EFFECT OF A THERMALLY ACTIVE COBINDER ON COATED PAPER PROPERTIES AND PRINT QUALITY

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ABSTRACT

Two cellulosic polymers (EHEC and CMC) have been evaluated in pilot coating trials with respect to their function as cobinder in two different coating formulations; one typical calcium carbonate-based top coating formulation and one clay-based light-weight-coated (LWC) formulation. For each grade the coating formulation was thus varied only by variation of the cobinder.

It was found, especially in the LWC formulation, that EHEC interacted strongly with the binder and reduced the amount of binder in the surface. Depending on the choice of cobinder, significant differences in wetting properties, gloss and print gloss were found. Only small differences were detected in the developed surface microstructure, as determined by visual evaluation of micrographs from environmental scanning electron microscopy. According to results from mercury porosimetry the variation in cobinder type gave no differences in porosity but significant variations in dominating pore size, which in turn correlated with the water absorption properties.

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INTRODUCTION

Cobinders are used in paper coating formulations in order to control the water retention as well as the flow properties of the coating color. The cobinder is added in only a small amount; typically 0.1-1.5 parts per 100 parts of pigment depending on the type of cobinder. Despite the low level of addition, the type and amount of cobinder in a coating color may have a significant effect on the final coating layer properties, such as roughness, gloss, wet ability and print quality (1-7).

Commonly used cobinders include natural polymers, such as starch and carboxymethyl cellulose (CMC), and synthetic polymers, which are often different types of polyacrylate products. Dahlvik et al. (8) made a fundamental study of the function of ethyl hydroxyethyl cellulose (EHEC) as a

cobinder in coating colors, and found that there may be pronounced interactions between the EHEC and the other components of the color, such as the pigment and the binder (latex) particles. The interactions were promoted by a temperature increase, as the EHEC, which is water-soluble at low temperatures, has a temperature-induced precipitation character and becomes increasingly hydrophobic upon heating. The interactions between EHEC and other components were characterized by studying the temperature-dependence of the viscosity. A viscosity increase with temperature was interpreted as indicating a pronounced interaction. The interaction between EHEC and pigment particles was in most cases substantial, but the degree of interaction was dependent on the type of pigment. A significantly larger amount of EHEC was adsorbed on clay than on calcium carbonate. A very strong increase in viscosity with increased temperature has also been detected with suspensions of EHEC and English clay (9).

A significant interaction is strongly related to the presence of styrene-butadiene binder, preferably with a high proportion of butadiene (8,9). In this context, interactions between EHEC and the surfactant used to stabilize the binder may be important. Previous studies have shown that solutions of EHEC in the presence of ionic surfactants are very temperature-sensitive and show a dramatic increase in viscosity on heating (10,11). Furthermore, it has been shown (11) that gel formation of an ionic surfactant and EHEC induced by heating is a result of a binding of the surfactant to the polymer at elevated temperatures.

It could thus be expected that the use of EHEC in a coating color will affect the properties of the final dry coating layer, as a consequence of interactions taking place between EHEC and other components such as pigment and binder particles. In the present study, two cobinders (CMC and EHEC) are compared with respect to the chemical and physical surface properties of paper, coated with two different coating formulations; one clay-based LWC (Light-Weight-Coated) formulation and one typical calcium carbonate-based top coating formulation.

EXPERIMENTAL

Materials

In the “top coating” formulation, the pigments were a ground calcium carbonate (Hydrocarb CC) from Omya Oy, Finland and an ultra-fine US clay (Miragloss 91). In the “LWC” formulation, the pigment used was delaminated US clay (Nugloss). Engelhard Pigments Oy, Finland delivered both clay pigments. Two model styrene-butadiene (SB) latexes (SB22 and SB10, with Tg of 22°C and 10°C respectively) from Dow Europe S.A., Switzerland were used as binders. Each formulation was varied only with respect to the cobinder, either CMC or EHEC being used, in amounts corresponding to a Brookfield 100 rpm viscosity of 1000 mPas of the coating color. EHEC was supplied by Akzo Nobel Surface Chemistry AB, Sweden and the CMC (Finnfix 10) by Metsa Specialty Chemicals OY, Finland. The average molar masses of the EHEC and the CMC were 60,000 and 66,000 respectively. The formulations are given in **Table 1**.

A 86 g/m^2 woodfree pigment precoated (7 g/m^2/side) base paper from MoDo Husum paper mill, Sweden was used with the top coating formulation, and the LWC formulation was coated on a 46 g/m^2 mechanical base paper from Myllykoski Paper, Finland.

	Top coating		LWC	
	pph	pph	pph	pph
GCC	70	70		
Ultrafine US clay	30	30		
Delaminated US clay			100	100
SB latex (SB22)	11	11		
SB latex (SB10)			11	11
EHEC	0.5		0.63	
CMC		1.15		1.1
Solids (%)	65	65	60	60
Coat weight (g/m^2)	11	11	11	11

Table 1. Coating formulations used in the pilot trials.

The coating trials were performed on the pilot coater of Dow Europe S.A., Switzerland. Both sides of the paper were coated with an applicator roll and a trailing blade at 1000 m/min and 1400 m/min for the top coating and the LWC formulations respectively. Drying conditions were applied to reach specified final moistures. The papers were calendered under constant conditions to enable differences in gloss properties of the papers to be detected. All the papers were printed in heat-set web offset as well as sheet-fed offset at KCL pilot plant in Espoo, Finland. The web offset printing was performed at a fixed print density with a printing-speed of 50 000 copies per hour. The sheet-fed offset printing was carried out under constant conditions at a speed of 5000 copies per hour.

Methods

Viscosity

The influence of temperature on the viscosity of pigment suspensions and cobinder-latex dispersions was evaluated using a controlled stress rheometer (StressTech, ReoLogica Instruments AB, Sweden). A constant shear rate of 4 s^{-1} was applied to the sample, using a bob/cup configuration, while the sample was heated in a water bath at 3°C/min. In order to obtain similar initial viscosity levels in the laboratory measurements, the calcium carbonate-containing coating color was evaluated at the solids content of 62% by weight and the clay color was evaluated at 60 %. The cobinder-latex dispersions, in relative amounts corresponding to the formulations, were evaluated at a solids content of 14 weight-% using a double gap configuration. The pH-value was 8.5 in all the measurements.

Uncalendered samples.

Burn-out

The unevenness of the mass distributions of the coating layers was evaluated with a burn-out test including image analysis, where the burn-out test was performed according to the principle described by Dobson (12). In this test, the sample is saturated with a solution consisting of 25 g/L of ammonium chloride in equal parts of water and ethanol. After saturation, the sample is dried under ambient conditions, followed by drying in a ventilated oven at a temperature of 225 °C. In this case the drying time in the oven was 5 minutes. During this heat treatment, the base paper

carbonizes and turns black, allowing non-uniformities in the coating mass distribution to be detected. An image analyzer from Kontron A.G., Germany, was used to determine the mean gray-tone value and the variance in the gray-tone of the burn-out samples. Frequency analysis with a band pass procedure was applied and the coefficient of variation of the gray tone value was reported for the intervals 2-4 mm and 4-8 mm. This coefficient of variation was taken as a measure of the non-uniformity in mass of the coating layer (13).

HG-porosimetry
Hg-porosimetry (AutoPore III, Micromeritics, USA) was used to obtain measures of the pore volume, the pore area and the dominating pore radius of the coating layers.

Croda staining
The ability of the coating layer to absorb printing ink was estimated by measuring the intensity of the ink stain according to the Croda test method. The contact times used before removing the excess of Croda ink were 30, 60, 180, 240, 540 and 960 s.

Dynamic water sorption test
The water absorption capability of the coating layer was evaluated with a dynamic water sorption tester, using an external pressure of 0.1 bar. The equipment is described in detail by Salminen (14). In the dynamic water sorption test, a reel of the paper is passed over a pressurized slit, filled with water. By maintaining a constant pressure and varying the speed of the paper, different contact times can be obtained. The absorbed amount of water is calculated as g/m^2.

Surface free energy
A dynamic absorption tester (DAT 1100), from Fibro Systems, Sweden, described in detail by Elftonson and Ström (15), was used to evaluate the surface free energy of the coated papers. In these measurements, a high-speed video camera is used to measure the contact angle between two liquids (water and tetrabromoethane) and the surface of the sample. From these measurements the surface free energy can be calculated.

Microscopy
A visual characterization of the coated paper surfaces was obtained using environmental scanning electron microscopy (ESEM).

Optical properties
Gloss, brightness (with and without UV radiation) and opacity were measured with standard testing equipment.

Calendered samples

Before printing, the top coated papers were calendered with 7 nips at 80 °C, using a line load of 230 kN/m and a speed of 500 m/min. The LWC papers were calendered at 200 kN/m at the same temperature and speed. The samples were further evaluated by measuring the paper gloss and the print gloss. Coated laboratory calendered (at room temperature, 20 kN/m, one nip per side) samples were studied by ESEM and by performing UV-scanning experiments.

UV-technique

The UV-scanning experiments were performed according to the principle described by Fujiwara and Kline (16), using a CS-9000 flying spot scanner, from Shimadzu Seisakusyo, Japan. The principle of the measurement is based on the absorption of UV radiation of the SB binder at certain wavelengths. An area of 64 x 64 mm^2 of each sample was analyzed, in lines, 4 mm separated from each other. On each line, measurements were made at 2 mm intervals. In this way, a three-dimensional profile is generated, showing the relative amount of binder in the surface. The mean value, $S_{\Delta 260}$, and the standard deviation, $V_{\Delta 260}$, of the amount of binder in the surface are automatically displayed.

Uncalendered and calendered samples

Both uncalendered and calendered samples were evaluated by standard laboratory methods; PPS H 1000 smoothness, the K&N absorption test, IGT dry pick, wet pick, ink refusal, ink set off and ink piling.

RESULTS AND DISCUSSION

Figure 1 shows the viscosity as a function of temperature for dispersions of EHEC and the corresponding two latexes used, as well as for dispersions of CMC and the corresponding latexes. Both EHEC-containing dispersions exhibited an increase in viscosity, starting at about 35°C with a local maximum at 50 – 55°C. The viscosity values were however much higher when SB10 was used.

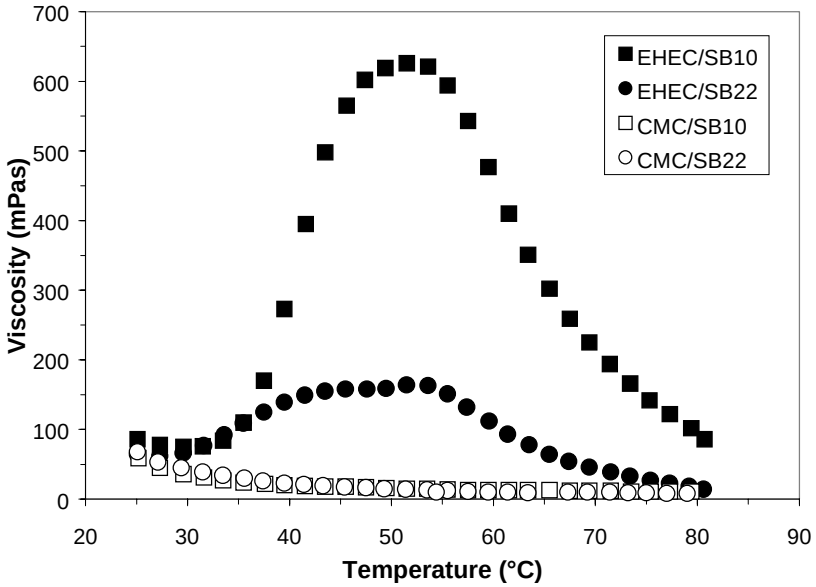

Figure 1. Influence of temperature on the viscosity of latex-EHEC and latex-CMC dispersions.

When CMC was used as cobinder, no temperature-related increase in viscosity was detected, but rather a continuous decrease in viscosity with increasing temperature. Clearly, there was a

temperature-induced interaction between EHEC and the SB-latexes, the softer SB10 latex (lower Tg) giving a stronger interaction. This behavior has also been reported and discussed in a previous study (8). When solutions of only EHEC or only CMC were heated, the viscosity decreased in both cases (17).

The dependence of the viscosity of the investigated coating colors on temperature is shown in **Figure 2**. Again, the presence of EHEC gave rise to a viscosity maximum at a certain temperature, again with the softer SB10 latex giving the highest viscosity. The effect of temperature on the viscosity of the CMC-colors was small, but the calcium carbonate-based color showed a slightly increasing viscosity with temperature. This might have been a result of an increasing solids content, due to a slight evaporation during the experiment. It can be seen in figure 2 that the end value of the viscosity of the carbonate-based color with EHEC as cobinder was similar to the end value of the corresponding color containing CMC. It can therefore be concluded that both carbonate-based colors underwent the same relative change (increase) in viscosity during heating.

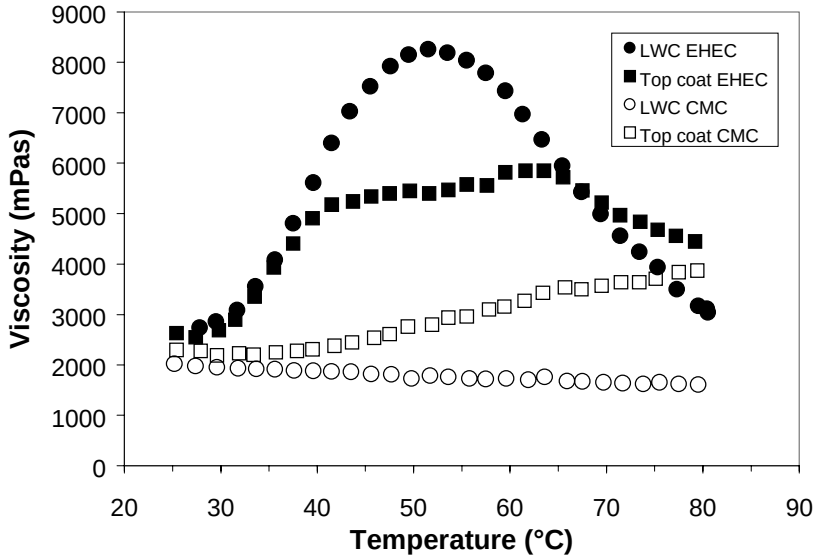

Figure 2. Influence of temperature on the viscosity of coating colors.

According to the Hg-porosity measurements of the uncalendered coating layers (**Table 2**), no significant differences in pore volume were found between the two top coated papers or between the LWC papers. Some differences were detected in the pore area and in the dominating pore radius. The pore radius can be related to liquid absorption characteristics and the ink setting properties of the coating layer, as a smaller pore radius has been shown to correspond to higher solvent (ink oil) absorption (18) and faster ink setting (19,20). When the top coating and the LWC formulations are compared, it can be seen that the top coating formulation resulted in a coating layer with somewhat higher values overall. This is a consequence of the difference in morphology of clay and calcium carbonate and thus in the tortuosity of the clay-based and the calcium carbonate-based coating layers.

	Top coating		LWC	
	EHEC	CMC	EHEC	CMC
Pore volume (cm^3/g)	0.44	0.44	0.26	0.26
Pore area (m^2/g)	21.9	24.2	9.6	10.4
Dom. pore radius (μm)	0.052	0.048	0.035	0.041
Calculated porosity (%)	52	52	39	39

Table 2. Data from Hg-porosity measurements of the coating layers.

Some optical properties of the uncalendered surfaces are listed in **Table 3**. In the case of the LWC papers, there were no significant differences in opacity or brightness, but the gloss values tended to be lower with EHEC. In the case of the top coated papers, the brightness was slightly higher when EHEC was used, possibly because less EHEC was used than CMC. As in the case of the LWC papers, the gloss values for the uncalendered top coated papers were lower with EHEC than with CMC.

	Top coating				LWC			
	EHEC	S.d.	CMC	S.d.	EHEC	S.d.	CMC	S.d.
Gloss (MD) %	21.6	0.7	22.9	0.8	12.4	0.5	13.6	0.5
Gloss (CD) %	17.3	0.6	19.4	0.5	11.2	0.3	12.2	0.3
Brightness (with UV) %	90.9	0.1	90.6	0.1	77.1	0.1	77.2	0.1
Brightness (no UV) %	86.8	0.1	86.3	0.1	77.3	0.1	77.3	0.1
Opacity %	94.2	0.1	94.6	0.1	92.3	0.2	92.3	0.2

Table 3. Some optical properties of the uncalendered coated papers.

There was a slight difference in the amount of SB-binder in the surface depending on the choice of cobinder, as measured with the UV-technique (**Table 4**). With EHEC, a slightly lower amount of binder was detected for both formulations, but the variation was slightly greater in the case of the top coating. In the LWC coatings containing EHEC, the standard deviation was lower. The smaller amount of binder in the surface when EHEC was used could be due to interactions between the EHEC and the binder, and possibly also the pigment, creating a more uniform binder distribution in the z-direction. The relative difference was greater in the LWC coating, which agrees well with the high interaction between EHEC-latex-pigment (figures 1 and 2).

	Top coating		LWC	
	EHEC	CMC	EHEC	CMC
$S_{\Delta 260} - 20000$	24151	24901	8847	9301
$V_{\Delta 260}$	716	682	802	939

Table 4. Results from UV scanning measurements (relative units).

Figure 3 shows results from the measurement of the contact angle of water. Relatively small differences were detected in the values of the contact angle on the top coated papers, especially at short contact times. In the case of the LWC papers, there were significant differences in these values already at a contact time of 0.1 s. In both cases, the contact angle was lower with EHEC than with CMC, which also agrees well with the measured amount of binder in the surface (table 4).

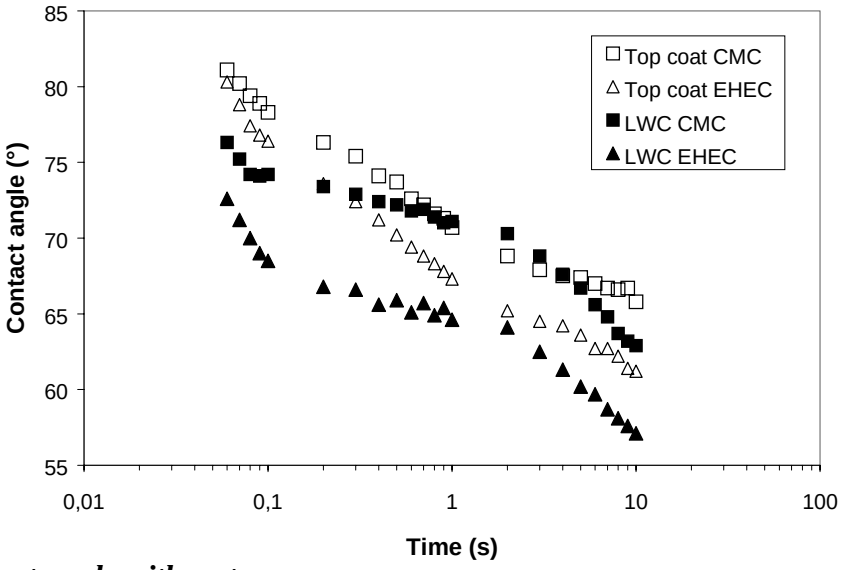

Figure 3. Contact angle with water.

The surface free energy followed to a large extent the trend for the contact angle. Values for the surface free energy at a contact time of 0.1 s are given in **Table 5**.

Top coating		LWC	
EHEC	CMC	EHEC	CMC
51.2	50.6	54.8	51.2

Table 5. Surface free energy (mN/m) at a contact time of 0.1 s.

Figure 4 shows the results of Croda stain experiments on the four papers. The top coated papers showed higher stain intensity values than the LWC papers, but there were no substantial differences associated with the EHEC or CMC. The intensity of the Croda stain can be considered to reflect the porosity of the tested surface. The results also correspond well with the data from the Hg-porosity measurements (table 2), in which the top coating formulation gave higher values, but no dependence of porosity on cobinder type was detected.

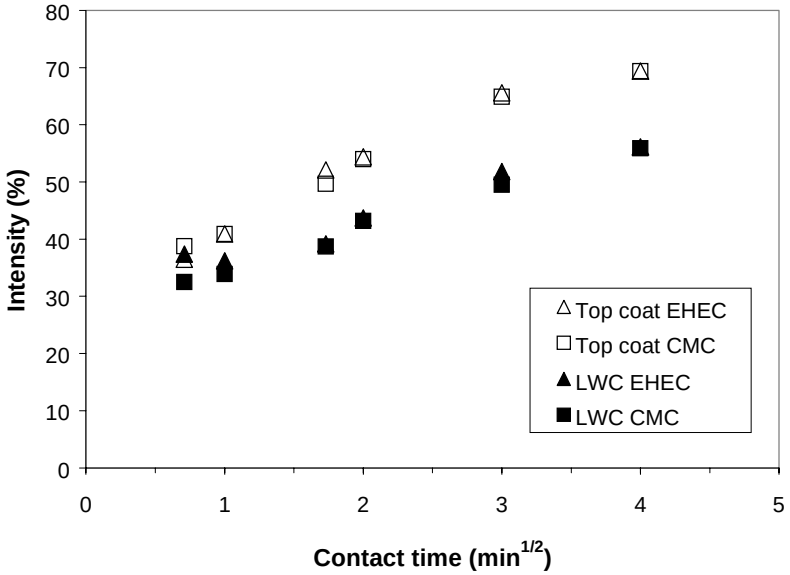

Figure 4. Intensity of Croda stains.

Figure 5 shows the water sorption capability of the different papers, using the dynamic sorption tester at an external pressure of 0.1 bar. When these results are compared with those given in figure 3 and table 5, it can be seen that the amount of water penetrating into the surface is not completely following the trend of the contact angle for water or the surface free energy. Instead, the differences in water absorption could perhaps be related to the microstructure and the pore size of the coating layers. EHEC most likely generates a different microstructure than CMC when using clay, by interacting more strongly with the pigment and binder particles. When using calcium carbonate, there is a moderate interaction between EHEC and the pigment. According to the data from the Hg-measurements, the use of CMC resulted in somewhat smaller pores in the top coating layer than the use of EHEC, while the opposite was found in the LWC layer. These data may explain the results of the water absorption measurements.

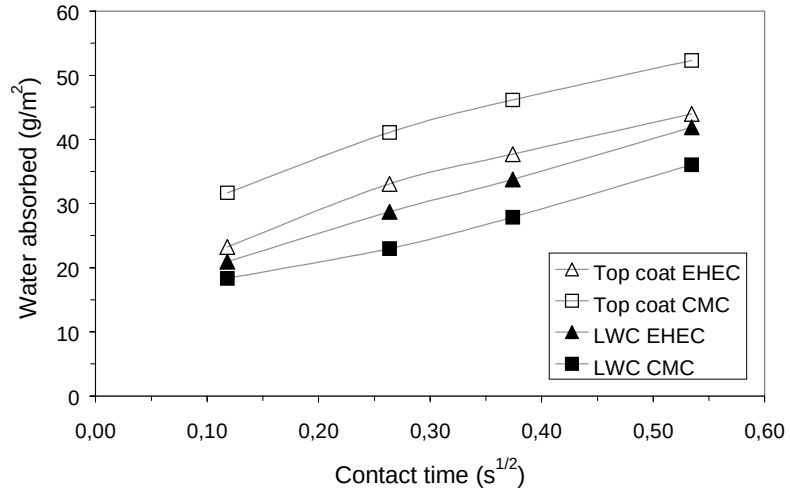

Figure 5. Water sorption at different contact times.

After calendering, higher gloss and higher print gloss were observed with EHEC in the top coated paper, as shown in **Figure 6**. The opposite was noticed for the LWC papers, as illustrated in **Figure 7**; in this case the use of EHEC resulted in a lower gloss and a lower print gloss. The reason for these gloss differences is not clear, but they may possibly be related to the micro-structure (roughness) of the surface and/or to the amount of binder in the surface of the coating layers (table 4).

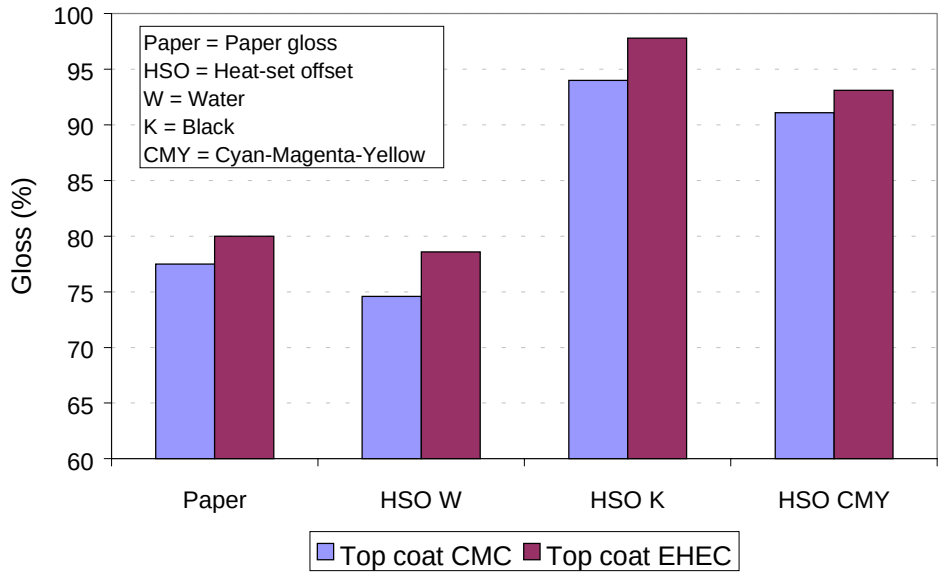

Figure 6. Paper gloss and print gloss for the calendered top coated papers.

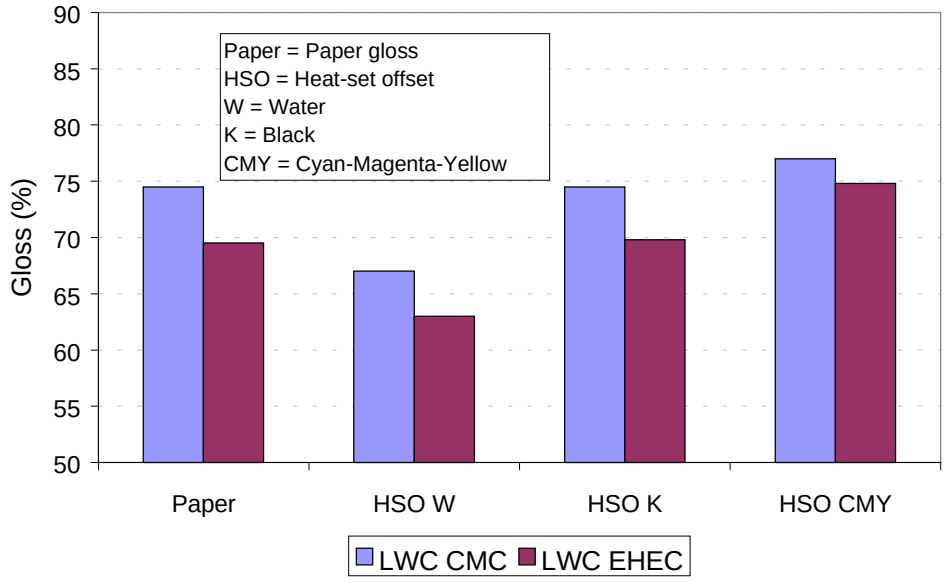

Figure 7. Paper gloss and print gloss for the calendered LWC papers.

Figure 8 shows the relation between print snap and dominating pore radius. The results indicate that there are more factors than only the pore size that influence the print snap. As a general trend, a smaller pore size corresponded to a lower print snap value. This is in accordance with other studies, showing a relation between pore radius and P&I slope, i.e. the ink-set rate (18) and between the P&I slope and the print snap (19). However, within each coating system, i.e. the top coating or the LWC coating, there was a discrepancy in the behavior of the system, as a higher print snap was related to a smaller dominating pore radius. Here, the surface microstructure or the binder level may have played a major role for the development of paper gloss and print gloss.

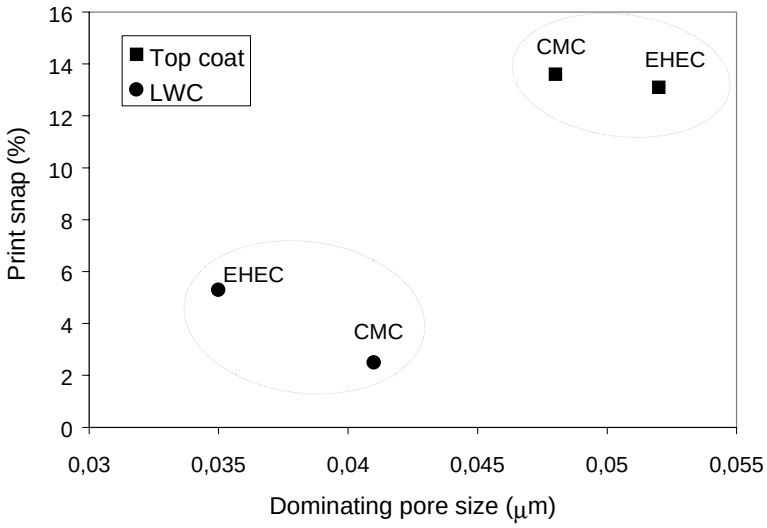

Figure 8. Print snap versus dominating pore size for the calendered top coated papers and the LWC papers.

From the visual examination of the surfaces using scanning electron microscopy the conclusion is that CMC and EHEC produced fairly similar microstructures. This is in agreement with the calculated porosity and the results of the Croda stain evaluation, both of which indicated no great differences in the pore structure characteristics with respect to the type of cobinder used. The relatively small differences observed in these results may indicate that the formed structure is rather weak and that it simply breaks down during the consolidation of the coating layer due to the capillary forces. Such a behavior has been noted for other aggregated systems (21). Another explanation could be that the time scale during blade coating is too short for any observable temperature-induced structure formation to take place. It is also conceivable that more sophisticated techniques in addition to microscopy (e.g. image analysis) are required to visually detect possible small-scale variations in the microstructure.

According to the results of the burn-out measurements (**Table 6**), EHEC gave a somewhat more uneven mass distribution of the coating layer on the top coated papers, which is possibly related to the higher standard deviation of binder content in the surface, as measured by UV-analysis. In the case of the LWC papers the results were reversed, which is also reflected in the data from the UV measurements. Although it could not be observed visually, the latter could be due to a somewhat more structured coating with the EHEC, resulting in a coating layer with a better fiber coverage and thus a more homogeneous coating layer. In this context, it can be noted that the

formulations containing EHEC required a higher blade load than the formulations containing CMC, which implies that interactions took place to some extent already in the wet coating color. This is also supported by the viscosity measurements (Figures 1 and 2).

	Top coating		LWC	
	EHEC	CMC	EHEC	CMC
Var coeff 2-4 mm	2.51	2.00	2.61	2.80
Var coeff 4-8 mm	1.88	1.41	2.08	2.15

Table 6. Results from Burn-out measurements.

During the web offset printing trials, the ink feed needed to achieve a constant print density was measured. It was found that the presence of EHEC in the LWC formulation resulted in a higher ink-feed requirement in all stations. For the top coating formulation, the relation was virtually the opposite; EHEC was associated with a lower ink-feed in all stations, except in the cyan station where the ink feed rates were equally high. A similar behavior was observed in the sheet-fed printing, where the rate of ink feed was kept constant. Here, the presence of EHEC resulted in a slightly higher print density on the top coated papers, while the print density on the LWC papers with this polymer was clearly lower. These results correlate with the results from the measurements of water sorption.

Table 7 presents results from the laboratory print evaluation of the coated samples. The values with CMC or EHEC as cobinder were overall fairly comparable, but in some measurements they differed to a certain extent. It is, for example, evident that the uncalendered IGT dry pick strength was somewhat lower with EHEC but, after calendering, especially with the LWC formulation, there was virtually no difference between the strengths of the CMC- and EHEC-containing coatings. Although the difference was greatly diminished after calendering, it is also noticeable that the surface smoothness (on the wire side) was higher when using EHEC in the top coating, a fact that could explain the gloss values given in figure 6. However, in the LWC coating (on the wire side) there were no significant differences in smoothness that would help explain the gloss values given in Figure 7.

		Top coating				LWC			
		CMC		EHEC		CMC		EHEC	
		FS	WS	FS	WS	FS	WS	FS	WS
Smoothness PPS H 1000	(μ)								
Uncalendered		2.3	4.3	2.2	3	4.1	3.7	4.6	3.7
Calendered		0.8	0.9	0.7	0.7	1.1	1	1.2	1
K&N	(%)								
Uncalendered		11.5	11.4	11.7	12.1	6.6	7.2	5.4	5.7
Calendered		6.7	6.6	6	6.6	0.5	0.8	0.5	0.3
IGT dry pick	(cm/s)								
Uncalendered		53	63	49	46	75	57	76	44
Calendered		49	54	49	53	60	53	63	47
Calendered		34	16	45	35	58	79	62	87
Wet pick	(Rating)								
Uncalendered		2	1	4	3	1	2	3	4
Calendered		3	1	4	2	1	2	3	4
Ink refusal	(%)								
Uncalendered		31.4	37.6	36.1	37.9	2.8	3.1	3.2	5.5
Calendered		35.4	33.3	33.9	31.1	2.3	4.2	4.2	3
Ink set-off	(Density)								
Uncalendered									
15s		0.34	0.27	0.24	0.25	0.37	0.56	0.23	0.45
30s		0.04	0.07	0.05	0.05	0.12	0.19	0.07	0.11
60s		0.01	0.02	0.01	0.01	0.02	0.03	0.01	0.02
120 s		0	0.01	0	0	0.01	0.01	0	0.01
Ink set-off	(Density)								
Calendered									
15s		0.34	0.47	0.43	0.49	0.86	0.99	0.73	0.89
30s		0.07	0.08	0.04	0.07	0.37	0.56	0.32	0.34
60s		0.01	0.02	0.01	0.02	0.1	0.18	0.06	0.12
120s		0	0.01	0	0.01	0.02	0.03	0.01	0.01
Ink piling	(Passes)								
Uncalendered		5	7	5	5	6	5	4	4
Calendered		5	5	4	5	5	4	4	4

FS = Felt side
WS =Wire side

Table 7. Results of the laboratory print evaluation.

CONCLUSIONS

Two cobinders, EHEC and CMC, were evaluated in pilot coating trials using two different coating formulations; one calcium carbonate-based top coating formulation and one clay-based LWC formulation. It was found that the choice of cobinder had a clear effect on the surface chemical properties of the coating layer. In both cases, but especially in the case of the LWC formulation, the use of EHEC was associated with a lower contact angle of water. Replacing

CMC with EHEC reduced the amount of SB-binder in the outermost surface of the coating layer, which could be one explanation to the lower contact angle. The lower amount of binder in the surface was probably due to a pronounced interaction between the three-component system consisting of EHEC, SB-binder and pigment, possibly giving a more uniform binder distribution in the z-direction. Measurements of viscosity as a function of temperature supported the occurrence of such interactions.

No significant effects on calculated porosity or on Croda stain intensity were observed with respect to the type of cobinder. However, EHEC and CMC generated variations in the dominating pore size, which correlated with the amount of water absorbed into the coating layer. In the case of the top coating, the use of EHEC resulted in a larger dominating pore radius coupled with a lower amount of absorbed water. This relationship was reversed in the case of the LWC coating, where EHEC gave a coating layer with a smaller dominating pore radius and a higher water absorption capability.

Clear differences in paper gloss and in print gloss were obtained between CMC and EHEC. For the top coating formulation, valid for calendered papers, increases in gloss and in print gloss were detected when EHEC was present, while the opposite relation applied to the LWC formulation. In the case of uncalendered papers, the presence of EHEC resulted in a slightly lower gloss value both for the top coated papers and for the LWC offset papers. The reason for the gloss differences is not clear, but it is most likely related to differences in the surface microstructure and/or to the amount of binder in the surface.

However, on the basis of solely a visual evaluation of environmental scanning electron micrographs, the differences in the surface microstructure between the coating layers due to the choice of cobinder were relatively small. The rheological measurements indicated a significant interaction between the components of the color upon heating when EHEC was used as cobinder. The higher blade pressure required may also be interpreted as a sign of an enhanced wet state interaction with this cobinder. The small differences in surface microstructure may find an explanation in e.g. that the formed structure is rather weak and that it simply breaks down during the consolidation of the coating layer due to capillary forces. Another reason may be that the time scale during blade coating is too short for any significant temperature-induced structure formation to take place. Furthermore, it is conceivable that more sophisticated techniques than used in this study (e.g. image analysis) are required to detect small-scale variations in the microstructure. Also worth noting is that the coating colors were applied to the paper surface at temperatures of 26-28°C. If the application temperature of the coating colors had been closer to the temperature of precipitation of EHEC, the effects on surface microstructure might have been greater.

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