Material Retention: A Novel Approach to Performance of Pigment Coating Colors

물질 보류 : 안료 코팅 처리를 위한 새로운 시도

Mr. Teuvo Piilola

CP Kelco Oy

제33회 펄프 · 종이기술 국제세미나

MATERIAL RETENTION:

A NOVEL APPROACH TO PERFORMANCE OF PIGMENT COATING COLORS

Ken McKenzie, Anne Rutanen, Jukka Lehtovuori, Jaana Ahtikari,

Teuvo Piilola

CP Kelco Oy

Äänekoski

FINLAND

ABSTRACT

Cost efficiency is today the primary requirement in the paper and board industry. This has led therefore, to a greater preponderance of products with specifically designed functionality to take account of current industry needs. Continually increasing machine coating speeds together with these new coating colour components have put more emphasis on the importance of the correct rheology and water retention of the coating colours to achieve good runnability and end product quality.

In the coating process, some penetration of the aqueous phase, to the base paper or board must occur to anchor the pre-coating to the base or the topcoat to the pre-coat. The aqueous phase acts as a vehicle not only for the binder, but also for the other components. If this water or material penetration is not controlled, there will be excessive material shift from the coating colour to the base, before immobilization of the coating colour will stop this migration. This can result in poor machine runnability, unstable system and uneven coating layer, impacting print quality.

The performance of rheology modifiers or thickeners on the coating color have tended to be evaluated by the term, “water retention”. This simple term is not sufficient to explain their performance changes during coating. In this paper we are introducing a new concept of ”material retention”, which takes note of the total composition of the coating colour material and therefore goes beyond the concept of only water retention. Controlled material retention leads to a more uniform z-directional distribution of coating colour components. The changes that can be made to z-directional uniformity will have positive effects on print quality as measured by surface strength, ink setting properties, print gloss, mottling tendency. Optical properties, such as light scattering, whiteness and light fastness delivery should also be improved. Additionally, controlled material retention minimizes changes to the coating colour with time in re-circulation giving less fluctuation in quality in the machine direction since it more closely resembles fresh coating for longer periods.

Use of the material retention concept enables paper and board producers to have more stable runnability (i.e. lower process costs), improved end product quality (i.e. better performance of used chemicals) and/or optimized use of coating colour components (i.e. lower total formulation cost).

SUMMARY OF RESULTS

As stated earlier, controlled material retention has a target of ensuring that the coating colour remains stable throughout the process and to control the mobility of the material in the coating layer prior to immobilization. Once both of these targets are reached the end product quality is more uniform both in machine and z-direction. Key observations from our work can be summarized as follows

- Controlled material mobility ensures uniform end product quality such as surface strength and whiteness.

- Blade induced pressure penetration is more significant with jet application compared to roll application and therefore understanding and control of the particle mobility under higher shear rates becomes more critical.
- The understanding of the influence of thickeners (and the mechanism of slip velocity) on the boundary layer is highly important in assessing their impact on machine runnability and end product quality.
- Penetration of material through excessive particle mobility can be controlled through modification of aqueous phase viscosity and immobilization properties.
- Insufficient control of material retention results in changes in the particle size distribution of the coating colour. This leads to deviations in the colour due to re-circulation of coating colour thus negatively impacting machine direction quality uniformity.

INTRODUCTION

Cost efficiency is today the primary requirement in the paper and board industry. Cost efficiency means maximized productivity (good runnability, minimum amount of broke – stable process) and optimized use of raw materials (maximum performance with minimum addition level – right component in right place) resulting in uniform end product quality. This has led therefore, to a greater preponderance of products with specifically designed functionality to take account of current industry needs. For example the development of the pigments and the latexes has a similar trend; smaller particles and narrower particle size distribution. Continually increasing coating machine speeds together with new or modified coating colour components have put more emphasis on the importance of the correct rheology and water retention of the coating colours to achieve good runnability and end product quality. Today the coating colour optimization is often done on a single component basis, but in order to be truly cost efficient, a more holistic view should be taken to ensure coating colour optimization.

The aqueous phase of the coating colour acts as a vehicle for its various components. If this water (and material) penetration is not controlled, there will be excessive material shift from the coating colour to the base, before immobilization of the coating colour will stop it. The migration rate towards the surfaces of primarily pigment particles, latex and OBA will have a significant impact on coated paper quality and machine runnability. This migration rate is exacerbated particularly if especially small size and narrow distributions of pigment and latex particles are used. This results in a greater rate of mobility, significantly influencing particle-packing behaviour and resultant end product quality.

In this paper we will demonstrate that it is possible to control mobility of the material by the correct choice of a thickener. This will be illustrated by end product performances such as surface strength, optical and printed paper properties showing the impacts of thickener type on the perceived improvements to z-directional distribution of the materials. Furthermore we will show that material retention can be evaluated and a predictive assessment to mill scale performance be made by indirect methods in laboratory scale. This will be of great benefit and importance to coating mills for cost effective performance of their coating units. This is achieved through the optimization of the location of the key coating components throughout the coating layer to maximize their performance. Traditionally coating colour research concentrates on fresh coating colour analysis. The results therefore, can be contradictory to mill scale findings as the stress factor of coating colour processing is missing, severely minimizing the value of the obtained results.

Historically, indirect methods such as low and high shear viscosity and static water retention have been utilized to evaluate coating colour performance and in many cases still are. These methods seldom take into account the influence of key factors such as base paper, coating colour circulation or coating process stabilization time. In order to achieve a more complete picture of the influence of coating dynamics, we have adapted known test methodologies, namely dynamic water retention (DWR), slip velocity and particle size distribution of coating colour to allow this. The combination of these methods allows us to monitor changes in coating colours during the coating process and suggest formulation modifications to maximize performance. /1/

In this paper four different coating colours were adjusted from the perspective of improved material retention according to the findings published in our previous paper /1/ of the methods developed. Paper coating, calendering and printing were done on pilot scale, the details of which are summarized later in this paper. Three different co-binding/thickening systems were chosen to assess their impact on effective control of material movement and thus z-directional distribution. Additionally, one further formulation with a lower latex level with a modified CMC was run to determine the impact on binder mobility, since there are obvious cost in use implications if successful. The pigments, additives and coating colour solids were kept constant. High shear viscosities were adjusted to the level that is considered appropriate for good runnability, by adjustment of the co-binding/thickening component. From experience this is targeted at 35 – 50 mPa·s using a capillary rheometer. The slip velocity can be used to assess the mobility of aqueous phase at high shear rates, and was adjusted to the level below 10 m/s (at 17 000 N/m^2), which under these conditions we have found to be suitable in the efficient control of material mobility.

Mobility of the aqueous phase

When coating colour is applied onto the paper, there is a natural penetration of the aqueous phase into the paper influenced by, the coating colour characteristics, by the base paper properties and the type of coater application/metering geometry. The aqueous phase contains pigment fines, binders, optical brightener, water soluble materials and free dispersing agents. It is therefore evident that the ability to control the mobility of these functional components are critical to ensure optimum machine performance and end product quality and uniformity.

In the blade coating process, the aqueous phase penetrates into the paper by both capillary and pressure forces. Pressure penetration is facilitated during coating application and under the blade during the metering phase. Base sheet penetration through capillary action, happens in the phases between coating application and blade metering and in the subsequent period until total coating immobilization occurs. Quantitatively it is difficult to separate out these two types of penetration, since both phenomena occur at same time regarding liquid penetration into the paper. It has been demonstrated /2, 3/ that pressure has a fundamentally more important influence on liquid penetration than contact time. It is important therefore to keep this in mind in relation to continuing increases of coater speed.

Capillary and pressure penetration relate to different characteristics of the coating colour. The wetting ability of the aqueous phase on wet pigments and on wet fibres has significance. If the aqueous phase wets fibres well, but doesn't wet pigments, both capillary and pressure penetration are high. The pigments adsorb different amount of water; clay more than calcium carbonate and fine pigments more than coarse. However under external pressure the pigment particles come closer to each other and they will lose some adsorbed water. Consequently the balance of surface energies and polarity of different components

control both the penetration rate and level. Increased solids of the coating colour at constant coat weight necessitates higher blade pressures, thus increasing the pressure penetration..

Increase in aqueous phase viscosity slows down penetration. Temperature has an influence on the penetration via the impact on aqueous phase viscosity. At high temperature the viscosity is lowered and the resulting penetration is greater. If the binder/co-binder is poorly adsorbed on the pigment, or bonds break down under pressure/shear forces, more binder remains in the aqueous phase and the resultant viscosity of the aqueous phase will increase through the different mechanisms described later in this paper. /4, 5/

There are several factors relating to the base paper, which also have influence on the amount of absorbed liquid. It has however been shown that modifications of colour have a greater influence on the penetration tendency of the aqueous phase, than changes in the absorption characteristics of base paper. /6/

In jet applications, a significantly lower pressure pulse prior to blade tip is applied on the coating compared to roll application resulting in a significantly thinner filter cake and a lower penetration of materials. A thinner filter cake before the blade is also the reason for a slightly higher dewatering under the blade. The highest pressure occurs under the blade tip. /7/ so it can be assumed that from a material penetration point of view in jet applications the role of blade load is greater than in roll applications. At higher speed the dwell time prior the blade becomes shorter and an even thinner filter cake is formed before the blade. Due to this the pressure penetration and dewatering tendency increases and the material flow control becomes even more critical, again impacting machine performance and end product quality.

EXPERIMENTAL

Thickeners

This work covered different types of commercial thickeners, which have different thickening mechanisms, resulting in different kinetic impacts on water and material retention. One of the thickeners was a conventional sodium carboxymethyl cellulose (CMC) used in paper coatings. Another thickener was a modified CMC, where the cellulosic backbone has been manipulated during the manufacturing process to provide improved material retention properties through enhanced water retention capability and faster immobilization through improved associative behaviour /1/.A further test point was an alkali swellable emulsion (ASE). Low molecular weight fully hydrolyzed polyvinyl alcohol was used in conjunction with the ASE synthetic. This is a typical industry practice to provide additional properties, which synthetics in general do not normally provide alone.

Water-soluble rheology modifiers impart their effect on a system through one or more distinct mechanisms. The thickening mechanism is strongly related to the chemical structure of the chosen rheological additives. The main types of mechanisms for thickeners when building their viscosity are presented in Table I.

Table I. Main mechanisms types for thickeners

	Conventional CMC	**Modified CMC**	**ASE**	**PVOH**
Associativity	+*	++*	+	+*
Aqueous phase viscosity	+++	+++	++	+

* = Depending on the pigment system

Base paper

The base paper used in the trials was pre coated un-sized wood free paper. The pre coat weight was 8 g/m^2 and the total grammage 91 g/m^2.

Coating formulations

Coating formulations used in this work consisted of the following:

- Narrow particle size ground calcium carbonate
- Fine china clay
- Carboxymethyl cellulose (Finnfix CMC)
- Typical alkali swellable emulsion

- Small particle size SB-latex
- Low molecular weight fully hydrolyzed polyvinyl alcohol
- Tetra sulfonated optical brightening agent

Formulation details are listed in Table II.

Coating colours were made to constant solids content at pH 8.5 and 9. The latex level in one coating colour using the modified CMC grade was decreased by one part in order to assess the effect of this specific product on the z-directional distribution of binder.

Table II. Coating colour formulations

Colour	Conventional CMC	Modified CMC	Modified CMC + less latex	ASE + PVOH
GCC	70	70	70	70
Clay	30	30	30	30
CMC	0.7	0.6	0.7	-
PVOH	-	-	-	0.4
Latex	10	10	9	10
OBA	0.5	0.5	0.5	0.5
Synthetic thickener	-	-	-	0.3
Solids, %	63	63	63	63
pH	8.5	8.5	8.5	9.0

Pilot data

Pilot trials were carried out at KCL (Keskuslaboratorio Oy, Finland). The essential trial conditions are presented in tables III, IV and V.

Table III. Coating conditions (Opticoat Jet-coating)

	Conventional CMC	**Modified CMC**	**Modified CMC + less latex**	**ASE + PVOH**
Speed, m/min	1200 and 1500	1200 and 1500	1200 and 1500	1200 and 1500
Beam angle, °	50	50	50	50
Blade dimensions	0.381/84 mm, 40°	0.381/84 mm, 40°	0.381/84 mm, 40°	0.381/84 mm, 40°
Pumping speed, %	45	35	35	35
Blade pressure, bar (1200 m/min)	0.63	0.58	0.57	0.66

The target moisture content was 5.0 %. The base paper was heated using electrically powered infra drier. The coated papers were dried using electrically powered infra driers and gas heated airfoil driers.

Table IV. Supercalendering conditions (Multical)

	All trial points
Nips	4+1+5
Temperature °C	70
Speed, m/min	750
Target gloss %	70

Table V. Printing conditions (Roland Favorit RVF)

	All trial points
Speed, sheet/h	5000
Printing inks	Rapida series (HostmannSteinberg)
Target densities	black 1.85, cyan 1.50, magenta 1.15, yellow 1.15

Coating colour analysis

Basic properties of coating colours (solids content, pH, static water retention, density and viscosity at different shear rates) were analyzed. Solids content was measured with Mettler-Toledo HR73 Halogen moisture analyzer. Viscosities of coating colours were measured with Brookfield RVDV-II+ viscometer (100 rpm), Hercules HI-shear viscometer DV-10 and with capillary rheometer (DT Paper Science) (capillary: 50 mm/0.5 mm). Static water retention (ÅA-GWR) was measured using constant coating colour volume 10 ml (5 µm membrane, 0.3 bar pressure, 2 min). Density was measured gravimetrically. Furthermore slip velocity was measured with capillary rheometer (DT Paper Science) /8/, dynamic water retention was determined with coater by DT Paper Science applying Novicoater method /1/ and the particle size distribution was analyzed using Coulter LS 13 320MW device. All measurements were performed after standardized handling at constant temperature (25 °C).

Coated and printed paper analysis

Standard paper analyses were performed to coated papers. In this paper we are presenting the results that are relevant from the material retention point of view. To these critical parameters were chosen surface strength, CIE-whiteness and print gloss.

Surface strength was measured with IGT AIC2-5 according ISO 3783 standard. CIE-whiteness was measured with Minolta CM 3700D according ISO 11475 standard. From 4-colour printed papers print gloss (90 % black, 67 % cyan, 67 % magenta and 67 % yellow) was measured with Hunter 75°.

Results

Coating colours

Viscosities

Properties of the fresh coating colours are presented in Table VI. There were differences in viscosities at different shear rates of coating colours since thickener dosages were selected in order that mobility of the aqueous phase was controlled. Coating colours with CMC as thickener had similar viscosities through the whole measured shear rate area. Coating colour with synthetic thickener had lower Brookfield viscosities and higher high shear viscosities that CMC colours. The viscosities at high shear rates are presented in Figure1.

Table VI. Properties of fresh coating colours

Fresh coating colour	**Conventional CMC**	**Modified CMC**	**Modified CMC + less latex**	**ASE + PVOH**
Solids, %	63.1	62.8	62.8	63.2
Density, kg/dm^3	1.47	1.45	1.45	1.44
Static water retention ÅA-GWR, g/m^2	145	150	135	125
BrRV viscosity (at 100 rpm), mPa·s	1400	1200	1300	750

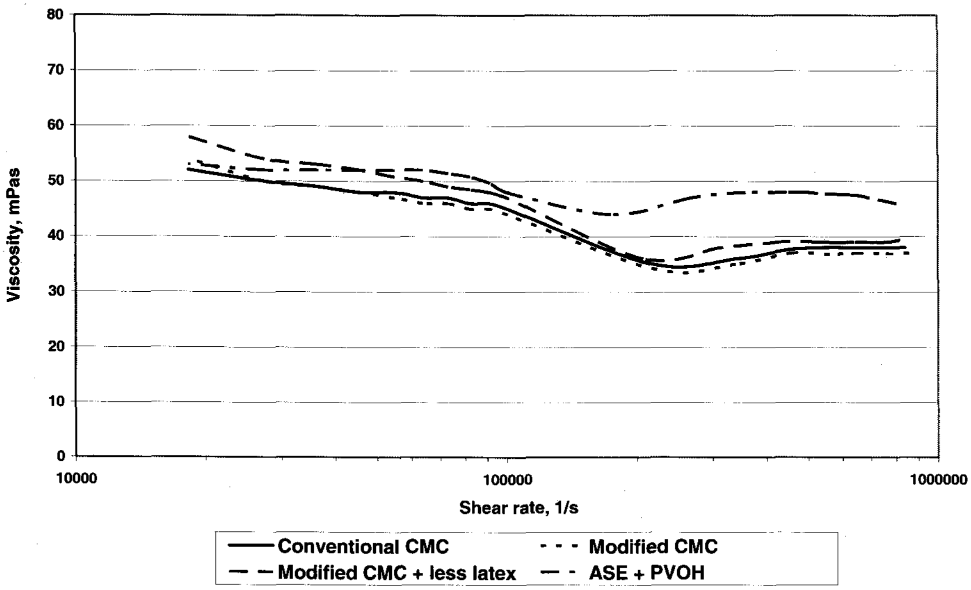


Figure 1. High shear viscosity curves of fresh coating colours (Hercules + capillary).

Properties of the coating colours after the pilot trial are presented in Table VII. Minor changes in basic properties were noticed and only major change happened in the density of the synthetic thickener coating colour; density decreased about 8% during the trial due to air entrapment. All coating colours were diluted slightly due to edge showers.

Table VII. Properties of coating colours after pilot trial

After trial	**Conventional CMC**	**Modified CMC**	**Modified CMC + less latex**	**ASE + PVOH**
Solids, %	62.8	62.5	62.5	63.0
Density, kg/dm^3	1.45	1.40	1.41	1.32
BrRV viscosity (at 100 rpm), mPa·s	1300	1200	1300	750

Water retention

The static water retention method (ÅA-GWR) is a measure of the amount of water released from the coating colour during a certain time under a defined pressure. The greater the value the worse the apparent water retention under these static conditions.

The dynamic water retention method (Novicoater DWR) is based on the actual change of the coating colour solids during the coating process. The lower the change in solids content of the coating colour, the better the water retention./1/ Although the static method results indicate that synthetic thickener coating colour has better water retention, there is virtually no differences in the results measured at dynamic conditions (see Figure 2.) Based on our previous experiences we can see that all the coating colours have good water retention, which combined with correct high shear viscosity levels is beneficial for good runnability. The differences seen here are not significant and is a further confirmation that our methods allow more targeted control of mobility.

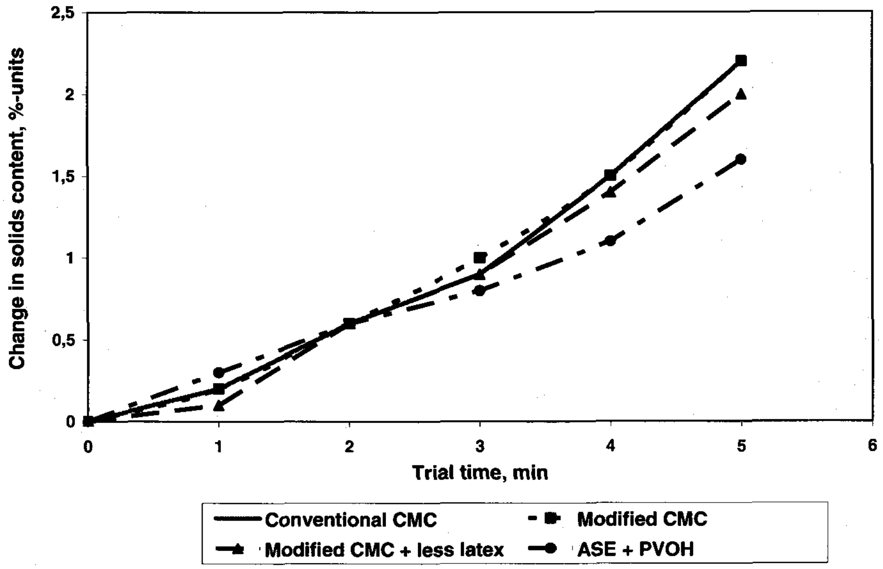


Figure 2. Dynamic water retention results of the fresh coating colours.

Slip velocity

Slip is an inherent characteristic of a pigmented coating suspension that depends on pigment particle packing behavior and solids fraction volume; the state of dispersion and the flowability of the continuous phase and is measured using capillary viscometry. A possible mechanism for the creation of a slip layer is a lower concentration of particles next to the capillary wall than in the bulk color, due to the particle migration and size segregation. These phenomena have been detected during shear flow with several optical methods and analyzed mathematically. The slip layer has a relatively high shear velocity and more material flows through the capillary tube than expected by theory with non-slip boundary conditions. Slip velocity can be related to easy release of water from the bulk color, lubrication ability of small particles (ball bearing effect) or polymer coils (viscosity of aqueous phase). /8/ It is essential to understand the control mechanism of the material mobility so that to the correct level of slip velocity can be determined. Thickener dosages in these coating colours were adjusted so that slip velocity of all coating colours was on a low level, which under these conditions is correct in order to control the material mobility efficiently. Slip velocities did not change significantly during the pilot trial coatings. Slip velocities of fresh coating colours are presented in Figure 3.

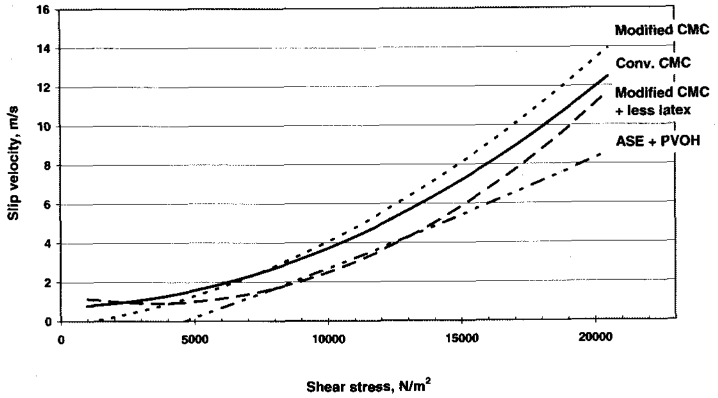


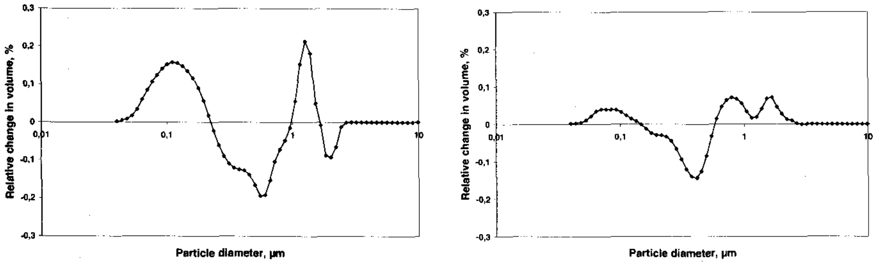
Figure 3. Slip velocity results of the fresh coating colours.

Particle size distribution

Coulter LS 13 320 particle size analyzer measures particle sizes with an assumption that all particles are round, and therefore it is not possible to get absolute particle sizes. However, studying the changes in particle size distributions is an effective way to monitor the stability of coating colours even if all particles are assumed to be round. The stability of coating colours can be monitored by measuring particle size distributions of fresh coating colours and coating colours after the run and by comparing particle size distributions to each other. Changes indicate phenomena such as coating colour homogeneity being compromised through excessive movement of particles of certain size (relatively in volume) or if aggregates are formed.

Particle size distributions of coating colours before and after the pilot trial coatings are presented in Figure 4. Coating colours with modified CMC were very stable and only small if any changes in particle size distributions could be seen during the pilot trial. Coating colours with traditional CMC or synthetic thickener/PVOH had some changes in particle size distributions during the trial even though the mobility of aqueous phase was controlled and therefore the mobility of particles should be restricted. This is most probably due to higher blade pressures required for these two coating colours. Higher blade pressure, as indicated earlier results in higher pressure penetration forces leading to preferential movement of coating colour components more towards the base paper. This leads to more difficult control of material movement. The reasons for higher blade pressures were higher capillary viscosity (synthetic thickener) and higher amount of coating colour applied to the paper due to higher flow rate of the jet (conventional CMC). To be able to control the movement of material with high blade pressure even more controlled material mobility is needed. Understanding the implications of this facilitates the correct choice of coating color composition.

Conventional CMC **Modified CMC**



Modified CMC + less latex **ASE + PVOH**

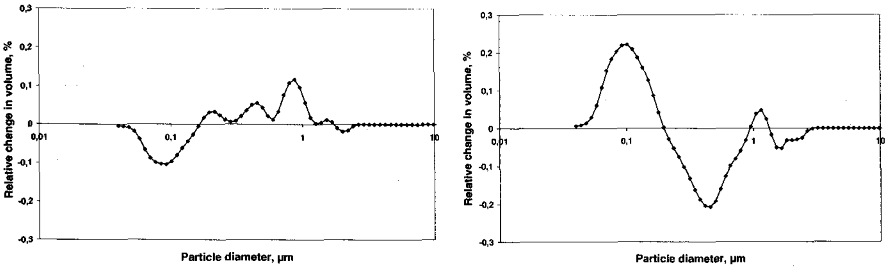


Figure 4. Particle size distributions of coating colours before and after the pilot trial.

Coated and printed papers

Controlled material retention allows the coating colour to remain more stable throughout the process and to control the mobility of the material in coating layer prior to immobilization. Once both of these targets are reached the end product quality is much more uniform both in machine and z-direction. Coating colour testing give indications about the coating colour stability and therefore also about machine directional uniformity. Paper tests enable us to postulate the impact on z-directional uniformity.

Surface strength

Surface strength of the papers was determined by measurement of picking and delamination tendencies in the laboratory (see Figure 5). These tests did not show any differences between the trial points. This indicates that significant reduction in binder level is possible if the material retention is properly controlled. The fact that CMC also functions as a binder in its own right (binder strength higher than with SB-latex /9/) becomes more significant when lower latex levels are considered as part of cost reduction programs.

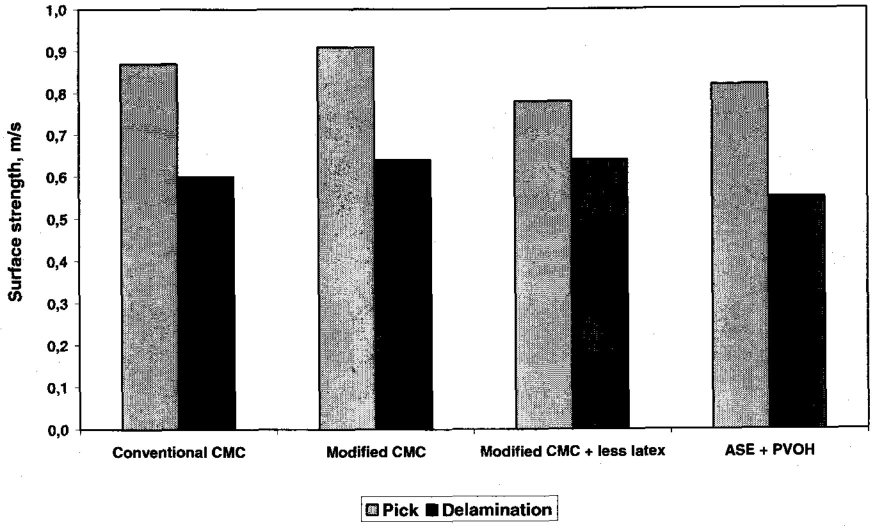


Figure 5. Surface strength (cd)

CIE-whiteness

CIE-whiteness was measured from the papers coated at 1200 m/min and 1500 m/min with equal coat weights (12 g/m^2). The results are presented in Figure 6. Changes in particle size distribution already indicated that there is more material movement in the synthetic thickener coating colour and the whiteness results are confirming this. Increased pressure penetration is most likely forcing material, particularly OBA more towards base paper and therefore resulting in lower whiteness level due to the location of the OBA. The difference is increasing with higher machine speed suggesting sub-optimal mobility control despite meeting slip and water retention targets.

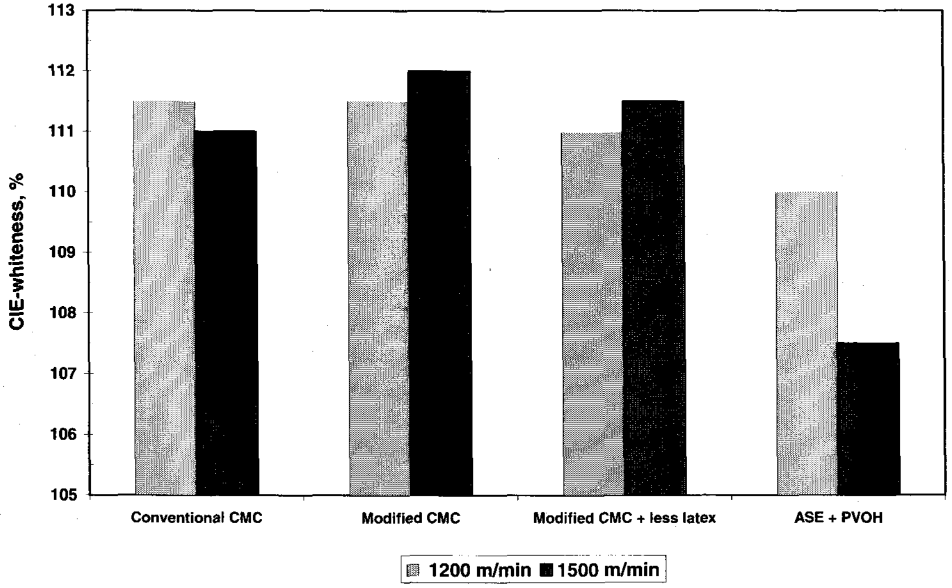


Figure 6. CIE-whiteness

Print gloss

In order to see the influence of co-binder systems on printability all the papers were calendered to the same gloss level. We have made the assumption that the papers have comparable micro smoothness levels as well. Print gloss results presented in Figure 7. show that there are minor differences between the CMC coating colours. It is known that latex reduction will give a more porous surface impacting the printability. Correct choice of CMC grade and addition level together with controlled material retention ensures that there are no changes in end product printability. Meanwhile the synthetic thickener coating colour gives much lower print gloss. Variations in print gloss we believe are most probably due to differences in component composition on the surface (i.e. latex level) and in pore structure as evidenced by the changes in particle size distribution shown earlier.. The air entrapment into the coating colour which can be a tendency of this system will also result in an even more porous surface structure.

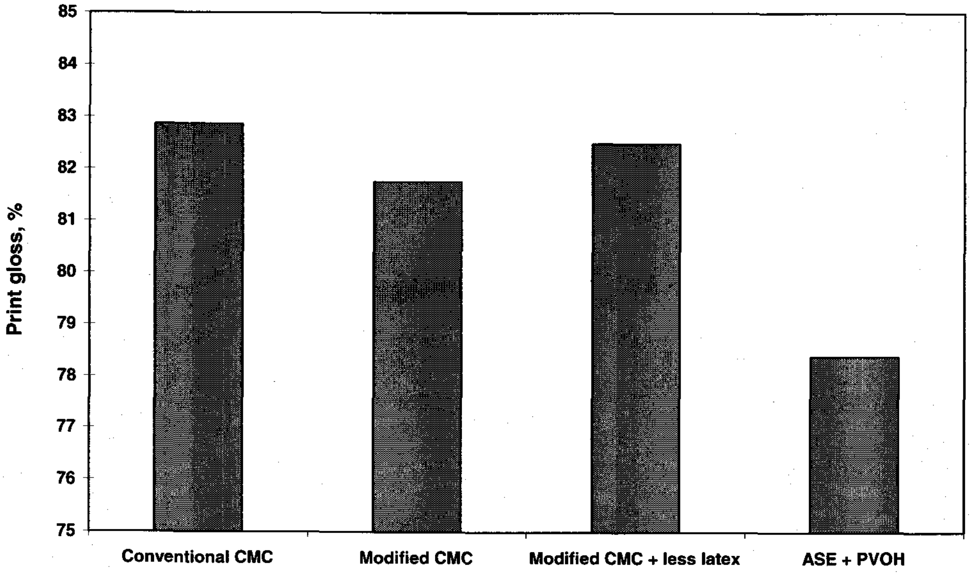


Figure 7. Print gloss

CONCLUSIONS

This concept of material retention takes note of the total composition of the coating colour material and therefore goes beyond the concept of only water retention. In this paper four coating colours were optimized to have best possible material retention without sacrificing the runnability. Actual coating results showed that even minor differences in coating conditions can have significant impact on end product quality. Therefore it is even more important to have a holistic view on the whole coating process including base paper, coating colour and process parameters.

The material movement due to pressure and capillary penetration can be controlled by aqueous phase mobility, immobilization properties and high shear viscosity. It is important to have all these parameters on the correct level simultaneously. Traditional methods of coating colour measurement, such as low shear viscosity, static water retention are not sufficient for determining potential performance; they are suitable only for quality control purposes.

The slow immobilization of the conventional CMC coating colour combined with the high blade load led to higher material movement, which could be seen in changes in particle size distribution. Although there were no major changes seen in this study with the CMC colors, this could lead to changes in end product uniformity in machine direction in continuous operation. High capillary viscosity of the synthetic thickener coating colour led to blade load induced pressure penetration causing major changes in particle size distribution and lower end product quality even in this short trial. Therefore it can be concluded that it was not possible to optimize both capillary viscosity and aqueous phase mobility simultaneously. Modified CMC coating colours with controlled material retention gave the most uniform results. This enabled the optimization of the latex level without changes in surface strength and print gloss.

As a final conclusion, controlled material retention leads to more uniform z-directional distribution of coating colour components. Additionally, controlled material retention minimizes changes to the coating colour with time in re-circulation giving less fluctuation in quality in the machine direction since it more closely resembles fresh coating for longer periods. Use of the material retention concept enables paper and board producers to have more stable runnability (i.e. lower process costs), improved end product quality (i.e. better performance of used chemicals) and/or optimized use of coating colour components (i.e. lower total formulation cost).

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