APPLICATION OF NANO-FIBRILLATED CELLULOSE AS A PAPER SURFACE TREATMENT FOR INKJET PRINTING

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ABSTRACT

A new method is proposed to increase the print density of inkjet prints by application of a layer of nano-fibrillated cellulose (NFC) to the base sheet of an uncoated woodfree fine paper treated with AKD. The hydrophilic NFC surface holds the inkjet pigments at the surface while the AKD acts as a barrier to liquid penetration. A combination of NFC and AKD gave higher print densities and at the same time reduced print-through compared to papers treated with AKD only. CLSM images confirm that ink spreading on and penetration in untreated samples is greater than the AKD samples. For the untreated samples, the ink covered the paper surface almost uniformly with a few areas where the ink did not cover. For the AKD samples, the ink droplets contracted on the hydrophobic surface, giving poor coverage as shown by the large number of uncovered areas.

INTRODUCTION

In inkjet printing, inks impact the paper surface in specific locations to form an image. Recent trends for short run high speed printing with inkjet technology increases the demand for a low cost paper that gives good printing results. The goal of this work is to explore the potential of NFC as a coating to improve inkjet print quality.

Absorption of inkjet inks by uncoated papers often leads to a number of print quality problems. For uncoated, unsized papers, the inks are in contact with wood fibers that promotes fluid penetration into the sheet. This penetration leads to low print density and high "print through." Papers intended for inkjet printing are often sized to reduce ink penetration, but too much sizing may also lead to a decrease in print density. Therefore, it may be beneficial to investigate a new method to reduce penetration of inkjet inks into uncoated papers while at the same time improving its print quality. For inkjet printing, it would be ideal for the paper to have a hydrophilic surface that can absorb the ink and spread in a uniform manner over the surface, and a hydrophobic interior to prevent ink penetration and print through.

In recent years, nano-fibrillated cellulose (NFC) has shown some potential for use in areas such as papermaking and coating processes [1-3], as well as a reinforcing component for polymers composites [4-5]. Cellulose nano-fibers can be produced either chemically or mechanically. Chemical methods include: acid treatment of wood fibers or micro-crystalline cellulose to give uniform nano-crystalline cellulose [6]. Mechanical methods usually consist of disintegrating wood fibers in a homogenizer under high pressure, after which the fibers are broken down into fibrils with diameters on the order of 20 nm [3]. Another method that uses both a chemical treatment followed by a mild mechanical method is TEMPO-mediated oxidation method for mechanically treated wood fibers [7, 8].
Hamada and coworkers showed that NFC coated onto synthetic fiber sheets, alone or mixed with kaolin did show a nice improvement in print density for these samples when printed with a laboratory flexographic press using water based inks [3,9]. The NFC layer, when applied at a high enough amount,

was able to capture ink pigments and hold them at the surface of the paper. The improvement for dye based inks was much less.

Inkjet inks spread or contract depending on the surface free energy of the paper. The hypothesis is that the inks contract on the less absorbent or hydrophobic surface, giving a lower observed print density. In this work, we propose that it is possible to increase the print density of AKD sized papers by adding a layer of hydrophilic NFC to the hydrophobic AKD papers. The sizing should provide the paper with a lower ink penetration and minimize print through and the hydrophilic NFC layer should give better ink spreading on the paper surface, leading to higher print densities.

EXPERIMENTAL PROCEDURE

AKD Treatment of Paper

A commercial woodfree fine paper was treated with a 1% solution of pure AKD wax (Raisares A, Ciba) in hexane with the purpose of creating a hydrophobic surface without changing the pore structure. The base paper has some internal sizing that gives a contact angle of near 90°. Following immersion of the samples in the AKD solution for ten seconds, the samples were left in a fume hood to allow the hexane to evaporate, and then oven cured for five minutes at 105°C. The control samples, without AKD or heat treatment, are referred to as the "0% AKD" samples. Samples treated with the 1% solution of AKD in hexane are referred to as "1% AKD."

Inkjet Printing Procedure

A desktop ink jet printer (X9350, Lexmark) was used to apply inks to the substrate. Pigment and dye-based magenta inkjet inks were provided by VTT Technical Research Centre of Finland. About 5 mL of each type of ink was injected into separate ink cartridges, and was allowed to sit for approximately 24 hours. This was done so that the sponges in the cartridges became fully saturated with ink. A "solid" area and a "gradient-filled" area were printed on an uncoated woodfree paper of different absorbency as changed by AKD treatment. Figure 1 shows the solid and gradient-filled areas that were printed. Print density was measured on the solid areas, but not on the gradient-filled areas. A microscope (Nikon) equipped with a camera was used to analyze the prints. The print density was measured with a standard reflection densitometer (Cosar, Graphic Microsystems).

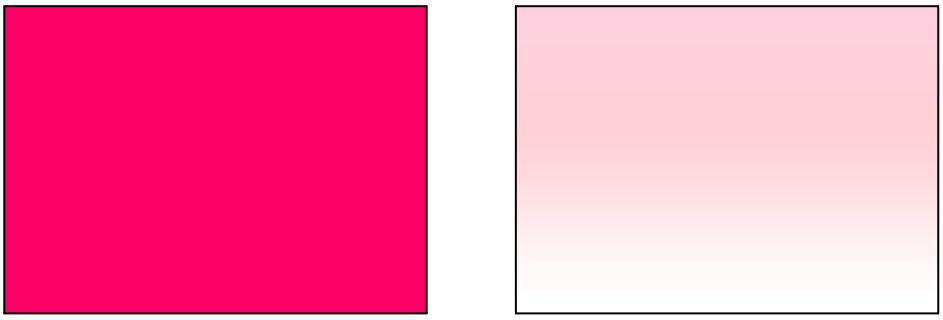


Figure 1. Solid area (left) and gradient-filled area (right) printed on 0% AKD and 1% AKD woodfree paper.

Application of Nano-Fibrillated Cellulose

The nano-fibrillated cellulose (NFC) suspension is obtained from a bleached softwood kraft fiber. The NFC was prepared by a pre-treatment method followed by mechanical treatment using a pilot-scale

refiner by the University of Maine Process Development Center. The pre-treatment is not essential to produce nano-scale material but reduces the energy need. Figure 2 shows FE-SEM images of the NFC suspension from Hamada and Bousfield [9], along with its viscosity-shear rate curve. They reported the width of an individual fiber to be about 20 nm. The viscosity of the NFC suspension was measured with a cone-and-plate rheometer. The initial solids content of the NFC suspension was approximately 3.5%. It is important to note that even at such a low solids content, the viscosity of the NFC suspension has a high initial viscosity at 1000 Pa·s and exhibits a clear shear-thinning behavior at high shear rates. A layer of NFC was applied at different coat weights by adjusting the gap of a wire-rod coater (RK Print Coat Instruments, UK) after which the samples were dried for about five minutes using heat lamps. A "3" rod was used throughout the coating experiments. NFC coat weight ranged from 2.0 to 5.0 g/m^2, based on differences in air-dried weight before and after coating. The samples were then calendered at 50°C, with a nip load of 100 kN/m. Some uncoated samples were also calendered as another control. Lastly, printing was done on a desktop printer as previously described.

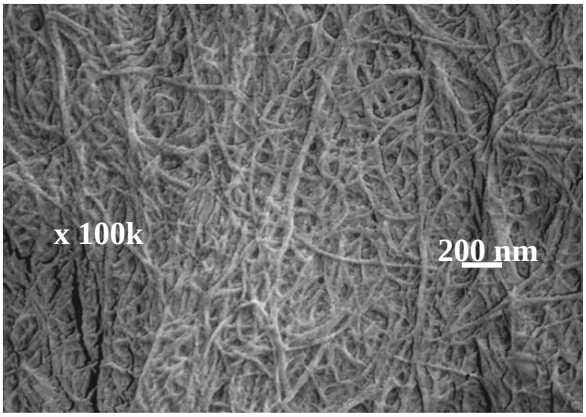


Figure 2 FE-SEM image of NFC (left) and its viscosity curve (right) from Hamada and Bousfield [9].

Quantifying Ink Distribution and Penetration using CLSM

Absorbance and fluorescence spectra of the pigment and dye-based magenta inks were measured to confirm that the inks were fluorescent. The inks were diluted with deionized water to approximately 0.10% before the absorbance measurements, since the original inks were simply too dark for any type of measurement. Figure 3 (left) shows the absorbance spectra of the diluted inks. Based on the maxima peaks, we can determine the excitation wavelength to use for the fluorescence measurements. For the fluorescence measurements, about 20 μL of each undiluted ink was placed on glass slides and was dried for 24 hours. Fluorescence spectra (Figure 3, right) were obtained using an excitation wavelength of 532 nm from the Argon laser. Based on these figures, we confirm the inks may be used as received and no additional fluorescent dyes are needed.

A confocal laser scanning microscope (Lecia TCS-SP2) was used to quantify ink distribution and penetration into uncoated woodfree paper before and after AKD treatment. A 63x oil-immersion lens was used as the objective lens. Confocal images in the z-direction were obtained with the series scan feature, using a step size of 0.80 μm. The total penetration depth scan was approximately 38 μm. After each sequential scan, the images were reconstructed and analyzed for ink penetration using the Leica software.

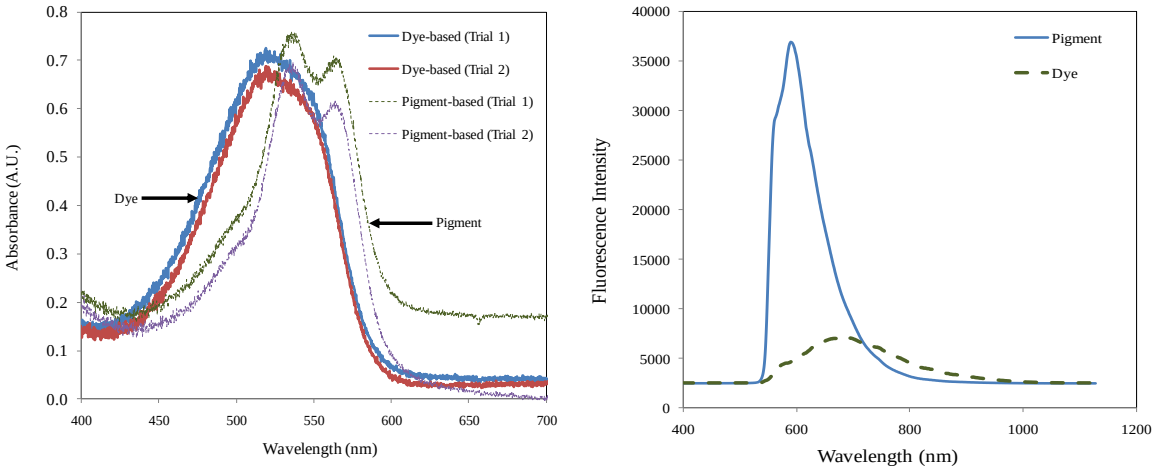


Figure 3. Absorbance spectra of the dye and pigment based inks (left) and its corresponding fluorescence spectra (right).

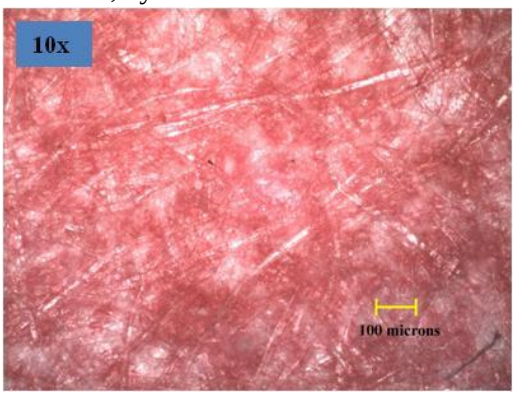
RESULTS AND DISCUSSION

Figure 4 shows optical images of solid areas printed on the 0% AKD and 1% AKD woodfree paper. For the untreated samples, both types of inks cover the fibers more than the AKD treated fibers. The print density is higher for the untreated samples for both inks as reported in Table 1. Also, for the AKD samples both types of inks do not appear to penetrate into the sheet as much as the untreated samples, but rather spread along edges of the fibers. We also see that the dye-based ink covers the AKD treated fibers more than the pigment-based ink, and that the pigment ink forms more uniform dots. A hypothesis is that the ink dots tend to contract on surfaces with high contact angle, as is the case for the AKD treated sample, therefore, giving a low print density. Conversely, the ink dots spread excessively on surfaces with low contact angle, as is the case for the untreated sample. This behavior does correlate with the contact angle and surface energy measurements shown by Luu et al. [10].

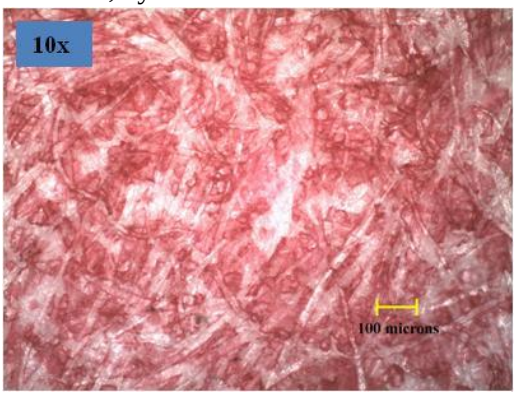
Table 1 summarizes the print density of the solid areas. It is evident that the paper surface energy has a dominant effect on the spreading and penetration of inkjet inks. This behavior is different from flexographic printing in that the pigments in water-based flexo inks is quickly immobilized on the paper surface and the print density is limited by the amount of ink transferred, which is proposed to be a function of the ink filtercake.

Figure 5 shows examples of ink dots formed on the 0% AKD and 1% AKD surfaces. At 40x magnification, it can be seen that both types of ink dots spread on the hydrophilic surface, giving higher area coverage. On the other hand, the dots contract on the hydrophobic surface and do not spread along the fibers, which should lead to lower area coverage and print density. Furthermore, dots formed with the dye-based ink are not as uniform as the pigment ink dots. The pigment ink dots appear to form a "ring" at the edge of the dot, which may be attributed to the fact that the pigments are concentrated at the outer edge of each drop. This again confirms that the AKD layer on the fibers is limiting ink penetration.

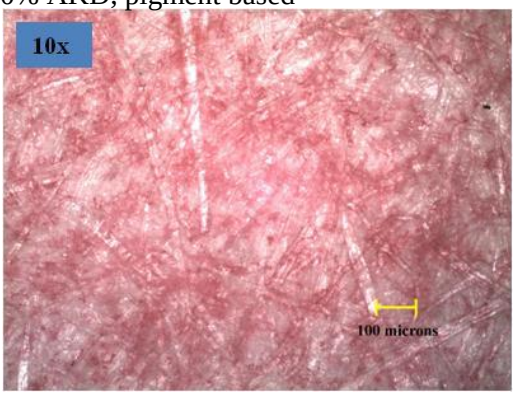
0% AKD, dye based



1% AKD, dye based



0% AKD, pigment based



1% AKD, pigment based

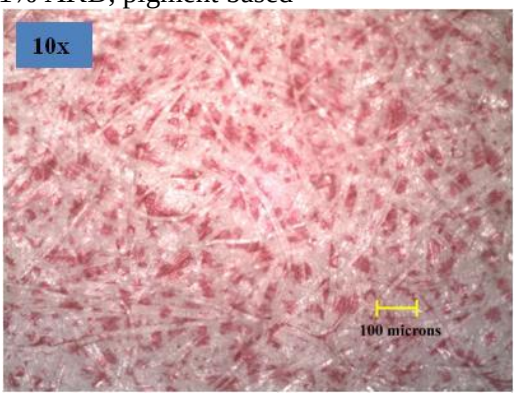


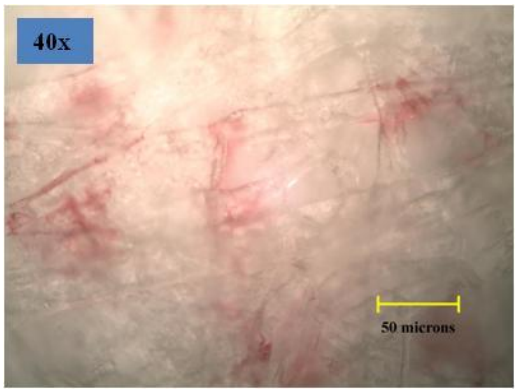
Figure 4. Solid area printed on untreated AKD woodfree paper using dye-based (top) and pigment-based (bottom) ink-jet inks. A 10x objective lens was used.

Table 1 Print density of solid area prints

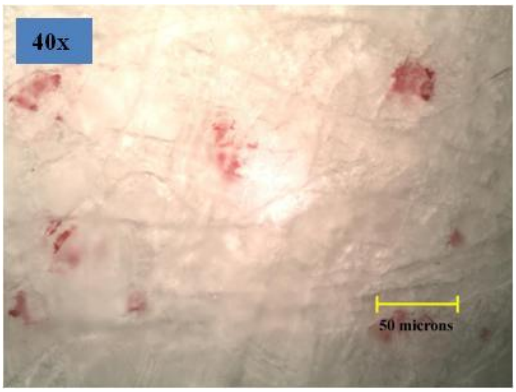
Sample	Dye-based	Pigment-based
0% AKD	0.71 ± 0.01	0.43 ± 0.01
1% AKD	0.59 ± 0.02	0.33 ± 0.01

Figure 6 shows optical images of solid areas printed with dye-based ink on two different paper samples: one with AKD size and the other with both AKD size coated with a NFC layer. After applying about 1.9 g/m^2 NFC to the 1% AKD sample, the ink covers the surface uniformly and gives an increase in print density. This ink spreading behavior after NFC treatment is also shown in Figure 6. Similar experiments were done on "gradient" prints and the same effects of AKD and NFC on ink spreading were observed. We propose that the hydrophilic NFC layer absorbs the ink droplets quickly, but at the same time, the AKD layer acts as a barrier to ink penetration. The ink is trapped at the paper-NFC surface, but does not "bead up" as is the case for paper treated with AKD only.

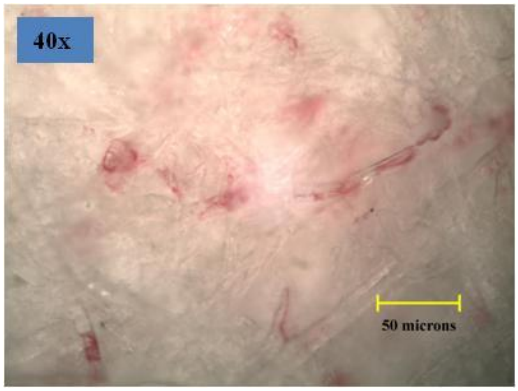
0% AKD, dye based



1% AKD, dye based



0% AKD, pigment based



1% AKD, pigment based

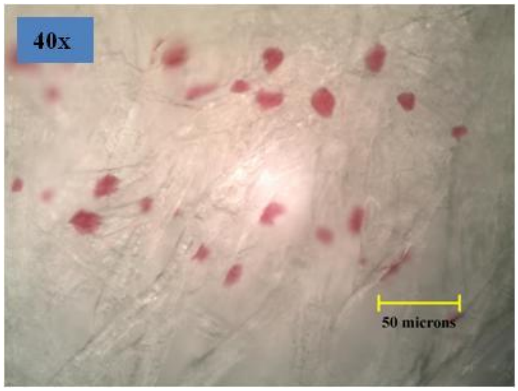
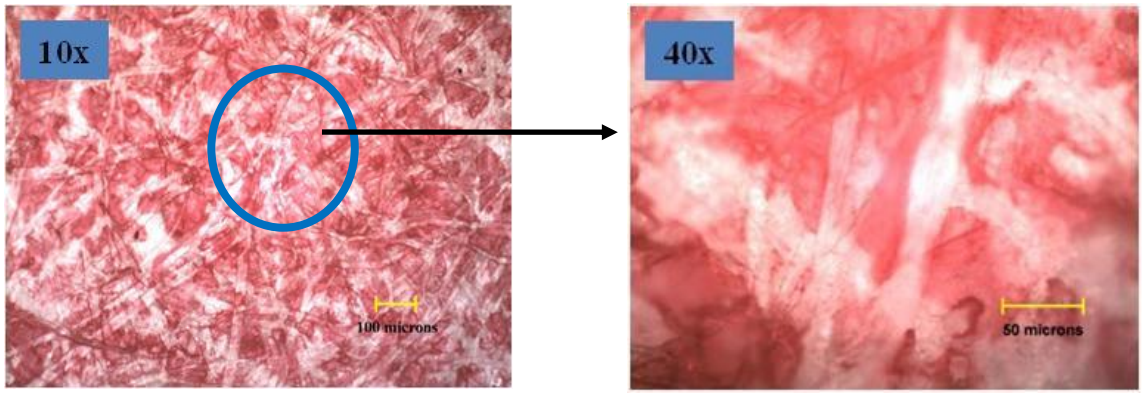


Figure 5. Gradient-filled area printed on untreated AKD woodfree paper using dye-based (top) and pigment-based (bottom) ink-jet inks.

1% AKD, calendered



1% AKD with 1.9 g/m^2 NFC, calendered

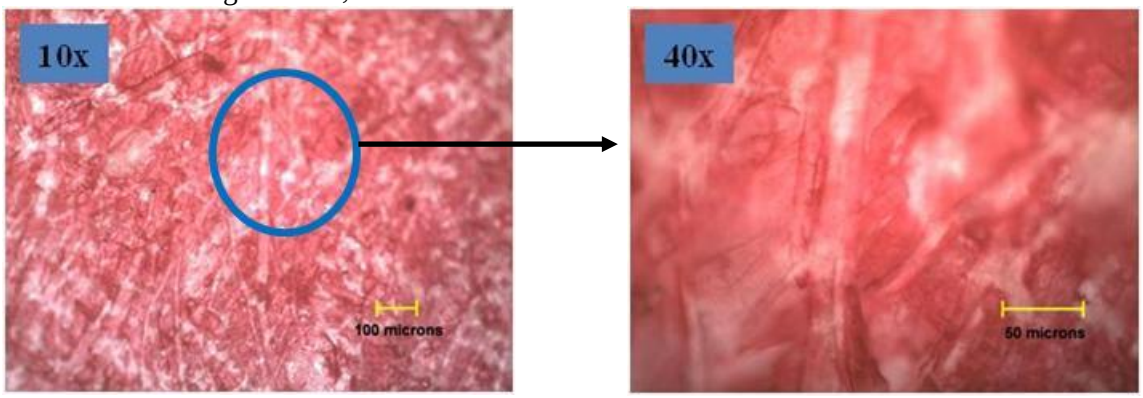


Figure 6. Images showing increased ink spreading along the fibers after application of NFC: (top) 1% AKD with calendering; and (bottom) 1% AKD with 1.9 g/m^2 of NFC and calendering.

Figure 7 shows the print densities of the dye and pigment-based inks for the different samples. Notice that the print density of the dye-based ink decreased from 0.76 to 0.63 after AKD size (without calendering), confirming our previous results where we showed that the ink dots actually shrink on the hydrophobic AKD treated fibers, which would explain the lower print density. After calendering of the 1% AKD sample, the print density increased from 0.63 to 0.74, confirming the previous linerboard study [10] where we demonstrated that print density increased with smoothness. After applying a NFC layer (about 2 g/m^2) to the AKD sample, the print density increased to 0.83. The slight drop in print density at 5 g/m^2 NFC coat weight, within error, suggests that the print density has reached the saturation value and additional NFC should not increase this value. Figure 7 also shows the print density of a HP Brochure Paper (180 g/m^2), which is a high-quality coated paper. Although the print density of the uncoated woodfree fine paper is far from the value of the HP paper, this study shows there is potential to increase the print quality of uncoated inkjet paper by using NFC. The important conclusion is that the hydrophilic NFC layer on the base paper increases ink spreading but at the same time AKD sizing limited ink penetration, which minimized print through as shown in Table 2. For the pigment based ink, there is nearly no change in print density after NFC treatment and appears that the prints show a saturated print density. It is possible that the ink pigments are immobilized or trapped on the NFC layer and cannot penetrate the base sheet, therefore the print density remains nearly constant.

A drawback of using the current NFC is its high water content, which may cause fiber swelling and possibly lead to changes in fiber structure during the coating process. In future work, it will be beneficial to develop methods to remove the excess water from the NFC but at the same time still be able to coat the paper surface.

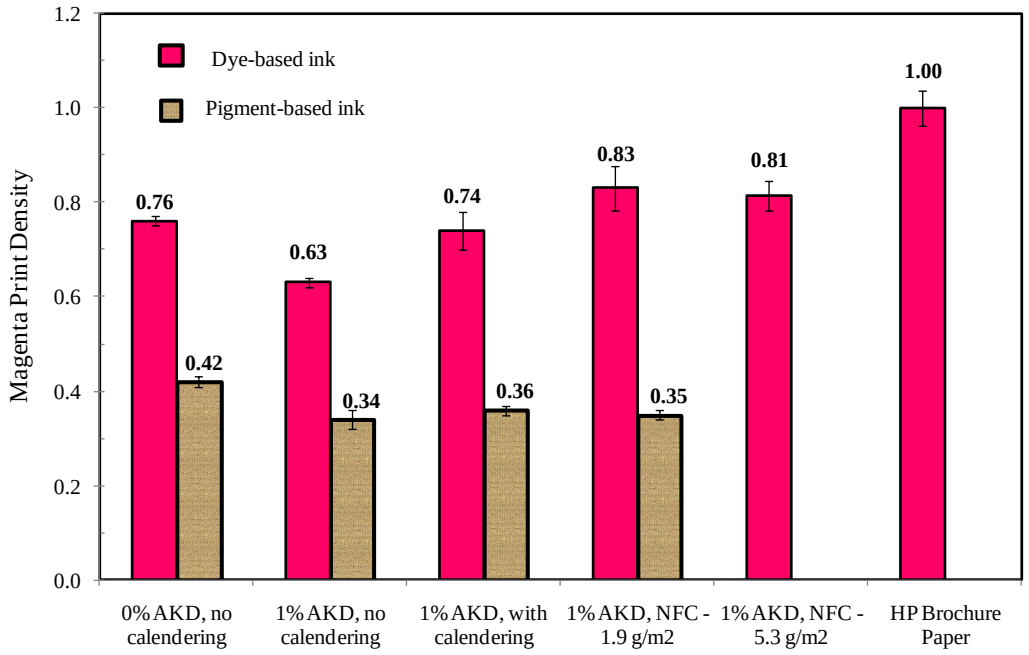


Figure 7. Print densities of solid area prints for dye and pigment-based inks.

Table 2 Print density of the solid area prints for the dye-based ink

Sample	0% AKD, no calendering	1% AKD, no calendering	1% AKD, calendered	1% AKD with 1.9 g/m^2 NFC, calendered
Printed Side	0.76 ± 0.01	0.63 ± 0.02	0.74 ± 0.03	0.83 ± 0.05
Reverse Side*	0.041	0.019	0.021	0.017

**Standard deviation of the reverse side PD ranges from ± 0.007 to 0.009*

Confocal laser scanning microscope (CLSM) results are shown Figure 8. This indicates the distribution of the dye-based ink jet inks on the uncoated woodfree paper before AKD treatment. The image on the left is an XY stack profile image calculated by the CLSM software. The image on the right is a 3D topography image calculated in a similar manner as the stack profile. The brighter areas represent the higher spots, and the darker areas are lower spots or pits. For the untreated sample the ink covers the paper surface nearly uniformly; however, there were a few low areas where the ink did not cover. The ink dots spread on the low contact angle surface, giving a high print density. The dark area on the upper left corner is a pit or low spot, as evidenced by the height surface profile shown in Figure 9. The height profile corresponds to the line drawn across the 3D image.

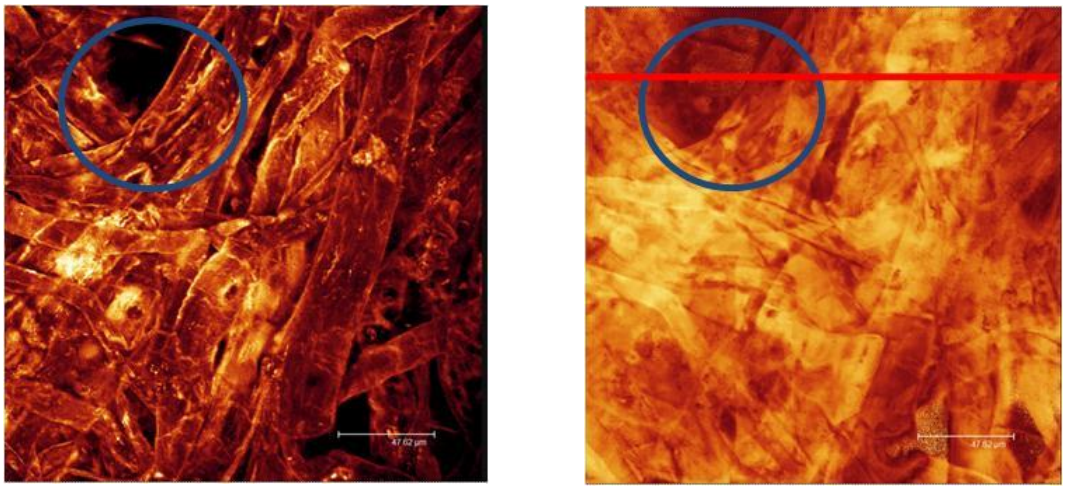


Figure 8. (Left): Stack profile image of the untreated sample printed with the dye-based ink-jet ink. (Right): 3D image of the same sample. The scale bars are 47.62 μm.

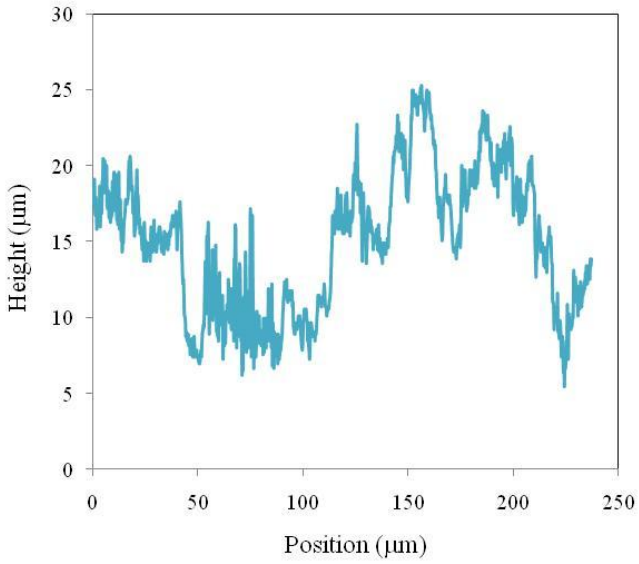


Figure 9. Surface profile of the pit shown in the 3D image from Figure 8.

Figure 10 shows the corresponding confocal images for the AKD woodfree sample. The hydrophobic surface has a dramatic effect on the spreading of the dye-based ink, giving poor dot coverage as evidenced by the larger number of uncovered areas shown in the left image. Similar trends were observed for the pigment-based inks, but the confocal images are not shown in this work.

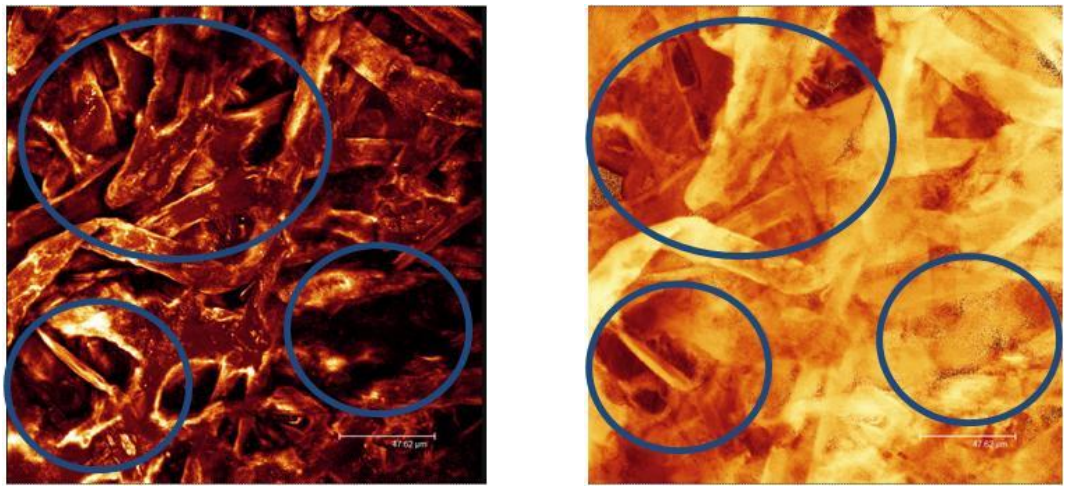


Figure 10. (Left) Stack profile image of the 1% AKD sample. (Right): 3D image of the same sample. The scale bars are 47.6 μm.

Figure 11 shows examples of fluorescence intensity profiles of the dye and pigment-based inks as a function of penetration depth for the untreated and AKD samples. The maximum fluorescence intensity and the penetration depth at which it occurs are summarized in Table 3. The AKD size reduced the maximum fluorescence signal. The lower intensity of the 1%AKD sample does seem to correlate to the lower print density and print-through for the AKD sample shown in Table 2. One unexpected result is that the AKD treated samples still give a broad peak in these curves while visual observation of the samples indicate that the dye and pigment are all at the surface of the sample. We currently do not have an explanation for the broad peak observed in the AKD samples.

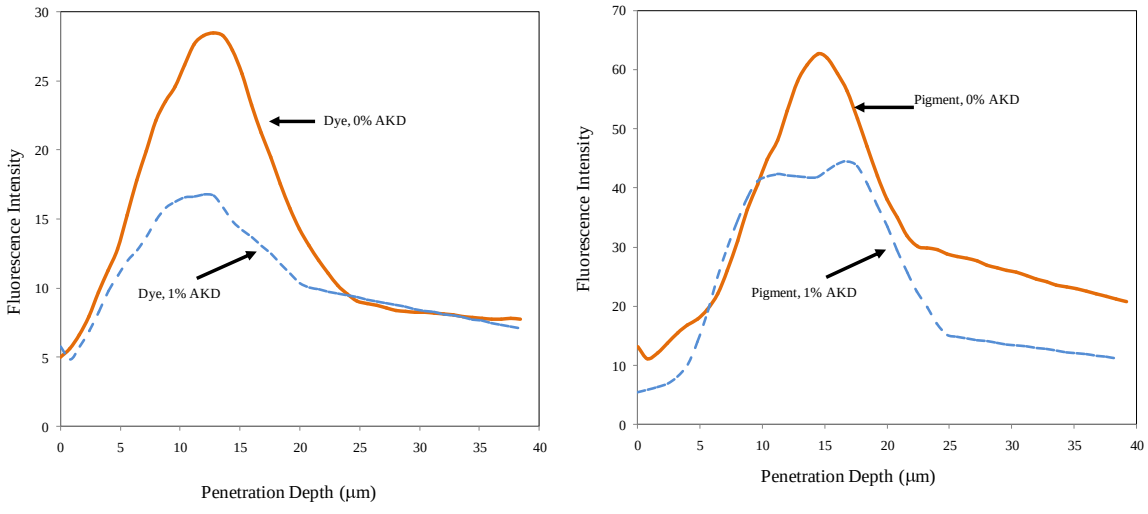


Figure 11. Penetration profiles of dye-based ink-jet ink (left) and pigment-based ink (right) in the untreated and AKD woodfree papers.

Table 3. Maximum intensity and penetration depth of the dye-based ink in the untreated and AKD woodfree papers.

Sample	Maximum Intensity	Penetration Depth (μm)
0% AKD	28.49	12.54
1% AKD	16.80	11.76

The presence of the NFC layer helps ink spread on a hydrophobic base paper. The ink drops are unable to retract and leave exposed areas of paper that lead to a decrease in print density. The NFC layer allows the spread of ink into lower regions of the paper surface. The NFC layers were not able to stop the movement or penetration of pigment or dye deeper in the paper surface. Even when the paper is hydrophobic, pigments and especially dyes do penetrate a significant amount. The hydrophobic base paper does help reduce print through.

SUMMARY

A new method to improve the print quality of ink-jet printed samples was explored. The method involved applying a layer of nano-fibrillated cellulose to the woodfree base sheet treated with AKD. The hydrophilic NFC surface helps the drops to spread in a controlled manner and not retract. This gives some improvement in the ink density in solid fill areas. The AKD treatment limits liquid penetration and reduces print-through. Pigments and dyes were able to penetrate through these NFC layers. The combination of NFC and AKD gave a higher print density and at the same time reduced print-through compared to samples treated with AKD only.

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REFERENCES

1. Schlosser, H. “Nano-disperse Cellulose and Nano-Fibrillated Cellulose – New Products for Paper and Board Manufacture and Coating.” IPW. (9). 2008: 41-44.

2. Mörseburg, K., and Chinga-Carrasco, G. “Assessing the Combined Benefits of Clay and Nanofibrillated Cellulose in Layered TMP-Based Sheets.” Cellulose. (16). 2009: 795-806.

3. Hamada, H., Beckvermit, J., and Bousfield, D.W. “Nanofibrillated Cellulose with Fine Clay as a Coating Agent to Improve Print Quality,” TAPPI Coating Conference, PAPERCON, 2010.

4. Zimmermann, T., Bordeanu, N., Strub, E. “Properties of Nanofibrillated Cellulose from Different Raw Materials and its Reinforcement Potential.” Carbohydrate Polymers. (79). 2010: 1086-1093.

5. Gardner D.J., Oporto, G.S., Mills, R., Samir, A.S.A. “Adhesion and Surface Issues in Cellulose and Nanocellulose,” Journal of Adhesion Science and Technology. (22). 2008: 547-567.

6. Araki, J., Wada, M., Kuga, S. and Okano, T.: Colloids Surfaces, A: Physicochem. Eng. Aspects, 142, 75-82 (1998).

7. Saito, T., Nishiyama, Y. Putaux, J. L., Vignon, M. and Isogai, A.: Biomacromolecules, 7, 1687-1691 (2006).

8. Saito, T. and Isogai, A.: Cellulose Commun., 14, 62-66 (2007).

9. Hamada H., and D.W. Bousfield, “Nano-fibrillated cellulose as a coating agent to improve print quality of synthetic fiber sheets”, Proc. Technical Association of Pulp and Paper Advanced Coating Fundamentals Symposium, (2010).

10. Luu, W.T., Kettle, J., Aspler, J., and Bousfield, D.W. “Influence of Ink Chemistry and Surface Energy on Flexographic Print Quality.” Proc. Technical Association of Pulp and Paper Advanced Coating Fundamentals Symposium, 2010.