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HIGH PERFORMANCE COATINGS CONTAINING UP TO 100% OF CALCIUM CARBONATE

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ABSTRACT

Calcium carbonate is now the dominant mineral used in paper coating. However, wide variations in the extent of its use exist even within the same type of paper or board.

Some of these differences are due to issues of local mineral availability and logistics, but others are due to the experience and sensitivities of individual mills.

In coated wood free grades, especially in Europe, it is not uncommon to be completely clay free. However, learning to run clay free has required a re-think on the control of coating solids, drying profiles and coating application.

Some board mills also run totally clay free, and in general where clay is used, it is used for its specific functionalities of physical coverage of a very rough base, for high uncalendered gloss and for improved activation of laser marking due to its specific beneficial impact on laser energy absorption.

The main benefits of an increased use of $CaCO_3$ are an increase in final sheet whiteness (blue shade), and lower cost of production, however, there may be challenges related to low gloss and coverage of the base. Therefore, the use of formulations containing 100% $CaCO_3$ requires a total system approach.

This presentation first introduces some typical formulations that are used in coated board and paper throughout the different regions of the world, and then explores the different ways in which an increased amount of $CaCO_3$ can generate maximum benefits.

The process of how to optimise coatings containing ultrafine $CaCO_3$ is described so that such coating can give equivalent paper and print gloss and physical coverage to those containing traditional amounts of glossing clay. Examples are then given for double coated woodfree and coated board which show that highest levels of performance can be achieved with coating containing up to 100% ultrafine $CaCO_3$ provided that coating colour solids, binder and co-binder concentrations are all optimised at the same time as the mineral.

Keywords: Coating color, gloss, optimisation, ultrafine $CaCO_3$.

INTRODUCTION

Many years ago, clay used to be the dominant mineral used in paper. However, the ability to produce under neutral pH conditions, an ever more demanding market requirement for high paper whiteness, and an increasing focus on operating cost has meant that calcium carbonate has now overtaken clay as the mineral of choice in the production of paper and board.

Since 2007, the global consumption of Ground Calcium Carbonate (GCC) in the paper and board industry has grown by over 10%, whereas kaolin consumption has decreased by nearly 30%. This trend seems likely to continue since there are strong cost drivers to utilise still higher amounts of GCC[1]. see Fig.1a,b.

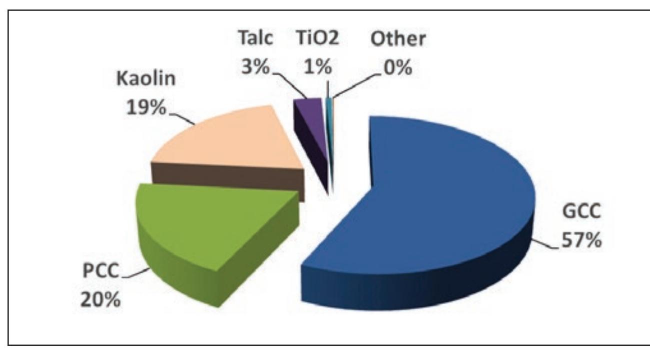

Figure 1a: Global mineral consumption 2013

Pigment	% Change 2007 to 2013
GCC	+13%
PCC	-3%
Kaolin	-27%
Talc	-247%
TiO2	-5%
Other	-75%
Grand Total	-2.7%

Figure 1b: Changes in consumption 2007 – 2013

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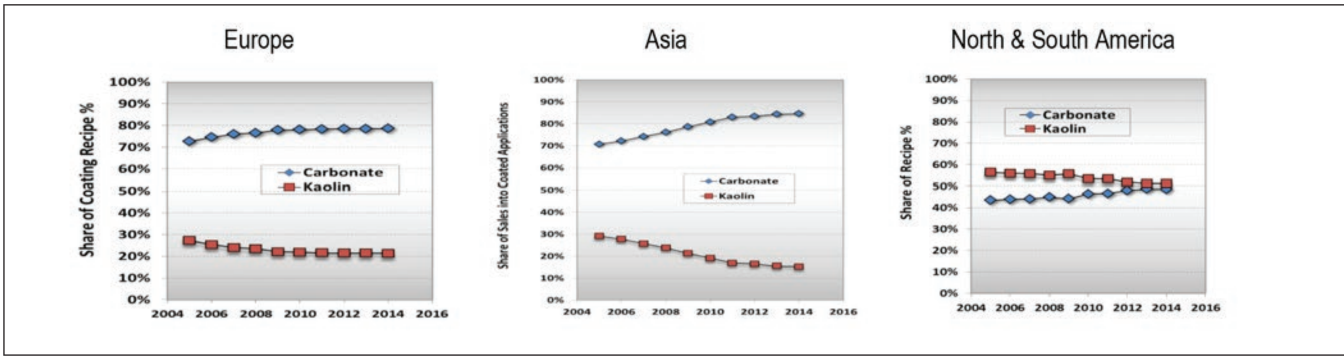

Figure 2. Mineral consumption trends in coating by global region

However, depending on local availability of minerals, and local "evolution" of coating equipment and practice, significant differences can still occur within different regions. See Fig 2.

These regional differences in mineral consumption are obviously translated in to differences in generic coating formulations. But, in addition, even within the same geographical region, papers with the same finished technical specification are often produced with formulations containing different types and very different ratios of calcium carbonate and clay.

For example, formulations for gloss and silk topcoats for Coated Woodfree range from containing 70:30 carbonate clay (particularly NA, SA and Japan) and high levels of binder (>11pph), to those with 100% carbonate and less than 8 pph binder. Indeed, clay free formulations are now well established on many major machines in Europe as well as some in Asia, especially because silk papers specially lend themselves to being produced with 100% ultrafine fine carbonates with little or no surface calendering.

Formulations for coated board also show wide variation. Certain producers use 100% calcium carbonate in both precoat and topcoat (GCC/engineered GCC/PCC), however it is still common to use some clay in to improve optical and physical coverage and laser marking[2].

Other ingredients, such as binders, co-binders and additives also often vary in quantity and characteristics to make the system a complex one. Even when considering just coated board, the ratios of pigment and binder can be very different between and within regions. See table 1.

In this paper, we outline the main differences in properties afforded by the different pigment types and also show some of the main levers which can be used to optimise formulation for good runnability and final properties. This is a review of a significant body of practical work carried out for research purposes and for customers within Imerys Minerals.

	North & South America		Europe		Asia	
	pre/middle	top (gloss)	pre/middle	top (gloss)	pre/middle	top (gloss)
Carbonate	100	70 - 30	100 - 60	100 - 70	100 - 60	100 - 60
Clay	0	30 - 70	0 - 40	0 - 30	0 - 40	0 - 40
latex	8 - 18	12 - 16	7 - 16	10 - 15	11 - 16	10 - ?
starch	8 - 0	0 - 5	5 - 0	0	?	?

Table 1. Typical range of pigment/binders found in Global coated board formulations.

In modern coating formulations, within the constraints of mineral availability and cost, minerals should be used for "what they are good at" as described by Nutbeem et al [3].

It is well known that calcium carbonate particles are blocky particles (low aspect ratio) with the potential (depending on the source raw material) for high whiteness (blue shade). Some typical values for different pigment brightness are shown in Fig 3a. It is also well known that clay particles generally have a significantly higher aspect ratio and lower brightness.

Therefore, in simple terms, clays should be used to maximise good physical coverage of a surface and to reduce surface porosity[4,5], whereas calcium carbonates should be used to achieve maximum whiteness and increase surface porosity. A summary table of strengths and weaknesses is shown in Fig 3b. In many cases a blend of different minerals is desirable to obtain the optimum balance of properties.

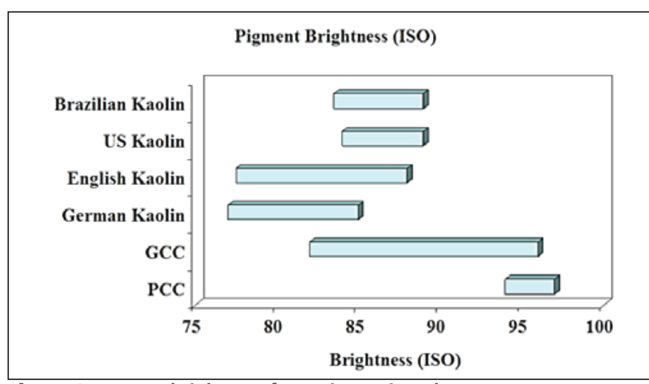

Figure 3a. Range brightness for various minerals

	Colour Solids	Paper Brightness	Paper Opacity	Fibre Coverage	Paper Gloss	Print Gloss
Coarse Ground Marble	++	+	-	+	--	--
Fine Ground Marble	++	+	-	---	-	--
Fine Ground Chalk	++	--	++	---	-	--
Fine Precipitated Calcium Carbonate	+	+	++	-	+/-	--
Fine Kaolin	-	-	+	+	++	++

Figure 3b. Strengths and weaknesses of various minerals

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This approach is especially interesting in multilayer coatings where each layer can provide specific functionality. This will be discussed further in the second half of this paper.

The key benefits of maximising the use of calcium carbonate are:

- Lower mineral cost
- Improved whiteness and blue shade (leading to lower OBA requirement),
- Faster ink setting rate (reduced problems of water interference mottle issues or set off)[6]
- Higher surface strength for a given amount of binder (this can translate in to a lower binder demand thus further reducing costs)
- Higher solids applications (reduced energy of drying).

Provided that a base paper is of high brightness, the simple replacement of clay by fine carbonate in the topcoat will significantly increase brightness and whiteness. However, because GCC particles show intrinsically poorer physical coverage and poorer dynamic water retention, properties such as paper and print gloss will be lower at equivalent coating solids. Therefore, operating a 100% carbonate topcoat requires the optimisation of the total system.

METHODS

This paper presents a collection of results from laboratory, pilot and industrial paper coating trials.

In all cases coating colours were prepared using 100 parts of each mineral pigment and a range of other additives including binders and co-binders.

Coatings were applied to woodfree and board base papers of varying grammages. Laboratory coatings were applied using a Heli-Coater™ with blade metering at a speed of >600m min-1. Pilot and industrial coatings used the equipment that was available at each site.

Coatweights were 11-13 gm^{-2} unless otherwise specified. Where identified in the text, papers were calendered to improve smoothness and gloss.

Standard properties were measured on both the coating colours and the finished papers/boards. Most methods, such as solids, low shear viscosity and static dewatering (AA GWR) on the coating colours and Gloss, Brightness and CIE Whiteness, and smoothness are described by their relevant Tappi and ISO norms.

However, in some cases proprietary methods were used for measurements. These include the measurement of print gloss, dry surface IGT strength (measured using low viscosity oil using an AIC2-5 unit (IGT) in accelerating mode with a maximum velocity of 2 ms^{-1}), dynamic dewatering of coating colours which measures the dynamic change in viscosity of a coating colour in contact with a base paper using a Paar Physica immobilisation cell (see Fig. 11), and the calculation of surface pore size from SEM images (Fig. 15).

Where particle size of pigments is referred to (Fig. 4), the values were measured in %mass fractions by a Micromeritics sedigraph.

RESULTS

Optimisation with increased amount of GCC topcoats

Sheet gloss is perhaps the most challenging issue with topcoats containing high levels of calcium carbonate. In general, at an equivalent particle size distribution, clay will give higher gloss than GCC. This is due to the lower microroughness of the coating containing clay and is related to the shape of the particles[7,8].

Optimisation of pigment particle size

When maximising the amount of GCC in a coating formulation, the first optimisation that is required is that of the particle size of the GCC itself. Ultrafine pigments are required in order to reach high levels of gloss[9]. See Fig 4.

Optimisation of coating solids

After the particle size, the most important factor to optimise is that of coating colour solids. Fortunately, "blocky" GCC particles have good rheology and, therefore, can be coated at much higher solids than formulations containing clay. In Europe, papermakers routinely coat topcoats in double and triple coated CWF and board and packaging grades at >70% solids without issues of dilatency.

Higher coating solids have a positive effect on paper and print gloss. For example, an increase in topcoating solids from 65% solids to 69% can increase gloss by around 5 units, when coated on a precoated smooth base (Fig 5.)

Higher solids will also help to improve the coating colour dewatering behaviour. The following example compares the AA GWR

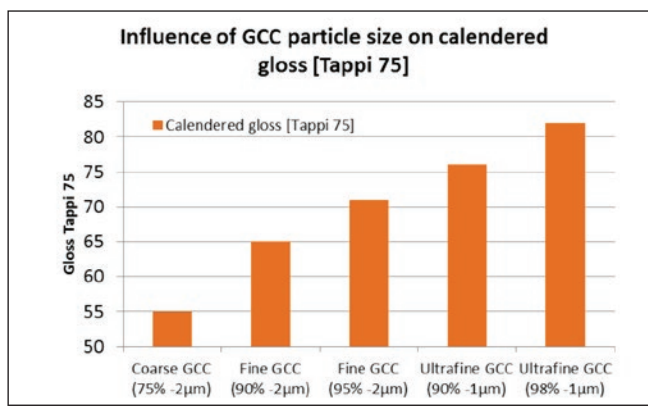

Figure 4. Effect of particle size on gloss of 100% GCC coatings

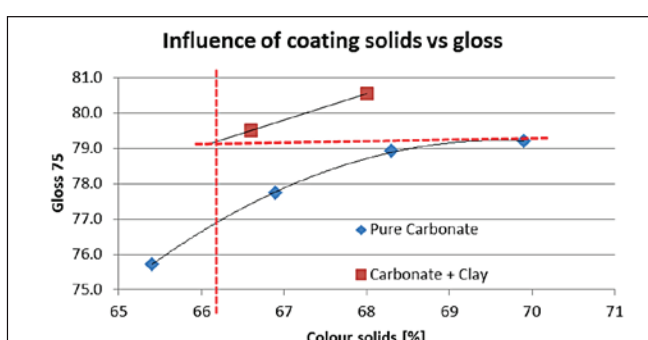

Figure 5. Effect of particle size on gloss of 100% GCC coatings

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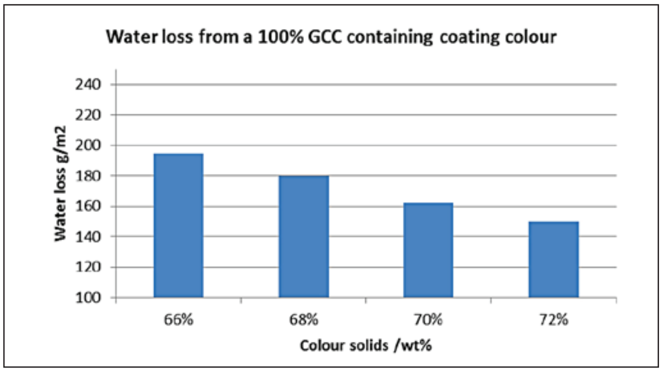

Figure 6. Effect of colour solids on water retention

static dewatering of fine broad GCC at 4 different solids levels to give an indication of the impact of varying solids content on dewatering. The method is described by Sandas *et al* [10]. As the initial coating colour solids content increases, the dewatering decreases. See Fig. 6.

The lower amount of water present in a coating colour at high solids obviously also has the additional benefit of requiring less drying energy – for example an increase of 4% in coating colour solids (66 to 70%) will reduce the energy needed to dry the coating colour by around 20-30kWhr/T. There have been several publications concerning the migration of binder during coating colour application, the consolidation and drying process[11,12,13] and the dewatering process and interactions between coating colours and basepaper[14,15,16]. An excellent review of the subject is given by Engstrom[17] and additional data is given in a second paper in this conference[18].

Optimisation of binder, co-binder and other additives

Another benefit of high solids coating associated with 100% calcium carbonate formulations is the possibility to make considerable reductions in binder concentrations. These reductions both reduce cost, and provide an additional route to increasing the gloss of the unprinted surface since binder level has a significant impact on gloss.

Typically, 100% ultrafine standard GCC formulations can be run with 2-3pph less binder compared to formulations with 20-30pph clay due to the reduced presence of pigment ultrafines in the pigment and the reduced migration of binder away from the topcoat. The intrinsic shape of the particles also plays an influence with the platey kaolin being stronger in the X-y direction but weaker in the z direction, which will impact the pick strength[19,20]. See Fig. 7.

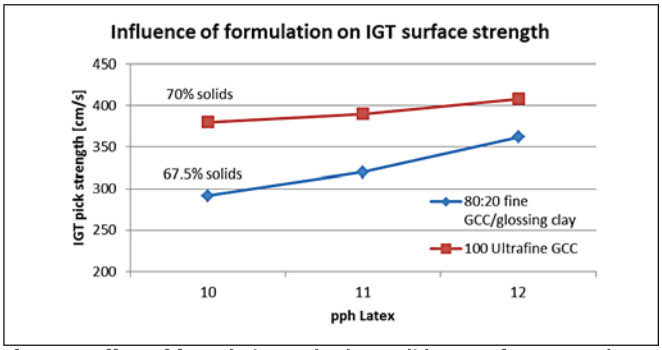

Figure 7. Effect of formulation and colour solids on surface strength

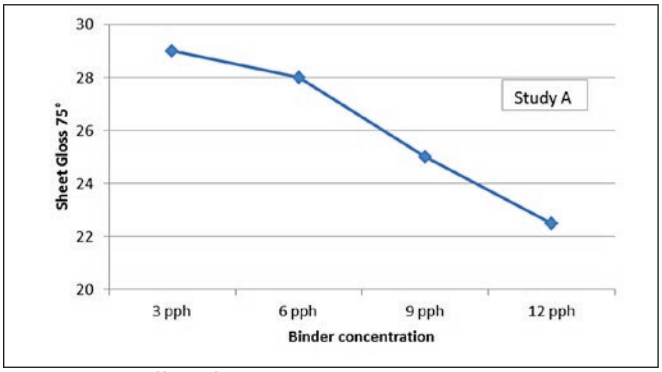

Figure 8a. The effect of binder level on uncalendered gloss (Study A)

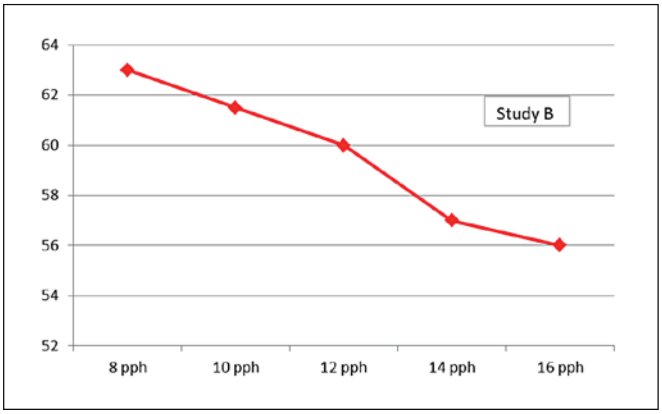

Figure 8b. The effect of binder level on calendered gloss (study B)

A reduction of 2 parts of binder should increase both the calendered and uncalendered paper gloss by around 1-2 units. See Fig. 8a and Fig. 8b.

The nature of the binder itself can also be varied in order to influence both paper and print gloss. Paper gloss is influenced by the particle size of the latex. See Fig. 9a.

Print gloss is impacted by the roughness of the paper substrate[21], the pore structure of the coating layer[22] and finally by the polar nature of the polymer chains and networks. Incorporating polar monomers such as acrylonitrile or butyl acrylate into the latex reduces the interaction with ink vehicle. The interaction between the ink oils and the binder chemistry will impact the rate that the ink will

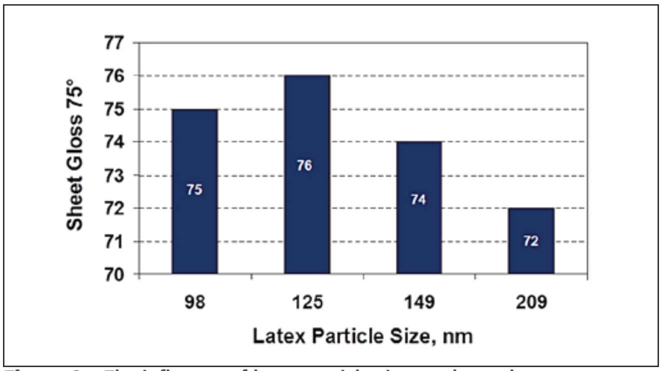

Figure 9a. The influence of latex particle size on sheet gloss

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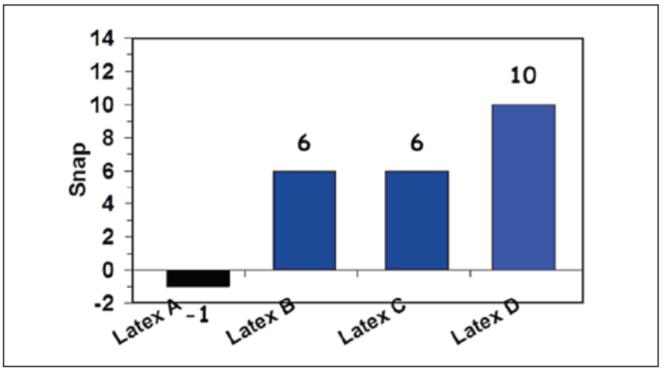

Figure 9b. The influence of latex on "snap" or Delta Ink gloss

immobilise and set, and this will impact the final print gloss[23,24, 25]. See Fig. 9b.

As pigment particle size becomes finer, the optimum binder particle size also needs to be finer. The finer latex is better accommodated within the coating pore structure, and ink tack development is slowed down leading to higher print gloss.

The choice of co-binder also can significantly influence both coating colour dewatering (ease of running at high solids), and paper gloss itself as a result of shrinkage during drying. An example of this is shown in Fig. 10.

Maximum gloss is often obtained with synthetic thickeners that allow the highest solids operating window. The example in Fig. 11 shows that changing co-binder from 0.5pph CMC to 0.2pph synthetic thickener improves the dewatering characteristics of a 100% ultrafine carbonate coating colour and, therefore, allows it to be run at 1 unit higher solids. The measurements were made using a Paar Physica immobilisation cell and precoated base paper with a shear rate of 2000s^{-1} .

Other optimisations that should be considered when using high levels of GCC in topcoats include the reformulation of additives such as OBA and OBA activators (eg. PVOH).

In particular, if the full whiteness gains that are obtained when replacing clay by ultrafine GCC in a topcoat are not required, then the concentrations of both OBA and OBA activators can be reduced, often by over 50% or repositioned to the precoat, since the increased transparency of a 100% ultrafine GCC coating will allow the fluorescence from the precoat to dominate sheet brightness. For example, in the graph in Fig. 12 below, the final sheet brightness +UV could be maintained with a reduction of OBA addition in the precoat from 0.7pph to 0.4pph.

One disadvantage of high solids coating is that the coating runnability window is smaller than when coating at lower solids.

However, many mills have taken on this challenge, and have found that this can be managed by both coating and formulation design. At high solids, bent blade application is generally preferred and should

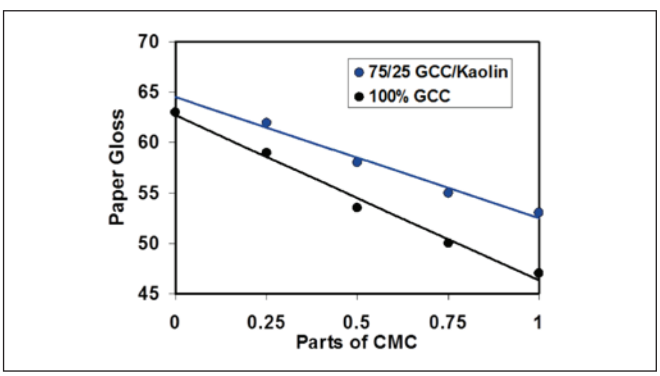

Figure 10. Effect of co-binder concentration on sheet gloss

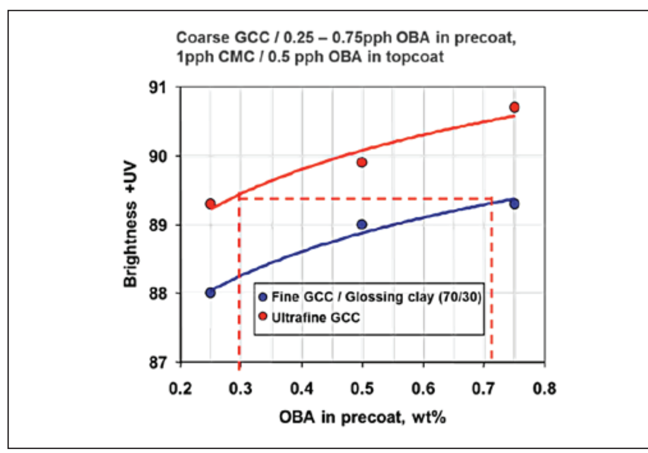

Figure 12. Potential for OBA reduction with high white 100% GCC formulations

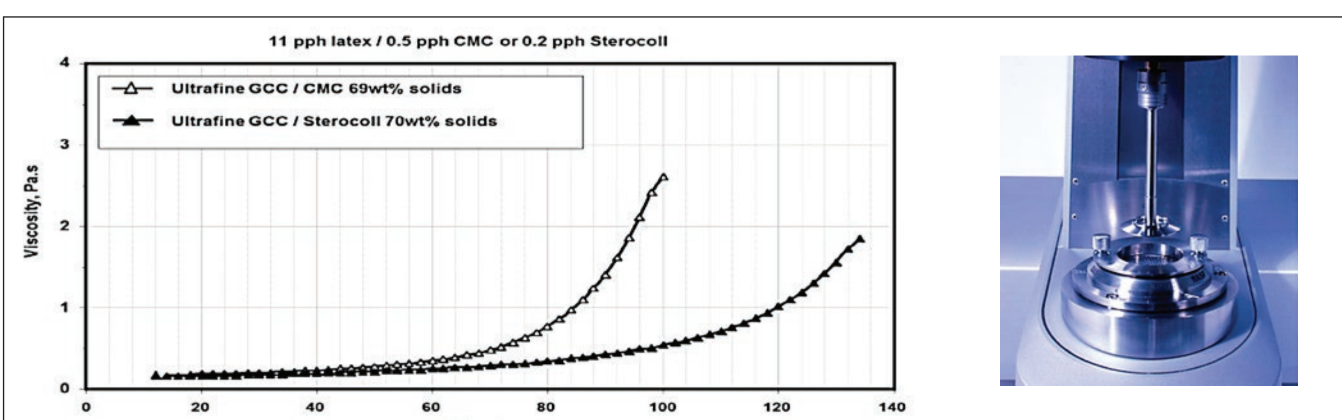

Figure 11. Influence of thickener on coating colour solids and dewatering (Paar Physica immobilisation cell)

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	Recommended for high solids coating especially with low coatweight
Blade angle	High
Blade extension	Low
Loading (enforcement)	Low
Pre-tension	3 - 4mm. Used to rigidify the blade and control ct wt profiles
Blade bevel	High
Blade type	Ceramic

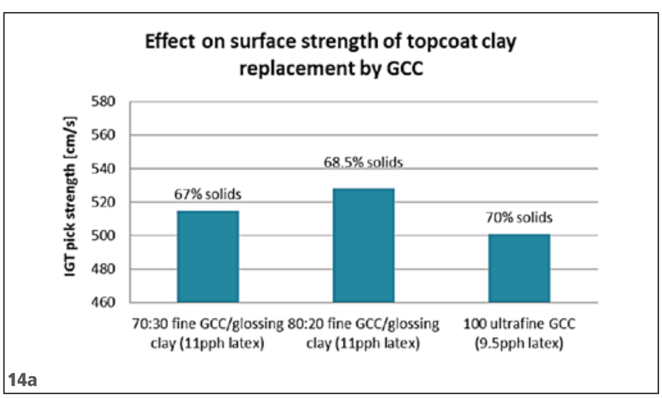
Figure 13. Practical recommendations for high solids coating with bent blade geometry

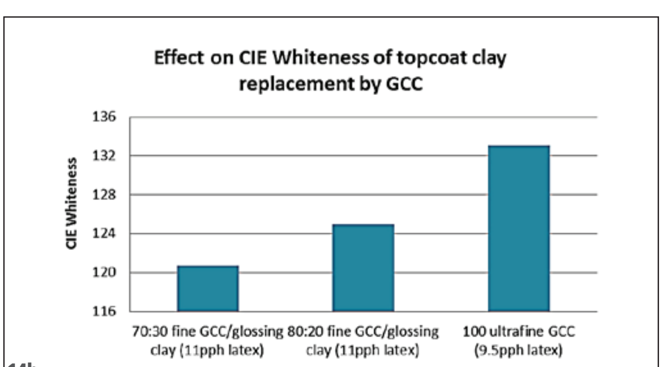
be carried out with high blade angle, low free blade extension and high blade bevel[26] (see Fig. 13). In addition, care needs to be taken to introduce the minimum amount of water with the showers at the base-coating interface and thickener needs to be chosen for maximum water retention.

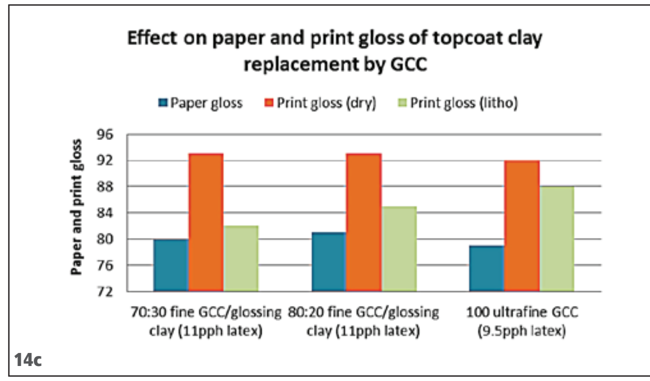
As shown above, all the levers of particle size, coating colour solids, binder type and concentration and choice of thickener will be needed when targeting maximum gloss with coating colours containing 100% calcium carbonate.

In order to match the gloss of a clay-containing coating, an all-carbonate coating will need to contain ultrafine particles, and will need to be coated at high coating colour solids, contain less binder and use optimised thickener.

Some of these modifications can be seen in the coating example below (Fig. 14a,b,c), where increasing colour solids and reduction in binder allowed paper and print gloss to be maintained whilst increasing CIE whiteness by 12 units.

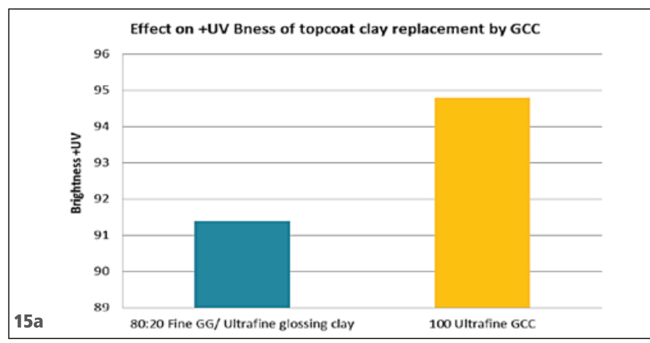


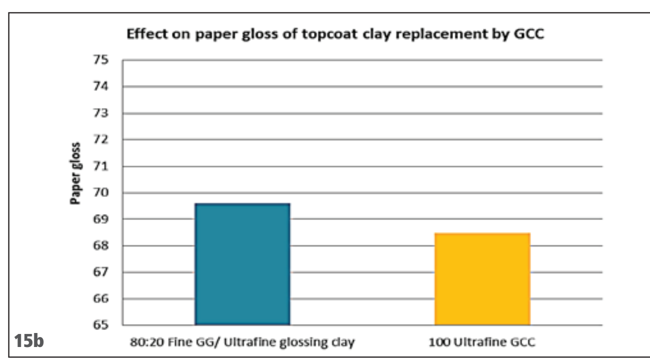


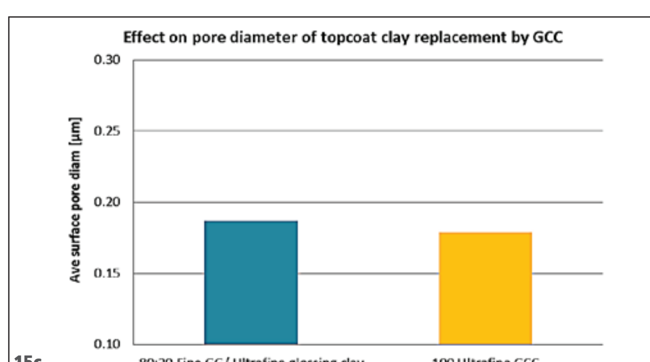


Figures 14a,b,c. Coating example of the potential of 100% GCC coatings (Improved strength & whiteness at equal gloss)

Another example is taken from mill trial results (Fig. 15a,b,c). In this instance, we looked at a double coated woodfree application,







Figures 15 a,b,c. Mill trial results for optimised use of 100% ultrafine GCC in topcoat. (Pore diameter data calculated by image analysis from SEM surface images)

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using a metering size press for the precoat and a blade coating for the topcoat. The precoat contained a standard coarse GCC.

In the topcoat, the standard was a blend of fine GCC and ultrafine glossing clay. This was changed to an ultrafine GCC with the particle size chosen to maintain sheet gloss and surface porosity. Paper quality was maintained whilst gaining over 3 units in +UB brightness.

Total system optimisation

So far, we have seen that optimisation of a single coating layer can allow increased use of calcium carbonate in topcoats, however, in multilayer systems often the best strategy is to optimise both precoat and topcoat together.

In Europe, the traditional way of making board was to use a strategy of low cost carbonates in precoat and clay/calcium carbonate blends in topcoat for coverage and gloss. However, over recent years, the European board industry has taken a total system approach and has moved to clay / carbonate precoats for combined optical and physical coverage of the basepaper, together with maximum high solids carbonate for topcoating.

In this approach, each pigment is used for its key strengths. (Fig. 16.)

In papers or boards containing multilayer coatings, the role of the precoat is to provide cost effective basepaper coverage. The topcoat must then provide a micro-smooth surface that is suitable for paper and print gloss development. It also controls the surface porosity to ensure fast ink setting and a homogeneous uptake of ink (low mottle)[27].

In the optimised system approach, inclusion of platey kaolins together with GCC in the precoat improves both optical and physical coverage of the fibres (Fig. 17).

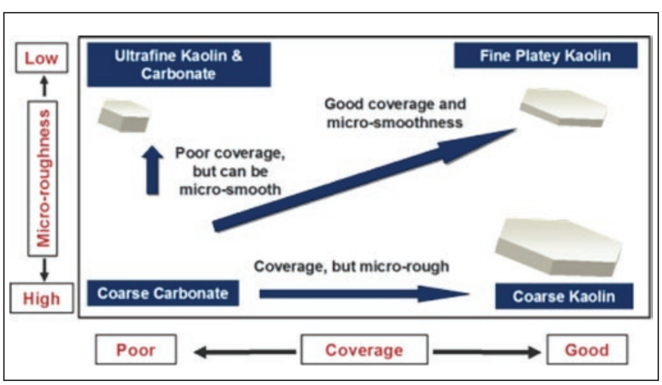

Figure 16. Illustration of pigment influence on the relationship between coverage and micro-roughness

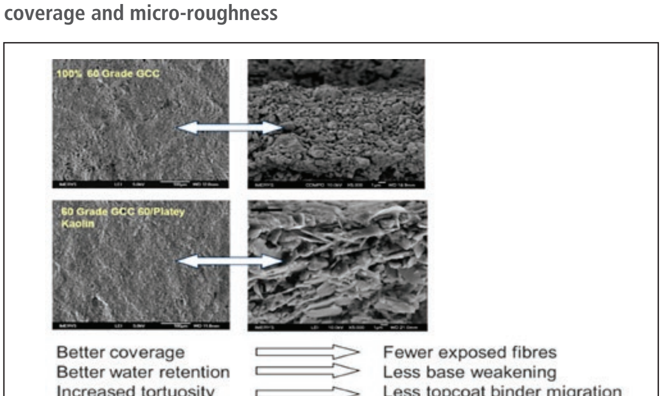

Figure 17. The influence of kaolin in precoat

The example below shows that, on a low brightness base, this approach can result in higher gloss, increased smoothness and higher final board brightness compared to a more traditional approach. (See Fig. 18a,b,c)

It should be noted that if the base board is sufficiently smooth and does not require the presence of clay for physical coverage, then a similar overall brightness gain can be achieved by using natural rather than high brightness calcium carbonates to provide improved optical coverage of the base layer.

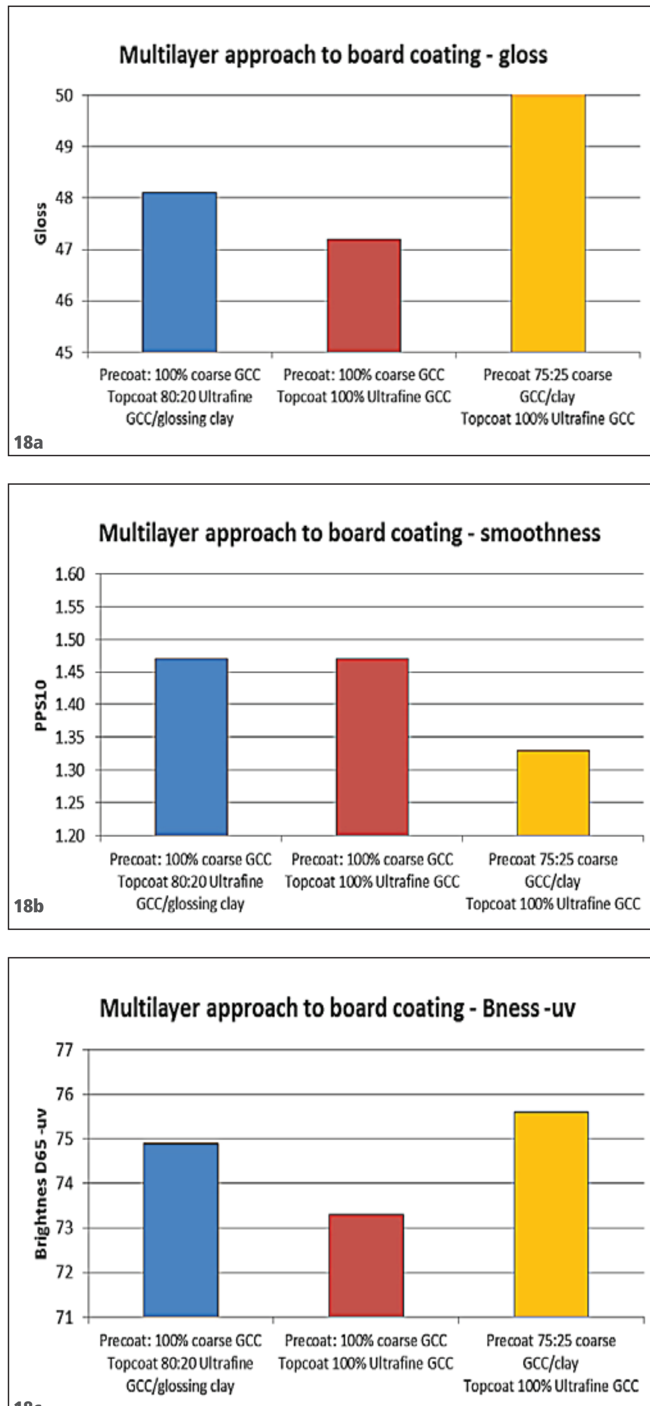

Figure 18a,b,c. Optimised board using a combined precoat and topcoat approach

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CONCLUSION

Calcium carbonate is the dominant mineral used in paper and board production. This paper has reviewed various approaches to maximising its use in coating formulations. Topcoats containing 100% Calcium carbonate can match the performance of traditional coatings provided that all aspects of the coating formulation are optimised, including mineral particle size, coating colour solids, and coating formulation. In particular, when producing double coated paper and board, the key strengths of both Calcium Carbonate and kaolins should be synergistically combined within the different coating layers in order to provide maximum optical and physical coverage of the base, as well as high whiteness and lowest chemical demand.

- Topcoats with 100% ultrafine CaCO3 can give:
- Improved shade and higher brightness – less OBA required.
- Similar gloss.
- Better water retention (at high solids).
- No pigment makedown required on site – (savings in energy, chemicals, maintenance and staff)
- No treatment of makedown waste water required.
- Overall formulation cost reduction. ■

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