

Optimisation of steep carbonate coating formulations with ultra fine platy kaolin

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⊕ KAOLIN

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ABSTRACT

Maintaining high paper gloss without compromising light scattering potential in steep particle-size-distribution carbonate coating recipes is non-trivial. While the use of fine blocky kaolin is accepted practice for gloss generation with standard carbonates, there is doubt over its compatibility with steeper pigment blends. This is because the enhanced light scattering potential of such coating systems is a result of large, clearly defined pores. As these become larger, there is a chance that the fine kaolin will partially fill them, thereby reducing the system's light scattering potential. Additionally, the partial filling of these pores would further increase the ink setting rate of the system. It is proposed that the use of ultra fine, but platy, kaolin may overcome these shortcomings. This assumes that the aspect ratio of the kaolin plates can be engineered to be sufficiently fine to aid gloss development, but concurrently have a large enough plate diameter to stop it from filling the voids created by the steep partner carbonate. The performance of coatings formulated with such a kaolin, a new product development, is reported here for the first time and is contrasted against that obtained from a fine blocky kaolin.

BACKGROUND

Mineral coating layers are used successfully to influence the interaction of light with paper. This interaction defines the visual experience by influencing paper gloss, shade, brightness and opacity. With the exception of gloss, the key contributor to these phenomena is the light scatter and light absorption characteristics of the system.

It is well known [1] that, for a given mineral coating pigment, engineering the particle size distribution in terms of mean particle size and the steepness [2] has a strong effect on light scatter potential. Similarly, the material choice and processing it receives will have a strong influence on light absorption, through the residual quantity and type of contaminant still present in the finished product [1].

Engineering the particle size distribution (psd) to create larger, better-defined, pores in the coating structure increases the light scatter potential of the system through more optimised scattering centres in terms of size. Generally, pore size is a factor of both mean particle size and the steepness of the particle size distribution. In practice this may be achieved by the removal of the ultra fine fraction from the mineral product which has two beneficial effects. Firstly it ensures that the spacing between scattering centres (pores) is sufficiently large to avoid 'optical crowding' [3], while simultaneously opening the coating structure by removing the fraction most likely to fill the resultant pores [4]. For calcium carbonates, this has been shown for coating applications based on both ground calcium carbonates (GCCs) [5] and precipitated calcium carbonates

(PCCs) [6]. The benefits to the finished paper have been shown to include higher sheet brightness and opacity [4, 5] and improved resistance to blistering during offset printing [4].

Development of print and paper gloss, however, is more complicated. Paper gloss, in particular, is highly sensitive to coating coverage of the base paper. The greater porosity of the steeper pigment coating structures leads to faster dewatering, and subsequently quicker immobilisation of the coating on application. In principle, this leads to better coating hold out and better coverage than standard psd carbonates. This is particularly important in LWC applications where increased base coverage at low coat weights leads to improved sheet gloss [2, 4] through lowering of macro-roughness. In double-coated and higher coat weight applications where base coverage is not an issue, gloss becomes dependent on roughness at a pigment scale. In such applications, the lack of ultra fine particles in the steeper product leads to greater surface micro-roughness and potentially lower sheet gloss in comparison to standard product [2].

An additional tool in the pursuit of paper (and printed paper) gloss is the use of partner kaolin in blends with the engineered carbonate. While ultra fine, blocky glossing clays are used extensively and successfully in many gloss grades with standard carbonates, there is concern that if used in blends with steep carbonate, they will effectively fill the newly appointed open pore structure and subsequently partially negate its high scatter potential. Previous work by *Nutbeam et al.* [2] has looked at the effect on coating structure of using such blocky glossing kaolin in partnership with steep carbonate. This work concluded that, while sheet gloss improved, the pore size of the resultant coating layer was indeed greatly decreased over a similar coating with no kaolin present, suggesting that the full benefits (such as enhanced brightness and opacity) of the steep carbonate system may not be realised. Performance was also compared with blends containing platy kaolin. This was found to disrupt the packing of the carbonate and led to greater preservation of the coating pore structure, but did not generate gloss to the same level.

If a platy, but truly ultra fine, glossing kaolin could be used, it is proposed that paper gloss may be developed without the detrimental effect on light scatter potential. The reason for this is that the platy kaolin would not be able to fill the voids created by the steep carbonate, and would instead bridge the pores, preserving them for light scatter generation. It is further hypothesised that the resultant coating structure might slow down the tack development of applied printing inks as the platy kaolin would result in greater ink hold out, thereby neutralising another potential technical shortcoming associated with the use of steep carbonate products.

Such kaolin would need to have an average particle size (equivalent spherical diameter) fine enough to generate gloss, but with an aspect ratio sufficient to give it significant plate surface area. The use of a new kaolin production grade exhibiting such physical properties in partnership with steep carbonate systems is reported in this work for the first time, and is contrasted against ultra fine, blocky partner clay. The reader should also be aware that this paper is reporting on the effects of a systematic change in the steepness of the carbonate as a blend component in coating applications. This has rarely been reported in the literature to the best of our knowledge.

EXPERIMENTAL DETAILS

A series of coatings were made using a range of calcium carbonates with increasing particle size distribution steepness in 70/30 blends with partner kaolin. Two different US kaolins were used: one ultra fine and blocky, and the other ultra fine and platy. The carbonates were fabricated by blending a standard psd, commercially available GCC (CaCO_3) with a commercially available rhombic PCC (CaCO_3) at different blend ratios as stated in Table 2. Details of the pigments used are given in Tables 1 and 2, and sedigraph measurements of the particle size distributions of the carbonate blends are shown in Figure 1. By means of reference, standard commercial GCCs tend to exhibit steepness values of approximately 34, while commercially available engineered-psd GCC with a similar 2-micron count has a steepness value of approximately 45. The steepness range of 34 to 57 assessed in this study, therefore, represents a full range of values and may represent the first study comprising the systematic variation of carbonate steepness

over a full range to be published. The pigments were formulated with 10pph Dow 920 latex, 2pph Nyलगुम A45 starch and 0.5pph Nopcote C104 (calcium stearate) to make the coating colour.

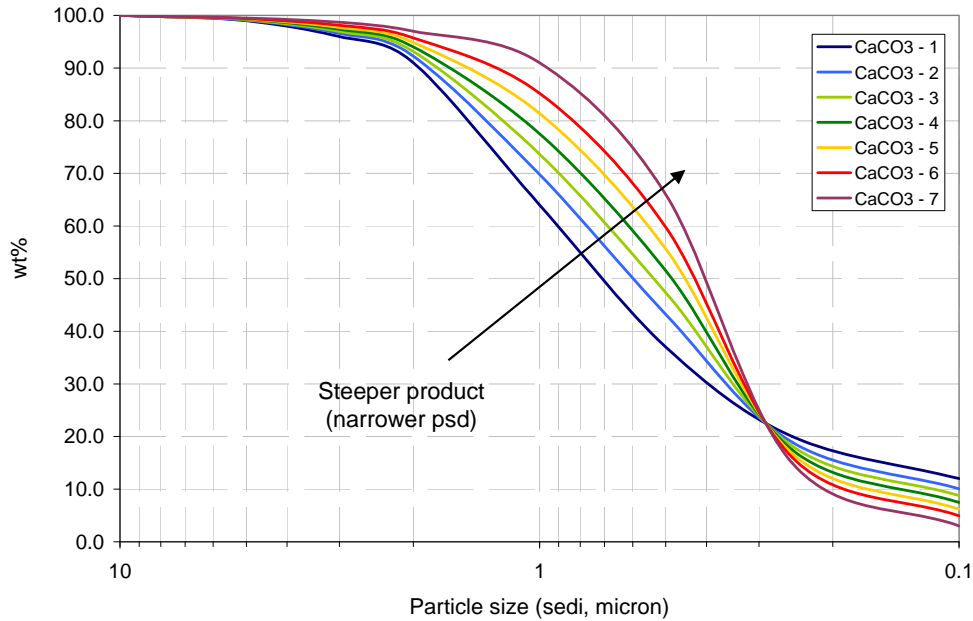
Table 1. Kaolin coating pigment properties

	Fine platy kaolin	Fine blocky kaolin
Brightness (D65/10)	88.3	88.0
L* (D65/10)	96.5	96.5
a* (D65/10)	-0.15	0.00
b* (D65/10)	2.37	2.54
<2µm content (%)	97	99
<1µm content (%)	89	99
<0.5µm content (%)	73	94
<0.25µm content (%)	47	68
<0.10µm content (%)	20	25
Mean particle size, D50 (µm)	0.27	0.19
Surface area (m2/g)	19.0	20.9
Average shape factor	29.5	9.5
Mean plate thickness (µm)	0.03	0.04
Mean plate diameter (µm)	0.97	0.40

Table 2. Calcium carbonate coating pigment properties

	CaCO ₃ 1	CaCO ₃ 2	CaCO ₃ 3	CaCO ₃ 4	CaCO ₃ 5	CaCO ₃ 6	CaCO ₃ 7
<2µm content (%)	91	92	93	94	95	96	97
<1µm content (%)	64	70	74	78	81	85	91
<0.5µm content (%)	37	43	47	52	56	60	66
<0.25µm content (%)	20	19	18	18	17	16	15
<0.10µm content (%)	12	10	9	8	6	5	3
Mean particle size, D50 (µm)	0.69	0.62	0.57	0.51	0.48	0.45	0.42
PSD steepness (D30/D70 *100)	34	35	37	40	43	48	57
%PCC in carbonate blend	0%	21%	36%	50%	64%	79%	100%

Figure 1. Sedigraph measurements of the particle size distribution of the different carbonate blends used in the study



A Helicoater with a pond head was used to apply a range of coat weights for each coating colour at 600m/min onto a 42gm² woodfree base. The application was performed using a 0.381mm thick blade set with a 2cm extension, at 45°. The coated papers were calendered using a Perkins laboratory calender with steel (20cm diameter) and cotton (30cm diameter) rolls for 10 nips at 87Kgcm⁻² pressure and 73°C at 36m.min⁻¹.

The calendered papers were conditioned at 50% relative humidity and 23°C for 24 hours before measuring their optical characteristics using an Elrepho 3300 with D65/10 illumination. The data was later interpolated to a common coat weight of 10gm². Kubelka-Munk theory [7, 8] was used to calculate the coating layer light scattering coefficient (S) and light absorption coefficient (K).

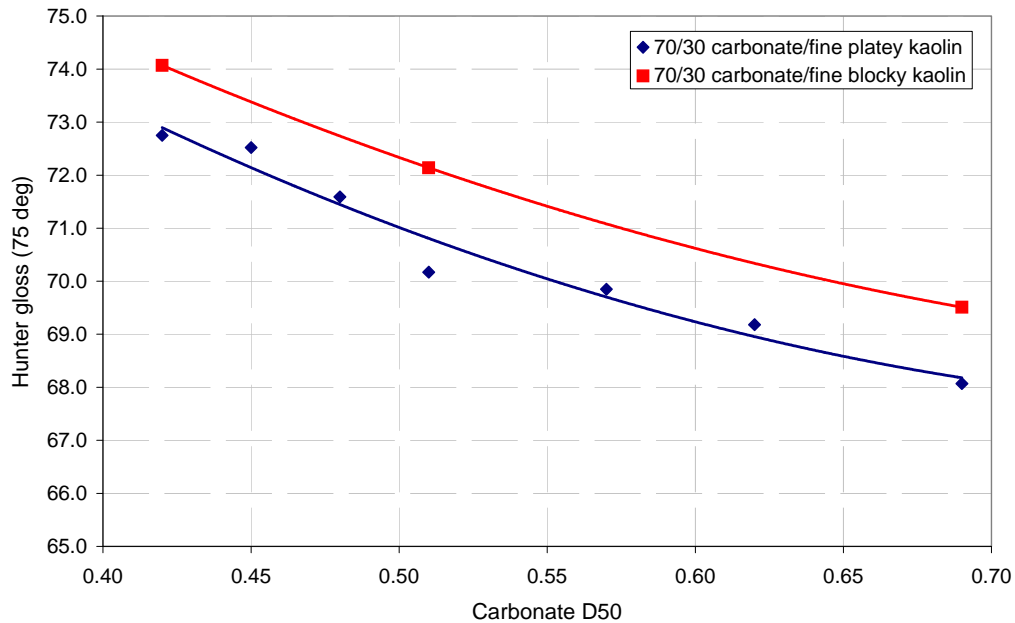
A Pascal 140/240 mercury porosimeter was used to characterise the pore structure of the calendered coating layer for each different coating colour, by analysing the papers exhibiting a coat weight closest to the target 10gm² (examples existed for all colours which had a coat weight of 10 +/-0.5 gm²). The pressure range employed during the characterisation was 0-190MPa. Samples from these same batches were also submitted for evaluation of printing ink tack development using an ISIT tack tester (Se Gan Ltd).

RESULTS

Paper gloss was measured using a Hunter glossmeter with illumination and detection at +/-75° from normal incidence. Figure 2 shows gloss development with mean carbonate particle size (D50) in the 70/30 carbonate/kaolin coating blends. It can be seen that there is a dependence of gloss on particle size. As expected, the use of finer carbonates give rise to higher gloss potential under equal calendering conditions. The range of carbonate D50 explored in this work has been deliberately kept relatively small, and results in a fairly modest range of achieved gloss (all paper sets give a gloss value within 4 gloss units of each other). Crucially, however, the data demonstrates that the fine, platy kaolin is able to develop gloss nearly as well as the fine blocky kaolin (equivalent results are within 2 gloss units of each other), despite having a plate diameter

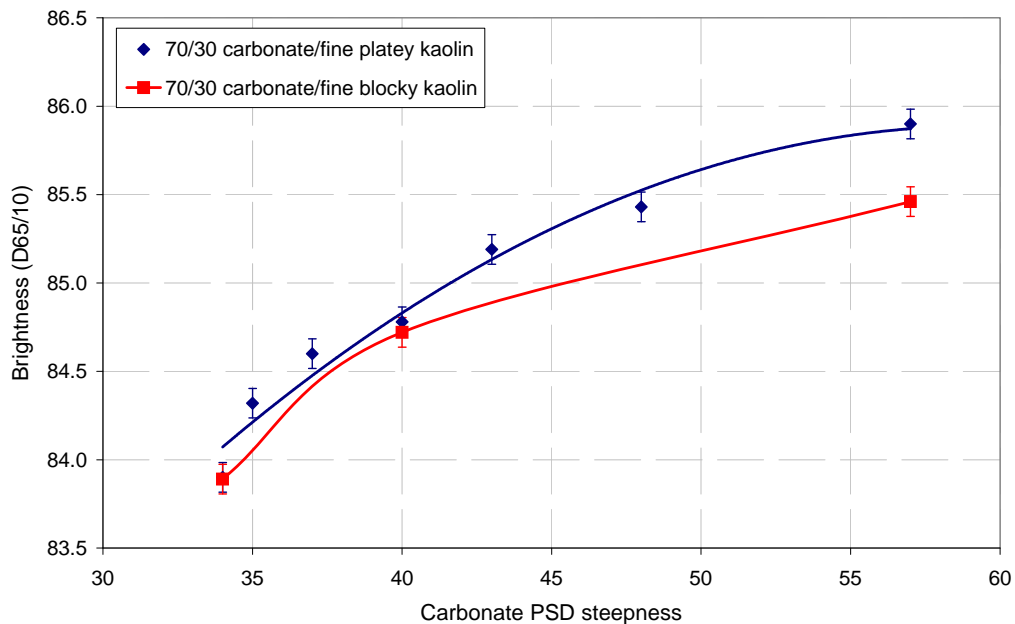
approximately 2.4 times as large. This suggests that the platy kaolin has a sufficiently fine mean particle size for gloss generation.

Figure 2. Gloss response of the coated and calendered papers as a function of carbonate D50



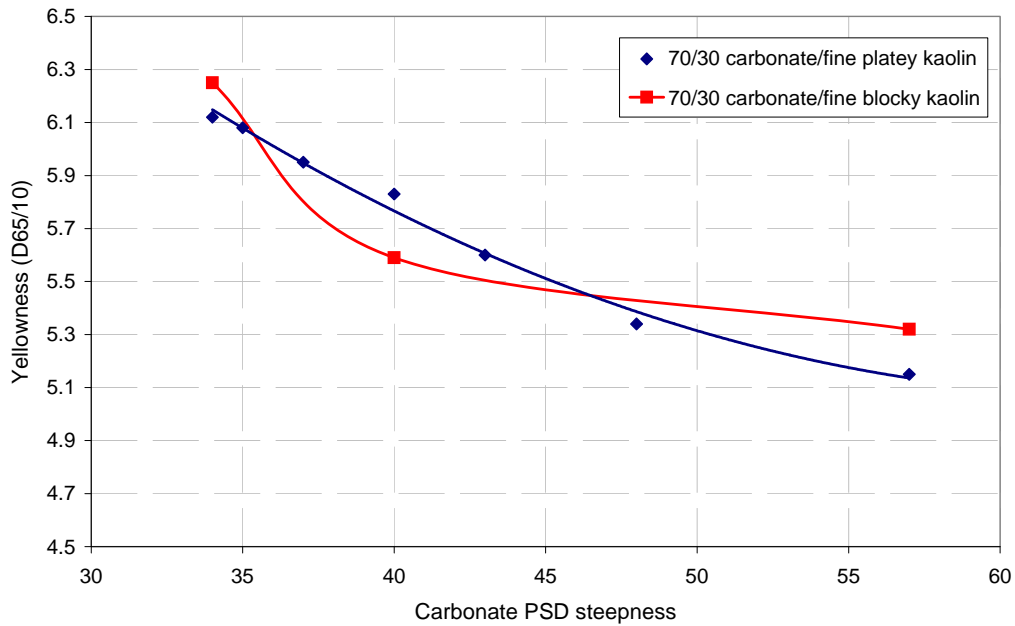
In blends with lower steepness (broader psd) carbonates, both kaolins give rise to finished paper with similar brightness. Figure 3 shows the development of paper brightness as a function of carbonate steepness. The graph shows, however, that the performance of the two systems diverges at higher carbonate steepness, with the platier kaolin system yielding almost 0.5 units of brightness higher than the blocky kaolin system at the highest carbonate steepness.

Figure 3. Paper brightness as a function of carbonate steepness (error bars represent the standard deviation in the measurements)



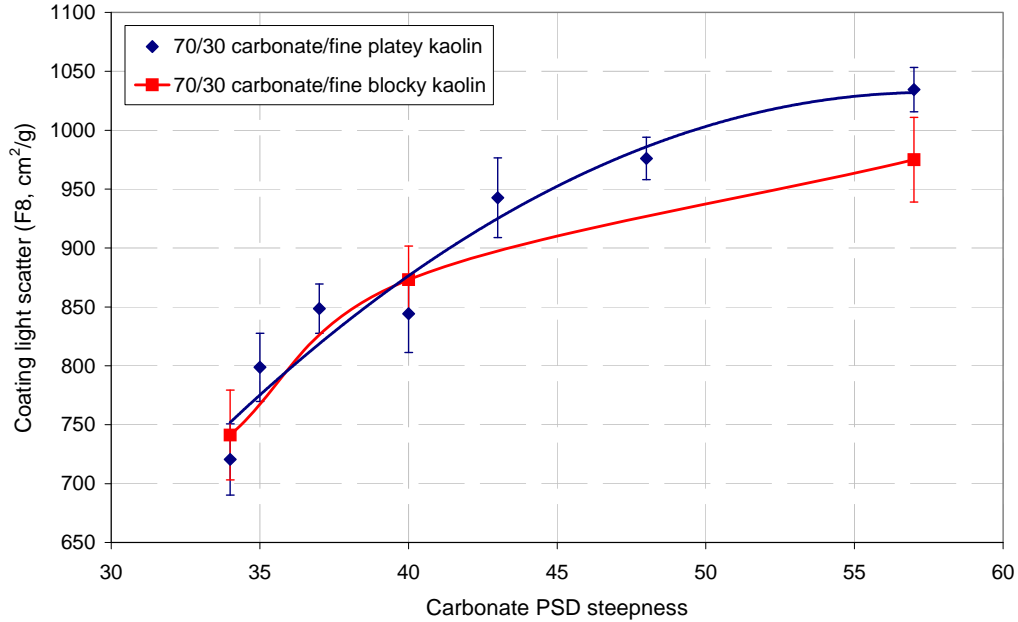
In order to understand the basis for the modest out-performance of the platy-kaolin in blends with higher steepness carbonate, the paper yellowness value was measured (Figure 4). The graph shows that the sheet yellowness is approximately the same for both kaolin systems, indicating that the difference in brightness performance between coating systems is not due to differences in light absorption. Instead, the out-performance of the platy system must be due mainly to enhanced light scatter. Light scatter as a function of carbonate steepness is depicted in Figure 5.

Figure 4. Paper yellowness as a function of carbonate steepness



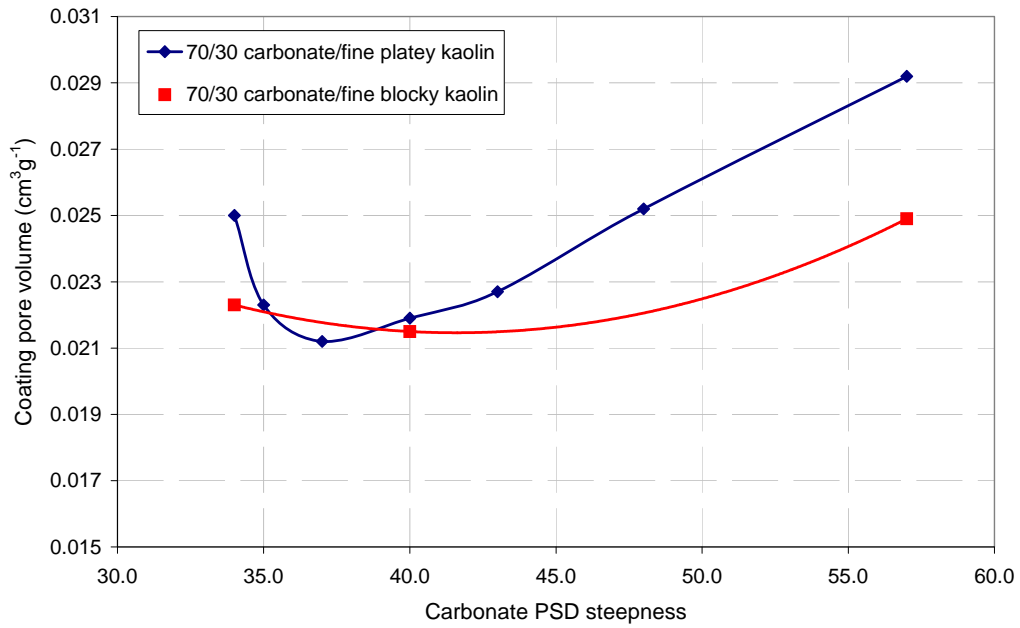
Since coating layer light scatter correlates well with carbonate steepness (Figure 5), this provides strong evidence that this is the major factor determining the optical response of the papers. Crucially, at standard carbonate steepness, both kaolin blends give rise to similar light scatter (and subsequently similar brightness values). However, as carbonate steepness increases, the light scatter potential of the two kaolin systems diverges slightly – with the fine blocky kaolin failing to generate the same level of light scatter as the fine platy kaolin for similar carbonate steepness.

Figure 5. Coating layer light scatter development with carbonate steepness (error bars represent the standard deviation in the 40 measurements which are used to calculate each individual data point)



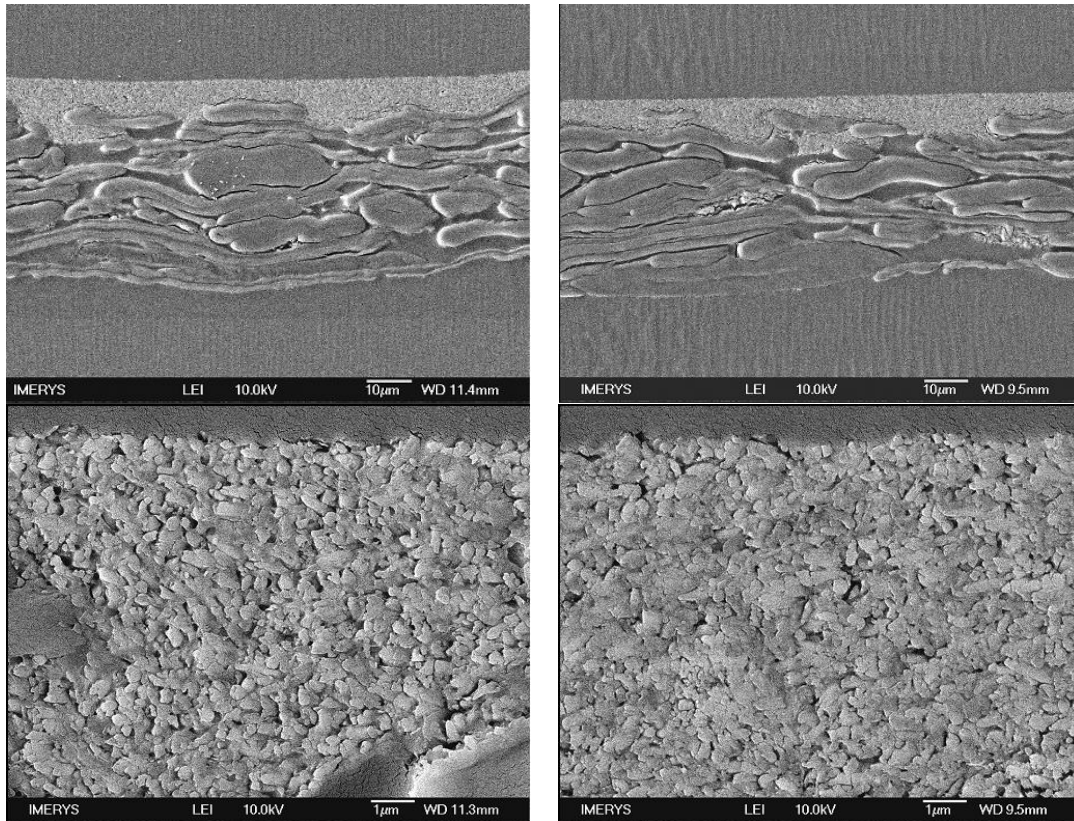
Mercury intrusion porosimetry helps elucidate an understanding of the cause of this modest divergence in light scatter generation. Figure 6 shows coating pore volume as a function of carbonate steepness for the two kaolin systems. The graph clearly shows that as the carbonate steepness increases, the coating pore volume increases, largely because there are fewer fines to fill the pores, yielding a more open coating structure. The rate of increase of void volume in the systems containing the fine platy kaolin is slightly greater than in the systems containing the fine blocky clay; suggesting that a proportion of the enlarged voids created by using steeper carbonates is being filled by the fine blocky kaolin. It is for this reason that the light scatter generation with carbonate steepness slightly under-performs in the fine blocky kaolin system. The fine platy kaolin does not easily fit inside the coating pores and hence acts to maintain the high void volume of the steep carbonate systems.

Figure 6. Pore volume dependence on carbonate PSD steepness



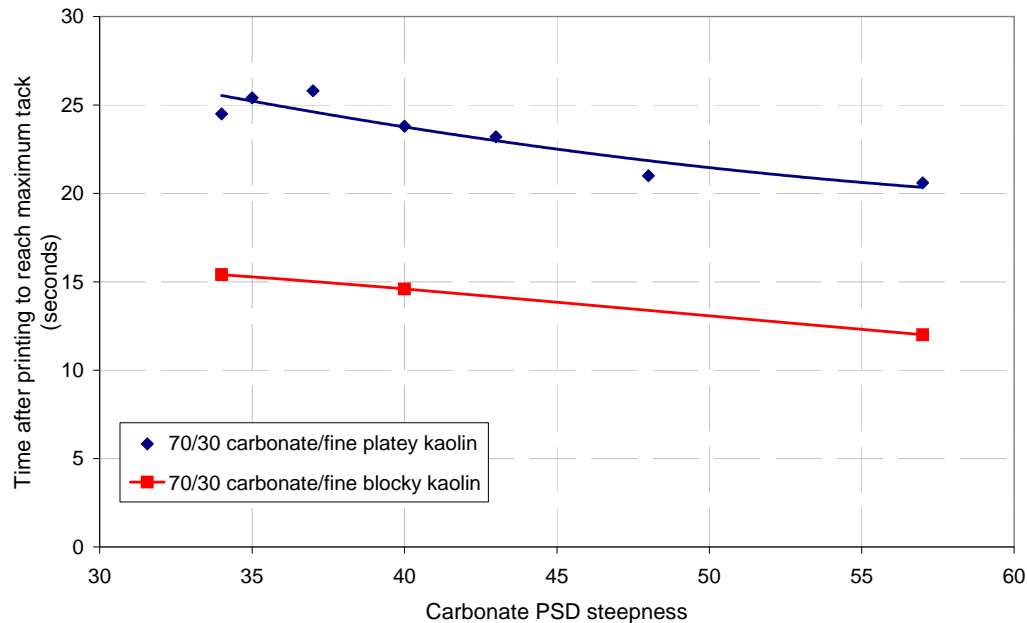
Scanning electron micrographs (SEMs) of paper cross-sections were prepared to visualise this phenomenon and are shown in Figure 7. The images show that the coating hold out is good in both systems as a result of the fast de-watering and rapid immobilisation of the coating structure. The high magnification images possibly show the pore structure preservation in the case of the platy partner kaolin over the fine partner kaolin, with the disordered kaolin plates central to the generation of the resultant structure in the bulk of the coating layer. The authors are keen to point out, however, that the micrographs only represent a small sample area and differences between coating structures are not dramatic, as befits the modest difference in papers.

Figure 7. SEM micrographs of paper cross-sections with the steepest carbonate blended with fine platy kaolin (left) and fine blocky kaolin (right)



Ink tack development as a function of time after printing was measured and the time to reach maximum tack force used as a proxy for ink setting rate. These results are shown in Figure 8. The graph shows the strong effect that the platy kaolin has on ink setting, enabling the tack development to be slowed even for formulations containing very steep carbonates.

Figure 8. Time after printing to reach maximum ink tack



Correlating this data with the pore structure information obtained by mercury porosimetry demonstrates that the mechanism for the differences in tack development between kaolin systems is linked to both the size and number of the pores in the coating structure created. The fine blocky kaolin systems are characterised by a larger number of pores that have a smaller average pore diameter in comparison to the systems containing fine platy kaolin. Making simple assumptions to relate the total coating pore volume with the average coating pore diameter shows that the blocky kaolin blends demonstrate 10-40% higher number density of pores than the equivalent carbonate steepness blend using fine platy kaolin. It is well known [9] that such coating structures demonstrate faster ink setting due to their high capillarity [10].

CONCLUSIONS

The use of fine, but platy, kaolin in blends with steep carbonates can help overcome some of the potential shortcomings associated with obtaining gloss while maintaining light scatter in steep pigment systems. In contrast to the use of fine blocky glossing kaolin, fine platy kaolin enables the open pore structure of the steep carbonate to be slightly better preserved, while remaining sufficiently fine to aid gloss development. We believe that this is a result of the fact that the plate diameter is too large to fill the larger voids created by using low-fines carbonates, whereas the blocky equivalent may partially fill these voids. In filling these voids, light scatter generation is slightly hindered, resulting in a modest negative impact on paper brightness and opacity. As a useful consequence of the coating structure created, the ink setting rate may also be controlled, easing pressure on possible complications such as poor print gloss or piling. In the current study, the fine platy kaolin was observed to demonstrate 40% slower tack development than the fine blocky equivalent.

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APPENDIX: ADDITIONAL PAPER MEASUREMENTS

Figure A1 – Additional measured sheet properties

Carbonate steepness	Opacity		Surface roughness, PPS1000 (μm)		Print snap (print gloss - paper gloss)	
	Fine platy kaolin	Fine blocky kaolin	Fine platy kaolin	Fine blocky kaolin	Fine platy kaolin	Fine blocky kaolin
34	72.1	72.1	0.72	0.79	5.93	2.49
35	72.6	-	0.71	-	2.82	-
37	73.1	-	0.73	-	3.15	-
40	73.0	73.3	0.74	0.76	1.83	0.86
43	73.8	-	0.73	-	-0.59	-
48	74.2	-	0.75	-	-0.52	-
57	74.5	74.0	0.74	0.76	0.25	-4.07



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