WEIGHT LOSS PHENOMENON OF PAPER AND THE MECHANISM FOR NEGLIGIBLE DAMAGE OF HEAT-INDUCED INKLESS ECO-PRINTING

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To eliminate the environmental pollution caused by the toxic and hazardous materials used in ink or laser jet printing, the authors have previously proposed a concept of heat-induced inkless eco-printing (HIEP), which is inspired by the yellowing discoloration of plant fibers. Based on the experimental studies on the thermogravimetry (TG) of paper, the yellowing of paper via heat-induction and a simulated printing test, the weight loss phenomenon of paper and the mechanism for the negligible damage to paper during HIEP are discussed. The paper lost weight drastically below 600 °C. However, this loss could be easily controlled by monitoring the temperature and heating time. No significant damage to the paper was evident upon HIEP as the degree of heat experienced during HIEP is far below that of the TG experiment; additionally, the evaporated water had a buffering effect. This study shows that the HIEP technology has valuable potential for practical applications.

Keywords: paper, cellulose, hemicelluloses, pyrolysis, printing, eco-material

INTRODUCTION

Paper-making and moveable type printing have played an invaluable role in the recording of human history, dissemination of culture, progress of science and technology and foundation of modern printing technology. The two aforementioned technologies are among the four greatest inventions in ancient China. Paper was invented approximately 2000 years ago, and moveable type printing was invented approximately 1000 years ago.[1,2] With the emergence and development of the computer, printing technology has evolved rapidly since the mid-20th century. Commercial dot matrix and laser printers were invented during the 1960s, and the first inkjet printer was introduced during the 1970s;[2] subsequently, thermal and 3D (nano) printers were invented more recently.[3] As discussed in a previous study,[4] laser and inkjet printers have been shown to have harmful effects on human health, and the use of ink adversely affects both the process of paper recycling and the environment significantly.[5,6] As a result, in recent years, the print industry has conducted extensive research on inkless or zero ink (Zink) eco-printing technology, whose core technique is focused on developing a new and distinct type of printing paper. For example, ZINK Imaging Incorporation[7] introduced a printing paper containing a significant amount of crystalline dye. As the printing technique that creates the dye resulted in various color changes in the paper due to heat during the printing process, ZINK developed a Pandigital inkless printer.[8] Dell Incorporation introduced photographic printing by applying a special layer on photo paper that could reflect lights of different wavelength, and they developed the Wasabi PZ310 mini-printer. In addition, other printing techniques have been introduced through changes in the nanometer microstructure of special materials on the surface of the paper or by utilizing liquid polymer;[9] this category of approaches is referred to as contact printing.[10-12] Furthermore, another recent printing technique has been introduced that has implemented eco-printing by utilizing natural pigment on printing paper.[13-15]

Although extensive effort has been focused on developments that have centered on manipulating the paper's molecular structure to achieve inkless printing, a radically different approach that can result in a paradigm shift for realizing inkless printing has not been reported in the literature to the best of the authors' knowledge. Recently, inspired by the inherent yellowing discoloration features of plant fibers,[16] as well as the rapid yellowing and discoloration of printing paper through heat energy, the authors proposed a radically new concept of heat-induced inkless eco-printing (HIEP) that does not require ink during the printing process and that can achieve the same printing results using only the currently used ordinary sheets of office paper.[4,17] This technique can eliminate the environmental pollution generated by the ink used in the printing industry. According to the thermogravimetry (TG) results in an earlier report,[4] the paper experiences significant weight loss[18,19] and yellowing discoloration[4,20] when the temperature reaches 480 °C. However, why does paper not experience any serious damage during HIEP? Based on experimental studies used to determine the composition of paper, TG, and heat-induced color blocks and simulated printing, the weight loss phenomenon and mechanism for negligible damage to paper during HIEP are discussed in this study along with various key technical parameters, such as the HIEP temperatures and time.

EXPERIMENTAL

TG and DSC curves of paper

In the experimental study that was conducted, the TG and differential scanning calorimetry (DSC) curves of the printing paper were obtained using a NETZSCHSTA499F3 instrument under simulated air atmosphere (10 mL/min oxygen + 40 mL/min nitrogen), and the corresponding heating rates were either 20 or 40 °C/min. The composition of the paper (Hoopoe® office paper, A4, 70 g/mm^2, DADONG PULP & PAPER) was determined by conventional methods.[21]

Experimental analysis of paper yellowing via heat-induction

To fabricate heat-induced color blocks, a wide ironing (Fig. 1a) head was applied by touching and sliding over the paper and was operated by hand at a certain speed at the current temperature. The experimental temperatures were set at 350, 400, 450 and 480 °C.

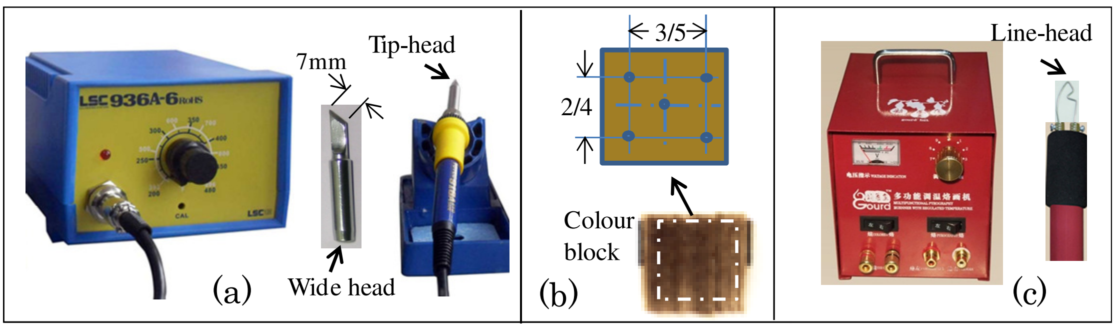

Figure 1: Controller and shape of its head for two electric soldering irons (a, c), and a sample of the color block with locations of 5 measurement points (b)

Using this method, color blocks approximately 7 mm wide by 8 mm long were drawn during each temperature, as shown in Fig. 1b. A stopwatch was used to record the time required to draw each color block. The psychometric lightness (L*) and chromaticity coordinates (x, y) were measured with a color luminance meter (TOPCON, BM-5A). Four color blocks containing 5 points (Fig. 1b) for each temperature were chosen for each group (the data capacity was 20).[4]

Printing simulation experiment

To examine the printing effect at higher temperatures, the 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 tip-head on the electric soldering iron at 350 °C or 480 °C (Fig. 1a)[4] and the line-head electric iron at 500 °C or 600 °C (Fig. 1c, type: zyx2-3-1, voltage: 220 V, and maximum temperature: 1000 °C). In the second method, the characters were written at 480 °C as a simulated scanning print.

RESULTS AND DISCUSSION

As previously mentioned,[4] the weight loss (pyrolysis) of the paper should be minimal once the paper has been printed and turned yellow. Therefore, the key to HIEP technology lies in determining the proper heat-induction temperature and time; the weight loss (pyrolysis) needs to be controlled to quickly achieve the required level of yellowing for printing. These issues are addressed in detail in the following sections.

Parameters influencing the weight loss (pyrolysis) of paper and their characteristics

As shown in Table 1, cellulose is the major ingredient in the paper and accounts for more than 60% of the total mass content; furthermore, hemicellulose and ash (filler) comprise 20% of the total mass. Water accounts for more than 5% of the total mass, and lignin is barely detected.

Both TG curves (Fig. 2a) of the paper at heating rates of 20 and 40 °C/min contain seven critical points (cp1-7), which separate the curves into eight stages. The temperature of the critical points increases with the heating rate. The weight loss of the paper mainly occurs during the third to fifth stages of the TG curves, which corresponds to two endothermic peaks and one exothermic peak in the DSC curves (Fig. 2b, D1, D2 and P1). Additionally, these main stages are roughly marked on the DSC curve for comparison with the TG curve. The locations of these peaks differ with the heating rate. Overall, the peak temperature increases with the heating rate (Fig. 2, Table 2). The total heat absorbed at different temperatures (Fig. 3) in the DSC curves (Fig. 2b) was obtained using ORIGIN. According to Li and Wang *et al.*,[22,23] who investigated the TG behavior of wood and biomass in air, these two endothermic peaks (Fig. 2 D1, III and D2, IV are mainly caused by the pyrolysis of hemicellulose and cellulose. The exothermic peak P1 (TG on IV) forms as a result of the following two reasons. First, the material burns at a high temperature (the process is referred to as “secondary combustion”) and releases the heat generated in the third stage of weight loss (Wang,[23] Tan,[24] etc.). Second, a transitional stage in the TG curve can be observed (Fig. 2a IV), because hemicelluloses and cellulose pyrolysis occur at different temperatures.[25] The total thermal solution in this stage has less than the required amount of heat absorption, which helps to form the exothermic peak. Overall, the pyrolysis process is endothermic (Fig. 3) because the amount of exotherms is greater than the amount of endotherms.

Subsequently, the authors focused on the effect of the heating rate on the weight loss (pyrolysis) of the paper. At a lower heating rate, the paper is heated for a long period of time to reach a certain temperature and loses more weight than when it is heated at a higher rate (Fig. 2a).

Table 1
Ingredients of paper

Major ingredient	Cellulose	Hemicellulose	Lignin	Ash (filler)	Water	Extractive
Average (%)	62.0	9.9	0.6	12.2	6.8	4.7

The total heat absorbed (Fig. 3) decreases, especially during the fourth stage (350-380 °C), because secondary combustion occurs fully and releases much more heat for pyrolysis than the process at a higher heating rate. Furthermore, the total heat absorption is constant above 530 °C.

Therefore, the heating rate affects the rate of paper pyrolysis and the associated product. Additionally, the critical temperature of paper pyrolysis is higher at a higher heating rate (Fig. 2a), which is consistent with the findings of Wang and Milosavljevic *et al*.[19,26]

Although pyrolysis requires much more heat at a higher heating rate, the rapid heating can significantly shorten the heating time to reach a specific temperature. In addition, rapid heating can reduce the weight loss of paper, which is desirable for the manufacturability and commercialization of the HIEP process.

Table 2
DSC temperature of the main peaks in the DSC curve

Peak No	D1	P1	D2	P2
20 °C/min	354	414	453	711
40 °C/min	378	423	451	751

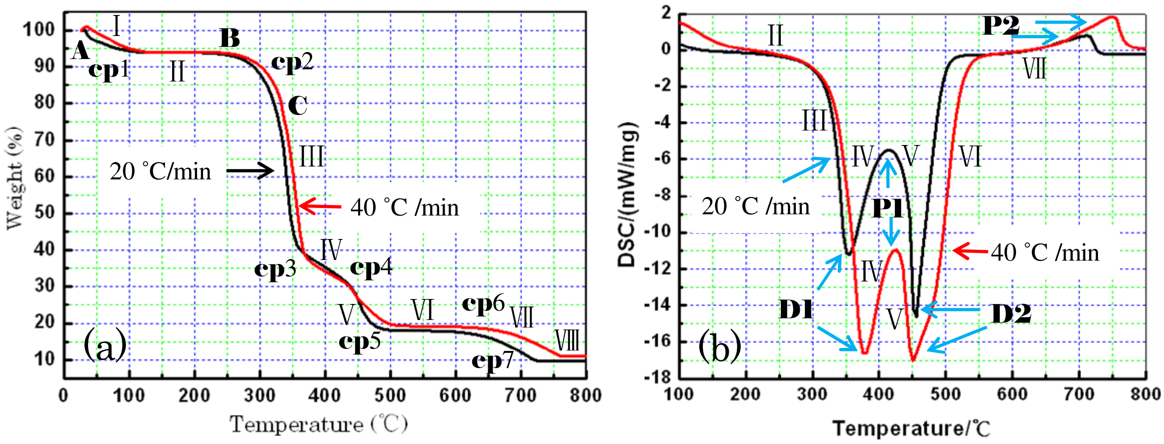

Figure 2: TG and DSC curves for paper samples

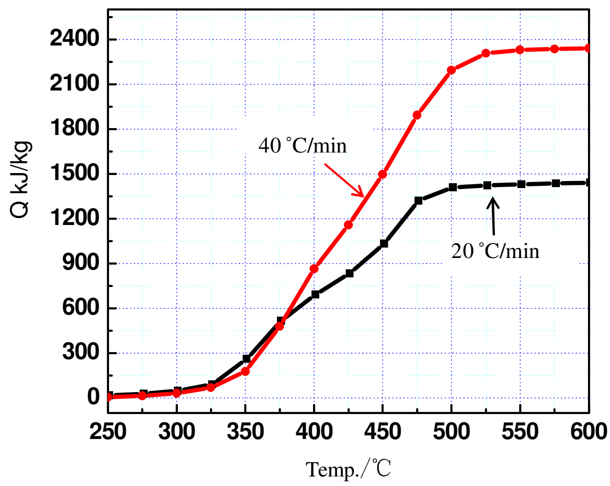

Figure 3: Endothermic curve of paper pyrolysis

Conversely, according to the TG results, the paper experiences significant weight loss when the temperature reaches approximately 500 °C (Fig. 2a). The question is, however, does the paper experience serious damage during HIEP? In the next section, this topic is discussed based on the experimental analysis of paper yellowing via heat-induction, the results of the printing simulation and the TG behavior of paper.

Heat causing paper damage and mechanism of its negligible damage during HIEP

The color blocks with the lowest and highest lightness L* at each temperature are shown in Fig. 4 as extreme color blocks to compare the color and technical parameters of the printing speed. Table 3 shows the results of different heat-induction times on the color blocks at different temperatures, indicating that the heat-induction time (t) and its standard deviation (σ) and extreme difference (δ_{max}) decrease as the heat-induction temperature increases. The extreme difference of the heat-induction time is approximately 20% to 30% and is caused by manual operation, and several differences in color can be observed between the two extreme color blocks at each temperature. However, the degree of variance is much smaller than the difference between each temperature. As shown in Fig. 4, the color blocks generated at 350 °C exhibit a yellow color, and the color blocks at 480 °C are darker. From the color analysis, the intuitive difference between each group is mainly caused by the lightness L* (Table 3), not the tone.

The results of the printing simulations at different heat-induction temperatures and times are shown in Fig. 5 (a-b) and Fig. 5 (c-d), respectively. The texts formed in the various modes are clearly visible, and there is no obvious damage to the paper. According to the TG results, the paper experiences significant weight loss when the temperature reaches 500 °C. However, the paper does not experience serious damage during HIEP because the heating time in the TG experiments is different from the heating time during HIEP.

Table 3
Temperature, time and lightness L* of the colour blocks in this experiment

Temperature	T (°C)	350	400	450	480
Average time	T (s)	7.14	5.4	3.03	2.58
Standard deviation of time	σ (s)	0.91	0.41	0.51	0.22
Extreme difference	δ_{max} (%)	30.1	17.1	20.1	19.0
Time of each dot	Δt (ms)	89	68	38	32
Average of lightness	L* (%)	26.2	17.9	14.2	14.4

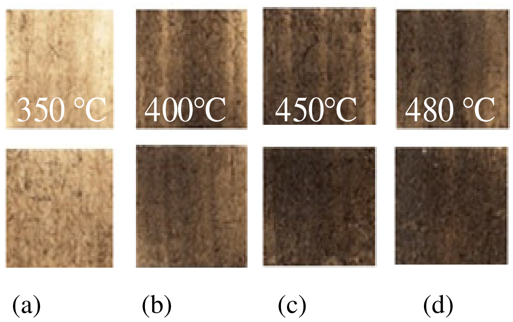

Figure 4: Color blocks generated by heat-induction

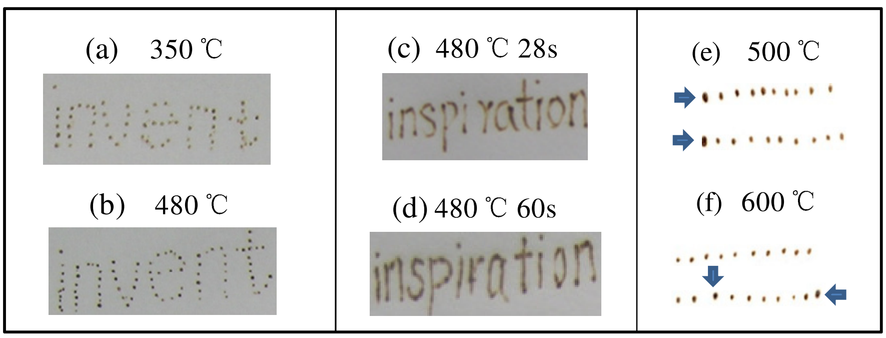

Figure 5: Simulation printing results at different temperatures by the print-click method (a, b, e, f), and scanning method (c, d)

The heating time depends on the HIEP speed (depending on the contact time between the printer head and paper), and the HIEP speed can be predicted by calculating the time to print one dot using the following formula:

$$\Delta t = t/(bn) \quad (1)$$

where b is the width of each color block (8 mm in this study); t is the time to form the color block by heat induction (the value is shown in Table 1); and n is the printed dot density. The value of n, according to the specifications of the thermal printer, is 8-23.6 dot/mm;[27] for this study, n has been conservatively defined as 10.

The time of heat induction of each printed dot (Δt) is calculated and listed in Table 3. According to Table 3, the time of crossing a printing dot is of approximately 30-90 ms between 400-480 °C. For example, at the heating rate of 40 °C/min, a 15 second time is required to increase the temperature by 10 °C during the TG measurements. On the other hand, the time to print each dot at 480 °C is considered as approximately 30 ms (see Table 3), which is less than 1/500 of the TG value. However, the heating process is continuous and cumulative in the TG experiment, and water (as an ingredient of paper, shown in Table 1) evaporates as the paper is heated, acting as a buffer. The degree of heat transfer differs by at least two orders of magnitude between the HIEP and TG experiments. Therefore, it is not difficult to understand the mechanism of negligible damage to the paper due to the heat causing paper damage during HIEP. As described above, the heat-induction temperature is much higher than that of paper (cellulose and hemicelluloses) pyrolysis, but the heating time is very short (several milliseconds), and there is a buffer effect of the water evaporated from the paper. Thus, secondary combustion of the paper will usually not occur, and there is minimal cellulose and hemicelluloses pyrolysis. Therefore, the paper does not experience any significant damage.

In addition, the weight loss phenomenon (paper pyrolysis) concludes when the temperature reaches 480 °C (Fig. 2a). Then, the paper loses weight very slowly in the subsequent six stages (approximately 500-600 °C); no additional pyrolysis occurs above 600 °C. According to a study by Tan *et al*.,[24] which discussed the relationship between the production and yield of biomass pyrolysis and heat-induction, cellulose and hemicelluloses have a higher char yield and lower gas yield between 400 and 600 °C. Furthermore, the char yield decreases and the gas yield increases rapidly between 600 and 800 °C. A high rate of carbonation will help paper carbonization and blackening for printing, and a low rate of penetration can reduce paper damage. However, if the heat-induction temperature is too high, the requirements for the material of the print head, printer security and other parameters of HIEP are also high. Temperatures ranging between 400 and 600 °C are reasonable for heat-induced printing. To verify this proposition, the results of the print and click simulation printing at 500 and 600 °C are shown in Fig. 5 (e, f). It is evident that a small number of heat-induced dots are severely damaged due to improper operation (Fig. 5e, f, arrow); however, a large number of dots can be produced with no obvious damage under appropriate control. The color (brightness L*) is much closer to that at 480 °C. This observation is consistent with earlier findings demonstrating that the paper becomes black above the critical temperature (430 °C).

In conclusion, it is obvious that the paper loses weight quickly between 400 and 600 °C. The paper weight-loss rate can be closely controlled by monitoring the paper heat-induction temperature and time. These findings provide a scientific basis to control paper weight loss upon yellowing and discoloration and to prevent damage based on the TG behavior of paper. Therefore, the HIEP has a highly promising practical value.

In summary, the main issue with heat-induced printing is the generation of the resulting yellow tones. As the findings in this research demonstrate, although this proposed technique is highly promising and offers a novel approach, the heat-induced printing is not yet a fully developed and mature technique to completely replace the currently used printing technology. As discussed in this paper, the pyrolysis and non-damage mechanism of printing paper, attributed to the pigments of heat-induced printing, results from the changes of molecular structure and carbonization that contribute to features such as durability and non-fading. If the aforementioned challenges can be overcome, the HIEP technology has the potential for a practical implementation as a viable approach for inkless printing and can be part of the printing industry. In fact, as a newly proposed technology, several of the key techniques and relevant concepts addressed in this research still need further in-depth study. As the next step, further study on the heat intensity of the printing process, the fiber decomposition process, optimal HIEP technical parameters and the paper's hemicelluloses (the substance that forms during the decomposition process), as well as how they affect the yellow discoloration, require further investigation. As discussed in a previous study,[4] further progress in the proposed HIEP also offers a broad topic for interdisciplinary research in biology, photochemistry, nanotechnology, paper-making, and color science. With an interdisciplinary approach for the continuation of this research, we will broaden and deepen the theory and applications of HIEP in the future, and the anticipated results will be reported in subsequent reports.[28-31]

CONCLUSION

The relationships between the heat-induction temperature, time and weight loss behaviors of paper were analyzed in this study. The yellowing of paper via heat-induction, technical parameters of HIEP and the mechanism of negligible damage upon HIEP were discussed.

1) The paper had several stages of weight loss in the TG experiments, and the paper lost weight drastically below 600 °C. Two endothermic peaks, corresponding to the hemicelluloses and cellulose pyrolysis, are observed in the DSC curves. Another exothermic peak, corresponding to the secondary combustion of a material that is difficult to decompose, is also observed. The obtained results show that a higher heating rate increases the heat-absorbing capacity of the paper and greatly reduces the heating time and weight loss of the paper. The weight loss of the paper can be easily controlled by monitoring its temperature and heating time. Therefore, these features of paper pyrolysis are expected to be important for the commercialization of HIEP.

2) The printing speed can be adjusted to a practical level when the heat-induction temperature is between 400 and 600 °C. The paper undergoes no significant damage during HIEP because the degree of heat transferred during HIEP is far lower than the heat transferred during the TG experiment. Furthermore, the buffering effect of water due to evaporation prevents damage to the paper. This finding shows that the technology has a highly promising practical value.

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