RECYCLED WOOD VS. VIRGIN NON-WOOD FIBERS IN PAPER – IMPACT ON THE CHEMICAL STABILITY OF BLACK SCREEN PRINTS

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Abstract

There are a number of factors to consider when choosing a paper substrate for a fiber-based graphic product. Physical, optical, strength and various properties of paper are limiting factors in the use of paper, especially when it is used as a packaging material. The requirements are additionally increased if the papers are subjected to printing in the creation of the graphic product. The print on the selected paper substrate must be stable to the influence of temperature, light, pressure and different chemical agents. Considering the depletion of forest resources, the demands for alternative resources for the traditional use of cellulose fibers in paper production are increasing. Thus, selecting the appropriate alternative source of biomass is a big concern. In this research, the changes in colorimetric values of black prints were analyzed after exposure to four chemical agents: water, sodium hydroxide, acetic acid and ethanol. Using black conventional and UV inks, prints were made with screen printing technology on paper substrates in which 30% of the pulp from recycled wood fibers was substituted with virgin fibers from wheat, barley or triticale straw. Compared to a paper substrate made from recycled wood fibers subjected to the same printing technique, it was observed that the replacement of part of the recycled wood pulp with virgin fibers of cereal straw in the paper substrate gave UV black prints a higher chemical stability, while the same replacement for conventional black prints caused reduced chemical stability to all observed chemical agents. In general, regardless of the printing substrate composition, black prints made with UV ink were more stable to all chemical agents than those made with conventional ink with the exception of ethanol.

Keywords: chemical stability, conventional and UV inks, paper substrate, screen printing, straw fibers

Introduction

Packaging materials may be exposed to various chemical agents such as water, alcohol, acid, oil, etc. during their life cycle. If the packaging material is expected to be exposed to a chemical, it is important that the ink or coating, or both, are not degraded, softened, or melted by that contact. Due to its environmental properties, paper and cardboard-based material are one of the oldest and most widely used types of packaging. Recycling is considered the best option for compensating for the loss of wood lignocellulosic raw materials from natural habitats around the world. Namely, recycling one newspaper can save 41,000 trees from being cut down[1]. However, first-class paper can be recycled a maximum of six to seven times[1,2]. Since the fiber length constantly decreases during recycling, the mass of recycled paper required in paper development increases with each recycling cycle as the fiber length decreases. It should be emphasized how recycled paper can never match the quality of virgin paper because recycled fibers have worse physico-chemical properties than virgin cellulose fibers due to the hornification effect of the fiber. This effect is a change in the outer layers of the cellulose that occurs during the drying process of the paper and during its exposure to the environment, affecting the paper's resistance properties[3,4]. On the other hand, the paper industry waste is very diverse in nature and composition and therefore cannot fully cover the demand and quality of the lignocellulosic raw material in the pulp and paper industry. The constant need for virgin fibers is a direct consequence of the deterioration of fiber properties during the life cycle of paper, and most mills augment their recovered pulp with some virgin fiber[5]. Contamination by a wide range of substances, the most important of which are the chemical components of mineral oils, and the increasing concern about their migration into packaged foods may limit the use of recycled paper in the production of paper-based food packaging and thus also lead to an increase in the demand for virgin fiber[6]. It is not surprising that the paper industry faces a constant need for virgin fiber to meet the various demands of the market. Part of these demands have been generated by the packaging industry's shift towards green alternatives by replacing plastic with fiber-based materials, such as paper and cardboard, which have a lower environmental impact. Given that wood has traditionally been the most intensively used source of virgin fibers, leading to overexploitation of forests in some parts of the world, the use of non-wood fibers for pulp and paper production is now showing increasing efforts even in countries with acceptable wood resources due to environmental concerns[7].

In this research, the chemical stability of prints on papers made under laboratory conditions from a mixture of pulp of recycled fibers and virgin fibers of cereal straw was studied, in order to gain insight into the possibility of using this type of non-wood raw material for papers and paper packaging intended for printing.

Experimental Part

Materials and methods

Preparation of paper samples for printing with screen printing technology involved several stages: the process for raw materials preparation, pulp preparation and forming paper substrates.

For the preparation of raw materials, straw of wheat (Triticum spp.), barley (Hordeum vulgare L.) and triticale (Triticale sp.) is collected after harvesting, purified and cut into dimensions up to 3 cm long. For pulp production, the process has included cooking, washing and a milling process. First, the prepared straw was weighed and the mass of NaOH was measured according to the parameter set to 16%. Then, both substances were mixed and boiled for one hour at a temperature of 120 °C and a pressure of 170 kPa with the aim of removing lignin, hemicellulose silicon, and the core of the fiber so that the fibers have the best possible interaction. This was followed by a washing process to remove the effects of NaOH and impurities in the fibers. And the final stage was defibration in the Holländer Valley Mill for 40 minutes to obtain a smooth pulp of fibers for paper production[8]. Finally, a paper substrate (42.5 ± 2.6 g/m^2) was formed from the mixture of obtained straw pulp and recycled pulp in a ratio of 3:7. Based on the chemical composition, four different paper substrates (marked as 100N, 70N30W, 70N30B and 70N30TR) were produced using a Rapid-Köthen sheet former (FRANK-PTI) according to EN ISO 5269-2:2004.

Black prints with dimension of 140x140 mm were gained by screen printing of laboratory formed paper substrates with Epta inks Hi-gloss conventional inks (KIIAN S.p.A., Italy) and with UltraGraph UVAR UV-curable inks (Marabu GmbH& Co., Germany) on a semi- automatic Shenzhen Juisun screen printing machine (Juisun, China) with a squeegee of a mechanical hardness of 75 Shore and a mesh line of 140 lines/cm. All prints were printed at a temperature of 23°C and a relative humidity of 50%. After printing, the UV prints were dried in two passes by UV irradiation. When printing on paper substrates of different composition, an effort was made to achieve a uniform coating of paint, which was monitored densitometrically[9] and shown in the results as the optical ink density of the prints.

Chemical resistance of the printed black ink was evaluated after contact with water, sodium hydroxide, ethanol and acetic acid based on the change in color CIE L*a*b* values measured using an X-Rite SpectroEye spectrophotometer at an illuminance of D50 and a standard observer of 2° i.e., from them calculated Euclidean color difference (ΔE^*_{00}). The chemical resistance test on paper substrates with 30% straw pulp (70N30W, 70N30B and 70N30TR) and reference paper without addition of straw pulp (100N) was performed in accordance with ISO 2836:2004 standard.

To assess the influence of each chemical agent on the prints made with conventional and UV ink by the screen printing technique, the difference between the black color within the L*a*b* system, before and after performing the test, was calculated according to Equation 1, using the untreated sample as a reference:

$$\Delta E_{00} = \sqrt{\left(\frac{\Delta L'}{k_L S_L}\right)^2 + \left(\frac{\Delta C'}{k_C S_C}\right)^2 + \left(\frac{\Delta H'}{k_H S_H}\right)^2 + R_T \frac{\Delta C'}{k_C S_C}\frac{\Delta H'}{k_H S_H}} \qquad (1)$$

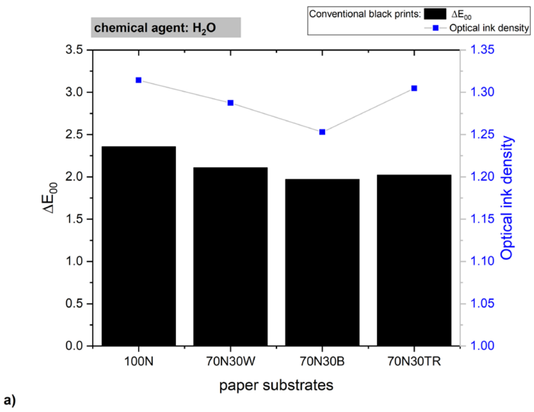
Where: ΔE^*_{00} represents the total color difference, ΔL' represents the difference in lightness between black prints before and after treatment with chemical agent, ΔC' represents the chroma difference between the black prints before and after treatment with chemical agent and ΔH' represents the hue difference between the black samples before and after treatment with chemical agent, R_T represents the rotation function, while k_L, k_C, k_H represent the parametric factors for variation in experimental conditions and S_L, S_C, S_H represent the weighing functions.

When the color difference value (ΔE^*_{00}) of prints after contact with chemical agents is below the value of 2, it is defined as a stable print with very small or hardly noticeable differences in color tone. If the color difference value is above 5, a standard observer sees the color of the print, before and after contact with the chemical agent, as two different colors, so such a print can be defined as a print with low chemical resistance.

Results and Discussion

Water resistance is the fundamental chemical resistance property of paper, especially when it is used as a packaging material. Namely, contact with water or moisture has very negative effect on the mechanical properties of paper and cardboard, as water-soaked corrugated cardboard can easily collapse with irreversible distortions[10]. Labels and markings printed on a paper substrate also suffer damage caused by water entering its structure and destroying the print on it. It is important to highlight that product which are stored in the freezer must have packaging with high water resistance. Whereas transport or tertiary packaging intended for outdoor use must have good resistance to moisture and rain. For a material to have good water resistance, it must combine water insolubility, low water absorption and low water vapor permeability. Insolubility implies that the material does not degrade under conditions of continuous immersion in water. Absorption of water into the paper material causes swelling, and when the swollen material dries, shrinkage occurs[11]. Alternating wetting and drying produces a cycle of swelling and shrinking which is a fatigue process that eventually weakens the paper used as a packaging material. While, low water vapor permeability is a property of primary importance for a material used as a packaging[12]. The results of water absorption inside the paper substrate made from recycled fibers (100N) and those made from admixture of recycled and straw fibers (70N30W, 70N30B, 70N30TR) determined using a Goniometer CCD video camera instrument with a resolution of 768 × 576 pixels, producing 50 frames per second confirmed how the addition of virgin fibers into pulp of recycled fibers increase absorption of paper substrate. Replacing 30% recycled fibers with virgin fibers in the pulp results in papers with 60% faster water absorption[13].

However, looking at the water resistance results of black screen prints in Figure 1, it is evident that the composition of the paper printing substrate does not play a decisive role in the water stability of the prints.



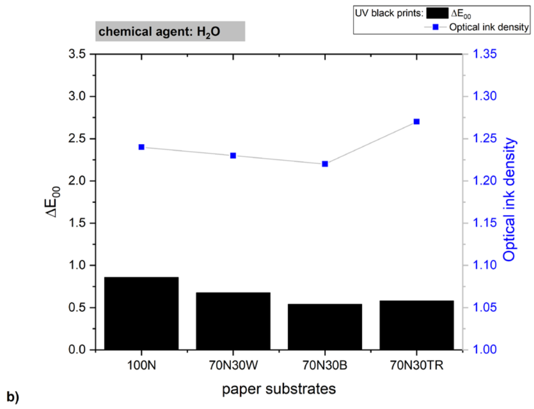


Figure 1: Water resistance of screen prints printed with black: a) conventional ink; b) UV ink

The results of black print resistance after contact with water are approximately the same regardless of whether the papers are made exclusively from recycled fibers or the pulp of recycled fibers is mixed with wheat, barley or triticale pulp. It can be seen that the type of ink, i.e., its composition defines the water resistance of the print. It can be seen that prints made with conventional black ink, which is dried by evaporation after printing, are more unstable to the action of water (Figure 1a) than prints made with black UV curable ink on the same paper printing substrates using same screen-printing equipment (Figure 1b). UV inks are dried immediately with UV radiation energy. This curing process hardens the ink on the paper surface, making it more durable and water resistant. The ΔE^*_{00} values for prints after contact with water were below 0.9 for all UV black regardless of the composition of the paper substrate used.

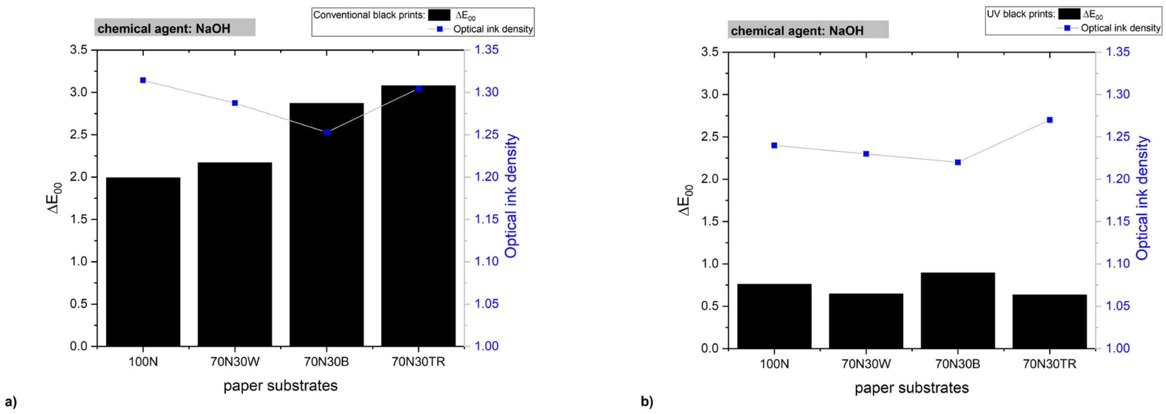


Figure 2: Alkali resistance of screen prints printed with black: a) conventional ink; b) UV ink

Alkali resistance is an important property, especially when a paper is intended to be used in the packaging of such materials or may come into contact with alkali solutions during transportation, storage or handling. Therefore, the ability of the black ink to remain unchanged in color under the action of sodium hydroxide was measured. For this test water solution of sodium hydroxide (1% NaOH) was used. The results in Figure 2 show a higher sensitivity of the conventional black ink to alkaline solution compared to the black UV ink printed on the same paper substrates. The results of ΔE^*_{00} values in the range of 2.0 to 3.1 for black prints made with conventional ink (Figure 2a) indicate that alkali can cause eye-visible changes in the color of the print, while values in the range of 0.5 to 0.9 indicate exceptional stability of black UV prints (Figure 2b).

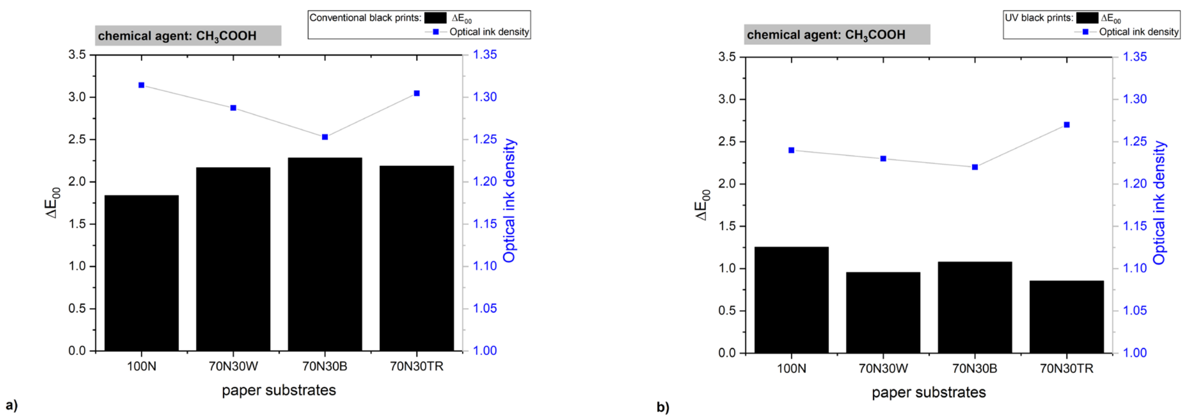


Figure 3: Acid resistance of screen prints printed with black: a) conventional ink; b) UV ink

The behavior of screen prints on paper substrates with 30% straw pulp (70N30W, 70N30B and 70N30TR) and reference paper without addition of straw pulp (100N) was much like with sodium hydroxide. Namely, for this test the water solution of acetic acid was also 1%. Compared to alkali, acetic acid has a slightly weaker effect on the change in the black color of the screen prints with conventional ink (Figure 3a), and slightly stronger effect on the change in the black color of UV prints (Figure 3b).

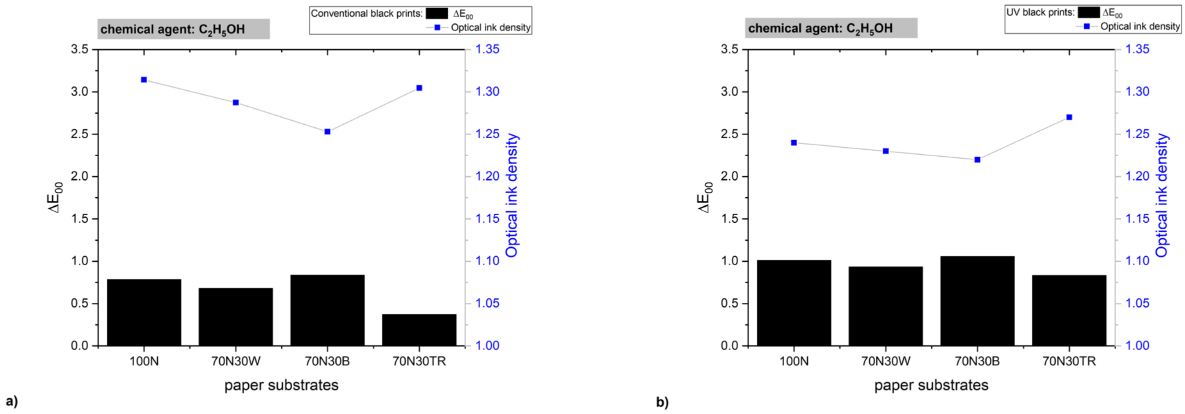


Figure 4: Alcohol resistance of screen prints printed with black: a) conventional ink; b) UV ink

From Figure 4 it is evident that black screen prints on papers made from the pulp of recycled fibers (100N) and recycled pulp enriched with virgin straw fibers, are the most stable on ethanol of all used chemical agents in the test performed. For this test denatured ethanol (96% C_2H_5OH) was used. The ΔE^*_{00} values for prints made with conventional and UV black inks were below 1.0 after contact with ethanol indicating high alcohol resistance for all black screen prints, regardless of the composition of the ink and the paper substrate used.

Conclusion

In this paper, it was confirmed that the composition of the printing substrate in relation to the composition of the printing ink has a negligible effect on the chemical stability of the print. In other words, the chemical stability of the print depends on the stability of the ink in contact with various chemical agents and is related to the state of the combination of pigment and binder. Due to the drying method, UV inks achieve a stronger bond between pigments and binders on the surface of the paper printing substrate, and thus a stronger chemical stability than conventional inks. Regardless of the composition of the printing substrate, black prints made with UV ink were generally more stable to all chemical agents than those made with conventional ink, with the exception of ethanol.

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