

Factors Affecting the Printing Strength of Kaolin-Based Paper Coatings

J.C.Husband, J.S.Preston, L.F.Gate, D.Blair and P.Creaton

⊕ KAOLIN

⊕ GCC

⊕ PCC

Factors Affecting the Printing Strength of Kaolin-Based Paper Coatings

J.C.Husband, J.S.Preston, L.F.Gate, D.Blair[†] and P.Creaton[‡].

Pigments for Paper Group, Imerys Minerals Ltd., Par Moor Centre, Par, United Kingdom PL24 2SQ,

[†]Dept of Chemistry, University of Edinburgh, King's Building, West Mains Road, Edinburgh EH9 3JJ,

[‡]School of Chemistry, University of Bristol, Cantock's Close, Bristol, United Kingdom, BS8 1TS.

Abstract

The mechanical properties of paper coating layers are very important in printing and converting operations. These include stiffness, resistance to fold cracking, dusting and pick resistance. In this work we have studied the pick strength of kaolin coated papers as a function of the coating pigment size, morphology and binder level.

We found that dry pick strength using oil depended on the pigment particle size. Coarse clays gave much higher pick resistance than finer clays. A similar trend was observed using oil-based inks. In the presence of water as a predamping fluid, the pick strength depended on the interval between predamping and printing. The coarse clay coatings had the greatest sensitivity to water, giving the lowest strength at short intervals, but the highest at long time intervals. Finer clay coatings were less sensitive to damping. The results indicate that the permeability of the coatings to water is the critical factor affecting wet pick resistance.

A new finding was that ink oils also reduce the strength of the coating layer. The extent of strength loss depended on the polarity of the fluid, being greatest with water and least with mineral oil. This effect of fluid may be a result of interruption of van der Waals bonding between latex and the kaolin surface. Hence the pick resistance of a coating layer is not a measure of its intrinsic strength, but is a result of the interactions between the ink and coating. Penetration of oil from the ink into the coating increases the applied stress through tack build, and simultaneously reduces the strength of the coating. Improving adhesion between mineral and binder may be the key to obtaining higher coating strength with offset inks.

Introduction

During printing the surface strength of a paper coating is a critical parameter. Papers can exhibit picking when subjected to the high stresses which develop during ink application. These stresses result from the tack build associated with the loss of ink solvent into the pores of the coating, and the consequent increase in cohesivity [1,2,4]. Picking as a result of the oil-based ink alone is normally referred to as "dry pick". Additionally, the offset process uses water, which is known to weaken the coating, leading to the phenomenon of "wet pick" [3,4].

In order to avoid picking, binder must be present in a sufficient amount to give adequate strength for the combination of pigment and basepaper in use. This is referred to as the "binder demand" of the pigment, but there is still some uncertainty about which pigment properties are most important in its determination. It is widely accepted that surface area is most important, although Cobb [5] was unable to show this. Dating back more than 50 years, her work clearly established a correlation of binder (casein) demand with the pore volume of the pigment in a coating layer. This is not unexpected, since porosity in a material reduces its strength because the voids have no load-bearing ability. Using this argument, pigments which increase the porosity of the coating should require more binder. However, such pigment designs may lose binder more readily into the basepaper, which might weaken the coating but paradoxically may strengthen the coating – basesheet interface.

Since Cobb's paper, there have been a surprisingly small number of published studies on coating strength. Parpillon *et al.* [6] measured the tensile strength of coating layers based on kaolin and calcium carbonate (GCC). They found that, at the same latex level, kaolin gave coating layers with about twice the tensile strength of GCC. Kaolin also gave greater elongation at rupture. These trends correlated with stiffness. The study also showed, not surprisingly, that both tensile strength and elongation to break increased as the level of latex increased.

Similar trends were observed as the T_g of the latex was decreased (ie. as the latex became softer). Dynamic mechanical and NMR experiments on the films suggested that the binder existed in discrete domains in the clay films but was spread more evenly over the GCC particles.

This explanation was also supported by the work of Lepoutre and Hiraharu [7] who investigated the differences in mechanical properties of coating layers based on calcium carbonate and kaolin, this time in the z-direction. Using the IGT pick test with oil, they concluded that the mechanical strength of the GCC coatings was higher than the clay. Using a rolling cylinder technique to measure z-directional strength, they found that the rupture energy of the GCC layer was higher than the clay, and therefore a higher level of binder was required for the clay coating to obtain similar strength to the GCC in the z-direction. Petterson *et al.* also investigated the wet pick strength of coated papers and concluded that GCC coatings were stronger than clay coatings under their experimental conditions [8]. They suggested that the role of water was to interfere with the adhesion between latex and pigment. Skeppstedt *et al.* [9] showed that surface treating calcium carbonate by in-situ polymerisation of styrene led to improved dry pick strength with SB latex binder. They attributed this to improved adhesion between the grafted mineral surface and the latex.

Lepoutre and Rigdahl [10] examined a wider range of pigments of different shape and related the in-plane elastic modulus of coating layers to the presence of voids. Hence in blends with clay, isometric GCC particles reduced the elastic modulus more than needle-shaped aragonite at the same adhesive level. Further studies of the z-directional strength of kaolin and GCC layers were reported by Inoue and Lepoutre [11]. They found that the peel energy of GCC layers was higher than kaolin layers at the same binder level, which in this study, somewhat unusually, was carboxymethyl cellulose. Coatings of monosized polystyrene pigment had the lowest peel energy. The critical binder content was determined from the peel test and correlated with pigment surface area. They concluded that coating layers based on plate-shaped clay particles were more resistant to in-plane stresses than isometric GCC.

Recently, some work has been published on z-directional coating strength of paper using a micro-indentor [12]. Although applied to coated paper the technique is in an early stage of development; the z-direction elastic stiffness estimated from the indentor showed order of magnitude agreement with that calculated from in-plane tensile measurements for coating layers containing calcium carbonate. For clay, the z-direction result was lower than the in-plane, which the authors suggested might arise as a result of the anisotropic nature of kaolin particles. An alternative view was provided by Granier and Sartre [13] who interpreted the strength of coatings in terms of acid – base character of the mineral and latex. In their model, the kaolin edges are basic and the faces acidic, so the acidic latex adheres much more strongly to the edges. Clearly, the effect of surface chemistry on binder – mineral adhesion should form part of any comprehensive theory of coating strength.

Our own recent studies of coating strength explored the relationship between in-plane and z-direction tensile strength of unsupported coating layers based on kaolins of different particle sizes and aspect ratios as a function of latex level [14,15]. This work showed that anisotropy in the coating layer as a result of the plate-shaped nature of kaolin particles leads to weaker tensile strength in the z-direction compared to in-plane direction. For a given set of fine clays, there was an inverse relationship between in-plane and z-directional tensile strength. Isotropic coating layers based on ground calcium carbonate (gcc) particles had similar tensile strength in the in-plane and z-direction. Compared to clays, gcc layers were weaker in the in-plane direction but stronger in the z-direction. In the present paper, our aim has been to establish whether the above trends determined for unsupported coating layers also apply to papers coated with the same pigments during printing. Therefore we used model coatings based on 100 parts kaolin, and plan to extend the study the carbonate containing coatings in future work. We believe that the results will be relevant to both web and sheet fed offset printing processes.

Materials and Methods

Materials

Two pairs of coating kaolins were used having approximately similar particle size distributions as determined by sedimentation. These were chosen to cover particle shape factor (SF) values from blocky (SF10-16) to platy (SF35-42). The mean (D50) particle size of the first pair was 0.40 μm esd. The second pair was finer, with a mean size of 0.20 μm . These four clays (FB, FP, UFB and UFP) were used in the previous study [15]. An

additional coarse high shape factor clay (CP) of mean size 2 μm was included in this study. The properties of the kaolins are summarised in Table I. Shape factor was measured using a proprietary technique [16]. The latex binder used throughout was a carboxylated styrene butadiene acrylonitrile copolymer of $T_g = 10^\circ\text{C}$ (DL920, Dow Chemical). The kaolins were slurried at the optimum solids using 0.3wt% of a sodium polyacrylate dispersant - (CED3546, Ondeo Nalco). For purposes of measuring the tensile strength of unsupported coatings, latex was added at levels between 3 and 17 pph based on clay. 0.3 pph of sodium carboxymethyl cellulose (Finnfix 10TM, CP Kelco) was also added as a thickener. After pH adjustment to 8.0, the colours were screened through a mesh of 53 μm aperture.

Table I. Physical properties of kaolins

Kaolin	Description	Particle size distribution by Sedigraph TM , wt% below					Shape factor	BET surface area, m^2g^{-1}
		2 μm	1 μm	0.5 μm	0.25 μm	D50 μm		
CP	Coarse platy	51	29	14	6	2.0	42	6
FB	Fine blocky	93	81	63	34	0.37	16	14
FP	Fine platy	90	74	55	31	0.44	34	16
UFB	Ultrafine blocky	100	99	94	68	0.19	10	27
UFP	Ultrafine platy	97	90	79	53	0.23	40	24
CP	Coarse platy	51	29	14	6	2.0	42	6

Experimental Methods

Preparation of unsupported coating films and the measurement of tensile strength both in-plane and in the z-direction was carried out using the methods described in our earlier papers [14,15].

Coated papers for print testing were prepared using these clays. The latex level for these experiments varied from 8 – 14 pph with sodium carboxymethyl cellulose added at 0.3 pph. The coatings were applied to a 46 gm^{-2} LWC mechanical basestock at 400 m min^{-1} using a laboratory cylindrical coater (Heli-CoaterTM) equipped with infra-red and hot air drying. The coated strips were supercalendered for 10 nips at a roll surface temperature of 65°C and a pressure of 89 kg cm^{-1} using a Perkins laboratory calender.

The mean pore size and volume of unsupported coatings and coated papers were measured by mercury intrusion using a CE Instruments Pascal 240 porosimeter. Corrections for glassware expansion were applied. When using coated papers, curve fitting was applied to separate the pores associated with the basepaper from the smaller coating pores.

The ink setting rates of the coated sheets were measured using the Ink Surface Interaction Tester (ISIT, SeGan, Cornwall) [1] using the Huber tack #1 and #3 inks used in the pick test.

The dry pick strength of the coated papers was measured using an IGT AIC2-5 unit. The unit was run in accelerating mode up to a maximum velocity of 2 ms^{-1} . 1 cm^3 of a standard pick oil of viscosity 17 Pa.s was applied and the print was assessed visually using low angle illumination to assess the speed and mode of failure, coating or basestock. Measurements were made in triplicate. See Appendix for more discussion of this test.

The wet pick strength was measured using a Prufbau Multipurpose Printability Tester. 0.5 cm^3 of ink (Huber tack #1 or #3) was applied to the distribution rollers 15 μl of distilled water to the damping unit. For initial experiments, a time interval of 4 s was used between damping and printing. The velocity at which picking first occurred was assessed visually and also the mode of failure was recorded. Again the measurements were performed in triplicate. In subsequent experiments, the delay time and volume of water was varied.

In all results given in this paper, picking was coating pick, not basestock or interface failure.

Print density values were assessed after printing using an IGT laboratory printing unit at a speed of 0.5 m s^{-1} at 500 N pressure. 0.3 cm^3 of magenta sheetfed ink was applied to give a 1 μm thick ink film. A portion of the

print area was predamped with 1 gm⁻² of water which results in a very short delay time of the order of 1 s. A Gretag SpectroEye densitometer was used to measure optical density.

Results

Tensile strength of unsupported coatings

Figures 1 and 2 show the tensile strength results for these clays in the in-plane (Fig 1) and z-direction (Fig 2). These are taken from ref [15]. Moving to finer or platier clays increases the in-plane strength but lowers the z-direction strength. The coarse platy clay (CP) is an exception to this trend, exhibiting a higher rate of strength increase with latex level and giving the strongest in-plane strength at latex levels > 5 pph.

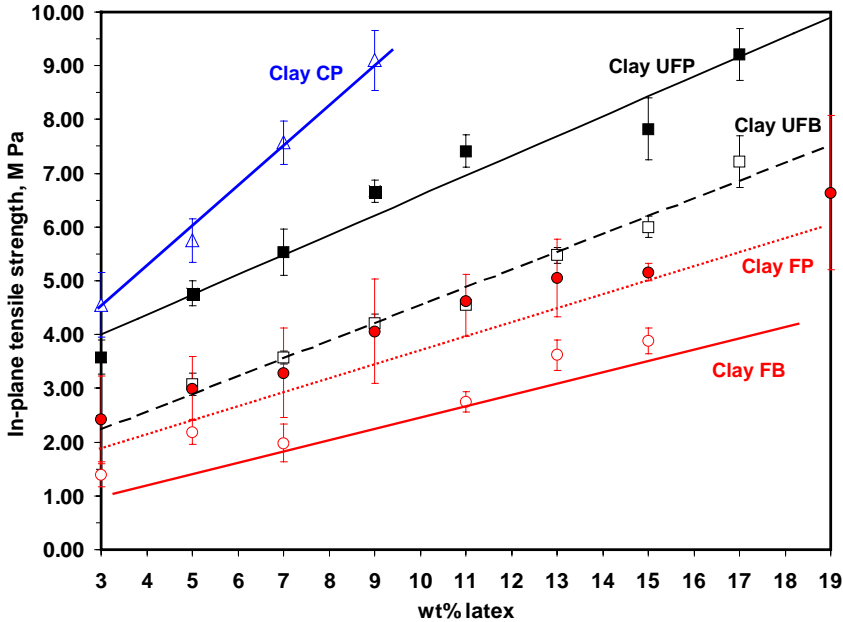


Figure 1. In-plane tensile strength as a function of latex level, all clays.

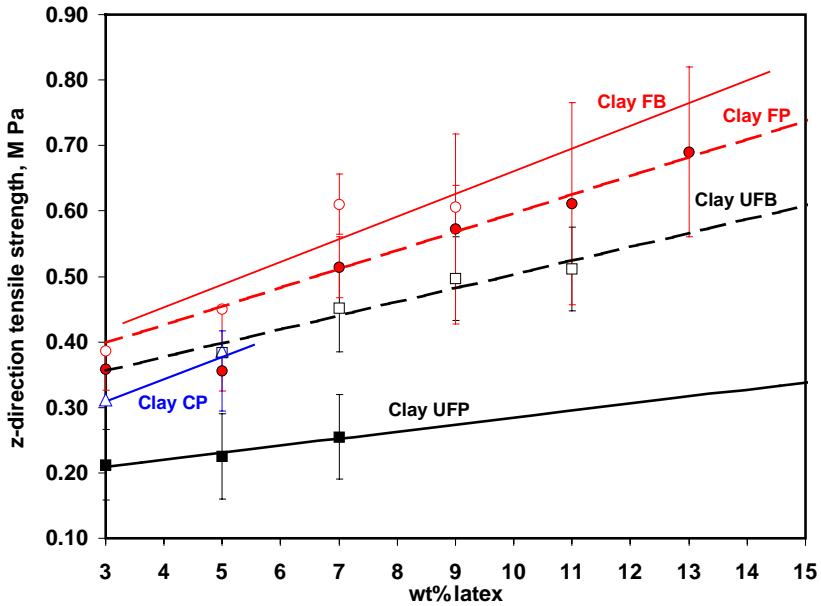


Figure 2. z-direction tensile strength for the coating films in Fig 1.

Tack development

The tack development curves for papers coated with kaolins FB, FP and CP at latex levels of 9.5 and 12.5 pph are plotted in Figure 3. The coarse kaolin CP gives coatings with the slowest tack rise and the slowest tack decay. Next slowest is fine platy kaolin FP, followed by fine blocky kaolin FB, showing the fastest tack decay. In all three systems increasing the amount of latex slows down ink setting, although the effect is secondary to the effect of changing kaolin. These results suggest that, in terms of ink vehicle penetration, the coarse platy clay CP gives the most closed coating surface, and fine blocky clay FB gives the most open coating surface.

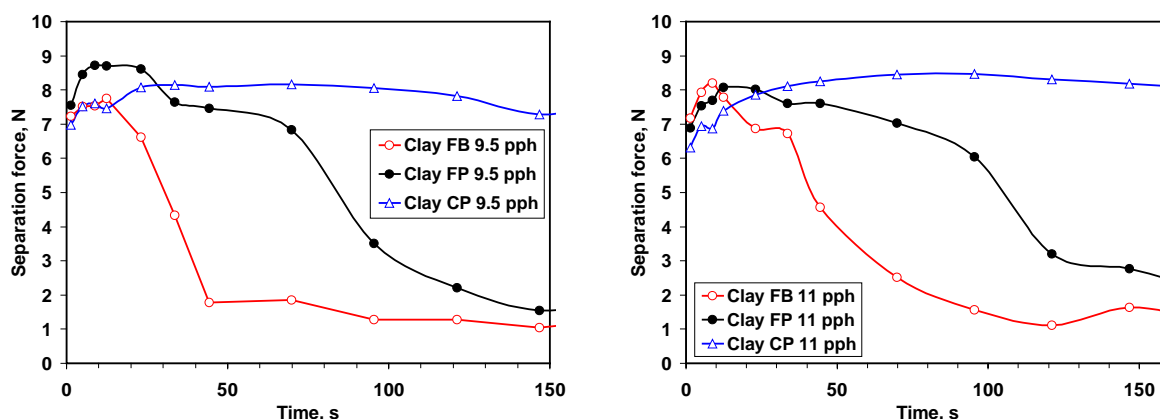


Figure 3. Tack development curves for coated papers containing kaolins FB, FP and CP at low and high latex levels using #3 tack ink.

Pick strength of coated papers

The results for the dry pick evaluation are shown in Figure 4. The results show that pick strength increases as the particle size of the pigment increases. There is no discernible influence of particle shape, since clay pairs FB and FP and UFB and UFP give very similar responses. The coarse platy clay CP gives a much higher rate of strength increase with binder level than the finer pigments, a similar trend to that given by the tensile strength in Figure 1.

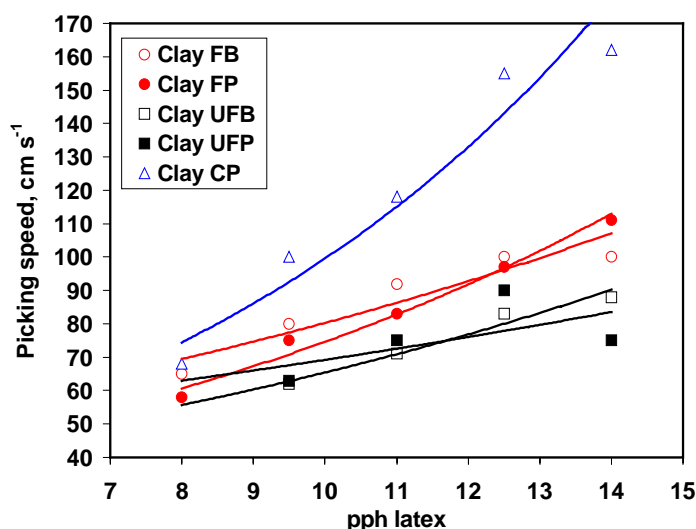


Figure 4. Dry pick strength of coated papers.

The pick speed of some of the papers was also measured on the Prubau tester using the Tack #3 ink with no predamping. The results (Figure 5) broadly follow the dry pick trends, showing that the coarse platy clay CP has the highest resistance to pick with this ink also.

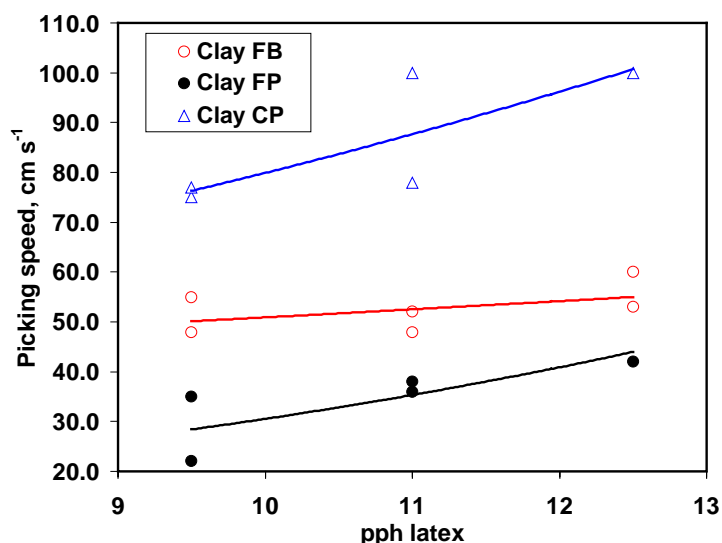


Figure 5. Comparison of pick resistance measured using #3 tack ink but no predamping.

As expected, the effect of predamping with water was to lower the picking velocity of the coating. However the delay time between damping and printing strongly influences this weakening effect (Fig 6). (The shortest delay that can be obtained with the Prubau apparatus is 1 s). The coarse platy clay CP has the greatest sensitivity to predamping, especially at very short delay times, when this pigment gives the lowest picking velocity of all the samples. At longer delay times, the situation is reversed and this pigment gives coatings with the highest picking velocity. It is interesting to note the reversibility of the detrimental effect water has on strength – given sufficient delay after damping the pick strength values in Fig 6 return to close to the undamped value. A similar trend towards lower pick velocity was found when the delay time was kept constant at 7 s but the volume of water increased (Fig 7). When a large volume of water was added, the effect on strength of increasing the amount of latex binder was small (Fig. 7). This implies that adding more binder is not an effective way to overcome severe wet pick issues, unless pore sealing effects can reduce the ingress of water (but this may induce water interference instead).

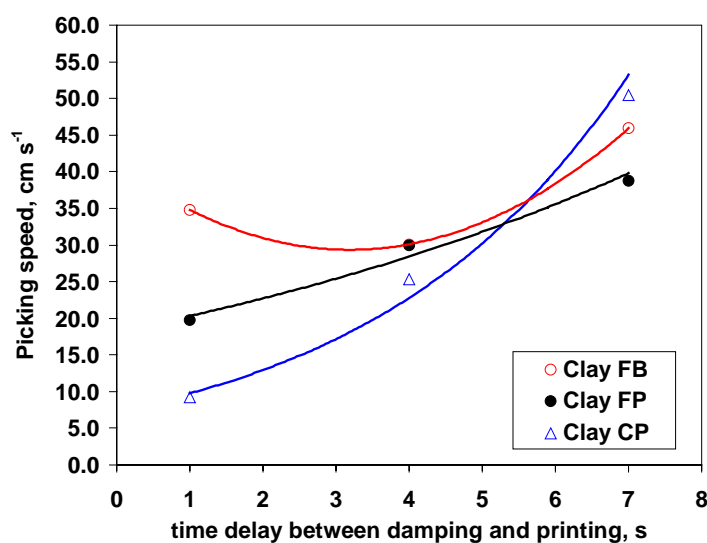


Figure 6. Effect of delay time between damping and printing, 11 pph latex and 10 μ L water for predamping.

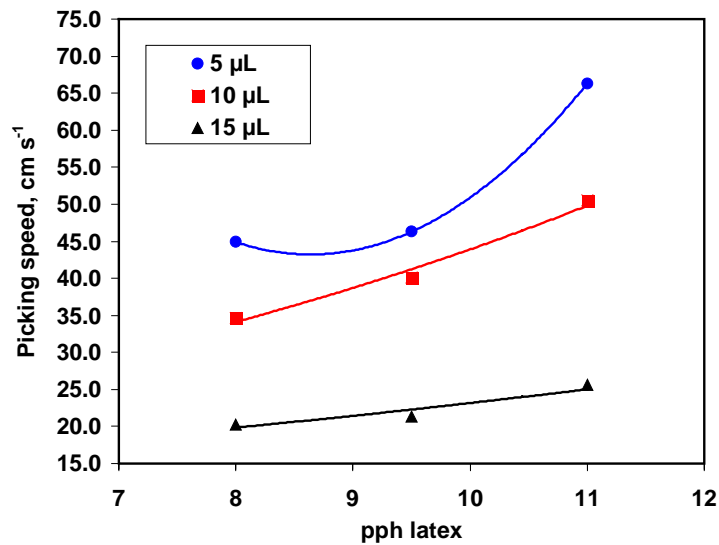


Figure 7. Effect of amount of water time used for predamping, Clay CP, constant delay time of 7 s.

Print density of printed papers

An offset printing evaluation using the IGT was conducted on the papers coated with clays FB, FP and CP. Table II summarises the print densities obtained in the litho and dry regions of the prints at 3 latex levels :

Table II : offset litho print densities of coated papers, 10 – 12 gm⁻² coat weight

Clay	Latex level, pph	Print density, litho region	Print density, dry region	Litho : dry ratio
CP	9.5	Wet pick	1.27	-
	11.0		1.26	-
	12.5		1.28	-
FB	9.5	1.34	1.33	1.0
	11.0	1.32	1.37	0.96
	12.5	1.31	1.36	0.96
FP	9.5	1.31	1.34	0.98
	11.0	1.30	1.36	0.96
	12.5	1.33	1.38	0.96

The coatings containing the coarse platy clay CP gave severe picking in the litho region and this made measurement of print density impossible. In the dry region, coatings with this clay had lower print density values than the finer clays. Both the finer clays gave litho : dry print density ratios between 0.96 and 1.0, indicating very little ink refusal. Hence there was no evidence for water interference in these coatings, even at the highest binder levels. It is interesting that the coarse platy clay coatings showed severe wet pick in the litho area, which corroborates the wet pick trends plotted in Fig 6. The delay time between damping and printing was about 1 s, the same as that observed to severely reduce the pick resistance in Fig 6.

Mercury porosimetry

Mercury intrusion results for coating films containing these clays are plotted in Figure 8. The coarse platy clay CP gives coatings with much larger pores (by a factor of 2) than the finer clays. The pore volumes are similar for all the clays. Also plotted are the results for coated papers, showing that both the pore size and volume are lower than in unsupported films. This suggests that the rod drawdown method used for the films gives a more

open structure than the blade coated papers, indicating less good platelet alignment, as expected. We were unable to obtain good pore volume data for the coated papers with clay CP, as the coating pore size overlapped with the basesheet pores. This confirms that the mean pore size is much larger than for clays FB and FP. The larger coating pore size given by clay CP means that, certainly at longer timescales, the permeability to free liquids will be high [17]. On the other hand the capillarity will be low, so there will be a smaller driving force for liquid imbibition. This will give a slow rate of ink setting since the driving force for oil removal from the ink layer is capillary pressure. It is likely that in coatings based on clay CP, the larger pores will increase the rate of permeability to water, leading to the trends shown in Fig. 6.

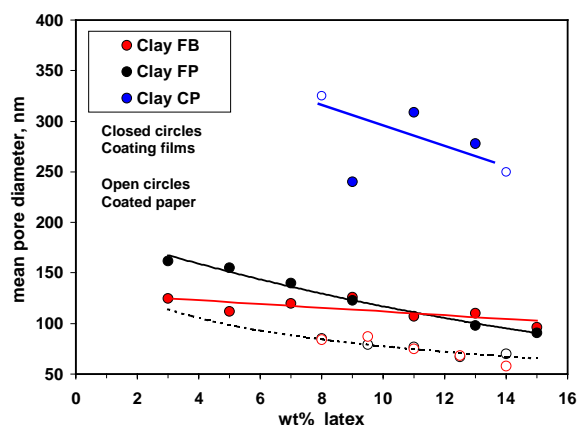


Figure 8a. Coating pore size by mercury intrusion porosimetry for clays FB, FP and CP.

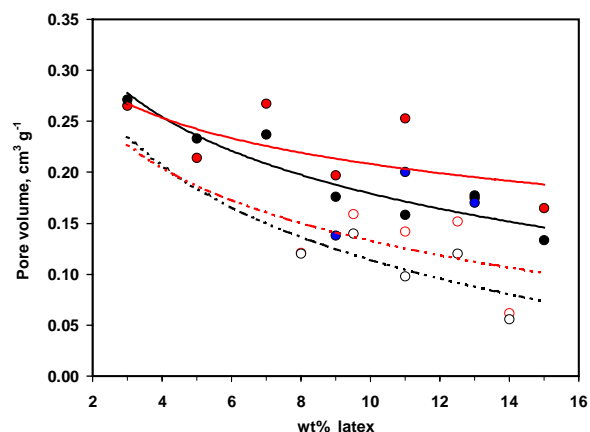


Figure 8b. Coating pore volume by mercury intrusion porosimetry for clays FB, FP and CP.

Effect of liquids on tensile strength of coating layers

Since the presence of water is known to weaken the coating substantially, it is possible that the presence of oils from the ink might have a similar effect. We studied this by soaking pre-cut tensile pieces of unsupported coatings based on ultrafine clay UFP in liquids of varying polarity ranging from water to vegetable, aliphatic mineral (obtained from an ink manufacturer) and silicone oils. The excess liquid was removed with filter paper and the in-plane tensile strength measured as described in ref [14]. The time between immersing the strips in liquid and measuring the tensile strength was maintained at about 60 s. Measuring the z-direction strength of saturated coatings was not possible since the method relies on adhesion to a water soluble tape.

Results are plotted in Fig. 9 for an immersion time of 60 s. The results for water reproduce the wet pick trends very well. The tensile strength falls from around 5 MPa at 12 pph latex to ~0.4 MPa when wetted. Note that when saturated with water, increasing the latex level has little effect on strength (compare with Fig. 7). Redrying the strips in air at room temperature restored the strength to close to the original level. A 50 / 50 mixture of isopropanol and water behaved in an identical way to water.

Experiments showed that oils also reduced the tensile strength of coatings. After 1 minute, the more polar vegetable oils reduced the strength by about two-thirds. Mineral oil, being less polar, had a smaller effect on strength. An experiment using silicone oil (BDH, 100 cs) showed this oil to be the least interactive, so that the strength was less affected (Fig. 10).

To check the possibility that the strips were not fully saturated with oil, a further set were prepared with an immersion time of 30 minutes. These results are plotted in Fig. 10(b). Clearly, strength continues to fall with time, but the effect of the polarity of the fluid is still evident. The caliper of the strips did not change after immersion for 30 minutes, indicating that no swelling of the coating had taken place.

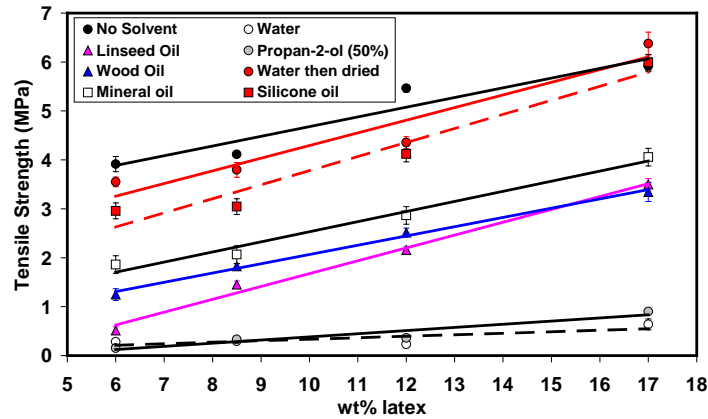


Fig. 9. Tensile strength of unsupported coatings at a range of latex levels based on Clay UFP after immersing in fluids of varying polarity (immersion time of 1 minute).

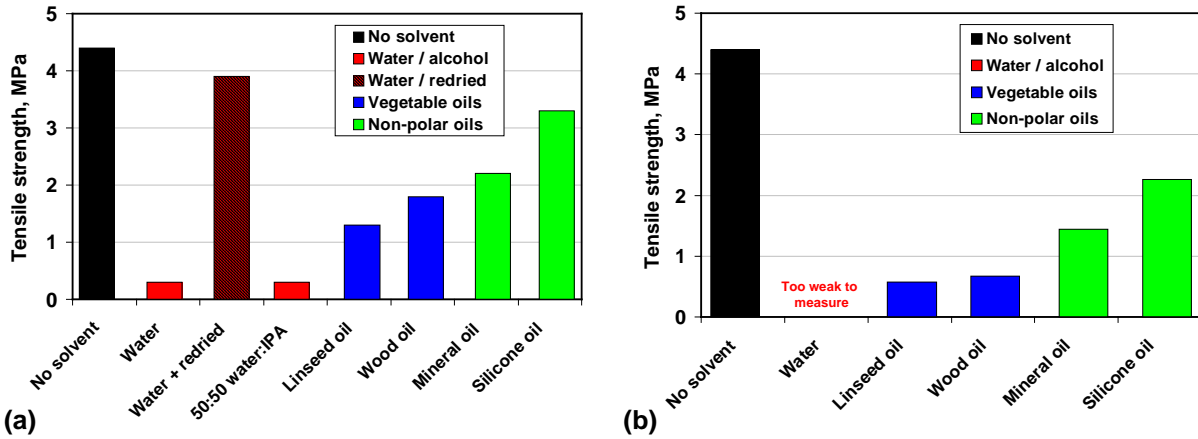


Fig. 10. Tensile strength of unsupported coatings based on Clay UFP saturated with fluids of varying polarity interpolated to 8.5 wt% latex. (a) after 1 minute, (b) after 30 minutes immersion.

We also made some coatings based on talc to compare with kaolin. Talc differs from kaolin in having basal surfaces with siloxane instead of hydroxyl groups [18] and therefore has a much lower affinity for polar fluids. We used a commercial talc slurry (C10, Mondo Minerals Oy, Finland), which also contains a wetting agent. The talc had a surface area of $5.5 \text{ m}^2 \text{ g}^{-1}$ and an average particle size of $2.0 \mu\text{m}$ esd.

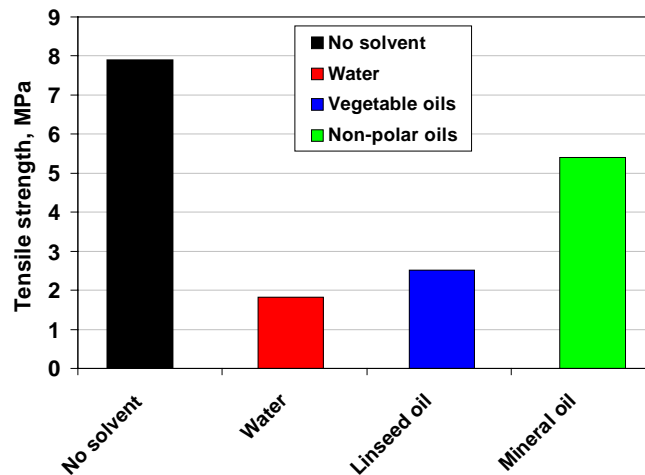


Fig. 11. Tensile strength of unsupported coatings of talc with 8.5 wt% latex after immersion for 1 minute.

The results (Fig 11) showed that talc coatings were significantly less sensitive than kaolin to water. Talc retained 23% of its dry strength when wetted for 1 minute compared to only 7% for kaolin. The effect of linseed oil was similar for both minerals, ~ 30%. The presence of a wetting agent, essential for slurry preparation, may complicate the interpretation of these results.

Rousu [19] studied the interaction between latex films and ink oils in some depth. She showed that certain types of oil, namely aromatic mineral oil and tall oil, were absorbed by latex films to a much greater extent than other vegetable and mineral oils. These oils also tackified the latex film. She also showed that acrylonitrile latexes, such as we have used here, had reduced oil interactivity. We plan to carry out further studies of the absorption of oils by the coating and the latex to understand the mechanism better.

Discussion

This study has shown that many factors influence the surface strength of coated papers during the offset printing process. Only some of these relate to the intrinsic strength of the coatings themselves, as measured by tensile testing on unsupported layers. Other important factors relate to the penetration of fluid, water or ink vehicle, into the pores and binder phase of the coating. When applying ink alone, penetration of ink vehicle from the ink into the coating controls the rate of tack build, and hence the force experienced by the coating during printing.

When we consider the strength of coatings in the presence of water, the situation becomes more complex. Our results have shown that coatings, which are inherently very strong when measured using the dry pick test, can be extremely weak when predamped. However, after the predamping water has evaporated from the coating layer, the strength is regained. Hence to successfully predict wet pick problems on the press, the delay time between damping and printing is a crucial factor.

A coating consisting of a very coarse kaolin had intrinsically high tensile strength, both in-plane and in the z-direction, when measured on unsupported coating layers. When coated onto paper, coatings based on this clay also had the highest dry pick strength. They also exhibited the highest strength when printed dry with a high tack ink. However, when predamped using a short delay time of the order of 1 s, these pigment coatings had the lowest wet pick strength. The strength was regained with longer delay times between damping and printing. Coatings with this pigment exhibited the slowest rate of ink setting. This is related to the large average pore size, hence low capillarity, which leads to a slow rate of removal of vehicle from the ink layer.

The mechanism by which water causes such a catastrophic strength loss is not understood. Latex binders are not hydrophilic and are unlikely to be affected by water. Petterson *et al* [7] concluded that water must attack the interface between the latex and pigment. Given the hydrophilic nature of kaolin, we think that the most likely explanation is that water temporarily forms a weak boundary layer which disrupts the bonding between the latex and mineral surface. The implication of this is that the latex – kaolin bonds are quite weak, probably originating from van der Waals forces, and not specific chemical bonds. Some support for this hypothesis comes from the observation that coatings based on talc, which has a hydrophobic surface, were less sensitive than kaolin to weakening by water. In future work we plan to compare binders such as proteins [20], starch [21], and polyvinyl alcohol [22] which take part in specific binding with clay surfaces.

When oil is the penetrating fluid, strength loss also occurs, but not to the same extent as we observed with water. The extent of strength loss was related to the polarity of the oil. With the more polar vegetable oils, after 30 minutes the effect on strength is almost as great as with water. A weak boundary layer may again be formed since the slightly polar vegetable oils also have an affinity for the kaolin surface [18]. It is well known that oily substrates are very difficult to glue. Silicone oil is non-polar and exhibited the least weakening effect. Hence the high pick strength of coarse clay coatings may in part be related to the slow rate of ink oil penetration, since the tack build and weakening effects will be low. It is also likely that, after printing, papers in which ink oil remains in the pores will have very weak coatings and this may contribute to various problems encountered after printing, such as scuffing.

In the Appendix we have attempted to calculate the stress applied to the coating at failure during the dry pick test. The results suggest that coating layers are about 2 orders of magnitude stronger than the stress applied during pick testing, and should not fail when they clearly do. It is possible that the timescale of stress

application in the tensile measurement is too slow. Another possibility is that of cavitation occurring in the nip exit leading to higher splitting forces than we calculated here. However, the established relationship between the picking velocity and oil viscosity for any given paper (see Appendix) suggests that the forces involved in picking can be related to the Newtonian behaviour of the oil film, which would rule out cavitation. A third reason, as detailed above, is that during printing, the presence of the oil weakens the adhesion between binder and mineral surface within the coating. It is also possible that picking may originate where there are flaws such as air bubbles in the coating.

Conclusions

This work has shown that :-

1. Coating pick resistance measured with oil-based fluids (dry pick) increases with the average particle size of the clay. This confirms industry experience. This trend is also seen for the in-plane and z-direction tensile strength of coating layers. There was no clear effect of kaolin shape factor on dry pick strength, unlike we observed in the tensile strength measurements.
2. When a water film was applied before the ink, the pick strength was reduced, especially for short delay times between damping and printing. The permeability of the coating to water was the key factor here. Coatings based on coarse clays that had the highest dry pick strength showed the lowest strength when predamped. This is probably related to their large pore size, which is thought to lead to a high permeability of the coating to water. The large pore size gives a low capillarity which reduced the rate of tack build with ink, and this lower tack force may contribute to an apparently higher dry strength.
3. A finding new to the literature was that the penetration of ink oils also reduces the strength of the coating. The polarity of the oil was a key factor. The mechanism has not been established, but it is likely that the oil can disrupt van der Waals bonding to form a weak boundary layer between the latex and mineral. It is also likely that oils are absorbed by the latex. One implication is that the process of ink setting and tack development is accompanied by a weakening effect on the coating as ink oil is imbibed. Since ink oils remain within the coating pores for some time after printing, the coating strength of freshly printed papers may be considerably lower than anticipated. This may contribute to strength-related problems during subsequent handling and converting operations.
4. Calculations of the forces associated with the dry pick test suggested that the maximum stress applied to the coating at failure by the film split at the nip exit was at least 2 orders of magnitude lower than the z-direction strength of the coating. The much shorter timescale of the pick test or the presence of flaws in the coating may explain why picking is observed.

In conclusion, measuring the tensile strength of dry coating layers is of value in providing a basic understanding of how mineral particle morphology, or binder properties, influences the material strength of the coating layer in isolation. However, in printing with offset inks, the coating strength is only one part of the story. Other factors include the rate of tack rise of the ink, since this determines the stress applied to the coating, and the extent of weakening of the binder – mineral adhesion by the oil phase of the ink. It is possible to envisage a coating which is inherently rather weak, but which gives a very slow rate of ink setting, hence tack build, which survives the printing nip without picking. It is also possible that a stronger coating, having a faster rate of tack build, and therefore more oil imbibition, would exhibit pick. The reason for this does not lie in the intrinsic strength of the coatings, but the different tack forces and weakening effects they experience.

The fundamental science behind the weakening effect of fluids such as oil and water is not well understood. Our results suggest that the polarity of the fluid is an important factor. This points to the nature of the bonding between latex and kaolin being relatively weak, and easily disrupted by polar fluids. Establishing the mechanism would represent a significant step towards engineering stronger coatings. More research is needed on this important subject, and colloid probe AFM techniques, for example, may offer a promising way to study this phenomenon fundamentally.

Acknowledgements

The authors are grateful to the board of Imerys Minerals Ltd for permission to publish this work, and to Dr A. G.Hiorns for helpful discussions.

References

1. Gane, P.A.C. and Seyler, E.N., "Tack development : an analysis of ink paper interaction in offset printing", Proc. TAPPI Coating Conf. (1994), pp.243-260, TAPPI Press, Atlanta,
2. Gane, P.A.C., Schoelkopf, J., and Matthews, G.P., "Coating imbibition rate studies of offset inks : a novel determination of ink-on-paper viscosity and solids concentration using the ink force-time integral", Proc. TAPPI International Printing and Graphic Arts Conf. (2000), pp 71-88, TAPPI Press, Atlanta,
3. Smith, D.A., Settlemyer, L.A., and McCoy, J.W., "An investigation of coated paper wet pick using scanning electron microscopy and the IGT Printability Tester", Proc. TAGA Conf. (1992), pp 320-345, TAGA, Rochester, New York,
4. Purfeest, R.D. and Van Gilder, R. F., "Tail edge picking, back trap mottle and fountain solution interference of model latex coatings on a six-color press predicted by laboratory tests", Proc. TAPPI Coating Conf. (1991), pp.461 - 472, TAPPI Press, Atlanta,
5. Cobb, R.M.K., "Coating adhesive demand – what pigment function governs it ?", TAPPI J., **41** (10), 581-600 (1958),
6. Parpillon, M., Engström, G., Petterson, I., Fineman, I., Svanson, S.E., Dellenfalk, B., and Rigdahl, M., "Mechanical properties of clay coating films containing styrene-butadiene copolymers", J.Appl.Polym.Sci., **30**, 581-592 (1985),
7. Lepoutre, P., and Hiraharu, T., "On the cohesion of clay and carbonate coatings", J.Appl.Polym. Sci., **37**, 2077-2084 (1989),
8. Petterson, I., Rigdahl, M., Fineman, I., and Engström, G., "On the wet and dry strength of coated paper", Trans. 8th Fundamental Symposium, Cambridge, Vol 2, 1985, pp. 655-671, Mech. Eng. Publications Ltd., London,
9. Skeppstedt, A., Borg, J., Mälhammar, G., Engström, G., and Rigdahl, M., "Surface treatment of CaCO₃ with polymers in order to improve the surface strength of coated papers", Proc. TAPPI Coating Conf. (1991) pp. 191-197, TAPPI Press, Atlanta,
10. Lepoutre, P., and Rigdahl, M., "Analysis of the effect of porosity and pigment shape on the stiffness of coating layers", J.Mater.Sci., **24**, 2971-2974 (1989),
11. Inoue, M., and Lepoutre, P., "Influence of structure and surface chemistry on the cohesion of paper coatings", J.Adhesion Sci. Technol., **6** (7) 851-857 (1992),
12. Barbier, C., Larsson, P-L., Östlund, S., Hallback, N., and Karathanasis, M., "On material characterisation of paper coating materials by microindentation testing", J.Coating Technol. Res., **2** (6), 463-471 (2005),
13. Granier, V., and Sartre, A., "Ordering and adhesion of latex particles on model inorganic surfaces", Langmuir, **11**, 2179-2186 (1995),
14. Husband, J.C., Preston, J.S., Gate, L.F., Storer, A, and Creaton, P., "The influence of pigment particle shape on the in-plane tensile strength properties of kaolin-based coating layers", TAPPI J., **5** (12), 3-8 (2006),
15. Husband, J.C., Preston, J.S., Gate, L.F., Storer, A, and Creaton, P., "A study of in-plane and z-direction strength of coating layers with varying latex content", TAPPI J., in press,
16. Gate, L.F., and Webb, T.W., US Patent 5,576,617 (1996),
17. Ridgway, C.J., and Gane, P.A.C., "Correlating pore size and surface chemistry during absorption into a dispersed calcium carbonate network structure", Nordic Pulp Paper Res. J., **21** (5), 563 – 568 (2006),
18. Trivedi. N.C., "Talc", in Pigments for Paper, ed. Hagemeyer, R.W., TAPPI Press, Atlanta, p. 200, (1997),
19. Rousu, S., "Differential absorption of offset ink constituents on coated paper", PhD dissertation, Åbo Academi University, (2002),
20. Whalen-Shaw, M., "Protein-pigment interactions for controlled rotogravure printing properties", TAPPI J., **67** (5), 60 – 64 (1984),
21. Husband, J.C., "The adsorption of starch derivatives onto kaolinite", Colloids Surfaces A, **131**, 145-159 (1998),
22. Toyoshima, K., in "Polyvinyl Alcohol", p. 331, ed. Finch, C.A, J.Wiley, New York, 1973.

Appendix

Calculation of the stress applied in the dry pick test

The dry pick test used in our laboratory involves the application of a film of viscous polybutyne-based oil of thickness $8\mu\text{m}$ to the coated paper substrate. The velocity of application increases through the action of an accelerating applicator disc [1]. The critical velocity at which the first signs of coating removal occurs is determined visually, in our case using a low power microscope and side illumination.

An important question is what happens at the critical velocity. We note [2] that the product of the pick velocity and the viscosity of the oil has a constant value for a particular substrate. This is possible because the oil displays Newtonian viscosity behaviour [2]. The existence of the relationship between pick velocity and viscosity implies that there must be a critical (extensional) stress which acts on the paper surface to cause pick.

The splitting of a liquid film at the exit of a rolling nip leads to a negative pressure being generated. As speed increases, the negative pressure also increases until it is large enough to cause failure at the coating surface. The assumption is made that the stress is acting vertically to the sample surface and therefore only the z-direction strength of the sample is important. There may be an in-plane force if the negative pressure is generated a significant distance from the centre of the nip, but we believe this is negligible due to the small size of the roll involved. The other potential in-plane force may be generated by the deformation from the roll surface, which will lead to an increase in the contact area in the nip and consequent stretching of the paper. Examination of the impression of the inked disc left on the paper strip after pick measurement allows us to calculate the longitudinal stretching of the coating. Results show that this is no more than 0.05 % in strain, and does not normally lead to coating failure.

An experimental investigation by Chopra and Tawashi [3] provides a useful set of data on the splitting force of films of viscous polymer solutions (lecithin) at short time scales. We have used these data to calculate the approximate forces involved in the wet pick test at failure, as follows :

The classical equation governing the force needed to separate two discs of radius a separated by a distance h when immersed in a liquid of viscosity η is as follows (equation 1) :

$$F.t = \frac{3}{4}\eta a^2 \left(\frac{1}{h_1^3} - \frac{1}{h_2^3} \right) \dots\dots\dots(1)$$

where F is the force needed to separate the plates by the distance $h_1 - h_2$ in time t .

Note that the force increases for diminishing film thickness and that this parameter has a third power dependence. This indicates the importance of film thickness and accurate metering of the volume of oil applied during the dry pick test. Equation (1) assumes that the liquid is Newtonian and that the separation rate is below a critical velocity where cavitation may begin. The Newtonian relationship between oil viscosity and picking speed suggests that this latter condition is adhered to.

Chopra and Tawashi measured the force at increasing rates of separation between two probes containing liquid of known viscosity values. They plot their data in the form of stress curves as a function of time for increasing separation rates. We used the data for their highest viscosity solution (6.2 Pa.s) to calculate the stress generated by the IGT pick oil as follows :

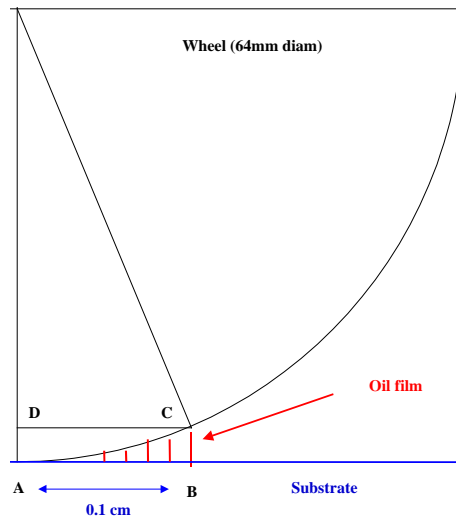


Figure A1. Schematic diagram of IGT tacky oil disc.

The rate of stretching of the oil film at a pick velocity of 100 cm s^{-1} was first calculated assuming the nip dimensions shown in Figure A1. In the time taken for the oil film to move from the nip zone at point A to the point B, the oil film will be stretched by a vertical distance CB. Suppose it splits at this point. Using trigonometry it can be calculated that the oil film is stretched by 0.00156 cm . At a pick velocity of 100 cm s^{-1} , the time taken to travel from A to B is 0.001 s . Hence the rate of stretching is 1.56 cm s^{-1} .

The fastest separation rate obtained by Chopra and Tawashi is 0.166 cm s^{-1} . Hence the IGT exceeds their experimental results by a factor of 10. However, we can extrapolate the peak stress values reported in [2] to the required velocity, which gives a peak stress of 1700 g cm^{-2} with reasonable accuracy (Figure A2). Next we corrected for the faster build up of stress with the IGT, which at 100 cm s^{-1} takes about 0.001 s to travel from A to B. This is 2 orders of magnitude less than Chopra and Tawaski's time scale of 0.1 s . We note that the stress rise is approximately linear with time, so we can estimate that in 0.001 s the stress will have risen to $1700 (0.001/0.1) = 17.0 \text{ g cm}^{-2}$.

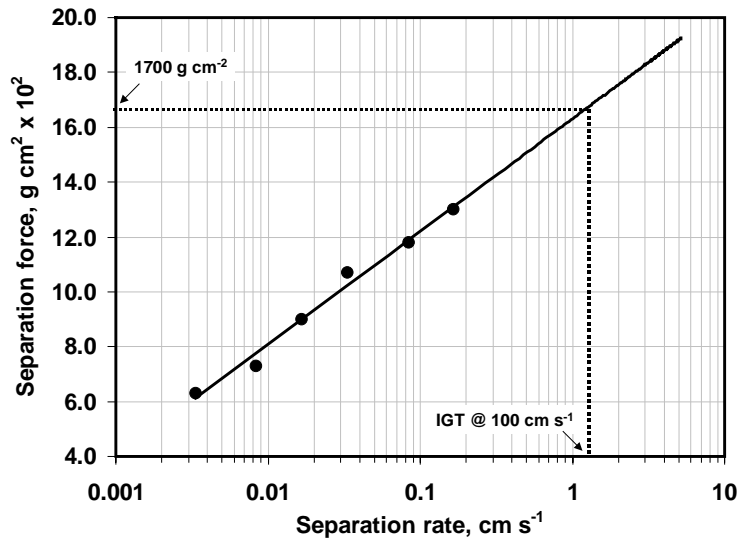


Figure A2. Separation force plotted as a function of separation rate for a lecithin solution of 6.2 Pa.s . Replotted from Chopra and Tawaski, ref 3.

There now remains one final correction to be made. The viscosity of the oil used was 17.5 Pa.s , higher than Chopra and Tawaski's polymer solution of 6.2 Pa.s . From equation (1) we see that the force F is linearly proportional to the viscosity so we can scale up our stress value by $17.5 / 6.2$ giving 50 g cm^{-2} , or 0.005 MPa .

This result for the maximum stress applied during the dry pick test at 100 cm s^{-1} is about a factor of 100 less than the z-direction tensile strength of the coating layers reported in Figure 2 (main text). However, these were not calendered, and the coated strips used in the pick test were. Consideration of the effect of calendering, which compresses the coating and reduces the porosity, leads to the conclusion that the z-direction strength after calendering would increase further, perhaps by a factor of 2 or 3.

References

1. IGT pick and blister test description, Applied Paper Technology Inc., www.appliedpapertech.com,
2. The pick test according to ISO 3783, IGT Newsletter 1, August 1997,
3. Chopra, S.K., and Tawashi, R., "Tack behaviour of coating solutions II", *J.Pharmaceutical Sci.*, **73**, 4, 477-481 (1984).



✦ **Europe**
Tel: +44 1726 818000

✦ **Asia Pacific**
Tel: +65 67 99 60 60

✦ **N. America**
Tel: +1 770 594 0660

✦ **S. America**
Tel: +55 11 2133 0055

Email
paper@imerys.com