Application of Confocal Laser Scanning Microscopy
To the Study of Backtrap Mottle

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Abstract

Backtrap mottle is a common printing defect that is difficult to correct. A good understanding of the mechanisms that leads to backtrap mottle is still lacking in the literature. A confocal laser scanning microscopy (CLSM) is used to evaluate samples that had different tendencies towards backtrap mottle. The coating structure is observed by staining the coating with a fluorescence dye. The final location of ink vehicle was observed by staining the resin with a fluorescent dye. Final prints that had backtrap mottle could be directly observed from the fluorescence of the magenta ink pigment. The distribution of magenta ink tends to be obscure on backtrap prints. Samples with uneven coated layer distributions correlated to the occurrence of backtrap mottle even though the coat weight is uniform. In addition, the contrast of fluorescence intensity was strong at portions of the thin coated layer: pore volume may decrease at region with thin coated layer. Samples with uneven ink resin distribution, tend to have backtrap mottle. Moreover, the resin hardly penetrates in regions with thin coated layers.

Introduction

Backtrap mottle is a printing defect that occurs in early down inks in a multiple nip printing. The ink density is not uniform within the sample. The printer cannot always adjust the press parameters to overcome this problem. A distinguishing characteristic of backtrap mottle is that a second or subsequent printing station is required for it to appear. It is well understood now that a non-uniform setting of the ink on the paper correlates well with this printing defect. However, it is not clear what factors in the coating layer that actually causes this non-uniform ink setting.

Some analytical techniques have been used to evaluate coated papers. Tomimasu and Arai et al. quantified the binder and pigment concentration at the top surface of coated paper by X-ray photoelectron spectroscopy (XPS) [1,2]. The relationship between print mottle and surface structure of coated paper was discussed. However, it was difficult to obtain the distribution of binder and pigments using XPS due to the limitation of resolution. Ultraviolet radiation absorption spectroscopy can determine the amount of latex in the coating, but this method is not very surface sensitive [3]. Micro-ATR (Attenuated total reflectance) /IR (infrared spectroscopy analysis) has been used for
mapping of binder on coated paper, but a good correlation with backtrap mottle was not established [4]. Whalen-Shaw et al. used electron probe microanalysis (EPMA) to characterize the backtrap mottle [5]. However, wide area can not be observed by this technique. Confocal Raman microscopy has recently been shown to produce excellent compositional maps of coating layers on paper [6-8]; the latex distribution relative to calcium carbonate is obtained by ratios of spectra signals with resolution of 2 μm in the planar dimensions. However, samples that had serious backtrap mottle had the same chemical uniformity as good sample. It is possible that the Raman technique also samples too deep into the structure to see differences or the non-uniformities that cause backtrap mottle are not chemical. Shen et al. measured the liquid absorbency of coated paper in sub millimeter scale by liquid-bridge probe. A good correlation has been obtained between absorption non-uniformity and the occurrence of print mottle [9]. This technique does not, however, give us a better understanding of what actually causes these non-uniformities.

Recent reports have shown that confocal laser scanning microscopy (CLSM) can be used to characterize coating layers and the penetration of ink into coatings and paper [10-12]. In these reports, ink was stained with a fluorescent dye and imaged with CLSM. To image the coating structure, again a fluorescent dye is used to stain the coating. While the laser beam is scanning on the specimen, the emitted fluorescent light is detected by a photodetector. The pinhole in front of the photodetector reduces out-of-focus information, and three dimensional information is obtained as a succession of optical depth images is scanned.

Here we use CLSM with fluorescent dyes to look at samples that have backtrap mottle. The distribution of coating binder was observed from the fluorescence stained with dye by CLSM: the coating layer thickness can be characterized at different locations in the sample with this step. The location of ink resin was observed as the distribution of resin stained with fluorescent dye by CLSM.

**Experimental**

**Coated papers**

The same samples as described and used by Xiang et al. [13] are used here. Sample A, B, C and D were produced by the pilot coater of S.D. Warren Technology Center. The change in the 6-color print would only be related to the designed difference in drying and not confounded by other factors: the samples have the same base paper, same coating and same coating weight. Sample A and B had good printing quality while sample C and D had backtrap mottle. The base stock was a 150 g/m² ground-wood free cover stock with typical northern mill pulp furnish, coated with 22 g/m² coat weight per side, dried with a designed combination infrared, early air foil and late air foil drying to a moisture of 6.0%. Last, the paper was on-line finished with soft-nip calendaring. The coating generically consisted of: 50 parts #1 high brightness clay, 10 parts calcined clay, 40 parts ultra fine clay, 14 parts SB latex and 2 parts starch with typical types of appropriate additives. The samples were printed with a commercial press using typical inks and
conditions. Parts printed by cyan and magenta inks on samples were directly observed using CLSM.

In addition, a coating was prepared from a calcium carbonate pigment (Carbopaque®, IMERYS), a kaolin pigment (KCS® Kaolin IMERYS) and a styrene-butadiene latex (620NA, Dow Chemical Co.). The coating color formulation was compounded from CaCO₃ 50%, kaolin 50%, and SB-latex 15%. Coatings were applied on the polyethylene (PE) film using a rod draw down coater. The coating weight was 65 g/m². Coated film was calendered at 0, 50, 100 kN/m (1 nip, 25°C). These samples were only used to estimate the relationship between fluorescence intensity and calendering.

**Pretreatment to observe coated paper**

Rhodamine B was used as a fluorescent dye for staining the coated paper due to its successful application in a previous study [12]. Rhodamine B has a strong fluorescence when excited by a wavelength of 514 nm. A 0.03 wt% of Rhodamine B was dissolved in ethanol. The coated papers were soaked for 3 minutes in this solution, rinsed with pure ethanol for 5 minutes, and dried.

**Pretreatment to observe the ink resin**

A 0.03wt% of Rhodamine B was added to an alkyd resin modified with linseed oil and was stirred. The resin was held to stain completely for 24 hours. The resin (50μm) was applied onto the coated and was wiped in 30 seconds after application. The samples were observed by CLSM after holding for 24 hours.

**Observation by CLSM**

Images were obtained using a CLSM (Leica TCS-SP2) equipped with x40 (HC PL APO, NA 1.25) or x100 oil-immersion objective lens (HCX PL APO, NA 1.40). Immersion oil (Refractive Index:1.518) was supplied by Leica. Excitation wavelength of 514 nm from an Ar laser (Power: 50 mW) was primarily used for the observation of the coated papers by CLSM. A diachronic beam splitter (DD458/514), which separates the fluorescent wavelength from the excitation wavelength, was used. The pinhole diameter was set to 50 µm. The detected wavelengths ranged from 535 nm to 635 nm. The shoulders of this detection window were assumed to be sufficiently away from the excitation wavelength to limit any crossover. Digital zooms of x1, x2 and x4 were used. Confocal images were obtained using both XYZ and XZY scan modes. In the case of XYZ mode, a sequence of XY (plane of the paper) frames was obtained at 0.1μm intervals in the z-(thickness) direction and was stacked as a maximum intensity projection (Z-stack image). In the XZY mode, XZ (paper cross-section) images were obtained through rapid depth scanning. Each image had 1024x1024 pixels.

**Other Measurements**

The cross sections of samples were observed as the secondary electron (SE) images by a scanning electron microscope (SEM: Hitachi SEMEDX). The electron beam was supplied at an acceleration voltage of 15kV and working distance was 16.5 mm.

The elements on the surface of samples were investigated using X-ray photoelectron spectroscopy (XPS: Perkin Elmer PHI-5600 ci ). The measuring conditions were as
follows; MgKα(1253.6eV) X-ray source: 15kV – 200 watts, vacuum in chamber: 10⁻⁶Pa, analysis area 800μmφ, take-off angle of the photoelectron: 45 degree. Narrow scan modes for atomic concentration were obtained with 58.7eV of pass energy and 0.5eV of step width.

The fluorescence spectra were obtained by a fluorescence spectrophotometer (Hitachi F-4500). Excitation wavelength of 514nm was used and the detected wavelengths ranged from 535nm to 700nm.

Results and Discussion

Observation of prints
Figure 1 shows the Z-stack images of offset prints by cyan and magenta inks on Samples A-D by CLSM. Bright regions indicate magenta ink pigment because magenta pigments have a strong fluorescence by CLSM. The distribution of magenta ink on samples A and B is clear but the distribution on samples C and D was unclear. These samples were printed in order of cyan and magenta. It was expected that magenta ink was not transferred due to the back trap of cyan ink as regards Sample C and D. However, the distribution of magenta ink could not be observed from optical images on the same magnification as CLSM because it was difficult to discriminate between cyan and magenta at the part of overlap. Samples with back trap mottle strongly correlate to sharp distribution of magenta ink pigments. This result was not expected because the mottle is seen with the eye in the cyan regions.
Table 1 shows atomic concentrations on coated papers by XPS. Oxygen concentration of Sample A and B was slightly higher than that of Sample C and D. However, the atomic concentrations of the others were not indicated the difference between good and bad quality. As a result, the surface composition of these coated papers was not concerned with the backtrap mottle because the change of atomic concentrations was not confirmed among samples. This lack of correlation of chemical composition with backtrap mottle agrees with a number of other results [8,14,15].

Structure of coated paper

Figure 1. Z-stack images of offset prints by CLSM
upper: good quality, lower: bad quality
λEX: 514nm  Detected Range : 535nm-635nm
Oil Lens X40, Digital Zoom X 1
Table 1  Atomic concentrations on coated papers by XPS

<table>
<thead>
<tr>
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<tbody>
<tr>
<td>C</td>
<td>50.7</td>
<td>52.7</td>
<td>53.9</td>
<td>51.2</td>
</tr>
<tr>
<td>O</td>
<td>34.9</td>
<td>34.8</td>
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<td>Si</td>
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<tr>
<td>Ca</td>
<td>0.7</td>
<td>0.9</td>
<td>0.7</td>
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</tr>
</tbody>
</table>

(Atom%)

Figure 2 shows SEM images of cross section of coated papers. The distribution of coating pigments can be observed by SEM. The coating structure of bad quality paper due to the backtrap mottle was remarkably different from that of good quality paper. Sample A and B formed flat coating layers, but sample C and D had uneven coating layers even though these samples had the same coat weight and were on the same base paper.

Figure 3 shows the cross section images (XZ images) of coated papers by the XZY method of CLSM. The important point is that this method does not require any sample preparation such as resin impregnation or cutting. In addition, the distribution and position of latex in the coating layer can be characterized because the coating binder was stained with Rhodamine B. Although same position could not observed by both SEM and CLSM, the distribution of binder was similar to that of pigments.
Figure 3. XZ Images of Coated Papers Stained with Rhodamine B
upper: good quality, lower: bad quality
λex: 514nm, Detected Range: 535nm-635nm
Oil Lens X100, Digital Zoom X 2

Figure 4 shows maximum intensity projections (Z-stack images) by XYZ mode of CLSM. Although sample A had some uneven contrast, the sample still appears uniform. The Z-stack image of sample B had good uniform fluorescence intensity. However, the extreme contrasts were shown on sample C and D. The contrast variation must come from the non-uniform coat weight distributions.
In a previous study, the fluorescence intensity of coated paper having high latex content was higher than that having low latex content [12]. Preliminary results obtained with a micro-IR ATR spectra did not show any differences in latex content between the samples.

Figure 5 shows the fluorescence spectra of coated layer stained with Rhodamine B. The coated layer was calendered by the different nip pressure. Fluorescence intensity increased with the increase of nip pressure. As coated layer was compressed by calender, the pore volume in coated layer would reduce. Although the binder in coated layer was stained with Rhodamine B selectively, a part of Rhodamine B would remain into small pores of coated layer even after samples had been washed to remove Rhodamine B in the ethanol. The washing time for five minutes might be too short for removing the fluorescent dye completely.
At least, it was expected that the contrast of fluorescence intensity was strong in regions of thin coated layers, for pore volume decreased at thin coated layer (lower in Fig.4).

Figure 6 shows Z-stack images of alkyd resin stained with Rhodamine B in each coated paper. Dark contrast indicates regions that the resin did not penetrate into the coating layers. Because the resin was completely cured by the oxidative polymerization after penetrated into coated papers, Rhodamine B was not dissolved into immersion oil at all during the observation with CLSM. Rhodamine B was expected to separate from ink vehicle during penetration into the coated layer. However, the distribution of alkyd resin as ink vehicle on the surface side of coated layer can be observed by this stain technique because fluorescence dye would be also penetrated into the paper some depth with the oils [11].
In the case of Sample A and B as good qualitative coated paper, the resin evenly penetrates into the coating layer. In the case of Sample C and D, however, the resin penetrates unevenly. Especially, the alkyd resin hardly penetrated regions of thin coated layer. The behavior of ink vehicle penetration in the wide area could be estimated by this stain technique. As a result, it was expected that ink vehicle penetrates unevenly into coated papers occurred backtrap mottle. Shen et al. also concluded that the occurrence of print mottle was related with absorption nonuniformity using a liquid-bridge probe [9]. Z-stack images of Sample C and D in Fig.7 showed that absorption nonuniformity of ink vehicle arose from uneven coated thickness. In addition, it was supposed that ink vehicle could not penetrate into thin coated layer which pore volume would decrease. This result again points to a physical non-uniformity that seems to cause backtrap mottle instead of a chemical non-uniformity.

It should be noted that the resin does not have pigments. There may be some possible steps, using pigments, to cause inks to have a more uniform absorption behavior. If the
resistance to absorption is moved to the ink layer, potentially a better printing result could be obtained, even if the paper uptakes pure oils in a non-uniform way.

Conclusions

The confocal laser scanning microscope was used to evaluate backtrap mottle. The backtrap mottle of prints could be directly observed as the fluorescence non-uniformity of magenta ink. The distribution of magenta pigments tends to be obscure on backtrap mottle prints.

The structure of coated papers was identified by CLSM with the stain technique. As a result, coated papers having uneven coated layer occurred the backtrap mottle. In addition, the contrast of fluorescence intensity was strong at portion of thin coated layer, for pore volume would decrease at thin coated layer.

The penetration of ink resin could be observed from the fluorescence of a resin stained with a fluorescent dye and imaged with CLSM. As a result, coated papers, which ink resin unevenly penetrated, correlate strongly with backtrap mottle. Furthermore, the resin hardly penetrated at portion of thin coated layer.

Acknowledgement

We thank the industrial sponsors of the University of Maine Paper Surface Science Program for their discussion and support of this project.

References


Application of Confocal Laser Scanning Microscope to the Study of Back Trap Mottle

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1) National Printing Bureau, JAPAN
2) Paper Surface Science Program (PSSP) University of Maine, USA
• **Back trap mottle (BTM)**

  Backtrap mottle is a printing defect that occurs in early down inks in a multiple nip printing.

• **Motivation**

  It is well understood now that a non-uniform setting of the ink on the paper correlates well with this printing defect. However, it is not clear what factors in the coating layer that actually causes this non-uniform ink setting.
Previous study

- XPS (X-ray Photoelectron Spectroscopy)
- ESEM (Environmental Scanning Electron Microscopy)
- Ultraviolet radiation absorption spectroscopy
- Micro-ATR (Attenuated total reflectance) /IR
- EPMA (Electron Probe Microanalysis)
- Confocal Raman microscopy

3D information on wide area can not be obtained by these analyses.
Objective of this study

To characterize the back trap mottle (BTM) on wide area by the CLSM
Basic Principle of a Confocal Microscope

Moving Sample Stage (Topside to Inside)

Collection of Focal Planes
How to obtain the depth profiles

(1) XYZ

Reconstruction
How to obtain the depth profiles

(1) XYZ

(2) XZY by galvo stage

No Preparation of Cross Sections
(Nondestructive Observation)
Experimental Samples

• **Good Printing Quality**: Sample A and B  
  **Bad Printing Quality**: Sample C and D (BTM Samples)

• Samples have the same base paper, same coating and same coating weight.  
  They were coated on different drying conditions.  
  Paper printed on a commercial press.  
  Expert ranking on prints.

• Parts printed by cyan and magenta inks on samples were directly observed using optical microscope and CLSM.
Applications of CLSM

1. Direct Observation of Prints
   (Comparison of CLSM and Optical Microscope)
   Observation of magenta ink

2. Structure of Coated Layer
   Stain coated layer with fluorescent dye

3. Distribution of Ink Resin into Coated Layer
   Use of resin stained with fluorescent dye
Optical Images of Offset Prints

Sample-A

Good Quality

Sample-B

Sample-C

Bad Quality

Sample-D
Optical Images of Offset Prints
Magenta Parts

**Sample-A**

**Sample-B**

**λ<sub>EX</sub>: 514nm**

Detected Range
535nm-635nm

Oil Lens X40
Digital Zoom X 1

**Sample-C**

**Sample-D**

**Non-uniformity of magenta ink is an excellent predictor of print quality. What causes non-uniformities though?**

**Z-stack Images of Offset Prints by CLSM**
Applications of CLSM

1. Direct Observation of Prints
   (Comparison of CLSM and Optical Microscope)
   Observation of magenta ink

2. Structure of Coated Layer
   Stain coated layer with fluorescent dye

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(Atom%) 

Samples seem to be chemically identical. Agrees with past work.
SEM images of cross section of coated papers

(Coat weights are identical for all)
Preparation of the Coated Paper Stained with Fluorescent Dye

[Procedure]

The coated papers were soaked for 3 minutes in the solution of Rhodamine B (0.03wt%) in ethanol.

The coated papers were rinsed with pure ethanol for 5 minutes.

Dry

Observation by CLSM
Sample-A (Paper) **Good Quality**

*λ_{ex}: 514\text{nm}*

**Detected Range**
535nm-635nm

**1 Step Size:** 2µm
**(25 Sections)**

*Oil-Immersion Lens X100*
*Digital Zoom X 2.0*

**XZY Animation of Coated Paper Stained with Rhodamine B**
Sample-D (Paper) Bad Quality

$\lambda_{\text{ex}}$: 514nm

Detected Range
535nm-635nm

1 Step Size: 2µm
(25 Sections)

Oil-Immersion Lens X100
Digital Zoom X 2.0

XZY Animation of Coated Paper Stained with Rhodamine B
XZ Images of Coated Papers Stained with Rhodamine B

Sample-A

Sample-B

\[ \lambda_{EX}: 514 \text{nm} \]

Detected Range
535nm-635nm

Sample-C

Sample-D

Oil Lens X100
Digital Zoom X 2

Good Quality

Bad Quality
Sample-A (Paper) **Good Quality**

\[ \lambda_{EX}: 514\text{nm} \]

Detected Range
535nm-635nm

Z-depth 15.8\(\mu\)m

Oil-Immersion Lens X40
Digital Zoom X 1

**XYZ Animation of Coated Paper Stained with Rhodamine B**
Sample-C (Paper) Bad Quality

λ_{ex}: 514nm

Detected Range
535nm-635nm

Z-depth 12.7µm

Oil-Immersion Lens X40
Digital Zoom X 1

XYZ Animation of Coated Paper Stained with Rhodamine B
Z-stack Images of Coated Papers Stained with Rhodamine B
Sample A

Sample B

co-added spectrum 1 at -1499, -5659 (Sample A)

co-added spectrum 2 at -1494, -5627 (Sample B)

2900 cm\(^{-1}\) (C-H Vibration)  
Area 500um X 500um

ATR Imaging of Coated paper
Sample C

co-added spectrum 4 at -1648, -5759

Sample D

co-added spectrum 3 at -925, -5591 (sampled)

2900cm⁻¹ (C-H Vibration)  |  Area 500umX500um

ATR Imaging of Coated paper
Fluorescence Spectra of coated layer stained with Rhodamine B
Applications of CLSM

1. Direct Observation of Prints
   (Comparison of CLSM and Optical Microscope)
   Observation of magenta ink

2. Structure of Coated Layer
   Stain coated layer with fluorescent dye

3. Distribution of Ink Resin into Coated Layer
   Use of resin stained with fluorescent dye
Alkyd Resin stained with Rhodamine B (0.03wt%)  

Coated Paper

About 50µl

30 Seconds

Wipe

Observation of resin by CLSM
Sample-A (Resin)  Good Quality

$\lambda_{\text{Ex}}$: 514nm

Detected Range
535nm-635nm

Z-depth 12.0µm

Oil-Immersion Lens X40
Digital Zoom X 1

XYZ Animation of Resin Stained with Rhodamine B
Sample-D (Resin)  Bad Quality

λ<sub>ex</sub>: 514nm

Detected Range
535nm-635nm

Z-depth  14.4μm

Oil-Immersion Lens X40
Digital Zoom X 1

XYZ Animation of Resin Stained with Rhodamine B
Good Quality

Sample-A

Sample-B

λ<sub>EX</sub>: 514nm
Detected Range 535nm-635nm

Bad Quality

Sample-C

Sample-D

Oil Lens X40
Digital Zoom X 1

Z-stack Images of Resin Stained with Rhodamine B
Conclusions

(1) The back trap mottle of prints could be directly observed as the fluorescence non-uniformity of magenta ink.

(2) The coated papers having uneven coated layer occurred the backtrap mottle. In addition, the contrast of fluorescence intensity was strong for portions of the thin coated layer, for pore volume would decrease at thin coated layer.

(3) The coated papers, which ink resin unevenly penetrated, correlate strongly with backtrap mottle. Furthermore, the resin hardly penetrated at portions of thin coated layer.
Acknowledgment

This research was supported by the industrial sponsors of Paper Surface Science Program at the University of Maine.
Sample-B (Paper) Good Quality

$\lambda_{\text{EX}}$: 514nm

Detected Range
535nm-635nm

Z-depth 12.5µm

Oil-Immersion Lens X40
Digital Zoom X 1

XYZ Animation of Coated Paper Stained with Rhodamine B
Sample-D (Paper) Bad Quality

\[\lambda_{ex}: 514\text{nm}\]

Detected Range
535nm-635nm

Z-depth 11.6\(\mu\text{m}\)

Oil-Immersion Lens X40
Digital Zoom X 1

XYZ Animation of Coated Paper Stained with Rhodamine B
Sample-B (Resin)  Good Quality

$\lambda_{\text{EX}}$: 514nm

Detected Range
535nm-635nm

Z-depth  8.4$\mu$m

Oil-Immersion Lens X40
Digital Zoom X 1

XYZ Animation of Resin Stained with Rhodamine B
Sample-C (Resin)  Bad Quality

$\lambda_{\text{EX}}$: 514nm

Detected Range  
535nm-635nm

Z-depth  15.4$\mu$m

Oil-Immersion Lens X40  
Digital Zoom X 1

XYZ Animation of Coated Paper Stained with Rhodamine B