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Laser Color Marking Using Thermo-Sensitive Recording Paper - Study of Condition for Magenta and Cyan Developing

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Abstract

Direct laser marking techniques are widely used for various applications. Laser marking method has technical issues for full-color marking due to its printing principles. We have conducted the study of condition for single magenta and cyan developing in the direct color marking method which selectively develops three color layers by direct laser irradiation to thermo-sensitive recording paper. We tried to estimate duration time for heating by thermal transfer simulation with one-dimensional model and conducted study of condition of laser irradiation based on a result of thermal transfer simulation As a result of the condition study, we revealed that non-contact direct single magenta and cyan color marking with laser was possible using our method. In this paper, we report on process to develop single magenta and cyan by laser irradiation.

Introduction

In recent years, direct laser marking techniques that print characters and a two-dimensional bar code to print targets are widely used for various applications. The targets cover a broad range of materials such as paper, plastics, metals, glass and wood. The recording principle of laser marking is a use for simple change of color of targets by carbonization or oxidation or engraving. For this reason, the laser marking method has technical issues for full-color marking that demand complicated color controls. Under such conditions, some laser color marking methods are reported such as the marking method on glass using light absorption by the effect of surface plasmon of metal nanoparticle [1]. on titanium or stainless material using light interference by thickness control of the metal oxide layer [2-4] and on plastic or paper materials using combination of chemical reaction by thermal process and fixing by UV exposing process [5,6].

Our approach which we have researched for laser color marking is a method irradiating laser to thermo-sensitive recording paper directly. The thermo-sensitive recording paper used in our research includes a plurality of each yellow, magenta and cyan developing layer. These color developing layers have thermal materials with different color developing threshold temperatures and are stacked in an ascending order of the threshold temperatures from a surface irradiated with the laser light. As we already reported, we conducted the study of the condition for single yellow developing whose threshold temperature is the alternatively highest among three primary color developing layers using such thermos-sensitive recording paper [7]. In this paper, we report on process to develop single magenta and cyan by laser irradiation.

Principles

The used thermos-sensitive recording paper has a plurality of each yellow, magenta and cyan developing layer (Fig.1). These color developing layers have thermal materials with different color development threshold temperatures and are stacked in an ascending order of the threshold temperatures from the surface. Regarding this thermos-sensitive recording paper, the layer whose color developing threshold is the alternatively highest and whose distance from the surface is the alternatively shortest is for yellow. The layer whose color developing threshold is the alternatively lowest and whose distance from the surface is the alternatively longest is for cyan. The layer whose color developing threshold and whose distance from the surface are alternatively middle is for magenta.

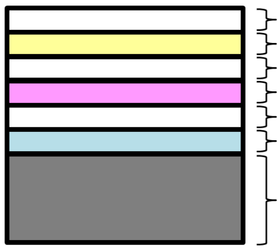

***Figure 1** Schematic illustration of cross-sectional of thermo-sensitive recording paper [7]*

It is possible to selectively develop yellow, magenta and cyan by thermal control as shown in Fig. 2 to the thermos-sensitive recording paper. As shown in Fig.2 (B), thermal control of following (M1) to (M3) steps is carried out for single magenta developing.

(M1) A surface temperature is raised rapidly.
(M2) The surface temperature is maintained at the range which is higher than the threshold of magenta and lower than the threshold of yellow.
(M3) Heating is stopped when the temperature at the magenta layer is higher than the threshold of magenta.

Moreover, as shown in Fig.2 (C), thermal control of following (C1) to (C3) steps is carried out for single cyan developing.

(C1) A surface temperature is raised rapidly.
(C2) The surface temperature is maintained at the range which is higher than the threshold of cyan and lower than the threshold of magenta.
(C3) Heating is stopped when the temperature at the cyan layer is higher than the threshold of cyan.

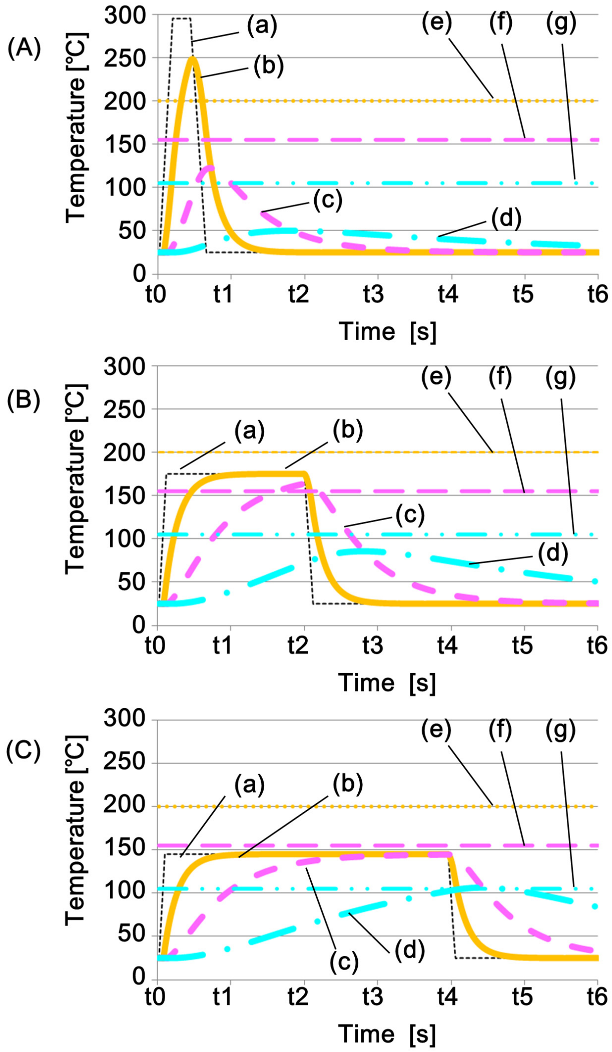

***Figure 2** Schematic illustration of thermal control for selectively single color developing: (A) Thermal control for single yellow developing, (B) Thermal control for single magenta developing, (C) Thermal control for single cyan developing, (a) Surface layer, (b) Yellow developing layer, (c) Magenta developing layer, (d) Cyan developing layer, (e) Threshold temperature of yellow, (f) Threshold temperature of magenta, (g) Threshold temperature of cyan [7]*

Methods

Thermal Simulation

We have made a one-dimensional model for thermal transfer simulation in order to estimate the conditions of laser irradiation which singly achieves magenta and cyan developing layers to the each threshold temperature. Thermal transfer simulation was conducted with this simple one-dimensional model in order to estimate duration time for single magenta and cyan developing. The condition of the simulation is shown in Table 1. In thermal transfer simulation, the temperature $\boldsymbol{T}$ was given to the boundary on the surface side and the time $\boldsymbol{t}$ until the heat conducts and the temperature of each color layer reaches the threshold temperature of each color layer was estimated.

Table 1 Conditions of thermal simulation [7]

Initial temperature [°C]	25
Boundary condition (Surface side)	Fixed temperature boundary
Boundary condition (Base Substrate Side)	Adiabatic
Grid resolution [μm]	0.1
Time step width [ns]	1

Laser Irradiation

Based on the result of thermal transfer simulation, laser beam is irradiated to the thermos-sensitive recording paper with some parameters such as power of the laser, scanning speed of the laser, and defocus distance. CO2 laser for heating process is used. The optical system (Fig. 3) which scans laser beam with galvanometer mirrors and condenses it with a F-θ lens was used.

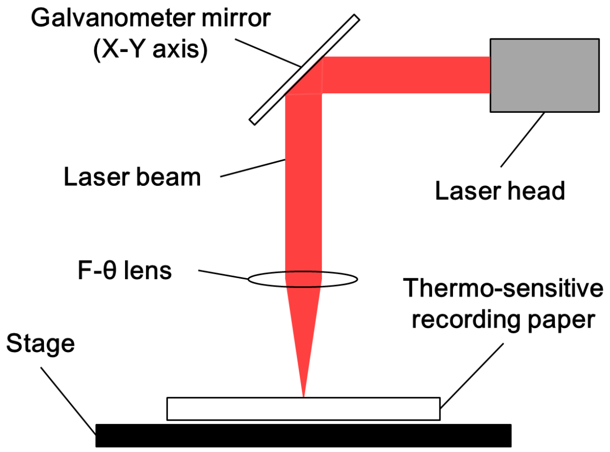

***Figure 3** Schematic illustration of optical system [7]*

The power of laser was controlled by duty and the frequency of laser is 25 kHz. The laser beam is scanned on the straight line of 5 mm as the shape of sawtooth wave on the conditions shown in Table 2 and the laser was irradiated in an area of square 5 mm on a side, and evaluated the color developing state.

Table 2 Conditions of laser irradiation

Parameter	Magenta	Cyan
Scanning pitch [μm]	483	115
Laser power [W]	1.00,1.02	1.10
Laser scanning speed [mm/s]	100,120	345-360
Defocus [mm]	4.2,4.4	4.0
Number of times of laser scanning	1	2

Evaluation of Color Developing

Color developing state of the thermos-sensitive recording paper after laser irradiation in the area of square 5 mm on a side is evaluated. Optical density of the area where laser was irradiated was measured and surface and cross-sectional were observed in order to confirm single magenta and cyan developing. Optical density was measured with densitometer RD-19I (Gretag Macbeth). Optical density was measured 3 times each to the same sample and the average was calculated as an optical density value.

The surface and the cross-sectional were observed with an optical microscope. In the surface observation, we qualitatively confirmed whether surface of the thermo-sensitive recording paper would have damage by laser irradiation and the state of color developing. In the cross-sectional observation, the laser irradiated samples were sliced with a design knife (NT cutter) whose angle of an edge is 30 degrees and the sliced samples were put on the slide glass and observed. The existence of color developing in each color layer was confirmed by slicing the samples to width which is thin enough for light to penetrate in the direction of the cross section when the cross-sectionals were observed with an optical microscope.

Results

Results of Thermal Simulation

As a result of thermal transfer simulation, the relation between the temperature ***T*** given to the boundary on the surface side and the duration time ***t*** for each color layer to reach each developing threshold, as shown in Fig. 4, is asymptotic to the color developing threshold value of each color layer.

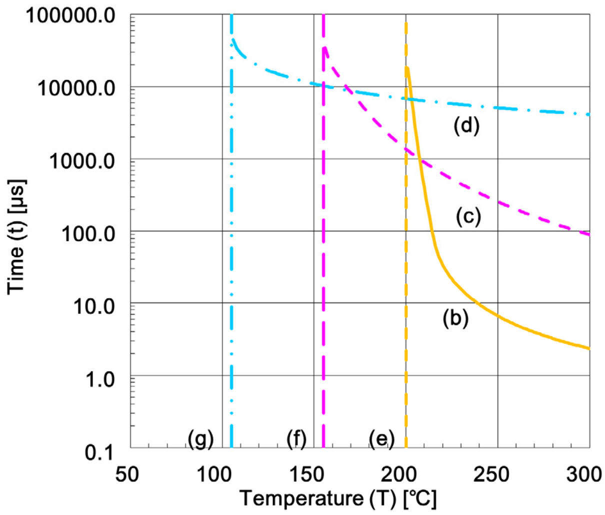

Figure 4 *Duration time for each color developing after giving temperature on surface: (b) Yellow developing layer, (c) Magenta developing layer, (d) Cyan developing layer, (e) Threshold temperature of yellow, (f) Threshold temperature of magenta, (g) Threshold temperature of cyan [7]*

Our discussing the result of the simulation, it was estimated that single magenta can be made to develop under the control of the temperature ***T*** given on surface and the duration time ***t*** such as ***T*** is higher than 160 degree Celsius and lower than 210 degree Celsius, and ***t*** is longer than 1000 μs and shorter than 9000 μs. Moreover, it was estimated that single cyan can be made to develop under the control of the temperature ***T*** given on surface and the duration time t such as T is higher than 100 degree Celsius and lower than 160 degree Celsius, and ***t*** is longer than 9000 μs.

Results of Evaluation

Laser was irradiated on the conditions shown in Table 2 based on the magenta developing conditions estimated in the simulation. The parameters were power of laser, scanning speed, and defocus distance. As a result, magenta developing was made on some conditions (Fig.5).

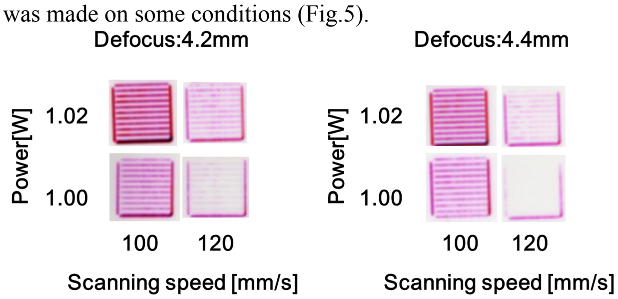

Figure 5 *Left: Image of laser irradiated thermo-sensitive recording paper when defocus is 4.2 mm. Right: Image of laser irradiated thermo-sensitive recording paper when defocus is 4.4 mm.*

As a result of observation of the surface of color developing samples, the irradiation conditions expected that single magenta was made to develop were three conditions shown in Table 3. In order to make the non-coloring area develop, laser was irradiated moving the irradiation position 9 times by 50 μm unit or 16 times by 30 μm unit on conditions (2). Moreover, laser was irradiated moving the irradiation position 9 times by 50 μm unit on conditions (3). As a result, the color developing samples as Fig. 6 were obtained.

As a result of the measurement of optical density of the three samples shown in Fig.6, the sample made with the way irradiation position was moved 9 times by 50 μm unit on conditions (3) (Bottom image) has the highest optical density. In order to bring out whether single magenta is developing in these samples, the cross-sectionals were observed with the optical microscope. Single magenta was developing in any samples as a result of the observation of cross-sectionals.

Table 3 Conditions for magenta developing

Parameter	Condition (1)	Condition (2)	Condition (3)
Scanning pitch [μm]	483	483	483
Laser power [W]	1.00	1.02	1.02
Laser scanning speed [mm/s]	100	120	120
Defocus [mm]	4.4	4.2	4.4
Number of times of laser scanning	1	1	1

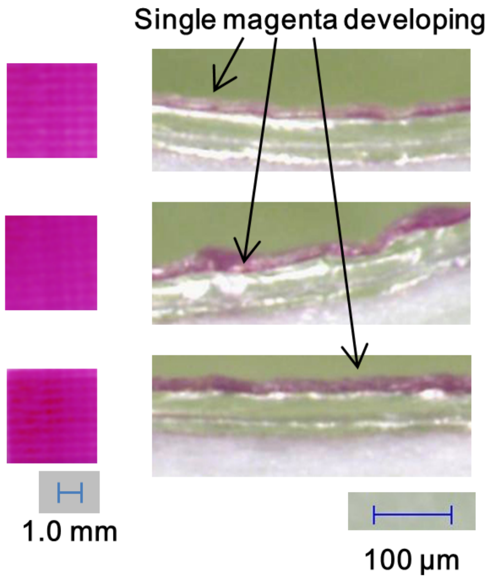

***Figure 6** Top: Image of laser irradiated thermo-sensitive recording paper when irradiating position is moved 9 times 50 µm each in condition (2) (left: surface, right: cross-sectional).Middle: Image of laser irradiated thermo-sensitive recording paper when irradiating position is moved 16 times 30 µm each in condition (2) (left: surface, right: cross-sectional). Bottom: Image of laser irradiated thermo-sensitive recording paper when irradiating position is moved 9 times 50 µm each in condition (3) (left: surface, right: cross-sectional).*

As magenta was made to develop, laser was irradiated on the conditions shown in Table 2 based on the cyan developing condition estimated in the thermal transfer simulation. The parameter of laser irradiation is scanning speed of laser. In these conditions, the reason why the number of times of irradiation is twice is that it was estimated through the simulation that longer duration time to give heat is necessary rather than duration time for single magenta developing in order to make cyan developing. Cyan developing was observed on all the conditions by laser irradiation. As a result of the cross-sectional observation with an optical microscope, single cyan was developing in the samples to which laser was irradiated on the condition of faster scanning speed than 355 mm/s, but magenta was mixed in the samples to which laser was irradiated on the condition of slower scanning speed than 350 mm/s (Fig.7).

Conclusions

We have conducted the study of laser irradiation conditions for single magenta developing and single cyan using the thermo-sensitive recording paper, based on the results of the thermal transfer simulation. According to the results of the microscope observation and optical density measurement of thermo-sensitive recording paper, we succeed in developing a method for selective magenta developing and cyan in some conditions of laser irradiation. Thus, our non-contact direct marking method enables full-color printing with a single laser, combined with a developing method for yellow that was already reported and substantiated. In addition, our process enables to raise possibility to make a smaller laser color marking unit because UV fixing process is not necessary in our process.

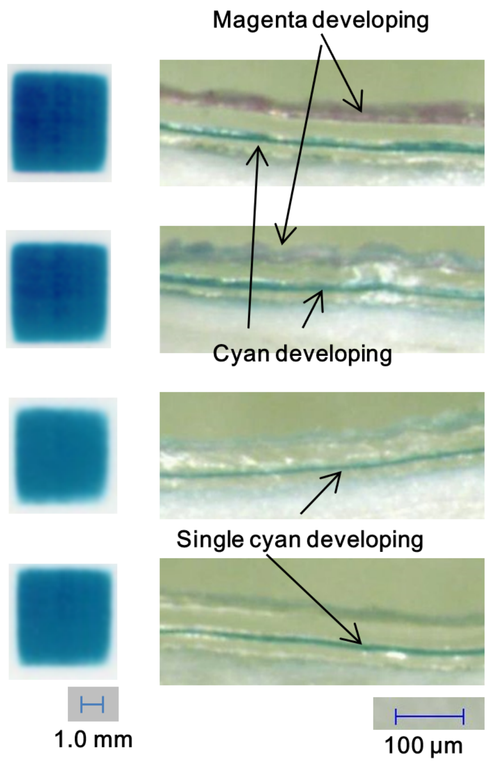

***Figure 7** Top: Image of laser irradiated thermo-sensitive recording paper when laser scanning speed is 345 mm/s (left: surface, right: cross-sectional). Second top: when laser scanning speed is 350 mm/s (left: surface, right: cross-sectional). Third top: Image of laser irradiated thermo-sensitive recording paper when laser scanning speed is 355 mm/s (left: surface, right: cross-sectional). Bottom: Image of laser irradiated thermo-sensitive recording paper when laser scanning speed is 360 mm/s (left: surface, right: cross-sectional).*

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