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The Behavior of Irreversible Thermochromic Inks in the Paper Recycling Process

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Abstract

Thermochromic printing inks are special chromogenic inks that change their color by exposure at a certain temperature, which is usually called the activation temperature (TA). The color change can be irreversible or reversible. The property of irreversible color change in relation to temperature exposure over time, allows the development of numerous indicators. As such, they can be used to monitor the storage and transportation of temperature-sensitive products, such as refrigerated and frozen foods, drugs, temperature-sensitive chemicals, or biological materials, etc. Since the ink formulation is an important factor in the deinking process, the aim of this research is to determine the recycling efficiency of irreversible thermochromic prints. Thermochromic inks differ from conventional printing inks in formulation and pigment size due to the presence of microcapsules that are much larger than conventional pigment particles. For this study, two irreversible thermochromic printing inks are printed by screen printing in full tone, on one printing substrate. To explain the behavior of these inks in the recycling process, the hydrophobicity of the sample surface was examined, as one significant factor in the flotation process using the contact angle of water. Recycling of prints was carried out in laboratory conditions, by chemical deinking flotation in alkaline conditions. Sheets were made for each sample before and after flotation. Optical properties of the recycled samples show that these inks are difficult to recycle. The deinking flotation method is not entirely the best method for recycling of irreversible thermochromic inks because slight differences in the optical properties of the laboratory paper samples before and after flotation are achieved. Future research should go in the direction of new techniques such as adsorption and enzymatic deinking.

Key words

optical properties, paper recycling, surface properties, thermochromic inks

1. INTRODUCTION

The waste paper recycling process and its use to produce new product reduces the number of trees that are cut down, as well as water and energy consumption conserving natural resources [1]. In order to obtain recycled fibers suitable for the production of recycled paper, the printing ink and other impurities must be separated to the greatest extent from the pulp suspension. The amount of residual ink in the suspension affects the final optical properties of the recycled paper. Therefore, a process for removal of printing ink is required. Deinking flotation is the most common process used for the separation of ink from the pulp suspension by means of air bubbles performed in a flotation cell. Inside the cell, the device blows out hydrophobic air bubbles that mix with the suspension and the hydrophobic ink particles cling to them and go towards the surface, while removable flotation foam (froth) forms on the surface [2–4]. Flotation can be aided by the use of different chemicals that increase the hydrophobicity property of the ink particles. Flotation efficiency is affected by various parameters such as the ability of the ink to bind to the air bubble, the ink to collide with the bubble, and the removal of flotation froth from the surface of the suspension during flotation [2, 4]. The brightness of the pulp is very often a measure of the efficiency of the flotation process since the removal of printing ink from the system affects the pulp's brightness [5, 6].

Smart materials are often discussed as materials that feel some stimulus from the external environment and create a useful response. Perhaps it is better to think of the answer, often called "smart behavior", which occurs when the environment reacts in a useful and reliable way, without affecting the material itself. Thermochromism is the specific ability of a substance, atomic group, or material to change its optical state. Materials that, within their complex structure, have a dynamic mechanism of color change due to the change in temperature that affects the complex formation, introduce an innovation to the market while offering improved product information transfer. Thermochromic mechanisms are divided according to the criterion of duration into reversible (multiple and temporary color change) and irreversible (single and permanent color change). Thermochromism in the printing industry is widely used precisely because of the new channel of information communication to the end user. Therefore, the thermochromic mechanism finds its benefits in terms of smart packaging, security printing, a multitude of promotional and marketing visuals. Thermochromic inks are composed of thermochromic pigments and vehicle. Thermochromic pigments are mainly encapsulated leuco dye-developer-solvent systems. Leuco dyes are colorless or weakly colored compounds which in reaction with a developer transform into a colored state [7].

Nowadays, more and more products on the market, precisely because of their competitiveness, strive to develop new functional properties that will attract consumers. Each new formulation will have a different effect on the environment, so it is necessary to determine the environmental impact of all new components, *i.e.* materials [8]. When it comes to reversible thermochromic printing inks, the research on their potential environmental and safety risks are limited. Thermochromic offset printing inks are very difficult to recycle by means of chemical deinking flotation method, while biodegradability studies showed that polymerized ink vehicle (vegetable oil + resin) in thermochromic offset ink is more stable than the polymer resin present in UV curable screen printing thermochromic ink (polyurethane acrylate) [9–11]. Additionally, another potential problem with thermochromic inks is the presence of bisphenol A (BPA) as one of the main compounds and its potential migration from the surface of the thermochromic print to artificial sweat solutions [12, 13], as well as the presence of BPA recycled paper made from thermochromic prints [14].

Thus, the aim of this study is to examine the possibility of thermochromic irreversible ink recycling and ink behavior in recycling process.

2. EXPERIMENTAL PART

2.1. Materials

In the preparation of experiment, two irreversible thermochromic printing inks were used, Kromagen Magenta MB60-NH (hereinafter 60MG), with an activation temperature of 60° C, and Termosil Red 75/80 (hereinafter 120MG) with an activation temperature of 75-80° C. Both printing inks were screen printed using semi-automatic screen-printing device (Holzschuher K.G., Wuppertal), employing 62/64 mesh for 60MG thermochromic ink, and 120 mesh for 120MG TC ink, on uncoated paper (120 g/m^2). All prints were made in full tone. The printing inks when exposed to activation temperature change color permanently, 60MG changes color from light pink to purple, while 120MG changes color from colorless to magenta.

2.2. Methods

2.2.1. Evaluation of surface wettability

The evaluation of surface wettability of paper and prints (inactivated and activated) were carried out by water contact angle measurements on DataPhysics OCA 30 Goniometer, using the Sessile Drop method. Measurements were performed at room temperature 23.0 ± 0.2ºC. The volume of water droplet was 1 µl. Contact angle was captured by CCD camera and measured 1–2 s after the droplet was formed. Average values of ten drops on different places of the same sample were taken and presented as mean±SD.

2.2.2. Paper recycling process

Printed paper samples were recycled by means of chemical deinking flotation under laboratory conditions defined by standard procedures described in ISO 21993:2020 [15], as presented in Figure 1. Unprinted paper and irreversible thermochromic prints were disintegrated in Enrico Toniolo disintegrator, while the flotation process was performed in the laboratory flotation cell. A certain amount of pulp suspension was separated after disintegration process before flotation (BF) and after flotation process (F) to prepare laboratory sheets of 45 g/m^2, using automatic sheet-forming device Rapid-Köthen Sheet, PTI.

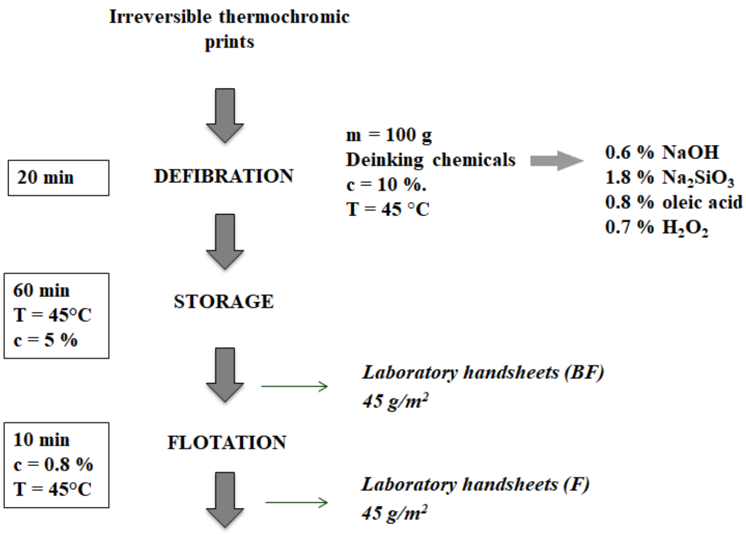

Figure 1.Shematic view of samples recycling process

2.2.3. Deinkability evaluation

The efficiency of recycling process was evaluated by measuring optical properties of laboratory handsheets made from undeinked pulp (BF) and deinked pulp (F). Evaluation of optical parameters was conducted according to standard methods: ISO Brightness (ISO 2470), CIE whiteness and colorimetric properties (ISO 11475) and ISO Opacity (ISO 2471) using Technydine Colour Touch 2 Spectrophotometer.

3. RESULTS AND DISCUSSION

In order to explain the behavior of the irreversible TC inks used in paper recycling, surface wettability of prints was determined. The contact angle of the water droplet on the substrate surface greater than 90° indicates that the substrate surface is hydrophobic while contact angle smaller than 90° indicates that surface is hydrophilic. Surface hydrophobicity can play a significant role in the deinking flotation process i.e., hydrophobic particles should be easier to remove from the pulp suspension.

The results of the contact angle measurements show that the unprinted paper substrate and the 120MG prints in the activated and inactivated state are hydrophobic (the water contact angle is greater than 90°) (Table 1). The results of the 60MG sample show that in the activated and inactivated state the print surface is hydrophilic with a water contact angle smaller than 90°. It is possible that this phenomenon occurs because the thermochromic inks composition. The components in printing ink binder can contain compounds with functional groups which give hydrophilic/hydrophobic character of the print. For example, vegetable oil in which the ester groups are present increase the hydrophilic character of the prints [16].

Table 1. Contact angle (θ) of unprinted paper and thermochromic printed surfaces

	Unprinted substrate	60MG	$60MG_{activated}$	120MG	$120MG_{activated}$
θ / °	96.65±1.03	85.3±1.07	86.51±1.37	112.02±1.14	103.39±0.67

To determine the efficiency of the recycling process, laboratory paper handsheets (45g/m^2) made before (BF) and after flotation (F) process were examined for their optical properties in the terms of ISO Brightness, CIE whiteness, colorimetric properties and ISO Opacity.

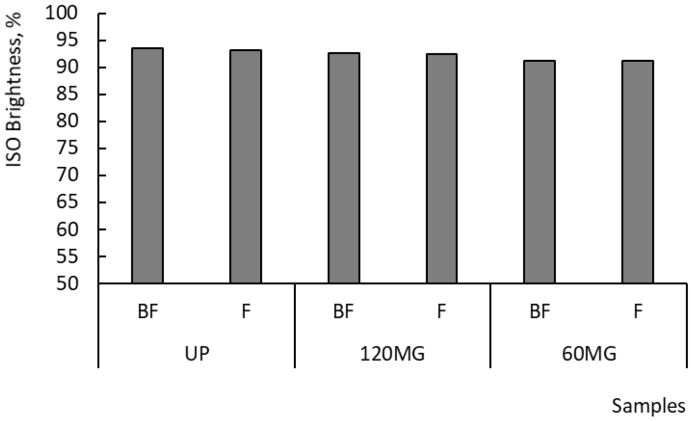

Figure 2. ISO Brightness of recycled fibres

The ISO brightness values of all samples are quite the same (Figure 2), with the highest value for the samples made of unprinted paper (93%), and followed by the samples made from 120MG (92%) and the lowest for the 60MG sample (91%). The flotation process had no effect on the ISO brightness change for all samples (Figure 2). The lowest ISO brightness value is obtained for the 60MG sample, probably due to the hydrophilicity of the printed surface (Table 1).

The values of the colorimetric parameter a^* (Figure 3) are highest for paper samples obtained by recycling of irreversible 120MG thermochromic prints, followed by recycled papers made from 60MG. The values on these samples are higher before flotation, which means that the ink particles are partially removed by flotation. A value of a^* indicates a shift to the red area, indicating a slight coloration of the laboratory paper handsheets. Although the higher hydrophilicity of the 60MG thermochromic print surface was expected to result in a higher ink residue in the pulp suspension, this was not obtained in this study. The value of the colorimetric parameter a^* indicates that the more hydrophobic TC ink (120MG) remained in higher share in the pulp, while the hydrophilic TC ink showed lower a^* value, i.e., has smaller residue in pulp suspension.

The results of the colorimetric parameter b^* (Figure 4) for the recycled paper (before and after flotation process) made from unprinted paper and 120MG thermochromic prints are quite the same, i.e., the flotation process does not affect the b^* values. The results of the paper obtained by recycling the samples printed with thermochromic ink 60MG show the lowest values of b^*, which indicates a smaller shift to the blue area compared to other tested samples.

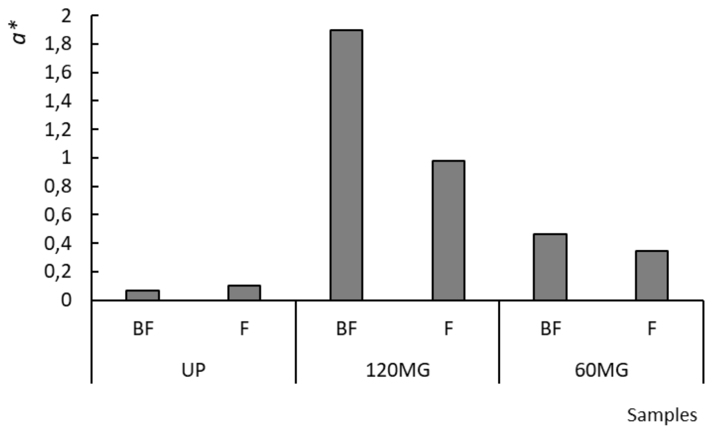

Figure 3. Colorimetric parameter CIE a of recycled fibers*

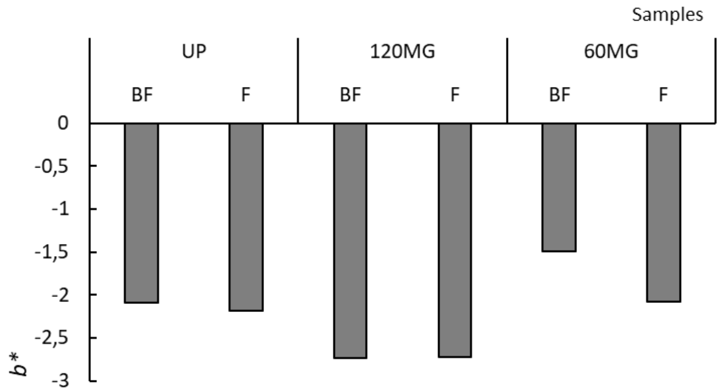

Figure 4. Colorimetric parameter CIE b of recycled fibers*

Larger changes in CIE whiteness values occur after flotation in all samples (Figure 5), but these changes are very small. For recycled papers made from unprinted paper samples, the whiteness value before and after flotation is almost identical.

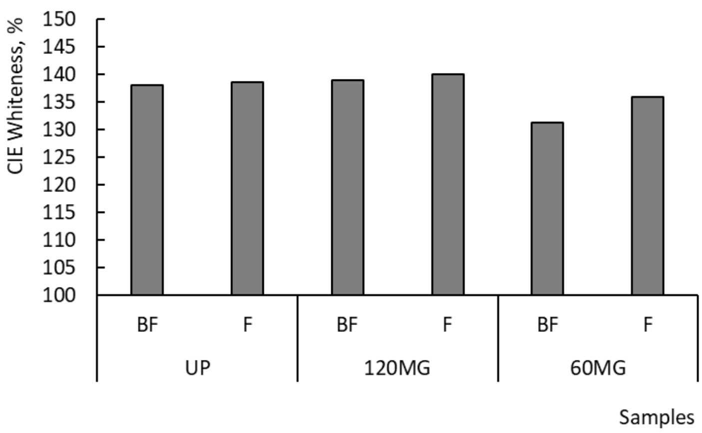

Figure 5. CIE Whiteness values of recycled fibers depending

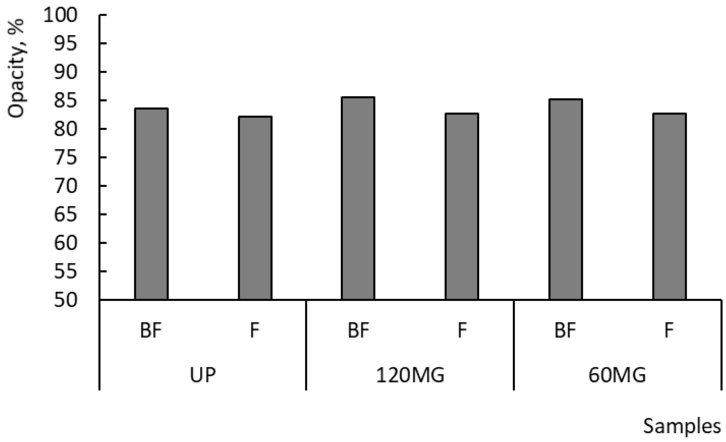

Figure 6. ISO opacity of recycled fibers

The opacity values of all samples are approximately the same (Figure 6). The results show that flotation process causes the loss of the fillers in the paper and the loss of them reduces the paper opacity. In samples obtained by recycling of unprinted paper, a decrease in opacity after flotation by about 1.37% is visible, while in samples obtained by recycling irreversible TC prints, a decrease in opacity is about 3.38% for 120MG and 2.95% for the 60MG sample, respectively. From this it could be concluded that the TC ink itself contributes to the loss of fillers, i.e., in some way it probably causes the filler particles to stick together resulting in higher removal in the flotation foam.

4. CONCLUSIONS

Despite the fact that the consumption of these kinds of printing inks is still limited, due to a Precautionary Principle it is necessar to examine thir possible impact on paper recycling process. The results of the optical properties of the recycled laboratory paper show that used irreversible thermochromic inks are difficult to recycle, although some changes were obtained by flotation, but the differences obtained are insignificant, i.e., very small. In addition, the flotation process reduces the opacity of recycled paper because flotation causes the removal of the fillers that serves as a substitute between cellulose fibers and paper. In addition, it can be assumed that a loss of optical brighteners occurred as well, especially in the TC ink sample which shows more hydrophilic character of the print surface. The deinking flotation method is not entirely the best method for recycling of irreversible thermochromic prints because slight differences in the optical properties of the recycled laboratory paper (obtained before and after flotation) are achieved. In addition, the colorimetric parameters indicate a slight coloration of the sheets of paper which may point to the release of colorants into the pulp suspension. Future research should be focused on new processes and/or chemicals research, such as adsorption or enzymatic deinking, which in other studies have proven to be successful methods for removal of poorly deinkable inks like water-based inks.

CONFLICT OF INTEREST STATEMENT

"The authors declare that there is no conflict of interest".

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