A Method to Characterize Coating Uniformity Using Confocal Laser Scanning Microscope

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Abstract

A new method on the coating layer uniformity was investigated. A method to characterize coating uniformity using a staining technique and a confocal laser scanning microscope (CLSM) was proposed. Burn out tests are compared to the CLSM technique in terms of coating layer evenness. The coating mass distribution was calculated using image analysis software from both methods.

A reasonable correlation was found between the burn out test and CLSM observation when the fluorescent dye was not rinsed from the sample. The CLSM method made quantification of coating mass distribution more rapid than the burn out test.

Keywords : coating, confocal laser scanning microscope, uniformity

1. Introduction

Among qualities of coated printing paper, appearance and printability are important and it is significantly understand what factors influence on those product qualities. The quality of coated paper is dependent on various factors such as composition and solid content of coating color, physical properties of base paper and types of coating process, and many methods have been developed to evaluate product qualities.

Ultra-violet radiation absorption spectroscopy can detect the distribution of styrene-butadiene latex on coated surface¹⁾. Photoelectron spectroscopy (ESCA), Raman spectroscopy and infra-red spectroscopy can determine

chemical compositions of coated surface²⁻⁷⁾. Confocal Raman spectroscopy can analyze chemicals inside a coated layer. They, however, are effective in analyzing mainly areas close to its surface, and no correlation has been found with printed quality yet.

Scanning electron microscope (SEM) is one of methods most commonly used to study the surface and cross section of coated paper⁸⁻⁹⁾. It gives very useful information on the uniformity of coated layer thickness, which is highly correlated with printed quality. It is necessary to prepare a smooth cross section of a sample, and many pretreatment steps are needed such as impregnation of resin, cutting by a microtome, grinding and gold vapor deposition. It also requires numbers of observation to get a reliable statistical result.

X-ray micro tomography can observe an inner structure of coated paper non-destructively¹⁰⁾. X-ray is very

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powerful in analyzing the inner structure, but it is not yet available for inspecting binder distribution. Its resolution is rough and is not enough to evaluate the uniformity of coated layer.

Recently, several papers have been published on evaluating paper quality using confocal laser scanning microscope (CLSM).

CLSM can observe a cross section of paper non-destructively after simple sample preparation. As it is non-destructive, it was reported to be useful for analyzing paper surface as well¹¹⁾, and several papers have been published on observing coated paper surfaces¹²⁻¹⁴⁾. They reported that clear and detailed images of coated layer could be obtained from coated paper as well as from its printed products by pre-staining with fluorescent dyes. One report said that CLSM could give information on a thickness distribution of coated layer and also on a distribution of alkyd resin¹⁵⁾. It is however not certain if it can evaluate the uniformity of coated layer thickness.

We were interested in verifying whether or not CLSM could evaluate the uniformity of coated layer thickness. Our evaluation by CLSM was compared with the traditional burn out method. To improve our evaluation by

CLSM, a new sample preparation method was studied. Further, coated layers were cross-sectioned and observed by SEM, of which images were compared with our CLSM images to validate our method.

2. Experiment

2.1 Materials

(Base papers for coating)

Three kinds of base papers were used in this experiment. Their physical qualities were summarized in **Table 1**. Regarding smoothness, the average roughness from the center (Ra) was calculated by using a laser scanning method based on ISO 4287-1997.

(Coating materials and color formulations)

Coating color formulations used in the experiment were listed in **Table 2**. Coating pigments had following average particle diameters respectively : ground calcium carbonate (Hydrocarb 90 by Omya Co.) : 0.6 μm , fine clay (Japangloss by KaMin Co.) : 0.4 μm , No. 1 clay (Capim DG by Imerys Co.) : 1.2 μm . They were determined by laser diffraction method using Mastersizer S by MALVERN Co. Using those coating colors, pilot test coatings were carried out with a spray coater and a blade coater, of which details

Table 1 Base paper properties

	I	II	III
Kind	wood-free	wood-containing	wood-containing
Basis weight (g/m ²)	48	38	48
Bulk (cm ³ /g)	1.21	1.50	1.62
Roughness Ra (μm)	4.01	4.78	5.46
Ash (%)	10	9	5

Table 2 Coating formulation for coating tests

Component		Pilot coating					
		Spray			Blade		
		A	B	C	D	E	F
GCC	pph	100	60	60	100	60	60
Fine Clay	pph	—	40	—	—	40	—
No. 1 Clay	pph	—	—	40	—	—	40
Styrene-butadiene latex	pph	13	13	13	11	11	11
Starch	pph	—	—	—	4	4	4
Lubricant	pph	0.5	0.5	0.5	0.5	0.5	0.5
Optical brightening agent	pph	0.1	0.1	0.1	0.1	0.1	0.1
Solid contents	%	65-55	55-50	55-50	65	65	65

will be described in the next chapter. The solid contents of coating colors were 65% for the blade coating and several consistencies between 65 to 50% for the spray coating. As for binders, colors for spray coating contained only styrene-butadiene latex. In those for blade coating, starch that intended to improve water retention was added at the rate of 4 pph along with styrene-butadiene latex, of which dosage was reduced by 2 pph from that of spray coating.

2.2 Coating trials

(Pilot coating trials)

Three kinds of base papers were coated with spray coater (OptiSpray by Metso Paper Co.) and blade coater (Nippon Paper industries Co.). In spray coating trials, coating speeds were 1,500, 2,000 and 2,500 m/min. respectively. Its coating weight was designed to be 8 g/m² on each side, and both sides were coated at the same time. As coated weight is dependent on color solid content, coating speed, size of nozzle and discharge pressure of coating color in spray coating, several sizes of nozzles and discharge pressures were tested to get a desired coated weight. In blade coating, the coating speed was 1,500 m/min. and the designed coated weight was 8 g/m². Coating was carried out on one side first and then on the other side.

2.3 Evaluation

(Uniformity of coated layer)

We wanted to know whether our method of using CLSM on measuring the uniformity of coated layer was useful or not. To do that, coated layer had to be stained with fluorescent dyes beforehand. As in the literature¹⁵⁾, coated samples were dyed with Rhodamine B from Wako Pure Chemical Industries. As Rhodamine B is excited by light of which wave length is 514 nm and emits strong fluorescence, dispersing Rhodamine B in coated layer makes coated layer observable. The procedure was as follows.

A coated paper sample was immersed in ethanol solution that contained Rhodamine B at the concentration of 0.03% for 30 minutes. Then, two kinds of treatments followed. One was the method established by Ozaki et al.¹⁵⁾ The stained sample was immersed in ethanol and washed for 5 minutes. It was further rinsed with fresh ethanol for 1 minute, and dried at a room temperature. The other was a new method tested by us, in which a stained sample was dried at a room temperature without rinsing. Our CLSM was TCS-SP 2 by Leica Co. Dry lens of 5 magnifications and oil lens of 40 magnifications were used for observations. Impregnating oil of which reflex index was 1.518 made by Leica Co. was used for oil lens. A light source was an argon laser of which power was 50 mW, and Rhodamine B was excited by a laser beam of 514 nm. Dichronic beam splitter (DD 458/514) separated an excited wave from a fluorescence wave. Airy 1 was adjusted to

get a pin hole of which diameter was 73 nm. The range of wave length to be detected was adjusted to the range from 535 to 680 nm which was the range of excited wave from Rhodamine B. The magnification of digital zoom was one, and conformal images were obtained with a XYZ scan mode. XY planes, that were parallel to paper surface, were selected stepwise in Z direction (direction of thickness) at an interval of 0.5 μ m, and an image on every plane was scanned. Each image was digitized with 1024 $\times$ 1024 pixels and was analyzed with an image analyzing soft ware (Image Pro) to get a standard deviation of its brightness.

To validate our method of using CLSM on the evaluation of coated layer uniformity, samples were evaluated with the traditional burn out test developed by Engstrom¹⁶⁾. The burn out solution was prepared by dissolving ammonium chloride into 50% ethanol solution to get the concentration of 25 g/l. A sample was immersed in the solution, and dried at a room temperature. Then, it was kept in an oven of which temperature was 225°C for 30 minutes. The treatment colors base paper brownish and leaves coated pigment white. An area that is covered with more pigment appears whiter than an area of less coated weight. If coating is distributed unevenly on paper surface, it looks mottled. A burn out sample was scanned by a scanner and digitized at the resolution of 1,000 dpi. Its variation in a gray scale was calculated as a standard deviation. The calculation was done with an image analyzing soft ware (Image Pro).

3. Result and discussion

3.1 The evaluation of coated layer uniformity

(Evaluation by burn out test)

Firstly, coated layer uniformity was evaluated by the traditional burn out test. After burnt out, a sample was scanned to get a gray scale image, from which a standard deviation of intensity (σ) was calculated. Fig. 1 shows two of them as typical models. Their base paper was base paper I. Picture (A) was coated with blade and the coated weight was 12.2 g/m² Picture (B) was by spray coating

Fig. 1 Pictures of burn out samples

- (A) Blade coated, Color G, Coating weight 12.2 g/m²,
(B) Spray coated, Color D, Coating weight 7.8 g/m²

Table 3 Standard deviation of burn out image

	Coating Color		Coater type	Solid Contents of Coating Color (%)	Coating Speed (m/min)	Coating Weight (g/m ² /side)	Standard Deviation
1	A	GCC	Spray	65	1,500	8	25.8
2				60	1,500	8	14.6
3				55	1,500	8	12.8
4				65	2,000	8	22.9
5				65	2,500	8	12.5
6	D		Blade	65	1,500	6	17.8
7				65	1,500	8	12.2
8				65	1,500	10	10.3
9				65	1,500	12	6.6
10	B	GCC + Fine Clay	Spray	55	1,500	8	12.8
11				50	1,500	8	8.4
12				55	2,000	8	13.6
13	E		Blade	65	1,500	8	13.4
14	C	GCC + No.1 Clay	Spray	55	1,500	8	17.3
15				50	1,500	8	9.6
16				55	2,000	8	10.3
17	F		Blade	65	1,500	8	13.3

of which coated weight was 7.8 g/m². As clearly shown, picture (B) that looked rougher gave a larger standard deviation. The result corresponded to visual inspection. **Table 3** summarizes standard deviations of samples coated on base paper I with blade and spray. The samples from No. 6 to No. 9 suggested that the standard deviation declined while the coated weight increased. It meant that at a larger coated weight, the base paper surface was more completely covered with coated layer. The fact verified that burn out images were suitable for evaluating coated layer uniformity, and it was represented by a standard deviation of its image intensity. In the spray coating, coated layer uniformity was influenced by operating factors such as the solid content of color and the coating speed. By comparing samples 1, 2, 3 and 10 with sample 11, and also sample 14 with sample 15, a lower solid content of color tended to produce a smaller standard deviation. By comparing samples 1, 4 and 5 with each other, a higher coating speed tended to give a smaller standard deviation. These results corresponded to understandings in the past that coating coverage was improved with reasonably low solid content and at higher coating speed¹⁷⁾. The method was reliable for evaluating coated layer uniformity.

(Evaluation by CLSM)

Fig. 2 Correlation between burnout and CLSM (rinsed)

Then, coated layer uniformity was evaluated by CLSM. Image pictures were obtained by the procedure described in Chapter 2. 3, from which their standard deviations were calculated. **Fig. 2** depicts correlation between standard deviations by the burn out method and those calculated from CLSM images taken from samples that were stained with Rhodamine B and then rinsed. Though the rinsing procedure was quite traditional, the correlation coefficient was

Fig. 3 Correlation between burnout and CLSM (not-rinsed)

very small and there seemed to be little correlation as shown in Fig. 2. Ozaki et al. reported that Rhodamine B combined with latex in coated layer and remained there after rinsed¹²⁾. Therefore, the distribution of Rhodamine B was more likely to represent the distribution of binder, and would be affected with latex that migrated along with water during drying and latex that impregnated into base paper. On the other hand, the burn out treatment was more related to the distribution of intensity caused by pigment.

So, we tried a method of staining with Rhodamine B without successive rinsing with ethanol. Standard deviations from the burn out tests and those from CLSM images without ethanol rinsing were plotted in Fig. 3. Though the correlation was not good enough, fair improvement was observed, compared with Fig. 2. In this method, it was reasoned that Rhodamine B still stayed in micro pores of pigment and its distribution was almost the same to that of pigment. So, the evaluation without ethanol rinsing is better for determining coated layer uniformity. Photos in Fig. 4 also support our reasoning. A sample in the left hand side had more uniform coated layer than a sample in the right hand side. When burn out images were

Fig. 4 Comparison between burn out and CLSM images
Left pictures ; Spray coated, Color E, Solid contents 50%, Coating weight 7.6 g/m²
Right pictures ; Spray coated, Color E, Solid contents 55%, Coating weight 8.1 g/m²
Top ; Burn out, Middle ; CLSM, Bottom ; CLSM not rinsed.

compared with each other, the former (top left) had a smaller standard deviation than the latter (top right). The result from CLSMs was contradictory. When CLSM images after rinsing were compared (middle left and middle

Fig. 5 SEM (top) and CLSM (bottom) images of cross section of coated papers

Table 4 Average thickness and standard deviation (σ) of the coated layer

Basepaper	Color	Coater	CLSM		SEM	
			Average Thickness (μm)	σ	Average Thickness (μm)	σ
II	A	Spray	5.8	2.1	8.8	3.7
	D	Blade	8.7	2.2	8.6	4.2
III	A	Spray	9.4	2.9	9.8	3.0
	D	Blade	10.1	3.1	9.4	3.7

right), one in the right hand side had a larger standard deviation. Without rinsing (bottom left and bottom right), their trend was similar to that of the burn out tests.

3.2 The evaluation of coated layer thickness

To further validate our method of evaluating coated layer uniformity, cross sections of papers were observed to measure thickness of coated layer. The cross sections of coated samples were observed by scanning electron microscope (SEM) and by CLSM. They are shown in Fig. 5 and these samples were coated by blade and spray coaters using the base paper III. For SEM, cross section samples were prepared by cutting out with a microtome. For CLSM, coated samples were stained by Rhodamine B without rinsing. With a stained sample, XY planes, that were parallel to paper surface, were selected stepwise in Z direction (direction of thickness) at an interval of $0.5 \mu\text{m}$, and an image on every plane was scanned and stored. The thickness of coated layer and its uniformity, expressed as standard deviation, were calculated with software (Image-Pro PLUS) in the both cases. In the SEM observation, thickness was measured at 50 points in the span of $135 \mu\text{m}$ along the direction of X, and was repeated three times. In the CLSM observation, thickness was measured at 50 points in the span of $345 \mu\text{m}$ along the direction of X, and was repeated ten times. Table 4 summarizes the average thicknesses and standard deviations of coated layers. The samples were coated on base paper I and II by blade and spray coaters respectively, and measured by SEM and CLSM. Regarding average thickness, those by SEM were almost the same to those by CLSM with one exception that was a sample coated on base paper II with spray coater. So, it is concluded that our method of staining and observing by CLSM can determine the thickness of coated layer. It is simple and does not need to prepare a cross section sample by microtome. Regarding the standard deviation of coated layer thickness, the result was contradictory by the observation methods. When a type of coating was concerned, those coated by spray gave smaller standard deviations than those by blade, regardless of the methods

of observation. As is shown in Fig. 5, the coated layer by spray coating was formed more uniformly on the contour of the surface of base paper than one by blade coating. With a different base paper, on the other hand, the relationship between CLSM and SEM was contradictory. Coated papers of base paper II gave smaller standard deviation values than those of base paper III under observation by CLSM. Under SEM observation, the relationship between them was reversed. As base paper II had a smaller Ra value, which meant smoother surface, than base paper III, the former would theoretically produce a coated layer of more uniform thickness. Therefore, we believe that the measurement by CLSM was more reliable. In the CLSM measurement, thickness was measured at more points than in the SEM measurement in which samples were laboriously prepared. The SEM observation might be affected by points in irregular surface areas.

4. Conclusion

We investigated the method of determining the uniformity of coated layer thickness by using CLSM. Our modification in staining samples that skipped rinsing gave a fair correlation with data by the traditional burn out method. Moreover, our new method could get data in a shorter time than the burn out method. It also measured the thickness of coated layer by observing its cross section and gave almost the same result as SEM observation. Our method could do it in a shorter time with more accuracy.

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