Chemical stability of prints made on hemp fibre based papers

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Abstract

For paper industry and consequently graphic industry it is very important that fibres used in paper production provide high quality and printability of the paper. In pulp and paper industry fibres of cellulose pulp derived still predominantly from wood, but in the last few years the consumption of non-wood raw materials for that purpose has grown. This work presents research on the chemical stability of printed hemp fibre based papers to water, alcohol and alkali. Evaluation of chemical degradation on prints was determined through the spectrophotometric measurements. Deviations in colour of prints have shown that highest chemical stability provides prints made on industrially paper formed from mixture of hemp and post-consumer fibres with high share of inorganic components. Further, bleached hemp fibres in handmade 100 % hemp fibre based paper give prints with the lowest chemical stability.

Keywords: chemical stability, hemp fibre, paper composition, printability

1. Introduction

A global deficiency of wood raw materials is nowadays present in the paper industry. Therefore, the alternative sources of virgin cellulose fibres for that industry sector are of great importance especially for further generations. Wood is still the most widely used raw material in the pulp and paper production, but the consumption of non-wood fibres has been showing the increasing trend in the last few years. Many useful fibres could be obtained from various parts of plants including leaves, stems (bast fibres), fruits and seeds. Leading users of non-wood fibres in papermaking are Asia and the Pacific countries [1]. At the present time, the most commonly utilized non-wood fibre is straw, but other non-wood fibres such as cotton, hemp, sisal and kenaf are also becoming more important in the manufacture of pulp and paper. Regardless to the fibre origin, wood (hardwood and softwood) or non-wood (agricultural residues, industrial residues and naturally growing plants), it is very important that selected fibres provide good quality of the paper. Hemp (*Cannabis sativa*) as new lignocellulosic fibre resources for pulp and paper industries has a number of advantages (long and strong fibre, low lignin content). This is an annual plant reaching a height of 4-5 m and yielding 12-14 tons of dry matter/yr ha. Only 80-150 days are needed for plants to be mature for fibre harvesting. Namely, 10-12 tons dry matter/yr ha can be harvested as fibre mass, 35% of which are long bast fibres and 65% are short core fibres. Hemp fibre for papermaking can have a fibre length from 15 to 55 mm. It is generally believed that the male plant is superior in respect of fibre compared to the female plant, therefore male hemp fibres are used in papermaking process [2, 3]. Main disadvantages are a lack of facilities for the extraction of cellulose from hemp which requires a special process and the cost of hemp pulp which is three to six times higher compared to conventional wood-based pulp production. Nowadays only 23 paper mills use hemp fibre and most of them are located in China and India. These mills generally produce special papers as cigarette papers, filter papers, art papers etc. [4].

For achieving the high quality final graphic product, the printability of paper and the stability of those prints are important [5]. The paper characteristics in various ways affect on quality of prints therefore the research presented in this paper focuses on evaluation printability and chemical stability of the hemp fibre based office papers. For that purpose these papers were printed by digital printing process. Created prints were tested for chemical stability to three different tests liquid agents: water, alcohol and alkali [6]. Evaluation of chemical degradation on the prints was observed through the Euclidean colour difference based on colorimetric values L*C*h°.

2. Experimental part

2.1. Materials

Three types of commercially available hemp fibre based papers (grammage 90 gm-2) were used for making prints:

Type 1 – handmade sustainable paper made from 100% hemp plant fibre with wildgrass is unbleached, uncoated printer-compatible (Laser and Inkjet) paper in natural colour with natural deckled edge. Paper manufacturer is Distant Village, US.

Type 2 – handmade sustainable paper made from 100% hemp plant fibre is non-chlorine bleached uncoated printer-compatible (Laser and Inkjet) paper in cream colour with natural deckled edge. Paper manufacturer is Distant Village, US.

Type 3 – hemp Heritage® uncoated natural white office paper made from a mixture of 25% hemp and 75% post-consumer fibre. Paper manufacturer is Green Field Paper Company, US.

These papers were printed in fulltone black colour by HP LaserJet 1320 office printer. This monochrome printer produce high-quality prints with 1200 dpi resolution using toner cartridge model Q5949A. Fulltone black prints were used as samples for evaluation of printability and chemical stability.

2.2. Methods

2.2.1. Chemical composition analysis of papers

The chemical composition of hemp fibre based papers used as printing substrates in this research was determined in accordance with the TAPPI standard T412 om-94 (moisture content), T413 om-11 and T211 om-02 (ash content: ignition at 900°C and 525°C). The amount of residues on ignition at 525°C and 900°C on oven-dry basis are related to calcium carbonate and clay content for all hemp fibre based papers. The percentages of calcium carbonate and clay were calculated by the following equations [7]:

$$CaCO_3,\% = (Ash_{525} - Ash_{900}) \times \frac{100}{44} \quad (1)$$

$$Clay,\% = (Ash_{525} - CaCO_3) \times 1.13 \quad (2)$$

Where:
Ash_{525} is the residue of ignition at 525°C
Ash_{900} is the residue of ignition at 900°C

2.2.2. Evaluation of printability

The optical properties of the printed papers were monitored with spectrophotometer X-rite DTP 20 at D65/10°, which are observed through colorimetric values: L* (lightness), a* (coordinate of green/red colour), b* (coordinate of blue/yellow colour), C* (chroma i.e. the direct distance of colour from the achromatic origin) and ho (hue i.e. angle measured in degrees from a 0° to 360°) were determined.

Both chroma and hue are derived from a* and b* values in CIE Lab colour [10] space using the following equations:

$$C^* = \sqrt{(a^*)^2 + (b^*)^2} \quad (3)$$

$$h^\circ = \arctan\left(\frac{b^*}{a^*}\right) \quad (4)$$

2.2.3. Evaluation of chemical stability of prints

The aim of the research was to evaluate the effect of hemp fibres on chemical stability of prints. The prints were tested for stability to the following agents in accordance with International Standard ISO 2836:2004 [6]. This standard defines methods of assessing the chemical stability of prints to liquid and solid agents, solvents, varnishes and acids. Used test liquid agent and defined contact time of the test agent is presented in Table 1.

Table 1. Used test liquid agent and contact time of the test agent

Test liquid agent	Contact time (t)
$H_2O_{distilled}$	24 hours
NaOH (w/v = 1%)	24 hours
C_2H_5OH (v/v = 96%)	5 minutes

According to this standard method of assessing the stability of prints is not equal for all used test liquid agents.

The method of assessing the stability or resistance of prints to water and alkali

Print sample was placed on a glass plate and set between four strips (two on each side) of filter paper soaked in the test liquid agent. Another glass plate was placed on top and the sample was put under pressure by applying one kilogram mass on top of the plate. Contact time of prints with water and alkali was 24 hours.

The method of assessing the stability or resistance of prints to alcohol

Print sample was placed in a glass tube containing ethanol and immersed for five minutes.

When the contact time expired, treated print samples were dried in an oven prior to assessment (t = 60 minutes, T = 40°C).

Dried chemically treated print samples were compared to untreated print samples and changes in optical properties caused by used test liquid agents were noted and discussed. Chemical stability of prints was monitored through changes in the optical properties of chemically treated samples.

The difference between printed sample before and after chemical treatments is calculated and expressed as ΔL*, ΔC*, Δh° and ΔE^*_{00} (Euclidean colour difference) [8, 9].

Where:

$$\Delta E^*_{00} = \sqrt{\left(\frac{\Delta L'}{k_L S_L}\right)^2 + \left(\frac{\Delta C'}{k_C S_C}\right)^2 + \left(\frac{\Delta H'}{k_H S_H}\right)^2 + R_T \frac{\Delta C'}{k_C S_C}\frac{\Delta H'}{k_H S_H}} \quad (3)$$

ΔL' is the transformed lightness difference between print before and after chemical treatment

ΔC' is the transformed chroma difference between print before and after chemical treatment

ΔH' is the transformed hue difference between print before and after chemical treatment

RT is the rotation function

KL, KC, KH is the parametric factors for variation in the experimental conditions

SL, SC, SH is the weighting functions

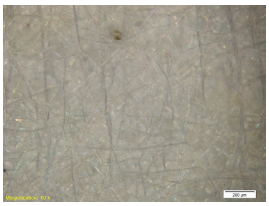
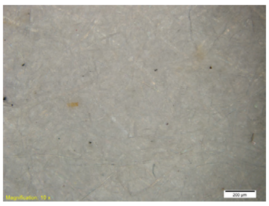
3. Results and discussion

3.1. Chemical composition analysis of papers

The chemical composition analysis of papers was done for a better understanding the impact of the hemp fibres in a printing substrate on printability and chemical stability. Gained results are presented in Table 2.

The results of chemical composition have shown how paper Type 3 has the highest content of ash (ash $_{525°C}$ = 7.01%; ash $_{900°C}$ = 4.21%) and the lowest content of moisture (2.66%). This paper is consisted from a mixture of 25% hemp and 75% post-consumer fibre and has a high share of inorganic components (6.35% of $CaCO_3$ and 0.75% of china clay) which are added during industrial process of making paper. Calcium carbonate and china clay are filler materials usually incorporated in fibres network during papermaking process to improve

Table 2. Chemical composition of the hemp fibre based papers

Paper	**Type 1**	**Type 2**	**Type 3**
Microscopic image*			
Moisture, %	4.95	5.17	2.66
Ash $_{525}$**, %**	1.84	2.38	7.01
Ash $_{900}$**, %**	1.36	1.72	4.21
$CaCO_3$**, %**	1.14	1.49	6.35
Clay, %	0.79	0.99	0.75

* The papers were imaged using an Olympus BX51 System Microscope at 100x magnification

the optical properties (whiteness, brightness, opacity, etc.) of paper sheet. In paper industry around the world a material used as filler varies according to their availability and economic factors. Important considerations for the selection of filler include optical properties, low cost, and compatibility with the papermaking process. While handmade papers with 100% hemp fibres (papers Type 1 and Type 2) have a small amount of those inorganic components. Paper Type 2 has slightly higher values of moister, ash, $CaCO_3$ and china clay content than paper Type 1. Therefore it can be concluded that chemical composition of the paper and the papermaking method (handmade/industrial) significantly affect the moisture content and ash content in the paper. Namely, handmade papers with 100% of hemp fibres absorb the most moisture from the air (Type 1 = 4.95%; Type 2 = 5.17%) comparing to industrial made paper (Type 3 = 2.66%) what is the consequence of the smallest share of ash (indicates the smallest addition of chemicals).

3.2. Evaluation of printability

Printability of hemp fibre based papers was evaluated based on spectrophotometric measurement results presented in Table 3.

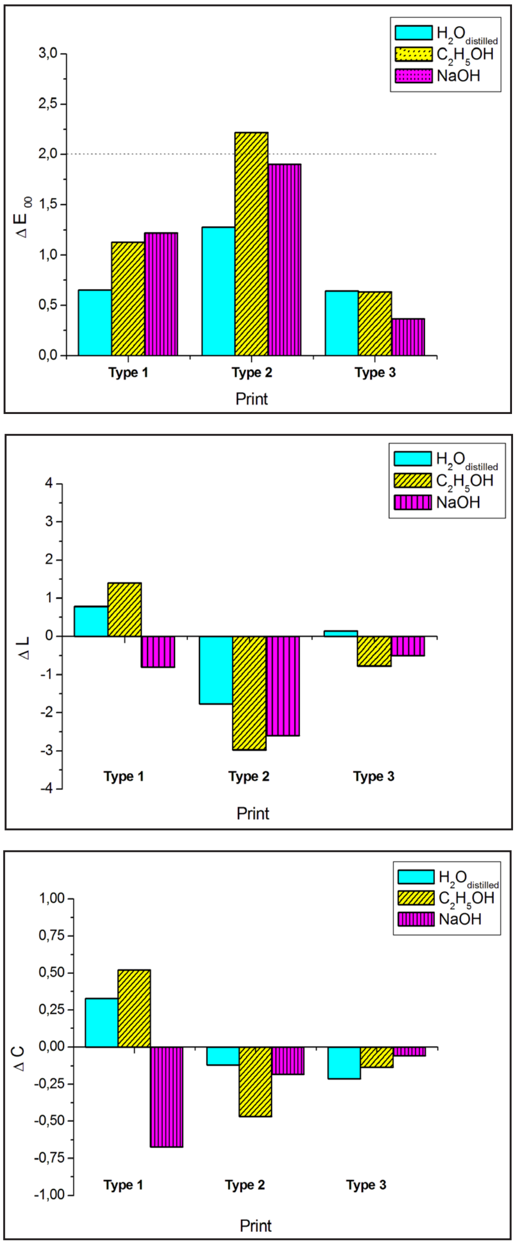
Table 3. Spectrophotometric measurement results of prints made on hemp fibre based papers

Print	L*	a*	b*	C*	h°
Type 1	23.039	1.685	2.563	3.076	56.567
Type 2	22.978	0.761	1.084	1.346	54.833
Type 3	23.854	0.617	0.473	0.79	37.349

By printing the hemp fibre based paper in full-tone black colour, measured L* value was expectedly low for all samples. The values of a* and b* measured after printing were low and positive (in the red and yellow part of the spectrum). Chroma as the saturation or vividness of colour was observed for all analysed papers types, where the paper Type 1 provide the most intense print of black colour (the highest C* value), while the print on paper Type 3 is the duller one (the lowest C* value). Hue angle as the basic unit of colour for all observed prints is measured in the first quadrant (between 0° = red and 90° = yellow).

3.3. Evaluation of chemical stability of prints

Evaluation of chemical stability of prints was done based on differences in colorimetric values (L*, a*, b*, C*, h°). In order to determine the influence of distilled water, ethanol and sodium hydroxide on the printed hemp fibre based papers Euclidean color difference (ΔE^*_{00}) was calculated according equation 3. While deltas for lightness (ΔL*), chroma (ΔC*), and hue (Δh°) are calculated as a difference between its value measured on a print and a value measured on chemically treated print. Gained results of these measurements, values of ΔE^*_{00}, ΔL*, ΔC*, Δh° are presented in Figure 1.



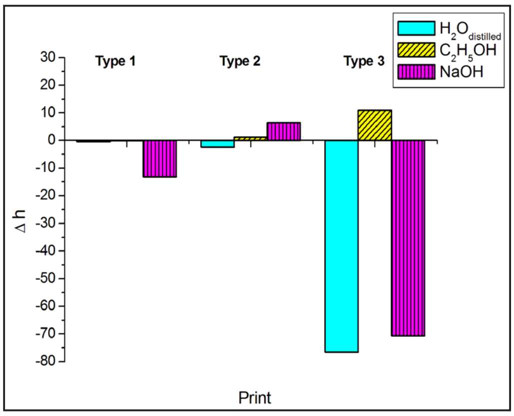
d 

Figure 1. Deviations in colour of prints before and after chemical treatments: a) ΔE^*_{00}; b) ΔL*; c) ΔC*; d) Δh°

As shown in Figure 1 all chemical agents that used influenced on the colorimetric values of prints.

Distilled water, ethanol and sodium hydroxide slightly influenced on prints determined through the ΔE^*_{00} (Figure 1a). Namely obtained ΔE^*_{00} on all chemically treated prints is in range from 0.35 to 2.25, which is not visible to an average observer [11]. Comparing the influence of all test liquid agents on prints Euclidean colour difference, water had the minor influence on ΔE^*_{00} values. Prints Type 1 and Type 2 have shown the same trend in ΔE^*_{00} changings after treatment with test liquid agents as follows: water < alcohol ≈ alkali. For print Type 3 ΔE^*_{00} values are lower and similar for water, alcohol, alkali that indicated the greatest stability of the print. This is a consequence of the chemical composition of the paper. High share of inorganic components in paper improve its printability and chemical stability.

In figure 1b the changes in lightness of prints (ΔL*) caused by the test liquid agents are negative (-) for print Type 2, which indicates that the print after chemical treatment became lighter (ΔL^*_{C2H5OH} = - 2.973; ΔL^*_{NaOH} = - 2.592; ΔL^*_{H2O} = - 1.765). It is interesting that other two papers (Type 1 and Type 3) as paper substrates has shown a minor changes in lightness/darkness of chemically treated prints. From all analysed test liquid agents, water has shown the smallest influence on lightness of prints regardless to the printing substrate. This parameter proves again that print Type 2 is the most instable paper and print Type 3 the most stable one.

As shown in Figure 1c, changes of chromaticity (ΔC*) for all prints are minor (ΔC* is in range from -0.06 to -0.67). As known [10] by increasing chroma value, a colour becomes more intense, while by decreasing it, colour becomes duller. It could be concluded that chemical treatment had caused increasing of colour saturation of prints (ΔC* are negative), except water and ethanol on prints made on paper Type 1 (ΔC* is positive). However, as all treatments have shown slight changes in chroma values of treated prints, these changes can be interpreted in interval of measurement error (ΔC* ≈ 0). Again, according to this observed parameter, print made on industrial paper made from mixture of hemp and post-consumer fibres (Type 3) had shown the highest chemical stability.

In Figure 1d gained results shown the degree of colour difference Δh°, where the most prominent is prints Type 3, especially after treatment with distilled water (Δh°_{H2O} = -76.642) and alkali (Δh°_{NaOH} = -70.682). For other prints the value of hue change Δh° are not so pronounced. Namely, on untreated prints measured hue angle of colour for all observed prints was in range 37° to 56° (Table 3), what indicate that prints Type 3 are the most reddish one while prints Type 1 and 2 are more yellow. After chemical treatment with distilled water and alkali prints Type 3 become extremely yellow which resulted in pronounced degree of colour difference Δh°.

From all obtained results it could be assumed that chemical composition of paper has important influence on chemical stability of prints. Beside origin of the fibres (wood, non-wood, recycled), the chemical additives in paper have an important influence on chemical stability of prints. In prints Type 1 and Type 2 the ink is in direct contact with hygroscopic virgin hemp fibres, while in print Type 3 the ink is in contact mostly with chemicals additives (mainly $CaCO_3$). Therefore the highest chemical stability shows prints made on industrially formed paper. On the other hand, bleached hemp fibres in handmade paper (Type 2) give prints with the lowest chemical stability regardless to test liquid agent used in this research.

Gained results in this research are in accordance with published results Bates et all, which have proven that coated papers and boards show greater chemical stability on alcohol, alkali and water than recycled papers [12].

4. Conclusion

The aim of the research was to point out the influence of hemp fibres in substrate on chemical stability of prints. A print is considered to be resistant to chemical substances when no alteration occurs after exposure to them or when no change in colour is observed. Taking into account all obtained results, the following could be concluded:

- The ΔE^*_{00} values are low and similar after exposure to all liquid agents for the print Type 3, that indicated the greatest chemical stability of the print.
- The delta of lightness parameter (ΔL^*) indicated that print Type 2 is the most instable print and print Type 3 the most stable one.
- According to the chromaticity (ΔC^*) all test liquid agents have caused slight changes in chroma values of treated prints. As well print Type 3 had shown the highest chemical stability.
- The delta hue parameter ($\Delta h°$) showed that the most prominent is print Type 3, which became extremely yellow.

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