Surface energy considerations for offset printing of coated paper and paperboard

JANET PRESTON, ANDREW FINDLAY, JONATHAN KEEN, AND ELI GASKIN

ABSTRACT: Offset printing of coated paper involves the complex interactions of ink with a surface that is characterized by three major properties: roughness, porosity, and related pore network structure 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 is much less studied and therefore the focus of this paper. The key results shown include:

i) Coating porosity has a negligible effect on SFE determination by contact angle using two fluids.

ii) 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.

iii) Wetting agent and corona treatment can impact water absorption rate and surface spreading of water, resulting in small differences in printability. Increasing the concentration of the surfactant on a coated surface indicates switching orientation of the surfactant molecules, giving a "step wise" printing result.

When looking to improve offset printability by selection of different pigments, the variation in SFE is less important than variation in either surface roughness or porosity.

Application: This paper studies the impact of sheet surface energy on offset printing and attempts to rank its importance against surface porosity and topography. Although the surface energy was shown to be less crucial than porosity for impacting offset printing, it still has the potential to be important for other aspects of converting, such as glueing, and a discussion on how to measure and control surface energy is useful.

Mineral based coatings are often employed to improve the surface properties of the paper to give higher print gloss and printed color density. Calcium carbonate and kaolin are the most commonly used minerals in this context due to the high levels of gloss, whiteness, and opacity that are possible [1]. The pigment chosen also plays an important role in controlling surface porosity and roughness and can be modified by selection of the pigment type (calcium carbonate, kaolin, talc) and shape [2-4], average particle size, and particle size distribution (PSD). The amount and type of latex and other binders and co-binders used, including coating color rheology modifiers, and the finishing of the paper (e.g., calendering) can have a significant impact on the porosity and surface chemistry of a coated paper [5-7]. 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 polarity [7], while keeping other bulk properties constant. Coating topography, porosity, and surface energy are the three major factors that can impact the final print performance of ink on paper, and in this work, the area of SFE contribution to the print quality is the main focus.

METHODS & MATERIALS

The coatings were applied to coated woodfree base paper using a Helicoater 2000C (T.H. Dixon & Co. Ltd.; Letchworth, England, UK) with short dwell head at 800 m/min and a coat weight of 12 g/m², with a drying cycle starting with infrared (IR) driers and hot air, followed by cold air. The formulation was 100 pph pigment, 12 pph styrene butadiene latex, 0.13 pph synthetic thickener, and pH 9.5. Calendering was performed using a Perkins laboratory supercalender (10 nips, 65°C, pressure of 68 bar, speed of 36 m/min) from B.F. Perkins & Sons (Holyoke, MA, USA). Samples were conditioned, tested, and printed at 21°C and 50% relative humidity.

Contact angles were determined in a sessile drop–goniometer measurement using two test liquids, water and bromonaphthalene, on a dynamic absorption tester from TQC Sheen B.V. (Capelle aan den IJssel, Netherlands). A pump system, with a 0.1 µl accuracy, drops 4 µl of water and 3 µl of bromonaphthalene onto the measurement surface, and the contact angles of these drops were taken at 0.1 s after application, which corresponds to the point at which the drop stopped oscillating on the surface. Young's equation (Eq. 1) was used to calculate SFE, and this is the

basis for all contact angle related techniques and relates contact angle, θ, to the interfacial tensions between all three phases present (solid-vapor, γ_{SV}; solid-liquid, γ_{SL}; and liquid-vapor, γ_{LV}) when a drop is at thermodynamic equilibrium on a surface, and this was then split into polar and dispersive components using the method developed by Owens and Wendt [8].

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

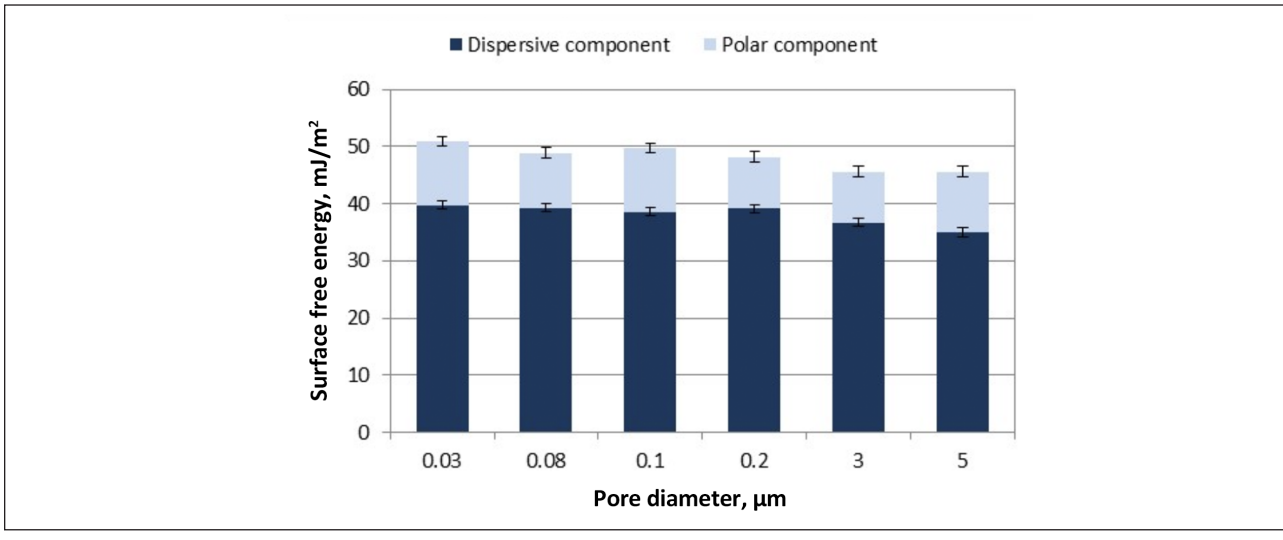
A Keyence Laserscape (Keyence; Osaka, Japan) was used to determine the root mean square (RMS) roughness of each surface, and this value was used to correct the contact angle using the Wenzel equation [9]. Mercury porosimetry was used for accessible pore size distribution and porosity evaluation using Thermo Scientific Pascal 140 and 240 porosimeters (Thermo Fisher Scientific; Waltham, MA, USA). Offset printing was performed using a laboratory scale IGT AIC2-5T2000 unit (IGT Testing Systems; Almere, The Netherlands) with simultaneous pre-damping (with 1 g/m² of water) so that ink rejection could be assessed. The ink applied directly to the paper is named the "dry" print density, and the ink applied to the predamped surface is called the "litho" print density. The ratio of litho-to-dry ratio (L/D) density gives a measure of ink rejection due to slow water absorption. A value of lower than 0.9 would indicate that there is some rejection of ink due to the predamping water. Print density was assessed using a GretagMacbeth D186 densitometer (GretagMacbeth; Regensdorf, Switzerland), 75° gloss, using a Technidyne glossmeter (Technidyne; New Albany, IN, USA) according to TAPPI Standard Test Method T 480 "Specular gloss of paper and paperboard at 75 degrees." Corona treatment was carried out on a Corona-Plus unit from Vetaphone (Kolding, Denmark) at an intensity of 85 W/min/m² [10].

RESULTS

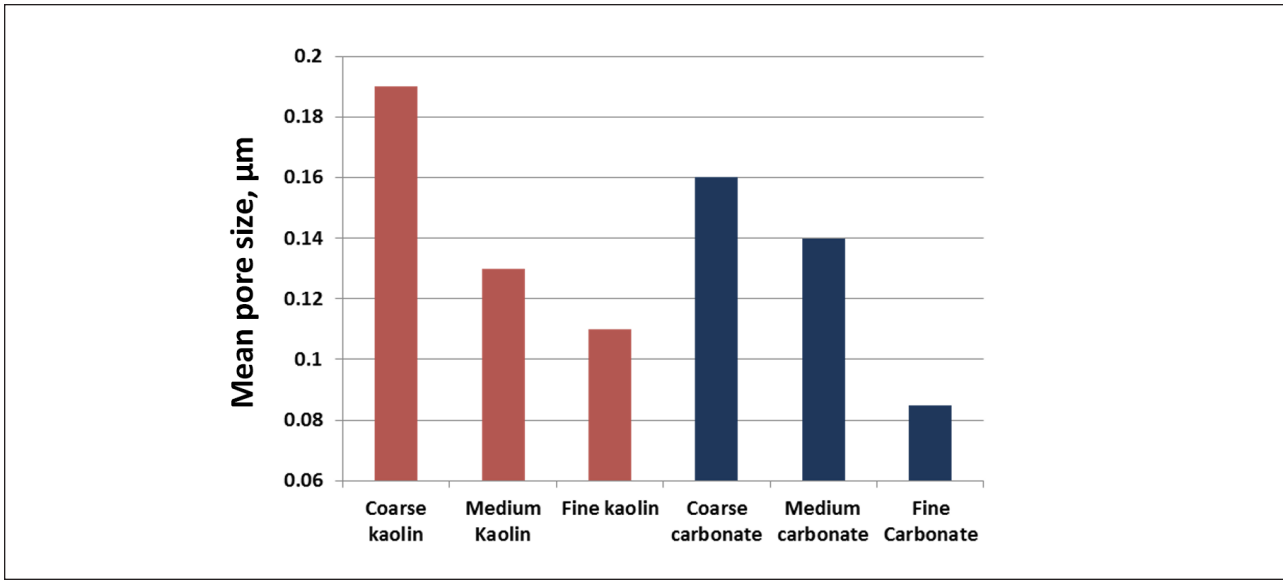
Impact of porosity on contact angle measurements

The impact of porosity on SFE determination was studied by using Cyclopore polycarbonate membranes. These were used as "smooth" model porous surfaces of the same material, where porosity was varied systematically (pore diameters from 0.03 to 5 µm). Increasing pore radius had no significant effect on SFE determination (**Fig. 1**) within the pore size range associated with coated paper (< 0.5 µm). This lack of dependency on surface porosity was also seen for pigment coatings (**Fig. 2** and **Fig. 3**) where the porosity and pore structure of coated papers was also shown to have little impact on SFE, although the porosity itself is known to have a highly significant impact on fluid absorption rate [5]. Furthermore, kaolin and carbonate are known to have different intrinsic surface energy values; however, after inclusion in a coating formulation, the surface energies were all the same (Fig. 3). It is probable that the soluble or flowable species present in coating colors (e.g., dispersant, latex, and any thickeners that may be present) are likely to become deposited on the pigment surface, thus defining the surface energy of the dried coating. Similarly, Tåg et al. [11] studied coatings with varying porosities and roughness that were prepared from different sized calcium carbonates and different calendering conditions but with the same surface chemistry (same binders). It was concluded that, at faster printing speeds, the impact on the coating porosity decreased in terms of fount solution absorption rate, as there was less time for capillary absorption to occur.

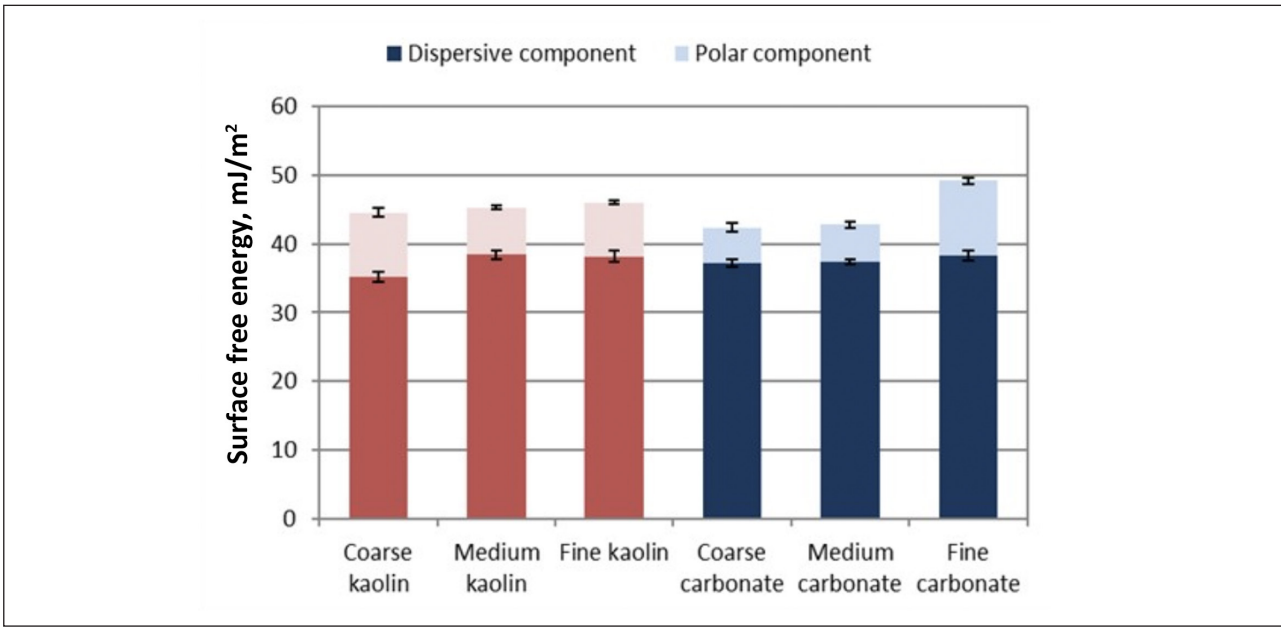
The "masked pigment" hypothesis was further tested by first making pigments with very different surfaces (as in **Table I**) and then assessing their surface energy as pressed tablets. These materials were then incorporated into coating colors, and after coating and drying, the surface energy



1. Impact of pore diameter on surface free energy (SFE) determination was studied by using Cyclopore polycarbonate membranes. Increasing pore radius did not seem to have a significant effect on SFE within the range of pore diameters that would be found in a paper coating (<0.5 um).



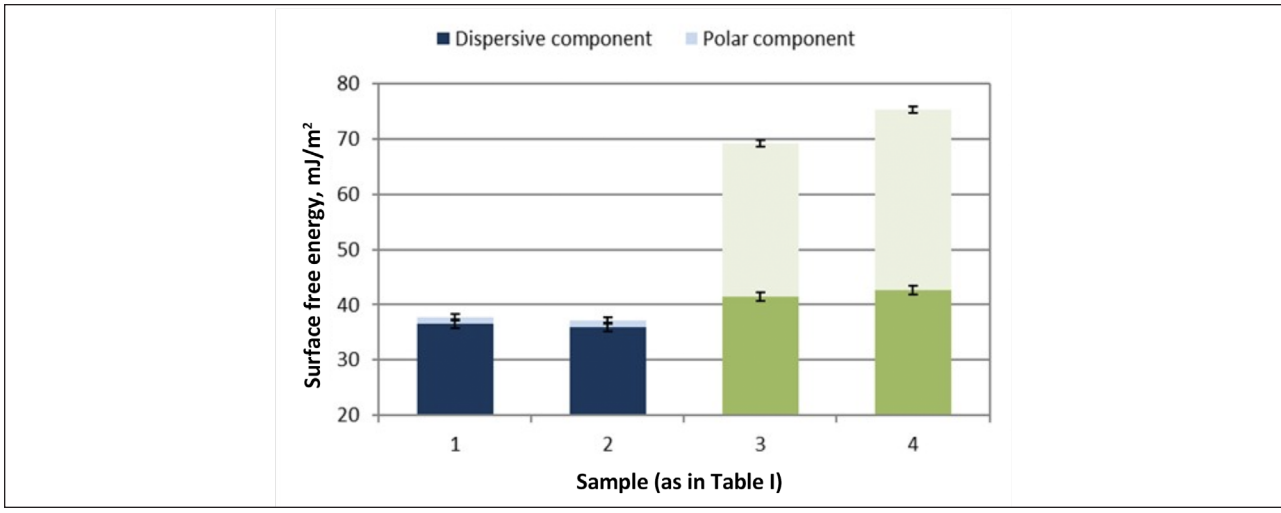
2. Mean pore size data for coatings containing particle-sized kaolin and carbonates. Coarser minerals give larger coating pores.



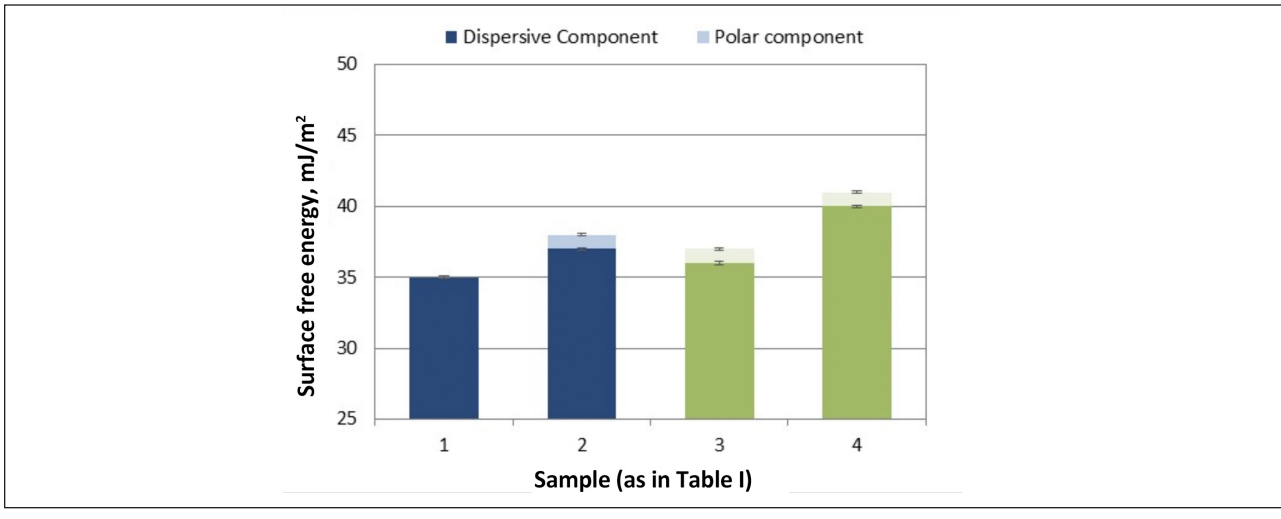
3. All samples showed relatively similar values for SFE, regardless of particle size distribution (PSD) or pigment type.

Sample	Treatment
1	Fatty acid coated GCC (hydrophobic), dispersed with hydrophobic dispersant
2	Fatty acid coated GCC (hydrophobic), dispersed with hydrophilic sodium polyacrylate dispersant
3	Uncoated hydrophilic GCC powder, dispersed with hydrophobic dispersant
4	Uncoated hydrophilic GCC powder, dispersed with hydrophilic sodium polyacrylate dispersant

I. Treated ground calcium carbonates (GCCs) prepared to further explore the masked pigment hypothesis. All four mineral samples were prepared, dried, and pressed into tablets for surface energy (SE) determination. They were then combined in a coating formulation as described in the text and applied to a paper surface, which was dried and the SE was remeasured.



4. The SFE comparison of pressed powder tablets. Uncoated carbonates (3 and 4) show a far larger polar surface component (γp) value than the coated carbonates (1 and 2).



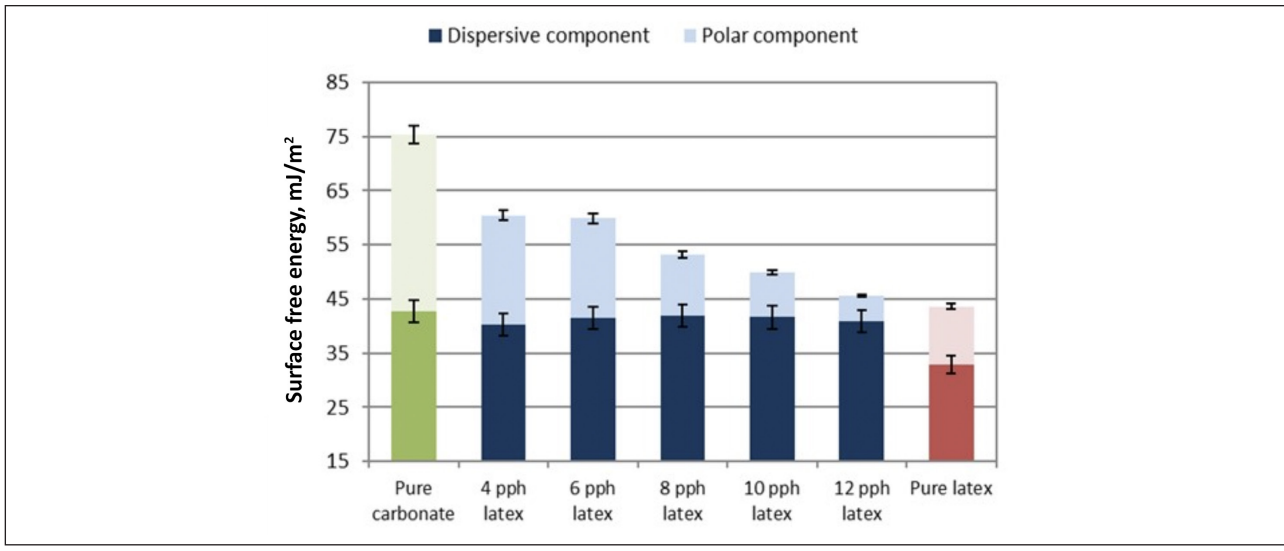
5. The SFE comparison of paper coatings formulated using carbonates from Table I. The polar surface component (γp) and total surface energy (γtot) differences are far smaller in paper coatings than the initial pigments.

was remeasured. It was shown that the large differences in surface energy of the pigment were significantly reduced in the final paper coating (**Fig. 4** and **Fig. 5**), suggesting that dispersant, thickeners, and latex were largely covering the surface of the pigment and masking their intrinsic surface energy. The printability of these papers was assessed in terms of print gloss, print density, and L/D ratio, and no significant differences were observed.

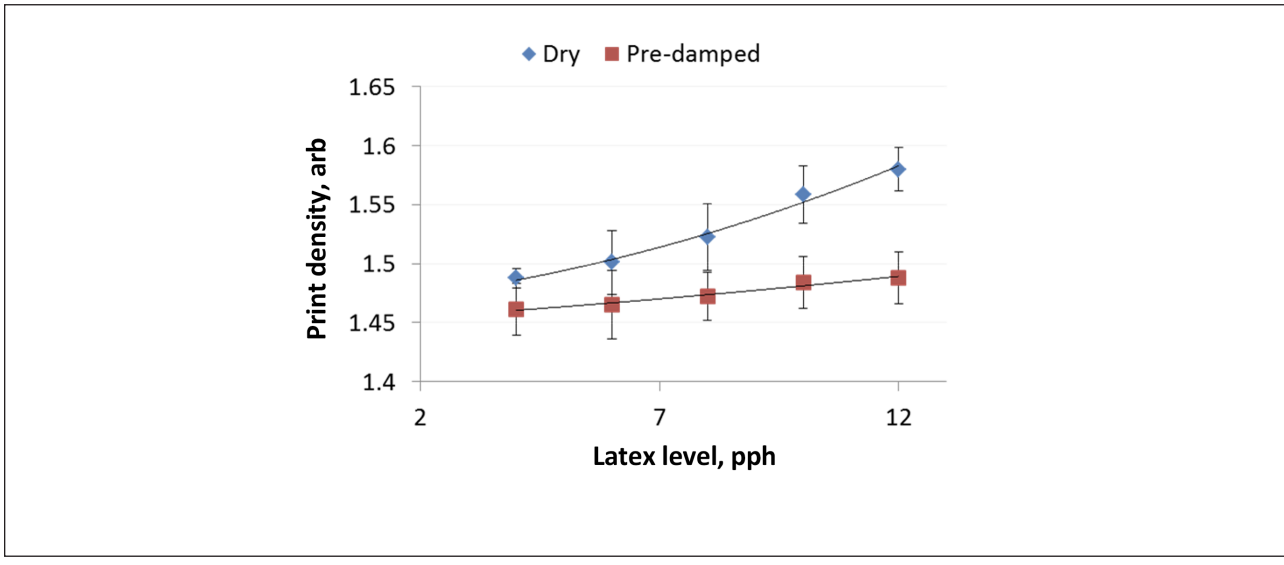
It has clearly been shown that significant differences in SFE of pigment can be effectively masked by the latex binder and other formulation additives in paper coatings, suggesting the dominance of the binders in impacting the coating surface. This was further explored by increasing systematically the binder level from 4–12 pph (**Fig. 6**) in a series of model coatings. To ensure no disturbing other factors, no other coating additives such as thickeners were used for these coatings. There was a decrease in total surface energy (γtot) and polar component (γp) of SFE 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 pigment [8].

The results for the printability assessments carried out on these papers are summarized in **Fig. 7** and **Fig. 8**. On both dry and pre-damped areas, higher latex levels showed an increase in print density, which results from a lowering in porosity of the coating. However, the increase in print density for pre-damped areas was not as large as the increase recorded for dry areas, indicating that a higher level of latex leads to proportionally more ink on water rejection (also seen as a slight decline in the L/D ratio, as shown in Fig. 8). It is, however, not really possible to determine if it is the more hydrophobic surface that is slowing the absorption of the predamping water or indeed simply the change in porosity.

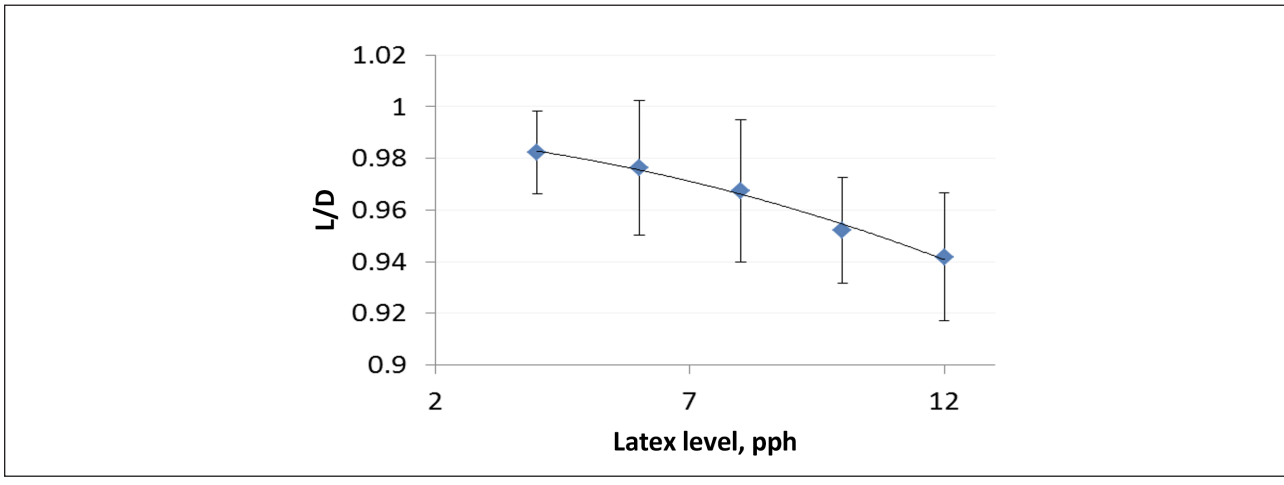
To disconnect the impact of changing porosity and polarity, two different methods of changing the surface energy



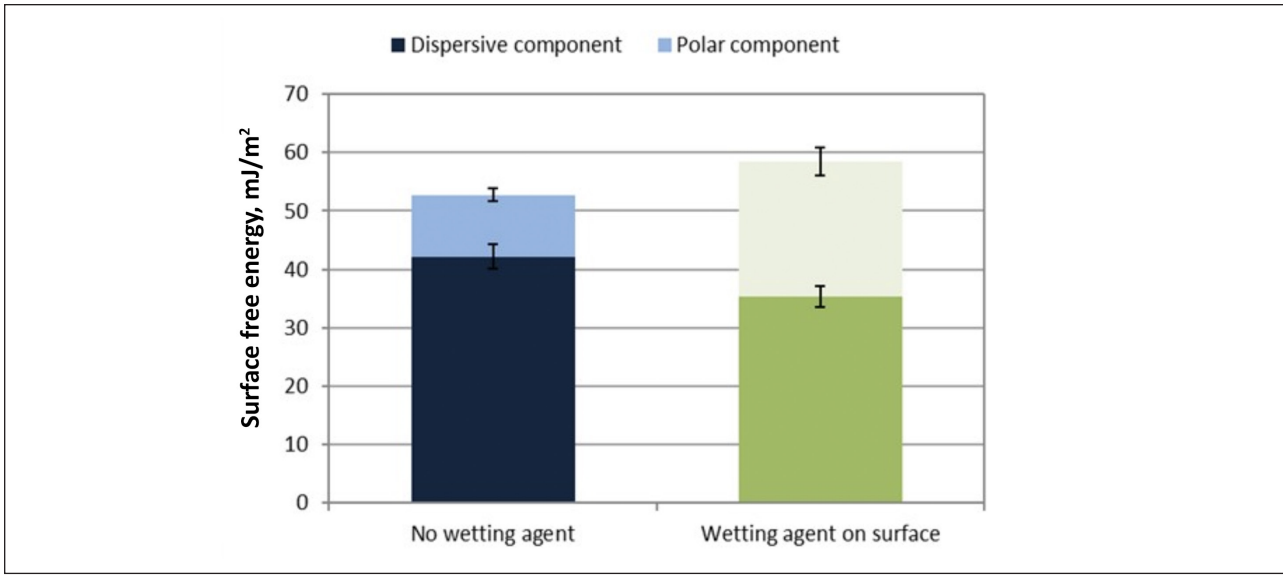
6. The SFE of paper coated with formulations having different levels of latex.



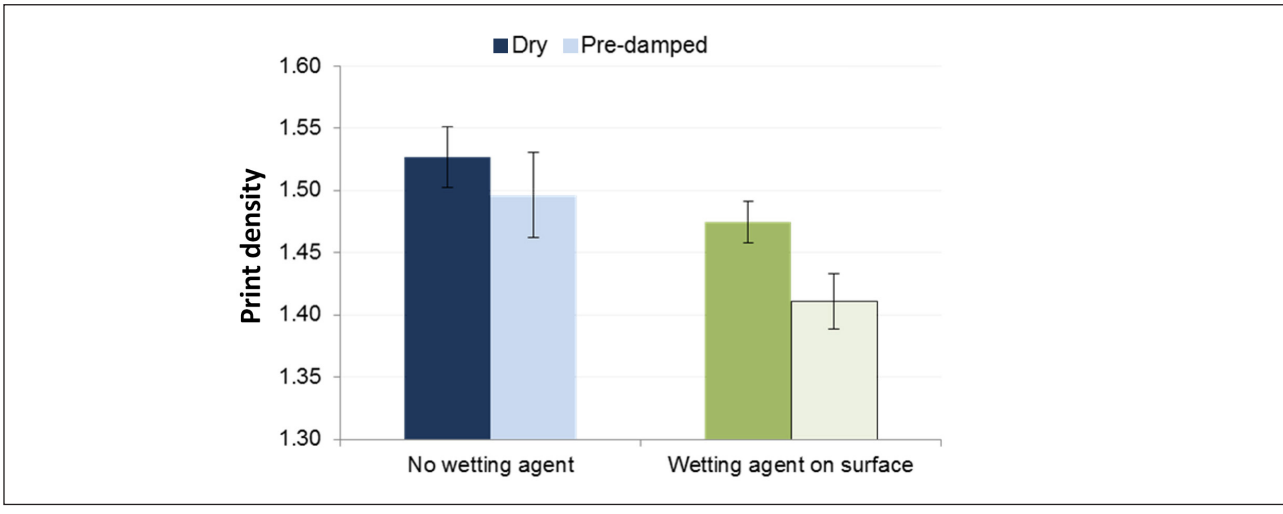
7. Print density in dry and pre-damped areas with increasing latex level (arb: arbitrary unit).



8. The litho-to-dry ratio (L/D) decreases with increasing latex level.



9. Effect of wetting agent on the SFE of coated paper.



10. Influence of wetting agent on print density showing a reduction in both dry and pre-damped density.

of the coating without changing the porosity were evaluated: the impact of wetting agent and Corona treatment.

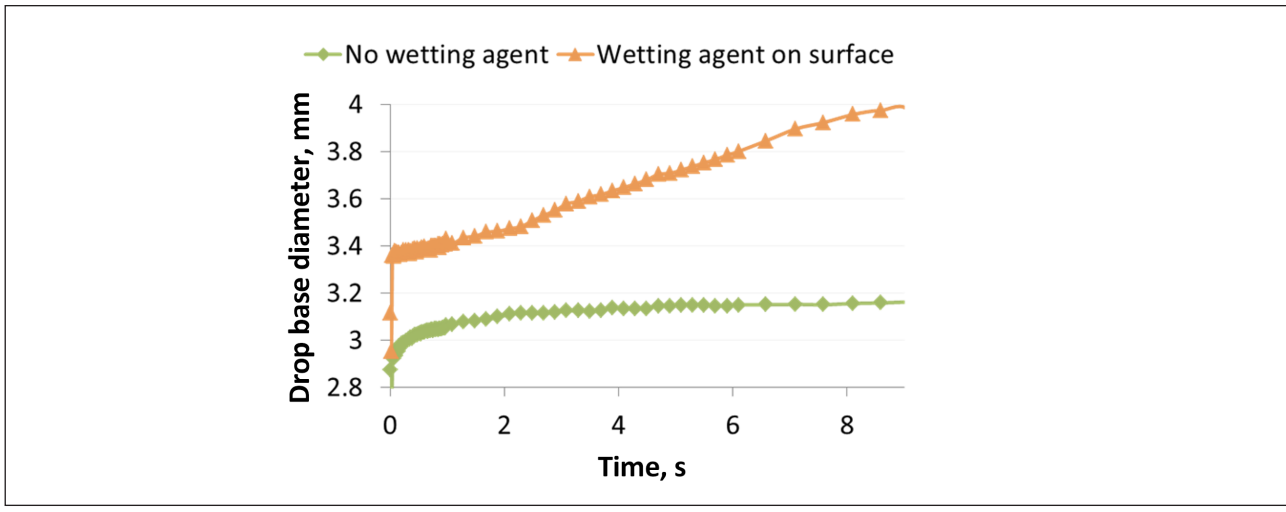
Wetting agent

In this study, a sodium dodecyl sulfate (SDS) wetting agent was applied directly to the surface of a dried paper coating. A control paper with no wetting agent at all was also included. The results (**Fig. 9**) showed that wetting agent applied to the surface of paper showed a reduction in dispersive component (γd) of surface free energy and an increase in γp, i.e., increased polarity and "wetting." The topography and porosity of the coatings remained unchanged. The print results are shown in **Fig. 10**.

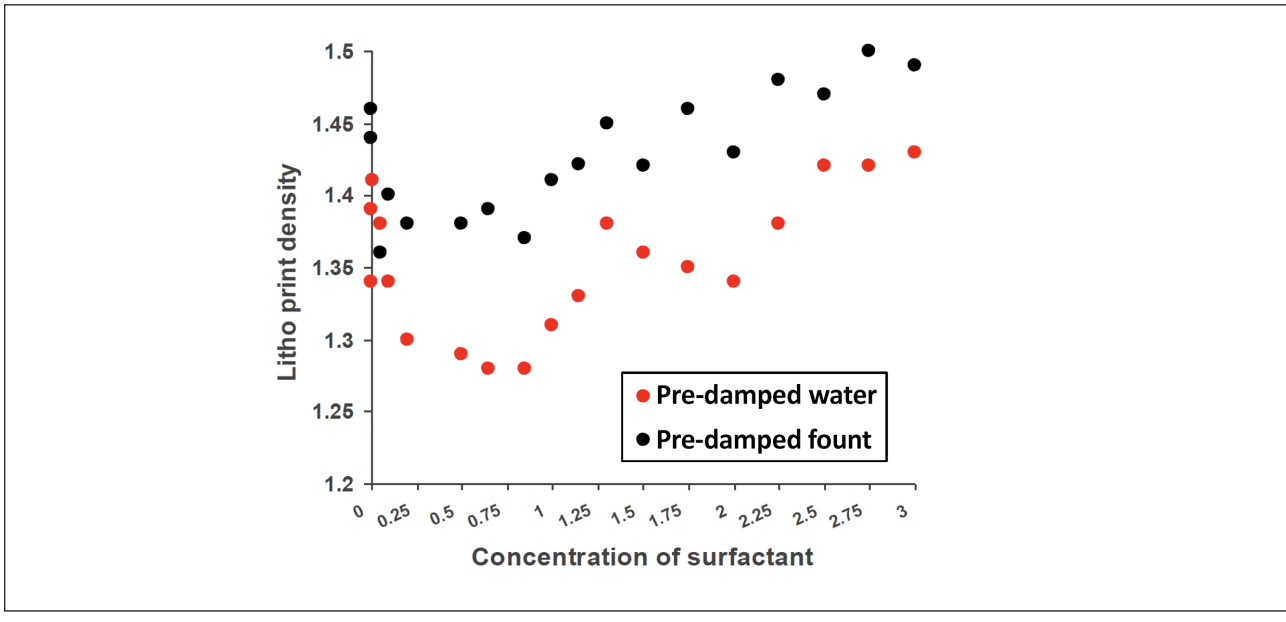
Wetting agent did not appear to overly impact the dry printability; there were only small reductions in dry print density for both samples. However, there was a significant reduction in print density for the pre-damped area of the paper with wetting agent on the surface. This was explained by looking 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 (surface spreading) than the control, as shown in **Fig. 11**. However, the rate of change of volume was similar to the control, suggesting rapid wetting but with minimal difference in absorption behavior. This caused the pre-damping water to form a film more readily and therefore interfere with printing to a greater extent, resulting in a reduction in print density.

Further analysis of impact of wetting agent/surfactant on a coated surface

A short exercise was carried out to apply increasing amounts of SDS surfactant by increasing the solution concentration to the surface of the coated paper prior to print-



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



12. Print density of surfactant treated surfaces after pre-damping with water and fount solution.

ing. During the printing process, both pure water and fountain solution (Vegra 4800, Vegra GmbH; Aschau am Inn, Germany) were used as pre-damping agents. In both cases, a stepwise response occurred, which suggests orientated layers build up that "switch" polarity. The fountain solution gives higher print densities than water, as it is more readily absorbed due to its lower surface tension (**Fig. 12**). A similar pattern is observed when measuring the contact angle of the fluids on these surfaces (**Fig. 13**).

However, buildup of too much fountain solution surfactant on the paper surface can result in ink rejection and a lower print density. At 10% fountain solution concentration, the litho print density is 1.42, while at 50% concentration, the litho density is decreased to 1.25.

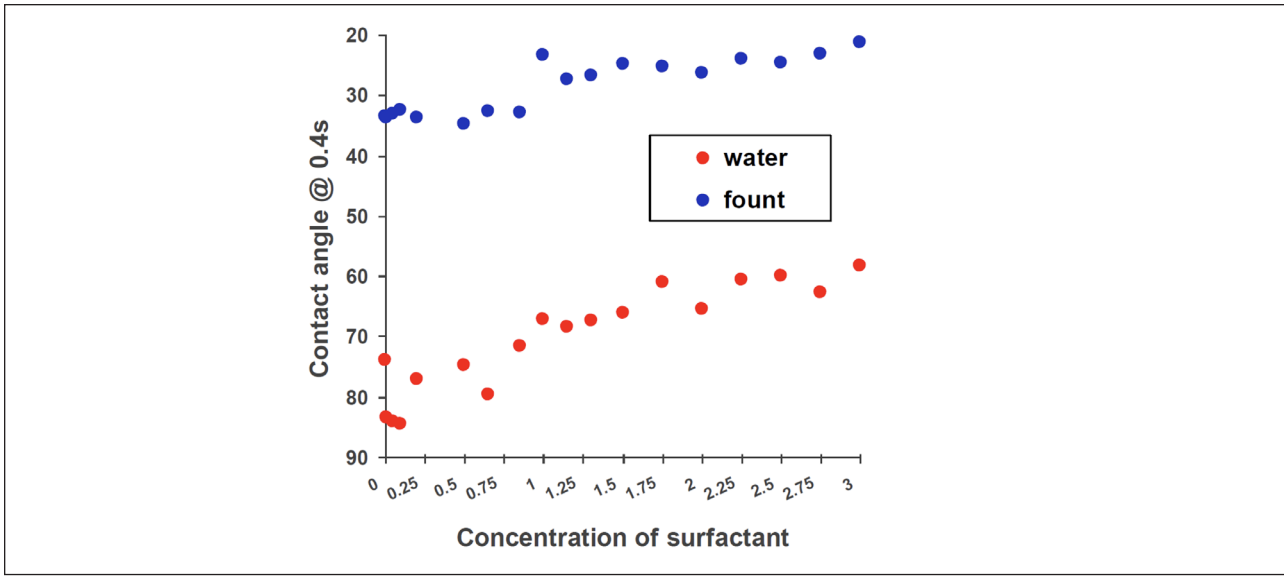
Corona treatment

Corona treatment has the ability to change SFE significantly (both γtot and γp increased with corona treatment), without majorly influencing other surface properties, such as porosity and roughness (**Table II**).

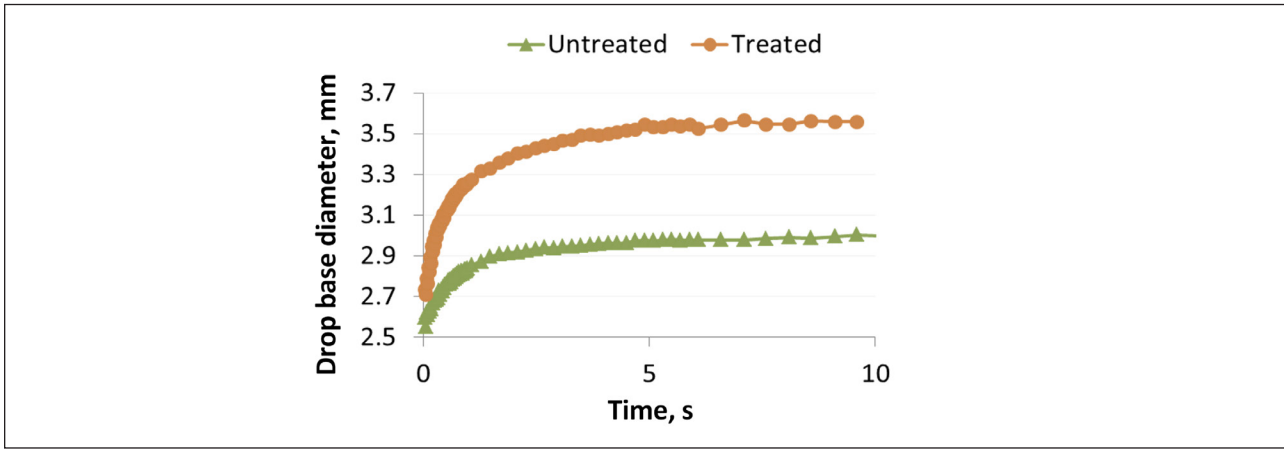
There was no difference in the dry print density between the treated and untreated surfaces; however, the litho

	Untreated	Treated
Polar surface energy (γp)	3.6	7.6
Total surface energy (γtot)	42.8	49.1

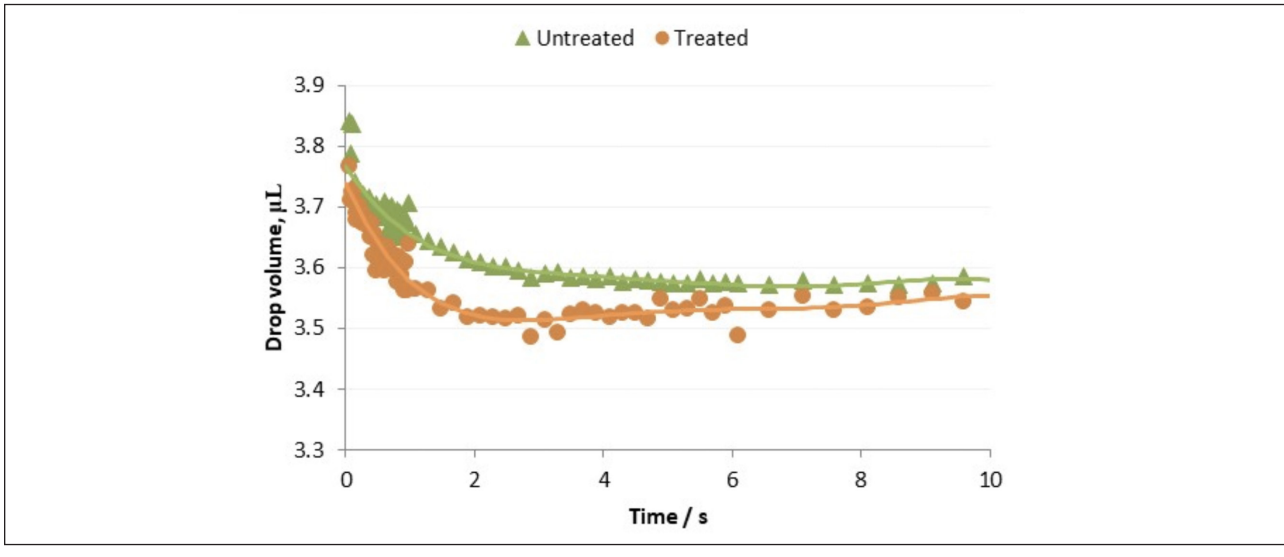
II. Surface free energy (mJ/m²).



13. Contact angle results show a pattern similar to print density. Surface is more hydrophobic at low sodium dodecyl sulfate (SDS) concentration, then more hydrophilic. Fount solution gives lower contact angles and higher print densities than water.



14. Corona treatment gives more drop spreading.



15. Corona treatment gives faster absorption.

print density was higher for the corona treated surface (moving from 1.30 to 1.38), suggesting a higher water absorption and less rejection of the ink by the water.

This was verified by the Fibro DAT water absorption and spreading curves (**Fig. 14** and **Fig. 15**), where it can be seen that after corona treatment, there is simultaneously faster drop spread and drop absorption (decrease in drop volume).

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 the bulk of the coating layer (e.g., by corona treatment) slightly improved the print density of pre-damped areas by more effectively removing the water present.

CONCLUSIONS

After correction of roughness differences using the Wenzel model, it was concluded that porosity of the coating surface had a negligible effect on SFE determination using contact angles determined at 0.1 s after drop application.

It is well known that the print quality of paper can be modified by changing pigment, but the results indicate that surface energy of the pigments themselves have little impact on surface energy of the final coated paper. Specifically, we demonstrated that identical particle-sized calcium carbonate pigments with hydrophobic or hydrophilic surfaces have very similar surface energies when incorporated into coating colors. In addition, we also showed that the SFE of a coating was actually dominated by the nature of the latex binder and thickener. The significant impact of the pigment on the printability is therefore likely to be related to the physical and structural aspects of the coating layer, such as the porosity and topography.

In experiments where the SFE was changed without modification of the surface roughness or porosity (using wetting agents or corona treatment), it was noted that very large changes in SFE 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 slightly decrease the litho print density due to ink rejection. Increasing wetting agent contact angle and spreading results helped explain why this was the case. The more hydrophilic surface caused the drop to spread sideways rather than penetrate into the bulk of the coating. This resulted in more ink rejection.

From this study, mills can understand how best to modify the surface energy of their coatings, such as by corona treatment. This could be important for other aspects of converting rather than just printing, such as gluing. Our next step is to look further at surface energy and its impact on converting operations like glueability.

ABOUT THE AUTHORS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We are interested in all aspects of the pigment coating formulation and their influences on final board properties. In the past, work has been extensively carried out and reported as to the pigment characteristics and how, when they pack together, they will impact the physical properties of the coating layer, such as pore structure. However, the area of surface chemistry has largely been ignored, and we thought it was a final part of the puzzle that needed further exploration.

The most difficult part of this study was in determining how best to measure the surface energy of paper coatings, such as how to apply a theory that is valid for a smooth, homogenous, and non-porous substrate to a surface that is none of these! We took a systematic look at each step in the measurement and also considered reproducibility before finally deciding on the conditions to use. We did not give up when confronted with the unexpected, but instead we worked through carefully and logically to best understand the findings and assess as to whether a result is real or is just a "flyer."

We were initially surprised to find that after applying surfactant solution to the surface of the paper, there was more rejection of ink due to slow water absorption rather than less. Looking at the Fibro DAT

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centration also impacted the print results, possibly due to a change in multilayer surfactant orientation. Corona treatment increased both the surface wetting and absorption of the water.

In offset printing, it is suggested 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, but it does have some impact on the water spreading and penetration/ink rejection. However, this report was limited to offset printing and other printing techniques, such as water based flexographic or inkjet, should be investigated. **TJ**

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