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INFLUENCE OF MULTILAYERED FILMS CONTAINING CELLULOSE NANOCRYSTALS ON THE PROPERTIES OF JAPANESE PAPER

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Abstract: *Cultural heritage objects are precious witnesses of the past, so our mission is not only to preserve them for future generations, but also make them available or open to the public. Among most fragile historic materials are paper-based materials. They are susceptible to various forms of damage and deterioration, and their preservation presents a challenging task for conservators. In recent years, the use of advanced materials with unique properties has been growing at an increasing rate, even in the traditionally slow-changing cultural heritage sector.*
This study models how historic paper would be affected by application of multiple coating layers containing different quantities of cellulose nanocrystals (CNCs). In our study, a 4 % CNCs aqueous suspension was used to treat the samples. In order to form a uniform layer, bar-coating method was used, and in addition, a specific layer thickness was formed in both single and multiple passes. The prepared samples were analysed for their optical properties (colour coordinates, yellowness, opacity, gloss), physical properties (Taber stiffness, weight, thickness) and surface properties (roughness). An increase of wet film deposit thickness (single layer applications) resulted in an increase of paper thickness, grammage, gloss, opacity, yellowness, the ΔE value and Taber stiffness, while its average surface roughness decreased. Multi-layer applications have gradually decreased paper thickness, while Taber stiffness remained unchanged.

Key words: Cellulose nanocrystals, nanocellulose, paper conservation, Japanese paper, coatings

1. INTRODUCTION

Cultural heritage objects are precious witnesses of the past, so our mission is not only to preserve them for future generations, but also make them available or open to the public. Among most fragile historic materials are paper-based materials. They are susceptible to various forms of damage and deterioration (Aleksić, Cigula & Pasanec Preprotić, 2022), and their preservation presents a challenging task for conservators. In recent years, the use of advanced materials with unique properties, such as nanocellulose, has been growing at an increasing rate, even in the traditionally slow-changing cultural heritage sector.
The term nanocellulose (NC) refers to nanoscale biomaterials derived from cellulose – an abundant, renewable, biodegradable and sustainable material. Apart from physical and chemical properties inherited from cellulose, nanocellulose possesses other unique properties, interesting to various research fields and industries. In order to achieve its optimal performance in a specific application, nanocellulose is usually modified.
Of the three main types of nanocellulose materials (cellulose nanofibers, cellulose nanocrystals and bacterial nanocellulose), cellulose nanocrystals (CNCs) are most commonly used (Huang, Xiaozhou & Dufresne, 2019). CNCs are rod-like nanoparticles with an average length of 100 to 200 nm and a diameter ranging from 5 to 20 nm (Ngo, Danumah & Ahvazi, 2018). They are traditionally prepared by acid hydrolysis of cellulose fibres with a strong acid (Mautner et al., 2018), although alternative methods are actively being developed in recent years. As properties of nanocellulose are affected by both the cellulose source and treatment conditions (Santmartí & Lee, 2018), method development for the preparation of crystals has become an intense research topic (Kontturi, 2018).
CNCs are known for their large specific surface area, thermal stability, low density, high crystallinity, great elastic modulus (Huang, Xiaozhou & Dufresne, 2019; do Nascimento et al., 2021), excellent tensile strength (Grishkewich et al., 2017), as well as optical transparency (Huang, Xiaozhou & Dufresne, 2019). These properties make CNCs a potentially desirable material for a wide range of applications – among which is conservation of cultural heritage materials. However, successful introduction of new materials to the heritage field requires thorough analysis and validation of both short- and long-term consequences of such application, as some of the materials can damage the historic object or change its appearance.

In recent years, all three types of nanocellulose have been evaluated for several treatments in conservation of wood (Walsh et al., 2017; Hamed & Hassan, 2019; Walsh-Korb & Avérous, 2019), painting canvas (Kolman et al., 2018; Nechyporchuk et al., 2018), silk (Wu et al., 2012) and notably – paper (Dreyfuss-Deseigne, 2017; Dreyfuss-Deseigne, 2017a; Völkel et al., 2017; Ghorbani, Samanian & Afsharpour, 2018; Operamolla et al., 2021). Previous studies have shown that CNCs are a promising material for consolidation of historic paper (Operamolla et al., 2021), and a natural polymer enhancer (Li et al., 2021), also omnipresent in coatings, adhesives, and within paper and pulp industry. Although nanocellulose as a coating agent is still being widely researched, it is well known that both thickness and formula play a crucial role in its performance (Li et al., 2021). However, studies in paper conservation have been dealing more with issues such as surface functionalization and removal of CNCs (Operamolla et al., 2021) and haven't considered in detail how paper properties are affected by different amounts of CNCs present. For these reasons, we aimed to investigate how different CNC quantities and layering affect optical, physical and surface properties of paper. It is expected that different quantities of CNCs and order of application of the layers will affect properties of paper and highlight benefits and drawbacks of both single- and multi-layer application solutions.

2. MATERIALS AND METHODS

All measurements were undertaken at 25 °C and 50 % RH.
Japanese handmade paper Takogami B (43 gm^{-2}, 70 % Kozu + 30 % Pulp, felt side (Japico-Feinpapier-VetriebsgmbH)) was used as the model paper.
The NC from this study originated from tree cellulose and was supplied by Nanocrystacell as a ready-made 4 % CNC aqueous suspension (hydrophilic, 90.3 % crystallinity, 1.04 g/cm^3 density, 10 – 15 mm wide and 150 – 300 long).
pH value is a crucial parameter for successful application of new materials and its compatibility with the original materials is of utmost importance. Another parameter that requires compatibility between the materials is viscosity, which is described as the measure of a liquid's resistance to flow. Low viscosity is a desirable property of coating materials, as it enables better flow into the pores of the substrate (Horie, 1987; Conservation Unit of the Museums and Galleries Commission, 1992). However, aqueous dispersions of CNCs are known to form gels even at lower concentrations (Ngo, Danumah & Ahvazi, 2018). To characterize suspension properties, we performed pH measurements and dynamic viscosity measurements using a WTW 340 pH meter and a RheolabQC rotational rheometer (Anton Paar GmbH). The viscosity was determined in a constant shear rate mode with the value of 0.02 s^{-1}.
CNC suspension was first redispersed with a magnetic stirrer set to 1000 rpm for 5 minutes, before ultrasonication with a Hielscher UP100H homogenizer. Ultrasonic time was divided into two 5-minute cycles, with amplitude control adjusted to 100%. Although commonly utilized application methods in paper conservation include a brush, a spray or a syringe, we utilized a non-conventional coating method with controlled speed and pressure to achieve a repeatable wet film deposit (RK Print Coat Instruments, 2022). The suspension was applied onto the paper substrate with a pipette. The K Control Coater, model 202 (RK PrintCoat Instruments Ltd) was used to spread the suspension at the speed of 4 m/min. In order to obtain different wet film deposits, we used coating bars #2 (12 µm), #3 (24 µm), #5 (50 µm) and #8 (100 µm). Some samples were coated in a single pass (single layer - SL) and others by gradually applying coating layers (multi-layer - ML), as recommended (Baglioni, Chelazzi & Giorgi, 2015). After applying each layer, samples were left to air dry. The wet film deposit thicknesses and coating bars used are shown in Table 1. Weight and thickness of the dry samples were measured with a digital analytical electronic balance (Mettler Toledo XS205, sample size 38x80 mm) and an EnricoToniolo DGTB01 digital micrometer with the weight pressure of 49.03 kPa.

Table 1: Wet film deposits

	Wet film deposit (µm) / coating bar (No.)			
Single layer (SL)	12/2	24/3	50/5	100/8
Multi-layer (ML)	12/2	24/2+2	48/2+2+3	96/2+2+3+3+3

2.1 Optical properties

To determine if any of the visually undesirable effects had occurred due to the application of CNCs, we investigated the associated parameters (CIE LAB coordinates, opacity, yellowness and gloss). Yellowness is commonly mentioned in relation to paper or pulp in need of a bleaching treatment, discoloration of aging paper (Feller, 1987) and paper exposed to different conditions (Johnston-Feller, 2001), but should also be considered when applying new materials. Since Japanese paper is of natural colour (slightly yellow), we measured both yellowness (according to ASTM E313) and opacity, using a Techkon SpectroDens device with measuring geometry of 0°:45° (Techkon, 2021). The measurement settings included the following: standard illuminant D65, a standard observer angle of 10 degrees and M1 measuring conditions. The unit was calibrated to absolute white. To measure opacity, we used a standardized ChromaChecker B&W Backer, in compliance with ISO 5-4 and ISO 13655.
CIE LAB coordinates (L* a* b*) were also measured with a Techkon SpectroDens device using the following settings: illuminant D50, a standard observer angle of 2 degrees, M1 measuring conditions and the sample on a white backing. The coordinates were used to calculate the colour difference (ΔE_{ab}) (Mokrzycki & Tatol, 2011).
As excessive shine can change the overall appearance of the paper surface, it is necessary to maintain acceptable levels of gloss during the conservation treatment. We investigated gloss levels using an Elcometer 407 Statistical Glossmeter with the standard measurement angle of 60°.

2.2 Surface roughness

Gloss, among other factors, depends on surface roughness (Wang et al., 2009). Surface roughness is an important parameter in determining the amount of coating applied (Pino, Pladellorens & Colom, 2010; Alam et al., 2012), as well as the method of application (Pino, Pladellorens & Colom, 2010). As applying coating layers also changes surface properties of paper, we measured average roughness (R_a) of the samples using a MarSurf PS 10 device (Mahr Federal Inc.).

2.3 Mechanical performance

A coating layer is intended to provide a certain mechanical reinforcement of the weakened paper, although enhanced structural strength is not always the primary goal of conservation treatments. Either way, the treated paper should retain some elasticity to avoid breakage. However, stiffness of the material, also known as an elastic modulus, is described as the resistance to being deformed elastically (Conservation Unit of the Museums and Galleries Commission, 1992). To measure the stiffness of paper according to the TAPPI T 566 method, we utilized a Lorentzen and Wettre bending tester (code 160). The instrument settings included the following: touch speed of 5^{o}/s, touch force of 2 mN and bending length of 25 mm.
As reversibility of the treatment with CNCs has been established by previous studies (Operamolla et al., 2021), we didn't include it in our research. It should also be noted that actual treatment of historic paper would require an analysis of both composition and degradation status prior to the application (Baglioni, Chelazzi & Giorgi, 2015).

3. RESULTS AND DISCUSSION

All measurements were repeated for at least 6 times, and tables and figures in this section report average values and standard deviations.
The pH measurement of the suspension resulted in a neutral value (pH value = 7.32), which is recognized as safe for use in paper conservation (Henry et al., 1989). The viscosity of the 4% aqueous suspension following the ultrasonication resulted in 890.4 ± 8.1 mPa·s, which is labelled as low viscosity (Horie, 1987). To achieve good penetration into the substrate, the suspension is expected to have low viscosity, as well as high surface tension (Conservation Unit of the Museums and Galleries Commission, 1992).
As shown in Figure 1, weight and thickness of the Japanese paper used in this research varied. The initial grammage was calculated higher than specified, measuring 46.83 gm^{-2} for paper coated by SLs and 49.30 gm^{-2} for paper coated by MLs. Application of the coatings had also increased the grammage. However, an increase of grammage proved to be more dramatic in the paper containing SLs (up to 5 gm^{-2})
Although the grammage of nearly all the samples increased with layer thickness, it seems that thickness itself decreases with addition of layers (ML).

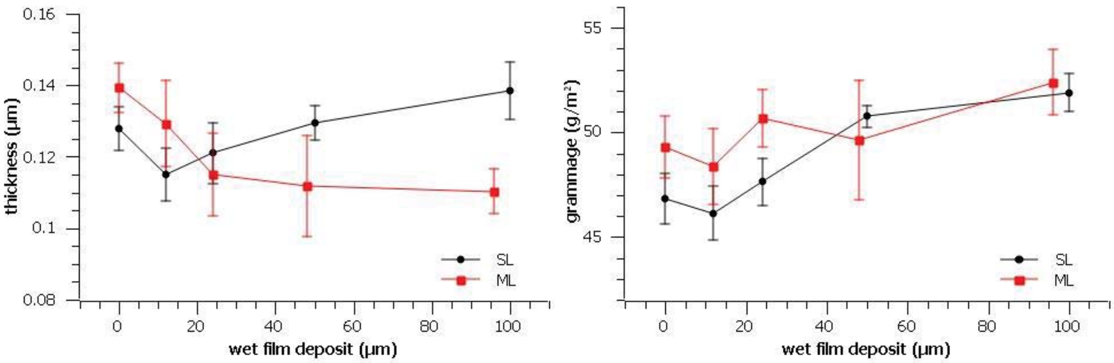

Figure 1: Changes in thickness (left) and grammage (right) of the samples in relation to wet film deposit thickness

Figure 2 shows changes in average roughness (R_a) due to the addition of coating layers containing CNCs. It seems that both SL and ML applications result in a decrease of roughness of the Japanese paper. However, when compared to the SL applications, the ML applications had decreased paper roughness more dramatically. These findings are consistent with previous results, in which ML applications had also resulted in a decrease of paper thickness.

The decrease in both thickness and average roughness of paper could be a result of the coating's penetration into the pores and crevices of the paper. In ML applications, this effect is even more dramatic, as each layer dries and forms a new surface to which the next layer is deposited.

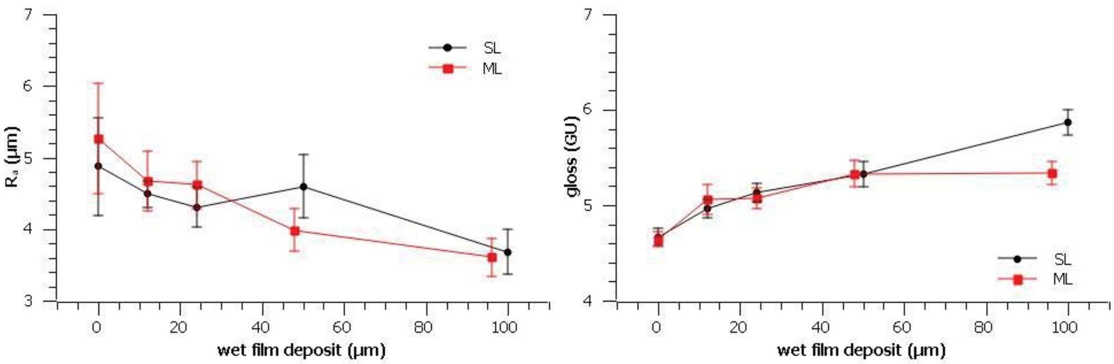

Figure 2: Average roughness R_a (left) and paper gloss (right) in relation to wet film deposit thickness

The data shown in Figure 2 indicates that both SL and ML applications have little effect on the gloss of Japanese paper. As expected, larger amounts of the CNCs will slightly increase gloss (up to 2 GUs).

Figure 3 shows that larger amounts of CNCs also result in colour changes. These changes manifest themselves in the form of darkening of the samples, causing the decrease of the CIE L* coordinate by 2 units (from 89.28 to 87.33 on paper gradually coated up to 5 times). Additionally, the colour of the samples shifted to even more yellow, causing an increase of the CIE b* coordinate by nearly 2 units (from 13.70 to 15.58 on the sample with wet film deposit of 96 µm).

Increased yellowness and darkening of the material have also been observed in other polymers used as consolidation agents of wood (Horie, 1987).

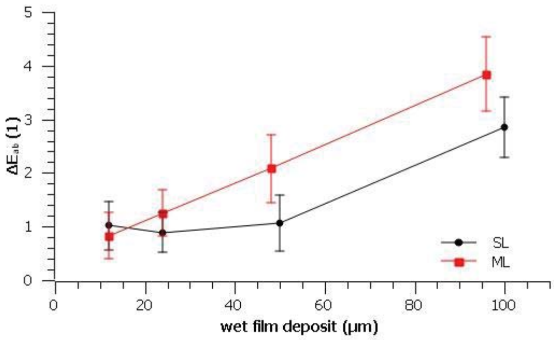

Figure 3: Color changes in relation to wet film deposit thickness

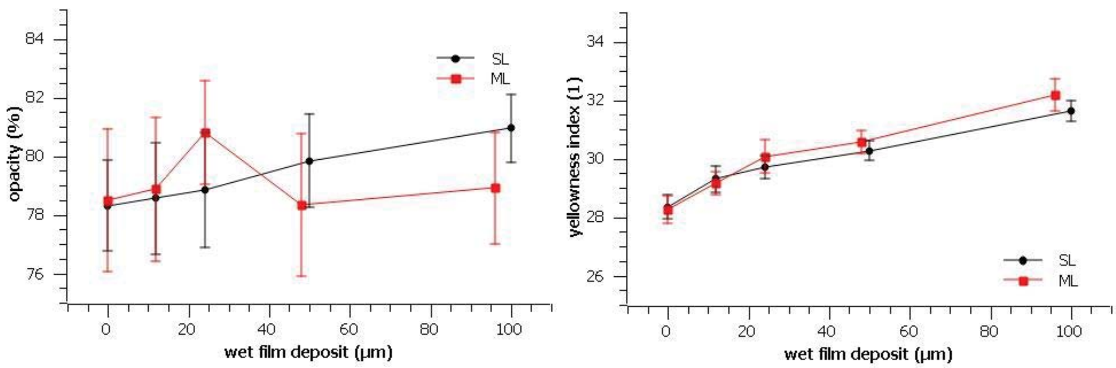

Figure 4: Opacity (left) and yellowness index (right) of the samples in relation to wet film deposit thickness

The data show that the opacity of the paper samples coated by a single layer of CNCs has increased with wet film deposit thickness but does not change for samples coated in MLs (Figure 4, left). This occurrence could be a result of better incorporation of CNCs into the paper structure, as seen in the aforementioned results for thickness and surface roughness (Figure 1, Figure 2). It should also be noted that standard deviation of the opacity measurements is larger than that of other measurements, which can be attributed to the non-uniform structure of the handmade paper.
We also observed that the yellowness index (YI) increases with the increase of wet film deposit thickness in both the SL and the ML coatings (Figure 4, right), which is consistent with colorimetric change ΔE_{ab} (Figure 3).

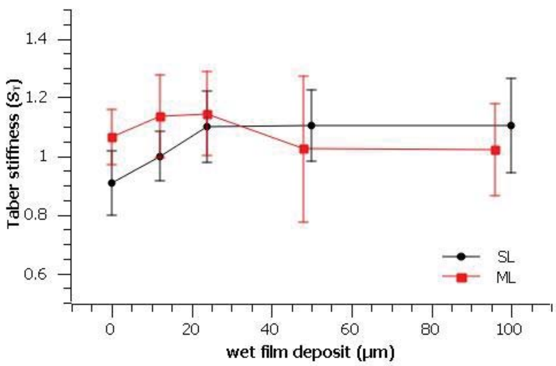

Figure 5: Taber stiffness of samples in relation to wet film deposit thickness

The results of Taber stiffness measurements shown in Figure 5 indicate that the stiffness of the samples coated by a single layer of CNCs increases up to a certain amount of the crystals added (wet film deposit of 24 µm), beyond which it remains constant. However, the stiffness of the samples decreased after the same amount (wet film deposit of 24 µm) was gradually added (MLs). It should also be noted that changes in the stiffness values of the samples vary from 0.1 S_T (ML coatings) to 0.2 S_T (SL coatings).

4. CONCLUSIONS

We conducted this research to determine the influence of different quantities of CNCs on the properties of Japanese paper, as well as benefits and drawbacks of both single- and multi-layer applications.
The results of the research showed that:

- An increase of wet film deposit thickness (SL applications) resulted in an increase of paper thickness, grammage, gloss, opacity, yellowness, the ΔE value and Taber stiffness, while its average surface roughness decreased.
- ML applications have gradually decreased paper thickness, while Taber stiffness remained unchanged. The decrease in paper thickness could be explained by penetration of the coatings into the pores and crevices of the paper. However, further research of the wetting properties and surface tension of the suspension needs to be conducted.
- The ΔE values for all coated samples did not exceed 3, which is considered the limit beyond which the human eye notices the difference. However, the ΔE values of the samples coated by a single layer of CNCs were lower compared to the ones coated by MLs.

Based on the results, it could be concluded that, although single- and multi-layer applications have affected paper properties differently in the short term, their long-term influence on paper is yet to be evaluated after performing accelerated aging tests.

5. REFERENCES

Alam, A., Manuilskiy, A., Thim, J., O'Nils, M., Lindgren, J. & Liden, J. (2012) Online surface roughness characterization of paper and paperboard using a line of light triangulation technique. *Nordic Pulp and Paper Research Journal*. 27 (3), 662 – 670. Available from: doi:10.3183/npprj-2012-27-03-p662-670

Aleksić, G., Cigula, T. & Pasanec Preprotić, S. (2022) An analysis of targeted properties of materials used for preservation and storage of heritage collections. *Journal of Graphic Engineering and Design*. 13 (1), 5 – 12. Available from: doi:10.24867/JGED-2022-1-005

Baglioni, P., Chelazzi, D. & Giorgi, R. (2015) Consolidation of Wall Paintings and Stone. In: *Nanotechnologies in the Conservation of Cultural Heritage*. 1st ed. Springer Dordrecht, pp. 15 – 59.

Conservation Unit of the Museums and Galleries Commission (1992) *The Science for Conservators Series: Volume 3: Adhesives and Coatings*. Ashley-Smith, J. (ed.) 2nd ed. Routledge.

Dreyfuss-Deseigne, R. (2017) Nanocellulose Films in Art Conservation: New and Promising Mending Material for Translucent Paper Objects.. *Journal of Paper Conservation*. 18 (1), 18 – 29. Available from: doi:10.1080/18680860.2017.1334422

Dreyfuss-Deseigne, R. (2017a) Nanocellulose films: properties, development and new applications for translucent and transparent artworks and documents. *Book and Paper Group Annual 36*. Washington DC, American Institute for Conservation, pp. 108–114. Available from: https://cool.culturalheritage.org/coolaic/sg/bpg/annual/v36/bpga36-20.pdf [Accessed 9th August 2022]

Feller, R. L. (1987) Comments on the Measurement of "Yellowness" in Pulp and Paper. In: *Book and Paper Group Annual 6*. Washington, D. C., United States, American Institute for Conservation, pp. 40–51. Available from: https://cool.culturalheritage.org/coolaic/sg/bpg/annual/v06/bp06-04.html [Accessed 9th August 2022]

Ghorbani, M., Samanian, K. & Afsharpour, M. (2018) Mechanical properties of Bacterial cellulose Nanofibers bio-composite as a long-lasting coating on the paper works. *International Journal of Conservation Science*. 9 (3), 389 – 400.

Grishkewich, N., Mohammed, N., Tang, J. & Chiu Tam, K. (2017) Recent advances in the application of cellulose nanocrystals. *Current Opinion in Colloid and Interface Science*. 29, 32 – 45. Available from: doi:10.1016/j.cocis.2017.01.005

Hamed, S. A. A. K. M. & Hassan, M. L. (2019) A new mixture of hydroxypropyl cellulose and nanocellulose for wood consolidation. *Journal of Cultural Heritage*. 35, 140 – 144. Available from: doi: 10.1016/j.culher.2018.07.001

Henry, W. (1989) Adhesives. In: *Paper Conservation Catalog*. Washington, D. C., American Institute for Conservation Book and Paper Group, pp. 1 – 127. Available from: https://cool.culturalheritage.org/coolaic/sg/bpg/pcc/46_adhesives.pdf [Accessed 10th April 2022]

Horie, C. V. (1987) *Materials for conservation: Organic consolidants, adhesives and coatings*. Rees-Jones, S.G. & Linstrum, D. (eds.) 2nd ed. London, Routledge.

Huang, J., Xiaozhou, M., Yang, G. & Dufresne, A. (2019) Introduction to Nanocellulose. In: Huang, J., Dufresne, A. & Lin N. (eds.) *NanoCellulose: From Fundamentals to Advanced Materials*. Wiley-VCH, pp. 1 – 20.

Johnston-Feller, R. (2001) *Color science in the examination of museum objects: nondestructive procedures*. Los Angeles, Getty Conservation Insitute.

Kolman, K., Nechyporchuk, O., Persson, M., Holmberg, K. & Bordes, R. (2018) Combined Nanocellulose/Nanosilica Approach for Multiscale Consolidation of Painting Canvases. *ACS Applied Nano Materials*, 1 (5), 2036 – 2040. Available from: doi:10.1021/acsanm.8b00262

Kontturi, E. (2018) Preparation of Cellulose Nanocrystals - Background, Conventions and New Developments. In: K.-Y. Lee (ed.) *Nanocellulose and Sustainability: Production, Properties, Applications and Case Studies*. 1st ed. CRC Press, pp. 27–44.

Li, A., Xu, D., Luo, L., Zhou, Y., Yan, W., Leng, X., Dai, D., Zhou, Y., Ahmad, H., Rao, J. & Fan, M. (2021) Overview of nanocellulose as additives in paper processing and paper products. *Nanotechnology Reviews*. 10 (1), 264 – 281. Available from: doi:10.1515/ntrev-2021-0023.

Mautner, A., Hakalahti, M., Rissanen, V. & Tammelin, T. (2018) Crucial interfacial features of nanocellulose materials. In: K.-Y. Lee (ed.) *Nanocellulose and Sustainability: Production, Properties, Applications and Case Studies*. 1st edn. CRC Press, pp. 87 – 128.

Mokrzycki, W. & Tatol, M. (2011) Color difference Delta E - A survey. *Machine Graphics and Vision*. 20 (4), 383 – 411. Available from: doi:10.1007/s10817-009-9143-8

do Nascimento, N. R., Pinheiro, I. F., Fioravanti Alves, G., Innocentini Mei, L. H., de Macedo Neto, J. C. & Morales, A. R. (2021) Role of cellulose nanocrystals in epoxy-based nanocomposites: Mechanical properties, morphology and thermal behavior. *Polimeros*. 31 (3), 1 – 13. Available from: doi:10.1590/0104-1428.20210057

Nechyporchuk, O., Kolman, K., Bridarolli, A., Odlyha, M., Bozec, L., Oriola, M., Campo-Frances, G., Persson, M., Holmberg, K. & Bordes, R. (2018) On the potential of using nanocellulose for consolidation of painting canvases. *Carbohydrate Polymers*. 194, 161 – 169.

Ngo, T.-D., Danumah, C. & Ahvazi, B. (2018) Production of cellulose nanocrystals at InnoTech Alberta. In: K.-Y. Lee (ed.) *Nanocellulose and Sustainability: Production, Properties, Applications and Case Studies*. 1st ed. CRC Press, pp. 269 – 287.

Operamolla, A., Mazzuca, C., Capodieci, L., Di Benedetto, F., Severini, L., Titubante, M., Martinelli, A., Castelvetro, V. & Micheli, L. (2021) Toward a Reversible Consolidation of Paper Materials Using Cellulose Nanocrystals. *ACS Applied Materials and Interfaces*. 13 (37), 44972–44982. Available from: doi:10.1021/acsami.1c15330

Pino, A. O., Pladellorens, J. & Colom, J.F. (2010) Method of measure of roughness of paper based in the analysis of the texture of speckle pattern. In: A. Albertazzi Gonçalves Júnior and G.H. Kaufmann (eds.) *Speckle 2010: Optical Metrology*. pp. 73871W1 - 73871W7-7. Available from: doi:10.1117/12.869655

RK Print Coat Instruments. (2022) *K Control Coater - RK Print Coat Instruments*. Available from: https://www.rkprint.com/products/k-control-coater/ [Accessed: 9 August 2022]

Santmartí, A. & Lee, K.-Y. (2018) Crystallinity and thermal stability of nanocellulose. In: K.-Y. Lee (ed.) *Nanocellulose and Sustainability: Production, Properties, Applications and Case Studies*. 1st edn. CRC Press, pp. 67 – 86.

Techkon (2021) *SpectroDens manual*. Available from: https://www.techkon.com/files/downloads/prospekte/SpectroDens%20Manual%20Web.pdf [Accessed: 6 September 2022]

Völkel, L., Ahn, K., Hahner, U., Gindl-Altmutter, W. & Potthast, A. (2017) Nano meets the sheet: Adhesive-free application of nanocellulosic suspensions in paper conservation. *Heritage Science*. 5 (1). Available from: doi:10.1186/s40494-017-0134-5

Walsh, Z., Janček, E. R., Jones, M. & Scherman, A. O. (2017) Natural polymers as alternative consolidants for the preservation of waterlogged archaeological wood. *Studies in Conservation*. 62 (3), 173 – 183. Available from: doi: 10.1179/2047058414Y.0000000149

Walsh-Korb, Z. & Avérous, L. (2019) Recent developments in the conservation of materials properties of historical wood. *Progress in Materials Science*. 102, 167 – 221. Available from: doi: 10.1016/j.pmatsci.2018.12.001

Wang, S., Ihalainen, P., Jarnstrom, J. & Peltonen, J. (2009) The effect of base paper and coating method on the surface roughness of pigment coatings. *Journal of Dispersion Science and Technology*. 30 (6), 961 – 968. Available from: doi: 10.1080/01932690802646447

Wu, S. Q., Li, M. Y., Fang, B. S. & Tong, H. (2012) Reinforcement of vulnerable historic silk fabrics with bacterial cellulose film and its light aging behavior. *Carbohydrate Polymers*. 88 (2), 496 – 501. Available from: doi: 10.1016/j.carbpol.2011.12.033