Application of ATR-IR measurements to predict the deinking efficiency of UV-cured inks

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ABSTRACT: In recent years, ultraviolet (UV)-curable ink has been developed and widely used in various printing applications. However, using UV-printed products (UV prints) in recovered paper recycling causes end-product dirt specks and quality issues.

A new method was developed that can distinguish UV prints from other prints by means of attenuated total reflectance infrared (ATR-IR) spectroscopy. Application of this method could allow more efficient use of UV prints as raw materials for paper recycling.

First, a mill trial was performed using UV prints alone as raw materials in a deinked pulp (DIP) process. Second, test prints were made with four types of UV inks: a conventional UV ink and three different highly-sensitive UV inks. Each print sample had four levels of four-color ink coverage patterns (100%, 75%, 50%, and 25%). Next, deinkability of all prints was evaluated by laboratory experiments. Finally, each print was measured using the ATR-IR method, and the relationship between the IR spectra and deinkability was investigated.

Mill trial results showed that UV prints caused more than 20 times as many dirt specks as those printed with conventional oil-based ink. There were variations in recycling performance among UV prints taken from bales used for the mill trial. Lab tests clearly revealed that not all UV-printed products lead to dirt specks.

In order to clarify the factors that affected deinkability of UV prints, the print samples were investigated by lab experiments. Key findings from lab experiments include:

- The number of dirt specks larger than 250 μm in diameter increased as the ink coverage increased.
- Higher ink coverage area showed stronger intensity of ATR-IR spectral bands associated with inks. These results indicate that deinkability of UV prints could be predicted by analysis of ATR-IR spectra.
- Finally, the method was applied for assessment of recovered paper from commercial printing presses. It was confirmed that this method made it possible to distinguish easily deinkable UV prints from other UV prints.

Based on these findings, we concluded that the ATR-IR method is applicable for inspection of incoming recovered paper.

Application: The developed method can determine the deinkability level of UV-printed products simply by analyzing the surface of those prints. Thus, it can be useful for incoming quality control in mills.

Due to the shrinkage of paper markets in Japan and exports of recovered paper to China and/or other countries in Asia, the amount of recovered paper as a raw material for secondary fiber has decreased. In addition, the development of new printing methods has given rise to different kinds of printed products in the market today. One that stands out as a trend is ultraviolet (UV) printing, which uses UV curable ink. Ultraviolet printing offers advantages such as reduction in volatile organic compounds (VOCs) and short job delivery times. However, acrylic resin, the major component of UV ink, forms a rigid coating layer on the paper surface after UV curing. This highly rigid layer is difficult to break down [1-4] and leads to unacceptable speck contamination in deinked pulp (DIP). For this reason, UV printed products (UV prints) have been regarded as raw materials to be avoided in the recycling process.

In our previous papers [5,6], we discussed a method that can distinguish UV prints from other printed products (such as products printed with oil-based ink) by means of attenuated total reflection infrared (ATR-IR) spectroscopy. We named this method the "ATR-IR method" [7-10]. When the method was applied in mills for recycled stock quality control, prints that gave poor-deinkability, such as UV prints, were sorted out more efficiently. Improved sorting reduced the incidence of dirt specks in DIP production.

The development of highly-sensitive UV (HS-UV) prints in recent years has made the pulp from these prints more easily deinkable [11]. The ease of deinking UV prints continues to be the subject of debate; for example, see the proc-

ceding of the INGEDE Symposium [12]. Thus, the development of UV prints is progressing. In order to maintain the productivity and quality of DIP, a deeper understanding of the deinkability of UV prints is required.

First, a mill test was performed as part of this study to establish the deinkability of conventional UV (C-UV) prints and HS-UV prints as raw materials. Second, to investigate the factors affecting the deinkability of UV prints, test prints were made with several types of UV-curable inks at various coverage ratios, and these test prints were evaluated for deinkability.

Finally, the application of the ATR-IR method for distinguishing easily deinked prints from difficult ones was examined. Up to this point, the method had been used only for distinguishing UV prints from those of other printing processes (such as prints made with oil-based inks or polystyrene coated prints). Laboratory deinkability tests revealed that not all UV prints were difficult to deink. In fact, some UV prints were as easy to deink as prints with oil-based ink. For more efficient use of UV prints as raw materials, it is necessary to sort UV prints by their level of deinkability. We explored the possibility of distinguishing easily deinked UV prints (those resulting in fewer dirt specks) from more difficult to deink UV prints (those resulting in more dirt specks) by evaluating the relationship between IR spectra and deinkability of several kinds of UV prints.

EXPERIMENTAL

Mill trial for comparing quality of UV and conventional prints as raw materials

A mill trial was conducted to compare the quality of UV prints and conventional prints (printed with oil-based ink) as raw materials. Three types of bales were collected from commercial printing presses for this mill trial:

- Conventional UV-curable ink (C-UV) prints only
- Highly-sensitive UV-curable ink (HS-UV) prints only
- Oil-based ink (OB) prints only

Table I shows the sources of the bales. Bales of C-UV prints were procured from printer B, those of HS-UV prints from printers A and B, and those with OB from printer C. The recovered paper grade of these prints was a mixture of sorted office waste (SOW) and colored ledger. All were evaluated in a DIP mill at Nippon Paper Industries. The comparison of deinking quality for each print as a raw material was based on the frequency of dirt specks in handsheets made from each deinked pulp according to TAPPI Standard Test Method T 205 sp-02 "Forming handsheets for physical tests of pulp." Specks were measured by image analysis (Easy Scan, Nippon Paper Unitec Co. Ltd.; Shizuoka, Japan), with only those larger than 250 µm in diameter being counted.

Test	Ink Type	Paper	Printer
1	C-UV	SOW/Colored ledger	B
2	HS-UV	SOW/Colored ledger	A and B
Blank	OB	SOW/Colored ledger	C

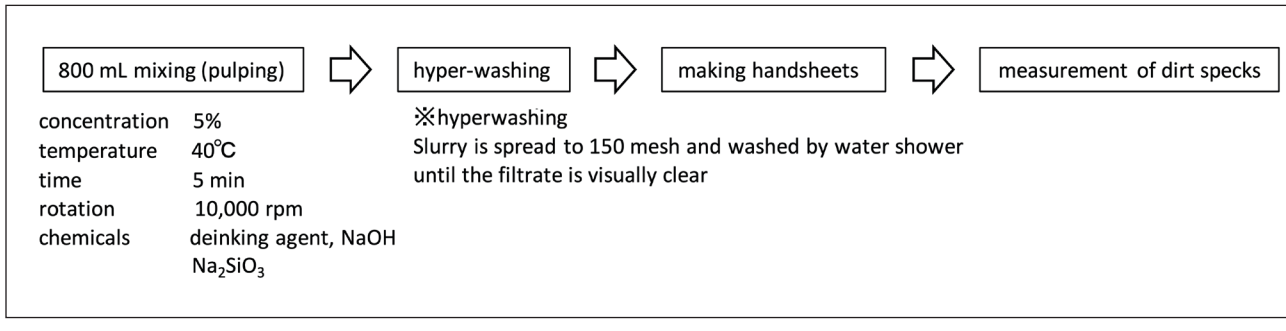
UV = ultraviolet; C-UV = conventional UV-curable ink; HS-UV = highly-sensitive UV-curable ink; OB = oil-based ink; SOW = sorted office waste.

I. Raw materials and printer sources for bales used in tests at Nippon Industries deinked pulp (DIP) mill.

Procedure for laboratory experiments

The HS-UV printing samples were taken from bales collected from printers A and B that were used for the mill trial. Then, those samples were evaluated by a laboratory experiment to investigate whether there was a difference in deinkability between products from each of the two printing presses.

The measurement procedure is shown in **Fig. 1**. First, print samples from printers A and B, respectively, were cut into 2 cm × 2 cm pieces by a shredder machine. Then, they were mixed with woodfree copy paper at a ratio of 1:9 on a weight basis. Next, the mixtures were disintegrated in a lab mixer at 5% consistency with deinking chemicals at 40°C for 5 min. A deinking agent (DP150, Nicca Chemical Co. Ltd.; Fukui, Japan), sodium hydroxide (NaOH), and sodium metasilicate (Na_2SiO_3) were used as the chemical package. Dosages of these chemicals were 0.2%, 0.7%, and 0.7%, respectively, based on dry weight of the pulp. At the completion of the pulping process, the slurry was hyper-



1. Schematic of the measurement procedure used in the deinkability test method (NaOH = sodium hydroxide; Na_2SiO_3 = sodium metasillicate).

Ink Maker	X		Y	Z
Ink Type	C-UV	HS-UV	HS-UV	HS-UV
Ink Coverage Ratio	100%, 75%, 50%, 25%	100%, 75%, 50%, 25%	100%	100%
Paper Grade	WFC			

UV = ultraviolet; C-UV = conventional UV-curable ink; HS-UV = highly-sensitive UV-curable ink; WFC = woodfree coated.

II. Print samples used for laboratory deinkability test and attenuated total reflectance infrared (ATR-IR) spectroscopy analyses.

washed through 150 mesh wire with openings of 100 µm. Washing continued until the filtrate was visibly clear. The number of dirt specks of 250 µm or larger in handsheets made from the pulps was measured by image analysis.

As outlined in **Table II**, test prints were made with four types of UV inks: a C-UV ink and three kinds of HS-UV inks. The C-UV ink was obtained from ink maker "X" in Japan, and HS-UV inks were obtained from ink maker X, as well as ink makers "Y" and "Z." Each test print had four levels of ink coverage patterns (100%, 75%, 50%, and 25%). A picture of the forms used for printing is shown in **Fig. 2**. Woodfree coated (WFC) paper sheets were used as a base paper for all prints. The region of the four-color part of the form was printed to an optical density target in the range of 1.90–1.95 using a Macbeth transmission reflection densitometer (GretagMacbeth RD-19, Videojet X-Rite K.K.; Grand Rapids, MI, USA).

The impacts of UV ink from the three ink makers and the ink coverage pattern on deinkability were investigated on the test prints. As shown in Table II, 10 kinds of print samples were tested: C-UV and HS-UV from ink maker X (ink coverage ratio 100%, 75%, 50%, 25%; 8 total prints); and HS-UV from ink makers Y and Z (ink coverage ratio 100%, 2 total prints). The evaluation of deinkiability was judged from the numbers of dirt specks in handsheets made from hyperwashed samples following the procedure shown in Fig. 1.

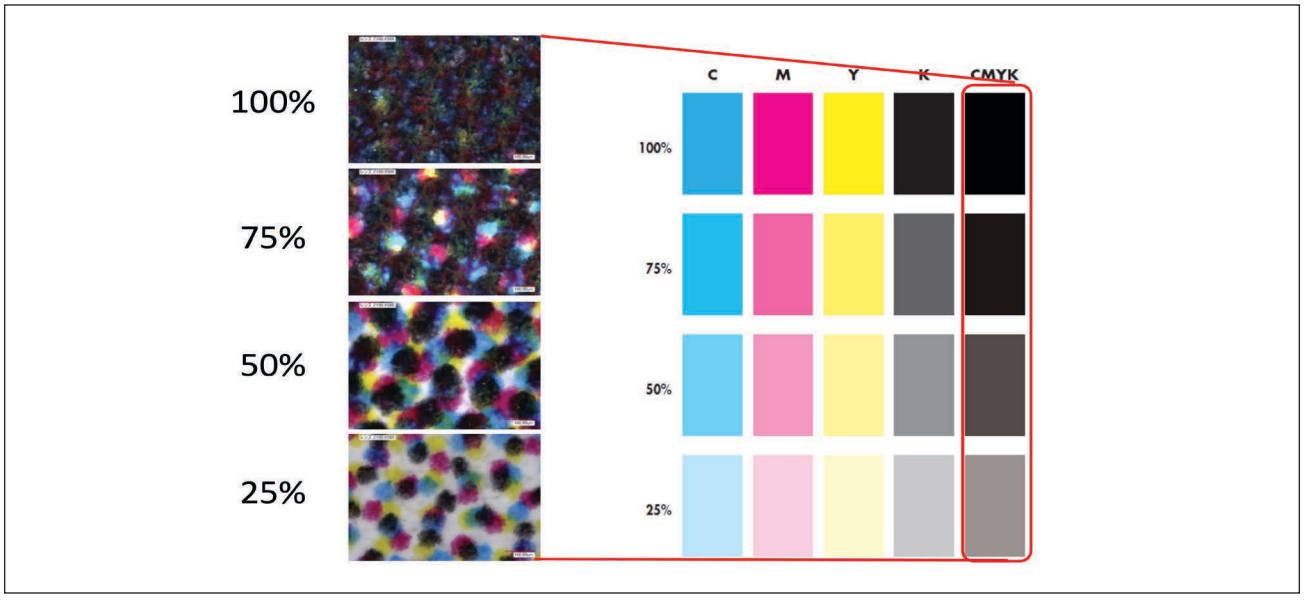
Application of the ATR-IR method

To obtain the IR spectrum, the surface of each sample shown in Table II was analyzed using the ATR-IR apparatus (Target ID, S.T. Japan; Tokyo) with ATR resolution of 4 cm^{-1} and zinc selenide (ZnSE) beamsplitter; in total, 16 samples were measured. By correlating IR peak patterns and results from deinkability experiments, IR spectra were classified into three patterns of deinkability: poor, good, and very good. Then, those spectra data were added to the database of the ATR-IR apparatus in order to update the ATR-IR method. Finally, printing samples taken from bales collected from printers A and B and were tested using the ATR-IR method to verify the usefulness of this method.

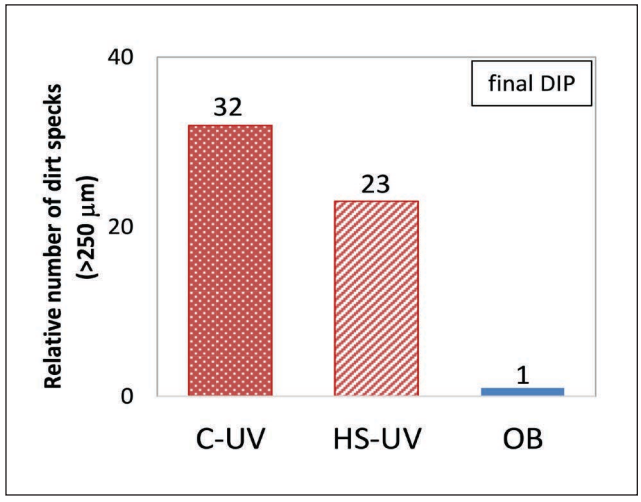
RESULTS AND DISCUSSION

Mill trial for investigating the quality of C-UV and HS-UV prints as raw materials

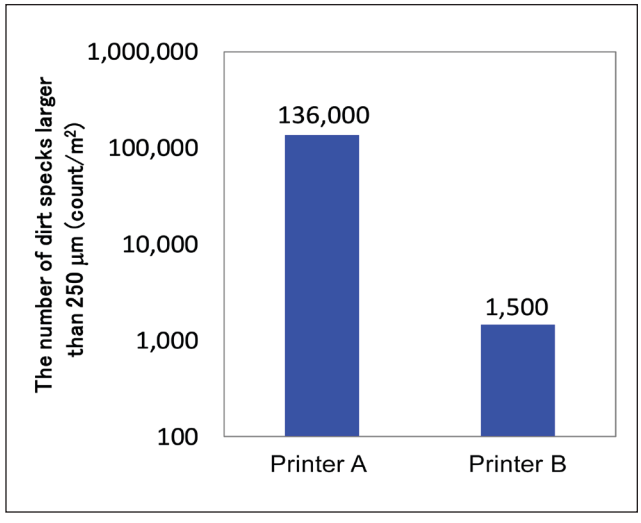
Figure 3 shows the number of dirt specks of C-UV, HS-UV,



2. Form and ink coverage patterns of test prints (C = cyan; M = magenta; Y = yellow; K = black).



3. Number of dirt specks from conventional ultraviolet-curable (C-UV), highly-sensitive UV-curable (HS-UV), and oil-based (OB) inks in the final deinked pulp (DIP) test. Relative value is used based on the number of OB.

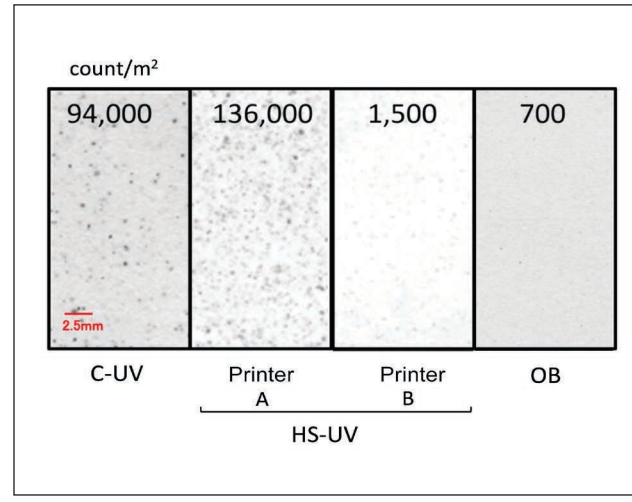


4. Number of dirt specks in samples from printer A and printer B after the laboratory experiment shown in Fig. 1.

and OB in the final DIP test. The relative number of dirt specks was based on the number of dirt specks in the OB. The relative number of dirt specks of C-UV and HS-UV was over 20 times more than that of OB. When comparing C-UV with HS-UV, HS-UV produced fewer dirt specks. However, it should be noted that whether the ink used was C-UV or HS-UV, unacceptibly large numbers of specks would result if these prints were used as the only raw materials.

Comparison of HS-UV print deinkability between printers A and B

Two kinds of HS-UV prints were used in the mill trial. One was from printer A and the other was from printer B. Laboratory work was performed to investigate whether there were differences in deinkability between the two sources. There was a large difference between the deinkability of



5. Images of handsheets after laboratory experiment shown in Fig. 1.

samples from printing press A and that from printing press B (**Fig. 4**; note log scale Y-axis).

Figure 5 shows images of lab-produced handsheets. The C-UV and OB sample results are also shown as comparative results, though these samples (C-UV and OB) were not taken at the same time as the mill test. It is easy to understand the difference in deinkability by comparing the images. The HS-UV samples from printer A actually showed more dirt specks than the C-UV sample. By comparison, samples from printer B had nearly as few dirt specks as the OB sample.

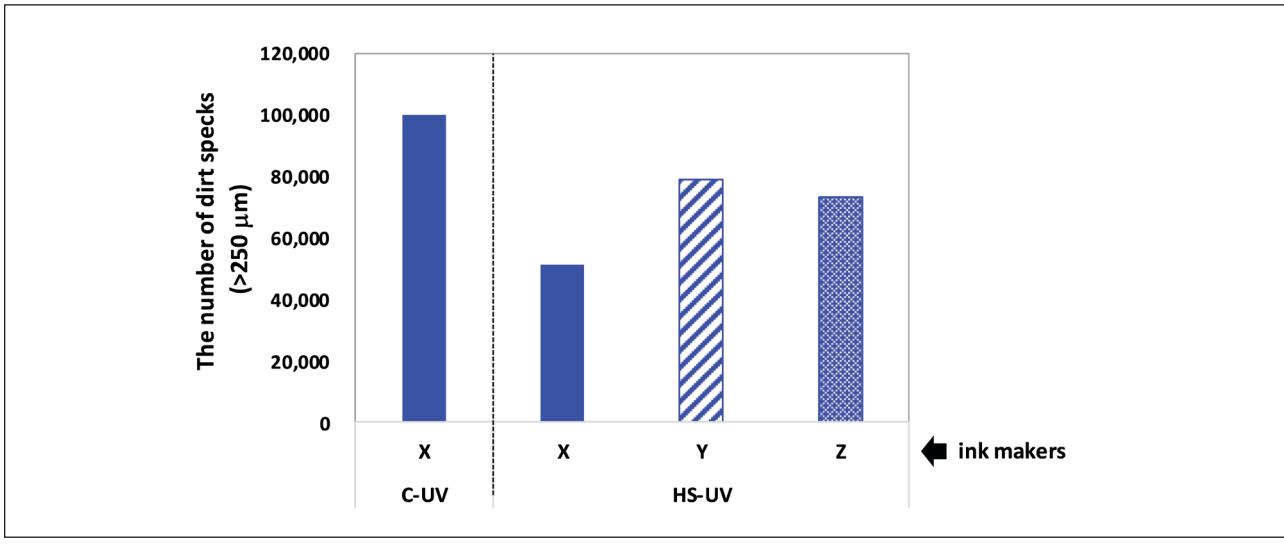
The results described here suggest that not all the UV prints were hard to deink. Some UV prints might become a cause of unacceptable dirt contamination, while other UV prints might not. Thus, it is important to understand what factors bring about these differences. For this purpose, we made test prints that had fixed ink coverage patterns using several kinds of UV inks; the pattern of these prints is shown in Fig. 2.

Comparison of deinkability of C-UV and HS-UV between different ink makers

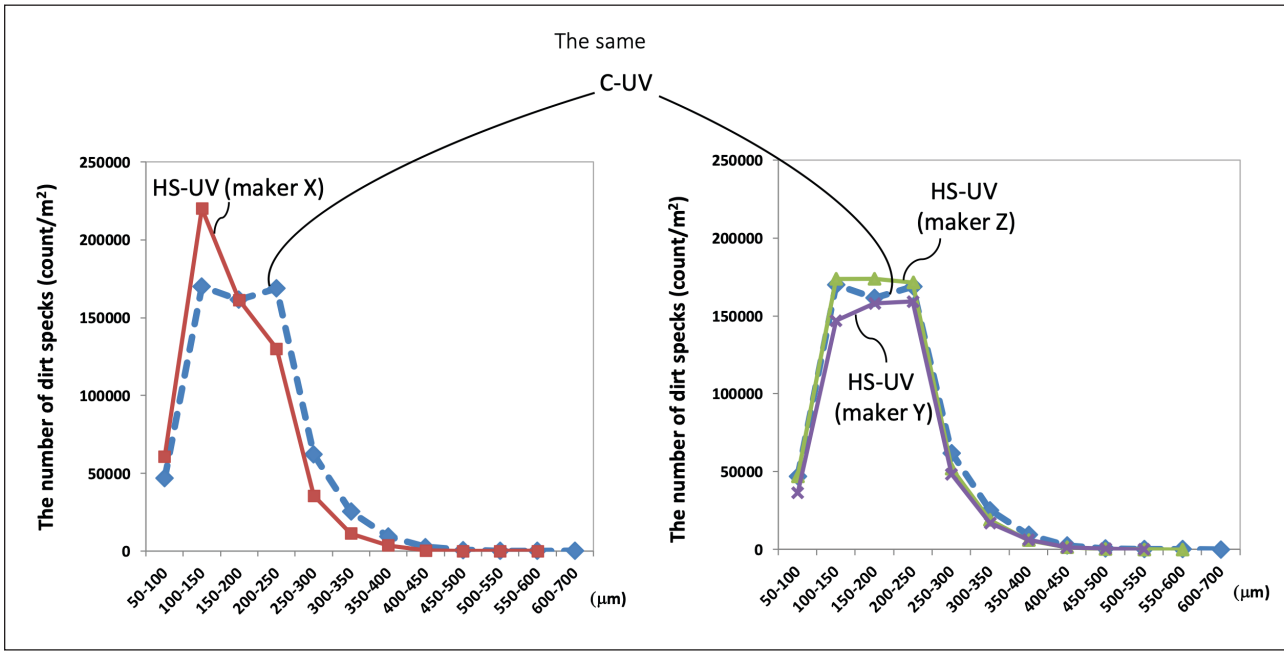
To examine differences in deinkability between several kinds of UV inks, laboratory experiments were performed with test prints. An area of 100% ink coverage ratio with the four color components (shown as CMYK in Fig. 2) in each test print was used.

Figures 6 and 7 show the results of the comparison. Figure 6 is a comparison of the relative deinkability of C-UV vs. three different HS-UV printed samples. Note that, to varying degrees, the HS-UV ink caused fewer dirt specks than did C-UV ink. This result suggested that the film from HS-UV ink was easier to break into small pieces than that of C-UV ink.

Figure 7 shows the distribution of the dirt specks by diameter. Note that the peak speck size of the HS-UV ink from ink maker X was shifted to the left side of the figure



6. Comparison of the number of dirt specks from C-UV and HS-UV inks in test prints.



7. Distribution of dirt specks by diameter: HS-UV from ink maker X vs. C-UV (left), and HS-UV from ink makers Y and Z vs. C-UV (right).

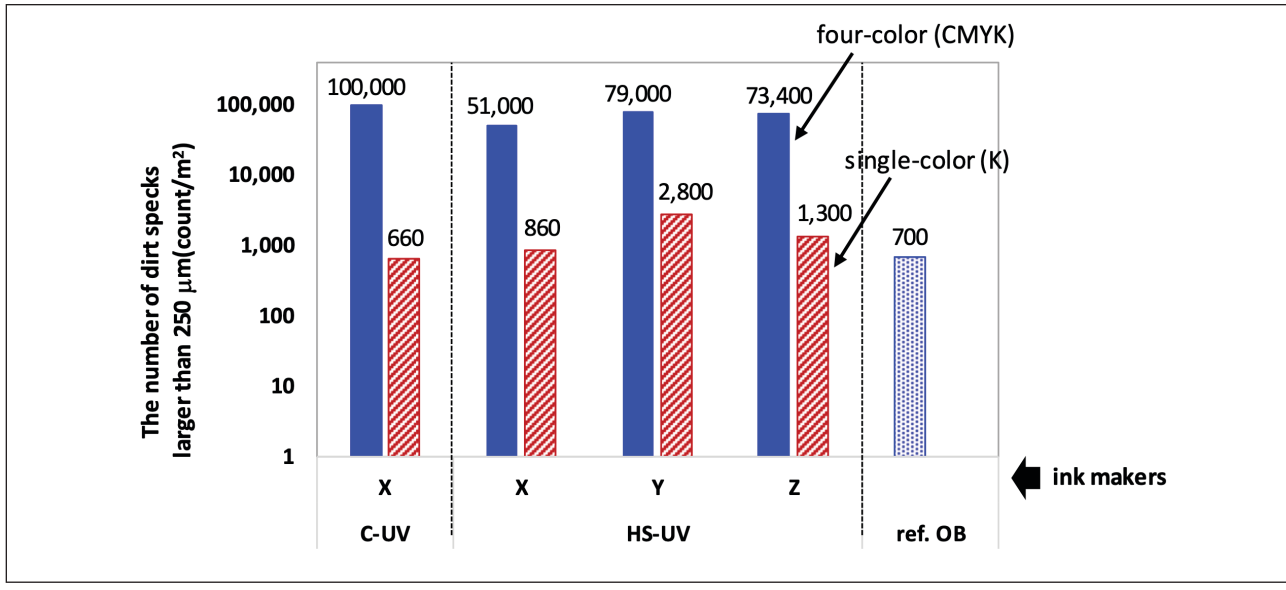
(smaller particles) compared with other types of ink. The increase in the number of dirt specks of 100–150 µm in diameter inferred that the HS-UV ink from ink maker X was more easily fractured during deinking than the other HS-UV inks tested in this laboratory experiment. Therefore, it was obvious that there were also differences in the deinkability of the HS-UV inks.

The impact of four color printing on deinkability was tested by using 100% ink coverage ratio of the four color components (CMYK as shown in Fig. 2) and also the single color component (K), respectively (note log scale Y-axis in **Fig. 8**). The number of dirt specks of OB (the same data shown in Fig. 5) is shown as a reference.

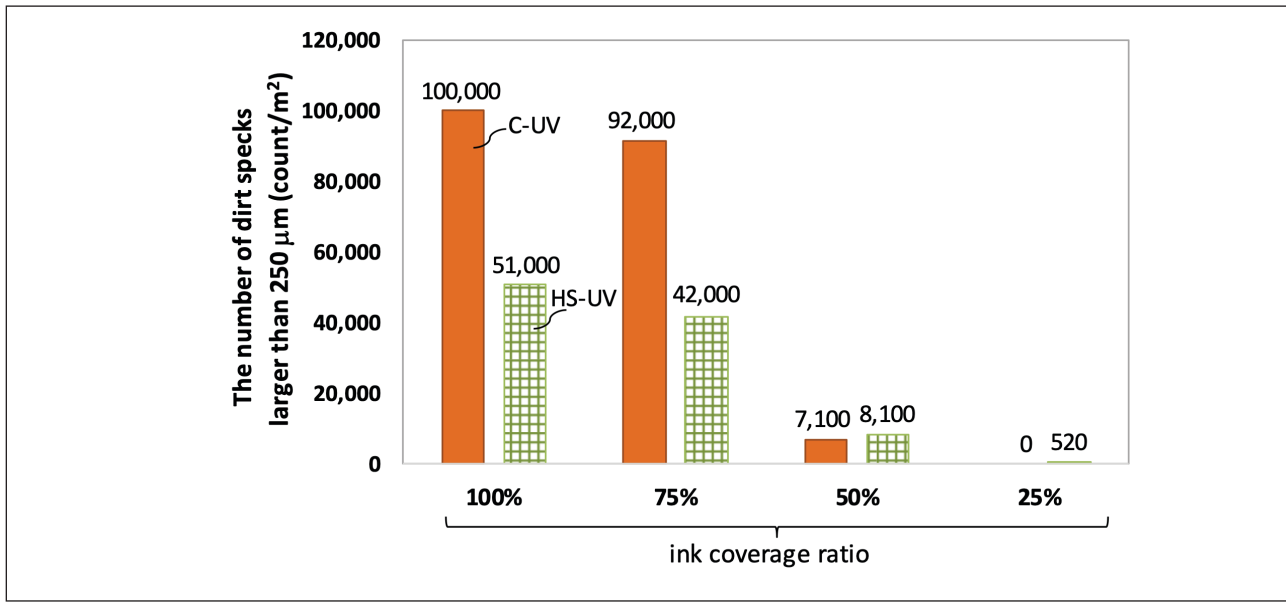
Clearly, single color prints caused far fewer dirt specks than four color prints. Furthermore, the number of dirt specks caused by single color prints was nearly the same level as that of the OB sample. Finally, the appearance of contaminants from C-UV ink and from HS-UV ink on single color prints was roughly the same. Therefore, the ink coverage printing pattern can strongly affect the deinkability of UV prints.

Investigation of ink coverage pattern's influence on deinking

Ink coverage patterns of 100%, 75%, 50%, and 25% were used for laboratory tests to investigate how much impact



8. Comparison of the number of dirt specks from the four color components (CMYK as shown in Fig. 2) with the single color component (K). Number of dirt specks from OB is shown as reference.



9. Number of dirt specks occurring at different ink coverage ratios (100%, 75%, 50%, and 25%) was examined with the laboratory experiment shown in Fig. 1.

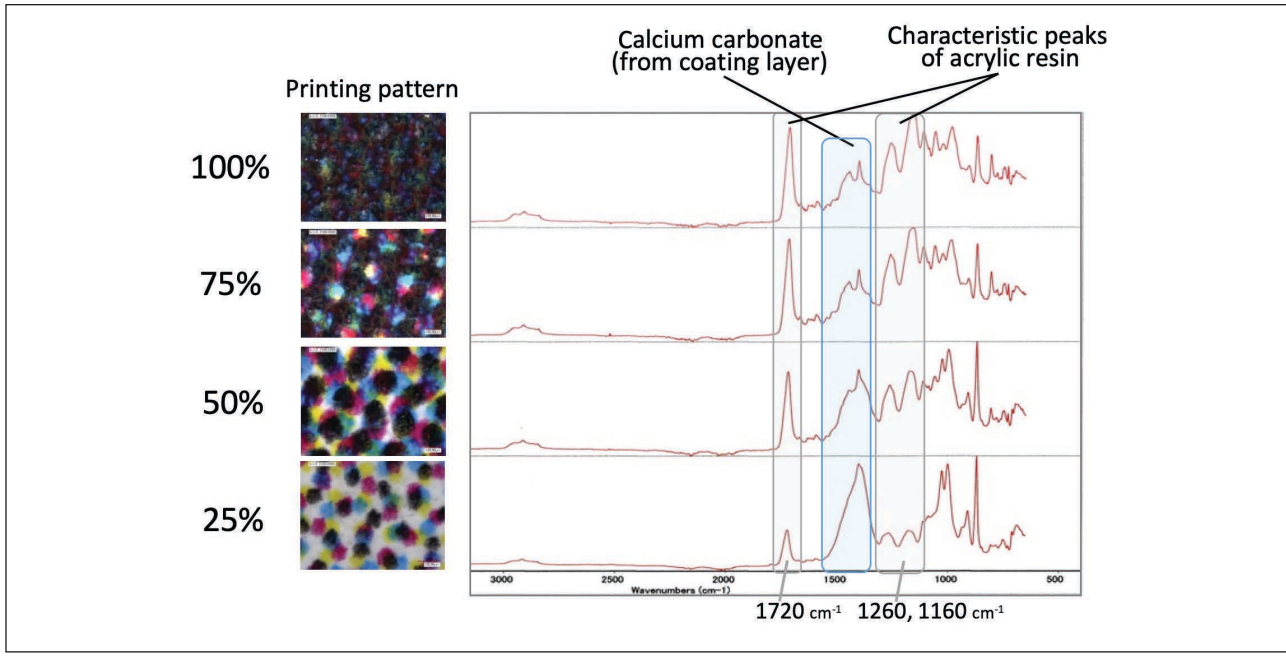
different printing patterns had on deinkability. In this test, C-UV and HS-UV inks from ink maker X were examined. Areas evaluated were the four color printing areas that are circled in red in Fig. 2.

Figure 9 shows that the number of dirt specks decreased as the ink coverage ratio was reduced. This tendency was confirmed for both C-UV and HS-UV ink, particularly below 75% coverage. There was not much difference in dirt speck content between ink coverage ratios of 100% and 75%. Ratios of 50% and 25% gave much smaller counts. These results suggest that ink coverage ratios under 50% may be more easily handled by the DIP process. At 25% ink coverage, there appears to be little detrimental effect on dirt content.

Application of the ATR-IR method

Results so far indicate that the ink coverage ratio has a large impact on deinkability. With the sharp difference in deinkability between ink coverage ratios of "100% and 75%" vs. "50% and 25%," it would be useful if one could use ATR-IR to distinguish printing patterns.

To achieve this goal, the surface of each sample shown in Table II was analyzed using ATR-IR apparatus to obtain IR spectrum. The IR spectra vs. ink coverage



10. The IR spectra of different ink coverage patterns. Characteristic peaks of UV prints are 1160, 1260, and 1720 cm^{-1}.

Ink Coverage Ratio	Surface of Prints	Intensity Compared with 2920 cm^{-1}	IR Spectra	Dirt Specks >250 µm (count/m^2)	Deinkability
100%, 75% Category I		more than 4.8 times		42,000～100,000	poor
50% Category II		3.8～4.6 times		around 8000	good
25% Category III		2.5～3.5 times		around 500	very good

around 2920 cm^{-1} | around 1720 cm^{-1} | around 1260, 1160 cm^{-1}

11. Relationship between IR spectra and deinkability results.

ratio is shown in **Fig. 10**. UV prints had three peaks at 1160, 1260, and 1720 cm^{-1}, which were characterized as acrylate. It was obvious that those characteristic peaks for UV prints were getting lower intensity as the ink coverage ratio decreased. This was accompanied by an increase in peak intensity at 1440 cm^{-1}, which was characteristic of calcium carbonate derived from coating. Judging from these results, ink coverage ratio can be predicted from IR spectra by the differences in peak intensity. Thus, we examined enhancing the ATR-IR method by combining these IR spectra and the results of laboratory experiments.

According to laboratory experiments, it is practical to divide the results into three categories:

- Category I: ink coverage ratio of 100% and 75%; deinkability is poor.
- Category II: ink coverage ratio of 50%; deinkability is good.
- Category III: ink coverage ratio of 25%; deinkability is very good.

To define the categorization by peak intensity, we measured 16 samples by means of the ATR-IR apparatus and examined each IR spectrum. We found that each category could be defined based on the average intensity of the peaks that were characteristic of acrylate (1160, 1260, and 1720 cm^{-1}) compared with that of 2920 cm^{-1} (Category I: more than 4.8 times; Category II:

between 3.8 to 4.6 times; Category III: between 2.5 to 3.5 times).

Finally, the spectra related to UV prints were stored in an ATR-IR database, as shown in **Fig. 11**. Hence, when UV prints were inspected with the ATR-IR method, they were categorized into three groups: poor, good, or very good. With this uploaded data from the ATR-IR method, UV prints from commercial printing presses that were used for the mill trial (Test 2 shown in Table I) were assessed. Eventually, prints from printer A were judged as poor, while those from printer B were very good. Therefore, we confirmed that this method made it possible to distinguish easily deinkable UV prints from other UV prints.

CONCLUSIONS

The following are key findings from this study:

- According to the final DIP image analysis, whether conventional UV or highly-sensitive UV ink was used, high levels of dirt contaminants are likely if these prints are used as the only raw material.
- Laboratory experiments in this study made it clear that not all UV prints are hard to deink.
- There were differences in the deinkability of HS-UV prints between two printers.
- Laboratory experiments using test prints revealed that the ink coverage ratio strongly affected the deinkability of those prints. Examination of several UV prints using the ATR-IR apparatus found that they could be distinguished based on the intrinsic peak intensity that reflected the UV ink coverage ratio.
- Laboratory experimental results and IR spectra were combined, and a database for enhancing the ATR-IR method was created. Deinkability of UV prints could be categorized into three types by means of the ATR-IR method: poor, good, and very good.
- Prior to upgrading the ATR-IR method, the method could only classify prints into UV prints, polystyrene overcoated prints, and prints made with oil-based ink. Now, the method can also determine the deinkability level of UV prints simply by analyzing the surface of those prints.

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We chose to study this topic because paper manufacturers have many product quality issues from dirt specks caused by ultraviolet-curable (UV) ink in paper used for recycling, and a way is needed to avoid them. Most UV-printed products (UV prints) have thus far been regarded as hard to deink.

We discovered that not all UV prints are difficult to deink, meaning that some of them may be used as raw materials in the recycling process. In addition, we also found a way to distinguish easily deinked UV prints (those carrying few dirt contaminants) from more difficult to deink UV prints (those carrying many dirt contaminants) using an attenuated total reflectance infrared (ATR-IR) spectroscopy apparatus. This discovery is new in this field.

Determining the deinkability between various UV prints was difficult. To address this, we made many test prints with different inks and analyzed them.

We found that some UV prints had nearly the same deinkability as conventional prints made with oil-based ink. If we can determine those usable UV prints, they can be used as a raw material for recycled paper products.

It was interesting to find that the IR spectra of printed inks differed in accordance with the deinkability of UV prints. We believe that the amount of printed ink directly affected the deinkability of the UV prints.

The deinkability of UV prints can be easily and promptly determined by analyzing the surface of the prints with the ATR-IR apparatus. Therefore, this approach is helpful for entrance quality control in mills.

Our next step is to apply this novel method in mills for entrance quality control. In addition, related industries in this field should work on developing easily deinkable inks and explore mill processes that can remove UV inks more efficiently.

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- Finally, the ATR-IR method was applied for the assessment of recovered paper from commercial printing presses, and the method's effectiveness was confirmed.

Due to diminishing supplies of recovered paper, expanding the usable pool of recycled paper is becoming more important. Sorting out prints that are hard deink by using the ATR-IR method is a first step in solving the problem of dirt contamination driven by UV prints.

Also, in light of the these findings, work on developing easily deinkable inks and exploring mill processes that can remove UV inks more efficiently should be considered among related industries. **TJ**

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