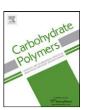
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Concept of heat-induced inkless eco-printing

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ABSTRACT

Existing laser and inkjet printers often produce adverse effects on human health, the recycling of printing paper and the environment. Therefore, this paper examines the thermogravimetry curves for printer paper, analyzes the discoloration of paper using heat-induction, and investigates the relationship between paper discoloration and the heat-inducing temperature. The mechanism of heat-induced printing is analyzed initially, and its feasibility is determined by a comparative analysis of heat-induced (laser ablation) printing and commercial printing. The innovative concept of heat-induced inkless ecoprinting is proposed, in which the required text or graphics are formed on the printing paper via yellowing and blackening produced by thermal energy. This process does not require ink during the printing process; thus, it completely eliminates the aforementioned health and environmental issues. This research also contributes to related interdisciplinary research in biology, laser technology, photochemistry, nanoscience, paper manufacturing and color science.

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1. Introduction

Historically, printing techniques have included two main methods: the use of bump technology, including stone carying techniques and 3D printing (Walker, 2008), and coloring methods (e.g., word printing in ancient China, laser printing and inkjet printing), which distribute dye regularly (Ray, 2004; Walker, 2008). Through a long development process, five categories of printers have been developed: dot matrix, laser, inkjet, thermal, and 3D (http://en.wikipedia.org/wiki/EP-101; http://en.wikipedia.org/wiki/Thermal printing; Walker, 2008). With applications in special areas, such as the dot matrix printing of tickets, the thermal printing of labels, and the 3D printing of model designs, these printing techniques have been widely used in commercial, industrial, office, news, and domestic contexts. 3D nano-printing has also been developed in recent years (Ferraro, Coppola, Grilli, Paturzo, & Vespini, 2010; Park et al., 2007). Modern printing can be considered "excellent" in terms of its performance, and the quality levels requested by customers can unquestionably be met. However, laser and inkjet printers can release significant volumes of fine particles, heavy metals, benzene, formaldehyde, styrene, and other carcinogens in the form of gases during printing (http://www.schmidtandclark.com/benzene-theprinting-industry; http://www.cancer.org/Cancer/CancerCauses/ OtherCarcinogens/IntheWorkplace/benzene). These substances

Thus, the concept of heat-induced inkless eco-printing (HIEP) is proposed (Chen. Xie. & Chen. 2010). This technology takes advantage of the tendency for paper to yellow, which is usually considered to be a disadvantage of printing paper (Carter, 1996; Davidson, 1996). Because the yellowing tendency of paper has been considered undesirable in previous studies (Beyer, Koch, & Fischer, 2006; Fromageot, Pichon, Peyron, & Lemaire, 2006), researchers have tended to focus on the elimination of the yellow color, for example, by bleaching or preventing light-induced yellowing during the production, usage, and storage of paper (Carter, 1996). In contrast, the technique presented in this paper harnesses this normally undesirable quality of paper. In this study, we discuss the relationship between the heat-inducing temperature and paper yellowing and discoloration based on the experimental TG curves of paper, heat-inducing, simulated printing, and current knowledge of the pyrolysis of biomass (the main component of this document). We also explain the mechanisms through which HIEP functions, addressing its feasibility, characteristics, and significance.

2. Methods

2.1. TG curves of paper

The thermogravimetric (TG) curves of printing paper (hoopoe® office paper, A4, 70 g/mm², DADONG PULP & PAPER) were measured by a STA 499 F3 (NETZSCH, Germany) under a simulated air

can deteriorate the living environment and affect human health. Paper recycling is also adversely affected when paper is colored by toner or ink (Chantigny, Angers, & Beauchamp, 2000).

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Fig. 1. An electric iron: its controller (a, b) and the shape of its head (a, c).

atmosphere (oxygen 10 ml/min + nitrogen 40 ml/min) at a heating rate of $20 \,^{\circ}\text{C/min}$.

2.2. Experimental analysis of paper yellowing via heat-induction

A soldering iron with a wide ironing head was used (Fig. 1). The head was used to touch and slide over the paper when operated by hand at a certain speed at a preset temperature. Heat-induced color blocks of approximately 7 mm wide and 8 mm long were produced. The psychometric lightness (L^*) and the chromaticity coordinates (x, y) were measured with a color luminance meter (TOPCON, BM-5A). The experimental temperatures used were 350, 400, 450, and 480 °C, and 4 color blocks containing 5 points each were chosen for each group (the data capacity was 20).

2.2.1. Printing simulation experiment

Characters were formed by two methods. In the first method, characters were formed from small heat-induced points produced by the print click method on the printing paper with the aforementioned tip-head electric iron at 480 °C (Fig. 1a). In the second method, laser ablation was performed with a laser (maximum power of 30 W, resolution of 0.025 mm), a high-speed stepper motor (maximum line speed of approximately 1 m/s), and control software. The power and line speed of the simulated printing were 13.5 W and 633 mm/s, respectively.

3. Experimental results and discussion

The thermogravimetric (TG) behavior of the paper can be divided into five stages before $500\,^{\circ}$ C, as shown in Fig. 2. Four critical points (cp 1–4) separating these stages occurred at approximately

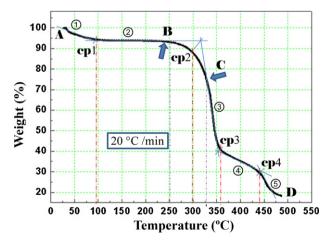


Fig. 2. The TG curve for the papers.

100, 300, 360, and 440 °C. The first stage corresponds to weight loss caused by evaporation. In the second stage, the rate of weight loss was the slowest. The third stage exhibited the fastest rate of weight loss and the highest percentage of weight loss. The weight loss continued in the fourth and fifth stages, in which the rate declined much more than in the third stage. In the TG curve, the BC transition (between the second and third stages) was the longest.

Heat-induced color blocks are shown in Fig. 3a, and the lightness (L*) and location of the chromaticity (x,y) are shown in Fig. 3b and c, respectively. Fig. 3a shows that the color did change through heat-induction at 350–480 °C, although the uniformity of the color was not sufficient because the technology was operated manually. The chromaticity (x,y) changes were slight, with x values varying from 0.40 to 0.38 and y values ranging from 0.39 to 0.37 (Fig. 3c, shown by the hollow circle). These values were mainly within the yellow color range (http://en.wikipedia.org/wiki/International Commission on Illumination). However, the lightness (L*) was greatly affected by the heat-inducing temperature and exhibited values of 26% to 14% under these experimental conditions (Fig. 3b). There was an initial rapid decline in the lightness as the heat-inducing temperature increased, whereas it was stable during the later stages.

Fig. 4a shows that the intermittent points formed clear text patterns during the printing simulation using heat-induction. Although some of the heat-induced points exhibited a small amount of damage, this effect may not alter the strength of the paper. Fig. 4b shows simulation printing by laser ablation, whose printing performance was similar to that of an existing commercial printer. Fig. 4c shows printing using a dot matrix printer manufactured in 1970 (Walker, 2008).

Next, we report the composition of the papers, their TG behavior and their discoloration through yellowing. Based on the aforementioned experimental results, the mechanism of HIEP and its feasibility is analyzed. As is commonly known, the main constituent of paper is biomass, of which cellulose is the major component, followed by hemicellulose (Chen & Li, 2010; Mosier et al., 2005). Many studies have investigated the pyrolysis and thermogravimetric behavior of paper biomass (Biagini et al., 2006; Wang, Wei, & Dong, 2007; Wang, Li, Xue, Yi, & Li, 2009). For example, Biagini has shown that hemicellulose and cellulose significantly decrease in weight at 260-320 °C and 315-380 °C, respectively, and pyrolysis nearly reaches completion (Biagini et al., 2006). The results of previous studies have indicated that the pyrolysis process generates three categories of products: liquids (bio-oils), solids (coke), and gases (Wang et al., 2007). The composition and quantity of pyrolytic products depend on the conditions under which the thermal decomposition occurs (e.g., the heating rate and residence time) (Biagini et al., 2006). These previous studies have aided the validation of the mechanism and feasibility of HIEP.

As indicated in Fig. 2, the paper weight decreased rapidly during the third stage, which started at 300 °C (cp 2). There was a longer transition region between the second and third stages (i.e., from point B to point C, see Fig. 2), which differed by approximately 80 °C. However, the length of the transition region in a single cellulose experiment was reported to be approximately 20-40 °C (Biagini et al., 2006; Wang et al., 2007). This difference in temperature occurred because, although the major constituent of paper is cellulose, it also contains small amounts of hemicellulose and lignin, and these three components have distinct TG characteristics. Thus, when specific experimental factors such as the paper constituents are considered, the results of this experiment can be viewed as consistent with the results obtained by Biagini (sp 2 315 °C) and Wang (sp 2 295 °C) in cellulose pyrolysis experiments (Biagini et al., 2006; Wang et al., 2007). Accordingly, the paper obviously loses weight at temperatures above 350 °C (see Fig. 2), which implies that paper (biomass) pyrolysis occurs rapidly (Biagini et al., 2006; Mosier et al., 2005; Wang et al., 2007). Fig. 3a shows that

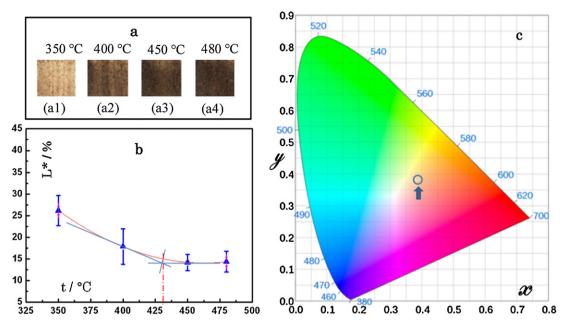


Fig. 3. Heat-induced blocks: (a) scanning photos, (b) corresponding lightness (L*), (c) chromaticity (x, y) (http://en.wikipedia.org/wiki/International Commission on Illumination).

temperatures greater than 350 °C used for heat-induction can cause paper yellowing, with slight variations (Fig. 3c). However, the lightness (L*) initially declines rapidly when the temperature increases, and it stabilizes at a value of 14% (Fig. 3b). The critical temperature is 430 °C, which is close to the temperature at the end of the fourth stage. These results are also consistent with the conclusion that biomass carbonizes at a higher temperature (Milosavljevic, Oja, & Suuberg, 1996). Accordingly, we can conclude that the yellowing process during heat-induction is nearly complete before the critical temperature is reached, and carbonized blackening mainly occurs above the critical temperature.

The comparison of the printing simulation results obtained using heat-induction with those obtained with laser ablation and a dot matrix printer from 1970 (see Fig. 4) shows that the clarity of the text printed by the three methods is similar. In other words, the quality level obtained by heat-induced printing is the same as that obtained using a dot matrix printer from 1970 (Walker, 2008), and the printing quality by laser ablation is better than that produced by a dot matrix printer. The characters formed by laser ablation are yellow in color because the temperature of heat-induction by the laser is below the critical temperature. Both Figs. 3 and 4 indicate that the heat-inducing technology can achieve the desired level of discoloration for printing, and laser ablation can form characters that are golden in color perfectly. Thus, the technology should be usable. Based on the aforementioned preliminary analysis and the characteristics of existing printers, the concept of HIEP can be characterized as follows. HIEP does not require any toner or ink. Using a special printer head, which can be improvised from an existing thermal, laser or dot matrix printer (Chen et al., 2010), the required

text or graphics can be formed on the paper via yellowing and blackening produced by thermal or laser energy. The energy derived from the energy supply unit or other heater (e.g., a light) is transmitted to the desired location on the paper by radiation, heat conduction, and other forms of heat transfer.

Finally, we illustrate the characteristics and significance of HIEP. To compare this new method with traditional print technologies, the aforementioned widely used "coloring method" must be defined in a complementary way. Specifically, the old method involves painting (writing) one or more colored materials (such as black ink) on a base material of a different color (such as white paper) to form the text. In addition to the most commonly used printers (e.g., inkjet and laser printers), thermal printers and rice paper pyrography also use this method (http://en.wikipedia.org/wiki/Thermal printing; Liu, 1999; http://en.wikipedia.org/wiki/Pyrography). Thermal printing on dedicated thermal paper uses a heat-induced chemical reaction and a coating of a compound on the paper to cause a color change. Similarly, the rice paper used for pyrography must be sprayed or brushed in advance with a thin slurry composed of a variety of chemicals (Liu, 1999). In other words, both of these techniques also involve the painting or writing of one or more colored materials (a coating) on a base material of another color to form words or patterns. Currently, almost all printing involves the application of a "paint color" to a "base material". However, a new printing technique has now been developed that requires only a single "base material" to achieve the effect of printing using the "coloring method".

HIEP has the potential to completely change the printing process. Heavy metals, organic polymers and other gases harmful to



Fig. 4. Printing: (a) by the simulated heat-induced method, (b) by laser ablation, (c) by a dot matrix printer (Walker, 2008).

human health will not be emitted from toner or ink during the product life cycle, including the printing process, the use of the printed materials, their storage or the recycling of waste. Thus, the use of this technology completely eliminates a range of issues associated with environmental pollution and human health risks created by toner and ink. This product is truly green and truly environmentally friendly, and it can be used in the office and home. The printing process is simple and easy to use, does not consume toner or ink, does not require an ink supply unit (system), only consumes heat energy for heat-induction, can effectively reduce toner and ink use in industry to improve the scale of production, can significantly reduce waste paper recycling costs associated with ink processing (Chantigny et al., 2000), and can help to improve the quality of recycled paper. Therefore, the concept of heat-induced printing is an important idea with significant applications. It can be widely and easily used in various printing devices and industrial production, and its use carries excellent social and economic benefits.

We hope that the heat-inducing (pyrolysis, or laser ablation) process can be used not only to achieve the yellowing and blackening required for printing but also to minimize paper weight loss to maintain paper strength and reduce energy consumption. Toward this end, a series of best practices should be determined through additional research. Researchers should determine the factors that affect the degree of paper yellowing. These factors might include the heat-inducing temperature or the technical parameters of laser ablation and can be expected to lead to the development of printing devices and high-temperature printer heads. The development of these parameters will require information about the pyrolysis of biomass (considering relevant aspects of the biology, heat transfer, and chemistry) and color science, as well as laser technology (for instance, laser ablation), nano-science (regarding nano-level pyrolytic carbonization on the surface of paper), photochemistry (regarding chromophores in photooxidization (Carter, 1996) and photodegradation (Davidson, 1996)), paper-manufacturing science (including information regarding biomass hydrolysis, enzyme treatment, graft changes and other chemical treatments (Carter, 2007) to make paper more suitable for this HIEP), high temperature materials science, and mechanical and transmission developments (because the printer heads will require sophisticated transmission and electronic control).

In short, the use of HIEP, which facilitates printing without ink, has a great deal of potential as a subject for basic science research and in a number of practical applications. After a number of years, this technology is expected to benefit mankind and lead to the challenge of providing full-color heat-induced printing. Thus, HIEP belongs to the same family as papermaking and movable type printing, which are among the four ancient Chinese inventions (Ray, 2004), and it would constitute another great invention in this area.

4. Conclusions

In this study, we have determined the TG curve for paper and explored heat-induction and simulation printing. We have investigated the relationship between the heat-inducing temperature and the yellowing and discoloration of paper, thereby analyzing the mechanism of HIEP and its feasibility.

1) Under the experimental conditions used, a heat-inducing temperature above 350 °C caused rapid paper pyrolysis and yellowing, and the color obtained varied slightly within the yellow spectrum. The lightness (L*) initially declined rapidly with increasing temperature and became stable at a value of 14%. The critical temperature was 430 °C. The yellowing process for heat-induction was almost entirely finished before the critical

- temperature was reached, and carbonized blackening mainly occurred above the critical temperature. Based on this these results and those of the simulation printing, HIEP should be feasible.
- 2) The concept of HIEP requires that the text or graphics were formed on the paper via yellowing and carbonized blackening produced by thermal energy. This technology is based on the principles governing the use of existing thermal and dot matrix printer technology, which can be used to develop a heat-inducing printer head. The energy can be transmitted to the desired location on the paper through the printer head. This process does not require any toner or ink, and it consumes only the energy required for heat-induction.
- 3) Almost all printing since ancient times has been performed using the primitive "coloring method", in which color and base materials are used, and the "bump method". In this study, we have proposed a new method of heat-induced eco-printing that does not require ink and can achieve the same results using only a single "base material" (i.e., paper).
- 4) HIEP will completely change printing. In the life cycle of the printed product, issues such as environmental pollution and human health risks caused by toner or ink and the recycling and reuse of waste paper no longer exist when this process is used. This printing process is also simple and easy to use in various industries. The development of HIEP represents a significant technological improvement, and it could be a landmark technology in today's era of worsening environmental pollution.

This study not only proposes the concept of HIEP, but it also creates a broad topic for interdisciplinary research in biology, photochemistry, nanotechnology, paper-making, and color science. We will broaden and deepen the theory and applications of HIEP in future research and present a series of relevant research reports.

Acknowledgments

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References

Beyer, M., Koch, H., & Fischer, K. (2006). Role of hemicelluloses in the formation of chromophores during heat treatment of bleached chemical pulps. *Macromolec-ular Symposia*, 232, 98–106.

Biagini, E., Barontini, F., Tognotti, L., Enrieo, B., Federiea, B., & Leonardo, T. (2006). Devolatilization of biomass fuels and biomass components studied by TG/FTIR technique. *Industrial & Engineering Chemistry Research.*, 45, 4486–4493.

Carter, H. A. (1996). The chemistry of paper preservation. Part 2: The yellowing of paper and conservation bleaching. *Journal of Chemical Education*, 73, 1068–1073.Carter, H. A. (2007). The chemistry of paper preservation. Part 5: Permanent paper. *Journal of Chemical Education*, 84, 1937–1940.

Chantigny, M. H., Angers, D. A., & Beauchamp, C. J. (2000). Decomposition of de-inking paper sludge in agricultural soils as characterized by carbohydrate analysis. Soil Biology & Biochemistry, 32, 1561–1570.

Chen, G.-P., & Li, C.-R. (2010). Analysis and application on influencing factors of paper shrinkage rate. *China Pulp & Paper Industry*, 31(20), 79–81 (in Chinese)

Chen, J. X., Xie, J., & Chen, F. (2010). A heat-inducing eco-printing method and print head device. 201010218623.8 & ZL 201020248698.6 (in Chinese).

Davidson, R. (1996). The photodegradation of some naturally occurring polymers. Journal of Photochemistry and Photobiology. B. Biology, 3, 25–33.

Ferraro, P., Coppola, S., Grilli, S., Paturzo, M., & Vespini, V. (2010). Dispensing nano-pico droplets and liquid patterning by pyroelectrodynamic shooting. *Nature Nano*, 5, 429-435.

Fromageot, D., Pichon, N., Peyron, O., & Lemaire, J. (2006). Thermal yellowing 353 sensitised by pre-photo-oxidation of non-deacidified paper Dominique Fromageot. *Polymer Degradation and Stability*, 91, 347–357.

Liu, Z. W. (1999). Pyrography method for rice paper. CN99122434.5 (in Chinese). Milosavljevic, I., Oja, V., & Suuberg, E. M. (1996). Thermal effects in cellulose pyrolysis: Relationship to char formation processes. *Industrial & Engineering Chemistry Research*, 35, 653–662.

Mosier, N., Wyman, C., Dale, B., Elander, R., Lee, Y. Y., Holtzapple, M., et al. (2005). Features of promising technologies for pretreatment of lignocellulosic biomass. *Bioresource Technology*, 96, 673–686.

- Park, J. U., Hardy, M., Kang, S. J., Barton, K., Adair, K., Mukhopadhyay, D. K., et al. (2007). High-resolution electrohydrodynamic jet printing. *Nature Materials*, 6, 782–789.
- Ray, K. (2004). Chinese inventions. http://www.sacu.org/greatinventions.html Walker, T. (2008). The history of print: From Phaistos To 3D. http://www.cartridgesave.co.uk/news/the-history-of-print-from -phaistos-to-2d/
- Wang, G., Li, W., Xue, Q. Z., Yi, Y. T., & Li, B. Q. (2009). Thermogravimetric behaviors of biomass' chemical components under air or syngas. *Journal of Fuel Chemistry and Technology*, *37*, 171–176 (in Chinese).
- and Technology, 37, 171–176 (in Chinese).

 Wang, W. G., Wei, J., & Dong, C. Q. (2007). Thermogravimetric and thermokinetic study on pyrolysis of cellulose. *Renewable Energy Resources*, 25, 23–26 (in Chinese).