

Instrumental Analysis-based Evaluation of Print Blanket Rubber Swelling

Asuka Uchida and Yasushi Ozaki

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Abstract

The rubber of print blankets and transferred rolls may deteriorate due to the swelling and extraction resulting from the interaction of solvents and ink on the printing machine.

A method of evaluating rubber deterioration had not previously been clearly established. In the present study, a technique for understanding the deterioration of rubber due to the effect of inks and solvents was developed using analytical instruments.

The process of rubber's swelling and extraction was evaluated in detail as an effect of the solvents and ink.

As a result, compatibility between rubbers and solvent/ink types can be predicted before printing.

To confirm the utility of the prior evaluation, two blankets were selected, and the printing test was carried out with a real machine. After that, printing qualities and states of blankets were evaluated. In the end, the condition of the blankets after printing was found to be in accordance with pre-printing assessments.

Introduction

The rubber in print blankets and transfer rolls deteriorates over time due to swelling and extraction(Furukawa,1957, Koshiji,2014). The surface rubber of such blankets plays a particularly important role in printing quality among rubber, ink and solvents must be selected to maintain stable printing electronics. Against such a background, favorable chemical compatibility quality with continued use.

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Because it interacts directly with substrates such as paper by transferring ink onto them. The specific qualities of the blanket are also affected by ink solvents as in the case of gravure offset printing used in the field of print.

We have evaluated penetration states of inks and solvents into blanket rubber and transfer rolls previously(Ozaki,2007,2008,2009).

Moreover, the relationship between ink/solvent systems and blanket rubbers must be clarified to predict printing conditions qualities before printing.

In order to maintain stable quality over continuous printing, compatible combinations of blanket rubbers and ink/solvent systems must be selected. Simple methods of visual check and palpation have generally been used. However, a reliable method of evaluating rubber degradation has never been established. Consequently, printing machine operators tend to select print blankets based on experience and intuition.

The objective of this study was to find a method to rapidly and accurately choose an appropriate print blanket for a given set of printing conditions, such as specific kinds of inks and solvents. In addition, it was necessary to determine the expected condition of the printing machine blanket.

In this study, we particularly analyzed the process of swelling and extraction in blanket rubber due to inks and solvents using ATR (Attenuated Total Reflection) imaging analysis system and gas chromatograph- mass spectrometry (GC-MS). Furthermore, two blankets were selected, and printing tests were carried out using a real machine. Following this, printing qualities and the resultant condition of the blankets were evaluated. Finally, the condition of the blankets after printing was in accordance with expectations of assessment results made before printing.

Experimental Materials

Four kinds of print blankets with differing structure and SP value (solubility parameter) of rubber were selected (Table1).

Two kinds of inks (Oil-based offset ink and UV curable offset ink) were dropped on print blankets (area:100mm²), and three kinds of solvents (ethanol, isopropyl alcohol (IPA) and petroleum ethers) with different properties were similarly dropped on the print blankets. These blanket samples were prepared for analysis.

	Rubber	Polarity (SP value)
Sample A	Acrylonitril-butadiene copolymer (NBR)	High (10.9)
Sample B	Ethylene-propylene terpolymer (EPDM)	Low (7.9)
Sample C	Isobutylene-isoprene copolymer (IIR)	Low (7.8)
Sample D	Polyester isocyanate (U)	High (10.0)

FTIR-ATR imaging analysis

ATR imaging analysis of Fourier transform infrared spectrophotometer (FTIR) was developed from the mapping technique of the infrared micro-spectroscopy. ATR imaging system was improved as a high-speed imaging instrument. 16 spectra were obtained simultaneously in ATR imaging system because 16 detectors were arranged in a line (Ohonishi,2013).

The chemical information of material surface can be obtained without pretreatment using ATR. As a first step, the chemical interactions between ink/solvent and rubbers were evaluated from ATR spectra and imaging ATR maps.

ATR imaging data on four kinds of original blanket rubbers were measured first. ATR imaging was carried out with an IR imaging system (Spotlight-400: Perkin Elmer Co.).

The measurement area was adjusted to 2mm x 2mm, and pixel size was 1.56 μ m. Spectral range was from 4000cm⁻¹ to 720cm⁻¹ at 8cm⁻¹ spectral resolution .Multiplication was assumed to be eight times.

Next, two types offset inks (5mg) and three kinds of solvents (100 μ l) were dropped on the original blanket rubbers and each ink or solvent was wiped off after two hours. Blanket rubbers were measured with an ATR imaging system again.

ATR spectra of blankets for printing test were obtained with one-way ATR (Agilent Technologies Ltd: 660IR). The measurement area was adjusted to 0.1mm².Spectral range was from 4000cm⁻¹ to 720cm⁻¹ at 8cm⁻¹ spectral resolution. Multiplication was assumed to be eight times.

Analysis of extraction components from rubbers with GC-MS

In order to identify the extraction components from rubbers in which the phenomenon was confirmed by ATR spectra, the extraction components of the rubbers were analyzed with a gas chromatograph mass spectrometer (GC-MS: JEOL Ltd. JMS700).

The solvent dropped on the surface of each rubber was collected by syringe after 2hours, 6hours, 24hours,and 48hours. The extracted solvents (1 μ l) were directly introduced into the injection of GC-MS and analyzed with GC-MS.

The analytical conditions were conducted in accordance to the split-less injection method with the following settings:

oven:50°C-250°C (10°C/minute), detector:MS (+),
column: DB-5MS(J&W Co.: 30m $\times$ 0.32mm $\times$ 0.25 μ m).

Printing test with a real printing machine

Sample A and Sample B in Table.1 were selected as the test blankets of printing machine. UV curable offset ink (acrylate based) and 3-metxy-3-methyl-1-butanol (high polarity solvent) were used for printing.

15000sheets were printed in the offset printing press (KOMORI Co.: LITHRONE 40inches) respectively, and the effect on the blankets and the printing quality of the sheets were evaluated.

ATR spectra of 4 printing line parts on two blankets before and after printing were obtained. In addition, the same parts of the blankets were measured as the ATR spectra 3 and 7 days after printing.

ShoreA-type hardness tester(Shimadzu Co.: DROMETER-JIS K6253) was prepared to measure hardness. Each hardness was measured on the same position as ATR spectrum obtained on blanket before printing and after printing (1000, 5000, 10000 and 15000 sheets) as well as 3 and 7days later. The surface hardness was shown by the mean value of measurements in four places.

The samples of printed sheets were evaluated as follow. The qualities of printing lines were observed in detail using an optical microscope. In addition, the printed sheets were compared visually.

Result and discussion

FTIR-ATR imaging analysis

“Extraction” was expressed as the phenomenon in which rubber components dissolve in solvents and inks, and “Swelling” was expressed as the phenomenon in which rubber expands due to the effects of solvents and inks.

Figure 1 shows the ATR spectra of the rubbers before and after dropping the UV curable ink on the surface of sample A. Change the spectra before and after ink dropping was confirmed. The peak intensities expressed as white arrows were increased after the ink dropping, and these peaks were dependent on the

ink components. Especially, an absorbance peak derived from an ink vehicle at 3400 cm^{-1} was detected by the swelling of the blanket surface. The absorbance peak at $3,400\text{ cm}^{-1}$ was assigned as the hydroxyl group.

On the contrary, the peak intensities expressed as black arrows were decreased after the ink dropping. For example, the absorbance peak derived from the blanket rubber at 1730 cm^{-1} was lower because rubber components were dissolved from the blanket surface (a phenomenon known as extraction). The absorbance peak at 1700 cm^{-1} was assigned as the carbonyl group.

Figure 2 shows two-dimension images of the hydroxyl group (3400 cm^{-1}) before and after ink dropping. Ink vehicle distributed richly in the white parts. When sample A, having rubber of high polarity, contacted with UV curable ink, “Swelling” occurred on the blanket rubber.

Figure 3 shows the two-dimension images of the carbonyl group (1730 cm^{-1}) before and after ink dropping. White parts decreased in the two-dimension image after ink dropping, to compare with that before dropping. This means that rubber components will dissolved in UV curable ink. Because rubber components dissolved in ink were removed with ink, the absorbance of carbonyl group in the blanket rubber reduced in **Figure 3**.

The distribution of swelling and extraction could be also visualized as two-dimension images with ATR imaging system.

2 types of inks and 3 kinds of solvents were dropped on 4 blanket samples in Table 1, and all samples were measured with ATR imaging system. As a result, high polarity samples A and D tended to evolve “Swelling” and “Extraction” together with UV curable ink vehicle, but Sample A and Sample D didn’t evolve “Swelling” and “Extraction” together with oil-based vehicle.

In addition, high polarity samples A and D tended to evolve “Swelling” and “Extraction” together with ethanol of high polarity, but Sample A and Sample D didn’t evolve “Swelling” and “Extraction” with petroleum ether that was of low polarity. Low polarity samples B and C tended to evolve “Swelling” and “Extraction” together with ink and solvents of low polarity unlike Sample A and Sample D.

In short, blanket rubber expressed “Swelling” and “Extraction” by inks and solvents of similar polarity to the rubber..

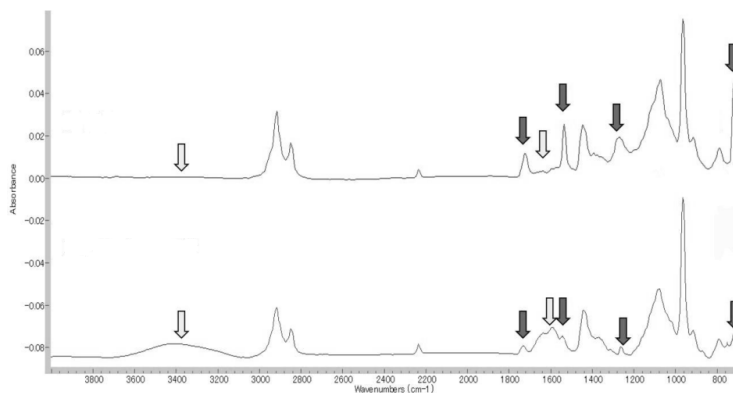


Figure 1. ATR spectra of rubbers before and after dropping the UV curable ink on the surface of sample A

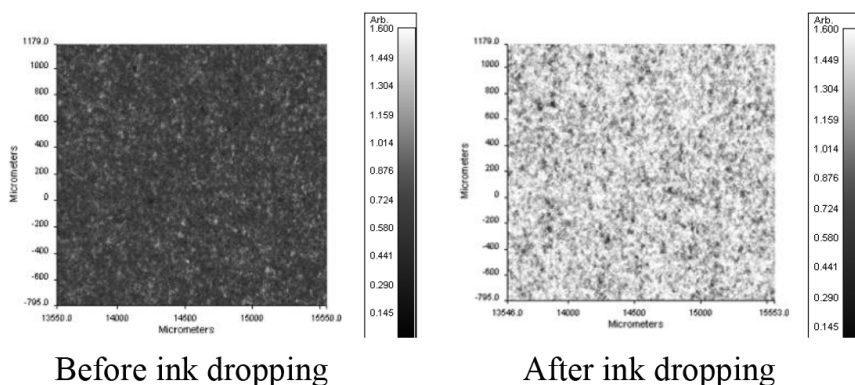


Figure 2. Two-dimension images of the hydroxyl group (3400 cm⁻¹) before and after UV curable ink dropping

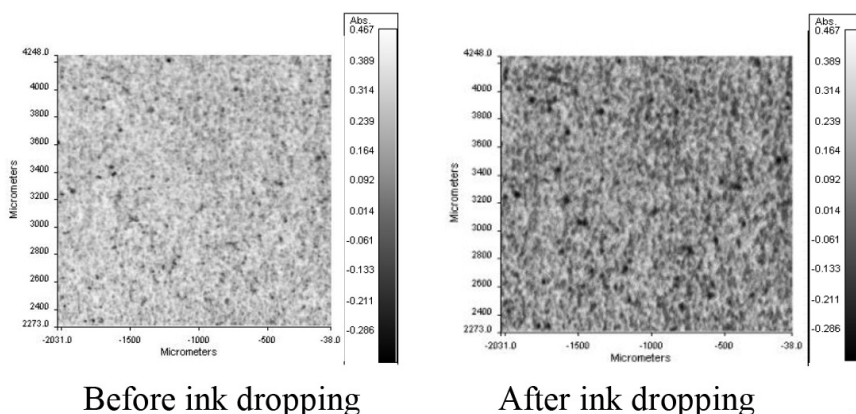


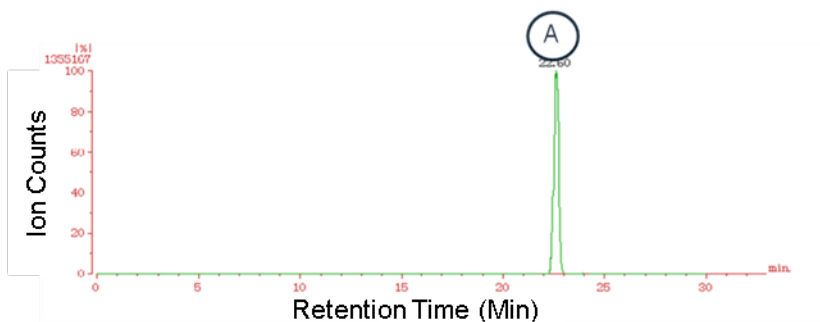
Figure 3. Two-dimension images of the carbonyl group (1730 cm⁻¹) before and after UV curable ink dropping

Analysis of extraction components from rubbers with GC-MS

Figure 4 shows TIC (total ion chromatogram) of extract with petroleum ether of sample B. Petroleum ether dropped on the surface of blanket rubber was collected by the syringe after two hours and twenty-four hours. **Figure 5** shows MS spectra identified each peak in Figure 4. One peak was detected from TIC of extract for two hours (Fig.4 (1)), and this peak was identified as the adipic acid ester (Fig.5 (A)). The adipic acid ester was used as the plasticizer of blanket rubber. Many peaks were detected from TIC of extract for 24 hours (Fig.4 (2)). Each peak was identified as the rubber component (Fig.5 (1-5)).

Figure 6 shows the relationship between the extraction time and the peak area of TIC. The adipic acid was instantly extracted with petroleum ether, and propylene diacetate of rubber components was secondly extracted, and finally many rubber components were extracted. It was found that the adipic acid was extracted with petroleum ether for short times and the rubber was taken to pieces over twenty-four hours. As a result, the components dissolved from the blanket surface could be identified in detail using GC-MS.

(1) Liquid extracted for 2 hours



(2) Liquid extracted for 24 hours

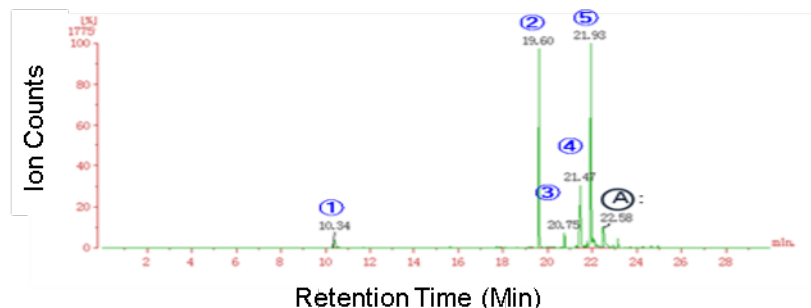


Figure 4. TIC of extract with petroleum ether of sample B

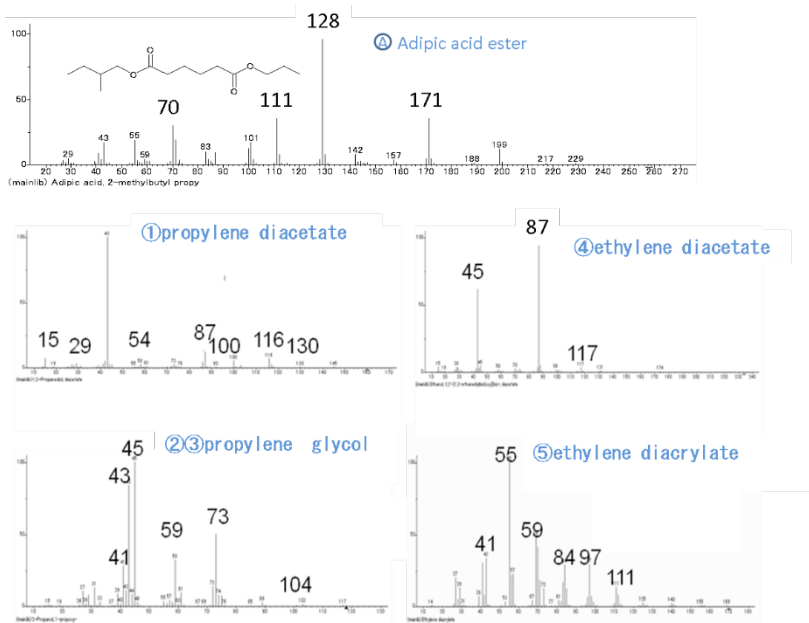


Figure 5. MS spectra identified each peak in Figure 4

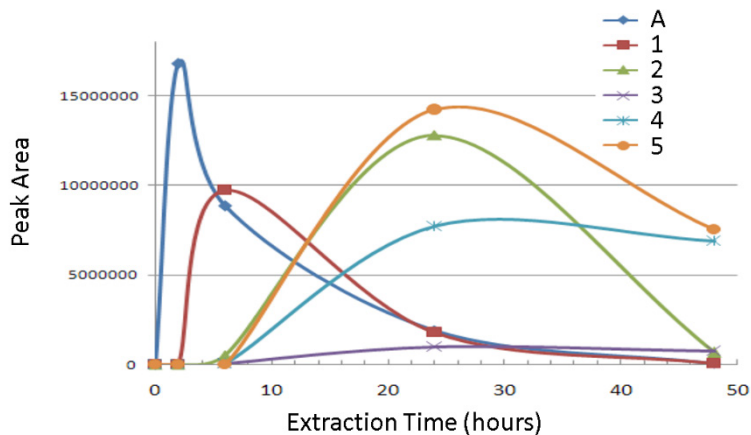


Figure 6. Relationship between the extraction time and the peak area of TIC

The process of the structure of the presence of the extraction with ink and the solvent, and the swelling and the extraction were able to be analyzed in detail by combining two kinds of analysis techniques.

Estimated result of adaptable blankets

The process of “Swelling” and “Extraction” of blanket rubbers with solvents and inks were clarified in detail using ATR imaging system and GC-MS.

Table 2 shows the estimated result of adaptable blankets with solvents and inks. The rank of adaptable blanket was in order of $\odot > \bigcirc > \triangle > \times$. Low polarity sample A was expected to fit on the printing by oil-based ink and to use petroleum ether for cleaning blanket. Sample B, having high polarity, would be conformed to UV printing and ethanol cleaning.

In these results, Sample A and Sample B were selected as blankets for the printing test with a real machine.

Solvent type (Polarity)	Petroleum Ether (low)	IPA (Medium)	Ethanol (High)	UV curable ink(High)	Oil based ink(Low)
Sample A	$\odot$	$\triangle$	$\times$	$\times$	$\odot$
Sample B	$\times$	$\bigcirc$	$\odot$	$\odot$	$\times$
Sample C	$\times$	$\triangle$	$\bigcirc$	$\bigcirc$	$\times$
Sample D	$\odot$	$\triangle$	$\times$	$\times$	$\bigcirc$

Rank: $\odot > \bigcirc > \triangle > \times$

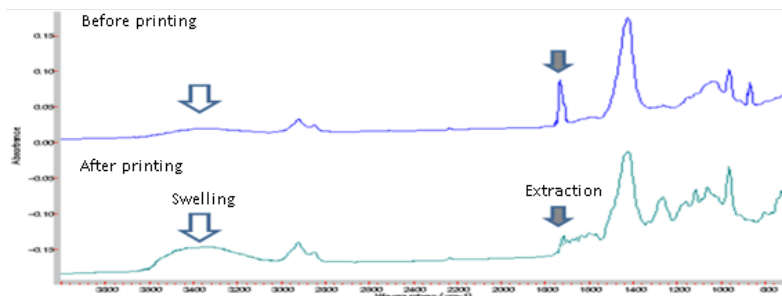
Table 2. Estimated result of adaptable blankets with solvents and inks

Printing test with a real printing machine

Figure 7 shows the ATR spectra of blankets before and after printing. In the case of Sample A, a peak intensity of hydroxyl group at 3400cm^{-1} appeared after printing, and a peak intensity of carbonyl group at 1730cm^{-1} decreased after printing. This meant that this blanket was swollen and was extracted. However, in the case of Sample B, swelling only occurred.

Figure 8 shows the peak area of hydroxyl group and carbonyl group before and after printing. Sample A was swollen by printing, but it returned to pre-printing conditions 7 days after printing. ATR peak intensity of carbonyl group of Sample A decreased after printing, and ATR peak intensity was not changed even if the blanket was left for 7 days after printing. This reason was considered that ink would penetrate in the blanket rubber while the blanket was leaving for long time.

(1) Sample A



(2) Sample B

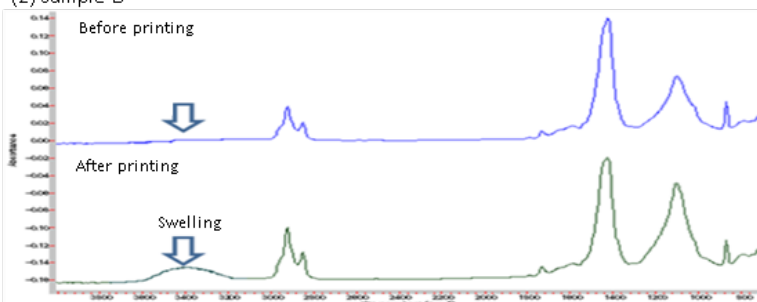


Figure 7. ATR spectra of blankets before and after printing
(1) Sample A, (2) Sample B

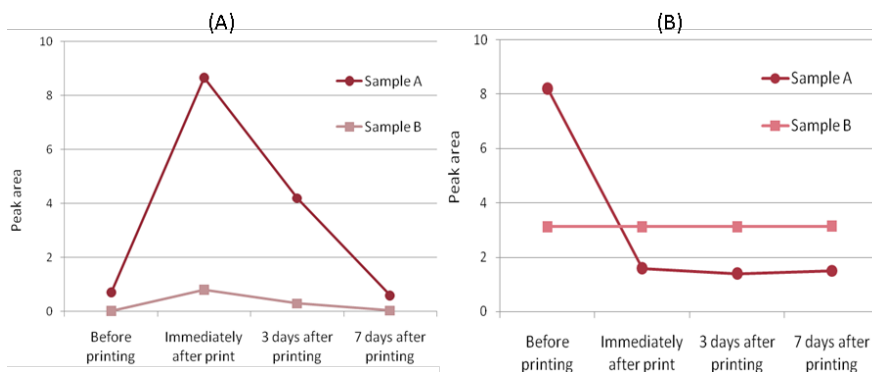


Figure 8. The peak area of hydroxyl group and carbonyl group before and after printing

(A) "Swelling" (hydroxyl group at 3400cm-1)

(B) "Extraction" (carbonyl group at 1730cm-1)

However, Rubber components of Sample A were removed from the surface of blanket after printing. Eventually, the state on the surface of Sample A was changed after printing by UV curable ink.

Whereas, ATR peaks area of hydroxyl group and of carbonyl group hardly been changed between before printing and after printing.

These results were conformed the estimated result of adaptable blankets with solvents and inks in Table 2.

Figure9 shows the change in hardness on blankets in the printing process. While hardness of Sample A increased in printing and decreased a little after printing, that of Sample B changed little in the printing process. It was found that the blanket rubber of Sample A was harder than that of Sample B on UV curable ink printing.

Figure 10 shows the optical microscope images of lines printed using blankets of Sample A and Sample B. The width of lines printed using the blanket of Sample A was twice as wide as that of Sample B. It was confirmed by printing test that the printing quality of Sample A was worse than that of Sample B. This reason was assumed to be caused by the change in blanket hardness after printing. It can be expected that hardness tester can be simply used as a tool for quality control.

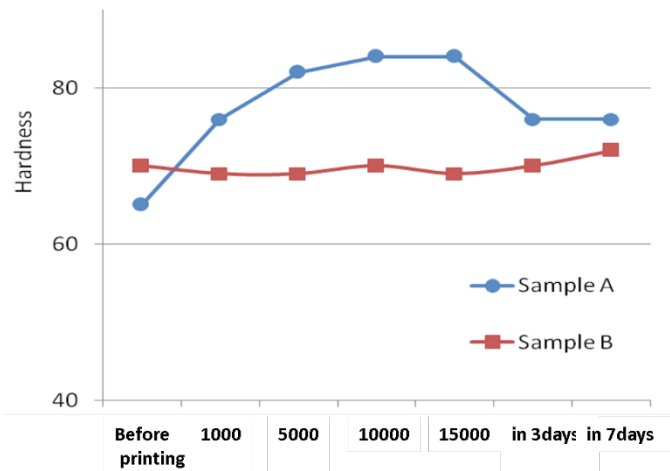


Figure 9. Change in hardness on blankets in the printing process

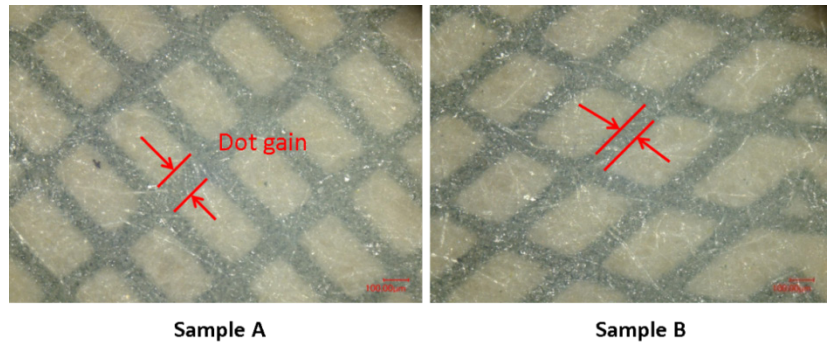


Figure 10. Optical microscope images of lines printed using Sample A and Sample B

Conclusions

The process of swelling and extraction in blanket rubber due to inks and solvents was analyzed using ATR imaging system and GC-MS. As a result, it was assumed that the combination of blanket rubber and ink/solvents having opposite polarity was suitable for printing condition.

The prediction so obtained from table test were confirmed by printing tests done with an actual printing machine.

In addition, it was found that the hardness tester was useful for quickly evaluating the state of the blanket on the printing machine.

In the future, we will be able to apply these techniques to resolve printing troubles caused by the degradation of the blanket.

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