Development of Paper Having Microporous Layer for Digital Printing

Shuichi Maeda, Toru Nakai, Akira Nakamura, Masakazu Hakomori, and Masaru Kato

Imaging Media Development Laboratory, Oji Paper Company, Tokyo, Japan

We describe the development of microporous paper sheet that meets the demands for print quality in different types of digital printing. The paper sheet contains a microporous layer that has a surface pore diameter of 0.5 to 30 μm and a density of 0.2 to 0.5 g/cm³. The microporous layer can be easily obtained by coating a sheet substrate with a stirred resin-containing liquid, which forms bubbles. Applications for the microporous paper sheet in digital printing include thermal wax transfer (including resin type), thermal dye diffusion transfer, direct thermal, solid inkjet and toner-based marking. In the first application, the microporous layer acts as an ink-receiving layer (see Fig. 1) due to the heat-insulating nature, the compressibility and the surface structure. The microporous paper sheet has a thermal conductivity of 0.25 W/(m·K) or less. The compression stress of the microporous sheet under a high compression of 10% by volume is controlled to 8 kg/cm² or less. The molten ink permeates sufficiently into the region of the microporous surface layer due to the presence of a large number (3,000/mm² or more) of fine pores distributed on the surface. Thus the microporous surface layer enhances the print quality for use in thermal wax transfer printing. Print qualities of the microporous paper sheets are quantitatively analyzed using automated image analysis systems with test targets that consist of basic image elements such as dots, lines and solid areas. The print qualities including dot raggedness, dot reproduction, line blurriness, line raggedness, tone reproduction, mottle, graininess and optical density of the microporous paper sheets are consistently higher than those observed for a plain paper sheet. For example, by measurement with the ISO-13660 draft standard, the lead line blurriness and raggedness of a microporous paper sheet are 27 μm and 1.8 μm, respectively, whereas those of a plain paper sheet are 57 μm and 7.4 μm, respectively.

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Introduction

There has been increasing interest in receiving sheets having porous layers for use in digital printing. The porous sheets can be used in a wide range of applications often for their porosity, low thermal conductivity and high compressibility, or for the three characteristics combined.

For example, Imoto and co-workers[1] have reported that a porous intermediate layer enhances sensitivity of the receiving sheet for thermal dye diffusion transfer printing due to its heat-insulating nature and elastic property. Takei and co-workers[2] have utilized hollow particles as a heat-insulator distributed in the intermediate layer for direct thermal paper in order to enhance the sensitivity. There have also been various reports describing the use of porous layers in direct thermal printing.[3]

Recently both Yamada and co-workers[4] and Tanaka and co-workers[5] have described a thermal wax transfer system that utilizes a large number of fine pores distributed on the surface of the ink-receiving sheet. In addition, Korol[6] has reviewed that these fine pores on the surface play an important role especially in thermal wax

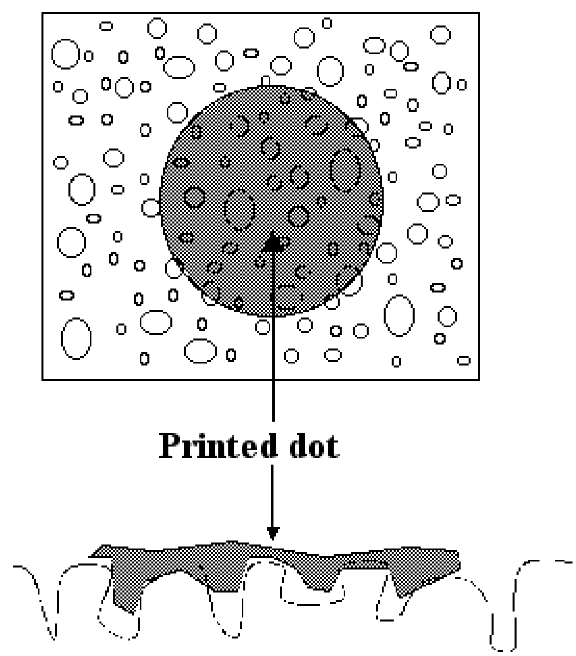

Figure 1. Surface and cross section view of a microporous layer for use in thermal wax transfer printing.

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Supplemental materials—Figures 5, 6 and 7 can be found in color on the IS&T website (www.imaging.org) for a period of no less than 2 years from the date of publication.

TABLE I. Composition of the Coating Liquid

Component	Part by solid weight
Aqueous resin: Polyurethane	100
Foam stabilizer: Salt of long-chain fatty acid	5.0
Viscosity control agent: Cellulose derivative	3.0

transfer printing because this system requires not only low thermal conductivity and high compressibility but also a high affinity to wax ink. In this system the molten ink permeates into the microporous surface layer due to the plurality of capillaries. The ink-receiving layer containing fine pores has been prepared in an indirect method as follows: a resin coating layer containing a water-soluble component is formed and then the water-soluble component is extracted and voids are generated by this elimination.[7]

However, from the industrial point of view, it is clearly preferable to find a direct method. The simplest route to obtain microporous paper having fine pores on the surface is to coat a sheet substrate with a coating mixture containing fine air bubbles. In our own research program we have focused on the preparation using a mechanical stirring method of introducing and dispersing air bubbles in a resin- containing liquid.

In the present work we describe the characterization and application of microporous paper sheets prepared using the direct method above. After describing the resulting characteristics from the structure of the microporous layers, we focus on the quantitative measurements of the print quality for use in digital printing with particular emphasis on thermal wax transfer printing.

Experiment

Preparation of the Microporous Paper Sheets

A typical preparation of microporous paper sheet is shown as follows: A mixture of air with a coating liquid (solid content of 30%) containing the composition given in Table I was stirred in a closed system at a mixing volume ratio of air/liquid = 0.5/1.0 with constant stirring of 1500 rpm using a continuous whipping machine. In this preparation air and coating liquid were continuously fed into the closed system (0.17 kg/min.). A large number of fine and dispersed air bubbles were observed in the resulting mixture as shown in Fig. 2.

Immediately after the bubbling treatment, an approximate 'equivalent circle' number-average bubble size, standard deviation, range and number were determined for the coating mixtures by counting more than 10,000 bubbles on several optical micrographs using DotAnalyzer-5000S digital image analyzer manufactured by Oji Scientific Instruments Co., Ltd.

One surface of a plain paper sheet having a weight of 127.9 g/m^2 was coated with the fine bubble-containing mixture using an applicator bar in a dry amount of 10 g/m^2. The coating was then dried to obtain a paper sheet having a microporous layer (Sample ID, MpP1).

The same procedures as described above were carried out except that the mixing volume ratio was changed to air/liquid = 2.0/1.0 (Sample ID, MpP2).

Characterization of the Microporous Layers and the Microporous Paper Sheets

The microporous layers have been characterized in terms of their morphology, density and pore size distribution. Scanning electron microscopy (SEM) studies

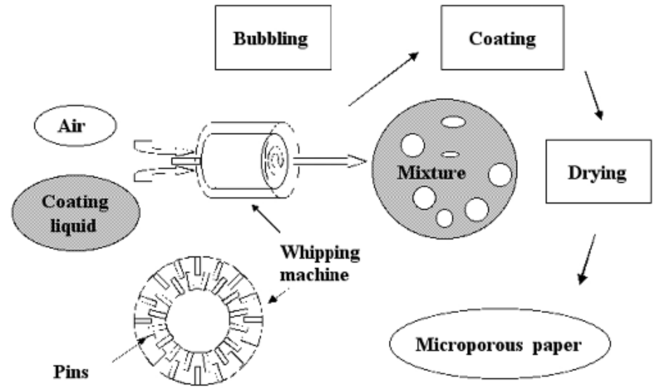

Figure 2. Schematic diagram for obtaining the microporous paper sheet using mechanical bubbling method.

were made using a JEOL JSM-5800LV instrument at an operating voltage of 10 kV.

The densities of the microporous layers were calculated from the thickness and weight data of the corresponding microporous paper sheets (MpP1 and MpP2) and the substrate paper (plain paper) assuming simple subtraction.

An approximate 'equivalent circle' number-average pore size, standard deviation, range and number were determined for the microporous surface layers by counting more than 10,000 pores on several optical micrographs using DotAnalyzer-5000S digital image analyzer manufactured by Oji Scientific Instruments Co., Ltd.

The microporous paper sheets (MpP1 and MpP2) have been characterized in terms of their thermal conductivity and compressibility. Thermal conductivity measurements were made on both the microporous paper sheets (MpP1 and MpP2) and the plain paper sheet by a laser flash method previously reported[8] using the LF/TCM (FA8510B type) instrument manufactured by Rigaku Cooperation.

The compression stresses of the microporous paper sheets (MpP1 and MpP2) and the plain paper sheet were determined using Strograph-M2 tensile compression apparatus manufactured by Toyo Seiki Seisakusho, under the following conditions: the microporous paper sheets and the plain paper were compressed at a rate of 0.5mm/min in the Z-axis direction, and then their stress-strain curves were monitored. The compression stresses under a compression of 10% by volume were determined from the stress-strain curves.

Print Quality of the Microporous Paper Sheets

The microporous paper sheets (MpP1 and MpP2) and the plain paper sheet were evaluated for use in thermal wax transfer printing in terms of their dot quality, line quality, solid area quality, uniformity and optical density. Two types of test targets designed by Quality Engineering Associates Inc. (QEA) and Oji Scientific Instruments Co., Ltd. (OSI) were printed on these sheets using a MD-5000 thermal wax transfer printer manufactured by Alps Electric Co., Ltd. These test targets consist of basic image elements such as dots, lines and solid areas for the quantitative print quality measurement.

Dot Quality

An APQS automated image analysis system manufactured by OSI was utilized in order to quantify the dot quality of the microporous paper sheets (MpP1 and

TABLE II. Experimental Data on the Coating Mixture

Coating mixture	Air/liquid volume ratio	Bubble evaluation: Bubble size (µm) Number average	Standard deviation	Range	Number/mm^2
MpP1	0.5:1.0	10.2	3.9	0.5-26.1	3100
MpP2	2.0:1.0	4.8	1.9	0.5-14.7	16000

TABLE III. Experimental Data on the Microporous Layers

Microporous layer	Density (g/cm^2)	Surface pore evaluation: Pore size (µm) Number average	Standard deviation	Range	Number/mm^2
MpP1	0.45	10.3	3.3	0.5-29.2	2600
MpP2	0.18	4.9	1.6	0.5-15.9	15700

TABLE IV. Experimental Data on MpP1, MpP2 and the Plain Paper

Paper sheets	Density (g/cm^2)	Thermal conductivity (W/(m·K))	Compression stress (kg/cm^2)
MpP1	0.82	0.245	7.6
MpP2	0.69	0.147	1.6
Plain paper	0.88	0.450	50.0

MpP2) in terms of dot raggedness and dot shape at 30% gray scale with solid magenta.

Line Quality

An IAS-1000 automated image analysis system manufactured by QEA was utilized in order to quantify the line quality of MpP2 and the plain paper sheet in terms of line width, blurriness and raggedness with cyan line using the ISO-13660 draft standard.

Solid Area Quality and Tone Reproduction

Both the APQS and the IAS-1000 system were utilized in order to quantify the solid area quality of MpP2 and the plain paper sheet in terms of solid area and tone reproduction.

Uniformity

Mottle and graininess were measured with methods developed by Jones and co-workers.[9] These methods were applied for the measurements of MpP2 and the plain paper using the IAS-1000 system.

Optical Density

A MacBeth reflective color density meter was used in order to quantify the optical density of the microporous paper sheets (MpP1 and MpP2) and the plain paper sheet.

Results and Discussion

Preparation and characterization of the coating mixtures, the microporous layers and the microporous paper sheets

As described in the experiment section, our microporous paper sheets can be easily prepared using the mechanical bubbling method. It can be said that this direct and simple method is more practical than the complicated method previously reported.[4,5]

Our experimental data on the coating mixtures, the microporous layers and the corresponding paper sheets are presented in Tables II, III and IV, respectively. The bubble size in the coating mixture is influenced by the mixing ratio of air with coating liquid as presented in Table II, with rather smaller levels being obtained at higher air volume. Presumably this is due to the difference in air pressure of the closed system. Air may be easily introduced into the coating liquid and dispersed in the coating mixture under high air pressure owing to high air volume. As a result smaller pores on the surface of microporous paper sheets were obtained when the air volume of coating mixture was higher.

The key technology in obtaining a successful microporous paper sheet for digital printing is control of the pore size distribution in the microporous layer. In other words controlling bubble size distribution in the coating mixture is critical because there is clearly a strong correlation between the pore size distribution and the bubble size distribution as presented in Tables II and III. In order to disperse and stabilize bubbles we utilize a foam stabilizer and a viscosity control agent in the coating liquid as presented in Table I. In addition, we have extensively examined the effect of other factors for controlling the bubble size distribution such as the stirring speed, rheology of the coating liquid and the nature of the component in the coating liquid. These results will be reported in detail elsewhere.[10] We finally obtain a large number of fine, stable bubbles with a diameter of 0.5-26 µm.

These stable bubbles produce a large number of fine pores on the surface layer with an average diameter of 0.5-30 µm as shown in Fig. 3. These fine pores play an important role in digital printing such as thermal wax transfer and solid inkjet. They enhance optical density and dot quality because the molten ink permeates sufficiently into the pores of the microporous surface layer due to the capacity and capillary attraction, and then fixes on the surface due to mechanical interlocking.

The microporous layers of MpP1 and MpP2 have significantly lower densities than that observed for the plain paper substrate (0.45 g/cm^3 and 0.18 g/cm^3 versus 0.88 g/cm^3). This is not surprising since our scanning electron microscopy studies suggest the microporous layer is clearly made up of fine porous cells, which give rise to a distinctive “beehive” morphology as shown in Fig. 4.

As anticipated from the “beehive” morphology, the thermal conductivity of the microporous paper sheets

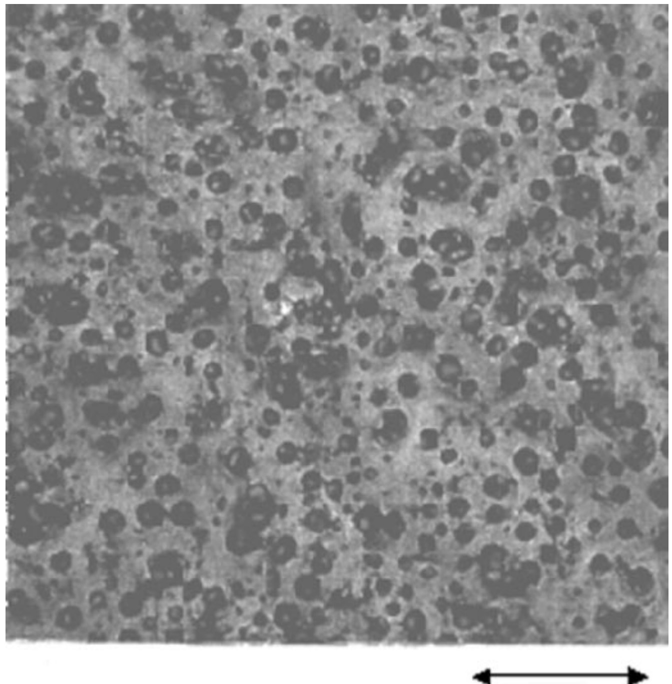

Figure 3. Scanning electron micrograph showing a large number of fine pores on the surface layer of MpP1.

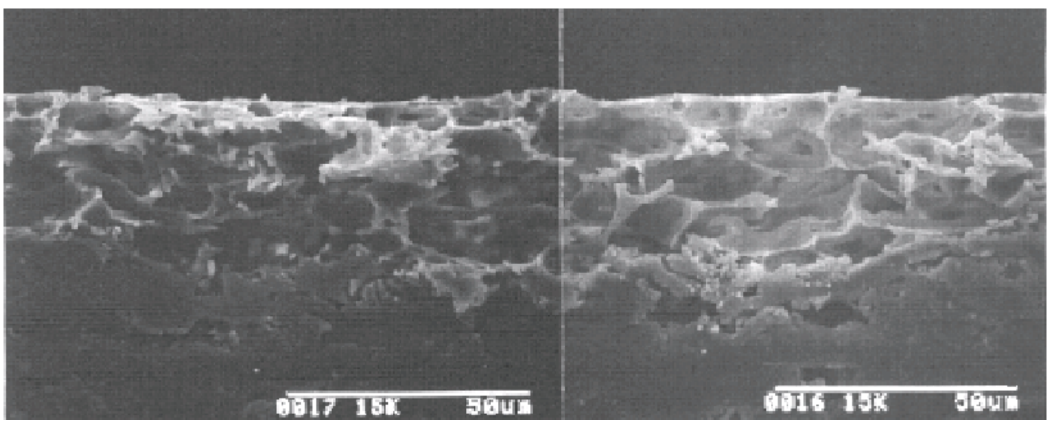

Figure 4. Scanning electron micrograph showing a distinctive "beehive" morphology.

(MpP1 and MpP2) are lower than that observed for the plain paper sheet (see Table IV). It is well known that thermal conductivity closely relates to the density of layer. Therefore there is no doubt that the low thermal conductivity of our microporous paper sheets result from the low densities of the corresponding microporous layers. The heat-insulating nature is very important in thermal printing as we along with co-workers have already demonstrated that a paper sheet having a heat-insulating layer significantly improve the sensitivities of thermal printing including direct thermal,[11] thermal dye diffusion transfer[12] and thermal wax transfer.[13]

As anticipated from the difference of the density between the microporous layers and the plain paper, the 10% compression stresses of microporous paper sheets (MpP1 and MpP2) are lower at least by an order of magnitude relative to that of the plain paper sheet (see Table IV). The low compression stress, in other words high compressibility, is also important in digital printing such as thermal wax transfer printing. The lower the compression stress of the sheet, the higher the softness of the ink-receiving layer and thus the higher degree of close contact of the ink-receiving layer with the ink ribbon in thermal transfer printing.

We believe our microporous paper sheet can be used in a wide range of applications in digital printing because the microporous layer acts as an ink-receiving layer, a heat insulating layer and a cushion layer due to high affinity to ink, low thermal conductivity and high compressibility, respectively. In our research program we have focused on thermal wax transfer printing because this system requires all three characteristics described above.

TABLE V. Dot Qualities of MpP1, MpP2 and Plain Paper

	Dot raggedness		Degree of circularity	
Paper sheets	Average	Standard deviation	Average	Standard deviation
MpP1	1.21	0.17	2.23	0.81
MpP2	1.09	0.02	1.50	0.10
Plain paper	1.31	0.25	2.53	0.99

TABLE VI. Line Qualities of MpP2 and Plain Paper

		Blurriness (μm)		Raggedness (μm)	
Paper sheets	Width (μm)	Lead	Trail	Lead	Trail
MpP2	120	27.1	40.0	1.8	2.4
Plain paper	110	56.6	96.2	7.4	4.3

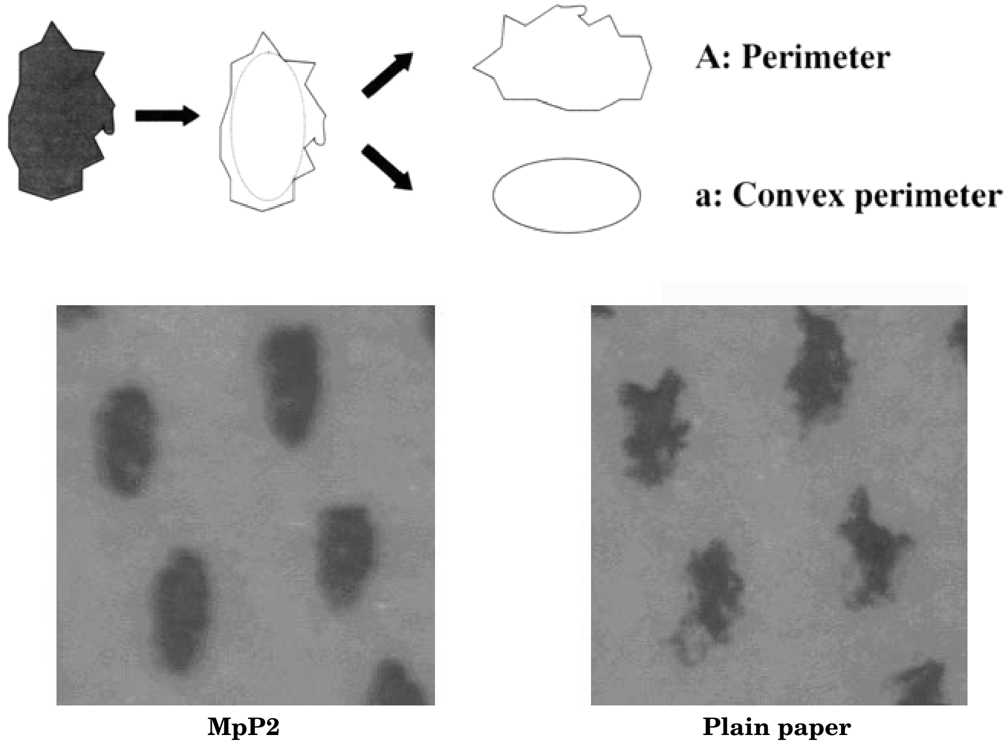

Figure 5. Optical micrograph showing dots at 20% gray scale with magenta of both MpP2 and the plain paper. Dot raggedness is defined as A/a.

Print Quality for Use in Thermal Wax Transfer Printing of the Microporous Paper Sheets

Dot Quality

Optical micrographs of dots printed on MpP2 and the plain paper are shown in Fig. 5. In this present work, in order to measure how rough a dot is, we defined the dot raggedness as the perimeter/convex perimeter. The lower the dot raggedness, the better the dot quality. A smooth convex object will have the minimum raggedness of 1.0. The dot raggedness of our microporous paper (MpP1 and MpP2) at 30% gray scale with solid magenta are lower than that of the plain paper. The dot raggedness of MpP2 is quite close to the minimum as presented in Table V.

We also defined the degree of circularity as $l^2/4\pi S$ (l:perimeter, S:dot area), in order to describe dot shape. The lower the degree of circularity, the closer to a circle. A circular object will have the minimum degree of 1.0. The degree of circularity of our microporous paper (MpP1 and MpP2) at 30% gray scale with solid magenta are lower than that of the plain paper. The degree of circularity of MpP2 is quite close to the circle as presented in Table V.

Line Quality

Optical micrographs of lines printed on MpP2 and the plain paper are shown in Fig. 6. It is clear, albeit qualitatively, that the line quality of MpP2 is much better than that of the plain paper. However, the quantitative measurements are preferable with an internationally recognized standard. The ISO-13660 draft standard, for example, prescribes methods for measuring blurriness and raggedness in order to quantify the line qualities.

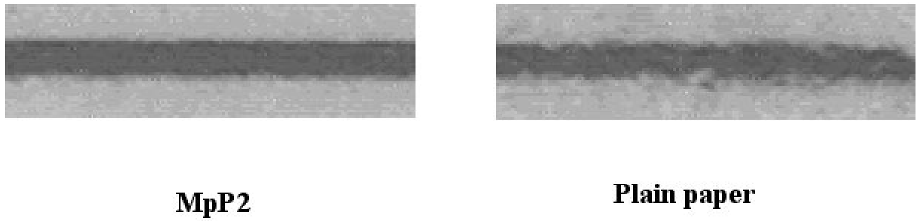

Figure 6. Optical micrograph showing lines with cyan of both MpP2 and the plain paper.

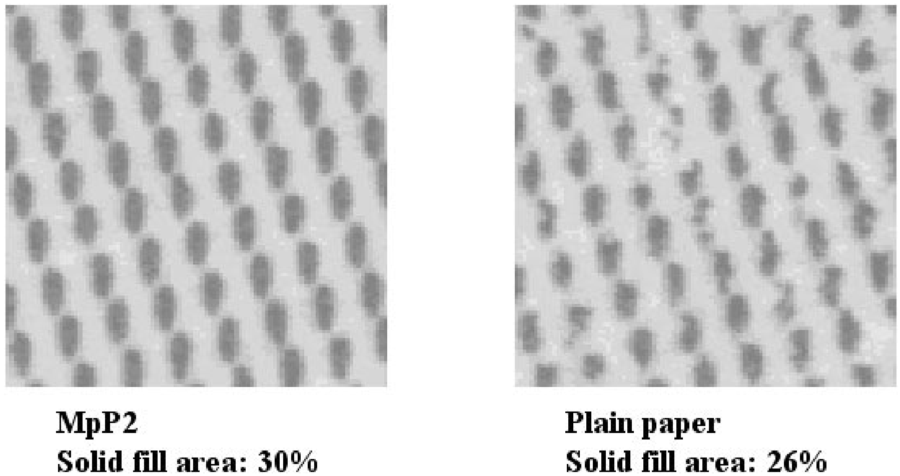

Figure 7. Optical micrograph showing dot images with 30% gray scale magenta of both MpP2 and the plain paper.

According to the definition described in ISO-13660 draft standard, blurriness is the appearance of being hazy or indistinct in outline; a noticeable transition of blackness from background to character. It is reported as the distance in micrometers. The lower the blurriness, the better the line quality. The blurriness of our microporous paper (MpP2) is reasonably low relative to that of the plain paper as presented in Table VI.

The definition of raggedness is also referred to the ISO-13660 draft standard. Raggedness is the geometric distortion of an edge from its ideal position. It is measured as the standard deviation of the residuals from a line fitted to the edge threshold. A ragged edge appears rough or wavy rather than smooth or straight. Therefore, the lower the raggedness, the better the line quality. The raggedness of our microporous paper is lower than that of the plain paper as presented in Table VI.

Solid Area Quality

Figure 7 shows dot images of both MpP2 and the plain paper at 30% gray level with solid magenta. The solid fill area of the microporous paper sheet (MpP2) as measured by the APQS system is higher than that measured for plain paper (30% versus 26%). This higher solid fill area leads to a higher optical density of the microporous paper relative to that of the plain paper. More importantly, with the microporous paper, essentially the designated solid fill area of 30% is reproduced. In addition, as shown in Fig. 8, the dot area distribution curve of MpP2 is surprisingly narrow and unimodal with standard deviation of 9%, while the plain paper exhibits a board distribution. These observations indicate the excellent dot reproduction of our microporous paper sheet.

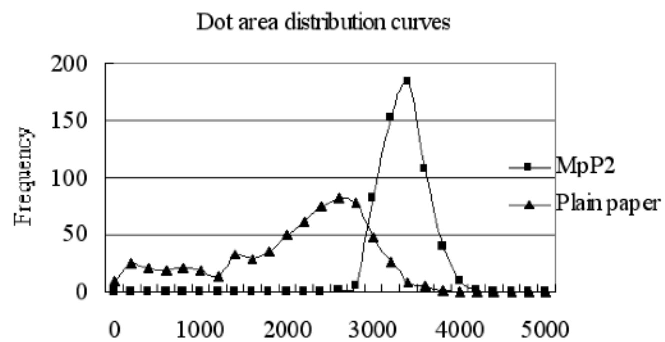

Figure 8. Dot area distribution curves of both MpP2 and the plain paper.

Tone Reproduction

Figure 9 illustrates the relationship between the actual solid fill area printed on MpP2 with magenta and the designated gray scale. The dashed line represents the ideal solid fill area expected from each gray scale level. All the experimental data points fall on and/or slightly above the ideal line with a correlation coefficient of 0.9995 and possibly larger deviations at 40% gray scale or more. This measurement indicates the excellent tone reproduction of our microporous paper sheet.

Uniformity

The ISO-13660 draft standard prescribes methods for measuring mottle and graininess which are matrices of “macro uniformity” and “micro uniformity”, respectively. In the case of measurement with ISO-13660, the region of interest (ROI) is subdivided into one hundred smaller

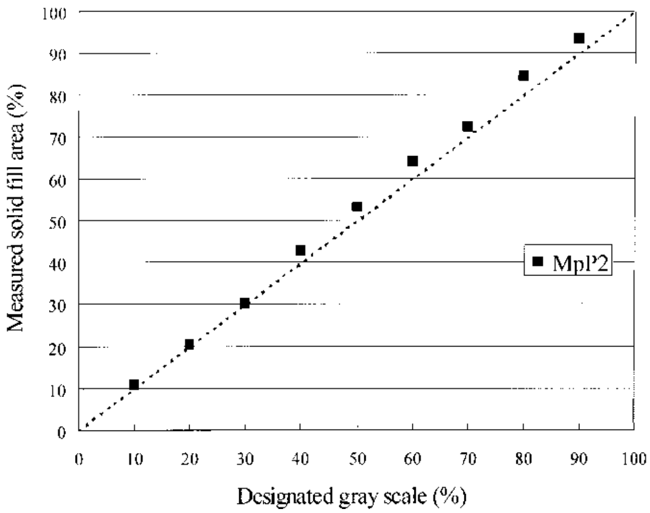

Figure 9. Solid fill area of MpP2 as a function of gray scale with magenta.

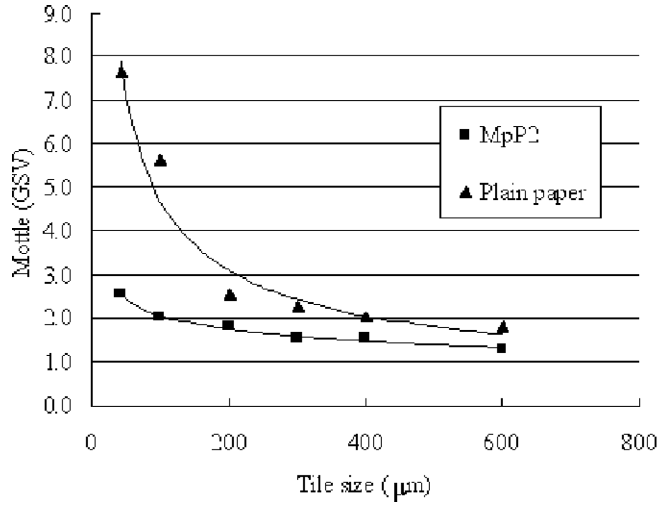

Figure 10. Mottle measurement taken at a range of tile sizes on areas printed with solid magenta of both MpP2 and the plain paper.

regions called tiles. The ROI prescribed by the ISO-13660 is 12.7×12.7mm and the tiles are 1.27×1.27mm. Each tile within the ROI is 30×30 pixels. Within each tile, the average optical density, m_i, and standard deviation of the optical density, σ_i, are calculated. The mottle can be calculated as the standard deviation of m_i, and the graininess by the equation as follows; Graininess=$(\Sigma\sigma_i/100)^{1/2}$

Although not mentioned in detail in this article, according to Jones and co-workers,[9] the ISO draft standard has limitations that make it inappropriate for analyzing mottle. In the view of these limitations, we decided not to apply the ISO method as is, but to use a variant with differences developed by Jones and co-workers.[9] The two differences are 1) the use of a variable tile size and 2) the use of simple gray scale values (GSV)-numbers between 0 and 255-as the unit of reflectance instead of optical density. The first point is extremely critical in view of the fact that human perception of reflectance variation is very sensitive to the scale of the non-uniformity.

Figure 10 shows mottle measurements taken at a range of tile sizes on area printed with solid magenta. When interpreting mottle data, larger values indicate more non-uniformity and smaller values indicate less non-uniformity. By using variable tile sizes, distinct differences in mottle between MpP2 and the plain paper become apparent, particularly at smaller tile size.

On the other hand, in the case of graininess, the ISO-13660 method was applied as is except that GSV-values were used instead of optical density. The graininess of the microporous paper sheet (MpP2) as measured using the ISO-13660 is much better than that measured for the plain paper (0.028 versus 0.066). From the data of both macro- and micro-uniformity measurements, we conclude that the microporous paper sheets appear quite uniform to the observer.

Optical Density

Figure 11 shows the relationship between the optical density and gray scale. The optical densities of our microporous paper sheets (MpP1 and MpP2) are consistently higher than that observed for the plain paper. These microporous paper sheets have advantages with respect to thermal printing because, as discussed earlier, the thermal conductivity and compression stress are much lower than those measured for the plain paper.

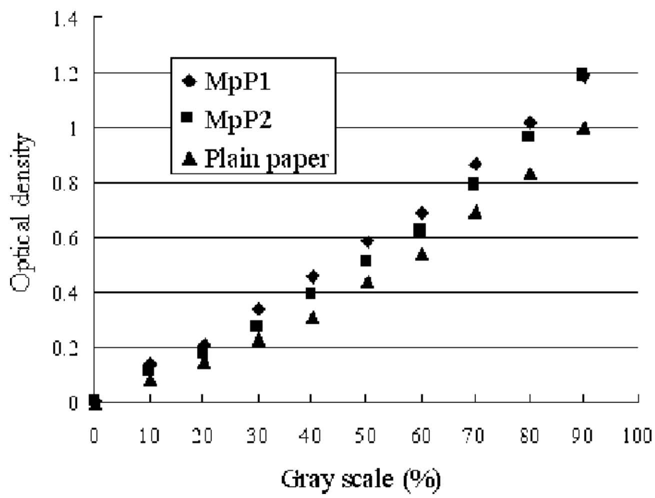

Figure 11. Optical densities of MpP1/MpP2 and the plain paper as a function of gray scale with cyan.

Figure 11 also shows that the microporous paper sheet having larger pores (MpP1) had a higher optical density relative to that having smaller pores (MpP2). This is perhaps surprising in view of the higher thermal conductivity and compression stress of MpP1 relative to that of MpP2. On the other hand, MpP2 had a significantly higher dot quality relative to that of MpP1 as presented in Table V.

In order to address this question we assumed that the pore size distribution on the surface of microporous paper sheets affects both the optical density and the dot quality in the thermal wax transfer system. We observed the microporous surface pores after thermal wax transfer printing using an optical microscope (not shown). The observation yielded useful, albeit qualitative, information on the print quality. The larger the pore size, the higher the ink-receiving capacity, which increases the solid fill area, in other words, enhances the optical density of the microporous paper sheet. Whereas with the smaller pore size, the higher uniformity of dots is at least in part due to the capillary attraction. We conclude that the pore size of these microporous paper sheets closely relates to both the capacity for embedding a solidified ink and the capillary attraction for absorbing a molten ink, with higher capacity and lower capillary attraction being obtained from larger pores. We found that it is preferable to control the pore dimension in the range 1-20 µm diameter for achieving a satisfactory balance of these properties.

Problems and the Solution of Microporous Paper Sheets

In general microporous layers potentially have undesirable characteristics such as blocking and poor strength of the layers. In practical usage the most useful approach to overcome these drawbacks is to find some materials for achieving a satisfactory balance of antiblocking and softness. We have extensively characterized some materials appropriate for achieving the balance in terms of their physical properties, surface chemistry and chemical structure.[14]

Advantages of our Microporous Paper Sheets

We note that our microporous paper sheets have the following three advantages that distinguish them from the porous paper sheets previously reported[4,5]: 1) facile preparation of the microporous layers; 2) facile recycling by using plain paper sheets as substrate instead of synthetic films; and 3) low cost.

Other Applications for the Microporous Paper Sheets

The other potential application areas for the microporous paper sheets include direct thermal, thermal dye diffusion transfer, solid inkjet and toner-based marking.

In collaboration with a copier and printer company we have recently developed an analogous microporous paper sheet for use in the last application. In the toner-based marking the microporous layer acts as a toner-receiving layer instead of an ink-receiving layer. Full details will be reported elsewhere in the near future.[15]

We note that the microporous layer also acts as an intermediate layer. For example, the microporous intermediate layers enhance the sensitivity of the receiving sheets for direct thermal[16] and thermal dye diffusion transfer[17] printing due to its heat-insulating nature and cushion property.

Conclusion

We have discovered a novel and facile method for the preparation of microporous layers that utilize a large number of fine air bubbles dispersed in a coating mixture. The resulting microporous paper sheets can significantly improve the print quality in thermal wax transfer printing, which otherwise has rather poor print quality when using a plain paper sheet. These microporous paper sheets have potential application areas in other digital printing systems; our work in these fields will be reported in detail elsewhere.[18]

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References

1. K. Imoto, S. Narita and Y. Kamikubo, *IS&T's 12th Int'l. Conf. on Digital Printing Technologies*, IS&T, Springfield, VA, 1996, p. 248.
2. K. Takei, T. Tsunoda, T. Akimoto and Y. Ugagame, Japanese Patent Publication H07-179055 (1995).
3. T. Amano and H. Sakai, Japanese Patent 2, 613,772 (1997).
4. K. Yamada, M. Takahashi and M. Katoh, *IS&T's 12th Int'l. Conf. on Digital Printing Technologies*, IS&T, Springfield, VA, 1996, p. 18.
5. H. Tanaka and Y. Hakamada, US Patent 5,521,626 (1996).
6. S. Korol, *5th Annual Nonimpact Papers Briefing*, Information Management Institute, Windham, Maine, 1997.
7. K. Kazui and K. Fukuda, Japanese Patent 2,684559 (1997).
8. M. Hakomori, M. Maeda, Y. Mizuhara, M. Kimura, T. Nakai, K. Asaeda, T. Nakata, and M. Oka, US Patent 5,631,076 (1997).
9. N. Jones, S. J. Sargeant, K. Sargeant, J. C. Briggs and M.-K. Tse, *IS&T's 12th Int'l. Conf. on Digital Printing Technologies*, IS&T, Springfield, VA, 1998, p. 161.
10. Manuscript in preparation.
11. S. Maeda, M. Hakomori, M. Maeda, and K. Nishikawa, Japanese Patent Publication H05-32053 (1993).
12. Y. Mizuhara, Y. Shimizu, H. Tsukamoto, and S. Hayashi, Japanese Patent Publication H11-301124 (1999).
13. M. Kimura and M. Hakomori, Japanese Patent Publication H07-228065 (1995).
14. S. Maeda, Japanese Patent Publication H09-315021 (1997).
15. Manuscript in preparation.
16. S. Maeda, Japanese Patent Publication H10-147060 (1998).
17. H. Tsukamoto, Y. Mizuhara and Y. Shimizu, Japanese Patent Publication 2000-52664 (2000).
18. Manuscript in preparation.