increased and gloss maintained while avoiding blister. The blister resistance of PCC is well documented (5, 6) and is something other small particle size pigments such as fine clay and ultra fine GCC have not demonstrated. Data from this study is shown in Appendix B.

In addition to the effects of moisture and temperature, the effect of differing calendering loads has also been studied. Mercury porosimetry shows that the coating pore volume decreases with calendering intensity. When using pigments that may need more pressure to reach a set level of paper gloss, or micro-smoothness, a decrease in overall porosity is expected in both the coating and base paper layers. Most reports on this subject focus on the final coated paper optics, strength, printability, and to some extent the mercury porosimetry showing the coating structure changes.

This paper will show that not only can the pore structure of the PCC coatings be maintained with moisture and pressure changes, but by taking advantage of both the inherent micro-smoothness of the small, aragonitic PCC, the pore structure of the substrate can also be maintained.

EXPERIMENTAL

The entire coating make-down, coating application and calendering process was performed on pilot scale at the Centre International de Couchage in Trois-Rivières, Quebec, Canada. Two different pigment systems were examined: a small particle size, narrow distribution aragonitic PCC and a medium, broader distribution ground calcium carbonate (GCC), both with Fine #1 clay. Please refer to Table I for a listing of each coating formulation and coating color characteristics. Characteristics of the pigments used for each coating are in Table II.

Table I – Coating Formulations

Coating #	1	2
PCC	70	
GCC		70
Fine #1 Clay	30	30
SBr Latex	14	14
Calcium Stearate	1	1
CMC	0.8	0.8
OBA	0.5	0.5
Dispersant	0.1	0.1
Application Solids, %	64.5	64.6
pH	8.69	8.56
Brookfield Viscosity, mPas @ 100 rpm	1394	1714
Hercules Hi-Shear Viscosity, mPas @ 4400 rpm	32.5	42.1
AA-GWR, gsm	218	206
Temperature, °C	30.8	31.6

Table II – Pigment Characteristics

	PCC	GCC	Fine #1 Clay
Average Particle Size, µm	0.42	0.68	0.21
Surface Area, m^2/g	11.7	12.4	22.3

Each coating color was adjusted to a pH of 8.5-9.0 as necessary. The application solids of the coatings were near 64.5% for both coatings. Each coating was applied at the target solids, achieving coated sheets without defects such as streaking, spitting or scratching.

The base paper used for this study was 62 gsm woodfree paper. The target coat weight was 14 gsm per side, applied via jet/blade. The blade used was 0.457mm with 45° bevel. For each coating formulation, the web was dried to three different moisture levels, targeting final sheet moistures of 5, 6 and 7% at the reel. The different moisture levels were reached through decreased drying in the floatation dryer sections as required.

Calendering was performed using an 11-nip supercalender at 400 m/min. Each coating at each moisture level was calendered at a set line load of 396 kN/m. Calendering load was also varied for each point to reach a target gloss. The target gloss was determined from the gloss achieved with the PCC formulation at 5% reel moisture. The temperature used for zones 1-3 remained at 90°C through all of the conditions.

Printing was performed at the Rochester Institute of Technology (RIT), in Rochester, NY, USA. The samples were printed HSWO on a Heidelberg Sunday® 2000 press. Blister resistance was successful for each of the trial points evaluated. No blistering was observed within the print surface, including those having a solid ink layer, for any of the trial points examined.

Paper testing was performed in constant temperature and humidity conditions according to TAPPI standards. Each property was tested by measuring 6 test points on 6 coated sheets (36 total measurements). The properties which were tested in this manner include gloss, opacity, brightness, roughness, porosity, caliper, print gloss and basis weight. Sheet bulk was calculated from values obtained from caliper and basis weight testing (bulk = caliper / basis weight *25.4). The print gloss and optical density testing was performed on printed samples from HSWO printing performed at RIT.

The target moistures at the reel after coating were 5, 6 and 7%. The moisture was adjusted to reach target levels as measured by an on-line scanner at the winder after coating. The reel moistures decreased significantly after calendering, changing the post coater moisture by approximately 2 to 3%. The final sheet moistures after calendering ranged from about 3 to 4%. The target moisture level, on-line scanner moisture at the winder after coating, and on-line scanner moisture after calendering were recorded for each trial point, and are shown in Table III. Results will be discussed using the pre-calendering moisture values as measured by the on-line scanner.

Table III – Online-Scanner Moisture of the Coated Paper after Coater & after Calendering

Pigment Slip	70/30 PCC/Clay			70/30 GCC/Clay		
Target Moisture After Coating	5	6	7	5	6	7
% Moisture, After Coater	5	5.8	6.6	4.9	6.0	6.8
% Moisture After Calendering	3.2	3.4	3.7	3.2	3.4	3.8

Aside from steps taken to wrap the reels in plastic directly after calendering until printing, no further efforts were made to control the moisture, and all comparisons are made based on the on-line scanner data.

This study was performed initially to determine how much of an advantage the open coating structure of a PCC coating had relative to the blistering in heat set web offset printing. Improved blister resistance was expected. One outcome that was not anticipated was a distinct shade differences between PCC and GCC coated paper at equal moisture content after calendering to an equal gloss target. The appearance of coated, calendered paper suggested that fiber crushing/calender blackening had occurred as moisture levels were increased, but to different extents between the PCC and GCC coatings. As this would be largely independent of coating compaction, an examination of the different coated papers and the substrate porosity through Mercury porosimetry was performed as a means of determining how the fiber structure of the paper below the coating was affected with increasing moisture. This report will detail the findings from that examination.

RESULTS

Quality coated gloss is dependent on two factors, micro-smoothness and macro-smoothness. Macro-smoothness is determined by the base paper. Deformation of the base can be achieved through a combination of variables such as pressure, temperature, and moisture. As Vreeland showed, by using a high enough temperature and moisture content, the Tg of the fiber could be used to mold the fiber to the coating. Vreeland (2) describes this equation, where

$$Tg = 234.2e^{-0.131m}$$

Tg = the glass transition temperature under the dynamic and moisture conditions existing in the nip, °C
e = the base of the natural logarithm
m = moisture content of the fibers in the web in % of the bone dry weight of the fibers

Using this equation and the moisture levels examined in this study, the Tg for each condition to reach cellulose Tg and mold to the coated surface was calculated (Table IV).

Table IV – Calculated cellulose Tg for moistures used for each coating

Coating #	1	2
Pigment	PCC	GCC
1st Moisture Level, %	5.0	4.9
Tg at 1st Moisture, °C	121.6	123.2
2nd Moisture Level,	5.8	6.0
Tg at 2nd Moisture, %°C	109.5	106.7
3rd Moisture Level, %	6.6	6.8
Tg at 3rd Moisture, °C	98.6	96.1

Vreeland’s equation for Tg predicts that there should be no deformation or loss of pore structure of the base sheet through thermal means. The calendering temperature used in this study was 90°C. Only at the highest moisture level used, targeting 7% off the reel of the coater, did the calculated cellulose Tg approach the temperature used during calendering. Both the PCC and GCC coating formulations had a cellulose Tg 5-10°C over the calender temperature used. Thus, the paper did not reach the predicted threshold necessary to reach thermal deformation.

Following the prediction that the deformation of the base will not occur through thermal means, the mercury intrusion shows that, as moisture is increased and pressure *decreased* to reach the equivalent gloss of the low moisture control, the pore volume of both the base and the coating can be maintained with the PCC coatings from 5-7% moisture. The GCC coatings did deform as moisture increased above 5%, starting at 6% and deforming even more at 7%. Refer to Figures 1 and 2.

The coated sheet porosity as measured with the Hagerty device also demonstrated that the total coated sheet porosity is maintained as moisture changes (Figure 3). If calendering is performed using a target line load, the total sheet porosity does change with increased moisture, as shown in Figure 4. The coated sheet porosity with the GCC coating is much more affected by increased moisture compared to the PCC coating. The overall change in coated sheet porosity from the low to high moisture level was 650 sec for GCC and 150 sec for PCC. Tables V and VI show the gloss and porosity averages and standard deviations of each of the trial points used in Figures 3 and 4. For additional details on testing methods, please refer to the Experimental section.

Figure 1 – Mercury Porosimetry: PCC Coating Calendered to 84 Sheet Gloss as Moisture Increases

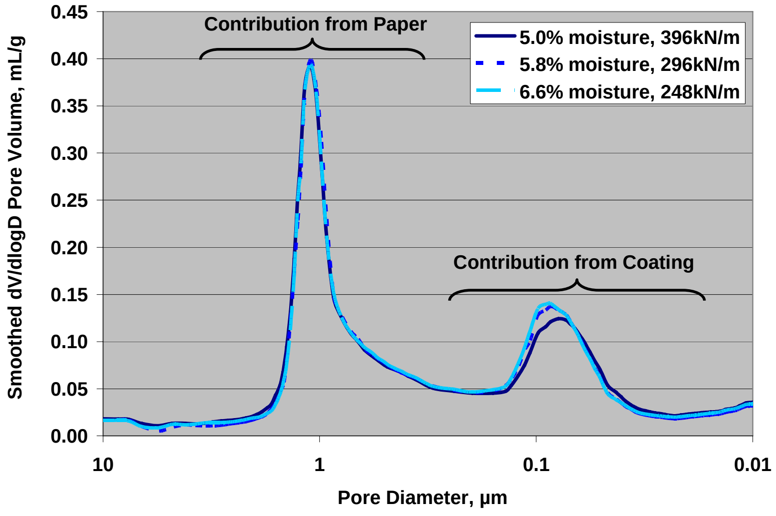


Figure 2 – Mercury Porosimetry: GCC Coating Calendered to 84 Sheet Gloss as Moisture Increases

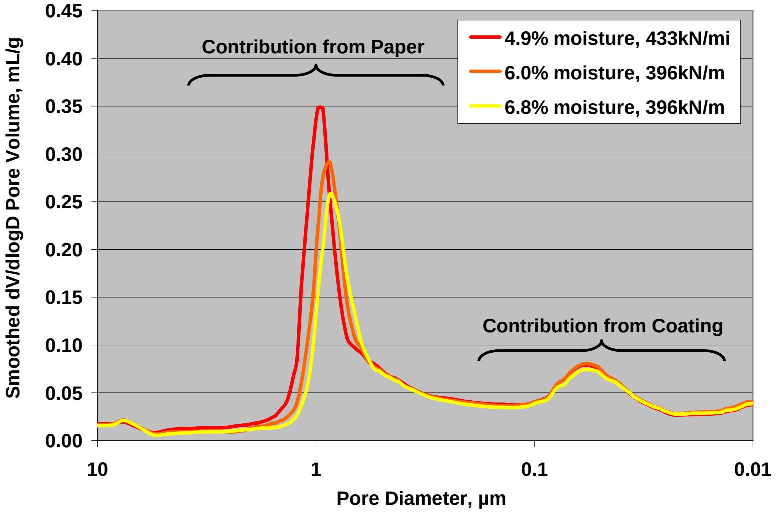


Figure 3 – Sheet Porosity as a Function of Moisture when Calendering to Equal Gloss

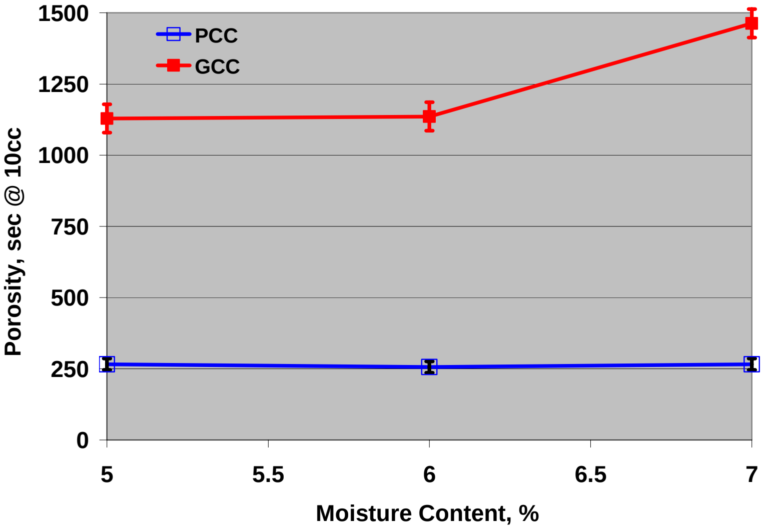


Table V – Gloss and Porosity Measurements when Calendering to Equal Gloss

Pigment Slip	70/30 PCC/Clay			70/30 GCC/Clay		
% Moisture, After Coater	5	5.8	6.6	4.9	6.0	6.8
Sheet Gloss						
Average, %	84.4	83.9	83.4	84.2	84.3	84.5
Standard Deviation	0.570	0.366	0.380	0.368	0.647	0.511
Haggerty Porosity						
Average, seconds @ 10mL	266	256	266	1129	1136	1463
Standard Deviation	4.9	5.0	6.2	47.8	29.8	47.8

Values correspond to those illustrated in Figure 3

Figure 4 – Sheet Porosity as a Function of Moisture when Calendering at Constant Line Load

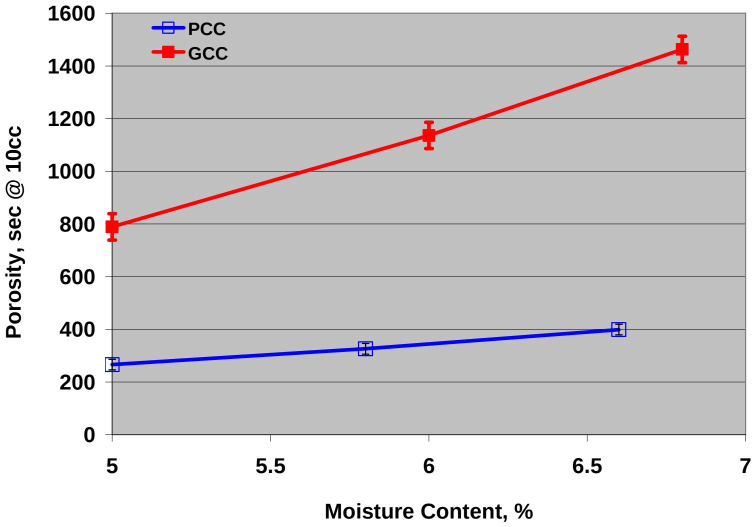


Table VI – Gloss and Porosity Measurements when Calendering at Constant Line Load

Pigment Slip	70/30 PCC/Clay			70/30 GCC/Clay		
% Moisture, After Coater	5	5.8	6.6	4.9	6.0	6.8
Sheet Gloss when Calendering at Constant Line Load						
Average, %	84.4	86.4	87.3	81.8	84.3	84.5
Standard Deviation	0.570	0.326	0.219	0.616	0.647	0.511
Haggerty Porosity						
Average, seconds @ 10mL	266	326	399	789	1136	1463
Standard Deviation	4.9	6.8	7.1	27.1	29.8	47.8

Values correspond to those illustrated in Figure 4

Although the thermal deformation calculations do not predict a loss of pore volume, some deformation of the base does occur if calendering conditions are changed. Figures 5 and 6 show the decrease in pore volume of both the coating and the paper regions as the coated paper moisture increased when calendering to an equivalent line load (396 kN/m). This decrease in pore volume was very similar for both the PCC and GCC coatings as moisture increased. The GCC coating decreased from 0.39 to 0.26 mL/g in pore volume, and PCC coating decreased from 0.39 to 0.29 mL/g over the same moisture range.

Figure 5 – Mercury Porosimetry: PCC Coating at Constant Line Loading with Increasing Moisture

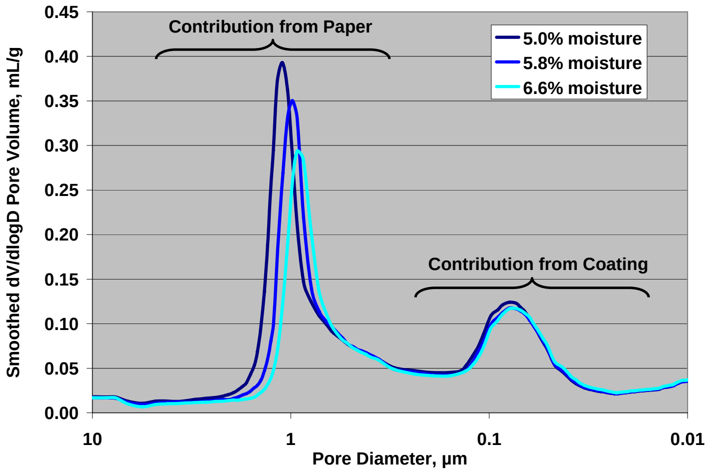


Figure 6 – Mercury Porosimetry: GCC Coating at Constant Line Load with Increasing Moisture

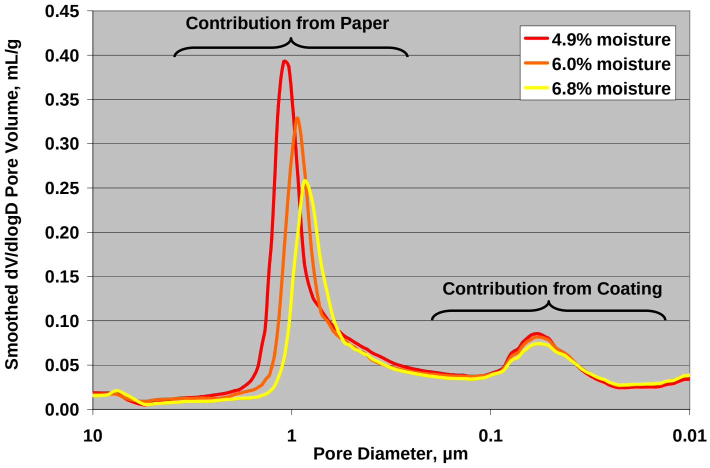


Figure 7 – Gloss as a Function of Moisture at Constant Line Loading

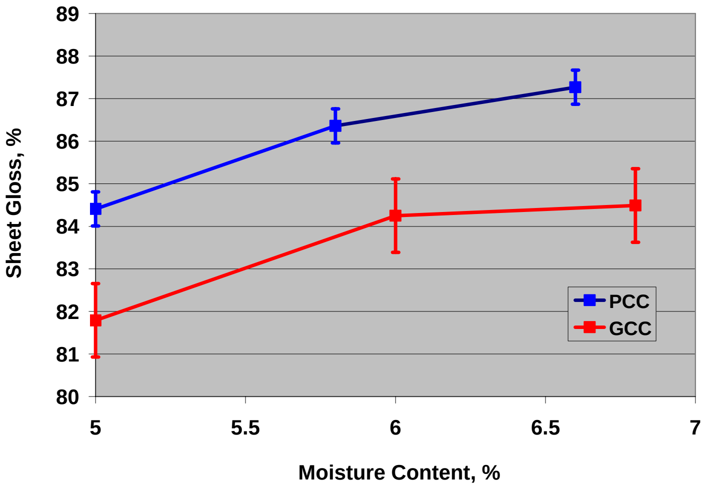
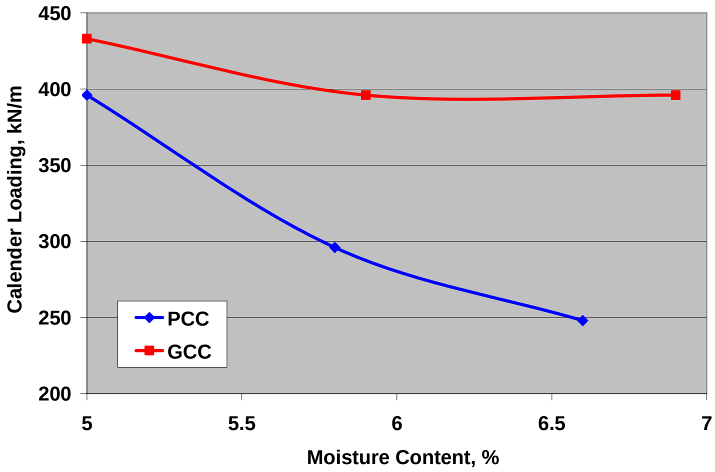


Figure 8 – Calendering Pressure as a Function of Moisture Content at Equal Gloss



The change in gloss is then attributed to a combination of pressure and moisture alone. Both the PCC and GCC coatings were calendered at equal line load and to equal gloss. As shown in Figure 7, the coated paper gloss of the PCC coating was much higher than that of the GCC at equal line load as moisture increased. This indicates that lower line loads could be used to reach target gloss compared to the GCC coating, which is illustrated in Figure 8.

The conclusion is that the PCC generates gloss more quickly, and that extra deformation from the base is not necessary. GCC still requires higher pressures to reach target gloss because more pressure must be used to attain good micro-smoothness in the coating layer, indicating that base deformation is necessary to reach good micro-smoothness and gloss with GCC. This concept is demonstrated through bulk and porosity. At equal calender loading, both bulk and porosity decreased with increasing moisture (Figure 9). When calender loading is adjusted to attain equal gloss, the sheet porosity and bulk are maintained with the PCC coating, but not with the GCC coating (Figure 10). Tables VII and VIII show the sheet bulk averages and standard deviations for each of the trial points used in Figures 9 and 10. For additional details on testing methods, please refer to the Experimental section.

Figure 9 – Sheet Bulk as a Function of Moisture Content at Constant Line Load

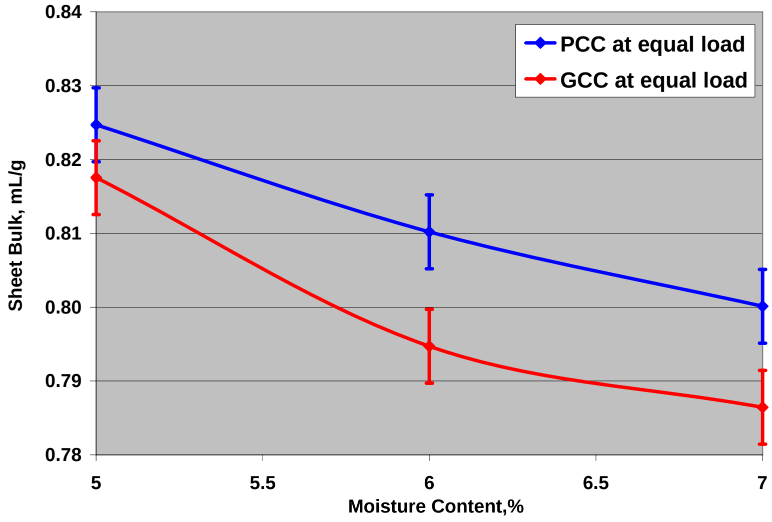


Figure 10 – Sheet Bulk as a Function of Moisture Content at Equal Gloss

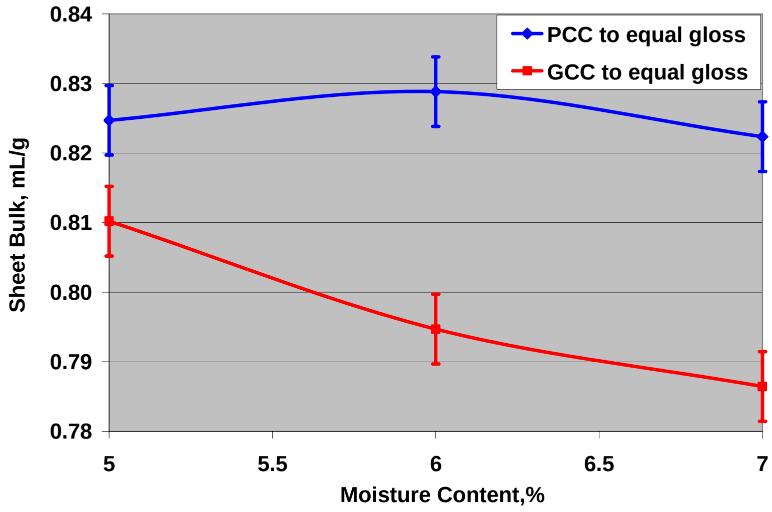


Table VII – Sheet Bulk Calculated when Calendering at Constant Line Load

Pigment Slip	70/30 PCC/Clay			70/30 GCC/Clay		
% Moisture, After Coater	5	5.8	6.6	4.9	6.0	6.8
Sheet Bulk, mL/g						
Average, seconds @ 10inL	0.825	0.810	0.800	0.818	0.795	0.786
Standard Deviation	0.012	0.010	0.016	0.008	0.010	0.011

Values correspond to those illustrated in Figure 9

Table VIII – Sheet Bulk Calculated when Calendering to Equal Gloss

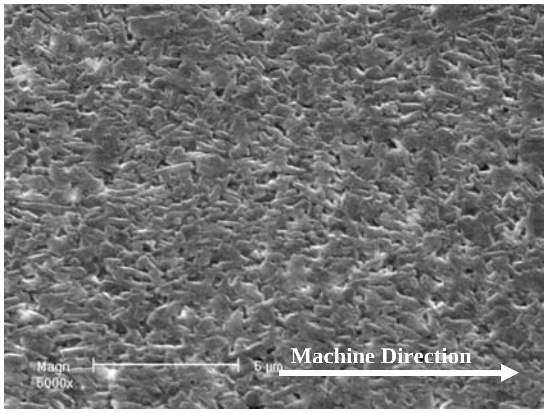
Pigment Slip	70/30 PCC/Clay			70/30 GCC/Clay		
% Moisture, After Coater	5	5.8	6.6	4.9	6.0	6.8
Sheet Bulk, mL/g						
Average, seconds @ 10inL	0.825	0.829	0.822	0.810	0.795	0.786
Standard Deviation	0.012	0.005	0.015	0.008	0.010	0.011

Values correspond to those illustrated in Figure 10

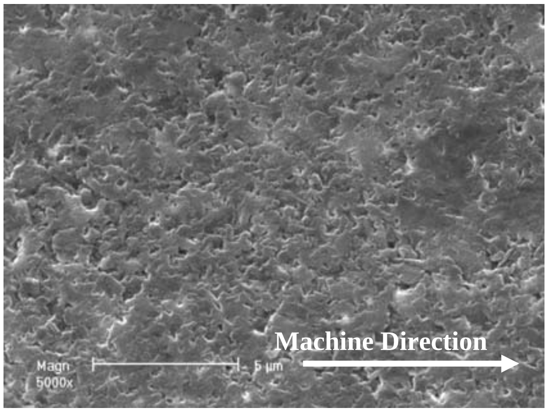
Micro-smoothness is derived from the coating pigments (1). Three conditions need to be met to attain good micro-smoothness from the pigments. First, there should be an alignment of pigment particles. There should be no large particles present, and last, shrinkage during immobilization should be minimized.

Aragonite PCC particles align in the shear field of the blade. By the very nature of the precipitation process, fine PCC, which has narrow particle size distribution PCC, has few coarse particles. Additionally, with the high aspect ratio of the particle, the particle alignment is maintained upon consolidation. Also, due to the inherent pore structure that narrow particle size distribution pigments provide, the structure is maintained during consolidation.

Figure 11 – SEMs of PCC and GCC Coated Paper Surface



Coated Paper with PCC at 5000 magnification



Coated Paper with GCC at 5000 magnification

GCC coatings have a random arrangement of particles at application, with very large and very small particles present. After immobilization, a random particle arrangement still exists, and particle alignment is not possible. The large pigment particles are still present, and the consolidation of particle during immobilization results in a compacted structure. These concepts are illustrated in Figures 12 and 13.

Figure 12 – PCC Particles Represented Before and After Immobilization

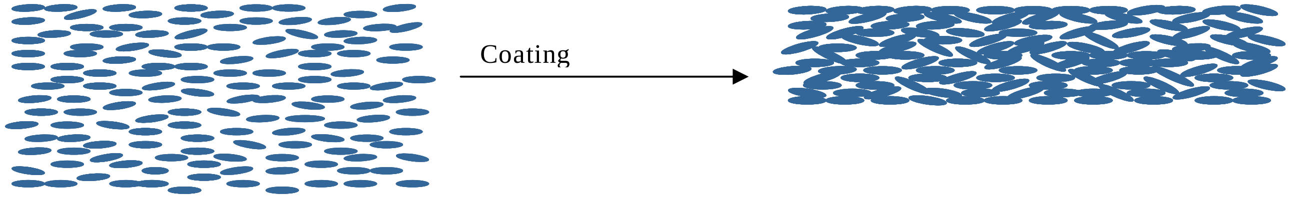
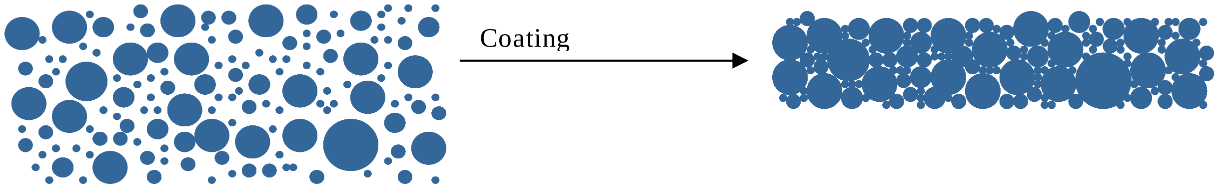


Figure 13 – GCC Particles Represented Before and After Immobilization



The result is that aragonite PCC pigments already achieve improved micro-smoothness through particle alignment, absence of large particles and preservation of the particle structure during immobilization. GCC pigments cannot achieve particle alignment because they have an aspect ratio very close to 1; have large particles present due to the broader distribution and consolidation of particles during immobilization. To improve the smoothness of GCC comparable to PCC, more severe process steps are required. This means that base paper deformation is required through higher calender pressures. As was previously shown in

Figure 7, PCC had much higher gloss with increased moisture at equal line load, and in Figure 8, had much lower line loads to reach the same gloss target compared to GCC. The result is that there is already inherent micro-smoothness with PCC present, and that smoothness and gloss are naturally more attainable without excess calendering of the base paper.

CONCLUSIONS

The pore volume of both the coating and paper substrate can be preserved during calendering through the use of increased moisture in conjunction with PCC. Negatives such as fiber crushing, blister, stiffness and loss of density can be avoided with aragonite PCC due to the ability of the PCC to maintain the coating structure during immobilization combined with the improved micro-smoothness resulting in a lesser need for calendering compared to other pigments such as GCC and clay.

ACKNOLEDGEMENTS

Discussions with Douglas Donigian were particularly valuable in conducting and preparing this research, and are very much appreciated. Time and talents of the team at CIC, the Web Offset team at RIT, Kimmo Huhtala and Bruce Evans of Specialty Minerals Inc. are also appreciated

REFERENCES

1. Oittinen, P., Limits of Gloss in Prints, No. 11, 1983 Paperi ja Puu, p. 718.
2. Vreeland, J., U.S. Patent No. 4,634,744 “Method of Finishing Paper Utilizing Substrata Thermal Molding”, Nov. 25, 1986.
3. Vreeland, J., U.S. Patent No. 4,749,445 “Method of Finishing Paper Utilizing Substrata Thermal Molding”, July 7, 1988
4. Linnonmaa, P., Todorovic, A., Roman, N., Donigian, D. and Ma, D. “Calendering Thermal and Moisture Effects on LWC Paper with Precipitated Calcium Carbonate Coating Applied by Metered Size Press”, TAPPI Metered Size Press Forum, 2002.
5. Dimmick, A. and Huhtala, K., “Quality Performance Using Increased Moisture Content at the Reel with Woodfree Coatings”, 2005 TAPPI Coating & Graphics Arts Conference Proceedings, April 2005.
6. Lehtinen, G., Aarni, E., Rajala, P. and Anderson, J., “Evaporation Energy Demands of Coatings Formulated with Calcium Carbonate Pigment”, TAPPI Coating Conference 2002.
7. Abrams, L. , Capano, P., Favorite, C., and Johnson, R., “Using Mercury Porosimetry to Characterize Coating Pore Structure and its Relation to Coating Optical Performance”, 1996 TAPPI Coating Conference Proceedings, p. 185 (1996)
8. Page, D.H., Seth, R.S. and De Grace, J.H., “The Elastic Modulus of Paper”, TAPPI Journal, September 1979, Vol. 62, No. 9, page 99.
9. Johnson, R., Abrams, L., Maynard, R. and Amick, T., “Use of mercury porosimetry to characterize pore structure and model end-use properties of coated papers – Part I: Optical and strength properties”, TAPPI Journal, Vol. 82, No. 1, p. 239.
10. Zhang, Z.R., Wygant, R. and Lyons, A., “A fundamental approach to understand the relationship between top coat structure and paper performance”, 2001 TAPPI Journal Peer Reviewed Paper, March 2001.

APPENDIX A

Materials used for the coating formulations included the following: OPACARB® A40 Precipitated Calcium Carbonate (registered trademark of Specialty Minerals Inc.’s affiliate in the U.S. and other countries), Hydrocarb® 90 GCC, Hydragloss® 90 Fine No. 1 coating clay, Dow XU 31294.5 latex, FinnFix® 10 Carboxyl Methyl Cellulose, Devflo™ 50 calcium stearate lubricant, Blancophor™ P optical brightener and Dispex® N-40 dispersant. Other named trademarks are owned by their respective owners.

APPENDIX B

Data and Figures from Dimmick, A. and Huhtala, K., “Quality Performance Using Increased Moisture Content at the Reel with Woodfree Coatings”, 2005 TAPPI Coating & Graphics Arts Conference Proceedings, April 2005

Full optical and physical testing, printing and print register as well as blister analysis were performed and demonstrated within the above reference to support statements made in the current work. Please refer to that paper for additional details.

Pigment Slips Used for Pilot Coater Application

Coating #	*1*	*2*	*3*	*4*	*5*
Narrow Particle Size Distribution PCC	*70*			*100*	
Broad Distribution GCC		*70*	*30*		*100*
Fine #1 Glossing Clay	*30*	*30*	*70*		

Online-Scanner Moisture of the Coated Paper after Coater & after Calendering

Pigment Slip	70/30 PCC/Clay			70/30 GCC/Clay			30/70 Clay/GCC			PCC		GCC		
Target Moisture After Coating	5	6	7	5	6	7	5	6	7	5	6	5	6	7
% Moisture, After Coater	5	5.8	6.6	4.9	6.0	6.8	5.0	5.9	6.7	5.0	6.1	5.0	6.0	6.8
% Moisture After Calendering	3.2	3.4	3.7	3.2	3.4	3.8	3.3	3.6	3.9	3.2	3.4	3.4	3.6	3.9

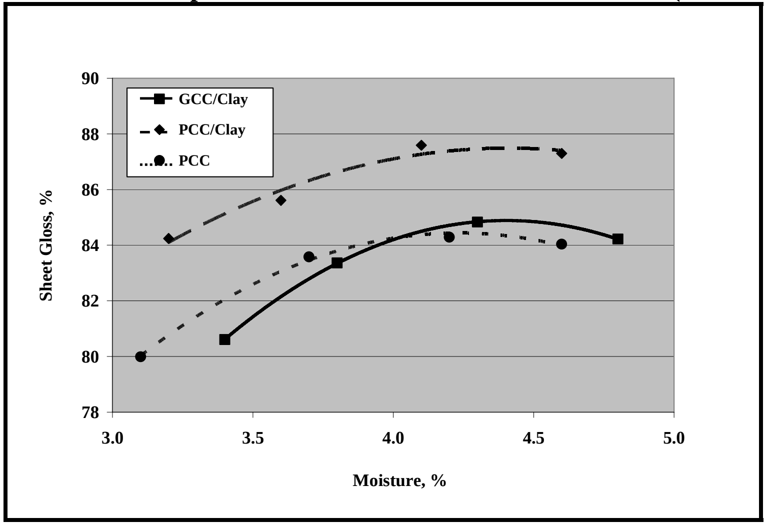
Note: A shortage of paper during the all-PCC coating trial point resulted in the loss of data for the 7% moisture level.

Line Load Comparison during

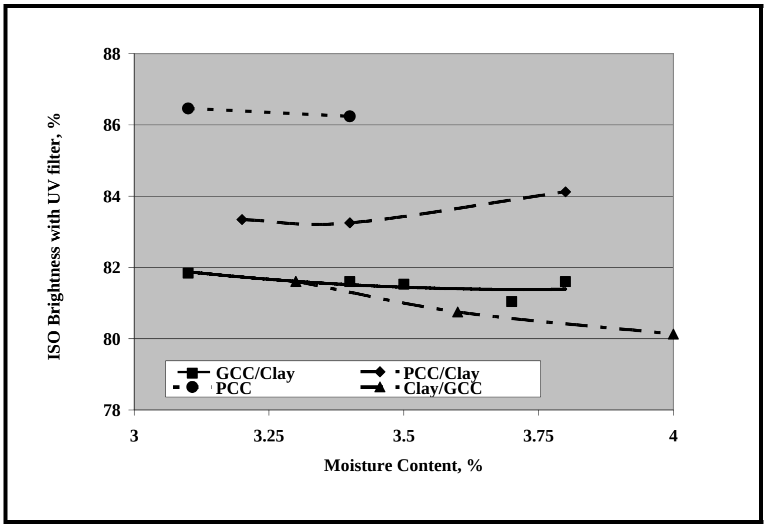
Pigment Slip	70/30 PCC/Clay			70/30 GCC/Clay			30/70 Clay/GCC			PCC		GCC		
% Moisture after Coating	5	5.8	6.6	4.9	6.0	6.8	5.0	5.9	6.7	5.0	6.1	5.0	6.0	6.8
% Moisture After Calendering	3.2	3.4	3.7	3.2	3.4	3.8	3.3	3.6	3.9	3.2	3.4	3.4	3.6	3.9
Gloss at Constant Line Load, 343 kN/m	84.4	86.4	87.3	81.8	84.3	84.5	88.6	88.9	90.3	81.9	83.9	71.6	73.8	76.6
Line Load to reach Target Gloss, kN/m	396	296	248	433	396	396	248	248	248	433	396	>433	>433	>433

Note: A shortage of paper during the all-PCC coating trial point resulted in the loss of data for the 7% moisture level.

Coated Sheet Paper Gloss as a Function of Sheet Moisture (at constant calender pressure)



Increasing Moisture vs. TAPPI Opacity of Coated Paper Calendered to Equal Gloss



Increasing Moisture vs. ISO Brightness of Coated Paper Calendered to Equal Gloss