Characterization of Penetration of Solvents into Press Blankets by Confocal Laser Scanning Microscope

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Blanket, Solvent, Penetration, Fluorescent, Dyes

ABSTRACT

The interaction of printing press blankets with ink oils and solvents can influence the printing results and the integrity of the blanket. Little has been reported on the penetration rate of various solvents into commercial blankets. A new method to characterize penetration rate is proposed here.

Three different blankets are contacted with three solvents. A technique is developed where a fluorescent dye is added to the solvents to allow the position of the solvent to be detected with a confocal scanning laser microscope (CLSM).

Top views of the samples reveal the distribution of the solvent within the surface structure of the blanket. The distribution does correlate with the blanket textures. Images of physical cross sections show that different solvents interact and penetrate into the blankets at different rates. These rates did not correlate to the contact angle of the solvent and the blanket but does relate to the relative densities of the samples as determined with back scatter electron images. The aliphatic solvent did not penetrate into one blanket type at all. Toluene penetrated to the rubber-fabric interface in 72 hours. The penetration rate seems to fit a diffusion mechanism.

Introduction

Ink solvents evaporate and penetrate into paper in the process of ink setting. Solvents penetrate into the blanket when the ink transfers to the blanket. Moreover, other solvents for cleaning also may penetrate into the blanket. These solvents can influence the printing quality because the solvents make the rubber swell that can change the ink transfer and its compressibility. In addition, solvents may degrade the blanket's mechanical strength by interacting with adhesives at certain depths within the blanket.

To help understand these issues, the penetration of solvents into blankets should be characterized. The amount of solvent in the substrates has been determined by gas chromatography-mass spectroscopy equipped with a purge and trap injector, a thermal desorption cold trap injector or a thermo-gravimetry technique (Middleditch,1988, Ghebremeskel,1994, Kunze, 1998). However, the techniques do not give information with regard to the internal distribution of solvents inside the blanket.

^{14}C-labeled binders of resins were used for the penetration of resin coatings into wood in the study of microautoradiography (Nussbaum,1998). Even if ^{14}C-labeled solvents are prepared, the penetration of solvent into substrates cannot be observed because ^{14}C-labeled solvents also evaporate. The selected dye carriers within plastic fibers were characterized by the electron microscopic analysis (Ravichandran, 1990) This technique cannot be applied to the blanket samples due to the limitation of resolution. In addition, a significant amount of time is needed to prepare samples in the embedding and cutting steps.

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In recent work, the observation of ink penetration into paper was characterized using confocal laser scanning microscopy (CLSM) (Ozaki,2005a,2005b). In these reports, ink stained with fluorescent dye was observed by CLSM. CSLM is established as a valuable tool for obtaining high resolution fluorescence images with minimal sample preparation. While the laser beam (Ar or He-Ne laser) is scanning on the specimen, the emitted fluorescent light is detected by a photodetector. Because a pinhole is placed in front of the photodetector, out-of-focus information is reduced. The plane of focus is selected by a computer-controlled fine-stepping motor which moves the microscope stage up and down. Full focus image can be obtained by stacking 2D images collected in series.

In this study, the penetration of solvents into printing press blankets using a CLSM stain technique is reported. Although solvents were gradually evaporated, the fluorescent dye dissolved in the solvents remained as a trace in the blankets. As a result, the penetration of solvent into the blankets could be estimated from fluorescence images of CLSM. Three different solvents and blankets are reported here.

Experimental

Three blankets with different surface textures were used in this study of the penetration of solvents. Three blankets were labeled as blankets A-C and were obtained from Day International. The blankets had a top textured rubber layer, a fabric layer, and a compression layer. The rubber type for all of the blankets is a vulcanized acrylonitrile-butadiene rubber.

Three solvents were used. One solvent was toluene. The others were an aromatic hydrocarbon and an aliphatic hydrocarbon.

Nile Red (Sigma-Aldrich Co. Ltd.) was used as a fluorescent dye for staining the solvents. A 0.03 wt% of Nile Red was added to each solvent. Nile Red was completely dissolved in each of the toluene and the aromatic hydrocarbon, but only a small amount of Nile Red was dissolved in the aliphatic hydrocarbon. As a result, the concentration of Nile Red in the aliphatic hydrocarbon was 0.005 wt% . Although Nile Red is degraded by the laser beams a small amount (Ozaki, 2005a), the slight change of fluorescence intensity is estimated not to be influenced the results.

The stained solvent was applied at a volume of 50µl on each blanket using a micro-syringe. To observe the penetration of solvents into blankets from cross section, the procedure shown in Figure 1 was performed: 1) contact dyed solvents with blankets by an excess amount, 2) wipe off excess solvent after one minute, 3) apply drop of solvent to blanket, and 4) cut samples with scissors at various times after contact. The initial wiping of the blankets was to force the solvent over the entire surface to obtain a uniform drop in the third step. The strips were cut to a width of about 5 mm. The cross sections are mounted on glass slides with double-sided tape. The center part of the drop was observed in the microscope.

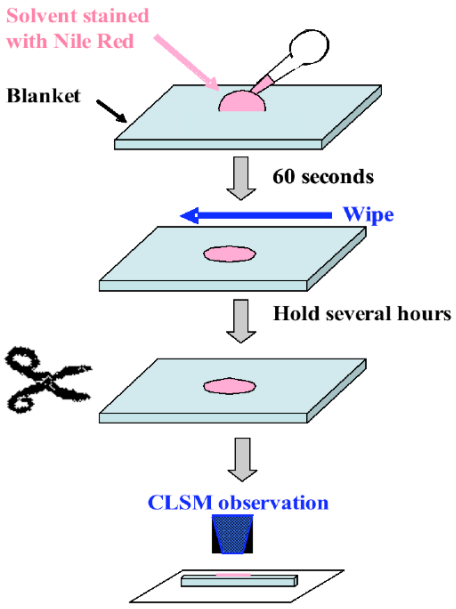

Figure 1. Sample preparation for CLSM cross section observation.

Fluorescent images were obtained using a confocal laser scanning microscope (Leica TCS-SP2). The x40 oil-immersion lens (HC PL APO, NA 1.25) was used as the objective lens to observe the blankets from surface. The x10 dry lens (HC PL APO, NA 0.4) was used to observe the blankets from cross section. Immersion oil (Refractive Index:1.518) was supplied by Leica. Excitation wavelength of 514nm from Ar laser (Power: 50mW) was used. A dichronic beamsplitter, which separates the fluorescent wavelength from the excitation wavelength of an Ar laser, was used (DD458/514). The pinhole size was set at the optimum value for each objective lens (Wilson, 1995). The detected wavelengths ranged from 535nm to 635nm for the excitation wavelength of 514nm. Confocal images in the z-direction were taken by 0.4μm/step and were reconstructed on the computer software. Image size of each frame was saved by 1024x1024 pixels.

The surface of each blanket was observed as the backscattered electron (BS) image by a low vacuum type scanning electron microscope (SEM: Hitachi SEMEDX). The electron beam was supplied at an acceleration voltage of 20kV and working distance was 15mm and a chamber vacuum was 15 Pa. The blanket surface are also viewed in an Environmental Scanning Electron Microscope (ESEM) (Electro Scan Model E-3, Phillips Electron Optics). A contact angle setup (CA-X, Kyowa InterFace Science Co.) was used to determine the contact angle: a small drop of the test liquid was applied to the blanket surface and the resulting drop was viewed with high power magnification. The images were recorded with a video camera for 30 seconds. The angle was determined through image analysis.

Results and Discussion

Figure 2 shows the back-scattered electron (BS) and ESEM images of three blankets. Blanket A has surface texture that looked rubbed and a moderate amount of filler. Blanket B has pores of 5-20μm in diameter as seen in Fig.2B. Blanket C has an uneven surface that looked like rubber chips as shown in Fig.2C. It appears that blanket C has the highest filler content in three blankets because most of the area on BS image showed a white color as seen in the top of Fig.2C. Blanket B seems to have the lowest density from the BS images. Different surface textures are often controlled in the manufacturing process by a grinding technique.

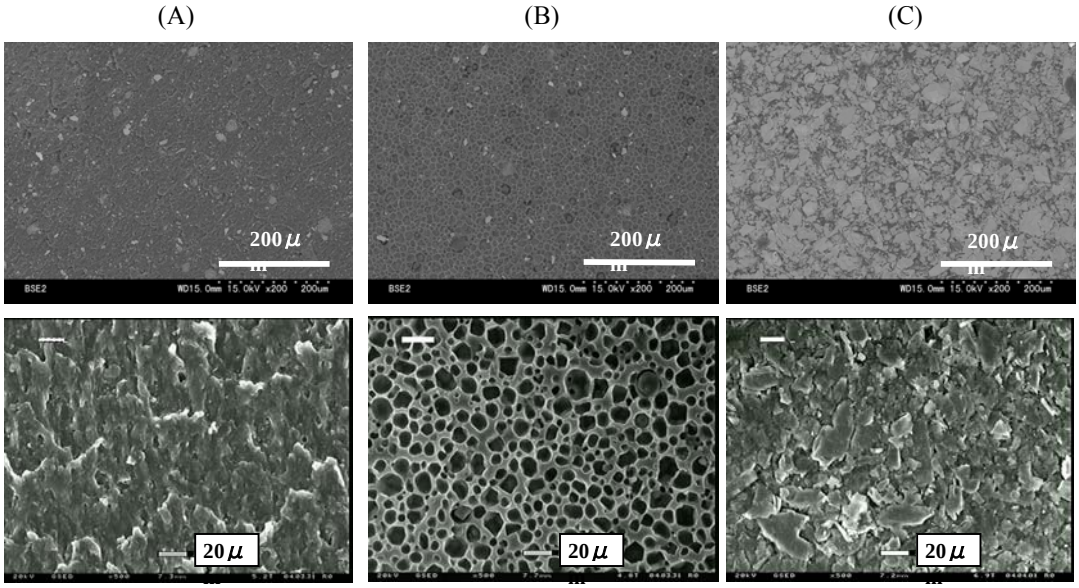

Figure 2. BS images (top) and ESEM images (bottom) of three blankets (A) blanket A, (B) blanket B, (C) blanket C.

As each blanket had a different color, color dye dissolved in solvents could not be used to observe the distribution of solvents. However, fluorescence dye could display the solvent location. Figure 3 shows the CLSM stack images of the three blankets. Bright parts show the fluorescence from Nile Red as the trace where toluene penetrated. The distribution of toluene around the surface of blankets could be observed by these fluorescence images. Toluene is distributed evenly on the surface of blanket-A as seen in Fig.3A, compared with Fig.3B and Fig.3C. Though, in the case of blanket B, the fluorescence intensity in the surface pores is high, the fluorescence along the pores is also detected. This result confirms that toluene fills in the pores first and then spreads into the blanket rubber. The distribution of fluorescence on blanket C was non-uniform. As the back scatter images indicate, blanket C may be made with non-uniform polymer types that leads to non-uniform solvent uptake.

The observation of fluorescence into the blanket is limited only to 30 μm depth from surface side because the laser beam could not transmit to the deep part of blanket. Some other recent papers have used the ability of the CLSM to obtain "optical" cross sections (Ozaki, 2005a,2005c), but this technique does not work well for these samples because the light cannot get out of the sample. The penetration of solvents into the blanket is observed from physical cross sections. Therefore, the results presented below and for future work could be obtained with a fluorescence microscope; the "confocal" aspect of this microscope is not needed.

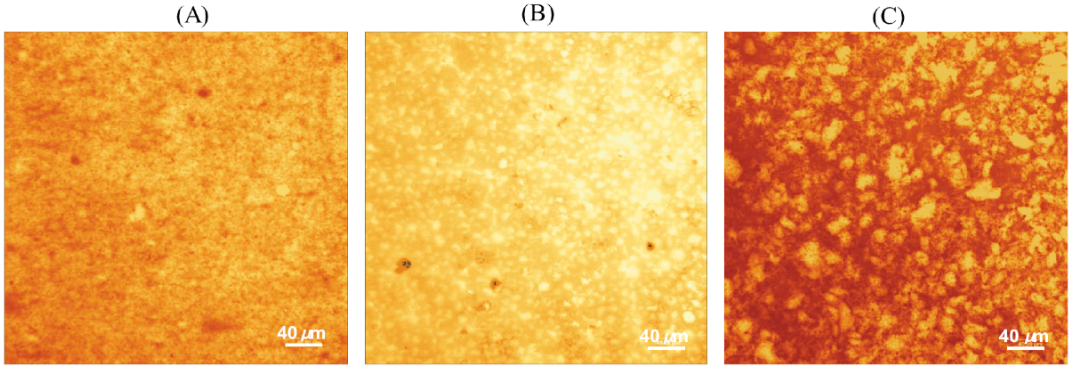

Figure 3. CLSM stack images for the three blankets. A, B and C are for blankets A, B and C, respectively.

Figure 4 shows the CLSM images of blanket A cross section 72 hours after contact with toluene. The reflected image represents the shape of blanket from the Z-stack image in Fig.4A. Sharp cross section images are obtained from the Z-stack image of reflected light even if a rough cross section is prepared with scissors. Rubber and the reinforced cloth are observed in the blanket. The thickness of the rubber layer of blanket-A is measured to be 380 μm The fluorescence image is expressed as the average intensity projection. The solvent penetration is observed well by the average intensity projection as in Fig.4B. Although some fluorescence spots are also observed in Fig.4B, these spots could have been generated in the preparation of cross section with scissors, but they also may come from the solvent finding defects in the interface layer. The depth profile of solvent into the blanket is characterized when the fluorescence image is overlapped with the reflected image as shown in Fig.4C. In this case, toluene arrives at the interface between rubber and the reinforcement cloth. As a result, these figures show that toluene penetrates to the depth of 380 μm in 72 hours.

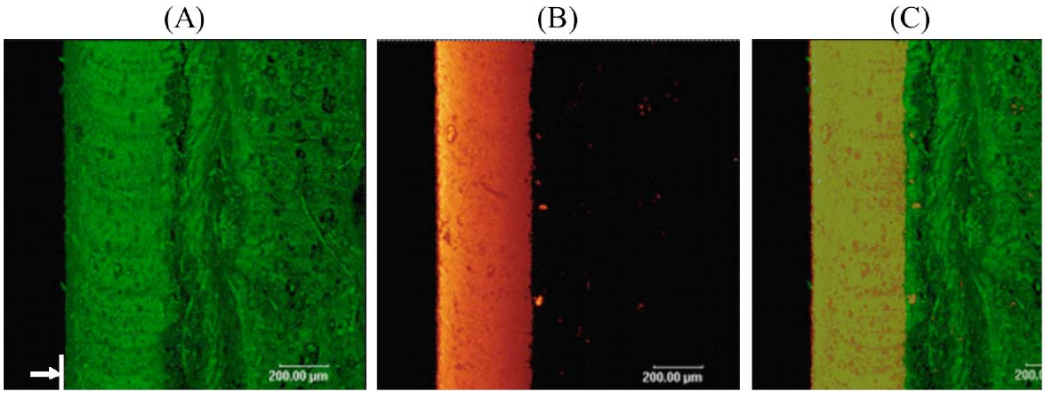

Figure 4. CLSM image of blanket A cross sections 72 hours later after contact with toluene (A) is the reflected image, (B) is the fluorescence image and (C) is the overlap of the two images.

Figure 5 shows the CLSM images of cross section of blanket A at different times after contact with toluene. The fluorescence intensity decreases within the deep part of the blanket. The figures show that the toluene gradually penetrates into the blanket. The penetration depth of solvents is not difficult to measure because the edge of fluorescence image ran parallel with the surface of blankets. This edge is rather sharp and had few signs of defects.

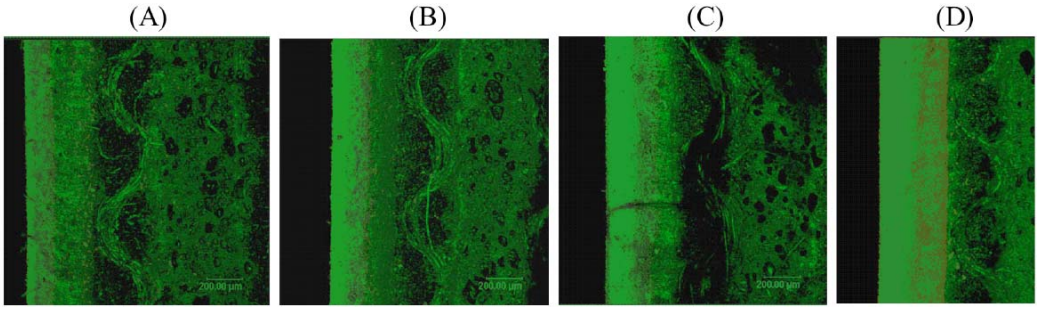

Figure 5. CLSM image of the cross section of blanket A after contact with toluene. A), B), C) and D) are 3, 11 45, and 120 hours after contact, respectively. Green is the reflected light and orange is the fluorescent light.

Figure 6 shows the relationship between the penetration depth of the three different solvents in blanket A as a function of time after contact. The solvents rapidly penetrate into the blanket for the first three hours and slowly penetrate after that time. Toluene reaches the interface between the rubber and the reinforcement cloth in 72 hours and did not penetrate beyond reinforcement cloth even after 120 hours. From the

perspective of blanket endurance and integrity, this result indicates that toluene potentially can interact with the adhesive between rubber and reinforced cloth after 72 hours. The aromatic solvent and aliphatic solvent also are able to reach the interface between rubber and reinforced cloth within 120 hours. The penetration rate of solvents in blanket A is in the order of toluene, aromatic solvent and aliphatic solvent. The penetration of all solvents resemble a diffusion type process.

Diffusion in the polymer should follow Fick's law of diffusion

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} \tag{1}$$

Where C is the concentration of solvent in the polymer, D is the diffusion coefficient, t is time and x is the distance from the surface. If a concentration of ten percent is assumed to be the position of the diffusion front, a square root relationship is obtained from the similarity solution to Eq. (1) that links the position of the diffusion front and time as

$$\delta = 2.4\sqrt{Dt} \tag{2}$$

where δ is the penetration depth. For toluene in blanket A, the diffusion coefficient that fits the results is on the order of 10^{-13} m^2/s. This value seems reasonable for diffusion in a polymer. The solid line in Fig. 6 shows the predictions of Eq. (2). The aliphatic diffusion coefficient is over an order of magnitude less than the toluene. The results in Fig. 6 indicate that there may be some physical absorption at short times before diffusion controls the results. At long times, the solvent penetration stops at the cloth-rubber interface and Eq. (2) no longer is valid.

The behavior of solvent penetration into blanket-A indicates that the Nile Red did not separate from solvents but moves with solvent in the blanket. As solvents on blanket are wiped after 60 seconds, it is expected that the behavior of solvent penetration depends on the amount of solvent in the initial penetration: there is not fresh solvent applied to continue the motion of the dye. Therefore, the solvent penetration could be observed by the stain technique with CLSM observation.

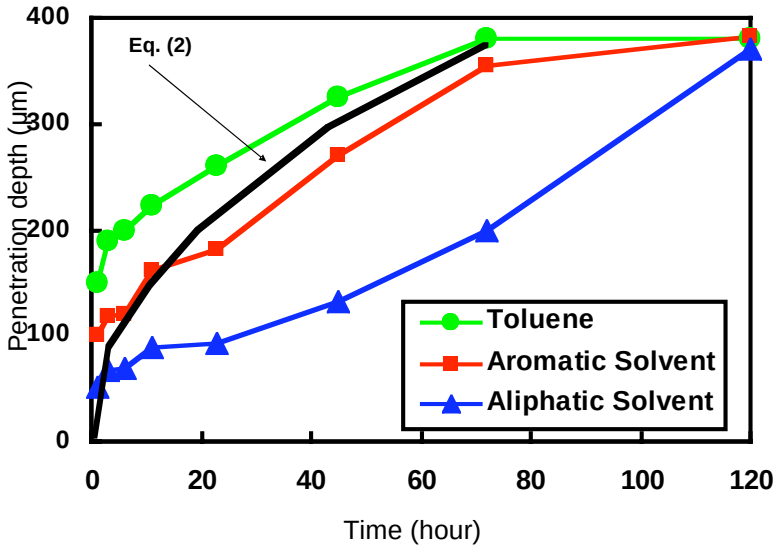

Figure 6. Relationship between penetration depth of solvents in the blanket-A and time. The solid line is the results from Eq. (2) with a diffusion coefficient of 10^{-13} m^2/s.

Figure 7 shows the relationship between penetration depth of toluene and time after contact for the different blankets. As the thickness of rubber in each blanket is different, the arrival times of solvents to the interface between rubber and reinforcement cloth are different. The penetration rate of toluene in the blankets are in the order of blanket B > A > C. The open pores in the surface of blanket B may help hold or start the diffusion process. These pores could help the diffusional process for blanket B. The high average density materials in blanket C could act to slow diffusion as the BS image in Fig. 1C indicates.

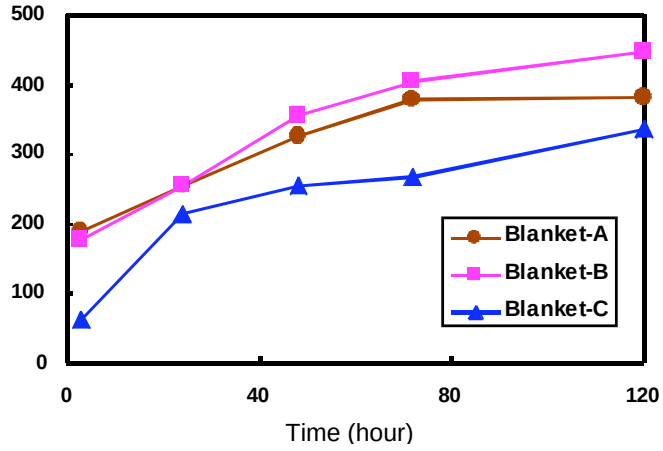

Figure 7. Relationship between penetration depth of toluene and the holding time

Figure 8 shows the dynamic contact angle of toluene on each blanket. Blanket A has the lowest contact angle. Blanket-B has the highest contact angle; this contact angle again may be a result of the porous nature of the surface. Blanket B did show a rapid decrease in the contact angle at short times: this result comes from the uptake of the toluene into the blanket at these short times. These results indicate that the wettability between toluene and blanket surface does not affect the penetration of toluene into blanket. The different surface textures can have a large influence on the contact angle.

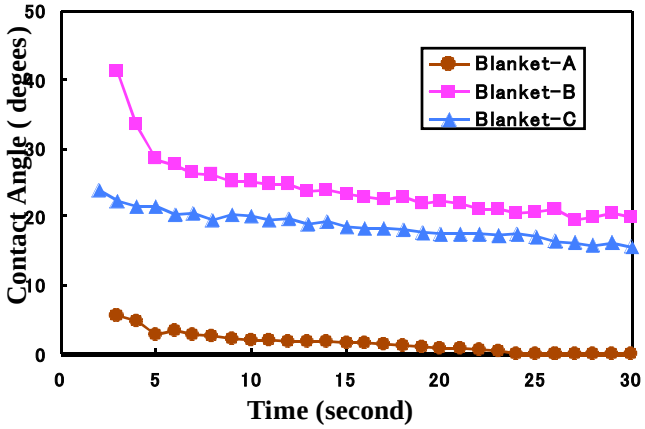

Figure 8. Dynamic contact angle of toluene on each blanket

Figures 9 and 10 show the penetration of aromatic solvent and aliphatic solvent into the three blankets. The rate of penetration of these solvents into the different blankets is similar to the results of toluene. All three solvents penetrate the fastest into blanket B. Blanket C was the slowest for all solvents and in fact, the aliphatic solvent did not penetrate into blanket C at all. The reason for this result is not clear but may be linked to the solvent-polymer interaction. The morphology of the blanket and the filler content in blanket rubber has a strong affect the penetration of aliphatic solvent.

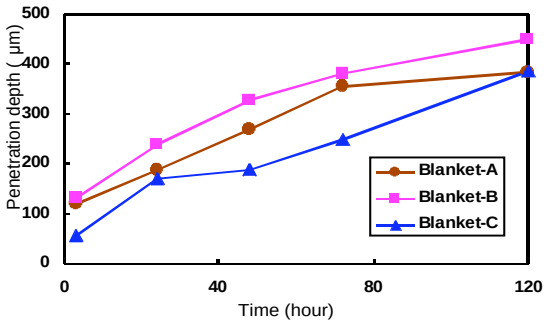

Figure 9. The relationship between penetration depth of aromatic solvent and time.

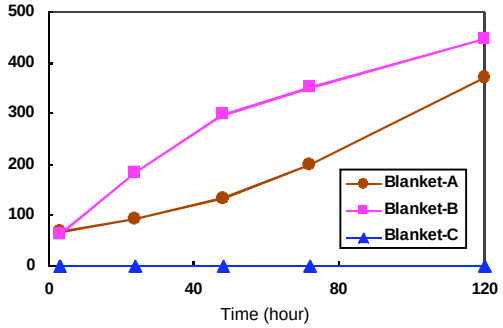

Figure 10. The relationship between penetration depth of aliphatic solvent and time.

Another open question is the influence of nip pressure and temperature on solvent penetration. This could be studied by contacting the blanket and the stained solvent in a rolling nip type device. After some time, the experiment could be stopped and the blanket cut to be imaged in the microscope. The confocal aspect of the microscope is not needed because physical cross-sections are taken here, but the fluorescence part of the technique is still needed.

Conclusions

A method to trace solvent penetration into blanket materials using a fluorescent dye and a confocal laser scanning microscope is developed. The method characterizes the rate of solvent uptake and can work for a range of blankets and solvents. The uniformity of solvent distribution in the top blanket layer can be observed. The depth of penetration is quantified by imaging physical cross sections.

Different blankets had different interactions and rates of uptake for different solvents. The depth of solvent penetration follows a square-root of time form. The rate of penetration did not correlate to the contact angle between the solvent and the blanket. These results indicate a diffusion type mechanism for solvent uptake and not absorption.

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