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The influence of coating structure and surface energy on Gibbs energy of ink oil imbibition during ink setting

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KEYWORDS: Gibbs free energy, Surface energy, Polar acid and base components, Coatings, Acrylate-acrylonitrile-styrene latex, Pore structure

SUMMARY: In this study of kaolin and latex chemistry influence on the specific Gibbs energy ($\Delta G$) in ink oil imbibition into a pilot coated solid bleached sulfate (SBS) board, we show that $\Delta G$ with coating structure variables (volume and diameter, $\Sigma(V/D)/m$) and surface energy parameters ($\gamma \cos \theta$) are affected by changes in kaolin and latex chemistry. We found that the base $\gamma$ amounts (from van Oss-Chaudhury-Good approach) on coated board surfaces were low compared to Lifshitz-van der Waals, $\gamma^p$ interactions while the acid $\gamma$ was very low, and in turn the acid-base, $\gamma^a$ portion. We conclude that the specific Gibbs energy concept combining $\Sigma(V/D)/m$ and $\gamma \cos \theta$ at interface suites better for characterizing capillary adsorption during oil-based ink setting than each parameter alone, especially when both pigment and latex chemistry are changed. Along with this study we also observed that two types of kaolin with constant $\gamma^a$ and different $\gamma^p$ changed $\Delta G$, and coated paper capillary adsorption in offset ink setting as seen in the different time needed to reach the maximum tack force, $t_{max}$, but with no effect on the maximum tack force, $F_{max}$, and the final tack. We further demonstrated that compared to styrene/n-butyl acrylate latex, n-butyl acrylate-acrylonitrile-styrene latex lowered $\gamma^p$ on coated board surface and $\Delta G$, and significantly increased $t_{max}$, and reduced $F_{max}$ and the final tack. We expect that the specific Gibbs energy approach may find applications in analyzing general interactions of porous coatings with polar and non-polar liquids on a macro-scale.

The critical parameters of coating structure having an influence on liquid imbibition on ink setting, film split and leveling are the nature of the liquid/solid/vapor interface as well as the capillary diameter and pore volume distributions. A commonly used method to characterize paper coatings is to determine the latter two parameters by mercury porosimetry. However, capillaries of a given volume with small diameters tend to have a relatively stronger influence on the ink tack build rate than capillaries with a larger diameter but a marginally larger pore volume (Ma et al. 2005). It was therefore felt that some relatively simple way of characterizing the pore structure and surface energy that correlates better with ink tack than pore diameter or volume distribution is needed.

A vast literature exists on both experimental studies and theoretical modeling of the penetration of liquids into porous media and their application to penetration of ink in paper or coating. However, to our knowledge previous work has not theoretically touched the very complex relationship between coating structure, binder chemistry and ink setting, and experimental studies of penetration mechanisms frequently require advanced instrumentation. Overviews are given (e.g. Van Gilder, Purfeerst 1994; Kan, Van Gilder 2004; Xiang et al. 2004). Recently, we proposed a Gibbs energy approach to the characterization of interaction of liquids with coatings and their penetration into porous substrates by capillary imbibition. Assuming cylindrical capillaries with spherical shape menisci, the specific change in Gibbs energy, when a liquid is imbibed into a porous medium at constant temperature and molar volume, $\Delta G$, can be calculated from equations (Ma et al. 2007)

$$\Delta G = -\frac{1}{m} \sum \frac{\Delta G_i}{\gamma \cos \theta} = -\frac{\pi D_i^2 h \gamma \cos \theta}{4} = -\pi D_i h \gamma \cos \theta$$

$$\Delta G_i = \frac{\Delta G_i}{\gamma \cos \theta}$$

where $\Delta G_i$ is the Gibbs energy associated with imbibition of liquid into a cylindrical capillary of height $h$, diameter $D_i$, and volume $V_i$; $\gamma$ is the surface tension of liquid; $m$ is the mass of a sample and $\theta$ is the contact angle of liquid on capillary wall. We showed, for a series of double coated papers, that $\Delta G_i$ correlates well with the rate of imbibition of ink as characterized by the development of ink tack. On the other hand, the total pigment surface area, the peak pore diameter, and the volume alone did not correlate with this rate.

$\Delta G_i$ can be treated as a product of coating structure variables (volume and diameter, $\Sigma(V/D)/m$) and surface energy parameters ($\gamma \cos \theta$), i.e. $\Delta G_i$ highlights the interactive properties of coating pore surfaces and a probe liquid (Ma et al. 2008). Using a non-polar solvent (diodomethane, DIM) on kaolin/calcium carbonate coatings in which the kaolin/carbonate ratio was changed, keeping the latex, dispersant and other additives constant, $\Delta G_i$ was predominantly determined by coating structure (capillary surface area). However, when binary solutions of formamide (FMD) and water on the same coatings were used, polar surface interactions were comparatively strong, as reflected in the changes of surface energy parameters.

The previous studies developed Gibbs energy analysis for capillary adsorption when the pigment type and kaolin/carbonate ratio change. This study focuses on the...
influence of structure and surface energy on ΔG, and on ink tack development when latex and kaolin chemistry are changed.

For a liquid on a smooth, non-deformable and non-absorbing solid surface, surface energy parameters (γcosθ) at interface are related to solid surface energy, γs, and solid-liquid interface energy, γSL, according to Young's equation

$$\gamma = \gamma_{SL} + \gamma_{L} \cos \theta$$  \hspace{1cm} [3]

van Oss et al. (1988) suggested that surface energy γ can be divided into two groups:

$$\gamma = \gamma^{AB} + \gamma^{LW}$$  \hspace{1cm} [4]

where the first term, Lifshitz-van Waals interactions, includes London (dispersion), Keesom (dipoles-dipoles) and Debye (dipoles-induced dipoles) interactions, and the second term denotes more short-range Lewis acid-base interactions. To take into account that material surfaces may contain both acidic and basic groups, the γext term in Eq [4] has been further divided into acidic and base parameters (van Oss 2006)

$$\gamma^{AB} = 2\sqrt{\gamma_a \gamma_b}$$  \hspace{1cm} [5]

where γa and γb denote acid and base parameters, respectively. In this approach (the van Oss-Chaudhury-Good-vOCG, approach), surface energy components can be determined by measuring contact angles for three liquids with known three liquids with known γa, γb, and γs, and solving for the components, using the equation

$$(1 + \cos \theta)\gamma_{L} = 2(\sqrt{\gamma^{LW}_{S} \gamma^{LW}_{L}} + \sqrt{\gamma^{LW}_{S} \gamma^{LW}_{L}} + \sqrt{\gamma^{LW}_{S} \gamma^{LW}_{L}})$$  \hspace{1cm} [6]

Experimental

Preparation and properties of coatings

Ground calcium carbonate (GCC) was from Omya AG, and fine kaolin was from KaMin LLC (Table 1). Styrene-acrylate based latexes (A and B) were from BASF AG. Latex A was styrene/n-butyl acrylate copolymer with glass transition point of 23°C at pH 6.5-7.5. Latex B was n-butyl acrylate-acrylonitrile-styrene copolymer with glass transition point of 4°C at pH 7-8, according to the manufacturer.

Coatings (Table 2) were applied, using a pilot coater at Trois-Rivières, PQ, Canada, on solid bleached sulfate board pre-coated at 400 m/min and 12 g/m² of 100 parts coarse ground calcium carbonate with 15 parts of latex, as well as optical brightener, thickener, dispersant, lubricant and cross-linker, the same chemicals as in top coat. The precoat formulation and process were the same in all experiments. The top coat weight was 12 g/m² of coating solids target at 64.5% with no on-line dilution. For details, see Ma et al. (2005). All coated board was calendered by a 2-nip pilot softcalender at 50 kN/m and 150°C surface temperature.

PPs-10 and TAPPI gloss were measured with TAPPI T555 and T480, respectively. Brookfield viscosity was measured at 100 rpm with #5 spindle and Hercules viscosity was measured at 4400 rpm with E bob.

Measurement of contact angles and determinations of surface energies

It was not possible to directly measure dynamic contact angles in small capillaries of the inhomogeneous industrial coatings used. The distributions of peak pore diameters in a range 56 to 88 nm were all similar. Therefore, when comparing samples, we neglected the impact of capillary diameter on vapor pressure, precursor, contact angle and liquid surface tension, and measured only static contact angles. Coated board samples were conditioned according to TAPPI T402, and sealed in a black plastic bag before contact angle measurements. The capillary dimensions investigated were in the range 30 to 195 nm as determined by mercury intrusion. Static contact angles on coated surfaces were determined by extrapolating time-dependent contact angles to t = 0 s.

Coating surface energy calculations were based on Eqs [4,6], using contact angles of a non-polar (DIM) solvent, two polar liquids (water, FMD), see Table 3, determined with a CAM 200 Optical Contact Angle Meter (KSV Instruments LTD, Finland) at the Laboratory of Forest Products Chemistry, Helsinki University of Technology, Finland. The DIM and FMD were from Sigma-Aldrich, 99%. The water was de-ionized, distilled and degassed. Samples were mounted on a horizontal flat metal base with double-sided tape. Contact angles on both sides of a drop profile were measured, and experimental set-ups are given in elsewhere (Ma et al. 2008). Time-dependent contact angles of solution drops on each coated paper surface were measured for 10 seconds,

### Table 1. Ground calcium carbonate and kaolin particle size distribution (PSD) and specific surface area (BET).

<table>
<thead>
<tr>
<th>Pigment</th>
<th>BET M²/g</th>
<th>Cumulative particle size distribution (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GCC</td>
<td>12.6</td>
<td>&lt; 5 μm 99.6 94.1 70.6 42 20.3</td>
</tr>
<tr>
<td>Kaolin, A</td>
<td>22.6</td>
<td>&lt; 2 μm 99.7 97.8 96.8 89.6 47.2</td>
</tr>
<tr>
<td>Kaolin, B</td>
<td>21.2</td>
<td>&lt; 1 μm 99.5 97.4 91.6 74.6 36.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>&lt; 0.5 μm 97.4 91.6 74.6 36.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>&lt; 0.2 μm 97.4 91.6 74.6 36.3</td>
</tr>
</tbody>
</table>

### Table 2. Pigment compositions of coatings, in parts by weight. In addition all coatings contained 0.15 parts polyacrylic acid (Ciba Chemicals), 15 parts latex (BASF) 0.5 parts carboxymethyl cellulose (CpKelco), 0.7 parts optical brightener (Bayer), 0.3 parts lubricant (Devden) and 0.3 parts cross linker (Bencen).

<table>
<thead>
<tr>
<th>Pigment</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fine kaolin, A</td>
<td>50</td>
<td>50</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>Fine kaolin, B</td>
<td>50</td>
<td>50</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>Latex, A</td>
<td>15</td>
<td>15</td>
<td>15</td>
<td>15</td>
</tr>
<tr>
<td>Latex, B</td>
<td>15</td>
<td>15</td>
<td>15</td>
<td>15</td>
</tr>
<tr>
<td>Carbonate</td>
<td>50</td>
<td>50</td>
<td>50</td>
<td>50</td>
</tr>
</tbody>
</table>

PPs-10, Smoothness, μm 1.13 1.13 1.10 1.10
Gloss, % 67.1 63.9 62.8 58.8
Print Gloss, % 93.5 93.4 93.7 93.2
Coating solids, % 64.5 64.6 64.5 64.6
Viscosity, Brookfield, mPas 2132 1784 2636 2384
Viscosity, Hercules, mPas 102.9 96.3 123.4 108.1
Blade loading, mm 1.9 2.0 3.6 3.1
extrapolated to $t = 0$ s and averaged from five measurements on both sides of drops.

**Pore size distributions**
Coating porosity (incremental volume and cumulative surface area corresponding to the equivalent diameter pores) was determined by mercury porosimetry using an AutoPore IV instrument from Micromeritics. Details are given by Ma et al. (2005).

**Determination of ink tack development**
The rate of tack build and decline was determined using a SeGan Ink/Surface Interaction Tester (ISIT), in the way described by Gane and Seyler (1994). The same sheet-fed offset cyan ink (Naturallith II PC, Sun Chemical) was used in all measurements. Details are listed elsewhere (Ma et al, 2005).

**Results**

**The influence of latex on coating rheology and board properties**
Type of latex had a strong influence on the thixotropic behavior of coatings (Fig 1). Latex B in coatings C and D induced flocculation that was relatively weak and broken by applied shear field during the rotation speed ramp-up in viscometer. On the return loop, all coating colors exhibited Newtonian flow behavior.

Kaolin A and B (Coatings A vs. C and B vs. D) behaved similarly except that kaolin B slightly reduced low shear and high shear viscosities, and coated board gloss. Compared to Coating A vs. C and B vs. D, notably, latex B produced lower board gloss, worse low shear and high shear viscosities and higher blade pressures on the coater, although all coatings had similar print gloss (Table 2).

**Contact angles of water, diiodomethane, formamide and hexadecane**
It is interesting to note that DIM contact angles on coatings with latex B were higher than those on latex A coatings while there was a little difference of contact angles between kaolin A and B (Fig 2). All contact angles of DIM tended to decrease as a function of time between $t = 0$ – 10 s with the contact angles on latex B that started at higher values decreased faster than those on latex A. Because the non-polar nature of DIM these contact angle and rate of decrease differences are particularly important for the study of polymer influence on Gibbs energy in ink oil imbibition. Extrapolated values of contact angles with standard deviation are given in Table 4. In fact, all liquids except hexadecane contact angles on latex B coatings were higher than those on latex A coatings.

The standard deviations were rather high for all the liquids tested except for hexadecane, implying that the differences between contact angles of DIM and FMD on coatings A and B are not statistically significant. The same is valid for the difference between C and D. Although the standard deviations in the contact angles are quite large, the results in Table 4 show that changing the binder has a significant effect on the surface energy in contrast to the negligible effect of changing the pigment composition.

**The capillary pore size and volume distributions**
Fig 3 shows logarithm of the differential intrusion volume vs. equivalent pore diameter determined by...
Contact angles were measured on all four samples. The large pore sizes around 0.25 µm are mainly due to the coarse precoat and the very low fraction of coarse particles from the top coat. Coatings A and B had very similar pore size and volume distributions. Coatings C and D had similar pore volume but different pore size distributions. Pore sizes and volumes of samples C and D with n-butyl acrylate-acrylonitrile-styrene copolymer were larger than those of samples A and B with styrene/n-butyl acrylate copolymer. This indicates that the different latex chemistry caused larger coating structure changes than differences between kaolin types used in this study.

**Ink tack development**

Fig 4 compares ink tack development on the four coatings. Interestingly, coating C with n-butyl acrylate-acrylonitrile-styrene latex produced a lower maximum tack force \( F_{\text{max}} \) than Coating A with styrene/n-butyl acrylate latex. The same held true for coating D relative to coating B. Compared to coating A with kaolin A, the B had the same \( F_{\text{max}} \) and final tack force, but different \( t_{\text{max}} \), i.e. the \( t_{\text{max}} \) of coating B with kaolin B was longer than that of coating A with kaolin A. Similar differences were observed between coatings C and D.

**Discussion**

**Surface energy of coated paper**

Measured contact angles had standard variations ranging from 2 to 6.3°. They were much higher than those on the supercalendered coated paper previously studied that were much smoother (typical PPs-10 smoothness was around 0.7 µm, Ma et al. 2007). The difference was more pronounced with coatings C and D. They could be due to higher surface roughness (Table 2) and/or chemical composition variations. The higher roughness could due to the low board compression in a two-nip soft calender, and the variation in chemical composition could be due to the ‘soft’ flocculation caused by coating ingredient interactions, as indicated by the rheological behavior (Fig 1).

**Kaolin and latex influence on surface energy**

The \( LW \) components of kaolins A and B are similar. This can be traced back to where they were mined from i.e. the same geological site. However, the base parameter of kaolin B was lower than that of kaolin A. Given the fact that there was a very small difference in surface area determined by BET (Table 1), the origin of such a large base parameter difference may be from the bulk mineral composition but it seems more reasonable to assume that it is due to surface chemistry modification in the processing of the kaolin. Effective utilization and conversion of the octahedral surface hydroxyls to change surface chemistry by chemical adsorption from simple cations to complex polymers has been a major subject in kaolin sur-
face chemistry modifications for coating, ink, rubber, plastic applications, to name only a few. The background of working on octahedral instead of tetrahedral can be basically reviewed in a theoretical study in which quantum chemical calculations within the framework of a very basic octahedral-tetrahedral 1:1 kaolin crystal structure demonstrated that carboxylate group of acetate bound to the octahedral surface hydroxyls via hydrogen bridge mechanism, and its interaction energy amounted to -70 kcal/mol. On the other hand, the acetate molecule interacted with tetrahedral surface through weaker hydrogen bonds, and the adsorption energies were only about -4 kcal/mol (Tunega et al. 2002).

Switching latex changed both $LW$ and base parameter levels. While the use of latex B certainly reduced $LW$ interactions, compared to latex A, it increased the base parameter slightly. For acrylate-containing latex, the type involved in this study, the size of alkyl group can affect both dispersive ($LW$ component in oil imitation) and polar surface energies. Changing from iso-octyl acrylate to ethyl acrylate resulted in a dispersive component decrease from 43.7 to 22.1 mJ/m$^2$ and an increase of the polar component from 0.1 to 16.7 mJ/m$^2$ (Chan, Van Gilder 2004). Functional group introduction into a polymer chain and/or to a chain end can significantly change polymer surface energy (Tsioulakis et al. 1999).

Surface concentration of polymer affects coating surface energy. The major difference between latex A and B according to their material safety data sheets (MSDS) is that latex B contains acrylonitrile (C-C≡N) group. However, energy dispersive spectrometer (EDS) measurements ($Fig$ 5) showed that no nitrogen could be detected near surface at low energy level of 7.5 kV while the latent carbon (lighter element than nitrogen) level was about -4 kcal/mol (Tunega et al. 2002).

However, energy dispersive spectrometer (EDS) at 7.5 kV. (Van Gilder, Purfeerst 1994). Our study shows that polymer (latex) chemistry has no significant influence on coating-ink chemical interaction. This is manifestly not true in current polymer chemistry (Kan, Van Gilder 2004). Thus, DIM is a better probe for chemical differences between coatings than hexadecane.

Surface energies of polymers have earlier been characterized in terms of dispersive and polar interactions (Wu, 1982). This approach was extended to the use of polar to the total surface energy ratio, $\gamma_s/\gamma_l$, and it was found that the higher $\gamma_s/\gamma_l$, the lower an oil-based ink setting rate was (Van Gilder, Purfeerst 1994). Our study shows that $\gamma_s/\gamma_l$ is sufficient for a full statistical analysis, it can be concluded from Table 6 that the lower $\gamma_s/\gamma_l$ tended to correlate with the longer $t_{\text{corr}}$. While this is in agreement with our previous studies, we emphasize that a higher value of surface energy parameter $\gamma_s\cos\theta$ at interface measured with non-polar solvent DIM resulted in a shorter $t_{\text{corr}}$.

Table 6. Summary of time to reach maximum tack, structural variable, surface energy parameter on Gibbs energy of imbibition (over pore size range of 0.03-0.195 $\mu$m) of all four coatings, determined by using diiodomethane.

<table>
<thead>
<tr>
<th></th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>Correlation, R</th>
</tr>
</thead>
<tbody>
<tr>
<td>$t_{\text{corr}}$, s</td>
<td>11</td>
<td>15</td>
<td>17</td>
<td>23</td>
<td></td>
</tr>
<tr>
<td>$\Sigma(\gamma/d)/m^2$, mJ/m$^2$</td>
<td>11.5</td>
<td>11.0</td>
<td>11.2</td>
<td>9.9</td>
<td>0.94</td>
</tr>
<tr>
<td>$\gamma^\circ\theta$, mJ/m$^2$</td>
<td>25.9</td>
<td>25.6</td>
<td>20.2</td>
<td>19.1</td>
<td>0.88</td>
</tr>
<tr>
<td>$\Delta G_i$, mJ/g</td>
<td>1202</td>
<td>1127</td>
<td>903</td>
<td>754</td>
<td>0.96</td>
</tr>
</tbody>
</table>

Fig 5. The key elemental analysis on coated sample C containing acrylonitrile (C-C≡N) group by energy dispersive spectrometer (EDS) at 7.5 kV.
not correlated to $t_{\text{max}}$, possibly due to the very low $\gamma^{\text{AB}}$ determined at $t = 0$ s. On the other hand, the correlation of $\gamma^{\text{AB}}$ and $\gamma$ with $t_{\text{max}}$ is rather consistent. This is not surprising because the coating surface energy, $\gamma$, was mainly determined by $\gamma^{\text{AB}}$ (Table 3), and dispersive forces are predominant in the ink oil imbibition into porous coatings. We note that the surface energy characterization methods used are different in the studies. This study directly characterizes coated board surface and pore structure with liquids while the previous studies characterize latex film alone with liquid contact angle, and inverse gas chromatography (IGC) in the Henry infinite dilution region. It has been suggested that IGC mainly assesses the high energy sites (Jacob, Berg 1994).

We recognize the complexity of contact angle hysteresis that has been a major subject in surface wetting in air and liquid environments (e.g. Marmur 1996, 2004), and that spreading of wetting line advances through kinetic and dynamic balances (Shanahan, 2001). Because of the small capillaries of inhomogeneous industrial coatings and variety ingredients of inks, in practice the Gibbs energy was calculated from measurements of drops of pure liquids of known surface energy on coated paper and board surfaces, assuming smooth, non-deformable and non-absorptive surfaces. Paper surface roughness effects on water drop drop spreading have been discussed in the literature (e.g., Modaresi, Garnier 2002; Werner et al. 2005). That the absorption of drops could be neglected in contact angle measurements was ensured by extrapolation of time-dependent contact angles to $t = 0$. This method is related to the front line of the advancing contact angle in capillary adsorption. If coating components, latex lattices in particular, swell during ink setting as proposed in previous studies (Xiang et al. 2004), our method may oversimplify latex and solvent interactions that are due to physisorption and/or chemisorption as a function of time. So far, we have not encountered difficulties by using contact angle at $t = 0$. This implies that due to the limit imposed by rheology coating ingredients are designed to be compatible, less strong polar interaction for example (Van Gilder 2004), and as such, our treatment is justified by those coating properties studied, and by the dispersive force predominance (loosely defined as physisorption) in coating and oil-base ink interactions.

Conclusions

Our results demonstrated that when both kaolin and latex chemistry were changed, the specific Gibbs energy concept that combines coating structure variables (volume and diameter, $\Sigma (V_i/D_i)m$) and surface energy parameters ($\gamma^{\text{p}}\cos \theta$) at the interface is a better method for the characteristics of capillary adsorption during oil-based ink setting than each parameter alone. Indeed, the change in latex chemistry contributed to both coating structure and surface energy changes. We found that the acid-base part of the surface energy ($\gamma^{\text{AB}}$) was low compared to the Lifshitz-van der Waals part ($\gamma^{\text{p}}$). We also observed that the Gibbs energy and capillary imbibition in offset ink setting was different for kaolins with constant $\gamma^{\text{p}}$ and different $\gamma$. This was seen in the different time needed to reach the maximum tack force, $t_{\text{max}}$, while there was no effect on the maximum tack force, $F_{\text{max}}$, and the final tack. We demonstrated that compared to styrene/n-butyl acrylate latex, n-butyl acrylate-acrylonitrile-styrene latex that lowered $\gamma^{\text{AB}}$ on coated board surface and the specific Gibbs energy, significantly increased $t_{\text{max}}$, and reduced $F_{\text{max}}$ and the final tack.

So far, we have demonstrated successful applications of Gibbs energy concept in the analysis of interactions of oil-based offset ink with porous coatings that with different contents of carbonates, kaolin and latex. We expect that such an approach may find applications in analyzing interactions of different porous coatings with polar and non-polar liquids.

Literature


