Development of Paper having Micro-Porous Layer for Digital Printing

Shuichi Maeda, Toru Nakai, Akira Nakamura, Masakazu Hakomori and Masaru Kato Imaging Media Development Laboratory, Oji Paper Company Tokyo, Japan

Abstract

We describe the development of micro-porous paper that meets the demands on print-quality in different types of digital printing. The paper contains a micro-porous layer that has a surface pore diameter of 0.5 to 30 μ m and a density of 0.2 to 0.5 g/cm³. The micro-porous layer can be easily obtained by coating a sheet substrate with a resin-containing liquid stirred forming bubbles. Application areas for the micro-porous paper in digital printing include thermal wax transfer, thermal dye diffusion, direct thermal, solid inkjet and toner-based marking.

In the first application, the micro-porous layer acts as an ink-receiving layer (see Figure 1) due to the heatinsulating nature, the compressibility and the surface structure. The micro-porous paper has a thermal conductivity of 0.25 W/(mk) or less. The compression stress of the micro-porous layer under a compression of 10% by volume is controlled to 8 kg/cm² or less. The molten ink permeates sufficiently into the region of the micro-porous surface layer due to the presence of a large number (3,000/mm² or more) of fine pores distributed on the surface. Thus the micro-porous surface layer enhances color density, dot reproducibility and continuous tone reproducibility in this application.



Figure 1. Surface view of a micro-porous layer for use in thermal wax transfer printing

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 et al.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 et al.² have utilized a 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.

Recently both Yamada et al.³ and Tanaka et al.⁴ have described a thermal wax transfer system which utilizes a large number of fine pores distributed on the surface of the ink-receiving sheet. In addition, Korol has reviewed that these fine pores on the surface play an important roll especially in thermal wax transfer printing because this system requires not only low thermal conductivity and high compressibility but also a high affinity to wax ink.⁵ In this system the molten ink permeates into the micro-porous surface layer due to the plurality of capillaries. The inkreceiving 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.⁶

However, from the industrial point of view, it is clearly preferable to find a direct method. The simplest route to obtain micro-porous 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 resincontaining liquid.

In the present work we describe the preparation, characterization and application (with particular emphasis on thermal wax transfer printing) of our micro-porous paper sheets.

Experiment

Preparation of Micro-Porous Paper Sheets

A typical preparation of micro-porous paper sheet is shown as follows: A mixture of air with a coating liquid (solid content of 30%) containing the composition given in Table 1 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 (0.17kg/min.). A large number of fine and dispersed air bubbles were observed in the resulting mixture.

Immediately after the bubbling treatment, one surface of a plain paper sheet having a weight of 127.9 g/m² was coated with the fine bubble-containing mixture using an applicator bar in a dry amount of 10 g/m². The coating was then dried so as to obtain a paper having a micro-porous 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).

 Table 1. Composition of the coating liquid

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

Characterization of the Micro-Porous Layers and Paper Sheets

The micro-porous layers have been characterized in terms of their density and pore size distribution.

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

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

The micro-porous paper sheets (MpP1 and MpP2) have been characterized in terms of their thermal conductivity and compressibility.

Thermal conductivity measurements were made on both the micro-porous paper sheets and a plain paper sheet by a laser flash method previously reported⁷ using LF/TCM (FA8510B type) instrument manufactured by Rigaku Cooperation.

The compression stresses of our micro-porous 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 micro-porous 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 Micro-Porous Paper Sheets

The micro-porous paper sheets (MpP1 and MpP2) and the plain paper sheet were evaluated for use in thermal wax transfer printing in terms of their color density, dot reproducibility and continuous tone reproducibility.

The images in 10 energy levels of continuous color tone were printed on these samples using MD-5000 thermal wax transfer printer manufactured by Alps Electric Co., Ltd. and Corel DRAW software.

A MacBeth reflective color density meter and an APQS automated image analysis system manufactured by Oji Scientific Instruments Co., Ltd. were used in order to quantify the print-quality of our micro-porous paper sheets.

Results and Discussion

Preparation and Characterization of the Coating Mixture, the Micro-Porous Layer and Paper Sheets

Our experimental data on the coating mixture, the micro-porous layers and the corresponding paper sheets are presented in Table 2, 3 and 4, respectively.

The bubble size in the coating mixture is influenced by the mixing ratio of air with coating liquid as presented in Table 2, 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 micro-porous paper sheets were obtained when the air volume of coating mixture was higher.

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

 Table 2. Experimental data on the coating mixture

The key technology in obtaining a successful microporous paper sheet for digital printing is how to control the pore size distribution in the micro-porous layer. In other words controlling bubble size distribution in the coating mixture is a key since there is clearly a strong correlation between the pore size distribution and the bubble size distribution as presented in Table 2 and 3. 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 elsewhere.⁸

		Surface pore evaluation		
	Density Pore size (µm)		Number	
Micro-porous	(g/cm ²)	Number	Range	$/mm^2$
layer		average	Range	/ 11111
MpP1	0.45	10.3	0.5-29.2	2600
MpP2	0.18	4.9	0.5-15.9	15700

Table 3. Experimental data on the micro-porous layers

As anticipated, the thermal conductivities of the microporous paper sheets are lower than that observed for the plain paper sheet (see Table 4). It is well known that thermal conductivity closely relates to the density of layer. Therefore there is no doubt that the low thermal conductivities of the micro-porous paper sheets arise from the low densities of the corresponding micro-porous layers. The heat-insulating nature is very important in thermal printing as several groups demonstrated that a paper sheet having a heat-insulating layer significantly improve the sensitivity of thermal printing including direct thermal, thermal dye diffusion and thermal wax transfer.

The compression stresses of the micro-porous paper sheets are also lower than that observed for the plain paper sheet (see Table 4). 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.

 Table 4. Experimental data on the micro-porous paper sheets

	Donsity	Thermal	Compression	
	$(\alpha/\alpha m^2)$	conductivity	stress	
Paper sheets	(g/cm)	(w/(mk))	(kg/cm^2)	
Plain paper	0.88	0.450	50.0	
MpP1	0.82	0.245	7.6	
MpP2	0.69	0.147	1.6	

Print-Quality for Use in Thermal Wax Transfer Printing

The print qualities of our micro-porous paper sheets in terms of color density are consistently higher than that observed for the plain paper sheet as shown in Figure 2. This is not surprising since it is known^{3,4} that a micro-porous surface layer acts as an ink-receiving layer and enhances print-quality for use in thermal wax transfer printing. We believe that these micro-porous paper sheets have advantages with respect to the thermal wax transfer printing because the thermal conductivity and compression stress is much lower than that measured for the plain paper sheet.

Figure 2 also shows that the micro-porous paper sheet having larger pores (MpP1) had a high color density relative to that having smaller pores (MpP2). This is perhaps surprising in view of the higher heat-insulating nature and lower cushion property of MpP1 relative to that of MpP2. On the other hand, the MpP2 had a significantly high dot reproducibility as presented in Table 5.

In order to address this question we assumed that the pore size distribution on the surface of micro-porous paper sheets affects both the color density and the dot reproducibility in thermal wax transfer system. We observed the micro-porous 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 enhances the color density of micro-porous paper sheet. Whereas the smaller the pore size, the higher uniformity of dots at least in part due to the capillary attraction. We conclude that the pore size of these micro-porous 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.



Figure 2. Color (cyan) densities of the micro-porous paper sheets as a function of energy level

Table 5. Dot reproducibilities (magenta) of the micro-
porous paper sheets at energy level of 2

Micro-	Roughness*		Degree of circularity*	
porous paper sheets	Average	Standard deviation	Average	Standard deviation
MpP1	1.28	0.18	2.43	0.87
MpP2	1.12	0.03	1.60	0.11

* The more convoluted the shape, the greater the value.

Figure 3 illustrates the relationship between the solid area made by magenta ink on the MpP2 and energy level. The solid line represents the area expected from the each energy level. All the experimental data points fall on and/or slightly above this theoretical line with correlation coefficient of 0.9995 and possibly larger deviations at energy level of 4 or more. This measurement indicates an

excellent continuous tone reproducibility of the microporous paper sheet.



Figure 3. Continuous tone reproducibility (magenta) of the microporous paper sheet (MpP2) as a function of energy level

General Problem and Solution of Micro-Porous Paper Sheets

In general micro-porous 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.⁹

Advantages of Our Micro-Porous Paper Sheets

We note that our micro-porous paper sheets have the following three advantages which distinguish them from the micro-porous sheet previously reported^{3,4}: (1) facile preparation of the micro-porous layer, (2) facile recycling by using plain paper as substrate instead of synthetic film and (3) low cost.

Other Applications of the Micro-Porous Paper Sheets

The other potential application areas for the microporous paper sheets include direct thermal, thermal dye diffusion, solid inkjet and toner-based marking. In collaboration with a copier and printer company we have recently developed an analogous micro-porous paper sheet for use in the last application. In the toner-based marking the micro-porous layer acts as a toner-receiving layer instead of an ink-receiving layer. Full details will be reported elsewhere in the near future.⁸

Conclusion

We have discovered a novel and facile method for the preparation of micro-porous layers which utilize a large number of fine air bubbles dispersed in a coating mixture. The resulting micro-porous 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 micro-porous paper sheets have potential applications in other digital printing systems; our works in these fields will be reported in detail elsewhere.⁸

Acknowledgement

We thank to the Oji Scientific Instruments Co., Ltd. for their assistance with the print-quality measurements by APQS system.

References

- 1. K. Imoto, S. Narita and Y. Kamikubo, *Proc. NIP12*, pg. 248. (1996).
- 2. For example, Unexamined Patent Publication (Kokai) No.7-179055, Japan.
- 3. K. Yamada, M. Takahashi and M. Katoh, *Proc. NIP12*, pg. 18. (1996).
- 4. US patent 5,521,626.
- 5. S. Korol, *Tutorial Notes*. *NIP12*, pg. 250. (1996).
- For example, Unexamined Patent Publication (Kokai) No.2-89690, Japan.
- 7. US patent 5,631,076.
- 8. Manuscript in preparation.
- 9. For example, Unexamined Patent Publication (Kokai) No.9-315021, Japan.

Biography

Shuichi Maeda is a research scientist at Oji Paper Company. He received his M.Sc. in polymer chemistry from Keio University and then joined the Central Research Laboratory at Oji in 1989. He temporarily worked on polymer colloids at Sussex University from 1992. After receiving his Ph.D. in 1994, he has been at the Imaging Media Development Laboratory at Oji. His current interests are polymer colloids, surface chemistry of foams and development of media for digital printing.