

Modelling the Latex Spreading on Clay

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In this manuscript a model was proposed in order to predict the extent of the latex spreading on clay pigment. The results from Scan Electron Microscopy (SEM) and X-ray Photoelectron Spectroscopy (XPS) were used to evaluate the predicted results. A good agreement of the predicted results was found.

Keywords: Latex, clay, coalescence, XPS, SEM

Paper coatings generally consist of a pigment, a binder, and some additives. Their main objectives are to improve the optical and printing properties of paper. For many years, most of the research effort devoted to the subject of paper coating has been aimed at establishing relationships between the various coating process parameters (e.g. color composition and rheology, method of application, substrate properties, and finishing conditions) and the properties of the coated paper. While differences in the performance of coated papers have been attributed to structural differences, relatively little was known about the development or consolidation of coating structure and the binder-pigment interaction process. In order to avoid complications, researchers have made many attempts to understand only the latex film formation [1]. Few researchers concentrated on understanding the fundamental of pigment-latex interactions. Atomic Force Microscopy (AFM) was used to study the ordering and adhesion of latex particles on inorganic surfaces (calcium carbonate crystal, mica, and silica) [2]. When the drying or annealing temperature is below the latex T_g, the particles remain spherical and their adhesion to the substrate is weak. In contrast, when the sample is dried or annealed at a temperature above latex T_g, the particles are deformed but they can not form a continuous polymeric film. Increasing the latex acid content enhances the extent of particle spreading. They concluded the importance of the acid-base concepts in the particles spreading and adhesion.

The effect of binder-pigment interactions was investigated with AFM in paint coatings [3]. It was found that the interaction between latex and TiO₂ particles is different depending on the polymer nature content (homogenous, soft, hard or mixture). TiO₂ particles were totally covered with latex particles; in other cases the bare, uncoated TiO₂ surface was observed.

In our earlier work [4] the evolution of surface structure and chemistry and the surface energy of wet-coalesced clay-latex coatings were followed. It was found that latex spreading rather than "binder migration" was responsible for the high styrene-butadiene (SB) area percent at the final stage of consolidation at the surface. Even at PVC as low as 40%, XPS results indicate that the surface is still heterogeneous and not covered totally with latex.

Drying in the presence of water (wet coalescing) was compared to drying in the absence of water (sintering) for clay-latex coatings [5]. As found from XPS, sintered coatings showed a higher SB area percent on the surface than did latex with a high glass-transition temperature (T_g)

and dried at room temperature. This was a result of latex spreading at the surface.

In this work a model is proposed for predicting the extent of latex spreading on clay pigment. The results from SEM and XPS were used to evaluate the predicted results.

Experimental part

Materials and methods

The coatings were based on kaolin pigment (Premier ECC International) and SB latex binder (GENCORP Performance Chemicals Co.). Two carboxylated SB latices with low T_g (-3 °C) and high T_g (50 °C) were used. The T_g of the latex has been changed by altering the S:B weight percentage during emulsion polymerization. The higher the styrene content, the higher the carbon contents. Acrylic acid at the same level with both latices, was used as a monomeric acid. Very slight difference in C:O ratio between the two latex was reported. The C/O ratio of the low and the high T_g latex are 51.28/1 and 51.7/1, respectively. The surfactant used in these latices was sodium laurel sulfate. Both latices have a density of 1.02 g/cm³, and they were supplied as emulsions, also they had the same level of carboxylation and similar particle sizes. The level of (internal) polymer cross linking changed by altering the level of chain transfer agent during emulsion polymerization. As provided by the manufacturer, the physical properties of the two SB latices are given below (table 1).

The supplied particle size by the manufacturer was measured by Hydrodynamic Differential Fractionated (HDF). However, when SEM was used to examine the latex particle size, a smaller size was obtained. SB latex particle size was measured over a line of packed particles of high T_g latex after drying. SB particle size was obtained as 0.133 μm only.

In order to prepare the coating layer, the clay pigment was first dispersed in water at 75% solids by weight, using 0.03 parts sodium polyacrylate (Dipex N-40) per hundred parts of pigments (pph). The dispersant amount of 0.03 pph was used because at this level a minimum in the measured viscosity of the clay suspension was observed, which is an indication of best pigment dispersion. The pH of clay suspension was adjusted between 8-9 with NH₄OH.

Later, coatings at 80% Pigment Volume Concentration (PVC) was prepared by mixing the clay and latex under a good agitation. In order to achieve smooth and applicable coatings the coating colors were further diluted to 60% solids by weight.

The coating colors were applied with a lab coater (K303) on a non-absorbent polyester film (Mylar). The lab

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SB Type	Solid, %	pH	Cross Linking, %	T _g , °C	Particle Size (µm.)
020281009	49.5	6.0	93%	-3.0	0.2046 ±0.01
020281010	49.6	6.1	70%	50.0	0.2109 ±0.01

Table 1
SB LATEX PHYSICAL DATA

coater (K303) was manufactured by RK print-Coat Instruments Ltd. The coating was applied with a rod draw down at medium speed of 0.67 m/min. The Mylar substrate was cleaned previous to the coating application with ethanol and left to dry at room temperature. The resulting coat weight was of order of 40 g/m and the coating thickness of 30 µm.

To study the coatings before coalescing, a quenching and freeze-drying technique was used [6]. In that technique, the coating structure at the moment of application (FD-0) was first quenched with liquid nitrogen then freeze dried.

Scane Electron Microscopy (SEM)

SEM was used to assess the morphological characteristics of the coatings surfaces. SEM manufactured by Amrai Corp., model Amr-1000 was used in this study. In order to overcome the problem of "charging", the SEM samples were coated with gold to increase electrical conductivity. A sputter gold coater, model Hummer VI-A by Anatech LTD, was used for coating the samples. The thickness of the gold coating was approximately 20 nm. This gold coating procedure allowed us to eliminate the charging artifact, and to get very clear pictures working at low beam energy of only 5 kV. Working with this low beam energy eliminated any thermal damage of the sample.

X-ray Photoelectron Spectroscopy (XPS)

XPS was used to investigate the surface composition of the coatings. X-ray photoelectron spectroscopy was performed with Kratos, X-Sam 800 instrument. All the samples were examined with Mg-Kα (1253.6 eV) at 15 mA. The pressure in the analysis chamber during sample analysis was 1x10⁻⁸ mbar. In order not to damage the carbon signal incorporated with the latex, the carbon element was scanned first, followed by a general survey of the sample, and then the rest of the elements (O, Al, Si and Na). The area under each element peak was calculated and the surface composition in atomic percentage was then calculated using the elements relative cross sectional area as supplied by the XPS manufacturer.

XPS study of the clay and latex, was conducted at the beginning of this study. Results are shown in table 2 and 3. The sulfur may originate from the initiator and from the surfactant. The ratio C/(Al+Si) for Premier clay used in this study is 0.25. This is similar to what was found in the literature for US clay [7].

A typical XPS general survey spectrum of a 40% PVC coating dried at room temperature is shown in figure 1. All elements except hydrogen can be detected with XPS. The Al, Si and part of the O and C signals come from the clay. The main part of the C signal originates from the SB latex and the rest is from the clay. The amount of carbon originating from each one was calculated with the help of the pure clay analysis (table 3).

Finally, the coating surface composition as area % was calculated as follow:

$$Clay\ Area\ \% = \frac{atom\%(Al + Si)_{Coating}}{atom\%(Al + Si)_{Pure\ clay}} \times 100 \quad (1)$$

	Low Tg SB Latex	High Tg SB Latex
C	78.0	85.3
O	15.0	10.6
Na	6.0	4.1
S	1.0	0.6

Table 2
XPS ELEMENTAL SURFACE COMPOSITION IN ATOM % OF SB LATICES

	Premier Clay
C	7.7
O	61.0
Si	15.9
Al	14.7
Na	0.7

Table 3
XPS SURFACE ELEMENTAL COMPOSITION IN ATOM % OF PREMIER CLAY

$$SB\ Area\ \% = 100 - Clay\ Area\ \% \quad (2)$$

XPS was used to investigate the coating surface composition of the 80% PVC coating before and after latex coalescence at room temperature (RT). The change in SB and clay content were expressed as area % based on measurements on pure clay as described earlier. The results are shown in table 4.

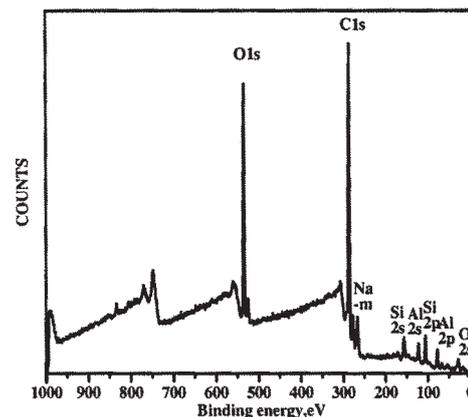


Fig.1 A typical XPS survey at 40% PVC, dried at room temperature

The Model

The model considers latex particles placed at the surface of a clay disc at the beginning of the consolidation process. As the consolidation process continues and the latex particles agglomerate, fuse and spread over the clay

Consolidation stages	SB area%
FD-0	15.78
RT	25.76

Table 4
XPS SB AREA% VARIATION BEFORE AND AFTER COALESCENCE OF 80%PVC COATING

disc, the SB form a continuous film on top of the clay disc causing an increase or decrease in the SB area %.

In the calculations, we used spherical SB latex particles of 0.13 µm diameter as measured from SEM. The clay pigment was considered as a disc of 2 µm diameter and with thickness of 0.2µm. This gives a 10/1 ratio, typical of delaminated clay. Figure 2 illustrates the model statement of the SB latex before and after spreading.

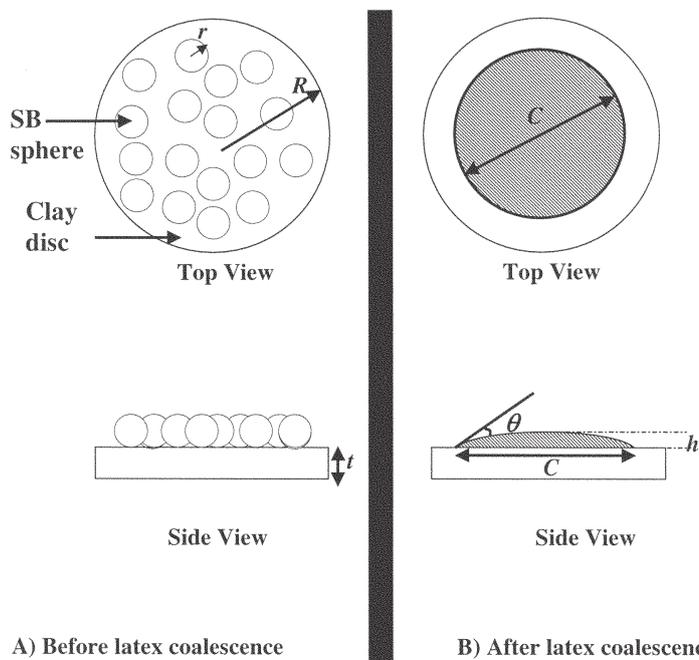


Fig. 2 Schematic diagram of the model statement.

Results and discussions

Before Latex Coalescence

The SB area % at the moment of application was calculated theoretically and compared to values obtained on SEM micrographs and XPS measurements. The theoretical SB area % before latex coalescence was calculated from the known volume ratio of clay and latex in the coatings, assuming that they are equivalent.

In addition, before the latex coalescence, the number of SB particles (n) is found from the known ratio of SB to the clay total volume and from the calculated ratio of a single SB particle to a single clay disc volume. The SB volume for a single SB (V) is expressed as a sphere volume Eq. (3) and the clay expressed as disc volume eq. (4)

$$V_{\text{Latex}} = \frac{4}{3} \cdot \pi \cdot r^3$$

$$V_{\text{clay}} = \pi \cdot R^2 \cdot t$$

Where r is the latex particle radius, R is the clay disc radius and t is the clay disc thickness. Theoretically, at 80% PVC the SB area % was calculated as 20%. The SB spheres were found as 134 surrounding one disc of clay, this means that only 67 spheres per one clay disc at the surface exist.

Latex Area from SEM

The latex area % before latex coalescence from SEM was calculated by assuming that the coating surface consists of SB particles in top of the clay particles. In order to find the SB area %, first the number of SB particles (n) in each micrograph was counted. SB area was then calculated as number of spheres multiplied by the area of one SB particle with radius r . Finally the SB area was calculated as the ratio between the SB area to the total area of the micrograph, as follows:

$$SB \text{ area} \% = \frac{n \cdot (\pi \cdot r^2)}{\text{Picture Area}} \times 100 \quad (5)$$

For four micrographs from two samples and at two different locations of 80% PVC coatings, the number of SB

latex particles was counted and the SB area % was calculated. The average number of SB latex particles was found as 83 particles per micrograph. Knowing the SB particle radius (r), the picture area and the SB particles number per micrograph, the SB area % was calculated from eq. (5). The average SB area % from SEM micrographs was found as 19.7% with a standard deviation of 5%. This SB area % at 80% PVC obtained from SEM is in agreement with SB area % of 20% obtained theoretically from the volume ratio, but higher than that obtained from XPS.

Latex Area from XPS

As shown earlier in the Experimental part, XPS area % at the beginning of consolidation from the freeze-dried samples (FD-0) at 80% PVC was 15.76%. This value falls within the standard deviation of the SEM value measured, but lower than the theoretical value.

The low SB area % at the surface as measured from the XPS means that a lower amount of SB on the surface at the beginning of consolidation have been detected by the XPS. Another possibility of the reason of low SB area % from XPS may be due to the effect of the surface voids on the XPS measurement. The presence of the voids on the coating surface affects the XPS analysis, since some of the signals from the coatings under the voids may count as if it is originating from the surface.

After Latex Coalescence

After latex coalescence occurs, the SB particles lose their identity and disappear, which make SEM pictures not helpful in predicting the SB area %. The extent of latex spreading on the clay pigment can however predict from the model, and compared to that found from the XPS measurement as shown below.

In order to predict the SB area % after coalescence, the assumption that the SB volume before ($n \cdot V$) equals the SB volume after (VV) latex coalescence was made eq. (4).

$$n \cdot V = VV \quad (6)$$

The left hand side of eq. (2), which represents the number of the SB particles and the volume of one SB sphere before coalescence, can be obtained from the calculated n and V as explained earlier.

However, after latex coalescence the volume of the SB lens is considered as the volume of a spherical lens, as shown in figure 2 (B).

$$VV = \pi \cdot h \cdot \left(\frac{C^2}{8} + \frac{h^2}{6} \right) \quad (7)$$

Here h is the height and C is the width of the SB latex lens after coalescence. The C value is required to calculate the SB area after latex coalescence and spreading. The C value can be calculated as function of the SB contact angle with clay pigment surface (θ). An additional equation used earlier for calculating the contact angle is then introduced to write h as a function of C and θ ,

$$h = \frac{C}{2} \cdot \tan \frac{\theta}{2} \quad (8)$$

Substituting eq. (7) and eq. (8) into eq. (6) results in a general equation to solve C (θ),
Namely,

$$C(\theta) = \left[\frac{\frac{n \cdot V}{\pi}}{\frac{\tan \frac{\theta}{2}}{16} + \frac{\left(\tan \frac{\theta}{2} \right)^3}{48}} \right]^{1/3} \quad (9)$$

In equation 9, n and V can be calculated as explained earlier, and the only unknown to solve C is the contact angle θ . Finally SB area % after spreading can be obtained by dividing the SB area to that of one disc of clay using the C value obtained and the radius of the clay disc (R) as

$$SB\ area\ \% = \frac{\pi \cdot \left(\frac{C}{2} \right)^2}{\pi \cdot R^2} \times 100 \quad (10)$$

We do not have a value for the contact angle of this latex on clay. In the literature, the contact angle of $31^\circ \pm 3$ for the spreading of SB latex on calcite surface was reported, using a scanning force microscopy (SFM) [8]. This value was used in our calculations.

To check the validity of this model and the contact angle selected the SB area % after latex coalescence at 80% PVC was calculated and compared to that found from XPS measurement. From XPS the SB area % increased from 15.78% before latex coalescence, to 25.76% after latex coalescence at 80% PVC. The number of particles calculated on the basis of the XPS results before latex coalescence is 49 particles. This would give a value of 1.02 μm for C, that is, 26% SB area %. This value is in good agreement with the SB area % obtained with XPS after coalescence. This indicates that the value of the contact angle of SB over clay may be close to 31° .

In addition, eq. 9 can be used to calculate the contact angle for any coating system directly from the XPS measurements. This is a useful approach to calculate the contact angle directly from the XPS measurements.

Conclusions

A simple model of latex particles on top of clay disc predicts well the extent of latex spreading over clay. The model input was SB sphere size, clay disc size and the contact angle of SB film over the pigment surface after latex coalescence. The model output is the width of the SB and the SB area % after spreading. Compared to the XPS results, a good agreement of the predicted results was found at 80% PVC, assuming a contact angle of 31° .

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References

1. KILL,S., Prog. Org. Coat. **57**, 2006, p. 236
2. GRANIER, V., SARTRE, A., Langmuir, **11**, 1995, p.2179
3. BUTT, H., KUROPKA, R., J. Coat. Techn., **67**, 1995, p.101
4. AL-TURAIIF, H., LEPOUTRE, P., Prog. Org.Coat. **38**, 2000, p. 43
5. AL-TURAIIF, H., LEPOUTRE, P., J. Appl. Polym. Sci. **82**, 2001,p. 968
6. STANISLAWSKA, A., LEPOUTRE,P. Tappi J., **79**(5), 1996, p.117
7. STROM, G. AND CARLSSON, G., NORDIC, Pulp Paper Res., **8**, 1993, p.105
8. UNERTL, W.N., Langmuir, **14**,1998, p. 2201

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