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Suitable Paper for Erasable Toner and the Role of Water in the Erasing Process

Takeshi Gotanda, Satoshi Takayama, Yumiko Sekiguchi and Kenji Sano
Corporate Research & Development Center, Toshiba Corporation, Kanagawa, Japan
E-mail: takeshi.gotanda@toshiba.ca.jp

Hiroyuki Maeda and Yuko Imamura
Toshiba Nanoanalysis Corporation, Kanagawa, Japan

Abstract. *The authors have revealed that paper having high smoothness, small pore size, and low drying ability is suitable for discoloring decolorable toner. In the heat erasing process, water accelerates the dissociation of leuco dye and developer and/or the diffusion of developer, considering the high dielectric constant of water and the solubility of developer in water. The authors have confirmed diffusion of the developer into paper from the toner in the heat erasing process by the direct evidence and results of energy dispersive x ray and time-of-flight-secondary ion mass spectrometry. © 2006 Society for Imaging Science and Technology.*
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INTRODUCTION

Paper consumption is increasing with the increasing number of computer-related products in the world. The reduction of paper consumption is an important issue to realize a sustainable society; because the material of paper is plant based, the papermaking process requires a great amount of energy, and paper accounts for 40% of the volume of large city trash.

Toshiba commercialized the decolorable (erasable) toner "e-blue™" in 2003.[1,2] This toner has a leuco dye colored by an interaction with a developer such as ethyl gallate (EG), as shown in Fig. 1. When paper is heated, an image printed by e-blue™ is decolorized due to dissociation of the dye and the developer. The paper can be used repeatedly after erasing. There are suitable printers for e-blue™ such as NX810 (Ricoh printer) and e-STUDIO350EB (Toshiba TEC multifunctional printer).

The result of life cycle assessment[3] indicates that use of a decolorable toner is an effective way to reduce the environmental impact. Furthermore, the costs associated with purchasing of paper and disposal of paper trash can be reduced.[4] Paper consumption can be reduced without reducing the number of times printing is repeated. The number of repetition times depends on the preference of the user, but the same paper can be used at least about five times in this heat erasing process.

We had found that the erasability of the decolorable toner depends on the paper brand and the condition of the paper. This paper discusses the relationship between the erasability and paper characteristics, such as *p*H, moisture, smoothness, gas permeability, pore size, and liquid absorbability.

ERASING TEST USING PLAIN PAPER

An erasing test was conducted as follows, using the decolorable toner (e-blue™, Toshiba Corp.). Printing was performed by the printer (NX810, Ricoh Co., Ltd.), using a 10 mm × 10 mm square pattern with ten steps of image density. The printed pattern was erased by the heat eraser (TMD-HE01, Toshiba Corp.). The eraser has two heaters in the body and the lid. Paper was placed between these heaters, heated to 140 °C for 2 h, and then cooled for 1 h. We measured the image density of the ten-step pattern using a chromaticity meter (CR300, Konica Minolta Holdings, Inc.), before and after erasing. The image density of the ten-step pattern was subtracted with the image density of the paper to compare the paper of different types, because the image density of the paper depends on the constituents of the paper, such as filler and size agents.

MEASURING METHODS FOR PAPER CHARACTERISTICS

To clarify the factors that influence the erasability, we measured the paper characteristics such as moisture content of the paper, *p*H of paper, smoothness of the surface, gas permeability, pore size, and liquid absorbability.

We regulated the moisture content of sample paper to avoid fluctuation of results due to moisture. All sample pa-

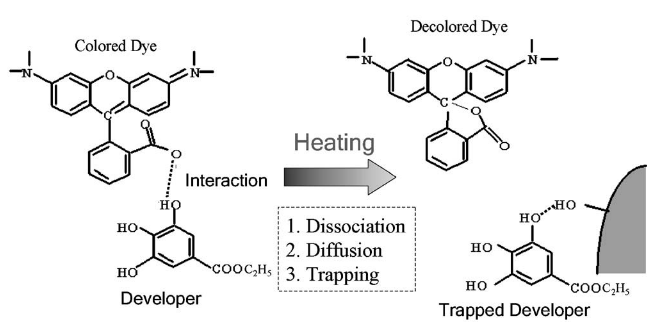

Figure 1. The principle of the decolorable toner.

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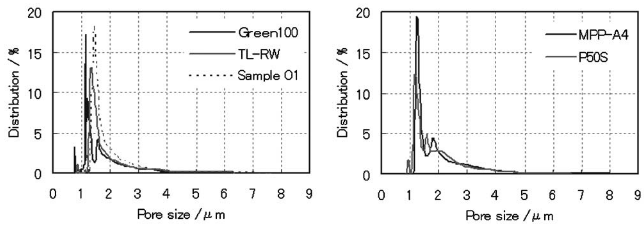

Figure 2. Pore size distribution of the paper. This measurement used Perm Porometer.

per was treated according to "JIS (Japan Industrial Standard) P8111; paper, board and pulps—Standard atmosphere for conditioning and testing," using an equilibrium state between ambient air (standard state: 23±1 °C, 50±2% RH) and paper.

pH of Paper (Ref. 5)

According to the method of JIS P8133, 2 g of paper sample was stirred in 100 ml of deionized water for 1 h at room temperature (20–25 °C), and then *p*H of the dispersed solution was measured by a conventional *p*H meter. The *p*H value defines as the *p*H of the paper.

Moisture Content of Paper (Ref. 6)

According to the method of JIS P8127, moisture content was estimated from weight loss after drying at 105 °C for 30 min.

Smoothness of Paper (Ref. 7)

According to the method of JIS P8119, paper smoothness was measured using a Bekk smoothness tester (Toyo Seiki Seisaku-sho, Ltd.). A piece of paper was inserted and pressed with the tester. The paper smoothness is defined by the time for a regulated amount of air leakage, because it depends on the rate of air leak in this tester.

Gas Permeability (International Standard Organization Gas Permeability) of Paper (Ref. 8)

Gas permeability is expressed by the flow rate (μm/(Pa s)) of air that passes through a paper across a pressure differential, using the Gurley densometer.

Pore Size (Average and Maximum) of Paper (Ref. 9)

The paper pore size was estimated from the pressure value required to press water out through pores of the wet paper sample. Pore size was calculated from the expression ($d=4\cdot B\cdot \gamma/P$ where d=pore size, B=capillary constant, γ=surface tension, and P=pressure) according to American Society for Testing and Materials (ASTM) F315-70 (1970) "Standard test method for pore size characters of membrane filters for use with aerospace fluids." A Perm Porometer (Porous Materials Inc.) was used. By this method, the pore distribution can be calculated from the gas volume flowing at different pressures, as shown in Fig. 2. Even in the case of wet paper, the result was reproducible and sufficiently practical to express the paper characteristic.

Water Absorbability of Paper (Ref. 10)

The water absorbability of paper is defined as the weight of absorbed water per second when the paper contacts water.

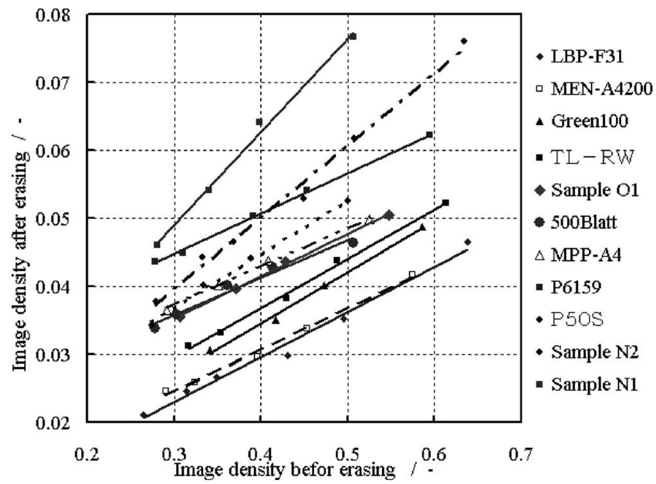

Figure 3. Results of the erasing test for 11 types of papers in using the heat erasing machine (TMD-HE0l). The moisture content is 5%.

According to a TAPPI method,[10] a dynamic previous test machine (Toyo Seiki Seisaku-sho, Ltd.) was used.

Drying Ability of Paper

We measured the drying ability of paper by an original method as follows. Ten sheets of paper were placed between two aluminum plates (2 mm thickness) of the same size as the paper in the heat eraser (TMD-HE01, Toshiba Corp.) and the paper was weighed before and after heating at 130 °C. Drying ability was calculated from the change of weight over 10 min. In this case, the moisture is expected to come out from edges of the paper.

RESULT OF ERASING TEST

We performed an erasing test to evaluate the effect of paper type, using 30 brands of paper. The results for 11 paper types (i.e., LBP-F31 (KOKUYO Co., Ltd.), MEN-A4200 (Mitsubishi Chemical Corp.), Green100 (Fuji Xerox Office Supply Co., Ltd.), TL-RW (Toshiba Business and Life Service Corp.), and Sample O1 (Oji Paper Co., Ltd.), 500Blatt (Toshiba TEC Corp.), MPP-A4 (Nakabayashi Co., Ltd.), P6159 (Toshiba Corp.), P50S (Toshiba TEC Corp.), and Sample N2 (Nippon Paper Industries Co., Ltd.), Sample N1 (Nippon Paper Industries Co., Ltd)) are shown in Fig. 3. The results showed that the image density after erasing depended on the type of paper.

We calculated erasability from the regression line for the image density before and after erasing, as the image density after erasing corresponding to an original image density (before erasing of 0.5). The value indicates the ease of erasing of the decolorable toner, i.e., when the erasability of decolorable toner is high, this value becomes small. The erasability was in the range from 0.037 to 0.077 according to the type of paper, as shown in Table I.

Effect of pH and Moisture Content of Paper on the Erasability of the Decolorable Toner

There are three types of paper, i.e., acidic paper, neutral paper, and alkali paper, depending on the additives to adjust

Table I. Erasability of 11 types of papers.

Name of Company	Type of paper	Other information	Erasability
KOKUYO	LBP-F31		0.037
Mitsubishi Chemical	MEN-A4200	-	0.038
Fuji Xerox Office Supply	Green 100	Waste paper 100%	0.043
Toshiba Business and Life Service	TL-RW	-	0.045
Oji Paper	Sample O1[a]	-	0.051
Toshiba TEC	500Blatt	-	0.051
Nakabayashi	MPP-A4	-	0.053
Toshiba	P6159	Heat transfer printing paper	0.060
Toshiba TEC	P50S	-	0.061
Nippon Paper Industries	Sample N2[a]	-	0.067
Nippon Paper Industries	Sample N1[a]	-	0.077

[a]Type of paper is unknown.

properties such as brightness and sizing effect. Generally, acidic paper contains aluminum sulfate as a sizing agent, and alkali paper has calcium carbonate as paper filler.[11]

The moisture content of paper changes from 5% to 12%,[12] when the air humidity changes from 30% to 70%. In electrophotographic printing which uses dry toner, the toner fusing process at 180 °C reduces the moisture content of the paper. We performed the heat erasing test for combinations of different moisture content and *p*H of the paper. The paper was chosen as follows: acid paper (*p*H 5.5, 6.5), neutral paper (*p*H 7.1), and alkali paper (*p*H 8.2, 9.3). The changes of the image density after erasing are shown in Fig. 4. We observed that the image density after erasing of neutral paper was lower than acid paper or alkali paper at all values of moisture content.

The blue color of the printed decolorable toner usually becomes colorless after heat erasing. However, we sometimes observed a slight yellowish color in the printed part on the heat erased paper. Hydrolysis of the dye is one of the candidate reasons for the yellowish color, since it frequently happened in the case of acidic or alkali paper.

When water content was 4%–8%, the image density after erasing was the lowest for all cases. This represents the region of suitable moisture content for heat erasing. The water is considered to be an accelerator of the dissociation of the leuco dye and the developer, because water has a high dielectric constant and ability to solvate polar molecules such as EG. Therefore, the developer can be extracted from the decolorable toner by water, and then the developer can diffuse into the paper. The water solubility of EG is 2.6 mg/ml (20 °C).

High image density after erasing is a problem for practical use. We have prescribed an upper limit value as a standard for the image density after the heat erasing: when the image density after erasing is less than 0.07, we can use the

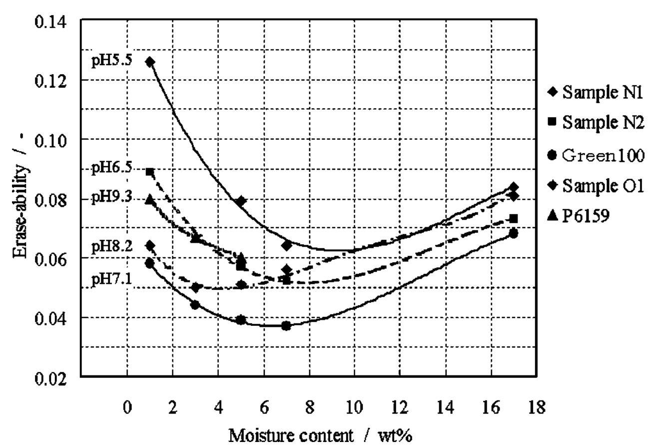

Figure 4. Moisture content and erasability in the different *p*H of the paper in using the heat erasing machine (TMD-HE01). The moisture content was changed intentionally.

paper comparable to double-side printed paper. The moisture content of paper is usually 3%–12%. In this moisture range, the image density after erasing of neutral paper and alkali paper was 0.07 or less as shown in Fig. 4. In other words, when we chose neutral or alkali paper, the image density after erasing is suitable for practical use.

EFFECT OF OTHER PAPER CHARACTERISTICS ON THE ERASABILITY

We calculated the correlation coefficient of the image density after erasing for smoothness, gas permeability, pore size (average and maximum), liquid absorbability, basis weight, thickness, and drying ability as shown in Fig. 5. Each data point corresponds to a different type (brand) of paper. (We could not measure correct pore distributions for three of the paper types, because their pore sizes were smaller than the limit of measurement, making it impossible to calculate their

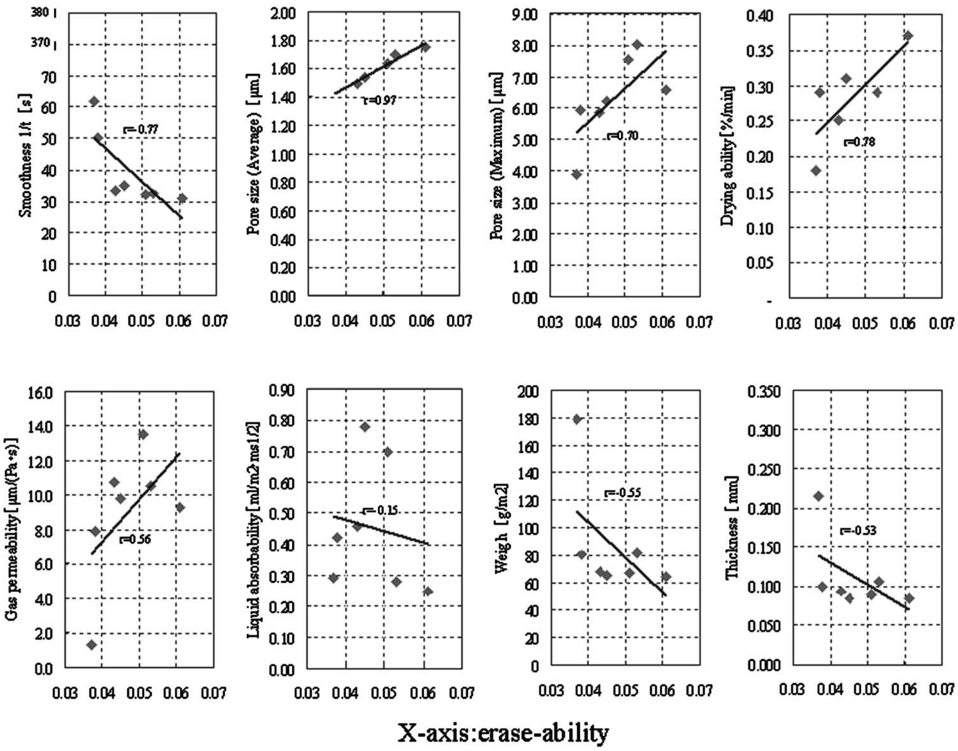

Figure 5. Correlation coefficients concerning paper characteristics and erasability. Each data point corresponds to a different type of paper, as following erasability; 0.037 (LBP-F31), 0.038 (MEN-A4200), 0.043 (Green 100), 0.045 (TL-RW), 0.051 (Sample O1), 0.053 (MPP-A4), and 0.061 (P50S).

average pore sizes.) The maximum pore sizes were measured for all types of paper, as shown in the graph next to the graph of average pore sizes.

The correlation coefficients for smoothness, average pore size, maximum pore size, and drying ability were 0.77, 0.97, 0.70, and 0.78, respectively, as shown in Fig. 5. The results suggest that a paper with high smoothness, small pore size, and low drying ability are easy to erase by heating. Note that statistically significant correlation point between paper smoothness, maximum pore size and drying ability, so that these variables are not independent.

As shown in Fig. 4, the image density after erasing changed with moisture content. Thus, we have regulated the moisture content of the paper to 5% before erasing in every test. However, the paper with high drying ability will lose moisture during heat erasing, and such paper is probably unsuitable for heat erasing. In other words, moisture holding ability is required for erasability. Higher smoothness and smaller pore size will be advantageous for holding moisture, because the water path for evaporation and diffusion is considered to be small. Therefore, it is reasonable that the erasability correlates with the paper smoothness and pore size.

DIFFUSION OF THE DEVELOPER INTO THE PAPER

We have confirmed diffusion of developer into paper from the toner by the following experiments.

We prepared the following samples: (A) A resin sample containing 4 wt % of EG, by heating the mixture of the toner resin, mainly polystyrene, and EG at 180 °C for 30 min. This sample was colorless.

(B) A piece of sample paper made by drying a piece of paper soaked in a saturated toluene solution of leuco crystal violet lactone (CVL). This sample paper was almost white.

A piece of the resin sample (A) (5 mm^3) was placed on the piece of sample paper (B) (20 m^2), and these samples were placed in an oven at 140 °C for 2 h. The heating conditions were the same as for erasing of e-blue™. We observed that blue color was developed under the resin sample (A) on the paper sample (B). This means that EG moved from resin into paper and reacted with CVL to develop the color. This is direct evidence that the developer moves from the toner into paper in the erasing conditions for e-blue™.

The following spectroscopic data supports the diffusion of developer into paper. We used energy dispersive x ray (EDX) spectroscopy to detect the atomic ratio in the paper before and after heat erasing for e-blue™ printed paper. The equipment used in the experiment was Genesis CDU (EDAX Corp.) and the acceleration voltage was 10 kV. The electron beam was irradiated on to the edge of the e-blue™ printed paper.

Table II shows the atomic ratio of carbon and oxygen for the paper and for EG. There was a tendency for the carbon ratio to be higher than the calculated value. In addi-

Table II. Calculated and measured ratios of C/O.

		C%	O%	C/O
Cellulose	Calculated value[a]	54.5	45.5	1.2
Ethyl gallate	Calculated value[a]	64.3	35.7	1.80
	Measured Value[b]	80.1	19.9	4.03

[a]Calculated from the molecular formula.
[b]Measured by EDX.

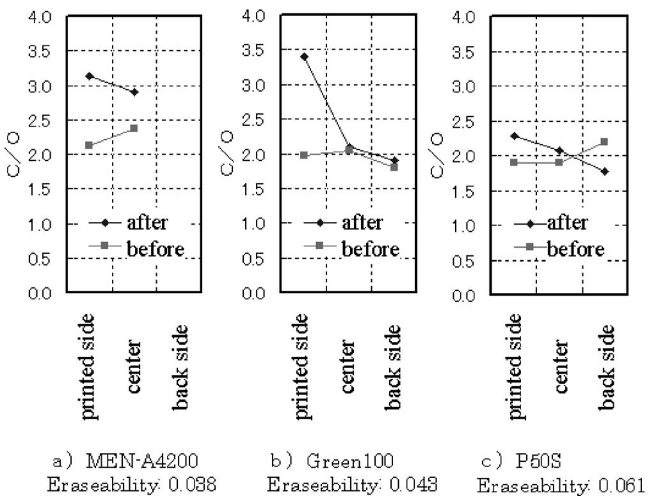

Figure 6. Change of C/O ratio in the cross section of paper for three types of paper, MEN-A4200, Green100, and P50S.

tion, Fig. 6 shows the change of C/O ratio detected in the paper after erasing of e-blue™ printed paper under the same conditions, where the original image density before erasing was regulated to be 0.1.

The most erasable paper, MEN-A4200, showed an increased C/O ratio from the e-blue™ printed side to the center of the paper in the direction of thickness. The medium eraseable paper, Green 100, showed an increased C/O ratio around the e-blue™ printed side. In the case of the less erasable paper, P50S, the C/O ratio change was small in all regions. The change in the C/O atomic ratio before and after heating indicates a transfer of materials into the paper. Thus, these results indicate that the developer diffuses into paper, and we have observed the diffusion capacity of the papers in this experiment.

Figure 7 shows the distribution of secondary ions from the paper using time-of-flight secondary ion mass spectrometry (TOF-SIMS). The thickness of the paper is about 70 μm. The secondary ions seem to be $M+=227$, which is considered to be an ion of EG ($M+=198$) with an added ethyl group fragment ($M+=29$).[13] Concerning the leuco dye (blue 203: Mw 539.72), the ion peak $M+=381$ was considered to be a secondary ion derived from the leuco dye, as shown in Fig. 8.

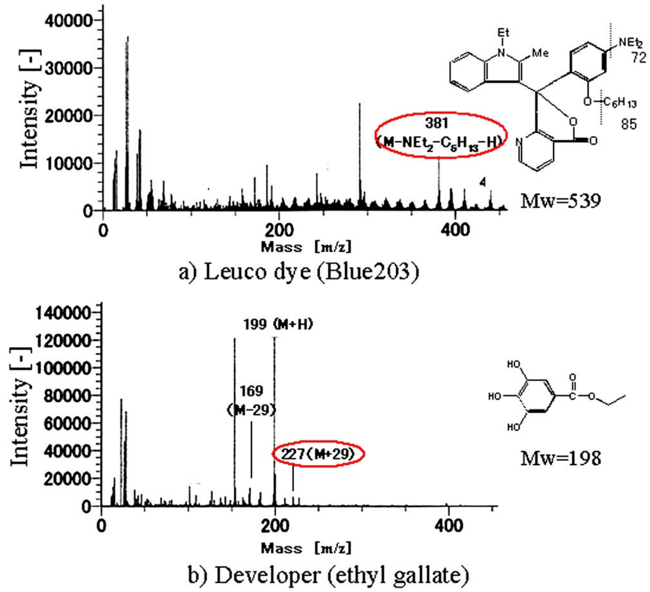

Figure 7. Mass spectra (fragment ion) of raw materials, the leuco dye (Blue203) and the developer (ethyl gallate).

The fact that the secondary ion distribution derived from the leuco dye before and after heat erasing did not change indicates that the leuco dye remained in the toner resin. It was a reasonable result, because the leuco dye has large molecular weight.

On the other hand, the distribution of the secondary ion of the developer changed after heat erasing. This is reasonable as the developer has relatively low molecular weight. In the case of paper with good erasability, the intensity of the developer in the mass spectrum was relatively small after heat erasing. This suggests that diffusion range of the developer in this paper is greater than in paper with poorer erasability.

These results support the contention that the developer diffuses into paper from the toner resin, and elucidate that the erasing results differ according to the kind of paper.

DISCUSSION

Heat erasing has three steps[1,2] as follows. The first step is the dissociation of leuco dye and developer. The second step is the diffusion of the developer in toner resin. The third step is the developer trapping by an erasing reagent such as starch[14] in the toner resin. We verified the further diffusion by direct evidence and the results of EDX and TOF-SIMS, that is, the developer such as EG diffuses from the toner into the paper itself.

Erasability depends on moisture content of paper as shown in Fig. 4. Each curve showed a minimum value of erasability, corresponding to the optimum condition for moisture content. Therefore, the moisture content is related to the dissociation of leuco dye and developer and/or the diffusing of the developer. On the other hand, we have revealed that paper with low drying ability has high erasability. The role of the water is considered to be an accelerator of the dissociation of the leuco dye and EG, because water has high

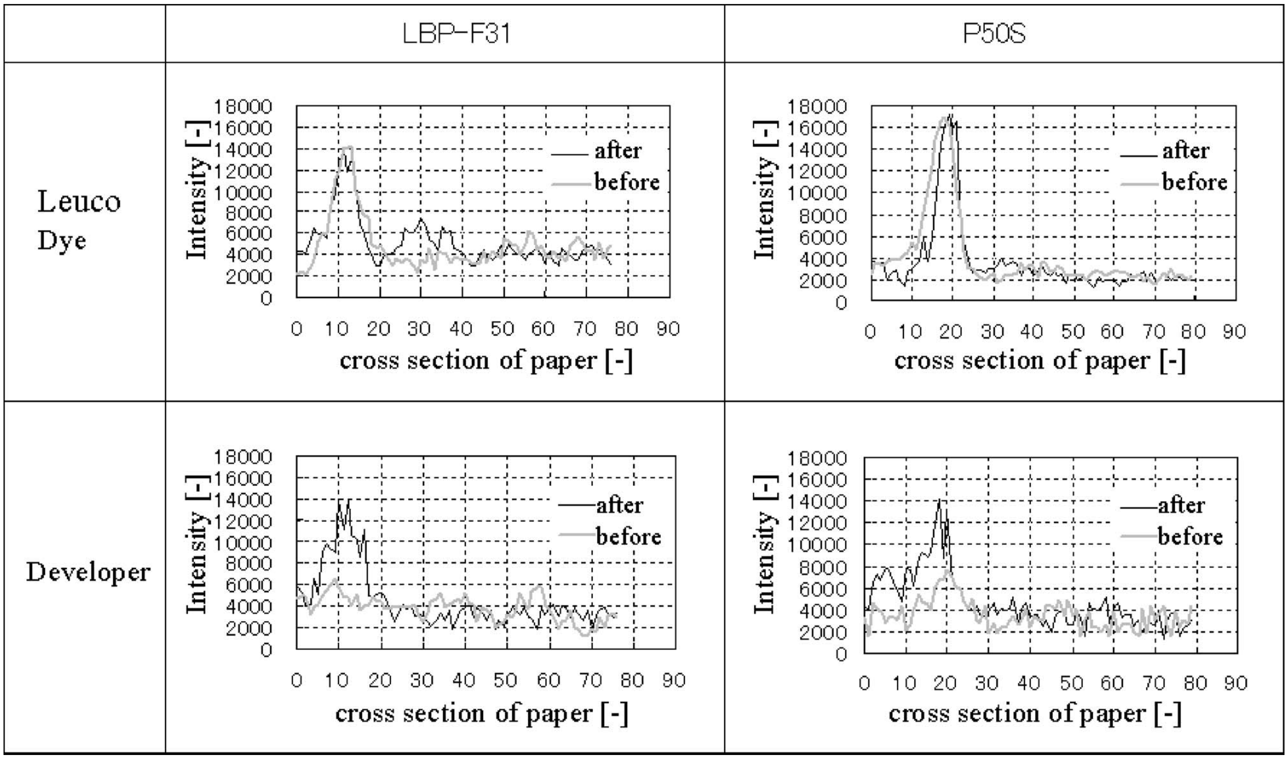

Figure 8. Change of detected intensity with TOF-SIMS in the cross section of the paper.

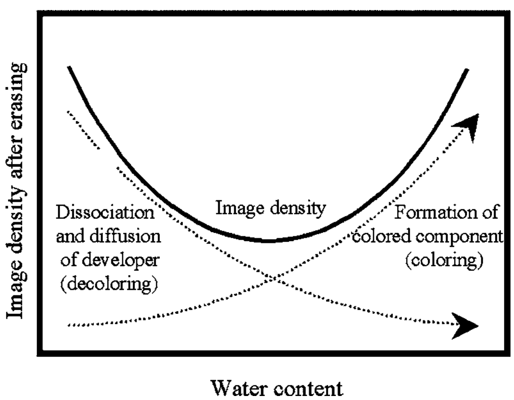

Figure 9. Image density after erasing depends on "dissociation and diffusion of developer (decoloring)" and "formation of colored component (coloring)."

dielectric constant and ability to solvate polar molecules such as EG. Considering the solubility of EG, we propose that the EG can be extracted from the decolorable toner by water, and then the EG can diffuse into the paper.

However, higher water content causes lower erasing performance as shown in Fig. 4. Considering the higher erasing performance of neutral paper, *p*H 7.1, acidity or alkalizity is the cause of the lower erasing performance. The residual image exhibited a yellowish color in the regions of higher water content in the experiment illustrated in Fig. 4. These facts suggest that there can be decomposition of the leuco dye and release of the colored components by acid or alkali under the water rich condition at 130 °C. Therefore, we summarize the possible explanation as shown in Fig. 9, which shows schematically how image density after erasing depends on: (a) dissociation and diffusion of developer; opposed by (b) formation of a colored component.

CONCLUSION

We have found suitable characteristics of paper for the e-blue™ decolorable toner as an effectively erasable paper. The results indicate that such paper, which has high smoothness, small pore size and low drying ability, is easy to erase by heat. The small pore size of the paper means that it will retain water, which is related to the drying ability. In the heat erasing process, water accelerates the dissociation of leuco dye and developer and/or the diffusion of developer, considering high dielectric constant of water and the solubility of developer in water.

We have confirmed diffusion of the developer into paper from the toner in the heat erasing process by the direct evidence obtained using developer containing resin on a sheet of paper containing CVL. Spectroscopic data obtained by EDX and TOF-SIMS supports the above discussion.

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