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BINDER MIGRATION IN PAPER COATINGS – A NEW PERSPECTIVE

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ABSTRACT

Clay or other minerals are coated onto fibrous paper to improve print and optical properties. The minerals are fixed to the fibrous substrate with a binder, either latex or starch. The coated paper is dried during manufacture, and if the binder migrates during this drying, there can be a deterioration in properties. Not only are there manufacturing considerations as to the choice of binder, but also environmental ones with regard to factors such as the energy used in drying. This work reveals new perspectives on binder migration which have been gained by a variety of approaches. Firstly, a critique is presented of the experimental methods which have been used by other workers. Then a comprehensive series of experiments is described. For ease of study, and because any effects are likely to be exaggerated, most of the experiments were carried out on samples which were 1.4 mm thick, some two orders of magnitude thicker than commercial coatings. However, the results were also replicated in less extensive tests on samples of thickness 55 µm. The experiments show that under a very wide range of conditions, including different coating thicknesses and drying temperatures, no latex migration is observed. Migration of starch was observed, however, and caused an increase in starch concentration at the surface during drying. If the sample was covered during the experiments, the system relaxed back and the concentration enhancement was reduced. The relationship between the particle size of the latex and starch, and the extent to which these particles might percolate through the void structures, was investigated by the application of the "Pore-Cor" software to mercury intrusion experiments. Also presented are the results of a mathematical continuum model, which accurately describes the migration of starch binder in terms of only two parameters, namely the evaporation efficiency and the diffusion coefficient of starch.

INTRODUCTION

Binder migration has been defined as "a differential movement of a binder or binders with respect to pigment particles leading to non-uniform binder distributions in coated paper and paperboard" [1]. It is widely regarded to be an important aspect of coating structure, with the degree of migration affecting coated sheet properties such as print mottle and coating strength [1,2]. Not only are there manufacturing considerations as to the choice of binder, but also environmental ones with regard to factors such as the amount of energy used in the drying process.

However, as several authors have pointed out [1,3,4], even after more than fifty years of study, a sound, fundamental understanding of the phenomenon has not yet been established. Most of the considerable volume of published work on the subject has been concerned with the investigation of the conditions which promote or minimise migration, rather than with the basic mechanism underlying the phenomenon. One of the reasons for the uncertainty has been the difficulty of obtaining reliable measurements [4]. Commercial samples consist of an uneven coating on an uneven substrate, with a coating that may vary in thickness from 20–30 microns to virtually zero over an area of a few square millimetres. It is hard to imagine how accurate measurements of coating binder distribution could be obtained from such samples, even using modern and sophisticated techniques. The researcher has a choice of persisting with extremely difficult but "real" coatings, or to reduce the experimental difficulties by working with better defined but "model" coatings, and either approach is open to criticism.

It is suggested here that the better option at present is to gain reliable results from well-defined coatings on a flat substrate, and use these to acquire some degree of understanding, at least for these model systems. Many previous workers have also employed a flat substrate, often plastic film, to generate coating samples of even thickness, although few of these have been concerned with investigating the basics of binder migration.

In order to alleviate the practical problems of analysis and to expand the experimental possibilities, the use of samples of significantly higher thickness was considered. The advantages of this approach are as follows: (i) the practical aspects of analysis are simplified – in particular, the ability to examine composition as a function of sample depth is greatly enhanced; (ii) since high thickness samples dewater and dry more slowly, any distribution processes are also likely to be slowed and therefore made easier to study; and (iii) increased coat weight has been reported to exaggerate migration [1,5,6]. A possible disadvantage is that the physical processes behind migration may change with coating thickness. We propose, however, that such changes do not occur, and this postulate is supported by our model described below. Previous workers have also used thick samples, for example Vanderhoff and Bradford [7] dried samples of low-solids polystyrene dispersions in 15-mm deep petri dishes, implying the use of thick sample, and Bernada and Bruneau [8] used 1-cm thick coatings to study drying and starch migration.

CHOICE OF ANALYTICAL TECHNIQUE

A range of experimental methods has been used by other workers in the study of binder migration. As part of the present study, a careful review of available techniques was made and the results of this appraisal are given below.

Pyrolysis gas chromatography [9–11]

This technique involves the heating of samples at a temperature sufficient to break down the latex polymer into volatile components, which are separated and analysed quantitatively by gas chromatography. The main weakness found in our laboratory was a lack of reproducibility, with the results showing a strong dependence on the precise conditions of pyrolysis. It is believed, however, that because of its sensitivity this technique has much potential if the practical problems can be resolved.

Electron microscopy [7,12–14]

The weaknesses of electron microscopy in this context are: (i) it can be difficult to identify binder in the coating image; (ii) selecting a representative field of view is a difficult problem in microscopy; and (iii) quantitative assessment of binder level is difficult, although modern image analysis makes this feasible provided unambiguous identification of the binder can be made.

ESCA-XPS [15–17]

XPS is a sophisticated technique which measures surface elemental composition by detecting and characterising photoelectrons emitted as a result of an X-Ray beam being directed at the sample. Its weaknesses in this context are: (i) the very shallow penetration depth of the method (5–10 nm), such that coverage of the particulate components of the coating by surfactant and dispersants would be expected to affect the results obtained; and (ii) the difficulty of understanding the effect of the porous nature of paper and board coatings on the technique.

UV spectroscopy [18–21]

A reflectance spectroscopy technique has been reported, utilising the absorption exhibited by SB copolymer in the UV region. UV radiation is shone normally at the surface of the sample and a detector is placed at 45° to the normal with the aim of measuring the intensity of reflected radiation. The corrected absorbance at a chosen wavelength (260 nm) is taken to be a measure of the quantity of latex present in the surface. The weaknesses of the method are: (i) the wavelength of the UV band used (about 240–280 nm) is of the same order as the size range of the voids present in a normal coating (20–500 nm), and a measurement of intensity at a single angle of observation will not distinguish between the extent of scattering and the quantity of absorbing species; (ii) the depth of sample accessed by the UV will depend on the degree of scattering, which in turn is a function of the void system present in the coating, and (iii) the method gives only relative results and therefore requires calibration.

ATR (surface) IR spectroscopy [22,23]

ATR uses a sample that is clamped against a reflecting crystal, through which an IR beam passes by multiple reflections. The beam interacts with the sample surface and an absorption spectrum is produced. The weaknesses of the technique are: (i) the penetration depth of the beam varies with its wavelength, and therefore changes across the spectrum used for measuring latex level; (ii) the method is relative and requires calibration against known samples in order to obtain estimates of surface latex concentration; (iii) the results depend critically on the quality of optical contact between the sample and the crystal, which in turn depends on the sample roughness and the clamping pressure; and (iv) the effect of void system is unknown.

Sectioning, ignition and gravimetric analysis [24]

With this method, coating samples are placed in a furnace and all the organic material is removed by ignition. This method was chosen for much of the present work, because it is simple and absolute. Nevertheless there are disadvantages: (i) coating samples have to be cut or abraded to determine the binder content at a particular depth in the sample; (ii) care has to be taken with regard to changes which might occur to the pigment during the ignition process; and (iii) any extreme surface effects, which might be significant in real coatings, would not be detected.

EXPERIMENTAL

Latices

Two carboxylated styrene-butadiene (SB) latexes of different particle size were synthesised in the laboratory. Latex 1, which was used for most of the work, had an average particle diameter of 160 nm measured by photon correlation spectroscopy. It was typical of a commercial coating latex, apart from the slightly low butadiene content of 25% by weight. The mid-point of the glass transition temperature of the polymer was 35°C, measured by Differential Scanning Calorimetry. Latex 2 had a finer particle size of 90 nm, but was identical in both monomer composition and index of molecular weight to the 160 nm product.

Pigments

English clay (SPS grade, produced by Imerys, St Austell, UK) was used as the pigment in most of the latex binder studies, but other pigments were also investigated as part of the overall programme.

Starch

A standard commercial coating grade of starch was used, Nylgum A-55, produced by Avebe. This material is an anionic phosphate ester of hydrolysed potato starch. It was freshly prepared for each experimental series by heating in deionised water at 95°C for 30 min, to yield a 30% solution. The solution was slightly cloudy, indicating the starch was not completely molecularly dissolved. In the absence of data for Nylgum A-55, the particle size was estimated to be of the order of 30 nm, based on the elution of 50% of Nylgum A-85 starch from 30 nm pores (25).

Coating mixes

Simple model coating mixes were used, consisting only of pigment, binder and water. Various levels of latex were used with respect to pigment, but only one level of starch. Details of the mixes are shown in Table 1.

Latex Formulation		Starch Formulation		
Pigment	100 to 85.0 (dry weight)	English clay (SPS)	96.0 (dry weight)	
Latex	0 to 15.0 (dry weight)	Starch	4.0 (dry weight)	
Water	to 63.5% solids	Water	to 62.5% solids	
Mix viscosity approx. 300 mPa s,		Mix viscosity approx. 1000 mPa s,		
Brookfield RVT, spindle 4,		Brookfield RVT, spindle 5,		
speed 100 rpm.		speed 100 rpm		

Table 1	Composition	and viscosity	of the	coating mixes
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Sample preparation

Sample preparation was similar for both latex and starch mixes. The thick samples were discs with a diameter of 50 mm. The samples had a thickness of 2.5 mm when first laid down, reducing to approximately 1.4 mm after drying. Some samples were also prepared which had the same mix composition, but which were only 55 or 60 μ m thick. The thin coatings were produced in the laboratory by hand draw-downs onto polyester sheet, using a Meyer bar.

Drying methods

Various drying methods were employed, including comparisons of low and high temperature conditions since higher temperatures and rapid drying have



Figure 1 Drying methods used for the various sample types

been reported to lead to increased binder migration [1]. The scheme for drying experiments is given in Figure 1.

For the simple evaporative drying of thick samples, the appropriate amount of coating mix was placed in a 50 mm diameter petri dish. As shown in Figure 1, some of the thick latex-bound samples were dried at 23°C, which was below the glass transition temperature (T_g) of the latex. For this low temperature drying, the relative humidity was controlled at 50% and the air flow over the samples was slow (less than 0.1 m s⁻¹). For the detailed starch experiments, samples were dried for the desired time, then plunged into liquid nitrogen and kept frozen for subsequent analysis. The high temperature drying of thick samples was carried out with a laboratory air-circulating oven at 70°C, which was the highest temperature that did not result in a disrupted coating, and was above T_g . The 110°C drying of dewatered samples was for 2 hours in a laboratory air-circulating oven.

The dewatering of thick samples was carried out using a specially



Figure 2 Dewatering cell

constructed pressure cell, as shown in Figure 2. The cell enabled an air pressure of 2 to 4 bars to be applied so that serum was expelled from the coating.

The dewatering caused the solids content of the mix to increase steadily with time up to a plateau value after about 60 minutes. The plateau value was found to be about 77% for the latex mixes and about 73% for the starch mix. After dewatering to this stage, the samples had sufficient mechanical integrity to enable them to be removed unsupported from the pressure cell. If desired, the drying process was completed by placing the dewatered samples in a laboratory air-circulating oven at 110°C for 2 hours. This temperature was also above the latex $T_{\rm g}$.

The thin coating drawdowns were dried either at 23° C and 50% relative humidity (air flow as above), or in a laboratory air circulating oven set at 110° C.

Analysis of coatings after drying

After drying, the thick samples were analysed by physically removing the top and bottom 5% by weight using a steel blade or steel file. Thin samples were sectioned by scraping off the top and bottom 5% by weight using the device illustrated in Figure 3, based on that described by Yamazaki and Munakata (26). Access to the bottom of the coating was obtained by careful separation



Figure 3 Scraping device for thin coatings

from the polyester with the aid of adhesive tape. Examination of the scraped surface by SEM indicated the process had caused little disruption to the coating.

The organic contents of the removed sections, and for most of the thick samples the remaining middle 90% section, were determined by ignition at 800°C in a laboratory furnace. Binder content with respect to pigment was calculated having made a small correction for the residue after ignition arising from the latex binder, and an allowance for the water content of the clay pigment (0.1%, and 12.3% for SPS clay respectively). The corrections were derived from ignition experiments on samples of pure binder and pure pigment.

Mercury porosimetry

A coating mix consisting of 15% (dry) Latex 1 and 85% SPS clay pigment, was spread or cast in the laboratory at thicknesses of 7 μ m, 55 μ m and 1.4 mm. The thinner coatings were dried under two conditions, 23°C and 110°C. The thick sample was dried at 23°C only. Similarly, dried samples of a 4% starch, 96% SPS clay mix, cast at thicknesses of 10 μ m, 55 μ m and 1.4 mm were also prepared.

These samples were then studied by means of mercury porosimetry, using a Micromeritics Autopore II porosimeter up to pressures of 414 MPa. The thick samples were lumps, and the thin samples were coated on polyester sheet. The latter were wound into spirals, and tied with nylon thread, before being inserted into the penetrometer. The mercury intrusion curves were corrected for the initial intrusion between layers of the spiral, and for compress-ibility [27].

RESULTS

Mercury porosimetry

The corrected mercury intrusion curves are shown in Figure 4. To emphasise the differences in the shapes of the curves, they have all been plotted on the same ordinate, namely 0 to 100% intrusion of the experimentally accessible void space within the sample bulk.



Figure 4 Mercury intrusion curves

For each binder, the void systems were found to be closely similar, regardless of thickness, providing some justification for the use of the thick samples in this study. The intrusion curve of the thick latex samples was closer to the oven dried thin samples than the air dried thin samples. This suggested that the long duration of the 23°C drying of the thick sample had resulted in somewhat more consolidation than that given by the thinner samples dried at 23°C, up to a level of consolidation similar to that caused by the oven drying of the thin samples. This is consistent with the findings of a previous study [28].

Drying of latex bound thick coatings on an impervious substrate at 23°C

For the first series of experiments, the coating mix was as shown in Table 1, with SPS clay pigment and various levels of the 160 nm latex.

The results given in Figure 5 show the analysis of the top and bottom 5% fractions and the centre 90% fraction of the dried samples. Each result quoted is the average value from up to seven repeated experiments. Data analysis indicated the 90% confidence limits for the average result were about ± 0.65 parts of organic material.



Figure 5 Latex distribution for unwashed thick samples containing 160 nm SBR latex, dried at 23°C on an impervious substrate

The results showed a slight excess of organic material in the surface 5% sections, which was consistent across all latex levels. At first sight this might be assumed to be a consequence of latex migration. However, it can also be seen that, irrespective of the latex level in the mix, the surface excess of organic material was found to be approximately constant at about 1% more than the charged level of latex polymer. In addition, the same excess of organic material was apparent even for the sample in which there was zero latex. Further investigation was clearly merited.

Sectioned samples were heated for 1 hour at 110°C, then washed in distilled

water at 60°C for 30 minutes and dried. Analysis of the washed samples (apart from the zero latex sample which disintegrated) gave the results shown in Figure 6. In this series, there was no evidence of excess organic material at the coating surface. For all sections, the level of organic material measured corresponded closely to the amount of latex polymer originally charged to the mixes.



Figure 6 Latex distribution for washed thick samples containing 160 nm SBR latex, dried at 23°C on an impervious substrate

In addition, analysis of the wash water by infra-red spectroscopy showed it to contain dispersant and surfactant species, which were identified as the stabilisers used in the preparation of the clay and latex dispersions. No latex was detected in the wash water. Qualitatively, more dispersant and surfactant was seen in the wash water from the top sections than from the bottom and middle sections.

Latex bound thick coatings on an impervious substrate: the effect of drying temperature

Another set of samples, again with SPS pigment and with levels of Latex 1 of 4% and 15%, was dried in petri dishes at the increased drying temperature of 70°C. The samples were washed after sectioning as before. The results, shown in Table 2, were similar to those obtained at the lower drying temperature.

Drying	Latex Particle	Latex Level	Lat	ex Level Measu	ured in
Temp (°C)	Size (nm)	in mix (%)	Top 5%	Middle 90%	Bottom 5%
23	160	4	4.1	4.2	3.9
23	160	15	14.7	14.7	14.8
70	160	4	3.8	3.9	4.0
70	160	15	14.5	14.5	14.7
23	90	15	15.3	14.6	14.9

Table 2 The effect of drying temperature and later particle size

Latex bound thick coatings on an impervious substrate: the effect of reduced particle size latex

Also given in Table 2 are the results of an experiment testing the effect of latex particle size. A mix of 85% SPS clay and 15% of Latex 2 (90 nm diameter) dried in a petri dish at 23°C again showed no significant evidence of latex migration.

Latex bound thick coatings on an impervious substrate: the effect of different pigments

Astraplate, an American delaminated clay, Superclay M, a fines depleted English clay and Carbital 90, a fine calcium carbonate (all produced by Imerys) were made into mixes as before, using Latex 1 as binder at a level of 15% by weight. With the colours based on American clay and the fines depleted English clay, pigment sedimentation proved to be a problem, preventing reliable results being obtained from the non-thickened model system.

Latex bound thick coatings: dewatering then oven drying

Drying a series of coating samples made from Latex 1 and SPS clay, by dewatering in the pressure cell and oven treatment, also gave no evidence of significant latex migration, as shown in Figure 7 and Figure 8. However, it



Figure 7 Latex distribution for unwashed thick samples containing 160 nm SBR latex, dewatered and oven dried

was interesting to note that with the dewatered series, the unwashed samples showed generally less surface enrichment of organic species than the unwashed samples dried on the impervious substrate. This was because the dewatering process expelled dispersant and surfactant from the sample, a process which was confirmed experimentally by examination of the IR spectrum of the expressed serum.

A dewatered (solids concentration 77%) sample of the mix containing 15% Latex 1 was also sectioned and analysed. The results, shown in Table 3, confirmed that there was also a uniform distribution of latex at this stage.

Drying	Latex Particle	Latex Level	Lat	ex Level Measu	ured in
Protocol	Size (nm)	in mix (%)	Top 5%	Middle 90%	Bottom 5%
Dewatered only	160	15.0	14.7	15.0	15.2

 Table 3
 15% Latex 1:85% SPS clay. Sample dewatered only



Figure 8 Latex distribution for washed thick samples containing 160 nm SBR latex, dewatered and oven dried

Finally, mixes based on the American clay and fines-depleted English clay bound with Latex 1 were dewatered and oven dried. This circumvented the sedimentation problem mentioned above. For these samples, the latex was found to be uniformly distributed with depth.

Latex bound thick coatings: summary of results

To summarise, there was generally no evidence of latex migration in the experiments using thick coatings dried either slowly or quickly, with a range of latex levels, with standard or fine particle size latex and with a selection of pigment types. Increased levels of water-soluble materials were detected at the drying surface, however.

Latex bound thin coatings dried on an impervious substrate

As indicated earlier, experimentation with thin coatings is considerably more difficult than with thick samples. However, top and bottom sectioning of 55 μ m (90g m⁻²) coatings using the scraping device shown in Figure 3 was found to be possible. Sufficient sample could be accumulated for analysis by



Figure 9 Latex distribution for washed 55 µm samples containing 160 nm SBR latex, dried at 110°C on an impervious substrate

ignition, by scraping up to 10 replicate samples. The flat, impervious substrate used was clear polyester film.

Figure 9 shows the results from 55 μ m coatings dried at 110°C, with analysis by ignition. Washing was attempted by gently wiping the sample surface with a damp lint-free cloth before sectioning, because after sectioning the amount of sample available was too small to wash separately. The results again provided little evidence for latex migration, although the surface section was consistently found to have slightly more organic material than the bottom section as a result of the limited washing.

A direct comparison of latex and starch

The results of an experimental series comparing thick samples using 4% of either latex or starch are detailed in Table 4. It can be clearly seen that with both of the drying regimes used, the starch bound samples showed a significant enrichment of organic material in the surface section (and a depletion in the lower section). A slight excess of organic material was

Drying	Binder	Binder Level	Binder Level Measured in		
		in mix (%)	Top 5%	Middle 90%	Bottom 5%
23°C	Latex	4.0	4.6	4.1	4.1
23°C	Starch	4.0	9.6	3.7	2.0
Dewatered then 110°C	Latex	4.0	4.7	3.9	3.8
Dewatered then 110°C	Starch	4.0	7.0	1.7	2.2

 Table 4
 A comparison between 160 nm latex and starch binder, unwashed thick samples

found in the (unwashed) latex coatings, as expected from the results discussed earlier.

This experiment indicated that a significant redistribution of the coating starch occurred during drying, and the following experiments were undertaken to investigate this finding further.

Starch bound thick coatings: dewatering and oven drying

Since the starch binder being used was largely soluble, it was not possible to clean samples before analysis by washing with water as was done for latex. All the results reported for the starch bound coatings would therefore be expected to contain a contribution from water-soluble materials present in the clay dispersion. No correction for this effect has been attempted.

Dewatering the starch bound coating mix (Table 1) to the plateau of its solids concentration with respect to time, followed by sectioning, showed that at this stage the starch was uniformly distributed with respect to the clay, but at a lower level than the 4% originally added, as shown in the first row of Table 5. A simple calculation showed that the level of starch remaining in the coating sample (2.2%) was consistent with the starch being quantitatively expelled with the water during the dewatering process. Analysis by IR spectroscopy of the serum forced out by the pressure cell confirmed that starch was the dominant component.

On oven drying a dewatered sample, starch enrichment occurred at the surface from which water evaporated. This could be demonstrated by removing a dewatered sample from the pressure cell and covering either the top or bottom surface (or indeed covering neither surface) before placing the sample in the 110°C laboratory oven. The results of these experiments are also shown in Table 5.

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Drying Conditions	Binder Level	Binder Level Measured in		
	in mix (%)	Top 5%	Middle 90%	Bottom 5%
Dewatered to FCC only	4.0	2.2	2.2	2.4
Dewatered, then 110°C with top face exposed	4.0	7.0	1.7	2.2
Dewatered, then 110°C with top and bottom faces exposed	4.0	4.8	1.6	5.3
Dewatered, then 110°C with bottom face exposed	4.0	2.6	1.4	6.7

 Table 5
 The effect of different routes of water removal on starch migration

Starch bound thick coatings dried on an impervious substrate

The next series of experiments was designed to try to determine *when* the excess starch arrived at the drying surface, using samples dried by evaporation at a temperature of 23° C.

By drying samples for specific times in petri dishes, followed by freezing in liquid nitrogen, sectioning and analysis by ignition, the accumulation of starch with respect to pigment in the top 5% of the samples could be followed as a function of time. The results obtained are given in Figure 10.

The time zero sample in this series gave a measured value of starch in the surface section which was very close to the charged amount of 4%. This was considered to be a useful validation of the experimental technique.

It can be seen from Figure 10, that starch enrichment at the drying surface commenced as soon as the drying process began. The build-up of starch was found to be complete after 10 hours drying, at which time the solids content of the mix was 78%. This corresponded closely to the second critical concentration (SCC), defined by Watanabe and Lepoutre [24] as the concentration at which coating consolidation is complete. The SCC was calculated to be 78.7% for this starch bound mix from the void fraction of the completely dried coating (determined separately as 41% by volume from a measurement of the dried coating density).

The coating colour in this experiment can be considered a three component mix of starch, clay and water, at least until the SCC when air begins to enter the system. The ignition experiments yield a value for the starch to (starch plus clay) ratio, ignoring the possible effects of water-soluble materials. By also measuring the total solids content of the sectioned samples, the relative amounts of all three components to each other can be calculated.



Figure 10 % Starch/(Starch + Clay) in top 5% section vs. drying time, for thick samples dried at 23°C on an impervious substrate

Performing such a calculation for this experiment yielded the results shown in Figure 11 and Figure 12. The figures present the starch to (starch plus water) ratio and the clay to (clay plus water) ratio as functions of time for the first 15 hours of drying. These ratios are approximately the concentrations for each of the solid components with respect to water. The data for the surface 5% sections are compared in each graph to the average values for the whole sample, calculated from the sample weight loss as water evaporated.

The results show that the starch concentration became significantly greater near the evaporating surface compared to the bulk as drying proceeded. In contrast, the clay appeared to be uniformly dispersed with respect to water for the critical first 10 hours of drying.



Figure 11 % Starch/(Starch + Water) vs. drying time for top 5% section and Whole sample. Thick samples dried at 23°C, impervious substrate



Figure 12 % Clay/(Clay + Water) vs. drying time for top 5% section and whole sample. Thick samples dried at 23°C, impervious substrate

Starch bound thick coatings dried on an impervious substrate: the effect of halting evaporation

If samples were covered by an impervious film part way through the evaporation-only drying process, it was found that the starch enrichment with respect to pigment that had developed, then diminished with time. An example is shown in Figure 13.

The obvious explanation for this observation is that starch and water were diffusing to eliminate the concentration gradient set up in the evaporation stage of the experiment. This diffusion process has been postulated by Hagen [29] but has not previously been observed experimentally. Clearly, this experiment could be used to measure a diffusion coefficient for starch in a coating mix, and this has been done as part of further quantitative analysis of these data. Interestingly, it was found that the rate of back-diffusion of starch was zero in samples dried for 12.5 hours, 1.5 hours after the SCC had been reached.

In order to carry out the mathematical modelling of the process, the starch



Figure 13 Relaxation in % Starch/(Starch + Clay) in top 5% section if evaporation is stopped after 4 hrs. Thick samples dried at 23°C, impervious substrate



Figure 14 Variation of % starch concentration by weight with time. Key as in text

concentration (weight of starch relative to weight of starch plus water) was plotted against time, and the stopped evaporation experiment normalised to the fully-evaporated experiment, Figure 14. The concentration at the top surface (\Box) can be seen to increase as drying occurs, whereas the concentration in the bottom layer (\triangle) stays almost constant. However, if the sample was covered by an impervious film part way through the drying, the system relaxed back as shown for the top (\bigcirc) and bottom (*).

Starch bound thick coatings dried on an impervious substrate: measurement of binder depth profile

Although difficult experimentally, it was found possible to freeze a sample which had been dried for 7.5 hours and section it to provide a complete depth profile from 12 layers. The sectioning was achieved by using a height adjustable sample holder and a steel file.

The results are shown in Figure 15, from which the nature of the starch concentration with respect to clay as a function of depth can be seen. This profile fits well to an exponential function and the area under the curve gave a good mass balance for the total level of starch originally charged to the mix (4%).



Figure 15 % Starch/(Starch + Clay) as a function of sample depth. Thick samples dried at 23°C for 7.5 hours, impervious substrate

As before, the results were recalculated in terms of the starch and clay dispersion concentrations. The results are given in Figure 16. A gradient in the starch to (starch plus water) ratio was seen with the high concentration near the evaporation surface, whereas the clay to (clay plus water) ratio was found to be almost constant with depth. This is in agreement with the findings of the time domain experiments (Figure 11 and Figure 12).

Another sectioning experiment using a sample dried for 12.5 hours was only partially successful, producing 8 sections from the top 25% of the sample before it disintegrated. The results obtained, however, also support those described above.

Thin starch samples on an impervious substrate

Using similar methods to those employed for the latex-clay study, 55 μ m coatings based on starch were drawn down on plastic film, dried and the surface and bottom 5% sections removed and analysed by ignition.

The results show that when drying at ambient temperature the extent of



Figure 16 % Starch/(Starch + Water) and % Clay/(Clay + Water) as functions of sample depth. Thick samples dried at 23°C for 7.5 hours, impervious substrate

surface starch enrichment with respect to clay was much less than for the thick coatings, and within experimental error, might even have been zero (Table 6). A significantly greater enrichment was observed when these thinner coatings, made with 4, 5 or 6% starch, were dried at 110°C (Table 6).

The results from the 55 μ m coatings agree qualitatively with the model proposed here, which is also capable of accounting for the levels of starch

Drying	Sample	Binder Level	Binder Leve	l Measured in
Temperature	Thickness	in mix (%)	Top 5%	Bottom 5%
23°C	1.4 mm	4.0	9.6	2.0
23°C	55 µm	4.0	4.3	3.3
110°C	60 µm	4.0	6.4	1.5
110°C	60 µm	5.0	7.7	2.4
110°C	60 µm	6.0	9.3	1.9

Table 6Comparison of thick coating with thin samples dried at 23°C or 110°C

enrichment actually observed. Further quantitative comparisons are in preparation.

DISCUSSION

Latex

The conclusions drawn from the present work might be summarised as follows. For thick coatings, no clear evidence for latex migration was seen. However, some enrichment of water-soluble materials was detected in the surface layer of these samples. In less extensive tests with thinner coatings, these general findings were repeated.

In view of the wealth of publications reporting significant degrees of latex enrichment at the coating surface, these results were somewhat surprising. There is, however, a number of concerns that can be expressed about the evidence for latex migration and about some commonly accepted beliefs. These are outlined below.

The experimental evidence for latex migration

The analysis of coatings for binder distribution is not an easy problem. As described in the experimental section, the common methods used for analysis have their drawbacks, some of which might seriously interfere with the results obtained and the conclusions drawn. In addition, the phenomenon of the accumulation of water-soluble materials reported in this work also has the potential to affect the analysis that is attempting to probe latex binder distribution.

Conceptual and theoretical treatments of binder migration

As well as the experimental problems, there are further concerns regarding the notion of latex migration. In order for migration to occur, there must be a driving force that causes latex particles to separate from pigment particles. A widely held view is that capillary rise provides the driving force, with latex binder being carried through capillaries, formed in the coating after the FCC, by the flow of liquid. There are some serious difficulties with this idea, however. Ranger [3] has questioned the existence of a freely available liquid reservoir that could supply the coating capillaries. He also raised the question of whether the capillary structure is capable of allowing latex particles to pass through easily. There must be serious doubts whether it can, since various studies [24,28,30] have shown that latex binder has a large impact on the

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degree of consolidation that a coating undergoes. This is strong evidence that at least some of the latex is part of the consolidating particle matrix, experiencing and responding to the consolidation stress and therefore not free to move within it. The large effect that latex has on consolidation suggests that the proportion of latex trapped in the matrix is substantial.

Some light can be thrown on this discussion by use of the "Pore-Cor" software, developed at Plymouth and available from Micromeritics, Atlanta. This software generates a void structure with the simplified geometry of a $10 \times 10 \times 10$ array of cubic pores connected by up to 3000 cylindrical throats. Each of these 'unit cells' connects to replicates of itself infinitely in each Cartesian direction. The generated structures are made to match the mercury intrusion characteristics of the experimental samples very closely, and allow for the shielding of large pores by smaller throats [31,32]. The structures can then be used to determine other properties. In this case, particles were flowed as a colloidal suspension into the top face of the simulated unit cell. Figure 17



Figure 17 Extent of migration (shown dark) of median sized latex particle through Pore-Cor simulation of void structure shows the 6.3% by volume maximum intrusion of 160 nm un-film-formed latex particles into a simulation of the final void structure of the thick latexbound structures.

The difference in size between latex and coating pigment is often cited, albeit implicitly, as the factor permitting their separation during the flow of the liquid phase during drying. It should be remembered, however, that most pigments have a highly polydisperse particle size distribution and possess a high proportion (on a number basis) of particles that are of the same order of size as latex particles. A large size difference between all the pigment particles and those of the latex should therefore not necessarily be assumed, and, as Figure 17 confirms, percolation is unlikely.

Finally, there is the issue of print mottle, a problem frequently ascribed to binder (often latex) migration. Mottle is commonly observed to be a feature of uneven coat weight, and the assumption is made that the degree of latex migration is different between high and low coat weight areas. The interested reader is referred to previously reported work [28] that identified structural changes in coatings, occurring as a function of coat weight and drying conditions. This study provided an explanation for variation in coating absorbency, and thus for print mottle, without the need to invoke the hypothesis of latex migration.

Starch

In contrast, starch was found to be capable of a significant degree of migration, either as part of the coating serum on dewatering or towards the drying surface on evaporative drying.

Figure 18 shows the Pore-Cor simulation of the maximum 98.4% intrusion of undissolved 30 nm starch particles into a starch-bound structure. When comparing Figure 17 and Figure 18, one must remain aware of several major approximations: (i) the structures measured by the mercury porosimetry are the end structures after drying, which will have smaller voids than are present during the drying process; (ii) the geometries of the void features are simplified into an array of cubes connected by cylinders; (iii) the latex will film-form if the drying temperature is above T_g , rather than move as particles; and (iv) the starch molecules will cover a size distribution spanning perhaps an order of magnitude either side of 30 nm. Nevertheless, the extent of permeation is so major that it has implications despite these approximations.

The results of this study pointed to a new explanation for the migration of water-soluble or very finely dispersed materials on drying a coating mix. At a drying surface, as water leaves the mix, pigment and solubles are forced into states of higher concentration. Pigment particles are able to respond almost



Figure 18 Extent of migration (shown dark) of median sized starch particle through Pore-Cor simulation of void structure (un-intruded region is the small light grey region near bottom centre)

instantaneously to eliminate the dispersion concentration gradient, perhaps because of the significant repulsive force between individual particles. The solubles respond also, but by the slower process of diffusion. The result is an observed increased ratio of solubles to pigment near the drying surface. The extent of solubles migration with respect to pigment according to this mechanism depends on the relation between the rate of water removal and the rate of diffusion of the solubles. Faster rates of water removal would be expected to result in more starch enrichment, in agreement with many reports in the literature.

MODELLING OF A PROPOSED MECHANISM

A mathematical model was developed to describe the postulated mechanism, using the rates of water removal and diffusion as the only two fitting parameters. The binder migration was treated as a one-dimensional convection/ diffusion problem within a structural continuum approximation. The model comprised 10 infinitely wide sheets of finite thickness, with assumptions as shown in Figure 19.





The evaporative boundary condition at the surface is (33):

$$-D_s \frac{\partial w_0(t)}{\partial x} = a(w_0(t) - w_a), \qquad x = 0$$
(1)

where $w_0(t)$ is the concentration of water in the surface layer at time t, w_a is the concentration which would be in equilibrium with the vapour pressure in the atmosphere remote from the surface, D_s is the surface diffusion coefficient, and a is coefficient with dimensionality LT⁻¹ which quantifies the efficiency of the evaporative process. Approximating the surface layer to a semi-infinite system during the time-step Δt , the solution is shown in equation (2). The

diffusion or dispersion of a species in a semi-infinite composite medium (33) is shown in Equations (3) to (5):

$$\frac{w(t+\Delta t)-w_0(t)}{w_a-w_0(t)} = \operatorname{erf}\frac{x}{2\sqrt{D_s\Delta t}} - \exp(hx+h^2D_s\Delta t)\operatorname{erfc}\left(\frac{x}{2\sqrt{D_s\Delta t}} + h^2\sqrt{D_s\Delta t}\right), \quad (2)$$

where $h = a/D_s$.

$$c_i = C_0 \sum_{n=0}^{\infty} a^n \left(\operatorname{erfc} \frac{(2n+1)l + x}{2\sqrt{D_i \Delta t}} - a \operatorname{erfc} \frac{(2n+1)l - x}{2\sqrt{D_i \Delta t}} \right)$$
(3)

$$c_{i+1} = \frac{2kC_0}{k+1} \sum_{n=0}^{\infty} a^n \operatorname{erfc} \frac{(2n+1)l + kx}{2\sqrt{D_1 \Delta t}},$$
(4)

where

$$k = \sqrt{D_i / D_{i+1}}, \qquad a = \frac{1 - k}{1 + k}$$
 (5)

The model was run by calculating the diffusion and evaporation over successive one hour time-steps. Full details will be given in a publication in preparation.

The close fit between simulation and experiment, shown in Figure 20, was achieved with only the two fitting parameters mentioned above, which in the model appeared as (i) the efficiency of evaporation *a*, which could be tested using different evaporation regimes, and (ii) a starch diffusion coefficient of 1.17×10^{-8} m² hr⁻¹, compared to a typical value for free diffusion of starch of 3.6×10^{-7} m² hr⁻¹.

The realistic value for the modelled starch diffusion coefficient provided strong support for the proposed mechanism for the migration of starch binder, and its detailed modelling.

CONCLUSION

In this study, we have identified very clear differences between the migratory behaviour of latex and starch in paper coatings. No latex migration was detected, either below or above its glass transition temperature. Explanations



Figure 20 Comparison of experimental and predicted starch/(starch + clay) in the top surface of the coating. SCC is the Second Critical Concentration

were proposed as to why previous work did appear to detect latex migration. By contrast, starch migration was observed. A physically straightforward mechanism was proposed, and successfully modelled to the extent that there was replication not only of the overall surface-concentration effects in thick coatings, but also the relaxation of the system if evaporation was stopped.

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Transcription of Discussion

BINDER MIGRATION IN PAPER COATINGS – A NEW PERSPECTIVE

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Theo van de Ven Paprican, McGill University

Amylose has a diffusion co-efficient 3–4 times of that of amylopectin thus in your coatings you should see a much larger gradient for amylopectin that for amylose. Have you looked at that?

Robert Groves

We didn't separate the starch. We simply took the commercial starch, although I realise that this is a mixture of components. It was interesting to see that in our experiments the commercial starch acted as a solution of a single material, for example in de-watering experiments where it was expelled quantitatively with the serum. One would expect there to be different diffusion behaviours for the different components of the commercial starch, with the final observed result being an average. Of course, other water-soluble materials such as surfactants and dispersants are also present and these will also be part of the mechanism we have described, with their own, probably different, diffusion coefficients. Our experiments describe a means of measuring the diffusion coefficients within the coating environment.

Ramin Farnood University of Toronto

I have a question regarding parameter alpha in the modelling part of your presentation it is related to mass transfer co-efficient, did you check with published equations for mass transfer to see how your fitted parameter matched these equations?

Discussion

Robert Groves

Unfortunately, I didn't know how to do that as there were two coefficients involved: a diffusion co-efficient for diffusion in the atmosphere away from the surface, and alpha which is actually the efficiency of transfer of the water from the sample surface to the adjacent atmospheric layer. So although I did have a look around in the literature, it was very difficult to find any parameters that were not totally specific to a system which was different to the one we studied. So I think probably the only way to get a handle on the parameter alpha would have been to do more varied experiments at different drying efficiencies and then start getting parameters experimentally. I certainly could not find anything in the literature which directly related to the combination of both alpha and the diffusion away from the surface, but if you know of some source I would be extremely interested to find out.

Kari Ebeling UPM-Kymmene Corporation

Is it possible to visualise a situation for the latex containing coatings where the drying speed is so high that the water frontier would move some of the latex towards to upper surface? The paper makers try to do it such that no water can get into the base sheet.

Robert Groves

In short, my opinion is "no". Ranger has pointed out that this is equivalent to saying, the less time there is for the migration process, the more it happens! For there to be an increase in latex movement with drying rate, one has to accept there is a capability for latex to move through the system. What is the driving force for this? Can latex particles move through the matrix? From our work, there is neither a convincing driving force nor the room for latex to move freely. The commonly accepted mechanisms for migration require latex to move after the first critical concentration; if water is evaporated more rapidly, one just attains the FCC more rapidly. Our experimental work and modelling with standard coating components, indicates that the matrix after the FCC allows no significant latex movement.

Peter Matthews

Can I just take the liberty as the second speaker to add that your question goes right back to the fundamentals of what is in the literature, as to whether there is a mechanism that is pushing things around in there. Such a mechanism would give rise to discontinuities at the first critical concentration and the second critical concentration, and you simply don't see them – which suggests, as Bob says, that that sort of shove doesn't exist.

Robert Groves

There is also an inconsistency in my opinion in the two main, currently held theories of binder migration (capillary rise and surface tension driven convection) and the accepted mechanism of coating consolidation first described by Watanabe & Lepoutre. The migration theories require that migration occurs after the FCC, but the Watanabe & Lepoutre paper clearly states that latex migration cannot occur after the FCC, since at this stage latex particles are trapped. This is an example of the contradictions that exist in this area.

Lars Wågberg Mid-Sweden University

When you look at the pore core model and the dimensions of all the throats that you have in this model and compare that to the size of the starch molecules, aren't you surprised that the diffusion is not more hindered than it is? Shouldn't the movement at the starch molecules be slowed down dramatically by all he narrow ducts?

Peter Matthews

Again we are talking about orders of magnitude. The starch itself has a huge range of sizes and we are looking at an order of magnitude slowing. Also, the diffusion coefficient is corrected in terms of diffusion through the volume of water; it is corrected for the porosity, so there is a correction for the fact that you have less water in the system. So what you are left with is the diffusion coefficient of the starch diffusing around the obstacles – factors such as the existence of the solid phase, the reduction in free water and so on are corrected out of the system. So, yes you may have expected a greater reduction in diffusion coefficient, but the model is so complicated I think I was just relieved that the hindered diffusion coefficient from the model came out less than the free diffusion value in the literature, rather than more!