness variations showed that most of the coating thickness variations exist at the length scales smaller than around 400 µm. Consequently, the major contribution to coating thickness variations comes from the base sheet surface profile, although only 50% of the variations were explained.

Autocorrelation analyses indicated the unique statistical properties of coating thickness variations that explain the rest of the coating thickness variations. A typical autocorrelation function for coating thickness variations showed close resemblance to a process of random deposition with some local levelling. At small length scales, in the order of fibre width, levelling occurs so that coating thickness variations are essentially determined by the surface profile at the corresponding length scale. At larger length scales, the same levelling suppresses the inherent coating thickness variations (random deposition), leaving only a trace of the effect of base sheet structures, creating contour-type coating.

In order to further examine the above observation and to investigate the universal properties of the coating thickness variations, a generic, random deposition model was constructed with this levelling effect. Coating thickness variation was investigated for the following three cases: (1) random deposition on a flat surface, (2) random deposition on a flat surface with levelling, and (3) random deposition on a rough surface with levelling. In all three cases, surface roughness (the rms of coating thickness) follows a universal behaviour: when plotted in logarithmic scales, roughness increases linearly with increasing coat weight (the total number of particles), and then reach a plateau value (saturation). In all three cases, correlation length grows with increasing coat weight but showed a tendency to reach a limiting value. This limiting value is clearly related to the system size in the case of flat surface, but in the case of rough surface, it depends on the surface features that are prevalent within the system size. Again the
correlation length in the fibre-width scales was found at a typical coat weight, which is a close resemblance to those observed experimentally.

A new method was developed for analysing coating microstructure uniformity using argon ion beam milling and FESEM, combined with a new image analysis procedure based on MCWS of SEI. The method gives large cross sections virtually free from artefacts and very high quality images which are particularly suited for quantitative analyses of coating microstructures. The result showed that a very thin layer of binder enrichment (500 nm) was present both at the coating surface and at the base sheet/coating interface. Another finding was that the binder almost exclusively filled up the small pores in the coating layer, whereas the larger pores were mostly empty.

Implications of this study are many. First, in order to improve the coating thickness uniformity from the point of base sheet, the focus should be on the selection of fibre (fibre width and thickness). The new method using argon ion beam milling and FESEM will have extensive applications for the problems related to coating microstructure uniformity, such as barrier properties and sintering behaviour of silver inks in printed electronics.
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REFERENCES


