

IMPACT OF SURFACE FREE ENERGY ON PAPER PROPERTIES AND OFFSET PRINTABILITY

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ABSTRACT

The performance of paper in many applications, including printing, is often determined by the nature of its surface. Although currently in decline, except in Asia, offset printing still accounts for around 40% of all print volume globally, and continues to dominate the high-quality end of the printing spectrum. This study focused on offset printing and the impact that different surface properties of a substrate can have on this process.

Offset printing of paper involves the complex interactions of ink with a surface which is characterised by three key interrelated properties: roughness, porosity and surface chemistry related to surface free energy (SFE). The effects of porosity and roughness are relatively well understood and are documented in the literature, whereas the influence of surface chemistry (SFE) is much less clear and has been studied to a lesser extent. Primarily this is due to the difficulty of measuring surface energy on non-ideal substrates, where extremes of surface features can impact the apparent surface energy (e.g., lotus effect).

Therefore, there were two primary aims for this study. The first was to make recommendations on the best method to calculate surface free energy (SFE) of paper considering its non-ideal nature. The second was to determine the relative impact of SFE on offset printability compared to other properties such as topography (roughness) and porosity.

The key results shown in this paper include:

A method to measure SFE on porous surfaces. The contact angle of a liquid droplet brought in contact with a porous surface is measured at 0.1 sec after contact in order to minimise inaccuracies caused by drop bouncing, wetting and absorption and corrected for surface roughness using the Wenzel model.

The observation that that surface porosity has a negligible effect on SFE determination by contact angle.

Demonstration that isolated SFE changes caused by use of wetting agent or corona treatment result in far smaller differences in printability than those obtained by modifying SFE and surface porosity simultaneously.

The chemistry of the latex polymer in the coating formulation

dominates the influence on SFE compared to pigment, with any surface energy differences present in the pigment being almost completely masked by latex.

It is therefore concluded that when looking to improve offset printability the variation in surface free energy (SFE) is significantly less important than variation in either surface roughness or surface porosity.

Keywords: Surface energy, paper coating, offset printing

INTRODUCTION

Offset printing

Offset lithography is one of the most common industrial printing processes due to cost-effective high-print quality and relative ease of the technique. This process uses a planographic printing plate and, as such, relies on differences in surface chemistry in order to distinguish image areas from non-image areas. It utilises the principle that the hydrophobic oil-based ink will be attracted to hydrophobic areas of the printing plate and repelled from hydrophilic areas. The surface interactions during printing are complex. The surface of paper is rough, porous and chemically heterogeneous and as a substrate, it is therefore far from ideal. Controlling the properties of paper is difficult; small changes in production processes and external conditions can lead to substantial differences in the paper's physical properties. The use of naturally occurring minerals and fibres introduces additional variability which cannot be accounted for and, therefore, it is virtually impossible to produce the exact same piece of paper twice.

Mineral-based coatings are employed to improve the surface properties of the paper often to give higher print gloss and printed colour density¹. Calcium carbonate and kaolin are the most commonly used minerals in this context, due to the high levels of gloss, whiteness and opacity possible. The pigment chosen also plays an important role in controlling surface porosity and roughness and can be modified by selecting the pigment type (calcium carbonate, kaolin, talc) and shape²⁻⁴, average particle size and particle size distribution (PSD). The amount and type of latex used can have a significant impact on the porosity of a coated paper⁵. Calendering is

often carried out to improve the gloss of coated papers by reducing roughness on all length scales⁶. However, this also results in crushing of the pores in both the base and coating layer. The heat from the calender also aids the process of latex film formation as reported by Carlsson⁷. Corona treatment is sometimes employed to facilitate substrate converting (e.g. lamination). It involves treatment of the substrate with high energy plasma to raise its surface energy by increasing its polarity⁸ whilst keeping other bulk properties constant.

Surface free energy determination on ideal and real surfaces

Although other methods have been reported^{9,10}, contact angle of a sessile drop on the substrate surface remains the most common for determining SFE. A drop is placed on the surface in question and allowed to reach an equilibrium contact angle. Images of the drop on the surface are captured and contact angle can then be determined with drop shape analysis software.

Young's equation (1) is the basis for all contact angle related techniques and relates contact angle, θ , to the interfacial tensions between all three phases present (solid-vapour, γ_{SV} ; solid-liquid, γ_{SL} ; and liquid-vapour, γ_{LV}) when a drop is at thermodynamic equilibrium on a surface.

$$\gamma_{SV} = \gamma_{SL} + \gamma_{LV} \cdot \cos \theta \quad 1$$

γ_{SV} can be considered equivalent to the SFE of the solid phase, γ_S , as it can be assumed that the vapour pressure of the solid is negligible.¹¹

A number of methods building on Young's equation have been developed which split γ_S into separate components based on the type of interactions which are responsible for the free energy of the surface. For example, Owens and Wendt¹¹ developed a model which split γ_S into the sum of two components, γ_S^d and γ_S^p . Here, γ_S^d is defined as the excess energy present at the surface of the material due to non-polar dispersion forces whilst γ_S^p is the energy due to polar, dipole-dipole interactions. According to van Oss et al^{12,13}, γ_S^p can be split further into interactions from Lewis acids (γ_S^+) and Lewis bases (γ_S^-). For these multicomponent methods, at least as many test liquids as there are components must be used. For instance, a three-component method must use at least three different test liquids with a range of polarity.

Young's equation assumes that all surfaces are perfectly smooth, impermeable, chemically inert and heterogeneous. This is clearly not the case for most real surfaces, especially paper. Wenzel¹⁴ was the first to investigate the dependence of contact angle on surface roughness. He realised that the apparent contact angle changes when observed on the same substrate but with different surface roughness present and developed equation 2.

$$\cos \theta^* = r \cos \theta \quad 2$$

This relates the apparent contact angle, θ^* , to the thermodynamically stable contact angle, θ , or Young's contact angle using a surface roughness factor, r , where $r = \frac{\text{actual surface area}}{\text{geometric surface area}}$.

Experimentally obtained apparent contact angles can therefore be corrected to the Young's contact angle before the calculation of SFE. The Wenzel equation (2) is based on the assumption that homogeneous wetting occurs. For instance, the drop completely penetrates the grooves of the substrate. For this reason, its use as a method for correcting apparent contact angles has limitations and some literature has reported that it can only be applied under certain conditions¹⁵. Heterogeneous wetting occurs when there are areas of a surface with different chemistry and a correction relating to this was developed Cassie-Baxter¹⁶

Measuring contact angles on porous substrates brings with it further complications; namely drop penetration into the substrate. This can lead to no stable contact angle being able to be measured as the drop is slowly absorbed. Washburn¹⁷ developed the capillary penetration model as a way of presenting the distance a liquid penetrates into a powder or porous medium as a function of time. For the case of a capillary, it was found that the square of the depth of liquid penetration, l , is directly proportional to the cosine of the contact angle, θ , as shown in equation 3:

$$l^2 = \frac{rt\gamma_{lv} \cos \theta}{2\eta} \quad 3$$

Therefore, if pore radius r , time taken for the penetration to occur t , surface tension of the liquid γ_{lv} , and viscosity of the liquid η , are known, the contact angle between the capillary and the liquid can be experimentally determined. Washburn models a porous body as equivalent to n cylindrical capillary tubes of radii r_1, r_2, \dots, r_n . However, real porous media do not have a constant pore radius throughout their pore structure and instead have a complex network of interconnecting pores. This limits the use of Washburn theory in real porous media such as paper.

Clearly, determining the SFE of a substrate such as paper is a complex problem with many factors influencing how a drop behaves when in contact with the surface. In this work, the substrate roughness was corrected using the Wenzel equation. The impact of porosity is further explored experimentally.

METHODS & MATERIALS

Substrate preparation

The impact of porosity on SFE determination was studied by using a model substrate - Cyclopore polycarbonate filtration membranes. These were used as "smooth" model porous surfaces of the same material where porosity could be varied systematically. SFE was determined for a range of pore diameters from 0.03 to 5 μm ,

For the coated papers, unless otherwise stated, coatings were applied to coated woodfree base paper using a Helicoater 2000C with short dwell head at 800 m min^{-1} and a coat weight of 12 g m^{-2} . Samples were conditioned, tested and printed 21 $^\circ\text{C}$ and 50% humidity. Calendering was performed by passing samples 10 times through a Perkins laboratory

supercalender at a temperature of 65°C, a pressure of 68 bar and a speed of 36 m min⁻¹. All papers were conditioned before and during testing. Formulations used throughout the work are summarised below:

1. Coating formulations used to generate data in Figures 6 to 11: the impact of pigment on SFE of coated paper - 100pph pigment, 12 pph Styrene butadiene latex, 15 gsm, pH 9.5
2. Coating formulations for the study of latex level (Figures 12-15) 100 pph pigment, styrene butadiene latex (12,10, 8, 6, 4 pph for colours numbers 1 to 5), coat weight 11-15 gsm, target viscosity 1400 mPa.s at Br 100 rpm, pH 9.5, solids 70 wt. %
3. Coating formulation for study of the effect of wetting agent (Figures 16-21). 100 pph pigment, 8 pph styrene butadiene latex, 0.13pph thickener, polar wetting agent. Solids 70 wt%, viscosity 1400 mPa.s, pH 9.5

Changes in surface energy from pigment to slurry to coating colour

In section 3.3 the impact of pigment surface energy compared to the whole coating colour surface energy was established by taking a more in-depth look at the colour making process. A range of physically similar carbonates with drastically different surface chemistries were used in an attempt to elucidate the extent of the role of pigment on the SFE of a paper coating. This was achieved by using hydrophobically coated and uncoated calcium carbonate powders. The SFE of these powders was measured on compressed powder tablets to observe the chemical differences in the pigments present at the beginning of the coating process. Hydrophobically coated carbonates are uncommon in paper coating due to the obvious difficulties of using a hydrophobic powder in an aqueous dispersion. More dispersant must be used to disperse hydrophobically coated carbonates than for untreated carbonates. Slurries were prepared with hydrophobic and hydrophilic dispersants to see if the nature of the dispersant had an effect on the SFE of a dried carbonate layer. Finally, the slurries were made into colours as described above in 1. The colours were coated by hand onto coated wood free base paper, SFE was evaluated and printability assessed.

Contact angle measurement & Surface free energy determination

Contact angles were determined using two test liquids, water and bromonaphthalene. This was carried out using a Dynamic Absorption Tester from Fibro System AB. A high-speed camera recorded the volume, base diameter, height and area of the drop as they varied with time allowing sorption and spreading characteristics to be analysed. In some cases, the Wenzel model was used to correct contact angle for roughness. Surface free energy was calculated according to the two component Owens-Wendt method using Equation 4, giving both the dispersive and polar components of SFE.

$$\frac{1 + \cos \theta}{2} \cdot \frac{\gamma_1}{\sqrt{\gamma_1^d}} = \sqrt{\gamma_s^p} \cdot \sqrt{\frac{\gamma_1^p}{\gamma_1^d}} + \sqrt{\gamma_s^d} \quad 4$$

Roughness

For in-depth analysis of paper surface roughness, confocal optical microscopy was carried out using a Laserscape from Keyence. Roughness profiles were determined from height data collected from ten tracks of 1024 points at 2 μm separation. Statistical roughness parameters such as the surface roughness factor, R_r , in Equation 2 or RMS roughness, a measure of mean roughness of a surface, could then be determined.

Porosity

Porosity was measured in units of Gurley seconds using a Messmer-Büchel Parker Print-Surf (dual head). A Gurley second³³ is defined, by test method TAPPI/ANSI T 460 om-11, as the time taken for 100 cm³ to pass through one square inch of paper whilst under a pressure differential of 1.22 kPa. Therefore, a low value in Gurley seconds translates to a high porosity. Mercury porosimetry was used for more detailed pore volume and pore size distribution data. This was measured using Pascal 140 and Pascal 240 porosimeters from Thermo Scientific.

Offset printing

Offset printing was performed using a laboratory scale IGT AIC2-5T2000 unit at a pressure of 500N and a speed of 0.5 m s⁻¹. This was performed with simultaneous predamping so that water interference could be assessed. Thus, for any given print, there are both dry and predamped printed areas. Print density was assessed using a Gretag Macbeth densitometer (D186 Zurich). Water interference was evaluated by calculating the ratio of predamped to dry print density; and is reported as L/D. Gloss was measured using a Technidyne gloss meter at 75° (TAPPI T480).

Corona treatment

Corona treatment was carried out on a Corona-Plus unit from Vetaphone. The intensity of the corona treatment was 85 W min⁻¹ m⁻².

RESULTS

One of the main aims of this report was to determine how best to measure the SFE of paper in the context of a non-ideal substrate and this was completed in two steps. First, variance of contact angle with time was examined for paper substrates in order to decide when was the best time to take contact angle after the drop made contact with the paper. Secondly, the impact of physical surface characteristics, such as porosity and roughness, on contact angle measurements on paper were assessed and discussed with respect to their impact on offset printability.

Paper as a substrate for contact angle measurements

As discussed previously, paper is a non-idea substrate on which to determine surface energy as roughness, porosity and chemical heterogeneity all contribute to difficulties in observing a stable contact angle and no equilibrium angle is reached, as is shown in Figure 1 for a coated paper. Absorption and wetting (spreading) of the water droplet occurs instantaneously and simultaneously (see

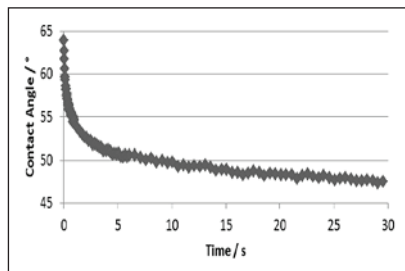


Figure 1. Contact angle of water droplet on paper substrate with time

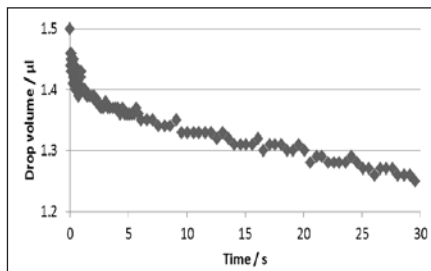


Figure 2. Water drop volume vs. time. Absorption can be seen to be occurring from 0 s.

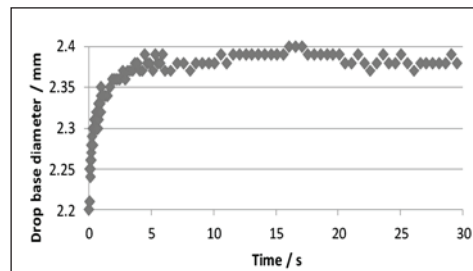


Figure 3. The rapid increase in the droplet base diameter shows instantaneous wetting & drop spreading

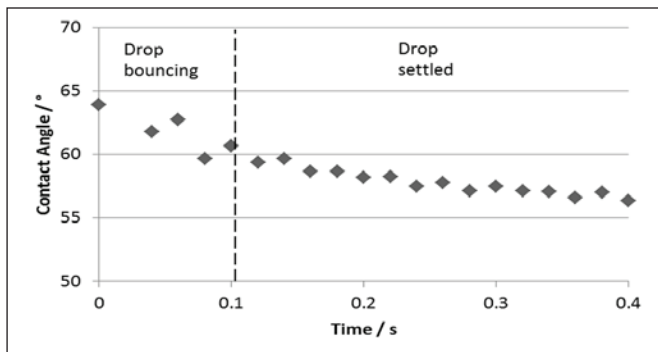


Figure 4. Expanded scale of contact angle variance with time on paper. Contact angle shows instability before 0.1 s due to momentum of drop as it is dropped onto the paper surface

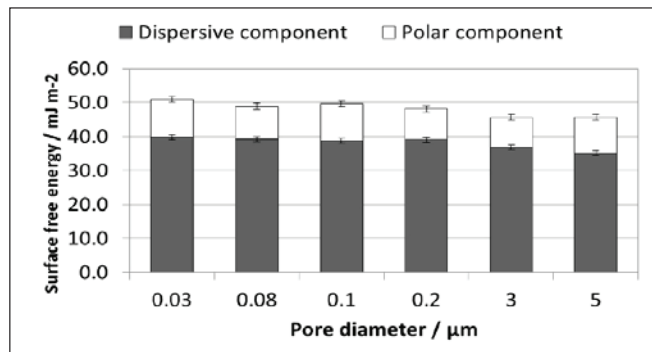


Figure 5. Impact of pore diameter on SFE determination. Increasing pore radius did not seem to have a significant effect on SFE within the range of pore diameters which would be found in a paper coating (<0.5 μm)

Figures 2 and 3). Figure 4 shows that contact angle is especially unstable before 0.1 s due to the momentum of the drop as it is dropped onto the paper surface (bouncing). Further information on analysis of fluid absorption into paper surfaces can be found in reference 5, by the author of this paper.

Due to the clear lack of any stable contact angle available, contact angles were taken at 0.1 s for both bromonaphthalene and water to minimise the effects of drop bouncing, absorption and wetting. Using equation 6, the polar component of surface free energy ("water liking") and dispersive component ("oil liking") were calculated.

Impact of roughness and porosity on contact angle measurements

Roughness and porosity are important factors when considering the rates of wetting and absorption as described by Wenzel and Cassie *et al.* ^{2,4,6,14,15}. In this study, the Wenzel model was chosen to correct contact angle for roughness.

To determine the impact of controlled roughness and porosity on surface energy – model substrates – cyclopore membranes were used and the results are summarised in Figure 5. It was expected that if porosity was to have an effect, a more porous surface may show a smaller contact angle at 0.1 s due to a higher rate of instantaneous absorption. The SFE for a more porous surface would therefore appear to be higher. However, this was not shown to be the case as increasing pore radius did not appear to have a significant effect on SFE determination, within the pore size range associated with coated paper (< 0.5 μm). This lack of dependency on porosity was also seen for pigment coatings (Figures 6 and 7) where the porosity of coated papers was also shown to have little impact on SFE determination. The impact of porosity on measurement of SFE was therefore deemed to be negligible as measured at 0.1 s time. However, it is well known that porosity, independently of surface energy in itself has a highly significant impact on fluid absorption rate ⁵.

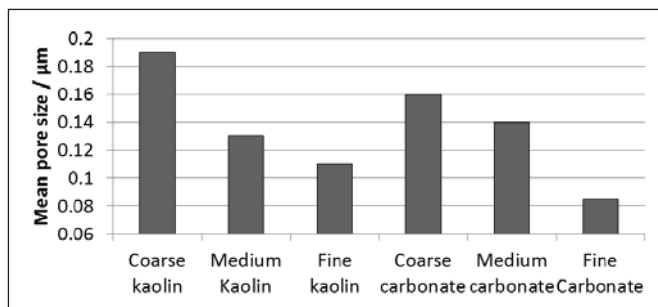


Figure 6. Mean pore size data for coatings containing coarse & fine pigments. Coarser minerals (larger size) give larger coating pores

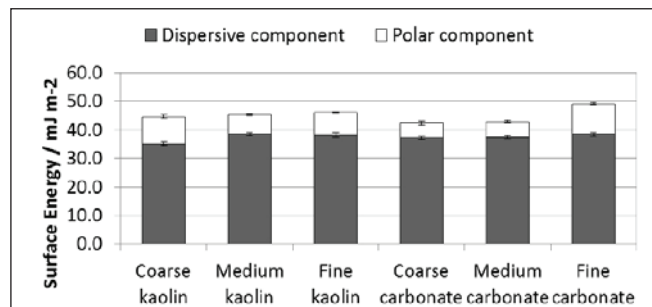


Figure 7. All samples showed relatively similar values for SFE regardless of PSD or pigment type

Impact of surface free energy on paper properties and printability - Pigment

Changing the formulation of a paper coating allows facile control of a number of physical surface properties which have been widely reported. However, the chemical impact of these changes has been studied to a far lesser extent. In this section, the formulations used were specifically devised to observe any chemical changes which may affect SFE. An initial study using different grades of kaolin and carbonate was carried out to determine the role pigment type and particle size distribution plays with regards to SFE determination. When these pigments were combined with dispersant, latex and thickener and coated onto a paper, a systematic reduction of pore size with reduction in mean pigment particle size for both kaolins and carbonates was measured (Figure 6). This was expected because the main property of a coating layer which is affected by PSD is its pore structure⁷ where a broader PSD with finer particles present allows better packing and therefore a smaller mean pore size. However, in Figure 7, it can be seen that the SFE of these is the same within error. The porosity is therefore once again playing an insignificant role in the SFE result. However, the differing pore structure in itself will play a significant role in determining the print quality.

Figure 7 shows that, within the bounds of this study, the type of pigment used did not significantly impact SFE measurement. Pure kaolin and pure carbonate both have polar groups present on their surfaces and may have been expected to show a large polar component of SFE and also significant differences between the two different mineral types^{40,41}. However, very little difference was observed with the coated paper and it was considered that this would be due to the latex forming a nearly complete polymer film on the paper surface and effectively masking the pigment particles.

The "masked pigment" hypothesis was then tested by taking a more in-depth look at the change of surface energy of the pigments as they go through the coating colour making process. The carbonates used throughout this study are summarised and identified in Table 1.

Figures 8-10 show a summary of the SFE of the carbonates through the colour making and coating process. It was shown that the large differences in surface polarity and overall SFE of carbonates seen in the early stages of colour making are significantly reduced in a final paper coating. This provided further evidence of latex covering

Table 1. A summary of the carbonates used for the investigation of pigment surface on the overall SFE of paper. Carbonates 2a and 2b are essentially identical carbonates although 2a was prepared from a powder and 2b was supplied already dispersed as a slurry. The same is true for samples 4a and 4b. The carbonates supplied as slurries were included so that the laboratory-based slurry making process could be compared to the commercial process

		Dispersant	
		Hydrophobic	Hydrophilic
Coating	Hydrophobic	1	2a, 2b
	Uncoated (hydrophilic)	3	4a, 4b

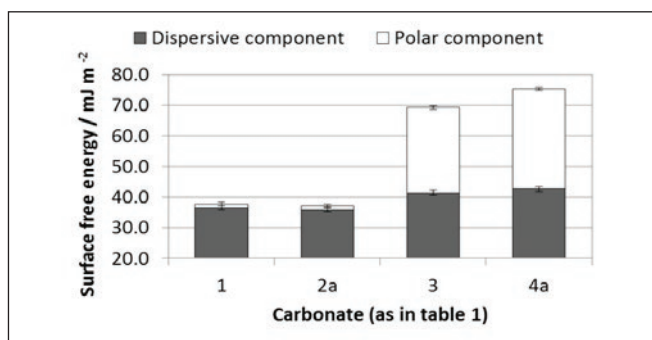


Figure 8. SFE comparison of pressed powder tablets (Table 1). Uncoated carbonates (3 and 4a) show a far larger γ_p value than the hydrophobically coated carbonates (1 and 2). There is also a small but significant difference in the γ_p value between carbonates 3 and 4a

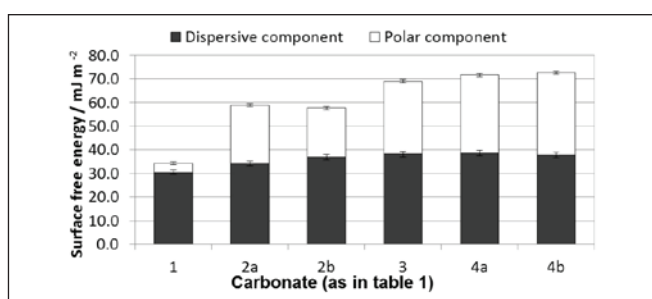


Figure 9. SFE comparison of slurries coated on polymer film (from Table 1) showing increasing γ_{tot} and γ_p with increasing hydrophilic character. Dispersant had less impact than carbonate surface coating. However, the combination of both hydrophobic dispersant and coating (1) gave the lowest γ_p and lowest total SE

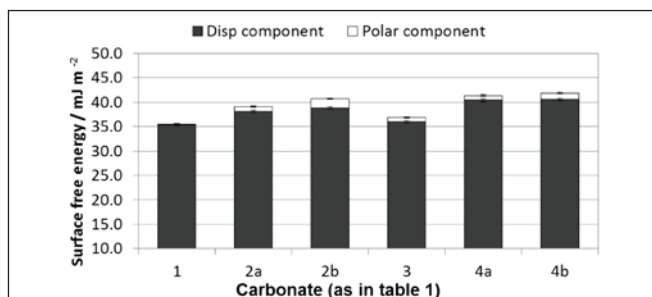


Figure 10. SFE comparison of paper coatings formulated using carbonates from Table 1. A trend can still be seen between γ_{tot} and relative hydrophilicity, but the differences seen as slurries and powders become far less obvious when the carbonates are in a paper coating. γ_p differences are also far smaller in paper coatings than powders or slurries

the paper surface and masking the chemistry of the pigment, where any differences which were still observed in paper samples were attributed to areas of pigment not fully covered by latex. The printability of these papers was assessed in terms of print gloss, print density and L/D ratio (shown in Figure 11), but no significant differences were observed.

It has clearly been shown that significant differences in SFE of pigment can be effectively masked by the latex binder and other formulation additives in paper coatings. It was therefore concluded that pigment plays a much less significant role in the surface chemistry of paper than latex does, and this was therefore evaluated further.

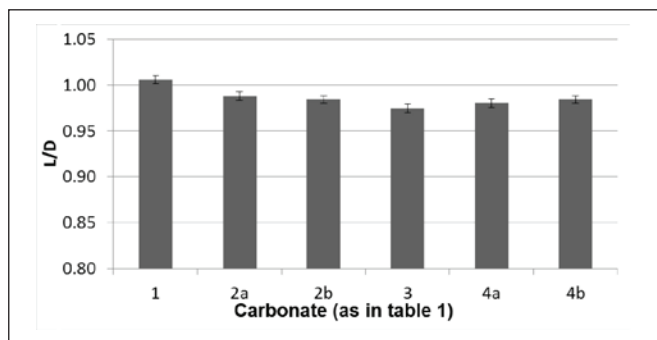


Figure 11. The print density of the predamped area (litho) / print density of the dry area (dry)

A value of 1 = same print density. There is no evidence from these results of ink rejection due to slow absorption of water (in which the L/D ratio would be lower than 0.9)

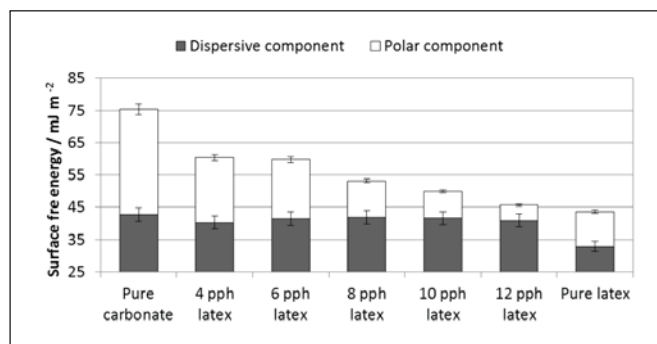


Figure 12. SFE of papers coated in formulations with different levels of latex present as shown in Appendix 1 Table A2. The pure carbonate and pure latex points are included as comparisons. Pure carbonate was measured on carbonate 4a from Table 1. Pure latex was measured on a dried film of the latex used for paper samples in this graph drawn down onto polymer film

Impact of surface free energy on paper properties and printability - Latex

As shown in Figure 12, the amount of latex in a coating colour was increased from 4 to 12 pph in increments of 2 pph. There was a decrease in γ_{tot} and γ_p for increased levels of latex, implying that for increased levels of latex in a formulation, a higher area fraction of the paper surface is covered by the non-polar latex rather than polar pigment⁸. This was backed up by the inclusion of SFE results for pure carbonate and pure latex, which highlighted the intermediate behaviour displayed by the paper surfaces. Latex-like character increased with increasing levels of latex in the formulation as would be expected.

The results for the printability assessments carried out on these papers are summarised in Figures 13-15. On both dry and predamped areas, higher latex levels showed an increase in print density, which results from a lowering in porosity of the coating (as shown by the Gurley results Figure 15). However, the increase in print density for predamped areas was not as large as the increase recorded for dry areas indicating that a higher level of latex leads to proportionally more ink rejection. This can also be seen as a slight decline in the L/D ratio (Figure 14) and would be expected as the increase in latex

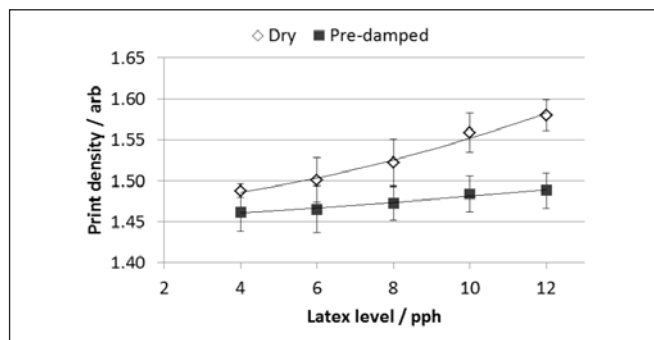


Figure 13. Print density in dry and predamped areas with increasing latex level

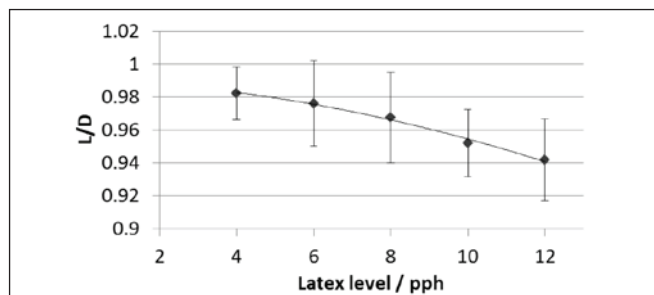


Figure 14. Relationship of L/D with latex level in a paper coating. L/D decreases with latex level

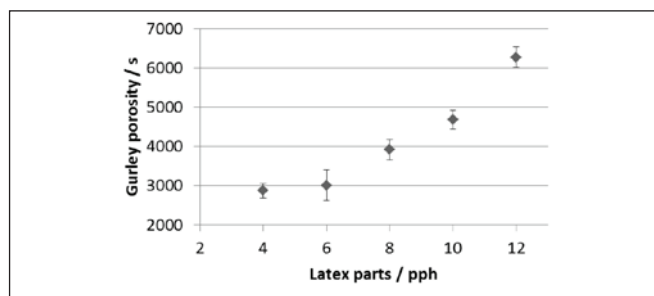


Figure 15. Relationship between Gurley porosity and latex level in a paper coating. Higher levels of latex afford a less porous structure characterised by a higher value of Gurley (s)

would prevent fast absorption of the predamping water. However, it isn't really possible to determine if it is the more hydrophobic surface which is slowing the absorption of the predamping water or indeed simply the change in porosity.

A clear link was shown between measured SFE and printability. However, due to the complexity of two properties changing simultaneously, two methods of changing the surface energy without change in the porosity or topography were selected; the impact of wetting agent and Corona treatment.

Wetting agent

Wetting agents are employed in industry to improve the wettability of polymers during processing. In this study, wetting agent was applied directly to the surface of a dried paper coating. A control

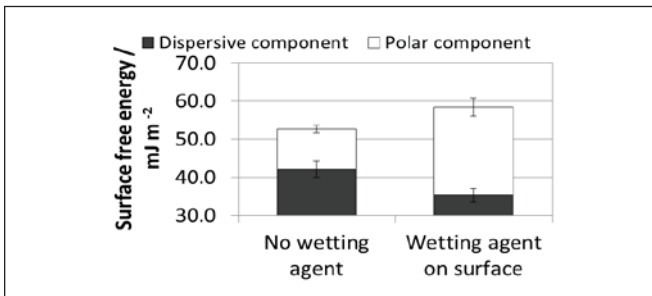


Figure 16. Effect of wetting agent on the SFE of coated paper. Wetting agent on the paper surface showed a reduction in γ_d , an increase in γ_p and an overall increase in γ_{tot}

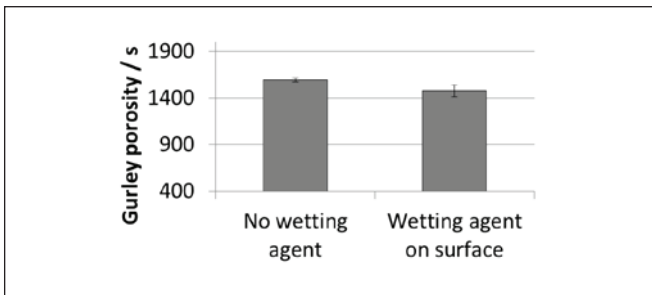


Figure 17. Effect on porosity of wetting agent applied to a paper coating surface. Porosity remains relatively unchanged and within error

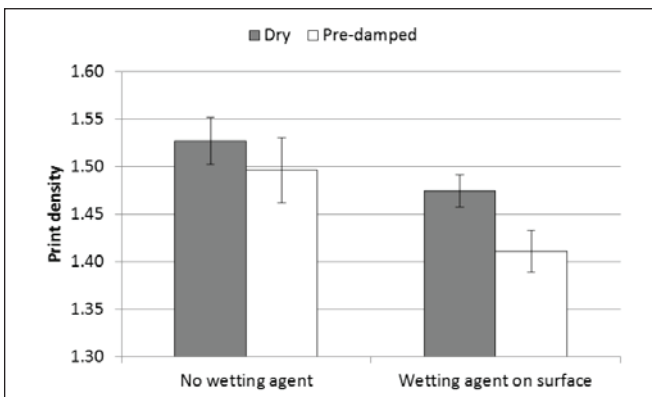


Figure 18. Influence of wetting agent on print density. There was a reduction in both dry and predamped density for the paper with wetting agent applied to its surface

paper with no wetting agent at all was also included. The SFE results are summarised in Figure 16.

Wetting agent applied to the surface of paper showed a reduction in γ_d and increase in γ_p . This was as expected for a surface treated with wetting agent, as these are chemical conditions which promote wetting. It was also shown as a means of changing SFE without affecting the bulk physical properties of porosity (Figure 17). The PPS roughness also remained the same within experimental error. These papers were printed, and the print density and gloss are shown in Figures 18 and 19.

Wetting agent did not appear to drastically affect dry printability. There were only small reductions in dry print density and dry print gloss for both samples and these could be considered within error. However, there was a significant reduction in print density for the predamped

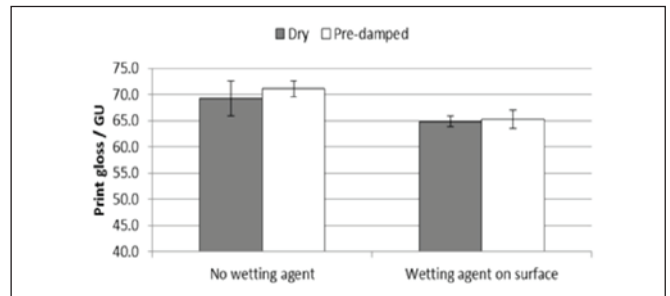


Figure 19. Influence of wetting agent on print gloss. Print gloss was also reduced in the sample with wetting agent applied to the surface

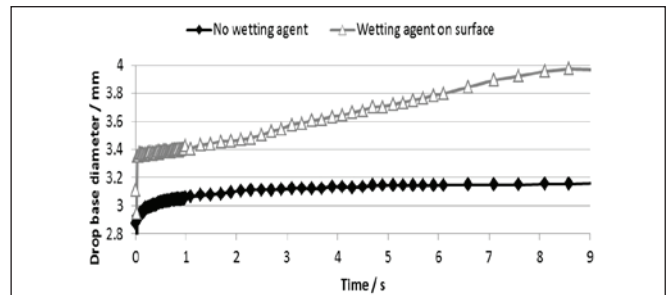


Figure 20. Wetting agent on the surface showed a larger initial increase in drop diameter and a greater rate of change indicating increased droplet spreading

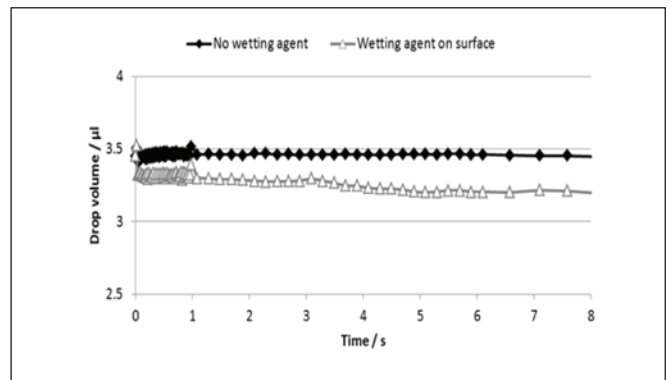


Figure 21. Wetting agent did not alter the volume absorbed significantly. Water spread on the surface rather than being absorbed into the coating

area of the paper with wetting agent on the surface. This was explained by looking at the water drop spreading and absorption characteristics on the coated surface. Wetting agent on the surface showed a higher rate of increase in drop base diameter Figure 20 (surface spreading) than the control. However, rate of change of volume was similar to the control, suggesting rapid wetting but with minimal difference in absorption behaviour (Figure 21). This caused the predamping water to form a film more readily and therefore interfere with printing to a greater extent resulting in a reduction in print density.

Corona treatment

Corona treatment has the ability to change SFE significantly without majorly influencing other surface properties such as porosity

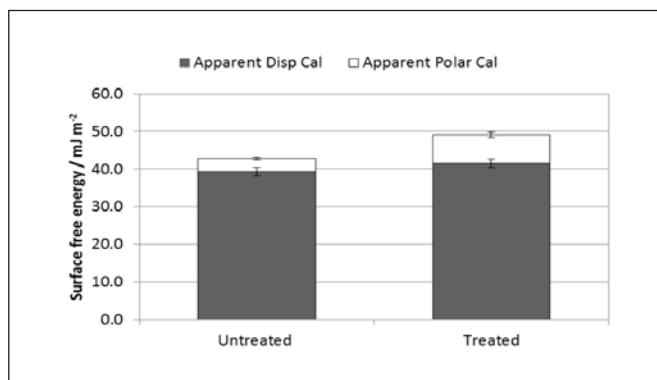


Figure 23. Effect of corona treatment on SFE. Both γ_{tot} and γ_{p} increased with corona treatment

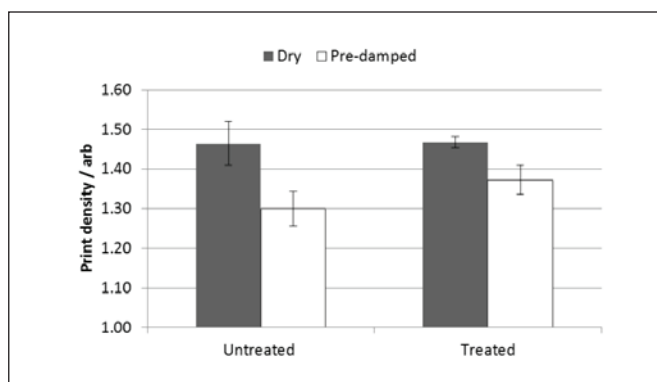


Figure 24. No change in the dry print density. The print density of the predamped area increased after corona treatment

and roughness¹². The effects of corona treatment are shown in Figures 23 and 24. There was no difference in the dry print density between the treated and untreated surfaces, however, the litho print density was higher for the Corona treated surface. This would suggest that this had a higher water absorption and less rejection of the ink by the predamping water.

Figure 23 showed that corona treatment had the most significant effect on γ_{p} . This is a widely reported effect of corona treatment and can be due to a number of processes depending on the method of corona treatment¹². The higher γ_{p} value of the treated paper did not seem to affect print gloss significantly, but an increase in predamped print density was observed (Figure 24).

As in the case of the wetting agent (section 2.5), a more detailed analysis of the droplet spreading (base diameter) and absorption (drop volume) gave some insight into the mechanisms occurring. In Figure 25, we see that the treated paper had a higher initial rate of spreading as well as a higher maximum drop base diameter. The water has spread across the paper surface. In Figure 26, we can see that a slightly higher initial rate of water absorption also simultaneously occurs for the treated paper allowing removal of the predamping water from the surface of the paper and therefore reduced ink rejection. This means that a higher print density can be achieved.

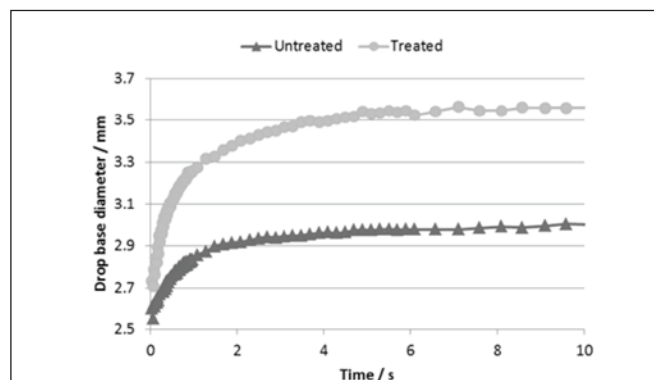


Figure 25. Initial rate of change of drop base diameter is higher for corona treated paper. The final maximum base diameter is also higher. Corona treatment → more drop spreading

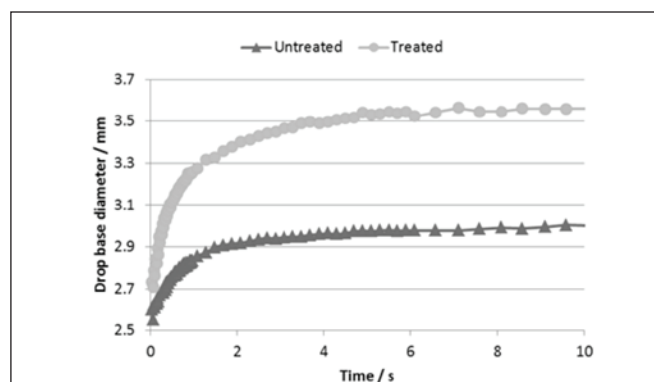


Figure 26. Initial rate of change of drop volume is higher for corona treated paper
Corona treatment → faster absorption

By separating the effects of chemistry and physical properties of papers with corona treatment, it was found that SFE has only a limited effect on printability. Most aspects of printability were unaffected, but the increased polar component of treated papers improved the print density of predamped areas slightly by more effectively removing the water present.

CONCLUSIONS

The first aim of this study was to report the best way to calculate SFE of paper using contact angle data. It was shown that 0.1 s value of contact angle was the best for these calculations in order to minimise inaccuracies caused by drop bouncing, wetting and absorption. Roughness-related differences in contact angle were corrected using the Wenzel model and it was concluded that porosity had a negligible effect on surface energy determination at 0.1s.

The second main aim was to gain a deeper understanding of the impact that surface free energy of paper has on printability in comparison to porosity and topography, and attempt to decouple these effects where possible. It is well known that the print quality of paper can be modified by changing pigment, but in this study, we show that changes in surface energy are much less important than changes in roughness and porosity. The results indicate that

pigments themselves have little impact on surface energy of the final coated paper, although it must be noted that the presence of sodium polyacrylate used to suspend the particles in aqueous coating colours, may have masked some of the effect of the surface chemistry of the pigment.

Specifically, we demonstrated that identical particle sized calcium carbonate pigments with hydrophobic or hydrophilic surfaces have very similar surface energies when incorporated in to coating colours. In addition, we also showed that the surface energy of a coating was actually dominated by the nature of the latex binder and other additives.

In experiments where the surface energy was changed without modification of the surface roughness or porosity (using wetting agents or corona treatment) it was noted that very large changes

in surface energy resulted in only small changes in offset print gloss and density. Application of wetting agent to the surface of the coating resulted in increased surface spreading of the water droplets, but not enhanced absorption into the bulk, which did decrease the litho print density slightly due to ink rejection. However, this was a severe case which would not generally be encountered in real paper coating situations.

In offset printing it may therefore be concluded that pigment surface energy is of less importance than its contribution to the paper roughness and porosity. The results also suggest SFE is less significant than porosity or topography in impacting offset print performance. However, this report was limited to offset printing and other printing techniques such as water based flexo or inkjet should be investigated. ■

REFERENCES

1. T. W. D. Dean, *The Essential Guide to Aqueous Coating of Paper and Board*, PITA, Bury, UK, 1997.
2. N. F. Santos and J. L. Velho, *Pulp Pap. Canada*, 2004, 105, 43–46.
3. J. Preston, PhD Thesis “Print gloss of coated surfaces” University of Bristol, 2001.
4. J. Järnström, P. Ihalainen, K. Backfolk and J. Peltonen, *Appl. Surf. Sci.*, 2008, 254, 5741–5749.
5. J. Järnström, M. Väisänen, R. Lehto, a. Jäsberg, J. Timonen and J. Peltonen, *Colloids Surfaces A Physicochem. Eng. Asp.*, 2010, 353, 104–116.
6. P. Vernhes, M. Dubé and J. F. Bloch, *Appl. Surf. Sci.*, 2010, 256, 6923–6927.
7. R. Carlsson, Karlstad University, 2005.
8. M. Pykönen, PhD Thesis Åbo Akademi University, 2010.
9. J. M. R. C. a Santos, M. H. Gil, A. Portugal and J. T. Guthrie, *Cellulose*, 2001, 8, 217–224.
10. D. Ansari, PhD Thesis University of Bath, 2000.
11. D. K. Owens and R. C. Wendt, *J. Appl. Polym. Sci.*, 1969, 13, 1741–1747.
12. R. J. Good and C. J. van Oss, in *Modern Approaches to Wettability: Theory and Applications*, eds. M. E. Schrader and G. I. Loeb, Springer US, Boston, MA, 1992, pp. 1–27.
13. C. J. Van Oss, M. K. Chaudhury and R. J. Good, *Chem. Rev.*, 1988, 88, 927–941.
14. R. N. Wenzel, *J. Ind. Eng. Chem. (Washington, D. C.)*, 1936, 28, 988–994.
15. Wolansky, Gershon & Abraham Marmur. “Apparent contact angles on rough surfaces: the Wenzel equation revisited.” *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 156.1 (1999): 381–388.
16. A. B. D. Cassie and S. Baxter, *Trans. Faraday Soc.*, 1944, 40, 546–551.
17. E. W. Washburn, *Phys. Rev.*, 1921, 17, 273–283.