5 Struktur gebende Calciumcarbonate und der Einfluss des Streichfarbenfeststoffgehalts auf die Papiereigenschaften Structure Giving Calcium Carbonates and the Influence of Coating Colour Solids on Paper Performance

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Zusammenfassung/Inhalt
Das Hauptziel dieser Studie bestand darin, Laufverhalten und Papierqualität verschiedener Calciumcarbonate mit enger und breiter Korngrößenverteilung über einen weiten Feststoffgehaltsbereich zu vergleichen. Dabei wurde das Wasserrückhaltevermögen aller Streichfarben auf ein gleiches Niveau eingestellt, um vergleichbare Bedingungen für alle Versuchspunkte zu schaffen.
Die Ergebnisse dieser Studie zeigen, dass Papiereigenschaften wie Weiße, Opazität, Papierglanz, Rauhigkeit und Druckglanz nicht signifikant vom Feststoffgehalt der Streichfarbe abhängen, wohl aber von der Partikelform und der Partikelgrößenverteilung des verwendeten Pigments. Die beste Papierqualität wurde in dieser Studie mit einem aragonitischen PCC mit enger Korngrößenverteilung erzielt.

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Abstract

There currently exist many structured and engineered pigments for paper coating, with new technologies for producing these pigments emerging frequently. As they become available for use, the knowledge of how to use these special pigments is imperative. Thus, a solids-performance relation was examined for precipitated calcium carbonate and ground calcium carbonate pigments, including a narrow particle size distribution (psd) aragonite precipitated calcium carbonate, a narrow psd calcite precipitated calcium carbonate, and ground products consisting of a narrow psd ground calcium carbonate, and a broad ground calcium carbonate. The results of this study indicated that there were no appreciable effects of the dilution of coating colours on optical coated paper performance when using high levels of precipitated calcium carbonate or ground calcium carbonate coating colours. The coated paper properties remained consistent over a 4%-units solids decrease. Previous work had demonstrated a decline in optical performance with lower coating colour solids. By controlling the key properties such as viscosity, water holding and immobilisation in this study, the performance of each pigment could be maintained despite coating colour dilution. These results demonstrate that narrow particle distribution pigments such as precipitated calcium carbonate can give enhanced coated sheet performance, even when used at lower coating solids, if attention is given to the rheology and water holding character of the coating. This means that different calcium carbonates can perform well with less than maximum applicable coating colour solids.

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1 INTRODUCTION

In high glossing grades, the availability of different structured or engineered pigments are becoming more prevalent. With these improvements in process technology, the application performance of these pigments can often become more challenging. This is certainly true with the increasingly narrow psds offered today. These changes in pigment characteristics may necessitate more care in designing the overall coating colour system, with specific attention to coating colour characteristics and coater parameters to optimise both coater runnability and end paper performance.

With these facts in mind, this study was designed to examine an array of calcium carbonates chosen to represent the different psds and morphologies used in the industry, while controlling the coating colour rheology, water holding and drying conditions. The main goal of controlling these key parameters was to optimise the potential of each calcium carbonate. Previous work had been done to compare a variety of different precipitated calcium carbonate (PCC) and ground calcium carbonate (GCC) coatings in a range of applications coating solids without accounting for the differences in rheology, water holding or pilot coater drying conditions (1, 2). By controlling the coating characteristics and application, this study would determine whether the trends previously seen with decreasing coating colour solids would be maintained with optimised coating colour and coater conditions.

Coater runnability and paper performances of calcium carbonates with narrow and broad psds were compared using a wide range of coating colour solids. This led to the ability to examine the calcium carbonate performance as a function of solids while using real-life applications and conditions.

2 EXPERIMENTAL

2.1 Pigments

The pigments used for this study consisted of four different calcium carbonate varieties: narrow aragonite PCC, narrow calcite PCC, narrow GCC, and broad GCC. Table 1 shows some of the physical properties of each of the calcium carbonate pigments examined. Each of these pigments is a commercial product, and possesses properties representative of what is commonly used in industry. Below are the distribution characteristics and Scanning Electron Microscope (SEM) images of each of the calcium carbonates used in this study (Figures 1 and 2).

Table 1: Pigment characteristics

Pigment Type	**Narrow Aragonite PCC**	**Narrow Calcite PCC**	**Narrow GCC**	**Broad GCC**
Average Particle Size, µm	**0,40**	**0,65**	**0,72**	**0,73**
Surface Area, m^2/g	**12,8**	**7,6**	**10,1**	**12,3**

Figure 1: Cumulative Mass Percent vs. Diameter

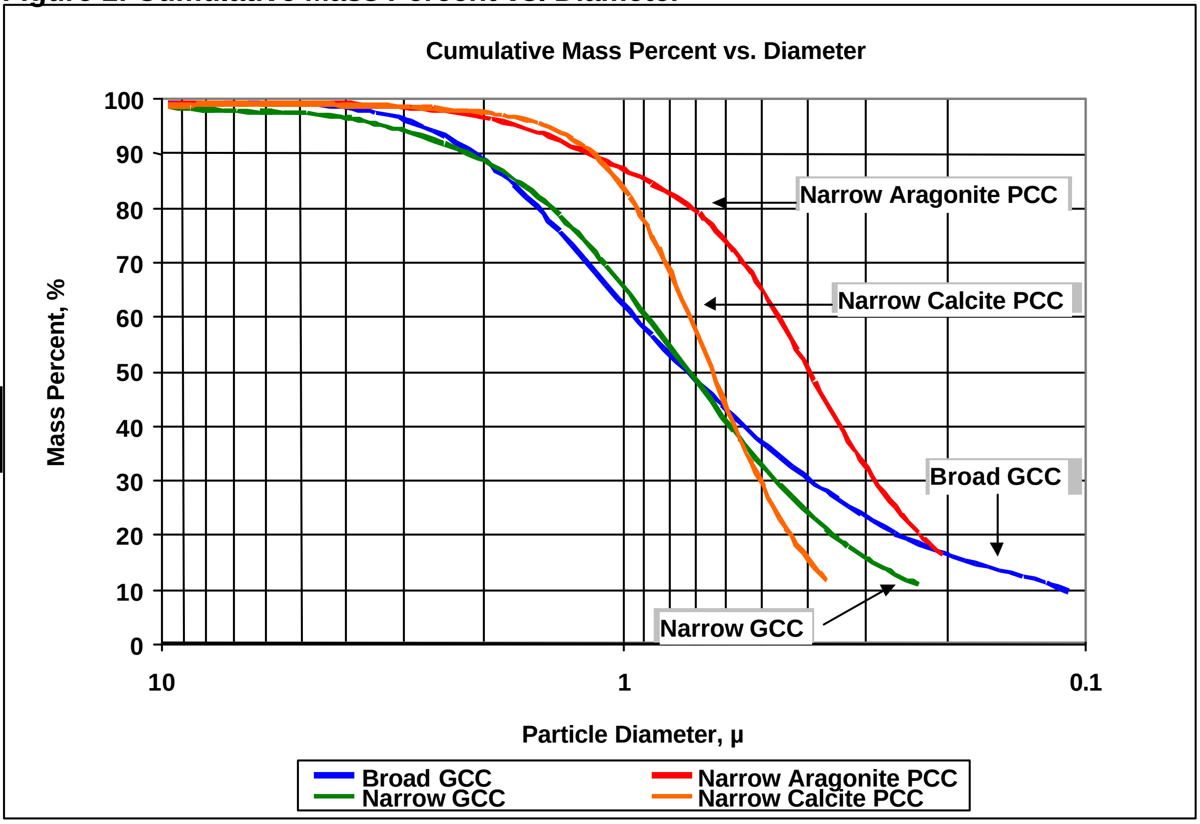
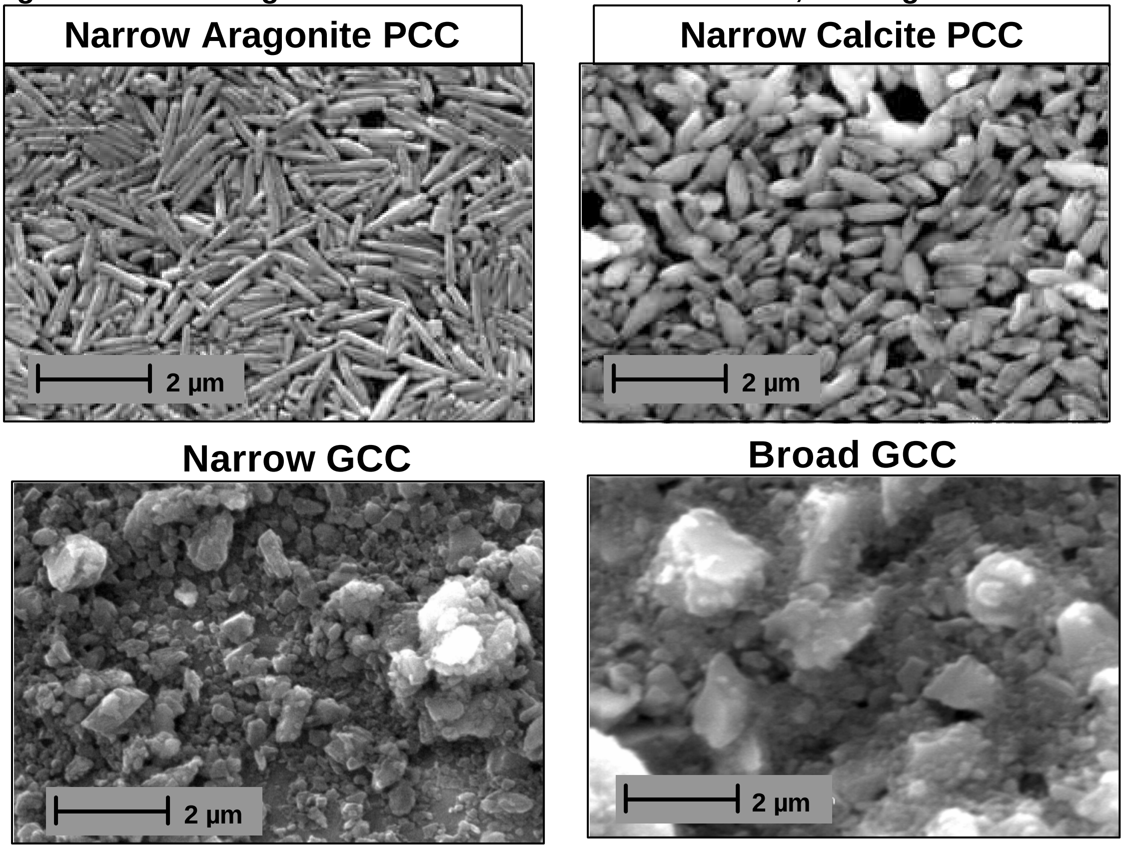


Figure 2 – SEM Images of Calcium Carbonates Used at 10,000 Magnification



2.2 Base paper

The woodfree base paper used in this study was mill precoated with blade, using a coarse GCC. Basic characteristics of the precoated paper are summarised in Table 2.

Table 2: Precoated paper properties

Dry Basis Weight	**86 g/m²**
Brightness	**88,9%**
Roughness PPS-10	**3,9 µm**
Opacity	**93,1%**

2.3 Coating Formulation

The coating formulation used throughout the study consisted of 80 parts calcium carbonate and 20 parts High Glossing clay. The binder and additive system included 12 parts SBA latex, 1 part Calcium Stearate, 0.8 part Carboxyl Methyl Cellulose, 0.5 part optical brightening agent, and 0.1 part dispersant.

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An alkali swellable acrylic polymer dispersion was used with each formulation to adjust the coating viscosity and water retention to a control target range for each coating colour solids application. The low shear viscosity target was 1500 cps as measured by Brookfield viscosity at 100 rpm.

2.4 Coater Application

The coating application was performed at the Centre International de Couchage in Trois-Rivierès, Quebec Canada. Each coating colour was applied to a European-style precoated woodfree base paper with a total dry basis weight of 86 g/m². The coater used was a Valmet Autoblade with jet applicator and blade. The blade thickness was 0,457mm with a bevel angle of 45^o for each trial point. The coating colours were applied at make-down coating solids and diluted until acceptable runnability was achieved. The acceptability of the coating performance is defined here as a clean blade with little/no build-up and a lack of scratching. A series of four different coating colour solids levels were run for each calcium carbonate formulation. The maximum runnable coating solids with each calcium carbonate determined the coating colour solids range for each series. Using the maximum as a starting point, the coatings were diluted by 1%-1,25%-units increments and applied.

Inherent differences in coating colour immobilisation were expected due to the differences in calcium carbonate distribution and particle size. To eliminate these immobilisation differences in the resulting coated paper properties, the drying was controlled throughout the coating process to keep the point of coating immobilisation for each trial point at the same place on the coater, and to dry each coated sheet with the same degree of intensity.

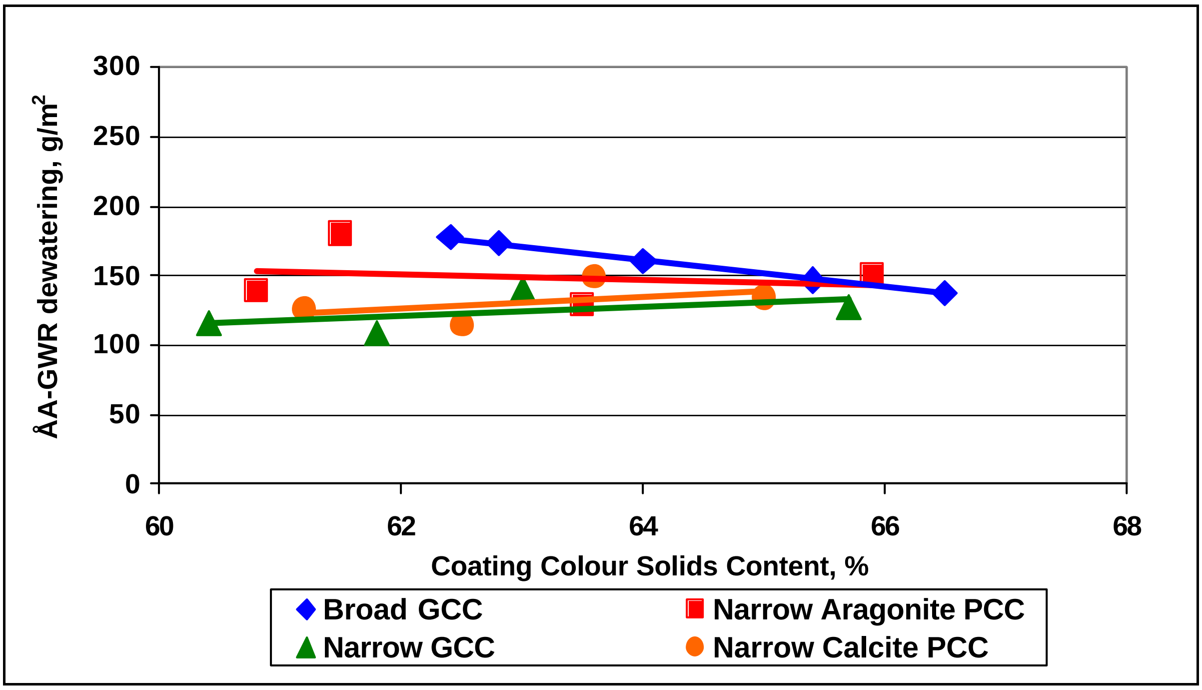
The coating was applied at 1500 m/min with 12 g/m² per side of paper. Target sheet moisture for the first side was 3,5% and for the second side 5,3%. An 11 nip off-line supercalender was used to calender the rolls. All the trial points were calendered at 400 m/min with three different nip loads (248 kN/m, 341 kN/m, 433 kN/m). Paper testing was performed on the coated paper according to TAPPI standards.

3 RESULTS & DISCUSSION

3.1 Coating Colour Characteristics & Coater Runnability

Controlling the water holding to a certain level for all colours was one key point in this study. Two different thickeners were used to accomplish this. The first was Carboxyl Methyl Cellulose, which was used at equal levels for each formulation regardless of pigment particle size, psd, or the coating colour solids. The second thickener used was an alkali swellable acrylic polymer. The polymer was used to adjust each coating colour to target viscosity and water holding without changing coating colour solids. Except for the series with broad psd GCC, where no acrylic polymer was needed, between 0,1 and 0,4 parts of the acrylic polymer was necessary to adjust the water retention and viscosity. Despite the large differences in coating solids content (a variation of about 6%-units), the water retention was adjusted to a fairly constant level. Figure 3 shows the water retention properties for all colours used in this study.

Figure 3: Water retention vs. Coating Colour Solids



Control of viscosity accompanied the control of the water retention. Figure 4 and Figure 5 summarise the low and high shear viscosity as a function of solids for all colours. Values for Brookfield viscosity scattered around 1500 mPas over the investigated solids range, with one outlying point. The exception was the trial point with broad psd GCC at the maximum applied coating colour solids, where the Brookfield viscosity reached 2100 mPas. Otherwise, the remainder of the trial points for each of the calcium carbonates examined over all of the coating colour solids levels was fairly close.

Figure 4: Brookfield Viscosity vs. Coating Colour Solids Content

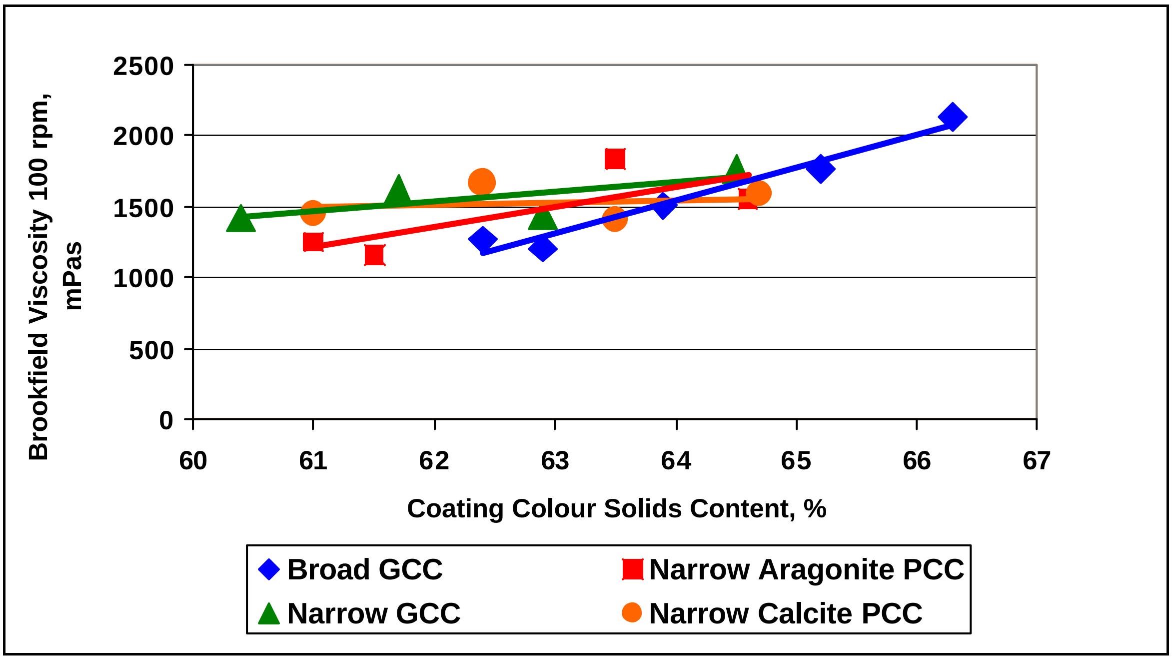
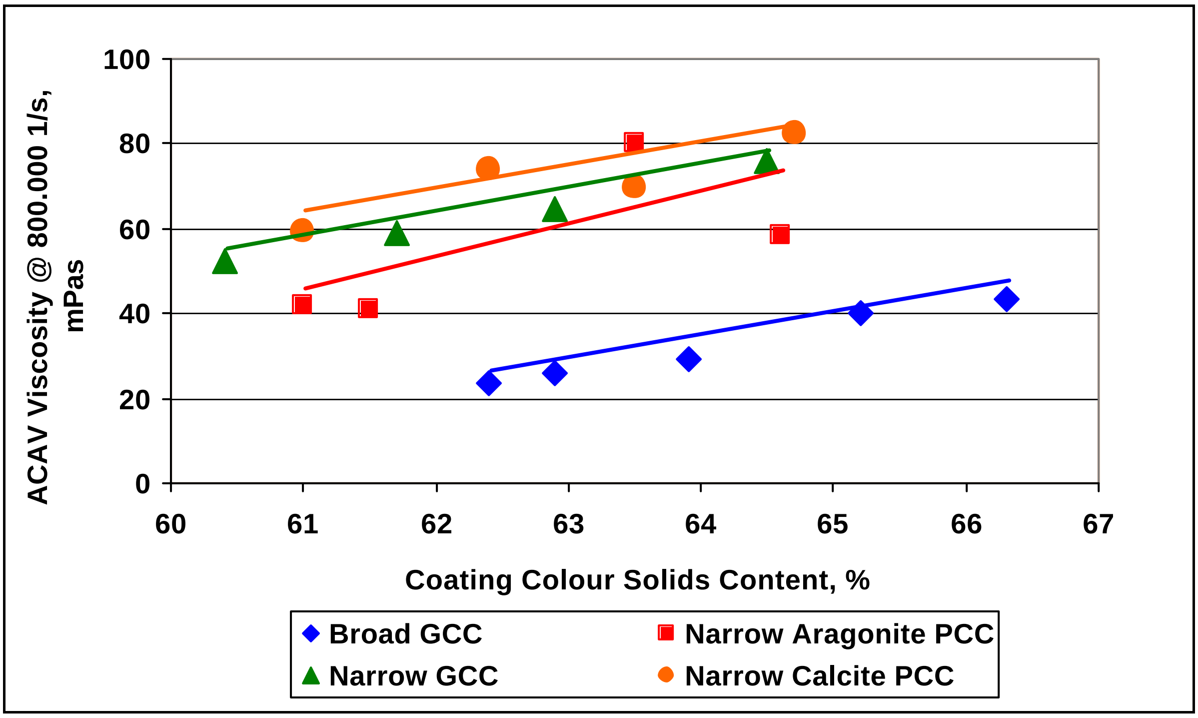


Figure 5: High shear viscosity vs. coating colour solids content



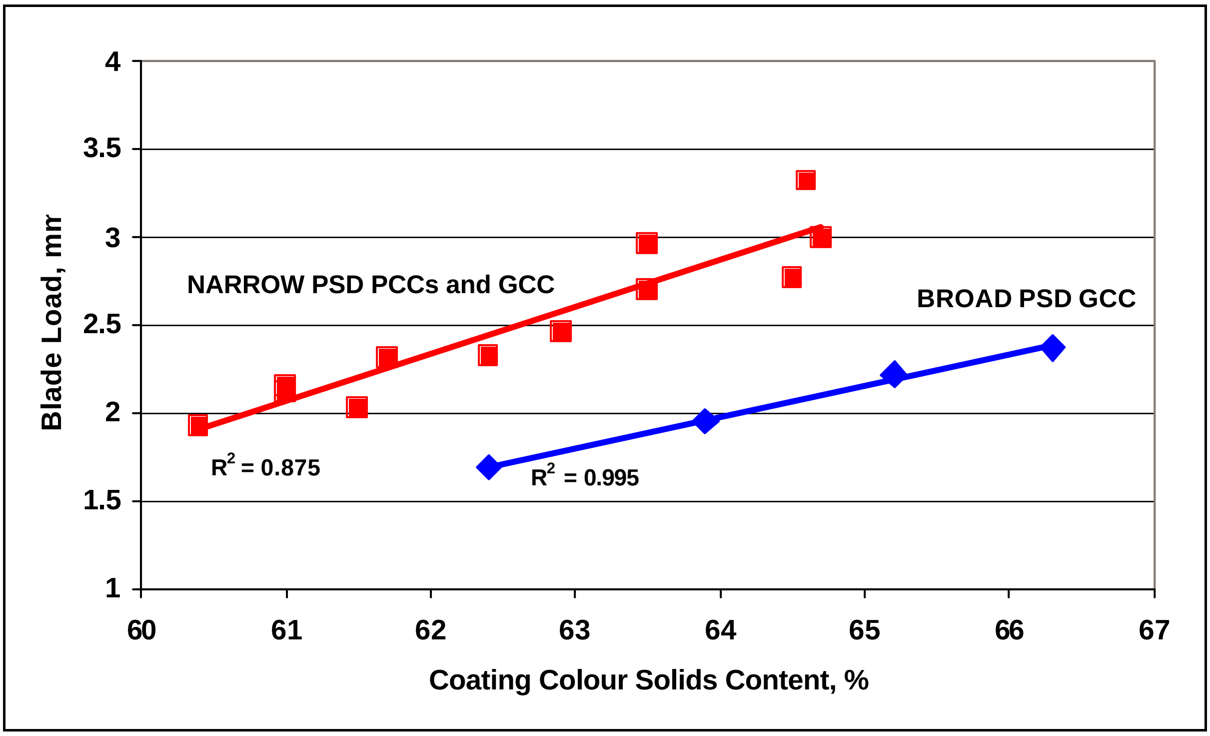
Although the purpose of the acrylic polymer was to adjust the coatings to an equivalent low shear viscosity and water holding, the resulting high shear viscosity was still affected by both coating colour solids content and calcium carbonate used. The difference in magnitude of the high shear viscosity between the pigments with steep psd and the one with broad psd is particularly noteworthy. This can be explained by differences in particle packing, e.g. that pigments with narrower psd show more open particle packing. Among the pigments with narrow psd, the aragonite PCC had slightly lower high shear viscosities that the narrow psd GCC and the calcite PCC.

Figure 6 demonstrates the relationship observed between the coater blade load and the coating colour solids. As expected, the correlation between the required blade load and the coating colour solids content shows the same separation between the pigments with narrow psd and the one with broad psd, as was observed with the high shear viscosity data shown in Figure 5.

In the chosen pigment blend with clay, the difference in the achievable maximum runnable solids contents between broad and narrow psd was less than 2%-units. No influence at all was noticeable when comparing the particle shape of the pigments with narrow psd. At the maximum achievable coating colour solids, all of the different calcium carbonates had acceptable runnability, with a generally clean blade without scratches.

As blade load is also one criterion for runnability it should be mentioned again that the broad psd GCC had a lower high-shear viscosity and required therefore lower blade loads. It must be mentioned at this point that no changes in blade geometry or blade settings (except blade load) were taken to optimise runnability, as this was not a target in this study.

Figure 6: Blade load vs. coating colour solids content



The maximum runnable coating solids achieved for the different carbonates are summarised in Table 3. Only minimal differences between the pigments with narrow psd were seen. The broad psd GCC ran at 1,5% - 2,0%-units higher solids content in this study. That this slightly lower solids content for narrow psd PCCs doesn't automatically result in higher drying costs was proven in previous studies (3). PCCs offer some compensation through easier drying and less specific energy consumption on a per-kilogram-of-water basis compared to GCCs.

Table 3: Maximum runnable coating solids content

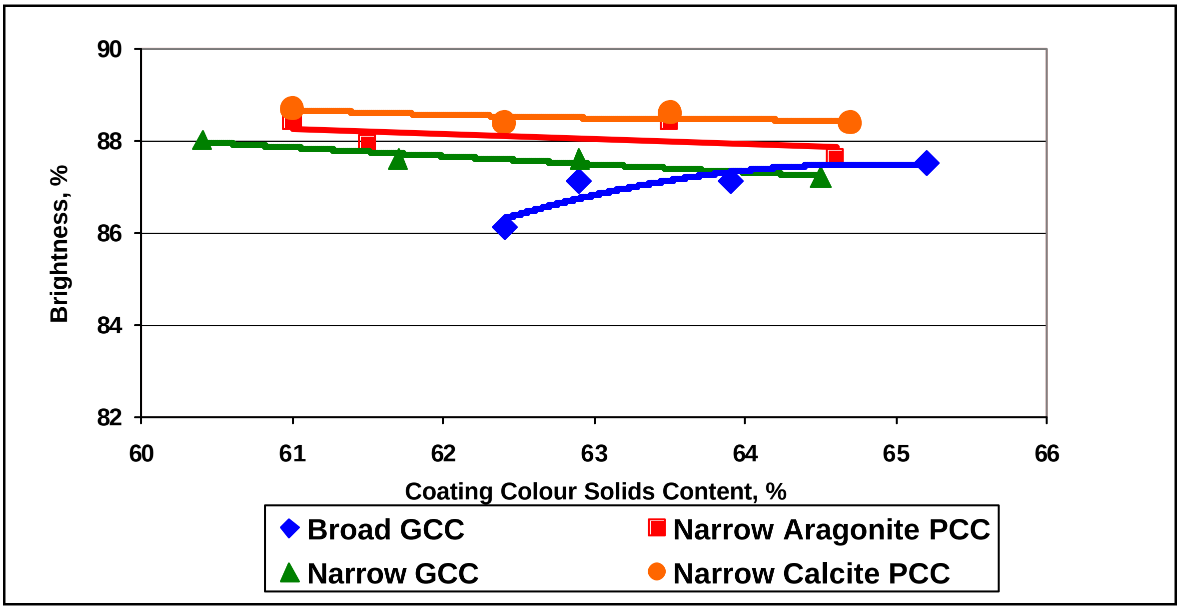
Pigment	Maximum Runnable Solids Content, %
Narrow Aragonite PCC	65,0
Narrow Calcite PCC	64,7
Narrow GCC	64,5
Broad GCC	66,5

3.2 Coated Paper Performance

Overall, there was very little influence of the coating colour application solids on the end performance properties. The major focus of this study was the optical properties, with some additional examination of the surface and porosity characteristics. It was felt that if there were an effect of dilution of coating solids on properties, these properties would be the ones that would be primarily affected.

An influence of the coating colour solids content on the brightness of the final paper was minor or not at all visible (see Figure 7). A slight indication for a decrease with decreasing solids content might be seen for broad psd GCC in the point with the lowest solids content. The prismatic PCC achieved the highest paper brightness even though it had the lowest pigment brightness of all carbonates in this study. Based on the results of previous studies, very high light scattering can be named as an explanation for this phenomenon. The very steep psd of the prismatic PCC results in a high coating porosity thus gives the coating layer a high internal surface, which again results in high light scattering.

Figure 7: Brightness vs. Coating Colour Solids Content



The opacity of the final papers seems to be relatively independent of coating colour solids content for all pigments used in this study. Figure 8 shows a very small change in the range of opacity values over the entire span of different solids examined. This was consistent for all of the pigments in the study. However, the narrower particle size distribution of the Precipitated calcium carbonate products resulted in higher coated sheet opacity, even though the average particle size of the GCC was similar to the larger calcite PCC. The increased opacity of the PCC products is due to the higher light scattering resulting from the narrower distribution, and gives higher opacity than the two GCCs, as is evident in Figure 9.

Figure 8: Opacity vs. Coating Colour Solids Content

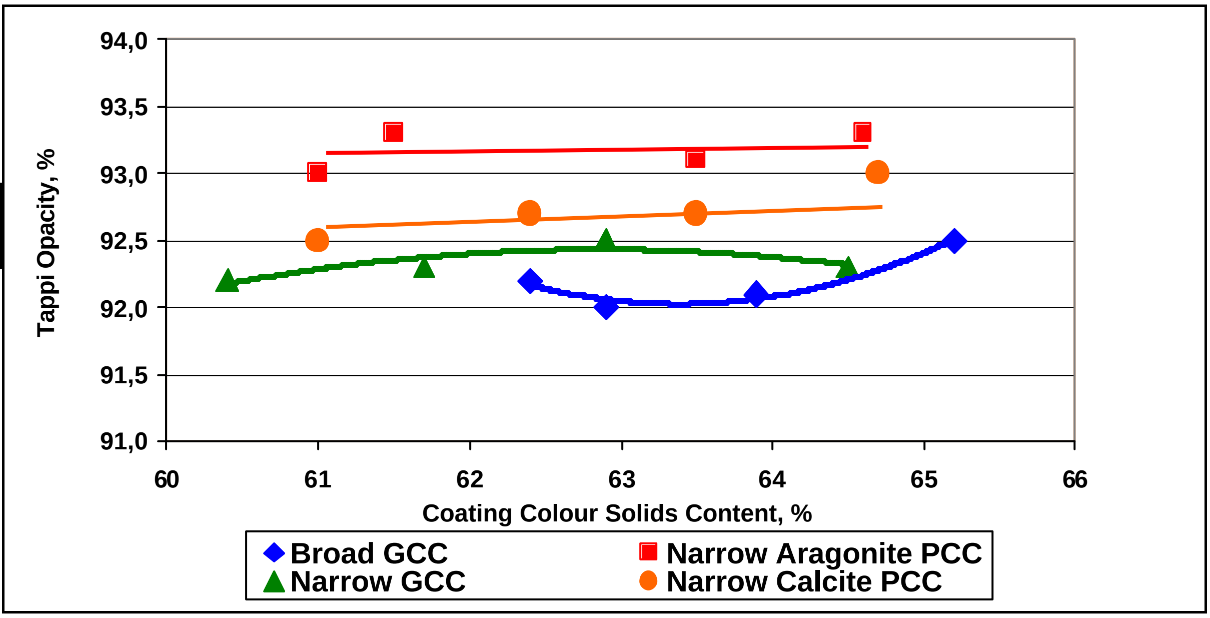
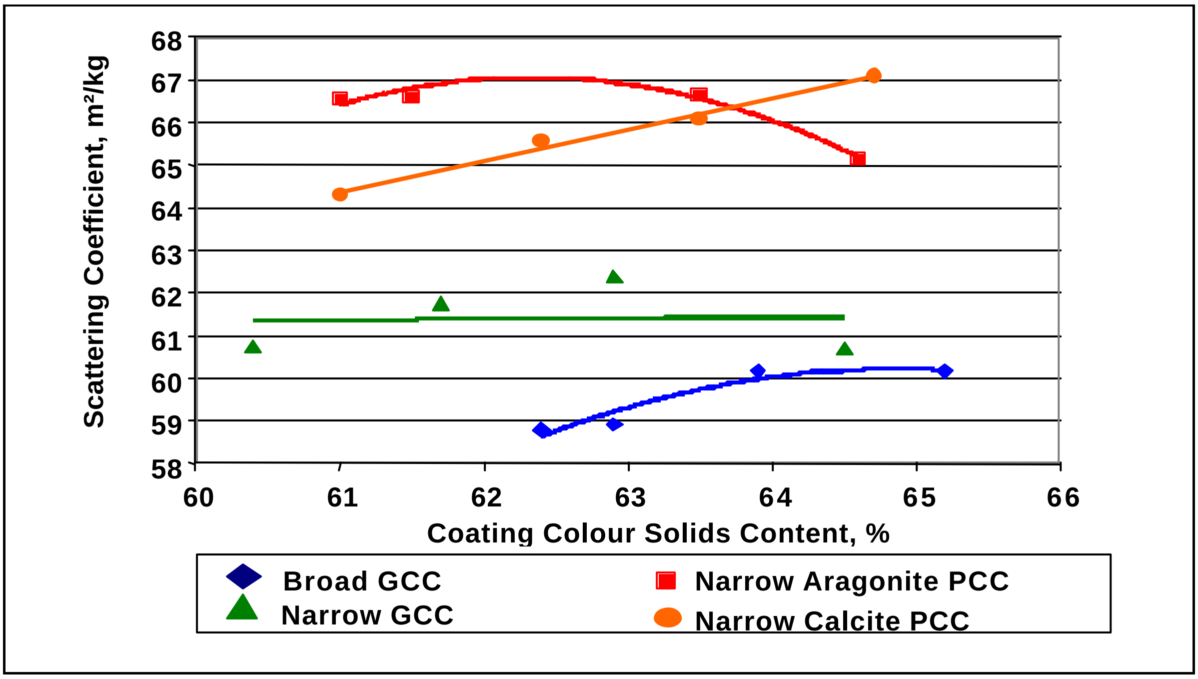


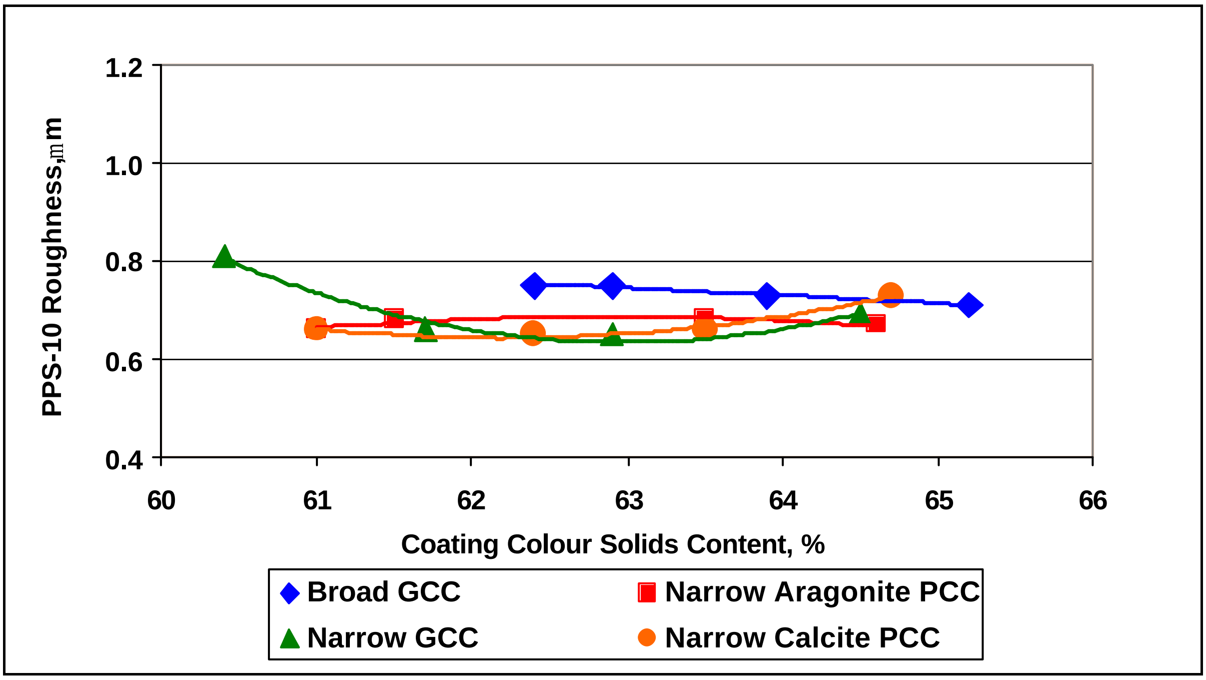
Figure 9: Scatter vs. Coating Colour Solids Content



Paper roughness, as demonstrated in Figure 10, showed no significant dependence of the coating solids content for all pigments in the investigated range. Also the level of the roughness was fairly similar for all pigment blends. More significant differences in roughness due to the differences in psd would have been expected in single coated applications.

Past studies had indicated that the aragonite morphology may benefit from lower coating colour solids applications. In this case, where water holding, rheology and coating immobilisation were controlled, there is no longer benefits to running at lower coating colour solids; coated paper properties were improved at the higher coating colour solids application. This study also demonstrates the common knowledge that good fibre coverage can be achieved regardless of the coating solids content.

Figure 10: PPS-Roughness vs. Coating Colour Solids Content



No influence of the coating colour solids content on sheet gloss was found for any of the calcium carbonates used in this study. This is contradictory to the results of previous studies, and shows the importance of water retention control in achieving maximum quality and runnability. This illustrates the fact that running at lower solids is not necessarily detrimental to sheet gloss if water holding is controlled. Instead, the sheet gloss was mainly influenced by the particle size and morphology of the pigments, as shown in Figure 11.

The highest overall sheet gloss at any application coating colour solids content was reached with the finest average particle size calcium carbonate (OPACARB® A40 PCC). This same fine pigment also was the only aragonite calcium carbonate included in this study, and with the different, needle shaped morphology and fine size, it gave distinctly improved sheet gloss compared to the other calcite calcium carbonates, as is evidenced in Figure 12.

As with the other paper properties examined, there were no changes in porosity with coating colour dilution. However, the optical properties support the porosity data in that the smallest average particle size/narrow distribution calcium carbonate had the most open coated sheet porosity. As the average particle size increased, the coated sheet porosity decreased, resulting in the coating with the coarse, larger GCC having the most closed coated sheet. This is demonstrated in Figure 13.

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Figure 11: Sheet Gloss vs. Coating Colour Solids Content

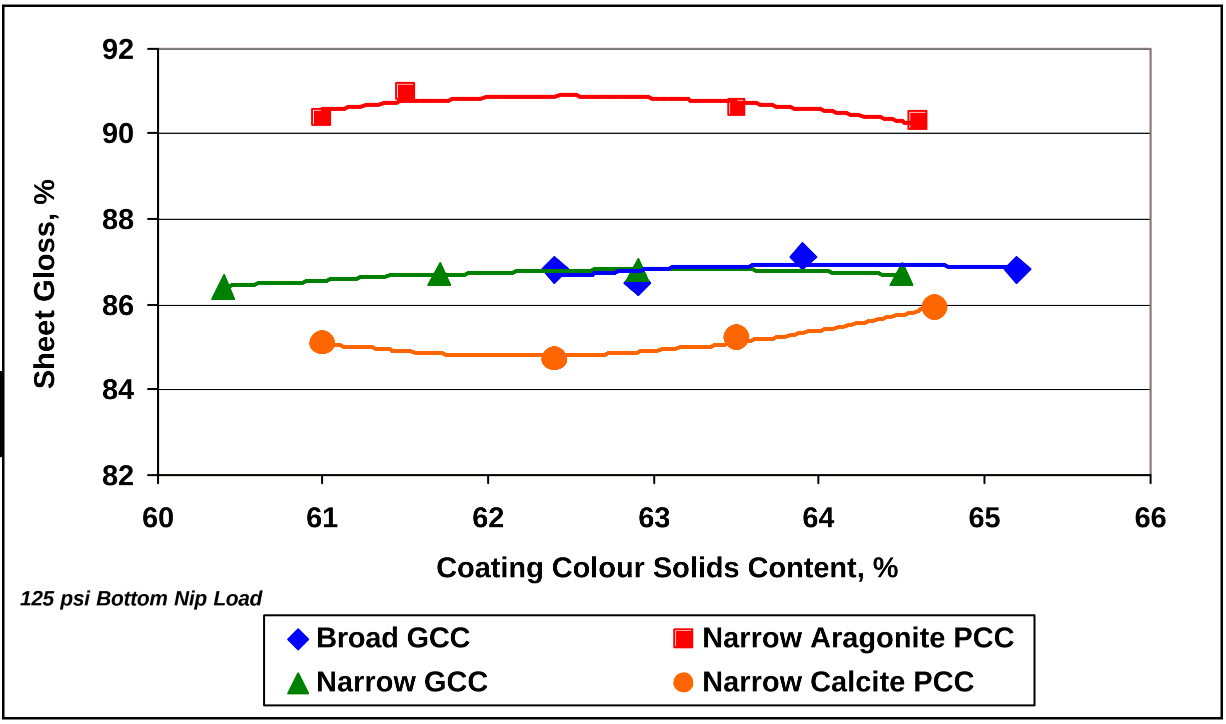


Figure 12: Sheet Gloss vs. Pigment Average Particle Size (Regressed to 64% Coating Solids Content)

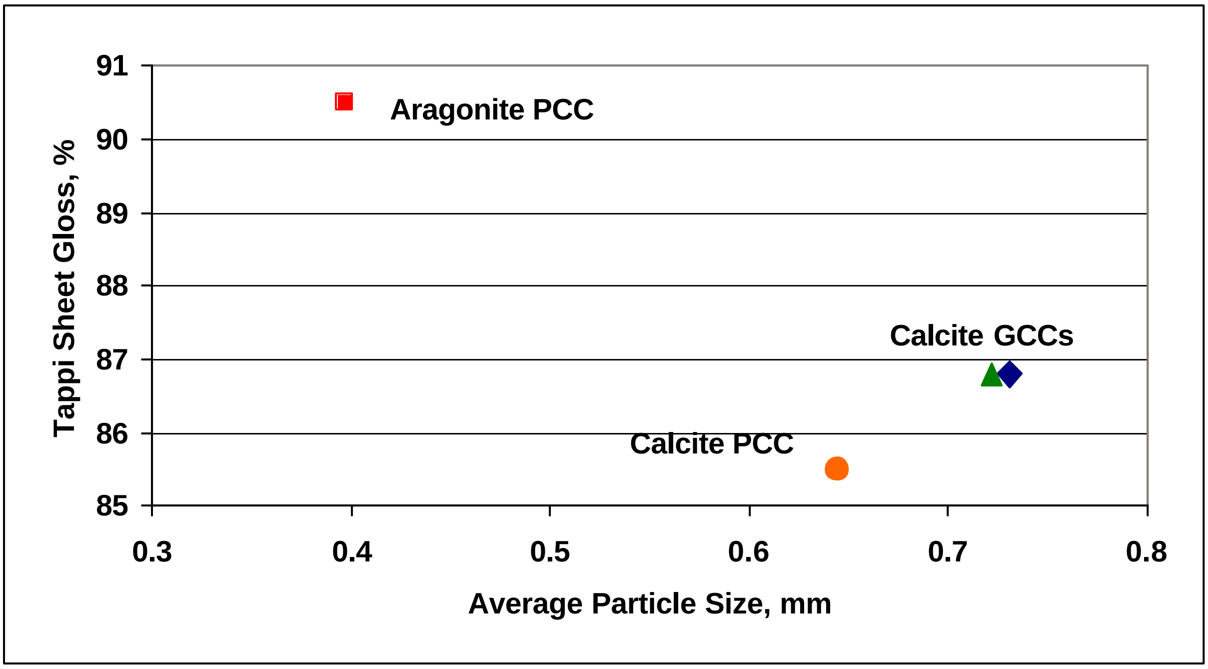
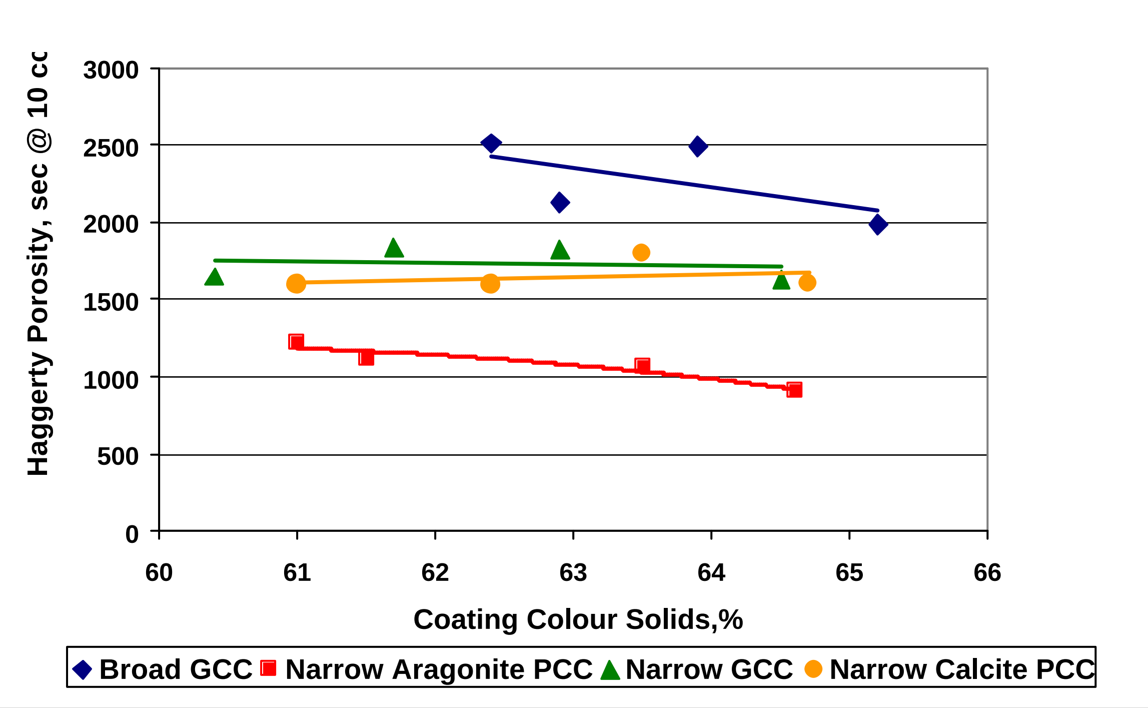


Figure 13: Porosity vs Coating Colour Solids Content



As the examined paper properties showed no significant influence of the coating colour solids content, the performance difference is also valid at the maximum runnable solids content. This is demonstrated in Table 4.

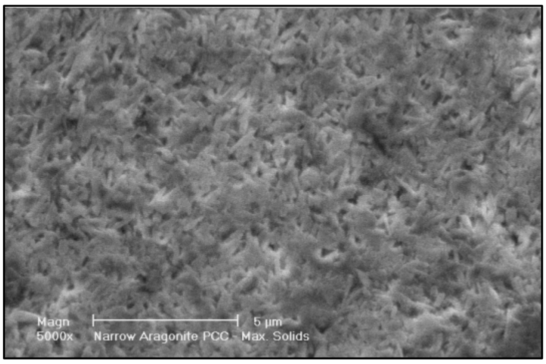
Table 4: Summary of paper properties at maximum runnable solids content

Pigment	Sheet Gloss, %	Brightness, %	Opacity, %	Roughness PPS-10, µm
Narrow Aragonite PCC	90,3	87,6	93,3	0,67
Narrow Calcite PCC	85,9	88,4	93,0	0,73
Narrow GCC	86,7	87,2	92,3	0,69
Broad GCC	86,8	87,5	92,5	0,71

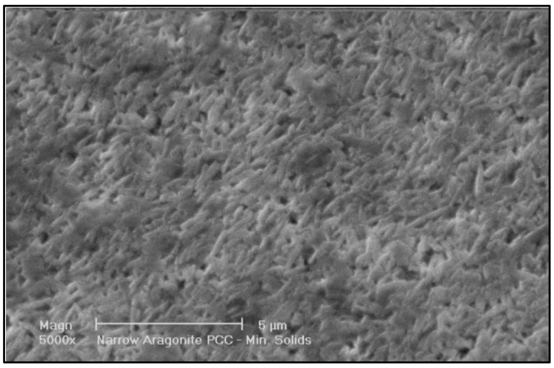
The SEM was also used to examine images of the coated paper for each calcium carbonate type at the maximum and minimum coating colour solids content to determine visually whether any differences existed in the appearance of the coated sheet with dilution. These images can be seen in Figure 14. No differences in coating coverage or general appearance within each pigment series were observed, with the exception of the broad psd GCC, which had a more open surface at minimum coating solids than compared to the same pigment, broad psd GCC, at maximum coating solids.

Figure 15 summarises the performance potential of the investigated pigments. Overall the best paper quality was achieved with the fine aragonite PCC. The combination of high glossing potential, high opacity due to the light scattering the natural high brightness of a calcium carbonate offers unique possibilities to the papermaker.

Figure 14: SEM Images of Coated Paper for Each Calcium Carbonate at 10,000X



Narrow Aragonite PCC at Maximum Coating Colour Solids Content



Narrow Aragonite PCC at Minimum Coating Colour Solids Content

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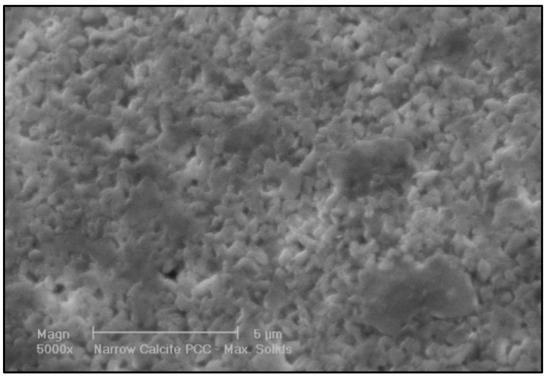
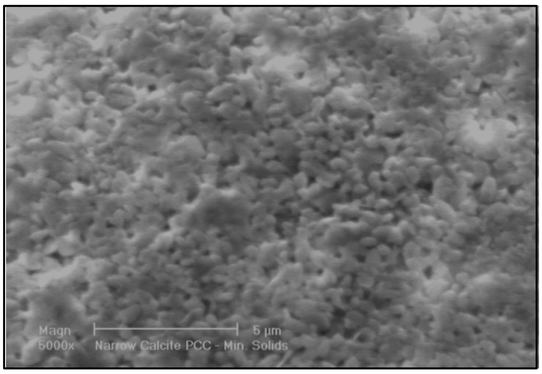
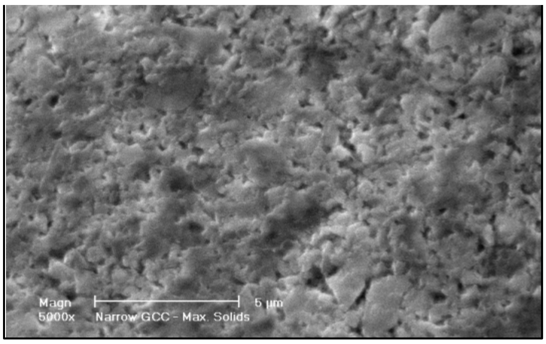


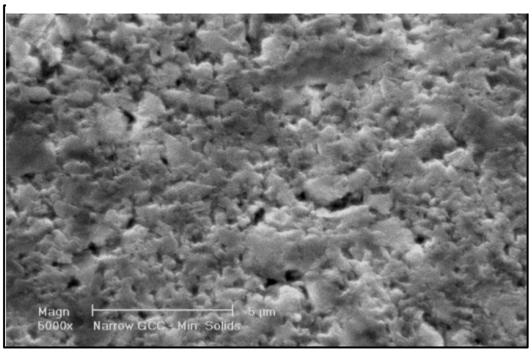
Narrow Calcite PCC at Maximum Coating Colour Solids Content



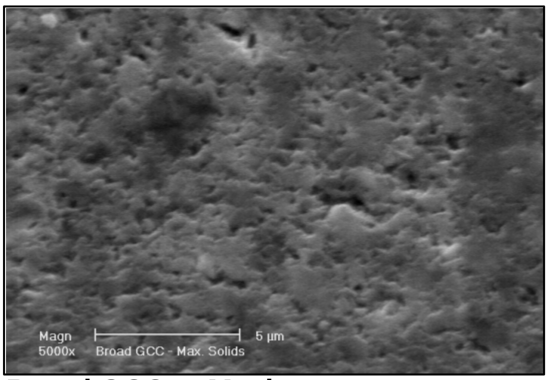
Narrow Calcite PCC at Minimum Coating Colour Solids Content



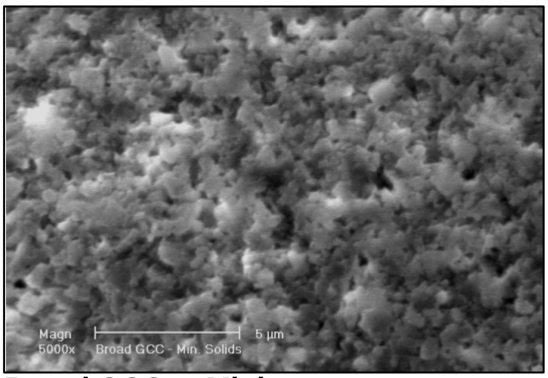
Narrow GCC at Maximum Coating Colour Solids Content



Narrow GCC at Minimum Coating Colour Solids Content

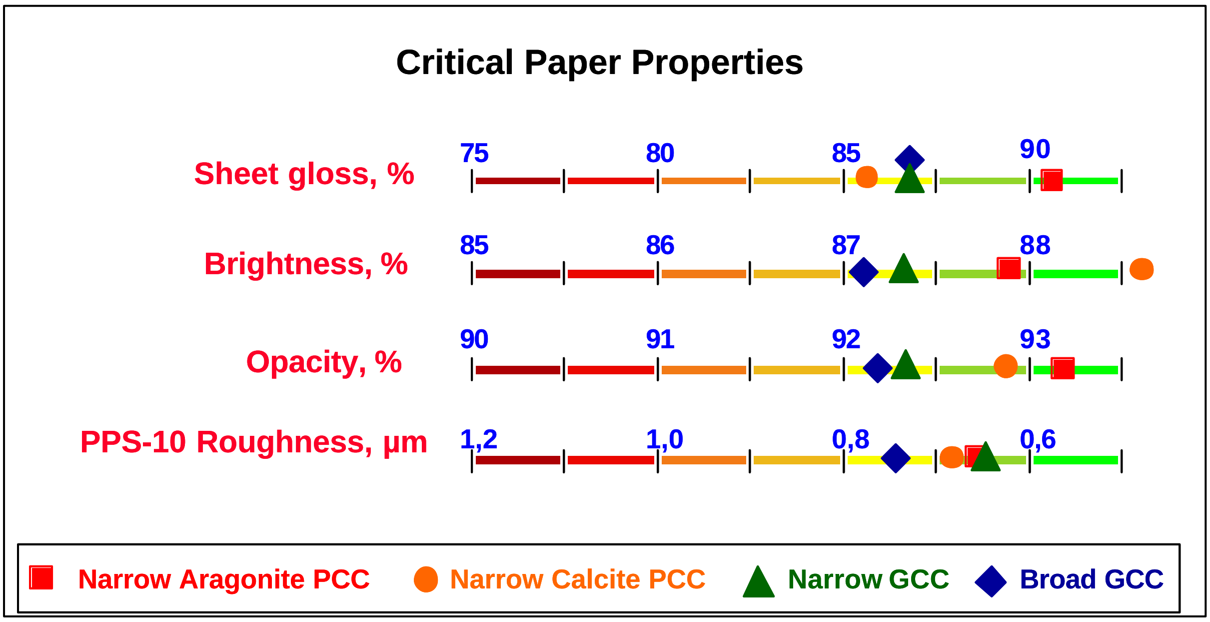


Broad GCC at Maximum Coating Colour Solids Content



Broad GCC at Minimum Coating Colour Solids Content

Figure 15: Summary of Critical Paper Properties (Regressed to 64% Coating Solids Content)



4 CONCLUSIONS

Comparing the results of this work to previous work, it was determined that:

1. The coated sheet performance of each calcium carbonate was maintained regardless of the coating colour dilution with control of coating colour viscosity, water retention, and drying conditions.
2. All of the narrow psd pigments performed the same with regard to maximum runnable coating colour solids, whether precipitated calcium carbonate or ground calcium carbonate, calcite or aragonite. The broad psd ground calcium carbonate was the only pigment with higher maximum coating colour solids within this study.
3. The coated sheet performance improved as the average particle size of the precipitated calcium carbonate decreased. The highest performance was seen with the smallest average particle size calcium carbonate, with the aragonite morphology.

5 ACKNOWLEDGEMENTS

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2. Hiorns, A., Proceedings of the 2001 TAPPI Coating Conference, “Calendering Response of Calcium Carbonates in Double Coating Woodfree Paper”, p. 127.
3. Alderfer, G., Aarni, E., Rajala, P., Anderson, J., Proceedings of the 2002 TAPPI Coating Conference “Evaporation Energy Demands of Coatings Formulated with Calcium Carbonate Pigment”, p. 412.

7 APPENDIX

The coating formulations used consisted of 80 parts calcium carbonate, 10 parts High Glossing Clay, and 10 parts High Gloss Premium Clay. The calcium carbonate portion varied between OPACARB™ A40 PCC, ALBAGLOS™ S PCC, less broad GCC, and broad GCC. The remainder of the coating formulation consisted of 12 parts Dow XU.30929.50 latex, 1 part Devflo™ 50 lubricant, 0.8 parts FinnFix® 10 Carboxyl Methyl Cellulose, 0.5 parts Bayer Blankophor™ P optical brightening agent, 0.1 parts Ciba Dispex® N-40 dispersant. Sterocoll® FD was added to reach Brookfield viscosity and ÅA-GWR dewatering targets for each coating formulation and solids test point.

The application of each coating formulation was done using a jet/blade configuration, using a woodfree, pre-coated base paper. The target coat weight per side was 12 g/m².

Paper testing was performed on the coated paper according to TAPPI standards.