THE EFFECT OF LASER INKLESS ECO-PRINTING ON THE CARBONIZED MICROSTRUCTURE OF PAPER

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The effect of laser inkless eco-printing (LIEP) on the carbonized microstructure of paper has been analyzed using two microscopes and a color luminance meter. It has been observed that after LIEP, the carbonized microstructure of paper presents three categories of features: small holes, cauliflower core-like clots, and fibrous features. When the printing power reaches a given value, pyrolysis and carbonization occur on the surface fibers of the paper. The higher the laser power, the more completely the fibers are broken down, and the formation of cauliflower core-like particles primarily occurs with high-level laser energy. In the carbonized microstructure, the transition zone of the printing boundary of the paper is typically several microns (or even zero microns), and the boundary is clear. It is concluded that when applying the proper parameter combinations, the fibers on the paper surface can undergo a large amount of carbonization and yellow discoloration, satisfying the printing requirements.

Keywords: paper, inkless eco-printing, SEM microscopy, microstructure, Zink

INTRODUCTION

Paper-making and moveable type printing have played an invaluable role in the recording of human history, the dissemination of culture, the progress of science and technology, and the foundation of modern printing technology. The two aforementioned technologies are among the four greatest inventions of 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 rapidly evolved since the mid-20th century. The commercial dot matrix and laser printers were invented during the 1960s, and the first inkjet printer was introduced during the 1970s;[2] thermal and 3D (nano) printers were invented more recently.[3]

As discussed in a previous paper,[4] laser and inkjet printers have been shown to have harmful effects on human health,[5] and the use of ink adversely affects both the process of paper recycling and the environment.[6] As a result, in recent years, the printing industry has carried out extensive research on inkless or zero ink (Zink) eco-printing technology. The core approach used in this field involves the development of a special new type of printing paper. For example, ZINK Imaging Incorporated[7] introduced printing paper containing a significant amount of crystalline dye. Using a printing technique that causes the dye to undergo various color changes upon heating during the printing process, they developed a Pandigital inkless printer.[8] Dell Incorporated developed a technique for printing photos that involves applying a special layer to the photo paper that can reflect light of different wavelengths and developed the Wasabi PZ310 mini-printer. In addition, other printing techniques have been introduced through changes in the nanometer microstructure of special materials or by utilizing a liquid polymer[9] on the paper surface. This category of techniques is referred to as contact printing.[10-12] In addition, another recent printing technique has been introduced that facilitates eco-printing by utilizing natural pigments on printing paper.[13-15]

Although extensive efforts have been focused on manipulating paper's molecular structure to achieve the goal of inkless printing, to the best of our knowledge, a radically different approach that can result in a paradigm shift for reaching the goal of inkless printing[4] has not been reported in the literature. Recently, we introduced the concept of heat-induced eco-printing technology implemented with ordinary paper without the use of toner or ink.[4,16,17] The main components of the paper are the cellulose and hemicellulose of the biomass,[18-20] and research on biomass pyrolysis,[21,22] thermal weight loss,[23,24] and carbonation mechanisms has been reported in numerous studies.[25,26] Some results have been obtained based on the biomass pyrolysis process (C-O and C-C bond cleavage[27]), such as the three categories of gas, liquid (bio-oil), and solid (coke); the composition and proportion of the pyrolysis products are dependent on the pyrolysis conditions (e.g., the heating rate and residence time).[25,28] The paper weight loss (carbonation) caused by laser inkless eco-printing (LIEP) may be similar to the weight loss observed with other techniques. However, the purpose of our eco-printing research is to ensure that the paper yellowing and blackening meet the printing requirements with as little weight loss as possible. This purpose is completely different from that of other research, which typically focuses on methods for rapidly converting biomass into bio-oil in a more efficient manner.[29,30] This paper focuses on the effect of printing using different LIEP parameters on the carbonized microstructure of paper.

EXPERIMENTAL

In earlier research, color blocks were produced by the contact method. The color blocks discussed in this paper are produced by LIEP, which is a noncontact method.

Printing simulation experiment and chroma determination

The printing paper used in this study (Hoopoe® office paper, A4, 70 g/mm^2, DADONG PULP & PAPER) is the same as in a previous report.[4]

Characters (color blocks) were formed by LIEP: 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.[4] According to the results of the color obtained from a pre-experiment with a number of printing parameters, the experimental parameters were designed as described in Table 1. The psychometric lightness (L*) and the chromaticity coordinates (x, y) were measured with a color luminance meter (TOPCON, BM-5A). For each sample, five color blocks that were 3 mm wide and 5 mm long were produced; each color block had two determination points. Each group had a total sample size of 10 points.

Microstructure observation

The microstructure of the paper in the region subjected to laser printing and the associated borders were observed directly using two microscopes: an Ultra Plus field emission scanning electron microscope (FE-SEM; Carl Zeiss NTS GmbH, Oberkochen, Germany) and a Carl Zeiss LSM 700 laser scanning confocal microscope.

RESULTS AND DISCUSSION

Carbonized microstructure of paper after LIEP

Figure 1 shows a set of SEM images. The laser power applied in the runs illustrated in the left column is lower than that of the runs illustrated in the right column (in the same row), and the images in each column are sorted by laser power from low to high. The laser power increases according to the image order (a-f). The print speed is given in the figure (the order in Figures 2-4 is the same as that for Figure 1) As shown in Figure 1, more intact fibers are only observed in the top left image (Figure 1a, with a wide arrow), which has the lowest print speed and laser power (see Table 1). The other images show a clot-like structure that resembles a cauliflower core pattern (Figure 1 with a triangle) accompanied by a large number of irregular voids (Figure 1 with an arrow and "V"). For the images produced at the same print speed (images in the same row), the diameter of the clots on the right side of each image row is smaller than that of the clots on the left side (Figures 2 c, d, e, f). The features on the left side of the first row have a fibrous appearance (Figure 1 a), and the features on the right side of each row have a clot-like appearance (Figure 1 b). This characteristic shows that the greater the laser power (at the same speed), the finer the fiber. The SEM images demonstrate this behavior as the laser power increases from (a) to (f). However, the slot diameter of one image did not follow this trend (Figure 1e) and it appears slightly larger than that of Figure 1 d. Although the power of

Figure 1 e is higher than that of Figure 1 d, the latter image has twice the print speed of the former image and a shorter laser ablation duration.

In addition, small faint holes (the circle in the image) can be observed in Figure 1. To further examine the carbonized microstructure (including the small holes), SEM images with a higher magnification (Figures 2 a-f) are provided for the same conditions as those represented in Figure 1. Images for paper without heat-induced printing (printed at a lower power) are provided in Figure 2 (g, h) for comparison.

Table 1
Parameters of LIEP

Velocity (mm/s)	100	350	550	750	1000
Power 0 (W)	/	/	3.0	/	/
Power 1 (W)	1.0	3.0	4.5	6.0	9.0
Power 2 (W)	1.5	4.0	7.0	9.0	15.0

Yellow discoloration is shallow in the series of Power 0. Chromaticity determination was not carried out (only SEM observation)

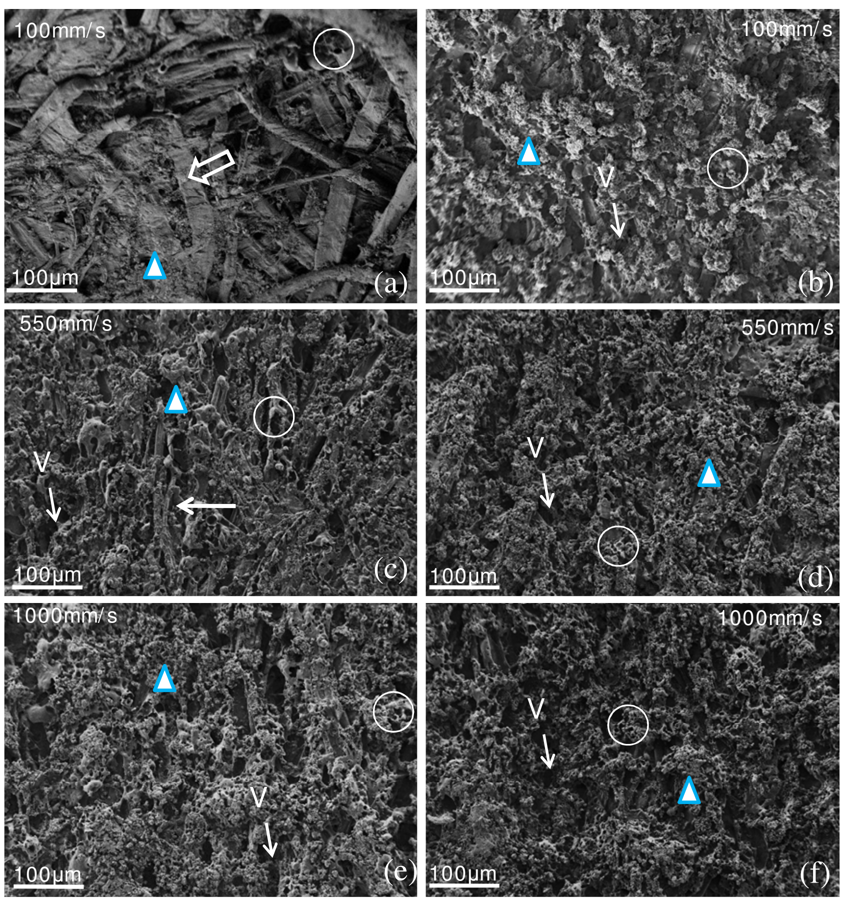

Figure 1: Low-magnification SEM images of the carbonized microstructure of paper after LIEP: (a-c) power 1 and (d-f) power 2

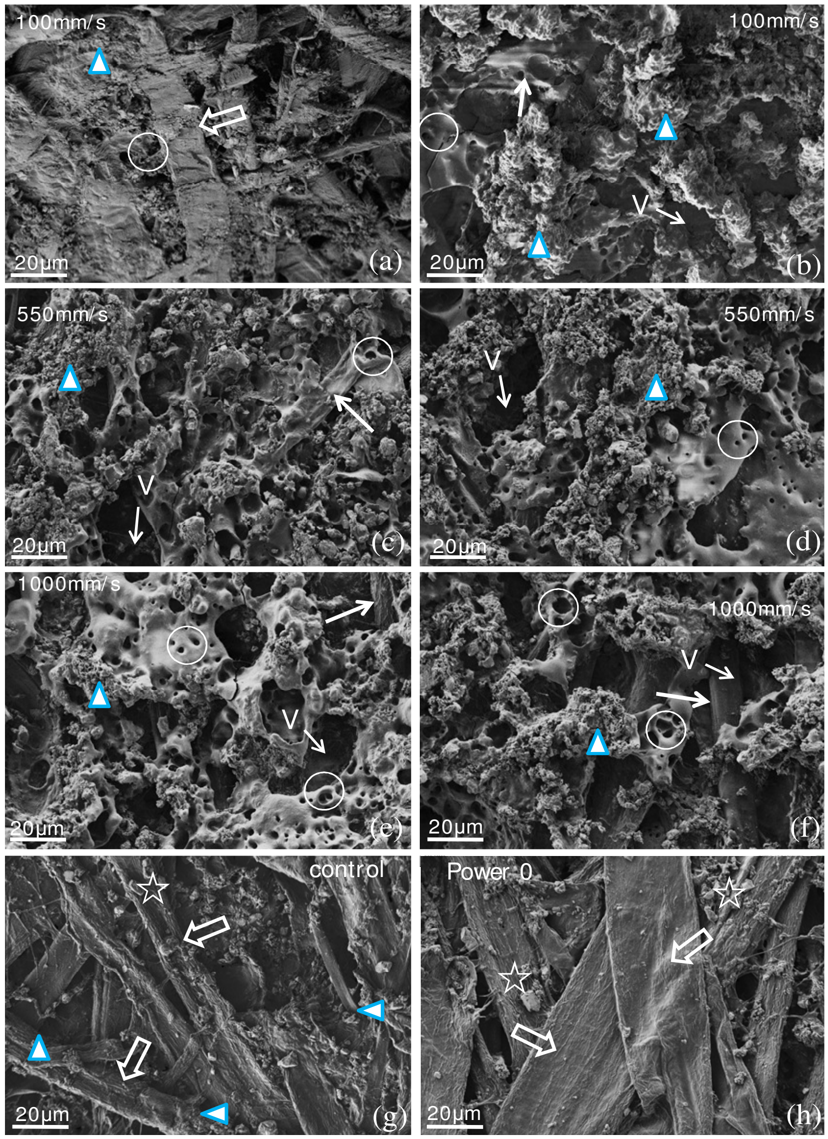

Figure 2: Typical carbonized microstructure and control sample: (a-c) power 1 and (d-f) power 2

Figure 2 clearly shows that the carbonized microstructure of the paper after LIEP can be described by three categories of characteristics: 1) small holes (Figure 2, circles), 2) cauliflower core-like clots (Figure 2, triangles), and 3) fibrous features (Figure 2a, wide arrows indicating the area in which the surface is no longer crumpled as in Figures 2 g, h. The small holes are primarily scattered on the surface of the material, which is quite smooth and soft; the surface of the material resembles microsludge (Figures 2 c, d, e) and feels like a softening material. In the samples (Figures 2 b, f), clot-like particle materials are always found (e.g., collections of powder that resemble clusters of flowers and feel like powdered materials). Concurrently, the majority of interspaces are distributed in the sludge, the slot materials, and the gaps themselves. Melted fibers can be observed at the bottom of the valley (Figure 2, the arrow marked with a "V"). Paper (before heat-induced printing) generally has a porosity (recesses and voids) greater than 50%;[31]

therefore, it can be concluded that the majority of the aforementioned interspaces were generated by the carbonation decomposition. Figure 3 shows SEM images of the print boundary under the same experimental conditions shown in Figure 1. The white dotted lines in Figure 3 indicate the division between heat-induced printing and non-heat printing, where the side marked by the letter "P" has been subjected to printing. In each photo, there is a clear and relatively clean dividing line, with a small width (only slightly wider than the white dotted line), while the transition zones from “no print” to “completely carbonized” are generally narrow. The lines are typically several microns wide, and in some cases, no obvious lines were found. The reason for this disparity may be that the laser diameter is small, and the laser energy can focus on print points. Therefore, the laser can print with a clear and clean boundary.

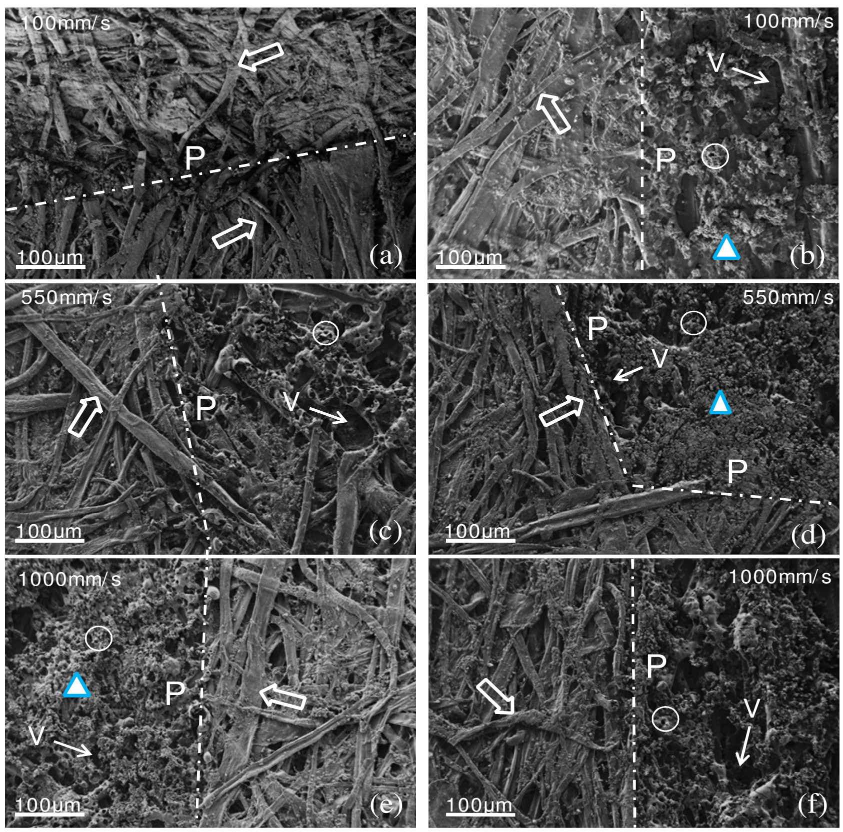

Figure 3: Carbonized microstructures of the boundary of LIEP: (a-c) power 1 and (d-f) power 2

Printing effect of LIEP

Figure 4(a) shows lightness L* curves for each sample together with the color blocks. The L* values are 23 to 42 under our experimental conditions, and approximately 25 under the power level 2. For the chromaticity (x, y), the experimental results indicate that the values of x primarily range from 0.38 to 0.41, while the values of y range from 0.36 to 0.38; these values are mainly distributed in the range of yellow tones without any large fluctuations. The differing appearances of the images corresponding to different power levels are primarily caused by the lightness L* (Figure 4a). This conclusion is consistent with the results obtained in a previous paper on direct heat-induced printing.[9] The power 1 samples have light yellow tones, and the lightness ranges from 40 to 50. A large number of fibers can be observed in the microstructure, especially when the lightness is close to 50 (Figure 2a). The fiber patterns corresponding to power 0 (the lowest power) are nearly the same as those of the paper without laser ablation. Just as a low laser power can be used to clean the fiber,[32] process conditions lower than the power 1 setting can be considered of no practical value in printing.

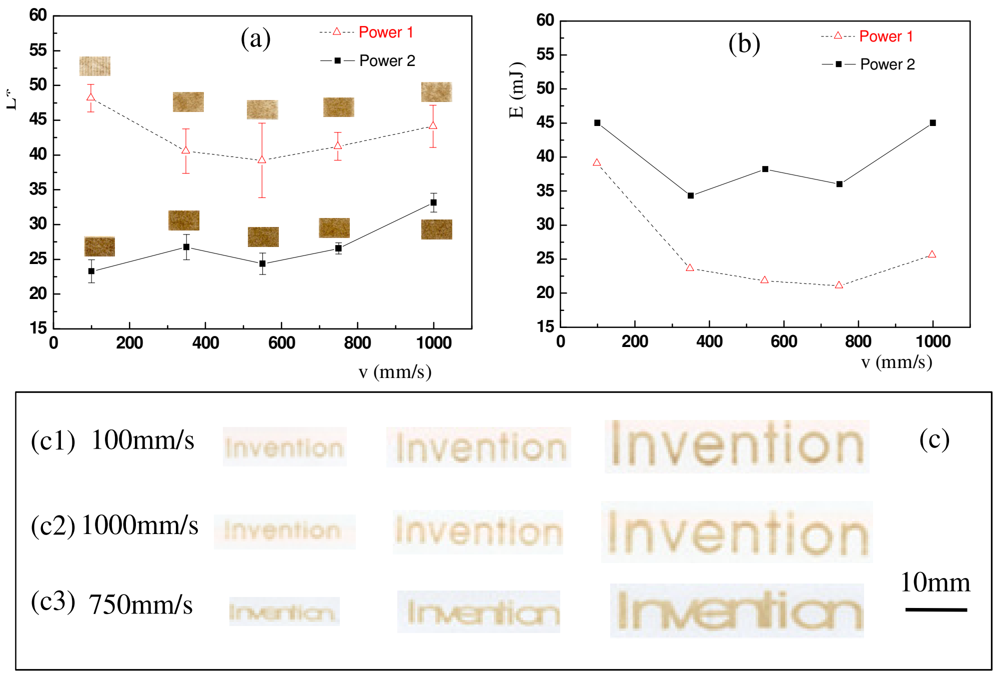

Figure 4: Relationship between the degree of yellow discoloration and LIEP parameters: (a) brightness values L* of the color blocks; (b) laser energy; (c) samples printed with different LIEP parameters for power 1 (c1, c2) and power 2 (c3)

To analyze the effect of printing, such as the relationship between the degree of yellow discoloration and the LIEP parameters, the laser energy E (J) used for each printing point (i.e., the smallest point that can be obtained by laser printing) can be expressed by formula (1) based on the laser power[33] and print speed.

$$E = P \cdot t = P \cdot d / v$$

where P (W) is the laser power, d (mm) is the smallest (unit) print point (i.e., resolution, 0.025 mm), and v (mm/s) is the line speed of printing (see Table 1).

Figure 4(b) is the E value curve of each sample. Figure 4(c) shows several examples of the printing effect. Although the tone and lightness of the print samples exhibit some differences, power settings 1 and 2 (shown in Table 1) can be applied to obtain a better printing effect.

Figure 4 shows that a lower laser energy can achieve adequate printing results; however, higher laser energies are required when the printing speed is too slow or too fast and when the lightness is too high. When the printing speed reaches 100 mm/s, the carbonization is poor with high lightness (if the laser energy is 1.2 W). However, if the laser energy is 1.5 W, the lightness decreases significantly. The microstructure (Figure 1b) also indicates that the fiber carbonization is incomplete because when LIEP was performed, each dot was subjected to printing for less than 0.3 milliseconds. Therefore, a critical laser power was reached. Laser ablation of the paper fiber is not likely to occur below this critical point, even if the print time is extended appropriately. The results of this experiment show that the critical power is a value between 1.2 and 1.5 W. As a result, three different LIEP parameter configurations can be applied, with corresponding microstructures. A fibrous microstructure and low-fiber carbonization can be obtained from power settings 1 and 2, respectively, and significant carbonization can be obtained from the other parameter settings. However, the paper surfaces undergo significant carbonization for all of the printing parameter settings (with the exception of the lower speeds and power setting 1), which can be determined from the aforementioned microstructure. The products of carbonization are sludge or slot materials, which can be removed by external forces, such as hand brushing or friction. The print quality should improve with waxing and other processing after LIEP.

To explore the depth of the printing impression after LIEP, Figure 5 shows the surface unevenness at the printing borders. A valley can be noted, as indicated by the letter "V" in Figure 5. As mentioned previously, this valley is primarily the void of the paper itself[34] rather than the product of laser ablation from LIEP. Thus, the depth of the recess formed after LIEP is considered to be between the heights (h_c) of the two-point line drawn in the same figure, which is less than 20 μm. Commonly, the thickness of printing paper is approximately 100 μm. Therefore, after LIEP, the thickness of the paper is still approximately 80% of its initial thickness. Thus, based on the results from this qualitative analysis of the carbonized microstructure, the paper retains sufficient strength after LIEP when using rational technical parameters. This finding is consistent with the viewpoint that the strength of the printed samples can be ascertained from visual inspection.

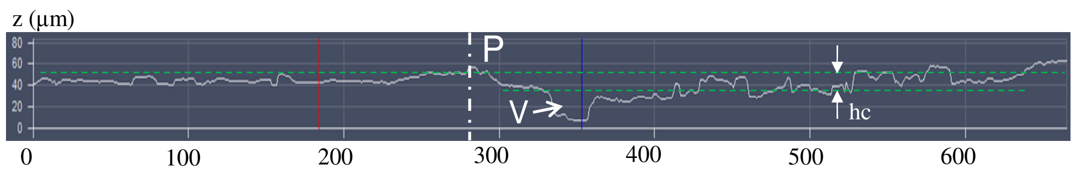

Figure 5: Unevenness of the printing paper surface for a velocity of 350 mm/s and a power of 3 W (magnification: 2000x)

This study has focused on the effect of printing on the microstructure of paper using a recently proposed eco-print technology. A better understanding of the mechanism requires further study of the influence of heat intensity during the printing process, of the fiber decomposition process, of hemicelluloses in the paper composition, and of substances formed during the decomposition process and their influence on yellow discoloration. An identification of the optimal LIEP technical parameters also requires further study. Further details will be reported in follow-up papers.[35,36]

CONCLUSION

This paper discusses the carbonized microstructure of paper, its degree of yellowing and its strength after the application of different LIEP parameter settings. The following conclusions were reached:

1) The carbonized microstructure of the paper after LIEP can be described as comprising three categories of features: small holes, cauliflower core-like clots, and fibrous features. When the printing power reaches a given value and laser ablation of the fiber on the paper surface and carbonization occur, a low laser energy produces a sludge with small holes, while a high laser energy produces cauliflower core-like particles.

2) For a given printing speed, fibers are broken down more completely at a higher laser power. Laser energy can be concentrated at the printing points and produces clear and relatively clean boundaries in the carbonized microstructure of the paper. The distance between the transition zone and full carbonation is typically only a few microns (or even zero microns).

3) From a qualitative perspective, the paper retains sufficient strength after LIEP when rational technical parameters are used. In terms of the relationship between the microstructure of the paper after LIEP and its degree of yellowing, the parameter combinations described in this paper all provided good printing effects. However, the printing process caused a significant amount of carbonization of the fibers on the paper surface (with the exception of the combination of low laser power and low speed). This carbonization can be removed by external forces. The print quality should improve with waxing and other processing after LIEP.

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