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The use of infrared and Raman microscopy to characterise the absorption of offset ink in paper

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Abstract

Previous studies have detected traces of mineral oils in food packaged in paperboard packaging, with the migration of the ink oil used on the outside of the packaging identified as a potential source of this contamination. This study examined the use of both infrared (IR) microscopy and Raman microscopy to evaluate their use in the detection of mineral oil migration from an offset printing ink through a bespoke set of laboratory made paper hand sheet samples. The IR microscopy was found to be largely unsuitable for this type of investigation due to the low IR reflectance of the materials used in the paper and the ink. Raman microscopy was able to clearly distinguish between the different ink and paper components and therefore characterise the migration within the paper samples. The initial results showed that the use of calcium carbonate pigments as a filler reduced the migration of mineral oil through the paper. For the coated papers, the majority of the mineral oil was detected within same region as the coating. This was in agreement with other studies that have examined the absorption of ink oils into the pore network of calcium carbonate paper coatings.

Keywords: food packaging, migration, mineral oil, paper filler, paper coating

1. Introduction

Printing inks consist of four main ingredients: pigments, binders, solvents and additives. Offset inks could contain mineral oils as a solvent. In the setting and drying process, the oils firstly penetrate into the paper or paper coating. Some papers are coated to improve print quality. The absorption of the ink oils into pigment-based paper coatings has been the subject of much research.

The absorption has been shown to be a function of the pore structure of the coating (Gane, Schoelkopf and Matthews, 2000), the chemistry of the coating (Rousu, Gane and Eklund, 2003) as well as the viscosity, surface tension and polarity of the oils (Tåg, et al., 2013). The absorption is primarily driven by capillary flow (Schoelkopf, et al., 2000), with diffusion into coating components such as latex (Rousu, et al., 2000a; 2000b) also occurring. Small quantities of alkyd and hard resin binders are also absorbed with the oils into the coating (Ström, Gustafsson and Sjölin, 2000). The majority of the binder materials remain on top of the coating, binding the pigment particles to the surface of the paper or paper coating. Due to the random fibre network, the ink absorption into paper is inhomogeneous (Kappel, et al., 2008), but paper-making parameters such as calendering and fibre refining have a strong impact on the absorption characteristics of a paper (Yang, et al., 2005).

The use of mineral oils in offset printing inks has become somewhat controversial in the packaging industry. When the food gets in touch directly with the packaging the use of mineral oil containing offset ink is forbidden. In the food sector, offset inks with vegetable oils are used as solvents. Despite all these measures, mineral oils in foods have still been detected by analysis. Traces of mineral oils have been found in dry foods such as rice, pasta and breakfast cereals (Droz and Grob, 1997). These can accumulate in the body and lead to organ damage (World Health Organisation, 2002; Van Heyst, et al., 2019).

It is widely known that the mineral oil contamination could originate from different sources in the production and delivery system, including from the lubrication oils from the machines used in farming and production; or the batching oils used in the jute bags that are used for transport and storage of products such as cocoa beans, rice and nuts (Moret, Grob and Conte, 1997). Paperboard packaging can contain a large percentage of recycled paper fibres, which were previously printed with offset inks containing mineral oil, for example, newspapers (Biedermann and Grob, 2010; Biedermann, et al., 2011; Vollmer, et al., 2011; Lorenzini, et al., 2010; 2013). If the packaged goods come into direct contact with the packaging, virgin fibres should, therefore, be used.

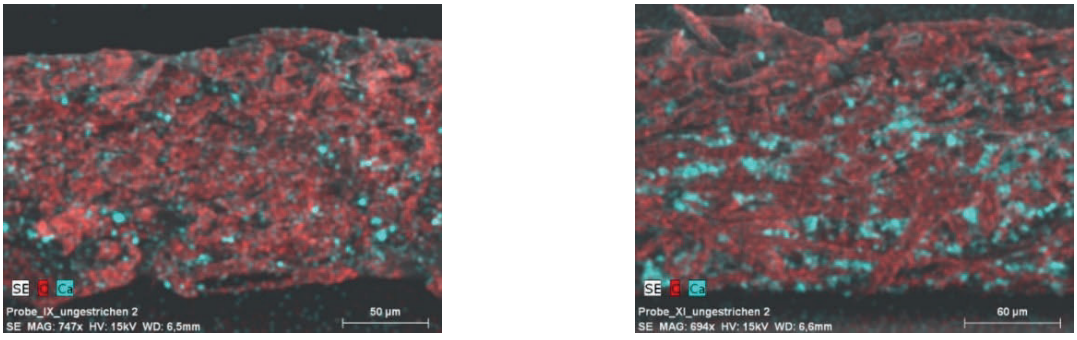
This investigation was part of a larger study into ink migration. Here we discuss the use of infrared (IR) and Raman microscopy to examine the migration of offset ink components through paper samples and present some initial results for different samples.

2. Methods

2.1 Sample preparation

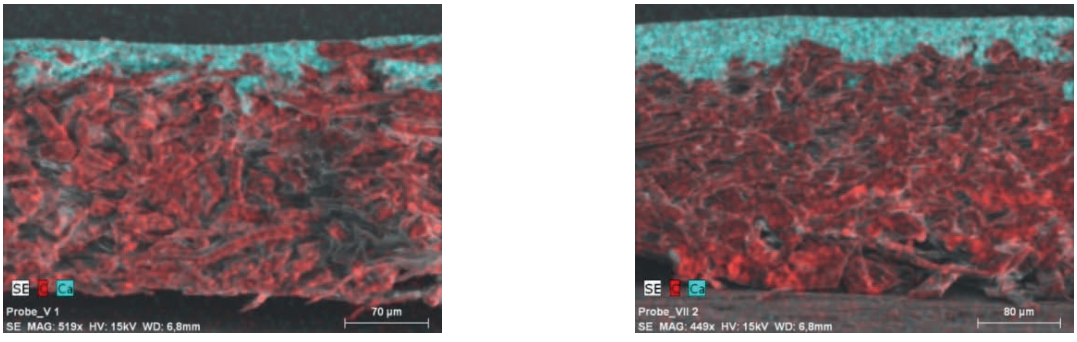
2.1.1 Paper samples

Initial studies examining offset ink penetration in a paper using commercially available papers proved inconclusive because the exact composition of the papers was unknown. Therefore, for this study, a structured set of hand sheet paper samples were produced using a Rapid Köthen Sheet former. Four different paper types were produced, all using the same type of bleached chemi-thermo-mechanical-pulp (BCTMP) fibres, each with a different combination of sizing and calcium carbonate filler content. In addition, different types of subsequent processing such as calendaring and coating were also used. The coating consisted of calcium carbonate pigments dispersed in a carboxyl--styrene-butadiene based latex binder.



a) *b)*

Figure 1: SEM/EDX pictures of uncoated paper with (a) low quantity of filler, (b) high quantity of filler



a) *b)*

Figure 2: SEM/EDX pictures of paper without filler with (a) single coating, (b) double coating

One potential problem with laboratory crafted hand sheets is an uneven retention of fillers and fibres. Therefore, to control the quality, imaging with Scanning Electron Microscopy and Energy Dispersive X-Ray Analysis (SEM/EDX) of unprinted paper-cross-sections were carried out. Figure 1 shows a comparison between two uncoated paper samples: one with a low quantity of filler and the other with a higher quantity of filler. The calcium carbonate filler shows up as light blue in the SEM/EDX images, while the fibres have a red colour. In both types of samples, the filler was relatively evenly distributed throughout the fibre matrix.

Figure 2 shows a comparison of two papers, one with a single and the other with a double-layer coating, both types of sample did not contain fillers. Since calcium carbonate was also used in the coating material, this also shows up as light blue in the SEM/EDX images.

2.1.2 Printing ink

For the print samples, a bespoke offset printing ink was used. This ink was comparable to typical sheet-fed ink containing mineral oil but did not contain additives such as wax. The ink was a process cyan containing copper phthalocyanine pigments. A suitable colour was needed that provided a strong colour contrast on the paper. While black would have provided the best visual contrast on the white paper, the inorganic carbon black pigments were not suitable for vibration spectroscopic methods because of their absorption characteristics. Cyan provided both a good visual contrast and also produced a strong Raman signal. In addition, the main ink's components such as the pigments, binder, mineral oil and the alkyd resin were provided as individual reference components for use in the IR and Raman spectroscopy.

2.1.3 Preparation of the samples

The laboratory paper samples (hand sheets) were printed with a 100 % solid tone on one side, using a printability tester (Prüfbau printability tester, Germany). For each sample, a controlled and constant amount of the ink was used. The same speed and nip pressures were used to produce each sample. For IR and Raman analysis, thin slices, named microtomes, are a commonly used approach to prepare samples. This involves first embedding the printed paper samples in a resin. When the resin is solidified, very thin slices are cut using a microtome blade. This approach was tried with both methacrylate and epoxy resins, but in both cases resulted in the ink bleeding. Therefore, in order to prepare the samples, a method was developed, where 10 mm × 10 mm layered blocks were made. These consisted of alternating layers of the printed paper samples with layers of polytetrafluoroethylene (PTFE) in between. The PTFE was used because it provided distinguishable IR and Raman spectra compared to the other materials. These layered blocks were then sandwiched between two thicker polyvinyl chloride (PVC) plates (Figure 3).

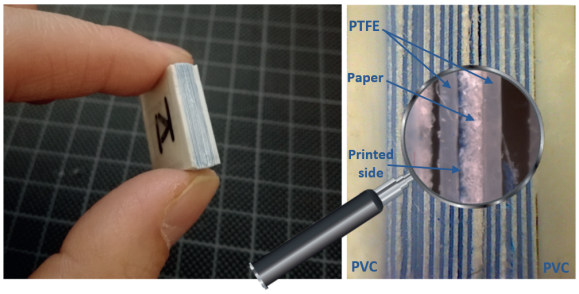


Figure 3: Paper-film-sandwich block, stabilized outside with two thick PVC-films

For the IR spectrometry, microtomes were produced from these sandwich blocks. One advantage of the Raman spectrometer over the IR spectrometer was that it could work with thicker samples; therefore, the sandwich blocks could be used directly in the instrument, eliminating the need to produce microtomes.

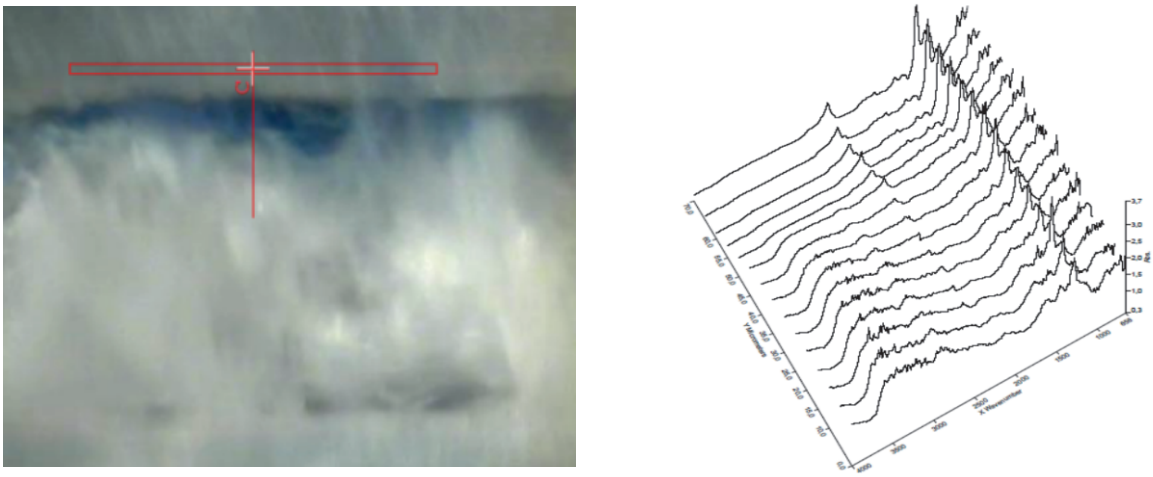
2.2 Sample characterisation

Methods were developed using both IR microscopy and Raman microscopy to characterise the cross-sections of the printed paper samples. Because the main area of interest of this study was to detect mineral oil migration in packaging, the printed samples were stored for a period of four months before characterisation, which would correspond to the lifecycle of a typical paper-based packaging.

2.2.1 IR microscopy

An infrared microscope consists of an IR spectrometer, an infrared detector, and an optical microscope. A Perkin Elmer Spectrum One FTIR Spectrometer with an Autoimage Microscope was used for generating infrared reflection-absorption spectroscopic (IRRAS) line scans from the microtome cuts of the printed paper sections. The results from a typical line scan are shown in Figure 4.

A total of 15 spectra with a repeatability of 64 scans per spectrum were recorded in each line scan. Measurement of the location of the individual printing ink and paper components were made by comparing the line scan spectra with the reference spectra of the base paper, paper coating, and ink as well as the individual ink and paper components to calculate a correlation coefficient.



a) *b)*

Figure 4: Line scan of the paper cross-section (a) and typical line scan spectra (b)

2.2.2 Raman microscopy

For Raman microscopy, a confocal Raman microscope alpha 300 R+ from WITec was used. From initial experiments, with different laser types, it was found that a green Nd:YAG Laser (λ = 532 nm) produced repeatable results in detecting the ink and paper components with a high signal-to-noise ratio. Furthermore, wavenumbers up to 3700 cm^{-1} could be reproduced. As the excitation laser radiation from the Raman spectrometer is much more intense than the resultant Raman scattering from the sample, a notch filter was used to prevent this excitation radiation from reaching the CCD detector and clouding the spectrum. A very narrow-band filter was used, so that the wavenumbers from the green laser (until approximately 70 cm^{-1}) were absorbed, therefore allowing the wavenumbers above approximately 80 cm^{-1} to be used for analysis.

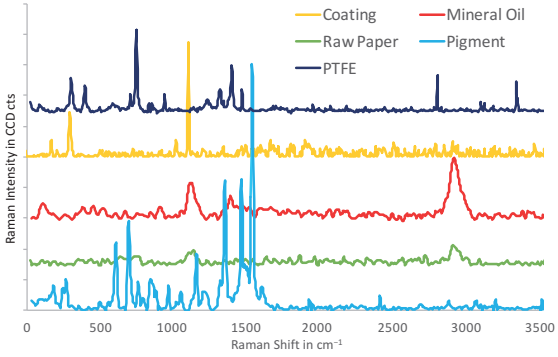


Figure 5: Relevant Raman spectra of the individual components

The individual Raman spectra of each of the main ink and paper components in the preliminary sample were measured to generate reference spectra in order to identify the unique signature wavenumber peaks of each component, which could then be used later to detect its presence in the printed paper samples. The Raman spectra of the main components are shown in Figure 5.

The pigment provided the clearest and most intense signal with few overlaps with those of the other materials. However, differentiation between the Raman spectra of the paper coating, mineral oil, and base paper was more difficult. All three materials produced a signal peak at approximately 1 100 cm^{-1}. The raw paper provided only two usable peaks at approximately 1100 cm^{-1} and 2900 cm^{-1}. The mineral oil also provided peaks in these regions. For this reason, the peak for the mineral oil band at 96 cm^{-1} was used for the evaluation. The mineral oil gives a significant signal in this area, which was absent in the spectra of the other materials (Figure 6). According to Cates, Strauss and Snyder (1994) it could be a CC torsion vibration.

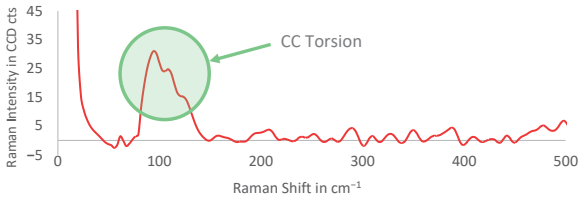


Figure 6: Raman spectrum of the mineral oil from a green laser (only the portion up to 500 cm^{-1} is shown)

Using the Raman microscope, the entire paper cross-section was measured during an image scan. A typical measurement region is shown in Figure 7.

Filters with different wavenumber bands were then created within the analysis software, in order to identify the different components based on the characteristic peaks determined from the Raman spectra.

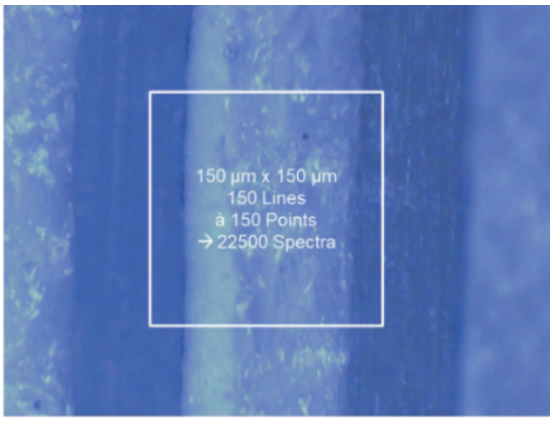


Figure 7: Magnification of sandwich block with a selected region for a Raman image scan

Examples of the most relevant filtered images are shown in Figure 8.

To measure the depth within the samples at which the different components were found, the filtered images were first vertically aligned to minimise skew, and then transformed into greyscale images. An example of a greyscale image for the filter selected for the pigment particles (1517 cm^{-1} to 1552 cm^{-1}) is shown in Figure 9.

The freeware software GNU Octave was then used to evaluate the average greyscale values as a function of the distance in *x*-direction. Figure 10 shows the plot of the greyscale values with the confidence interval for the cyan pigment component generated from image in Figure 9.

The plots of the five types of filtered images (PTFE, pigment, coating, mineral oil and base paper) have been combined into a single diagram shown in Figure 11.

For this preliminary sample, approximately the first 7 µm of the image was the PTFE film. This was followed by the pigment up to approximately 14 µm. The coating layer reached approximately to 40 µm.

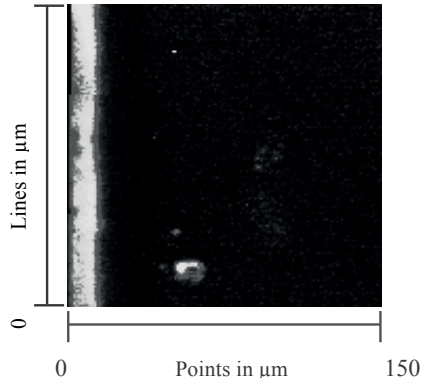


Figure 9: Greyscale image of the Pigment filter (1517 cm^{-1} to 1552 cm^{-1})

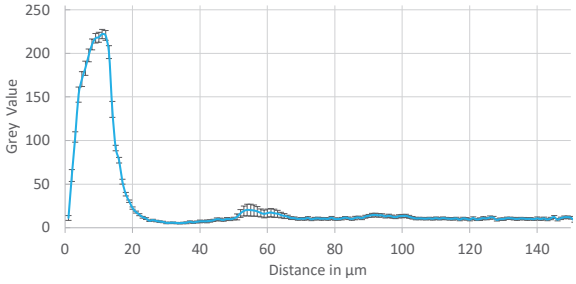


Figure 10: Average greyscale as a function of distance with error bars of the pigment distribution

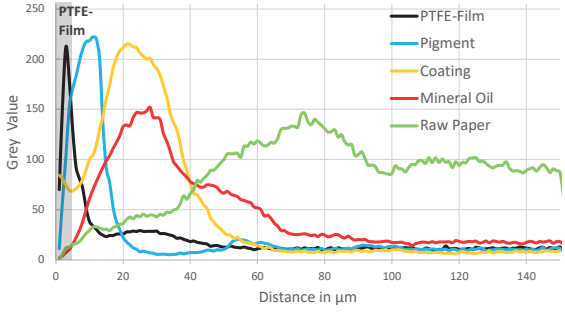
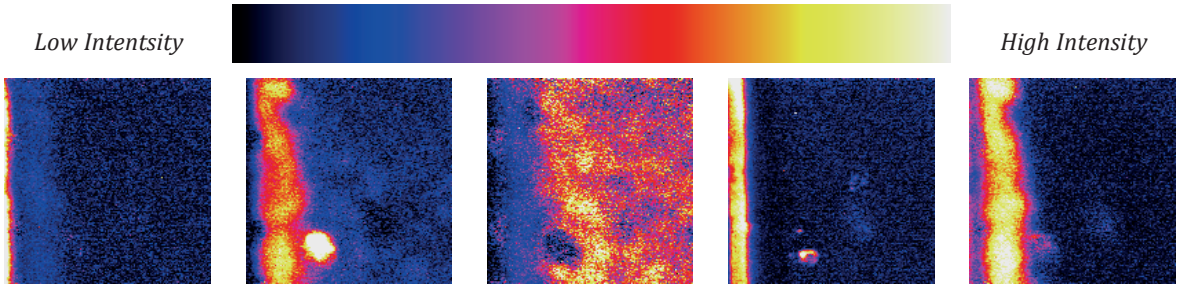


Figure 11: Results of the grey value intensity distributions of the individual materials of the preliminary sample of printed coated paper without filler



PTFE-Film (716 cm^{-1} to 750 cm^{-1}) | *Mineral Oil* (93 cm^{-1} to 98 cm^{-1}) | *Raw Paper* (1101 cm^{-1} to 1130 cm^{-1}) | *Pigment* (1517 cm^{-1} to 1552 cm^{-1}) | *Paper Coating* (270 cm^{-1} to 310 cm^{-1})

Figure 8: Filtered images of a Raman image scan of a printed and coated paper without filler

There was some overlap between the pigment and the coating layer, which could be due the pigment penetrating slightly into the coating surface or due to the unevenness of the coating surface topography. It is also possible that the ink contained some $CaCO_3$ as filler. The mineral oil seems to be mostly contained within the coating layer. For this sample, the cyan pigment and mineral oil penetrated to approximately 65 µm in one area, due to a probable flaw in the coating layer (Figures 8, 9, 10). Otherwise the migration of the mineral oil would have stopped at 40 µm.

All of the filtered images from all paper combinations were processed using this approach.

3. Results and discussion

3.1 Results of the IR microscopy

Figure 12 shows a typical result of a correlation analysis between the IR reference spectra from the IR-spectrometry measurements and the line scan from the IR microscope, shown here for the same example of the printed coated paper.

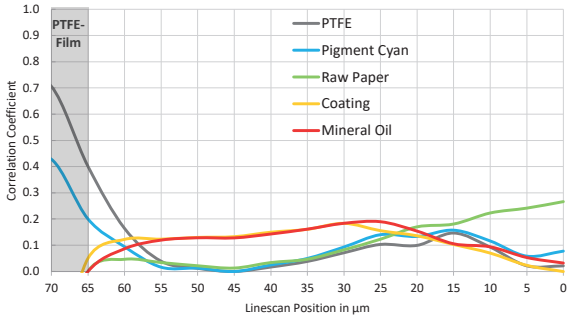


Figure 12: Result of the correlation analysis for the sample of printed coated paper without filler

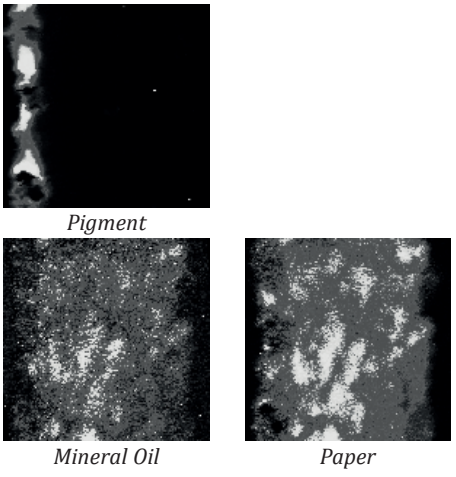
Also here the mineral oil seemed to be contained almost entirely within the paper coating – approximately also 40 µm penetration depth, with reduced further penetration into the fibre network. This is a possibility, based on the findings of other studies (Rousu, Gane and Eklund, 2003; Rousu, et al., 2000a; Ström, Gustafsson and Sjölin, 2000).

With IR microscope, only relatively low reflectance intensities from the line scan spectra could be detected. Despite the use of thin microtome samples and special reflective slides, too much of the IR radiation was absorbed inside the sample, resulting in very low correlation coefficients for the ink and paper components. Also, the 5 µm aperture of the instrument did not provide enough resolution to accurately determine the migration depth. For these reasons, IR microscopy was deemed to be unsuitable for this type of study.

3.2 Results of the Raman microscopy

The results from the Raman microscope showed no such problems. A typical result is shown in Figure 13 for an unsized, uncoated paper without filler. For the uncoated papers, without fillers, the mineral oil was detected throughout the complete fibre network. These also showed a high concentration of pigments on or near the paper surface, with some penetration into the fibre network to an approximate depth of 30 µm. High levels of the mineral oil were detected throughout the entire depth of the paper, therefore showing that the mineral oil from the ink had migrated through the paper.

For the uncoated papers that also contained fillers, a high concentration of mineral oil was detected in the region near to the paper surface, which shows that the calcium carbonate particles acted as a brake to hinder the oil migration. A typical greyscale filter images for



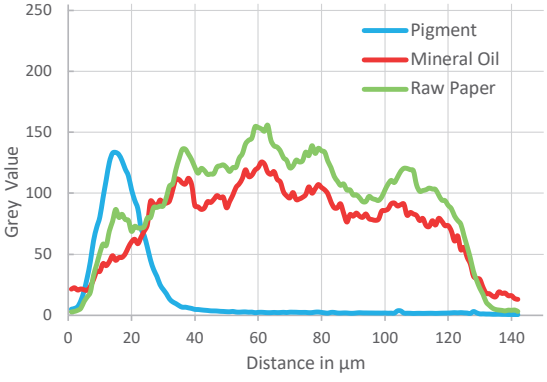


Figure 13: Greyscale filter images and plots from the printed cross-section of an unsized, uncoated paper without filler

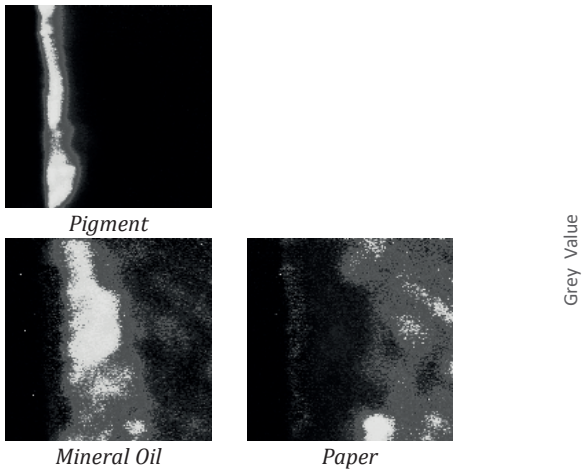


Figure 14: Greyscale filter images and plots from the printed cross-section of an uncoated paper with filler

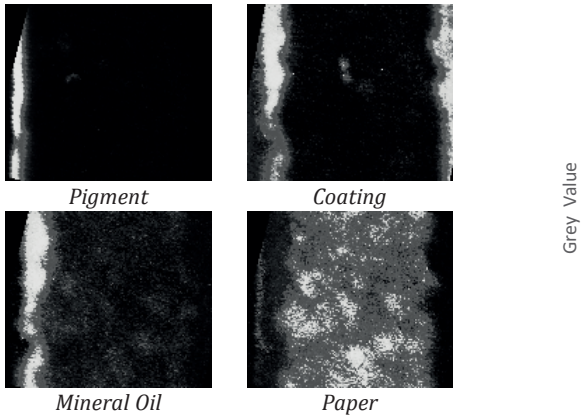


Figure 15: Greyscale filter images and plots from the printed cross-section of a coated paper

the pigment, mineral oil and raw paper and subsequent average intensity plot for a printed and uncoated paper with filler are shown in Figure 14.

For the coated papers, the bulk of the mineral oil was detected within the paper coating, with comparatively little oil detected within the paper fibre network (Figure 15).

4. Conclusions

Methods were developed using IR microscopy and Raman microscopy to characterise the distribution of offset printing ink components in paper cross-sections. IR microscopy proved to be unsuitable for this type of study because the intensity of the reflectance spectra was ultimately too low to quantify the amount of mineral oil and other materials present within the paper samples. Also, due to the limited spatial resolution of the instrument, it was not possible to accurately quantify the depth of the migration. Raman microscopy proved to be more suited to this application. With carefully selected filters based on characteristic peaks in the Raman spectra, it was possible to differentiate the different components and therefore to analyse the penetration depth of mineral oil in the base paper. The initial results showed that in the papers without calcium carbonate fillers and/or coatings, the high concentrations of mineral oil from the printing ink were found throughout the entire paper structure and therefore could potentially reach a product inside of the packaging. Migration was greatly reduced with the inclusion of fillers. The amount of mineral oil detected in the fibre network of the coated papers was relatively low, with high concentrations of the mineral oil detected within the layer of the paper coating. These results were in-line with the findings of other studies (Rousu, Gane and Eklund, 2003; Rousu, et al., 2000a; Ström, Gustafsson and Sjölin, 2000). However, since mineral oil was still detected within the paper fibre network of the coated papers albeit in lower concentrations it is highly feasible that over time the mineral oil from a printing ink could migrate through a coated paper based packaging and reach the content inside.

Acknowledgements

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