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Mechanistic insights into the weakening effect of water and oils on paper coatings containing latex adhesives during offset printing

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ABSTRACT

The phenomenon of “wet pick” during printing is well known to paper coating and printing technologists. Recent work has highlighted the reversible effect of water on the tensile strength of coating layers, and has shown that the mineral and vegetable oils commonly used in ink formulations have a similar, if smaller, detrimental effect on strength.

In this study, we show that the coating strength decreases as the dielectric constant of the penetrating fluid increases. In the adhesive science literature, a similar correlation has been observed for various types of adhesive joints, and can be explained in terms of ion-pair bonding. We have tested this theory for mineral-based paper coatings containing latex adhesive, and found that it underestimates the loss of strength observed experimentally. In the latex-mineral bond, contributions from other mechanisms such as van der Waals forces are also likely. This knowledge should ultimately allow the design of more effective pigment – binder combinations better able to withstand weakening in the presence of fluids used in printing.

KEY WORDS

Printing, coated paper, kaolin, calcium carbonate, styrene – butadiene latex, acrylic latex, fountain solution, linseed oil, mineral oil, dry pick strength, wet pick strength, ammonium zirconium carbonate, ion-pair bonds.

1. INTRODUCTION

During the offset printing process on coated paper, high levels of stress are experienced by the coating layer. This is as a result of the increasing tack force developed by the ink layer as it loses its oil-based vehicle into the pore structure of the coating. Gane and co-workers showed that this is a result of increasing cohesivity of the ink [1,2]. When the tack force develops too quickly, or the coating strength is inadequate, the phenomenon of “dry pick” is observed, in which fragments of coating are removed by the ink.

Additionally, in non-image areas of the print where aqueous fountain solution has been applied, the coating is weakened and subsequent printing with ink can cause a similar phenomenon known as “wet pick”. Pettersson and co-workers [3] considered that water could attack the interface between the binder (usually a carboxylated styrene-butadiene latex) and mineral, typically kaolin or calcium carbonate dispersed with sodium poly(acrylate). This weakening by water is temporary and is related to the rate of absorption of water by the coating [4-7].

In our earlier publications, we studied the effect of water on the pick strength of a number of mineral-based coatings on paper. The results for kaolin-based coating layers [5,6] showed that the strength in the absence of water (dry pick strength) decreased as the particles became smaller and surface area increased. After the coatings had been predamped with water before ink application to measure wet pick strength, the opposite trend was observed, i.e. the coatings with the highest dry pick resistance had the lowest wet pick resistance.

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When calcium carbonate coatings were compared, the trends were different [7]. The dry pick strength again decreased with increased fineness, but this time the wet pick strength followed the same trend. The results were explained in terms of the permeability of the coatings to water, with the platy nature of kaolin causing water to become trapped between particles as a result of the tortuosity of the coating pore structure.

In an attempt to study the effect of fluids, Reinius and co-workers prepared free-standing coating layers and measured their tensile strength after exposure to fluids such as water and mineral oil [4]. The results showed that considerable weakening occurred. Husband and co-workers [5-7] extended the range of fluids further and demonstrated that the degree of weakening of a coating layer was related to the polarity of the fluid, so that the polar oils such as linseed oil had a greater weakening effect than mineral oil. It was also shown that water had a catastrophic effect on the strength, but this effect was completely reversible if the water was left to evaporate under ambient conditions.

Very few studies have been published on the mechanism by which latex adheres to mineral surfaces and the effects of fluids, such as water, on the adhesion. This is clearly central to developing stronger coatings or more efficient binders. Using NMR, Dellenfalk and Svanson [8] obtained evidence for reduced segmental mobility of the latex chains when bound to kaolin, indicating some kind of interaction. The interaction became greater with heat treatment for several hours. Parpillon and co-workers [9] also used NMR to compare kaolin and calcium carbonate coatings. Their results suggested that the latex binder existed in discrete domains in the clay coatings but was spread more evenly over the ground calcium carbonate particles. Skeppstedt and co-workers [10] demonstrated that surface modification of the mineral (calcite) surface using grafted polystyrene improved the pick strength of paper coatings containing a styrene-butadiene latex binder. They suggested that the compatibility between pigment and binder had been improved by the surface treatment.

A number of authors have used AFM in order to study the adhesion of individual latex particles on model inorganic surfaces. Granier and co-workers [11,12] studied carboxylated styrene-butyl acrylate latex particles on silica, mica and calcite surfaces. Using the AFM they showed that adhesion of latex to the surface increased from silica, which had the weakest adhesion, to calcite, where the adhesion was so strong that latex particles could not be moved using the AFM tip. The results were interpreted in terms of acid – base character of the mineral and latex. Applying this model to kaolin, the kaolin edges are basic and the faces acidic, so the acidic latex may be expected to adhere more strongly to the edges.

Unertl [13] also used AFM to study the adhesion of carboxylated SB latex particles to dispersant-free calcite. By measuring the contact angle of the latex particles after spreading on calcite, he estimated the contribution of dispersion and acid-base interactions to the work of adhesion. Values for γ^D were between 22 – 49 mJm⁻² and γ^{AB} 37-64 mJm⁻². Commercial coating grades of calcium carbonate differ from pure calcite surfaces in having a dense adsorbed layer of poly(acrylate) [14], which may have a detrimental effect on the adhesion of latex. No studies have been found which investigate the effect of dispersant or water and oils on the adhesion.

The reversible detrimental effect of fluids, especially water, on the strength of adhesive joints is well known in the literature. A number of studies exist on weakening of epoxide-bonded aluminium joints [15-19]. Comyn [16-18] suggests a mechanism based on the weakening of ion-pair bonds by the fluid. The attraction of this mechanism for us was that, when immersed in a fluid, the bond strength is inversely related to the polarity of the fluid, in fact the dielectric constant, and can therefore be quantified. In this paper we discuss our results in the light of this mechanism.

2. THEORETICAL BACKGROUND

2.1 Weakening of ion-pair bonds

An ion-pair bond is defined as a pair of oppositely charged ions held together by Coulombic attraction without the formation of a covalent bond [20]. If the ions are not separated by liquid molecules, the bond is designated a “tight ion-pair”. Comyn [16-18] suggests that, if ion-pairs contribute to adhesion, the attractive interfacial force between two adhering surfaces can be quantified by the following equation :

$$F = q_1 q_2 / (4 \pi \epsilon_0 \epsilon_1 r^2) \quad (1)$$

Where F = force between 2 ions having charges q_1 and q_2 , separated by a distance r , and ϵ_0 and ϵ_1 are the dielectric constants for free space and the medium separating the ions, respectively.

We can therefore express the original value of the force for a “dry” bond (F_1) as :

$$F_1 = (A / \epsilon_1) \quad (2)$$

Where A is a constant term assuming that the charges remain constant as does the distance between them. We can rewrite equation (2) as follows :

$$A = (F_1 \epsilon_1) \quad (3)$$

When the joint is immersed in a liquid of dielectric constant ϵ_2 , the new value of the force (F_2) will be :

$$F_2 = F_1 (\epsilon_1 / \epsilon_2). \quad (4)$$

Values of dielectric constants for the liquids used in our study are given in Table 1 [21] :

Table 1. Dielectric constants for a range of typical liquid media used in printing

Medium	Dielectric constant
Air / vacuum	1
Mineral (paraffin) oil	2.2
Linseed oil	3.2 – 3.5
2-Propanol	18.3
Water	80

We assume that the original dry bond has free space separating the ions, and that the dielectric constant (ϵ_1) = 1. Hence when a liquid of dielectric constant ϵ_2 penetrates the bond, the strength falls as $1/\epsilon_2$. It is apparent that this gives us a method of testing the theory by measuring the residual tensile strength when a coating is immersed in a liquid and comparing with the theoretical residual bond strength calculated from equation (4).

3. MATERIALS AND METHODS

3.1. Materials

Two clay pigments, a coarse platy kaolin, Capim RGTM (designated CP), and an ultrafine platy kaolin (designated UFP), Contour XtremeTM from Imerys Minerals and one ground calcium carbonate pigment (GCC), were used in this investigation. The kaolins were produced from sedimentary deposits. The properties of the pigments are summarised in Table 2. The mean shape factor of the kaolin samples (defined as the average plate diameter / thickness) was measured by stopped flow conductivity using a patented technique [22]. The GCC was an experimental coarse grade, which gave coherent self-supporting coating films. Films prepared from finer GCC pigments were found to be too brittle to handle. The particle shape of the calcium carbonate was irregular, having a shape factor close to 1 (not measured). The pigments were dispersed at the maximum solids using an optimum dose of an appropriate sodium poly(acrylate) dispersant. For the kaolins, this was Accumer 9300 (Rohm & Haas, Valbonne, France) and for the GCC, Dispex[®] 2695 (Ciba, Bradford, UK).

Table 2. Physical properties of pigments

Pigment	Particle size distribution by Sedigraph [®] , wt% material below stated size (equivalent spherical diameter)					Shape factor	BET surface area, m ² g ⁻¹
	2µm	1µm	0.5µm	0.25µm	Average size, D50, µm		
Kaolin CP	51	29	14	6	2.0	42	6
Kaolin UFP	97	90	79	53	0.23	40	24
GCC	66	25	5	1	1.5	~1	5

In most experiments, the latex binder used was a commercial carboxylated styrene butadiene acrylonitrile copolymer of T_g = 10°C (DL920, Dow Chemical, Horgen, Switzerland), designated SBN. The latex was added at levels of 8.5 and 12 parts per hundred parts of mineral by weight (pph). In some experiments, other latices were used. Two were commercial acrylic latices designed for paint formulations, Primal[™] 016 (designated A1), and Avanse[™] 412 (designated A2), from Rohm & Haas, Valbonne, France. An experimental styrene-butadiene copolymer latex with a high level of carboxylation, 6.5 wt%, designated SBHC, synthesised by EOC (Evergem, Belgium) was also included. 0.3 pph of sodium carboxymethyl cellulose (Finnfix 10[™], CP Kelco, Åänekoski, Finland) was also added as a thickener. After pH adjustment to 8.0, the suspensions were screened through 53µm. In order to remove air bubbles, the suspensions were centrifuged at 4000 rpm for 10 minutes.

The latex surface energy was estimated from contact angle measurements on dry films of each latex coated onto a polyester substrate (Yupo FEB110, Yupo Europe GmbH, Düsseldorf). The approach was similar to that described by Kan and Van Gilder [23]. Before coating, the latex suspension was adjusted to pH 8 using NaOH. The polar (γ_s^p) and dispersion (γ_s^d) components of the surface energy were estimated by using the procedure of Owens and Wendt [24] from the equilibrium contact angles measured for water and 1-bromonaphthalene (Alfa Aesar, Heysham, UK). A Fibro DAT 1100 instrument (Fibro System AB, Stockholm, Sweden) was used. Results are summarised in Table 3.

Table 3. Surface energy and its components of latex films (in mJ m⁻²)

Latex	γ_s^d	γ_s^p	γ_s
SBN	35.9	20.5	56.4
SBHC	23.6	34.0	57.5
A1	33.0	9.9	42.9
A2	33.0	11.2	44.2

These results show that the SB latices have higher total surface energy values and are more polar than the acrylics. This probably reflects the level of surface carboxylation, with the high carboxyl latex showing the most polar character. Less is known about the acrylic latex chemistry, but the values measured here are similar to those reported by Kan and Van Gilder for styrene – n-butyl acrylate binders [23].

3.2. Experimental Methods

Coating films were prepared by drawdown using wire wound bars. The substrate chosen was a poly(ethylene terephthalate) film having a thickness of 13µm (Terinex Ltd., Bedford, UK).

Coatings acceptable for tensile testing were found by experience to require a thickness of at least 50 µm. This was achieved by using a wire-wound bar designed to give a wet film thickness of nominally 150 µm (RK Print Coat Instruments, Royston, UK). Following drawdown and drying with a hot air stream, we found that the majority of pigment-binder combinations could be easily separated from the substrate and were sufficiently self-supporting to handle. Typically, 100µm thick dried coatings were produced. For measurement of tensile strength in the plane of the coating, the coatings were cut into a barbell shape using a template designed for testing rubber samples. The length of the barbell was 50mm, and the width of the central bar was 4mm. The

thickness of the coating was measured using a digital micrometer gauge accurate to $\pm 2 \mu\text{m}$ (Messmer Instruments Ltd., Gravesend, UK). The ends were attached via rubber-faced clamps to a tensile tester (Testometric 350, Rochdale, UK). An extension rate of 10 mm min^{-1} was used for the tensile testing, which was carried out at 23°C and 50% RH. Load and elongation-at-break were recorded for each sample. The strength was calculated by dividing the load (N) at break by the cross-sectional area of the sample over which the load was applied to give the tensile strength in force per unit area (MPa). Five measurements were made on each sample, and the mean value calculated. In the following figures error bars signify the standard deviation.

A number of samples were equilibrated in atmospheres of varying relative humidity (RH) before tensile testing. This was done in a humidity cabinet (WKL34, Weiss Gallenkamp Ltd., Loughborough, UK) set at 22°C with relative humidity values between 30 and 90%. Figure 1 shows that at 90% RH strength loss occurred within 3-4 hours, and in practice coatings were equilibrated for 16 hours and placed in sealed poly(ethylene) bags, only being removed prior to measurement of tensile strength. Experiments showed that the loss of moisture from the coating during this operation was insignificant.

Samples of mineral oil and linseed oil were obtained from an ink manufacturer. A 50:50 mixture of 2-propanol : water was also used. In order to measure tensile strength in the presence of fluids, coating strips were immersed in the fluid, and the excess was carefully removed using filter paper before tensile testing. Figure 2 shows the kinetic response of strength to immersion time for kaolin and two oils. From this plot, an immersion time of 10 minutes was chosen for the study.

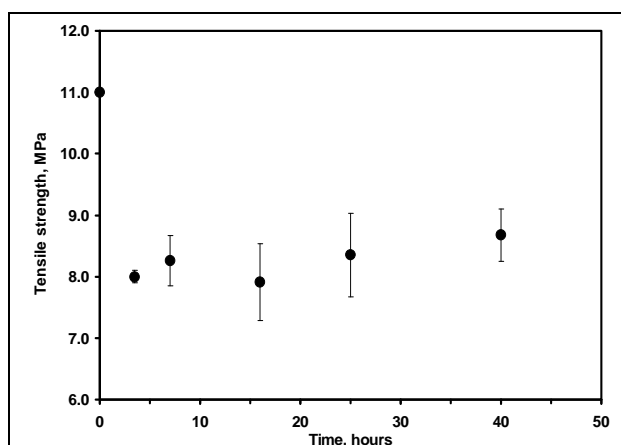


Figure 1. Tensile strength as a function of equilibration time for coatings in 90% RH air at 22°C (kaolin CP / 8.5 pph latex SBN).

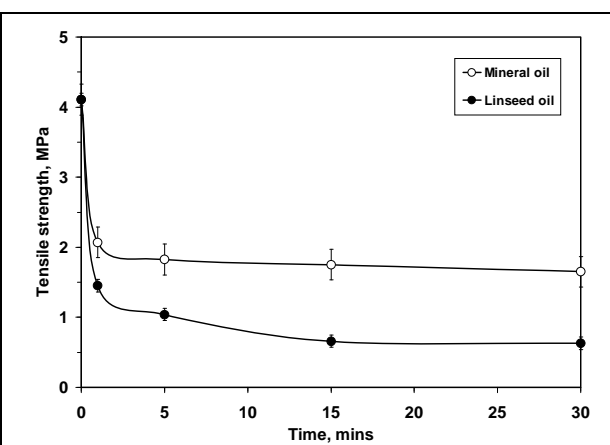


Figure 2. Tensile strength as a function of immersion time for kaolin coatings in different oils (Kaolin UFP / 8.5 pph latex SBN).

The total pore volume and average pore size of the dried coating films was measured by mercury intrusion porosimetry using a Pascal Model 240 porosimeter (CE Instruments Ltd., Wigan, UK). Corrections for glassware expansion were applied and the contact angle for mercury was taken as 141° .

4. RESULTS

Before we could calculate the residual strength after immersion in different fluids, it was necessary to estimate the intrinsic strength of the coating layers in the absence of any moisture. The strength as normally measured in a conditioned atmosphere of 50% RH is likely to be lower because of the presence of moisture in the coating. An approach similar to that used by Brewis and co-workers for epoxide joints was used [25]. We estimated the intrinsic strength by measuring the tensile strength after conditioning coatings in different relative humidity environments and extrapolating to 0% RH. Figure 3 shows that for kaolin CP and UFP coatings below about 50% RH, the strength is only slightly affected, only beginning to fall significantly as RH increases above 50%. GCC-based coatings behaved differently in showing weakening only at higher humidity levels, close to 90% (Figure 4). GCC coatings were much weaker than kaolin coatings, leading to a larger standard deviation in the measurements. The existence of a critical humidity for weakening has also been found for epoxide-bonded

aluminium joints [25], Figure 5. It should be noted that these were equilibrated at 50°C and therefore at 50% RH the water vapour pressure will be higher than in our experiments [26].

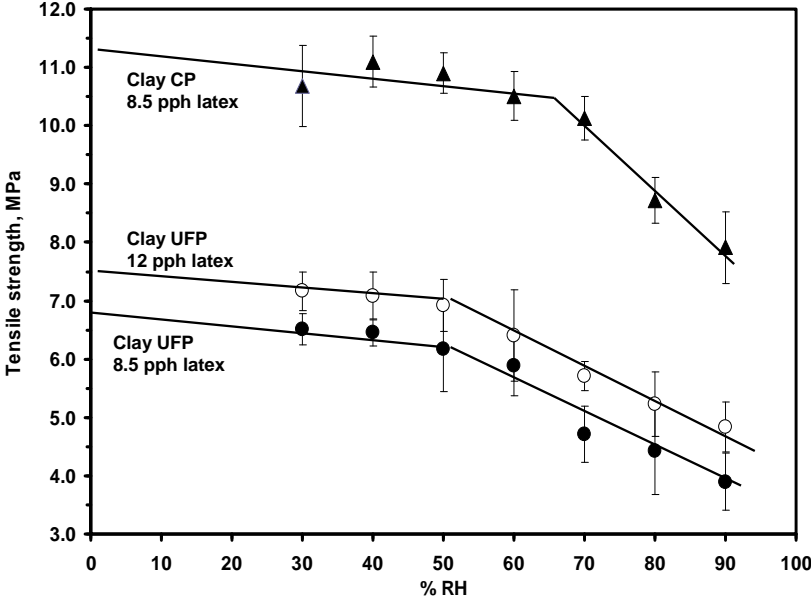


Figure 3. Sensitivity of tensile strength to RH, kaolin – latex coatings, 22°C.

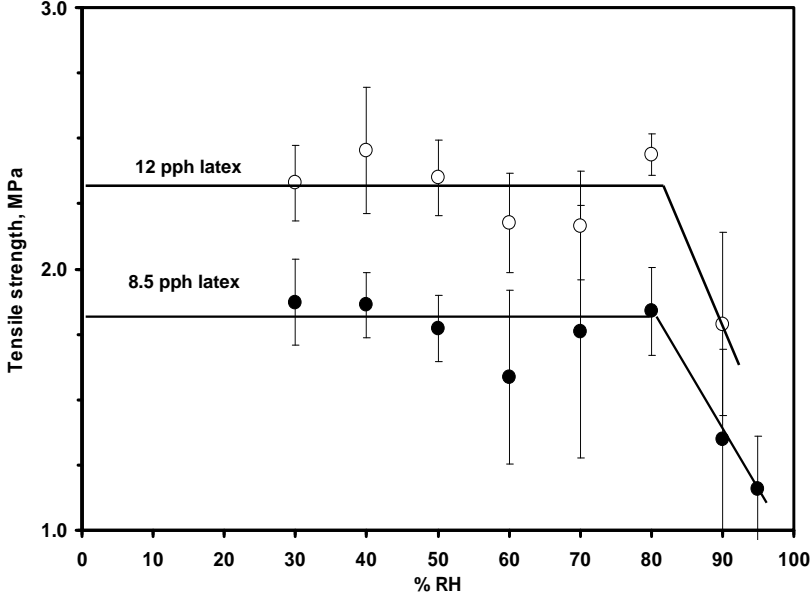


Figure 4. Sensitivity of tensile strength to RH, calcium carbonate – latex coatings, 22°C.

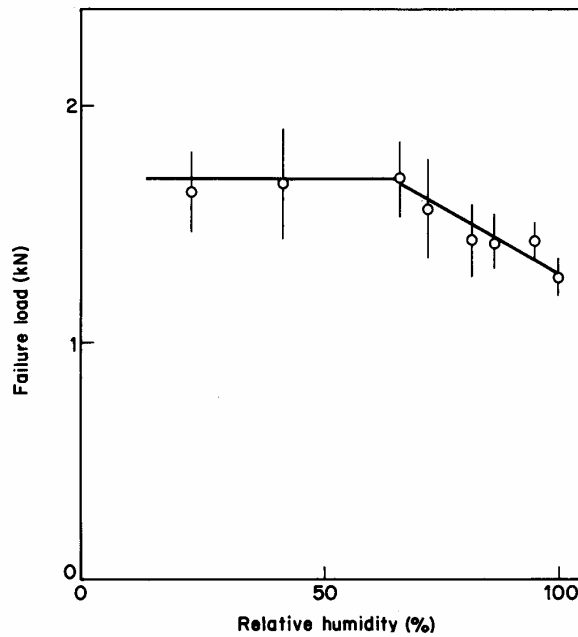


Figure 5. Sensitivity of failure load to RH, epoxide-bonded aluminium joints at 50°C after 10,080 hours exposure. From Brevis [25].

Figures 3 and 4 allowed extrapolation to give the intrinsic strength of the coating at zero moisture content. We used this value to calculate the % residual strength after immersion in different fluids and compared it with the predicted residual strength calculated from equation (4). These are summarised in Table 4. Duplicate values indicate separate experiments.

Table 4. Comparison of calculated and measured residual strength after saturation with different liquids

Pigment	SBN latex pph	Coating pore diameter nm	Coating pore volume cm^3g^{-1}	Tensile strength MPa (0 RH)	% residual strength			
					Mineral oil	Linseed oil	2-propanol water 50:50	Water
Theoretical (from equation 4)	-	-	-	-	46	28 - 31	2.0	1.3
Kaolin CP	8.5	240	0.14	11.3	23	11	<1	<1
Kaolin UFP	8.5	55	0.175	6.8	23, 42	9, 16	<1	<1
Kaolin UFP	12	52	0.182	7.4	21	12	<1	<1
GCC	8.5	480	0.187	1.8	19	10	<1	<1
GCC	12	440	0.144	2.3	18	11	<1	<1

In all cases there is a lower measured residual strength than estimated from the effect of the dielectric constant on the ion-pair interaction. The results for each fluid are quite consistent for all the mineral systems and binder levels.

We also studied the effect of water on the tensile strength of pure SBN latex films, of typical thickness 500 μm . These were prepared by drying in a vacuum oven on a smooth substrate. Latex was used after adjusting to pH 8 using NaOH. Bubble-free areas of the film were selected for tensile testing. Bars of latex were cut using a scalpel and the cross-sectional area measured before testing. Samples were immersed in water for periods of up to 40 hours.

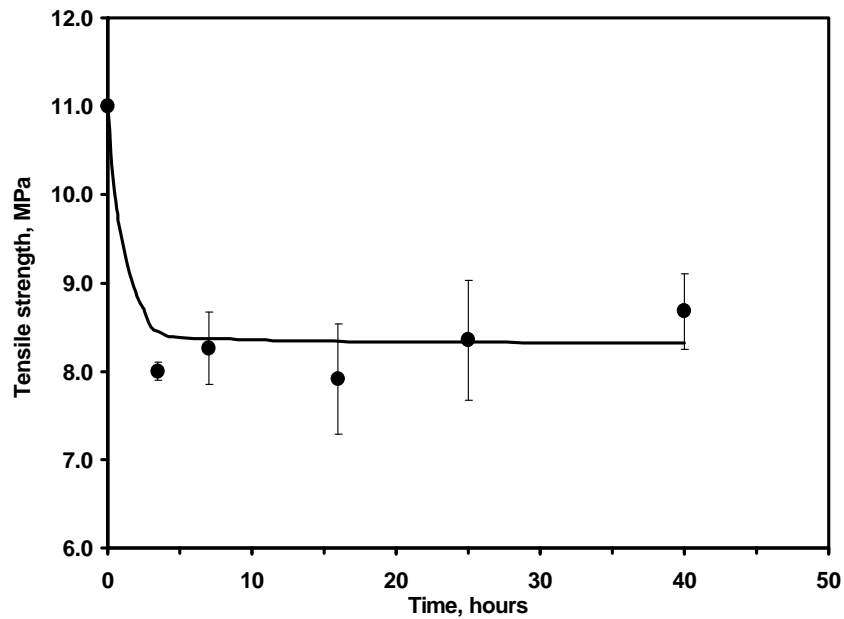


Figure 6. Effect of water immersion time on tensile strength of pure SBN latex films.

Results show that compared to the coatings in Table 4, the loss in strength was relatively small, even after immersion for 40 hours (Figure 6). The tensile strength fell from 11 MPa to 8.4 MPa. This implies that in coating layers, water principally attacks the mineral-latex bonds, not the latex interparticle bonds.

We also investigated the role of the latex polarity in terms of water sensitivity. Two acrylic latices intended for the paint industry, designated A1 and A2, were used. These were compared to our standard SBN latex in a coating containing GCC. Results are summarised in Table 5.

Table 5. Effect of latex composition on residual strength after saturation with different liquids

Coating	Tensile strength MPa	% residual strength		
		Mineral oil	Linseed oil	Water
GCC + 8.5 pph SBN latex	1.51 ± 0.02	19	10	<1
GCC + 8.5 pph acrylic latex A1	0.90 ± 0.12	46	16	29
GCC + 8.5 pph acrylic latex A2	0.72 ± 0.02	54	24	50

The results suggest that the less polar acrylic latices offer greater resistance to weakening by fluids than the standard SBN. The resistance to water is improved beyond the resistance to linseed oil, an observation which might be explained if the polar oil were absorbed by the latex itself. The observation that water resistance is improved is not unexpected, given the requirement of paint films for wet rub resistance. The mechanism behind this improvement may lie in the reduced polarity of the latex, reducing its affinity for water [23]. However, the acrylic latices give weaker coatings before wetting, which may be a result of other differences such as the thermo-mechanical properties, which we did not measure. Without a greater knowledge of the polymer chemistry it is difficult to speculate further on the mechanisms behind these results.

A second approach to increasing water resistance in the coatings industry is to use zirconium compounds, such as ammonium zirconium carbonate (AZC), as cross-linkers. These compounds are capable of forming covalent bonds between OH and COO⁻ groups [27]. We evaluated the effect of adding AZC (Bacote 20, MEL Chemicals, Manchester, UK) to a poly(acrylate)-dispersed GCC coating. An experimental grade of SB latex containing a high level of carboxylation, 6.5 wt%, designated SBHC was used for this. Results are summarised in Table 6.

Table 6. Effect of AZC on residual strength of coatings after saturation with different liquids

Coating	pph AZC (as solution)	Tensile strength MPa	% residual strength		
			Mineral oil	Linseed oil	Water
GCC + 8.5 pph SBHC latex	0	0.97 ± 0.12	18	18	<1
GCC + 8.5 pph SBHC latex	0.25	1.35 ± 0.21	30	17	<1
GCC + 8.5 pph SBHC latex	0.50	1.68 ± 0.13	37	24	<1
GCC + 8.5 pph SBHC latex	0.75	1.84 ± 0.12	30	25	19

These experiments showed that the tensile strength of the coating layer was increased by a factor of almost 2 at the highest AZC addition. Some benefits in resistance to fluids were conferred by the AZC addition. However, an improvement in resistance to water was only seen at the highest level of addition.

One factor not considered so far is the role of the poly(acrylate) dispersant in the adhesion of latex to mineral surfaces. Due to the requirement for colloidally-stable, high solids coatings, the mineral surface is covered by a layer of adsorbed poly(acrylic acid) [14], as is the latex [23]. The hydrophilicity of the surface is at least partly influenced by the nature of the counterions associated with the dispersant. The use of sodium-neutralised poly(acrylic acid) increases the affinity of the interface to water. An experiment was conducted to compare sodium-neutralised poly(acrylic acid) with an ammonium-neutralised version, commonly used in water-based paint formulations. The dispersants used, Dispex[®] N40 and A40, Ciba, Bradford, UK, were poly(acrylates) of similar molecular weight (4,000 – 5000 g mol⁻¹) differing only in the counterion present. They were both added at a dose 0.3 wt% on GCC. The results are summarised in Table 7.

Table 7. Effect of poly(acrylate) counterion on residual strength of coatings after saturation with different liquids

Coating	Counterion	Tensile strength MPa	% residual strength		
			Mineral oil	Linseed oil	Water
GCC + 8.5 pph SBN latex	Na ⁺	1.11 ± 0.17	27	11	<1
GCC + 11 pph SBN latex	Na ⁺	1.76 ± 0.12	19	10	4.3
GCC + 8.5 pph SBN latex	NH ₄ ⁺	1.62 ± 0.17	30	18	5.6
GCC + 11 pph SBN latex	NH ₄ ⁺	1.95 ± 0.05	27	21	8.7

These results confirm that the presence of sodium ions leads to an interface which is more readily weakened by water and oil. The observation that the sodium form in each case gives the weaker tensile strength is also evidence that the dispersant is more hydrated in the “dry” state – using Na⁺, the number of water molecules that can be co-ordinated increases with the degree of neutralisation, and after drying, this may lead to a relatively hydrated poly(acrylate) layer [28]. The NH₄⁺-neutralised form evolves ammonia on drying, leaving the protonated form of the poly(acrylate), which co-ordinates fewer water molecules.

The reversible nature of the weakening effect was also studied. After immersion in the relevant fluid, samples of coatings were allowed to dry under ambient conditions and the strength re-measured. With the oil-saturated samples, we also weighed the strips after 3 months in air to follow the loss of solvent by evaporation. Figure 7 shows the results. Strength loss is reversible when water and mineral oil are used, but with linseed oil the strength is permanently reduced. The reason is revealed by the mass change measurements. Linseed oil does not evaporate, but remains in the sample which shows a slight gain in mass after 3 months. This is because linseed oil dries chemically by atmospheric oxidation [29]. Hence printed papers are weakened permanently by

the presence of vegetable oils in the pores of the coating layer. The contribution of this weakened coating to handling problems such as scuffing and ink rub is not known.

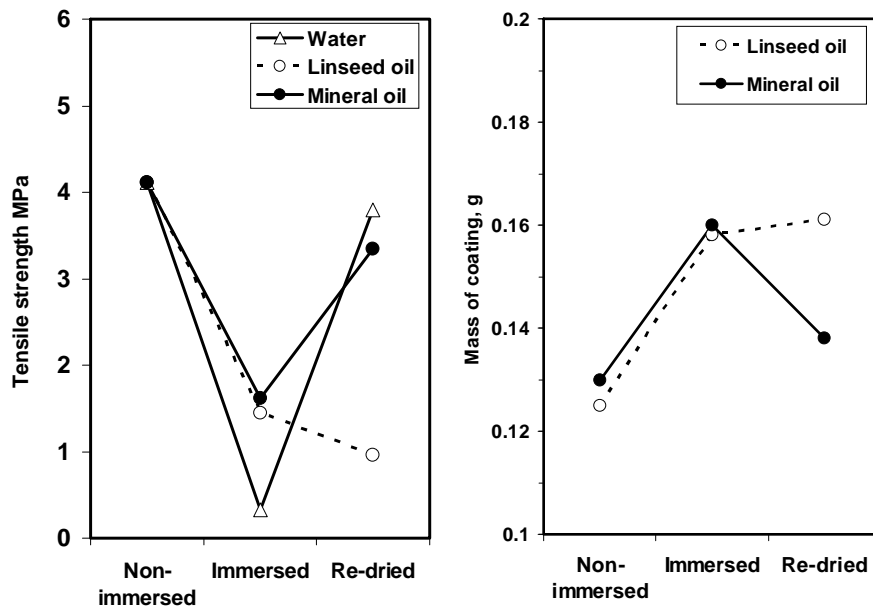


Figure 7. Left, reversibility of strength loss after immersion in water and oils followed by air drying. Right, mass of coatings before and after immersion in oils and air drying. Kaolin UFP, 8.5 pph latex SBN.

5. DISCUSSION

The strength behaviour of coating layers in the presence of moisture shows some similarities with epoxide-bonded joints. Both exhibit a loss of strength in the presence of water, which is reversible when the water is removed. Ink oils also cause weakening of the coating, which is permanent if vegetable oils are present in the ink. These remain in the coating pores and dry by oxidation. In this case the coating strength remains low, which means that printed papers have reduced surface strength. The effect of this on post-printing handling problems, such as scuff and ink rub, is not known.

Workers studying epoxide adhesives have discussed the mechanism involved in this strength loss in terms of ion-pair bonding, which is sensitive to the dielectric constant of the medium between the adhesive and the substrate.

Our results for kaolin and calcium carbonate coatings containing a latex adhesive are in qualitative agreement with this theory. When immersed in different fluids, the extent of tensile strength loss increased with the dielectric constant. However, the strength loss was about 50% greater than the theory predicted in all cases. A possible explanation lies in the assumption in equation (1) that the distance between charge centres is constant whatever the medium between them. Since water or oil molecules have finite sizes, this condition may not apply if water or oil molecules increase the separation between charges compared to that with free space only.

Coatings containing SBN latex were found to be sensitive to water vapour, in the same way as epoxide-bonded aluminium joints. Both systems exhibited a critical relative humidity above which the strength was significantly reduced. For the coarse kaolin coatings we found this critical RH was slightly higher than for the fine kaolin-based coatings. The significance of this critical RH has been discussed by Brewis et al. [25]. They suggested a mechanism involving salt hydration, where the salt-hydrate formed depends on the water vapour pressure. We suggest that capillary condensation is taking place above the critical RH. This results in a continuous film of water occupying the pore space of the coating which can then cause weakening. The pore size of the coating layer is likely to influence the critical RH at which the film becomes continuous, and coatings with large pores should require a higher critical RH to form a continuous liquid film. The calcium carbonate coatings have pores

which are an order of magnitude larger than the fine clay coatings (Table 4). Measurement of the weight of water absorbed by these coatings as a function of RH would help to resolve the mechanism.

It has been shown by Rousu [30] that different oils interact with latex films to different extents, and, therefore, the weakening effect may not just be related to the latex-mineral bond, but may also indicate lower cohesion within the latex film itself. Our experiments showed that latex films alone were not weakened substantially by water, even after 40 hours. This is evidence that water is attacking the interface between latex and mineral, as suggested by Pettersson and co-workers [3]. Ion-pair interactions between carboxylated latex and mineral surfaces may take place between acid groups and cations associated with calcite or kaolin surfaces, although preadsorbed dispersant may hinder or prevent this. Decreasing the polar nature of the binder by substituting an acrylic paint latex conferred greater resistance to weakening by fluids. Kan and Van Gilder [23] suggest that the rate of water penetration into the coating may be reduced with less polar latex. A significant improvement in tensile strength and some increase in water resistance using carboxylated latex were seen when ammonium zirconium carbonate was present. Zirconium-based cross-linkers are thought to confer water resistance by reacting with carboxyl groups and converting ionic to covalent bonds [27]. The carboxylated shell only exists on the outside of the latex particle, and the bulk of the polymer consists of styrene-butadiene, which is more likely to bind via van der Waals interactions. Unertl has provided evidence from AFM measurements that both dispersion and polar (acid-base) interactions contribute to the adhesion of carboxylated SB latex to clean calcite [13]. The flow properties of the polymer at temperatures above the T_g are likely to assist interlocking with the mineral surface, but will be easily displaced by a water film, which has a strong affinity for kaolin, for example. During drying, as the water film retreats, capillary forces will then renew the intimate contact of the rubbery latex with the surface, so strength is regained.

The effect of poly(acrylate) dispersant on the mineral – latex bond was also tested. The presence of Na^+ counterions was shown to enhance the sensitivity of the coating to water. This is explained in terms of the high co-ordination number of Na^+ ions [28]. Using NH_4^+ -neutralised poly(acrylate), which converts to the protonated form after drying, gave improved water resistance. This approach is used in the production of water-based paints [31].

A potential criticism of this study is that we have measured in-plane instead of z-direction tensile strength. In the printing nip, the coating experiences predominantly z-direction stresses which may lead to coating failure [6]. We found that it was not possible to measure z-direction strength in the presence of water and oils since our method relies on holding the coating between double-sided adhesive tape joints. In the case of isometric ground calcium carbonate coatings, we have shown that the in-plane and z-direction tensile properties are the same [32]. In the case of platy clay coatings, the strength is lower in the z-direction. The factor of importance with respect to latex adhesion is thought to be the extent of interaction with faces and edges of the particles, which have different chemistries. This may influence our results with kaolin.

CONCLUSIONS

The weakening effect of fluids such as ink oils and water on kaolin and calcium carbonate coatings containing latex adhesives has been studied. The in-plane tensile strength of both kaolin and calcium carbonate-based coatings was found to fall with increasing dielectric constant of the penetrating liquid. Previous work in the literature indicates that if the mechanism involved the weakening of ion-pair bonds, the residual strength after immersion in a liquid would be proportional to the reciprocal of the dielectric constant of that liquid. For kaolin and calcium carbonate coatings containing latex adhesives, we found that the residual tensile strength after immersion in different fluids was about 50% lower than predicted from this relationship. Hence a different or additional mechanism may be involved.

Compared to coatings, the tensile strength of pure latex films was much less affected by immersion in water. Coating layers retained less than 1% of the dry strength, whilst latex films retained as much as 76% of the dry strength. This result implies that it is the latex – mineral bond that is attacked by water, not the latex film itself.

The nature of the mineral – latex bond needs further study. Considering the chemical structures of latex and mineral particles, we suggest that more than one mechanism, physical or chemical, is likely to apply in these complex systems. Conversion of ionic to covalent bonds using zirconium was found to give much improved dry strength, and some improvement in resistance to fluids. Ionic bonds are formed by carboxyl groups, but van der

Waals interactions are more likely for the S-B polymer backbone. Both are weakened by fluids, and the above results together with previously published work using AFM suggest a combination of these mechanisms could explain the observed effects of liquids on coating strength. Less polar acrylic latices gave improved wet strength and this may be through a reduction in the rate of water penetration into the coating. Mechanical interlocking of the soft latex film with the mineral surface is also likely to contribute to adhesion.

A long term goal of this work is to stimulate the development of pigment – binder systems which are capable of resisting the weakening effect of liquids, and which are, therefore, more efficient in attaining the required strength. This will only be possible when we have a deeper understanding of binder-mineral adhesion on a molecular level, especially how it is affected by fluids.

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