Asian Journal of Chemistry; Vol. 23, No. 6 (2011), 2515-2519

ASIAN JOURNAL OF CHEMISTRY

www.asianjournalofchemistry.co.in

Printability Properties of Some Alkaline Sulfite-Anthraquinone-Methanol Handsheets

GULNUR MERTOGLU ELMAS[1,*] and SINAN SONMEZ[2]

[1]Faculty of Forestry, Istanbul University, 34473 Istanbul, Turkey
[2]Faculty of Technical Education, Marmara University, Istanbul, Turkey

*Corresponding author: Tel: +90 212 2261100/25019, E-mail: mertoglug@istanbul.edu.tr

(*Received*: 4 June 2010; *Accepted*: 10 February 2011) AJC-9602

Alkaline sulfite-anthraquinone-methanol, an organosolv pulp production method, is an environmentally friendly method. Alkaline sulfite-anthraquinone-methanol pulps are produced from fast growing *Samsun poplar clone* (*P. deltoides*) and grown in Istanbul, *Robinia pseudoacacia* and *Pinus pinaster* grown in Turkey as a raw material. In this study, alkaline sulfite-anthraquinone-methanol pulps were used to make hand-sheets. Then, the optical and printability properties of alkaline sulfite-anthraquinone-methanol hand-sheets were compared. It was found that the use of *Samsun poplar clone* in making hand-sheets resulted in decrease surface roughness and increase brightness, gloss and opacity. In addition, it had the highest print optical density and print chroma. Although the use of *Robinia pseudoacacia* in making hand-sheets decreased print mottle, *Pinus pinaster* increased print mottle. However, *Pinus pinaster* had the highest delta gloss. The *Samsun p. clone* provided the best print contrast which is beneficial to print readability.

Key Words: Alkaline sulfite-anthraquinone-methanol pulp, *Populus deltoides*, *Robinia pseudoacacia*, *Pinus pinaster*, Printability.

INTRODUCTION

Sulfide or kraft pulping, is used in the production of pulp, which contains concentrated acidic or alkali solutions. These compound solutions have sulphuric elements that cause environmental pollution. The paper industry is one of the most environmentally polluting industries. To reduce environmental pollution to the least possible level and to maintain continuous control of the process, an expensive investment is necessary. The cost of such investments leads to the increase of pulping production unit investment. The alkaline sulfite-anthraquinone-methanol (ASAM) cooking method is used in paper pulp production as a responsible alternative[1]. In this method, alkaline sulfite-anthraquinone-methanol is used as the cooking solution.

Bleaching, being a delignification process is in one sense performed with the most chlorinated compound. These compounds, which are mixed into wastewater, threaten to cause human health problems. Lignin based bleaching agents have proven to result in higher yields, without including chlorinated elements. Alkaline sulfite-anthraquinone-methanol pulping has come into prominence as a bleaching process that manufactures pulp without using chlorinated elements. According to Patt *et al.*[1], the main benefit reported for ASAM pulping, regardless of the raw material used, is its high yield, which may considerably contribute to the maintenance of low environmental pollution, which entitles it to be called environmentally-friendly. The present study evaluated the suitability of the *Samsun poplar clone* (5 year-old *Populus deltoides*), *Robinia pseudoacacia* and *Pinus pinaster* woods grown in Turkey as to their pulp yield and their optical properties in hand-sheets. Primary attention is given to the comparison of their optical and print properties.

EXPERIMENTAL

Samsun poplar clone (*Populus deltoides*), grown in the plantation area of the Poplar and Fast Growing Forest Trees Research Institute of Izmit, Turkey was used as a raw material. Furthermore, *Robinia pseudoacacia* and *Pinus pinaster*, grown in the Turkey (Istanbul), were used as samples, which were prepared in industrial chip size (28.3-56.7 points length, 4.3-11.3 points thickness, 28.3 points width). Later, the chips were put into a 10 L-rotating laboratory digester, were pretreated by steaming and then pulped. Cooking liquor composition and pulping conditions are given in Table-1.

Handsheets obtained from unbleched pulps were tested by TAPPI and ISO standard methods. All samples were conditioned for 24 h at 50 % relative humidity and 23 °C (73.4 °F) before testing. They were tested based according to TAPPI and ISO test methods. Opacity (ISO 2471), ISO brightness (ISO 2470) and yellowness index (ASTM E-313) were determined according to ISO standards. Optical properties were tested with

TABLE-1
CONDITIONS ALKALINE SULFITE-ANTHRAQUINONE-METHANOL PULPING FOR SOME WOOD SAMPLES

Raw material	SPC	RP	PP
(as oven dried) (Na_2SO_3/NaOH) %	3.63	3.63	5.39
AQ %	0.1	0.1	0.1
Methanol % (V)	10	10	10
Pulping time (min)	120	150	170
Maximum temperature (ºC)	170	170	170
Maximum pressure (bar)	12	13	13.5
White liquor pH	11.6	11.6	12.0
Black Liquor pH	8.12	9.5	9.0
ºSR	24	25	24
Wood/Liquor ratio	1/6	1/6	1/6

SPC = *Samsun p. clone*; RP = *Robinia pseudoacacia*; PP = *Pinus pinaster*

3300 type Elrepho spectrophotometers. Drainability (Schopper Riegler ISO 5267-1), laboratory sheets preparation (ISO 5269-2), standard conditioning (ISO 187), grammage (ISO 536), opacity (ISO 2471), ISO brightness (ISO 2470), were determined according to ISO standards. Paper roughness was measured using a PPS ME-90 (1000 kPa, soft backing) based on TAPPI T555-OM-99. Paper gloss was measured at 75° using a Novo-Gloss™ Glossmeter based on TAPPI standard T480-OM-99.

Hand-sheets produced from the ASAM pulps were printed on an IGT Testing System. It used the C1 printability tester for offset inks. The sheet samples were cut (142 × 842 points). For each test, three sheet samples were pressed to the C1 printability tester at 23.7 kPa pressure using a Micheal Huber München Resista Cyan 43FY0RS sheetfed ink, according to ISO 12647-2. The sheet samples were printed in a climate-controlled room (23 °C and a relative humidity of 65 %). Print density values of samples were measured with a GretagMacbeth spectrophotometer at 100 % tint on the printed samples. The density values were again measured during printing, just after printing and 2, 4, 8, 12 and 24 h after printing. Print gloss values of samples were measured at 75° on the 100 % cyan tint using a Novo-Gloss™ glossmeter on TAPPI standard. Print mottle was measured by image analysis using Verity IA software[2]. A first ten angstroms dynamic contact angle-measuring device, FTÅ200, was used to measure the change in contact angle of de-ionized water with time[3]. Water drops spreading (simulating aqueous ink spreading) were observed concurrently.

RESULTS AND DISCUSSION

Alkaline sulfite-anthraquinone-methanol (ASAM) hand-sheets from *Samsun poplar clone, Robinia pseudoacacia* and *Pinus pinaster* pulps of optical and printability properties were determined seperately.

Alkaline sulfite-anthraquinone-methanol paper brightness and gloss: Brightness is an important physical property. Obtaining contrast in printing or writing demands a bright paper surface. Superficial reflection, absorption, reflection within non-uniform parts of paper and fiber, reflection without and the opacity of paper all affect brightness. Brightness is measured at 457 nm wavelengths by a blue filter[4], which best separates white colour tones (R457 brightness-ISO brightness). Paper brightness is affected positively by print contrast and colour reproduction and is one of the key factors for print appeal. As shown in Fig. 1, *Samsun poplar clone* had higher brightness value than *Robinia pseudoacacia* and *Pinus pinaster*. *Pinus pinaster* had the lowest brightness value, 31.5 %.

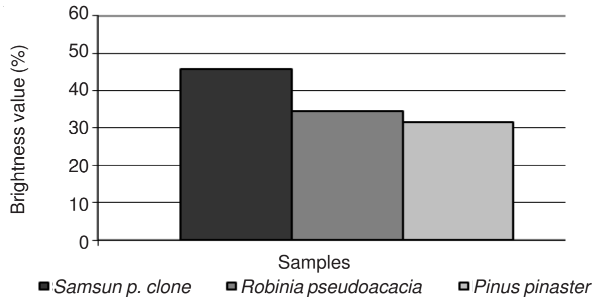

Fig. 1. Brightness values of hand-sheet samples

Gloss affects the visual appearance of printed products[5]. More uniform gloss is perceived as higher quality. The high gloss is also associated with surface physical properties[6]. In other words, the higher the gloss, the higher the smoothness. In addition, the paper gloss is affected by particle size, colloidal stability, drying conditions, binder level and composition[7]. Fig. 2 shows that the least Hunter Gloss 75º value was measured for *Robinia psedoacacia*. The Hunter Gloss 75º value of *Samsun poplar clone* was higher than *Pinus pinaster*. This could be due to the surface structure.

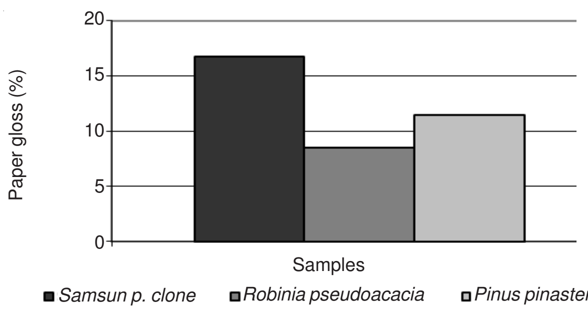

Fig. 2. Gloss values of hand-sheet samples

Alkaline sulfite-anthraquinone-methanol paper opacity: Opacity is determined by measuring the quantity of light transmitted through the paper. The opacity value is obtained by division of reflectance value by the reflectivity value. The application of this value is used to determine how much a printed image will pass through to the other side. Increased show-through of the printed image from the back side of the paper will decrease print contrast, which affects the visual appearance of the printed image[4]. In addition, printing opacity is associated with ink properties as well as paper properties. Obtained opacity values of ASAM paper samples, *Samsun poplar clone* had the highest opacity values (96.9 %), nevertheless *Pinus pinaster* had the lowest opacity value (93.5 %) as shown in Fig. 3.

CIE whiteness and yellowness: Brightness and whiteness are the most important determinates for contrast. In other words, increasing the brightness and whiteness increases the contrast between the paper and printed image[7]. Whiteness is determined by CIE 1931 system. CIE Whiteness values of the

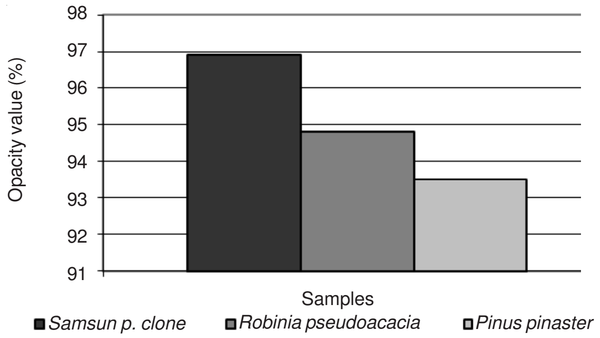

Fig. 3. Opacity values of hand-sheet samples

ASAM paper samples were compared[8]. According to the CIE whiteness values obtained from ASAM paper samples, *Samsun poplar clone* had the highest CIE whiteness values (W; -7.3 T; -11.1) and *Pinus pinaster* had the lowest CIE whiteness values (W;-61 T;-11.1) (Table-2). Alkaline sulfite-anthraquinone-methanol E-313 is a test method that is used to determine yellowness indices of white or colourless samples in the absorption-blue spectrum (Table-2).

TABLE-2
OPTICAL PROPERTIES OF ALKALINE SULFITE-ANTHRAQUINONE-METHANOL HAND-SHEETS SAMPLES

Optical properties (%)		*Samsun p. clone*	*Robinia pseudoacacia*	*Pinus pinaster*
CIE Whiteness	W	-7.3	-23.8	-61.0
	T	-11.1	-17.1	-20.2
Yellowness	(YI)	21.3	22.5	33.7

Surface roughness: Roughness of paper is the most important determinant for a good print[9]. Also, lower surface roughness leads to a reduction of the dot gain and an increase of the gloss[6]. In addition, the surface roughness significantly affects the ink transfer on the surface of paper[10]. Fig. 4 demonstrates that *Robinia pseudoacacia* had the highest surface roughness. However, *Samsun poplar clone* had the lowest roughness value, thereby resulting in good print results in offset printing (Fig. 4).

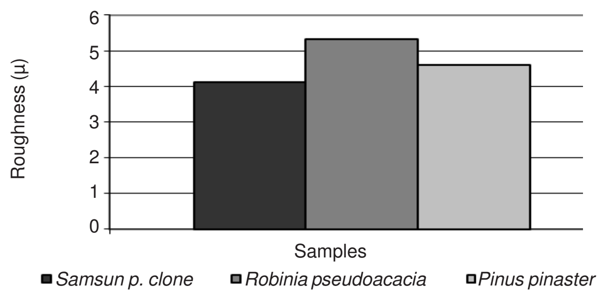

Fig. 4. Surface roughness values

Contact angle and droplet volume: A surface with a high water contact angle indicates low surface energy, which cause poor wettability. Low contact angle shows that the coated surface has better water absorption. The change in contact angle with respect to time represents water spreading. This condition reflects better wetting, better adhesiveness and higher surface energy. Fig. 5 shows the change of water contact angle on the paper samples over 6 s. The initial contact angles of the samples with additives are comparable to the control. The *Robinia pseudoacacia* had a higher initial contact angle. It showed that the *Robinia pseudoacacia* had a low surface energy. The *Pinus pinaster* was much more hydrophobic as compared to *Samsun poplar clone* and *Robinia pseudoacacia*. During the 6 s test, the contact angle of *Samsun poplar clone*, *Robinia pseudoacacia* and *Pinus pinaster* declined slowly. This indicates less ink spreading or ink immobilization. This could also provide improved image resolution and sharpness.

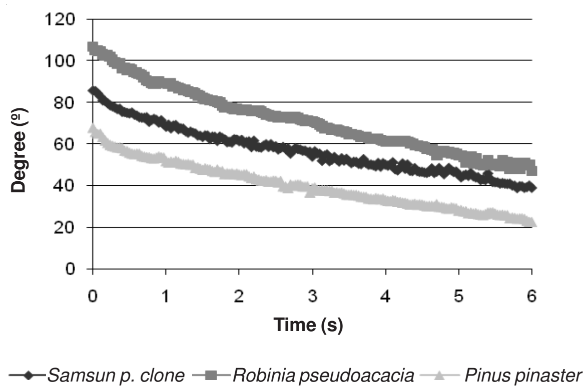

Fig. 5. Surface contact angles of hand-sheet samples

The change of droplet volume was also recorded and it is shown in Fig. 6. The data was normalized to the initial readings. Combining the data with the above contact angle results, indicates that *Pinus pinaster* showed less ink spreading than *Samsun poplar clone* and *Robinia pseudoacacia*, because the fountain solution will spread and absorb, inhibiting the spread of hydrophobic ink. Compared to *Samsun poplar clone* and *Robinia pseudoacacia*, the contact angle of the *Pinus pinaster* samples declined slower, while the remaining drop volumes dropped faster than the *Samsun poplar clone* and *Robinia pseudoacacia*. This indicated that the water droplet would be well fixed on the spot with less spreading, so does ink.

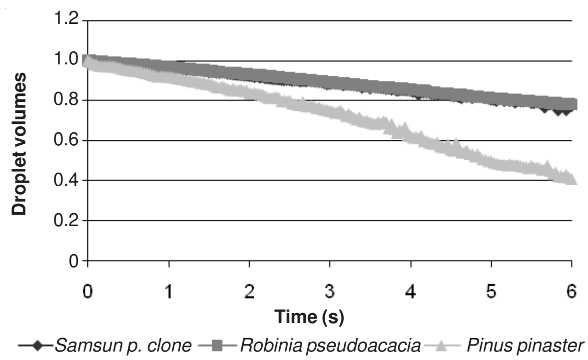

Fig. 6. Water droplet volumes

Print optical density: Print optical density shows the contrast between print and substrate. It has effects in determining dot gain and print contrast[11]. Lower dot gain and higher colour contrast indicate a good print. The substrate physical properties of smoothness and porosity have an important effect on print optical density. Also, printing conditions and machine settings affect print optical density. Table-3 shows that the printed ASAM sheet samples were completely dried after 24 h

TABLE-3
PRINT OPTICAL DENSITY VALUES OF PRINTED HAND-SHEET SAMPLES

Time (h)	*Samsun p. clone*	*Robinia pseudoacacia*	*Pinus pinaster*
0	1.4	1.12	1.29
2	1.32	1.08	1.23
4	1.27	1.05	1.19
8	1.27	1.05	1.17
12	1.22	1.00	1.14
24	1.22	1.00	1.14

printing. Although, *Samsun poplar clone* lost more print optical density than the others after 24 h printing (0.18), it had the highest print optical density value at after 24 h printing (1.22). Therefore, *Samsun poplar clone* was more hydrophilic than the other papers. The more absorbent paper results in lower print optical density. *Robinia pseudoacacia* had lower print optical density than the other samples at first measurement. This means that it's ink acceptance is lower than other samples due to having the least surface energy.

CIE L*a*b* an print lightness: Print optical density is not enough to determine a good print. A different printing process can result in different print optical density values. Print optical density is important for controlling a printing process, as long as printing conditions do not change, such as substrate, ink and the printing press itself. But, the acceptable print optical density for obtaining target colour values is related to CIE L*a*b* values. So, the values of CIE L*a*b* after printing are given in Table-4.

TABLE-4
CIE L*a*b* VALUES OF HAND-SHEET SAMPLES

Samples	L*	a*	b*
Samsun p. clone	57.4	-27.1	-48.7
Robinia pseudoacacia	61.1	-22.8	-44.2
Pinus pinaster	60.8	-29.8	-46.7

Print lightness is a major indicator for a good print. Therefore, the higher the print lightness, the lower the colour saturation. CIE L* shows print lightness, which is measured using a spectrophotometer after printing. Fig. 7 shows that the print lightness difference of *Samsun poplar clone* was lower than other samples. But this difference was not significant.

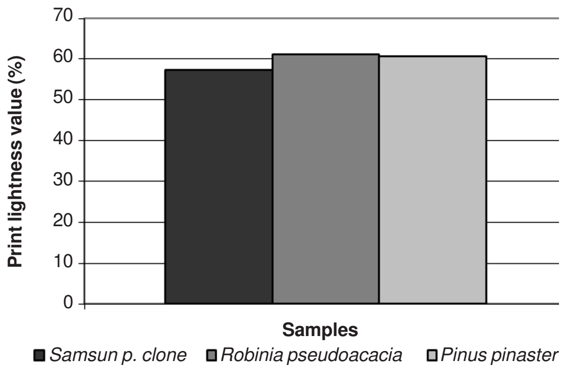

Fig. 7. Print lightness (L) values of printed hand-sheet samples

Print chroma: The term chroma means 'colour'. It shows colour saturation value[12]. It was calculated as:

$$\text{Chroma (C)} = \sqrt{a^{*2} + b^{*2}}$$

High print chroma demonstrates a large colour gamut, which is an important indicator for a good print. Actually, print chroma value of the *Samsun poplar clone* was obviously higher than *Robinia pseudoacacia*. But the print chroma values of *Pinus pinaster* were as much as the print chroma values of *Samsun poplar clone* (Fig. 8).

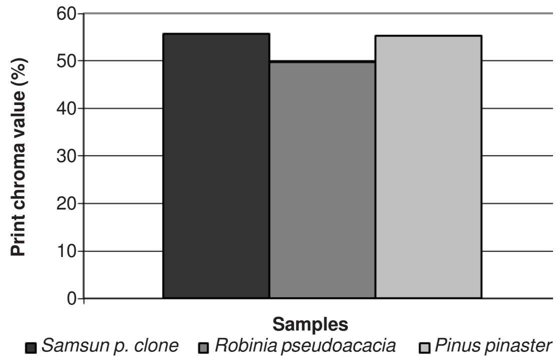

Fig. 8. Print Chroma values of printed hand-sheet samples

Print mottle: The mottling is an important index to quantify the printability. The variations in surface roughness influence the ink transfer and are responsible for a form of mottling. The improvement of the surface roughness has a consequence of decreasing the mottling index. A good print has a lower mottle[13]. The mottling index values for the 100 % solid area were measured[14]. These measurements show that *Robinia preudoacacia* had lower print mottle, so their mottling values were lower the others. *Pinus pinaster* had the highest print mottle values (Fig. 9).

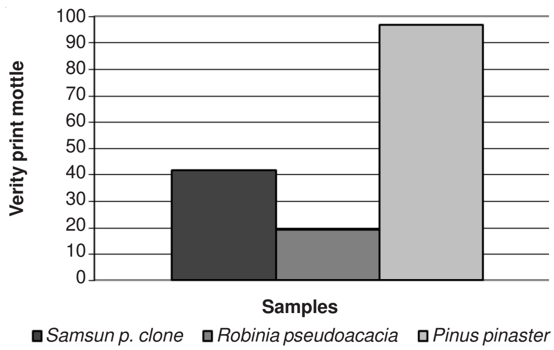

Fig. 9. Print mottle values of printed hand-sheet samples

Delta gloss: The surface properties and ink ingredients influence each other and positively or negatively affect the final print results[15]. The printability of a paper, which is its ability to receive ink and produce a high-quality image, needs to be good for the paper to be acceptable. A good printed paper has lower ink demand and higher print gloss at a given print optical density[16]. Ink ingredients and its amount is a significant predictor of a glossy print quality[17]. Therefore, delta gloss is an important determinate for printability measure of paper. The delta gloss is the gloss difference between the gloss after printing and the gloss before printing all at the same angle[5].

In this study, both gloss values were measured using Hunter Gloss 75°. Then, the delta gloss values of hand-sheets were calculated from these measurements. These calculations show that although, *Pinus pinaster* had lower paper gloss than *Samsun poplar clone*, thus it had better delta gloss than *Samsun poplar clone* and *Robinia pseudoacacia* sheets after printing. Therefore, it is concluded that paper gloss had a significantly effect on ink gloss (Fig. 10).

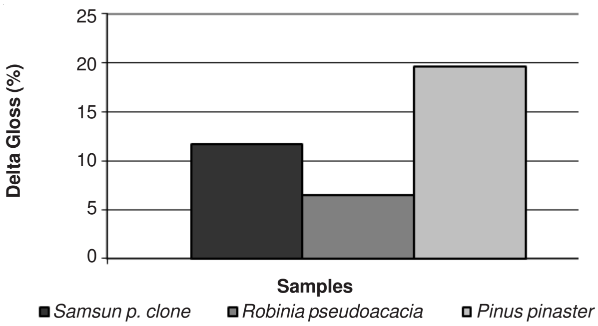

Fig. 10. Delta Gloss values of hand-sheet samples

Readability: Interference with the visual appearance of the printed image increases or decreases, depending on which ink and which paper colours are used. Contrast between paper colour and printing colour is important effect on readability. Optimal contrast is necessary, otherwise, it is difficult to comprehend the words. This can result in increased eye strain, lower reading comprehension and longer reading times.

Fig. 11 demonstrates that *Robinia pseudoacacia* had a lower contrast value between paper colour and print colour. Also, *Pinus pinaster* had lower contrast than *Samsun poplar clone* due to increased print mottle and lower colour contrast. Thus it may conclude that *Robinia pseudoacacia* and *Pinus pinaster* do not provide a suitable surface for printing longer texts.

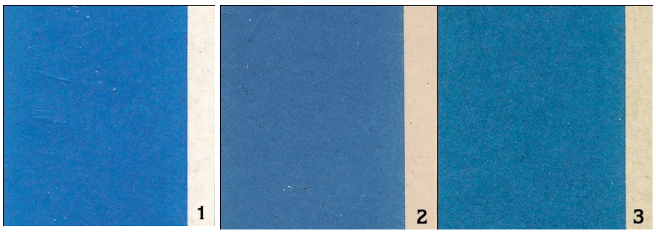

Fig. 11. Scanning views on *Samsun poplar clone* (1), *Robinia pseudoacacia* (2), *Pinus pinaster* (3) samples after printing

Conclusion

This study examined the printability properties of alkaline sulfite-anthraquinone-methanol (ASAM) hand-sheets that are produced from the fast growing *Samsun poplar clone* and *Robinia pseudoacacia* and *Pinus pinaster* which are grown in Turkey. These pulps were found to affect hand-sheet optical properties. *Samsun poplar clone* was shown to decrease surface roughness and increase paper brightness, gloss and opacity values, which also yielded good print quality. However, *Pinus pinaster* decreased paper brightness and opacity.

Meanwhile, *Samsun poplar clone* increased print optical density, but decreased print lightness. In addition, it increased print chroma, which led to a wider colour gamut. Therefore, the application of *Samsun poplar clone* provides better colour reproduction in offset printing.

This study also revealed that the pulps influence the print mottles. Specifically, *Pinus pinaster* increased print mottle, in contrast, *Robinia pseudoacacia* decreased print mottle. However, *Robinia pseudoacacia* significantly reduced the print optical density. As a result, *Pinus pinaster* and *Robinia pseudoacacia* also present a weak performance on colour contrast. *Samsun poplar clone* provided the best colour contrast which is beneficial to print readability. *Pinus pinaster* had a lower initial contact angle which indicated a high surface energy. Therefore, *Pinus pinaster* will increase ink spreading. This negatively affects the ability to obtain a good print with better shadow detail.

REFERENCES

1. R. Patt, O. Kordsachia and H.L. Shubert, in eds.: R.A. Young and A. Masood, Environmentally Friendly Technologies for the Pulp and Paper Industry, ISBN: 978-0-471-15770-0, John Wiley & Sons Inc. (1998).
2. R. Rosenberger, Proceedings TAGA, Vancouver, BC, Canada, The Correlation of Macro Print Mottle to Surface Topography as Measured by an Optical Surface Topography System (2003).
3. O. Carmody, R. Frost, Y. Xi and S. Kokot, *J. Surf. Sci.*, **601**, 9 (2007).
4. Y.J. Wu, A. Pekarovicova and P.D. Fleming, Proceedings of the 59th TAGA Annual Technical Conference, USA, How Paper Properties Influence Colour Reproduction of Digital Proofs for Publication Gravure (2007).
5. M. Juuti, T. Prykäri, E. Alarousu, H. Koivula, M. Myllys, A. Lähteelä, M. Toivakka, J. Timonen, R. Myllylä and K. E. Peiponen, *Colloids Surf. A*, **299**, 101 (2007).
6. T. Schuman, B. Adolfsson, M. Wikström and M. Rigdahl, Progress in Organic Coatings, 54, 3, Surface Treatment and Printing Properties of Dispersion-Coated Paperboard, pp. 188-197 (2005).
7. H.K. Lee, M.K. Joyce and P.D. Fleming, Proceedings of the IS&T NIP19: International Conference on Digital Printing Technologies: Influence of Pigment Particles Size and Packing Volume on Printability of Glossy Inkjet Paper Coatings, USA, pp. 613-618 (2003).
8. J.E. Levlin and L. Söderhjelm, Pulp and Paper Testing, 17. Papermaking Science and Technology, Fapet Oy, ISBN 952-5216-17-9 (1999).
9. R. Xu, P.D. Fleming, A. Pekarovicova and V. Bliznyuk, *J. Imaging Sci. Technol.*, **49**, 660 (2005).
10. R. Xu, A. Pekarovicova, P.D. Fleming and V. Bliznyuk, Proceedings of TAPPI Coating and Graphic Arts Conference, TAPPI Press, Atlanta, GA, USA, Physical Properties of LWC Papers and Gravure Ink Mileage, pp. 365-373 (2005b).
11. J. Johnson, C. Andersson, M. Lestelius, L. Jarnstrom, P. Ratto and E. Blohm, *Appita J.*, **62**, 5 (2009).
12. R.W.G. Hunt, 9th IS&T/SID Colour Imaging Conference, Scottsdale, AZ, USA, Saturation, Superfluous or Superior, pp. 1-5 (2001).
13. J. Ahlroos, M. Alexandersson and J. Grön, *Tappi J.*, **82**, 94 (1999).
14. J. Preston, A.G. Hiorns, N. Elton and G. Ström, *Tappi J.*, **7**, 11 (2008).
15. M.C. Béland and J.M. Bennett, *Appl. Optics*, **39**, 2719 (2000).
16. Z. Yuan and C. Heitner, *Tappi J.*, **7**, 4 (2008).
17. J.S. Preston, N.J. Elton, J.C. Husband, J. Dalton, P.J. Heard and G.C. Allen, *Colloids Surf. A*, **205**, 183 (2002).