Gloss and surface structure through a paint PVC ladder

N J Elton, Surfoptic Ltd
A Legrix, Imerys Minerals Ltd

Summary

This note illustrates the use of the Imaging Reflectometer for studies of paint by examining how the gloss and surface structure change as a function of pigment volume concentration (PVC). The range of PVC covers gloss to matt formulations. Of particular interest is the evolution of surface roughness and its effect on gloss. Gloss reaches a maximum at the critical PVC (CPVC) which is the formulation having the minimum binder concentration necessary to give a coating without air voids. The gloss behaviour is explained by changes in surface microroughness and refractive index and the analysis gives useful insights into how the surface structure changes around the CPVC. The gloss of the model paint formulation at all PVCs is lower than expected, and this behaviour is shown to be due to discrete surface defects.

Introduction

In terms of visual appearance, gloss is one of the key features of paints. The subject is discussed in some detail in the literature. Comprehensive reviews are given by Zorll (1972), who gives considerable detail on measurement techniques and also discussed the variation of gloss with pigment volume concentration (PVC); Simpson (1978) who discusses (amongst other things) the role of refractive index and presents data on optical microroughness; and Braun (1991) who extends the discussion of the influence of pigment particles on paint gloss.

Goniometric gloss measurements of paint are discussed by Colling et al (1968), Guillaume (1969) and Zorll (1972). More recently, Gate and Preston (1995) used gloss goniophotometry (which is closely related to the polarised light reflectometry method) to determine the refractive index and angular scattering of emulsion paints formulated below the critical pigment volume concentration (CPVC).

In this note, polarised light reflectometry is used to study a range of model paints at different pigment volume concentrations. Roughness and refractive index measurements obtained by this technique relate directly to gloss properties. It is shown how the measured data can explain gloss variations, and how discrepancies between observed and model gloss can be used to obtain further information about the surface structure.

Experimental

Paint samples were prepared by Imerys Minerals Ltd as a model laboratory formulation based on titanium dioxide and fine calcined kaolin pigments in a vinyl acetate ethylene binder, but with no coarse mineral extenders. Details of the formulation are given in the Appendix. The kaolin-binder ratio was varied to create paints covering the range of pigment volume concentrations (PVC) 20% – 55% at 5% intervals. The paints were applied to a smooth polyester film substrate using an Erichsen drawdown bar on a Coatmaster 509MC bench coater at 25mm/s to give coatings at a nominal wet thickness of 100 µm.

Standard paint laboratory measurements included: gloss (ISO 2813 standard: 60° incidence at 4.4° acceptance; 85° incidence at 4° acceptance; referred to a black glass standard $n_{589.3}$ = 1.567), stain resistance, dry hiding, also Kubelka-Munk scattering and absorption coefficients (S and K).

Reflectometer measurements were made using a standard Surfoptic SIRS75 Imaging Reflectometer with manual sample changer. The usual reflectometer parameters were measured, namely refractive index, gloss (3° and 20° acceptance angles), microroughness (roughness at a scale smaller than the wavelength of light), macroroughness (roughness on a scale much larger than the wavelength of light, measured as the distribution of surface slopes). Ten measurements were made at random points over the paint surface using the large measurement spot. Each measurement covers an elliptical area on the sample with major axes approximately 12 x 3 mm.

Basic Results

Figure 1 shows some of the main standard paint measurement results, made on the dry films. The CPVC occurs around 40% as indicated by the abrupt decrease in stain resistance and increase in scattering at higher PVCs owing to the incorporation of air voids into the film. Film gloss reaches a minimum around 35 – 50% PVC depending on the angle of incidence. The gloss data are interesting because the 85° gloss reaches a minimum at 50% PVC, but then shows a very significant increase as the PVC increases further. Gloss data at 60° show a barely significant increase above 50% PVC. One of the objectives of reflectometer measurements was to explain these observations in terms of surface structure.

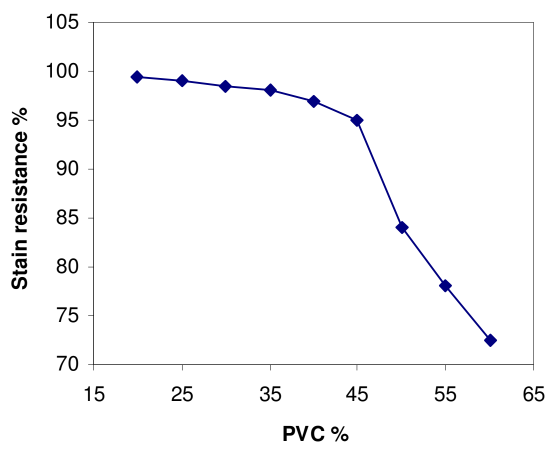


Figure 1a Stain resistance vs. PVC

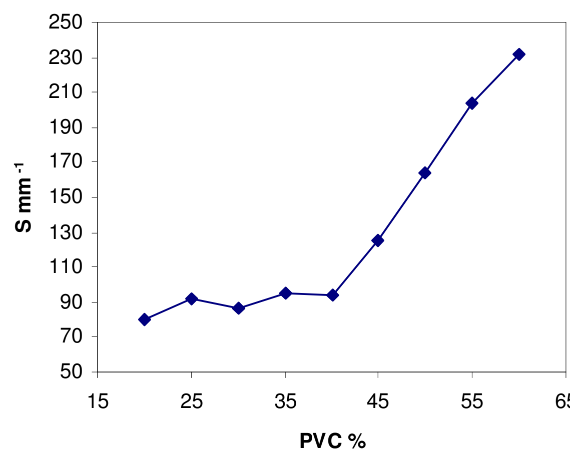


Figure 1b Kubelka-Munk scattering coefficient S vs PVC

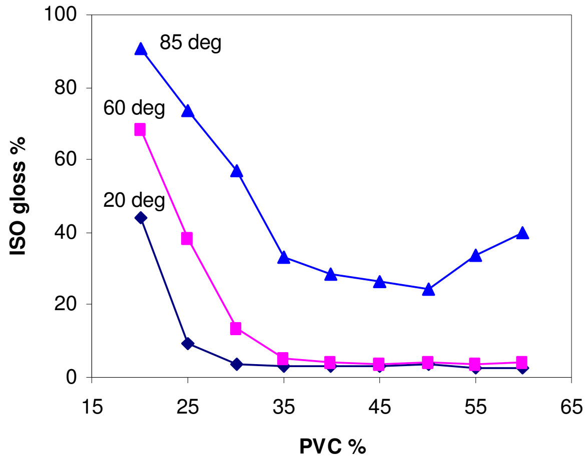
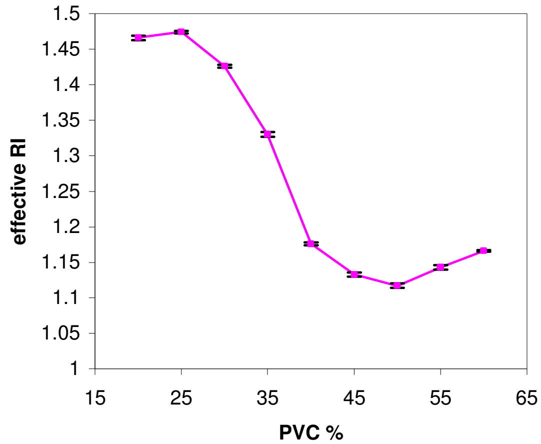


Figure 1c ISO gloss at three angles of incidence (after 7 days) vs PVC

Figures 2a-d show the basic reflectometer results as a function of PVC for the main measurement parameters. Macroroughness (as determined automatically) was effectively zero (instrument limited) across the sample range owing to the smooth substrate. The reflectometer gloss (measured at 75° incidence) shows a significant increase above 50% PVC for both 3° and 20° acceptance angles. These trends agree with the 85° incidence ISO glosses. Error bars represent 99% confidence limits on the ten repeat measurements.

For these paint formulations, refractive index is expected to be a measure of air void fraction at the surface. Titanium dioxide has a very high refractive index, but varies little in concentration through the formulation. Kaolinite has a similar refractive index to the binder, so changes in relative concentrations are not expected to produce significant changes in the refractive index of the mixture. The shape of the refractive index curve is similar to that for gloss, i.e. there is a large decrease up to 50% PVC, followed by a significant rise at higher PVC values. Microroughness shows the inverse behaviour, rising to 45-50% PVC, then falling. These observations show that as the ratio of pigment to binder increases, so the surface becomes rougher (at a sub-wavelength scale), and also "contains" more air. As discussed below, these effects are not independent, but do correlate well with the observed changes in gloss.



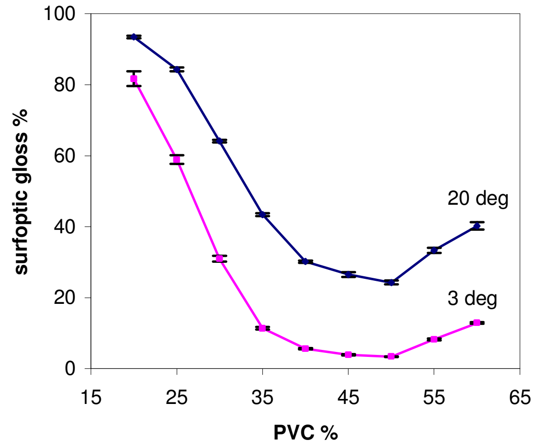


Figure 2a Refractive index vs PVC. Error bars are 99% confidence limits in all Fig 2 plots.

Figure 2b Gloss (20° and 3° acceptance angles) vs PVC.

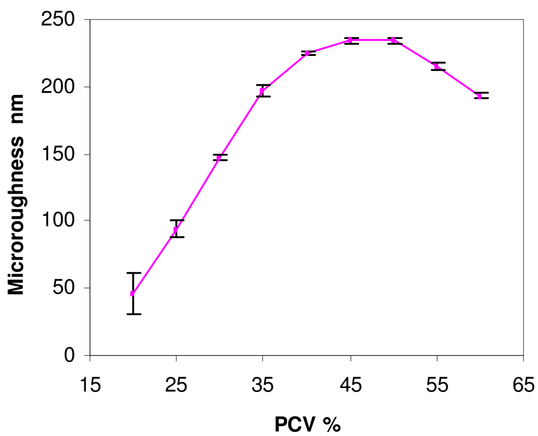


Figure 2c Microroughness vs. PVC

Surface structure through the PVC ladder

In these paint films, as PVC increases, the presence of pigment particles causes the surface to be increasingly distorted (Braun 1991), as illustrated schematically in figure 3. Above the CPVC, air begins to be incorporated into the paint film, and the surface generally becomes both rough and porous, although the porosity may not be connected until the PVC is very high.

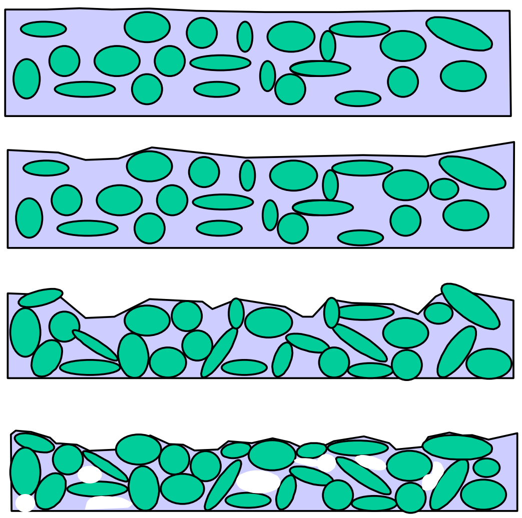


Figure 3 Illustrating development of microroughness of a pigmented film as PVC increases.

Well below the CPVC, pigment is dispersed with in the film and surface tension ensures that the surface is quite smooth.

As the PVC increases, particles become closer packed and start to distort the surface creating microroughness. Length scale of the microroughness features is typically sub-micron.

At the CPVC particles are close packed, but there are no air voids.

Above the CPVC, air is incorporated in the coating layer.

It is well known from ellipsometric studies that refractive index depends on surface microroughness (e.g. Azzam & Bashara 1989). In ellipsometry, a microrough surface is often modelled as a smooth “effective medium” composed of air and substrate, and the measured refractive index (the “effective” refractive index) is representative of this mixture of air and solid substrate (figure 4). Therefore, some correlation may be expected between the measured refractive index and microroughness and is shown in figure 5.

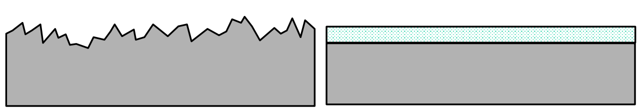


Figure 4 For refractive index determination, a microrough surface can be modelled as an “effective medium” - a smooth layer with effective refractive index intermediate between that of the solid material and air.

The refractive index is very similar for the two lowest PVC formulations, but then falls steadily with increasing microroughness reaching an inflection point at 50% PVC which is close to the CPVC. Either side of the inflection point, refractive index rises as microroughness falls, but the rate of change is significantly slower above the CPVC (figure 5) – i.e. the change in refractive index above the CPVC appears less dependent on the microroughness amplitude. This behaviour can be explained by considering that the void fraction of the effective medium depends not only on the roughness amplitude, but also on the spatial distribution of solid material.

At the CPVC and above, the surface structure becomes relatively complex as surface porosity develops. The binder causes pigment particles to be cemented together at contact points: voids form between the particles, but generally, they are no longer embedded in binder.

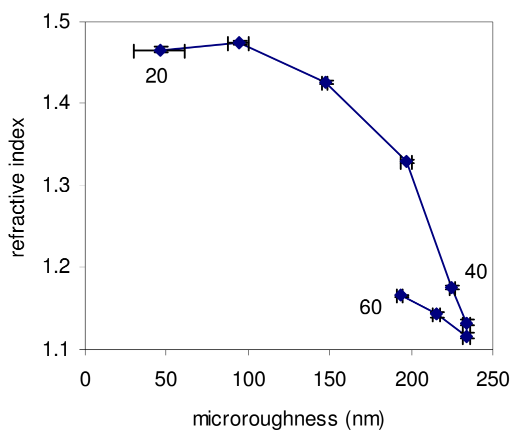


Figure 5 Correlation between refractive index and microroughness through the PVC ladder. (Numbers on graph indicate direction of PVC change.)

This change in surface structure is marked by the change in stain resistance and other parameters (Figure 1), but it is interesting to note that the transition point occurs at different PVC levels for the different measurements: 45 - 50% PVC for stain resistance; ~45% PVC for scattering coefficient and 35 - 50% PVC for gloss depending on what is taken as the transition. Although gloss does not reach a minimum until 50% PVC, most of the decrease has already occurred at 35% suggesting that incorporation of air into the paint film structure begins at the surface rather than in the bulk. Differences between physical methods for determining the CPVC have been discussed elsewhere (e.g. Bierwagen et al 1999; Schaake 1988 and references therein), and in practice, the CPVC may not be a well defined point, but rather a range (Bierwagen et al 1999).

The question of structure around the CPVC is discussed further below.

Gloss

It is possible to calculate gloss from refractive index and roughness (Elton 2008). It is useful to compare calculated and measured gloss because the degree of agreement can provide useful clues about the surface structure. For these paints, standard reflectometer measurements indicate that the surface is macro-smooth, so it is expected that gloss should be accounted for by just refractive index and microroughness. The model does not take into account directional-diffuse scatter from the microroughness, and therefore should underestimate gloss at lower angles of incidence (e.g. < 75°) or wide acceptance angles (> 5°) where the diffuse-directional scatter is relatively more significant. Figure 6 shows measured and predicted gloss as a function of PVC. The agreement at 75° and 85° incidence is very poor, with the measured gloss being much lower than that predicted. This observation suggests that some other mechanism of gloss-loss exists at all PVC levels. The shape of the model gloss curves, however, does follow the data quite well, suggesting that the rise in refractive index and drop in microroughness above the PVC are responsible (in part at least) for the observed change in gloss. At 60° incidence, the observed gloss is higher than the predicted. This behaviour is expected, because at 60° incidence, diffuse scatter (from multiple-scattering within the paint film) and directional-diffuse scatter from the surface microroughness contribute more significantly to the gloss, but are ignored in the model (Elton 2008).

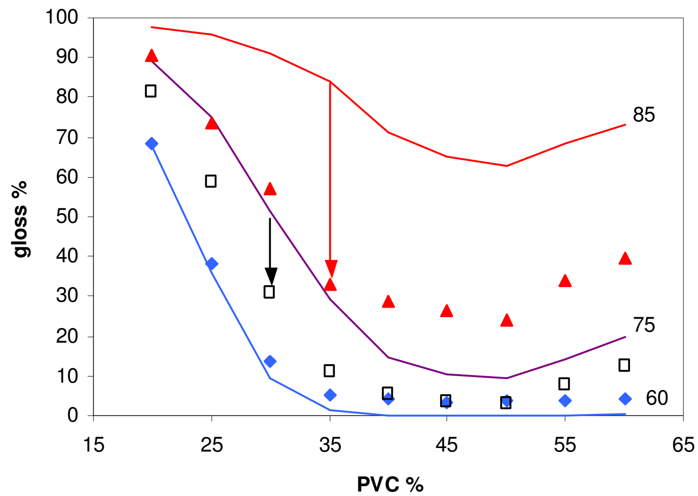


Figure 6 Predicted (solid lines) and measured (points) gloss versus PVC.

More detailed examination of the forward scattering pattern measured by the reflectometer shows significant scatter which varies with PVC as illustrated in figure 7. Reflection from a macrosmooth surface produces a narrow and bright specular spike. In routine measurement the reflectometer adjusts exposure of the scattering pattern according to the intensity of the brightest parts of the image. The sensor has limited dynamic range, but by deliberately overexposing, detail can be obtained for the less-intense wide-angle scatter over an angular range up to approximately ± 10° about the specular angle. The gloss model for a macrosmooth surface assumes all light is reflected specularly. For these paints, this is clearly not the case, and some light is being scattered at wider angles. The distributions of directional-diffuse scatter due to the microroughness do not account for this scattering as they are expected to be much broader. The additional scattering is greatest around the CPVC.

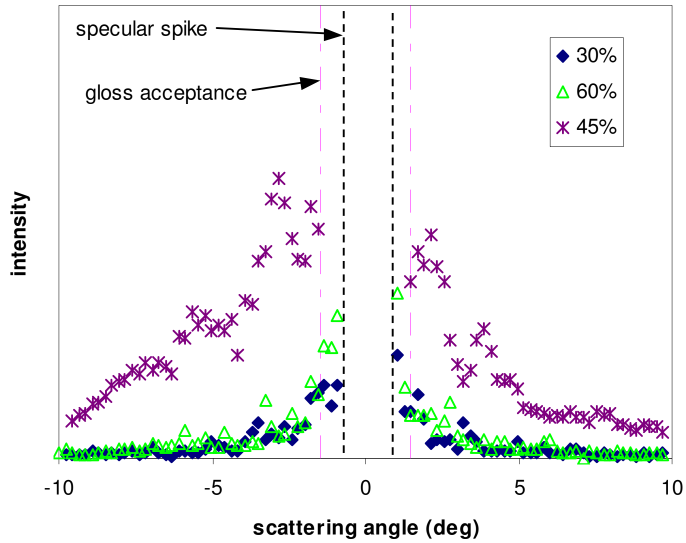


Figure 7 Angular scattering (in plane of incidence) for 35%, 45% and 60% PVC. Scattering patterns are overexposed to show less-intense details at wider angles. Specular data are excluded from the plot.

It is postulated that the surface contains discrete regions of characteristic roughness rather larger than the wavelength of light giving rise to additional scattering (governed by geometrical optics). The profile of such a surface is illustrated schematically in figure 8 and the scattering can be described by a mixture of two surface types: Total reflectance = f * (reflectance from macro-smooth regions) + (1-f) * (reflectance from macro-rough) regions, where f is the area-fraction of macro-smooth regions. This type of surface has been discussed by Colling et al (1968) and appears quite common in paint systems.

Figure 8 Illustrating a microrough surface with occasional discrete regions of macroroughness. Length scale is tens of microns.

Applying this idea to the gloss model by choosing values of f arbitrarily to obtain good agreement for the 75° data, also makes the 85° model a better fit to the data. Shadowing may be significant at 85° and would tend to lower the gloss relative to the other angles of incidence, but has not been considered.

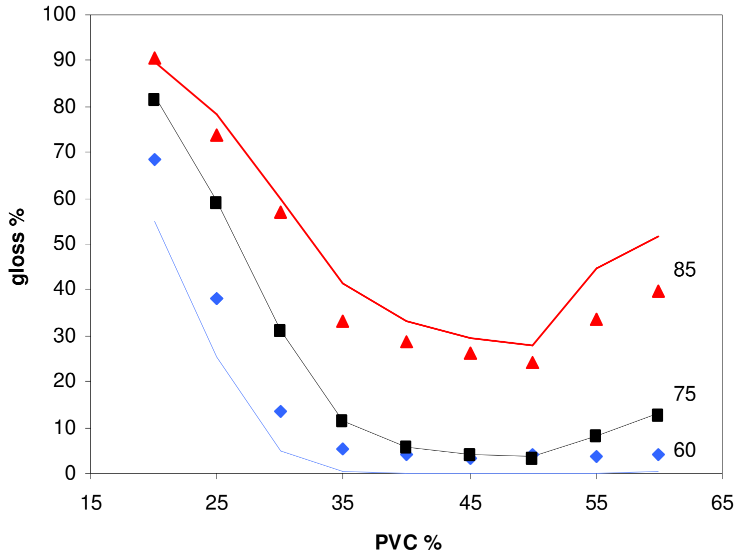


Figure 9 Predicted (solid lines) and measured (points) gloss versus PVC after correction for the presence of some macro-rough regions in the film surface. The scaling factor was chosen to give correct results at 75° incidence. At 85°, shadowing is expected to reduce observed gloss relative to the model. At 60° incidence, diffuse and directional-diffuse scatter are relatively more important and explain qualitatively why the observed gloss is higher than the model predicts.

Figure 10 shows an electron micrograph of the surface of the 55% PVC paint. The surface does contain discrete 'bumps' as inferred from the reflectometry data. The size of the features is such that they can appropriately be described by a facet model for light scattering. As shown above, such features are very deleterious for high angle gloss.

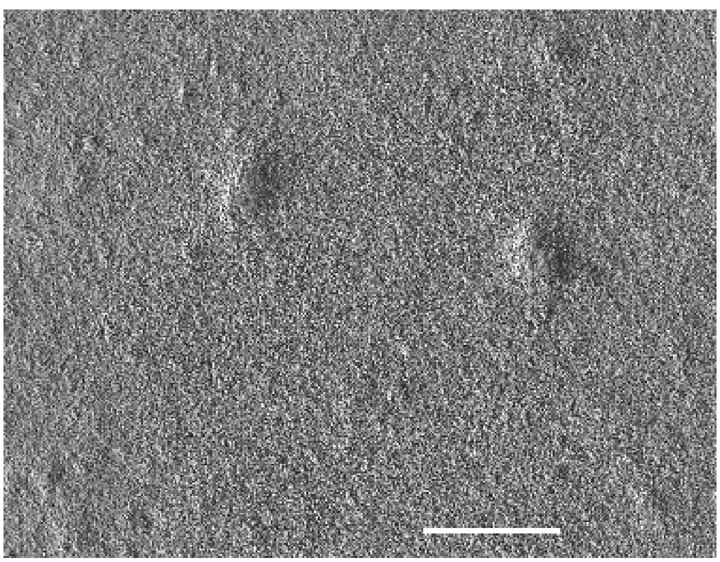


Figure 10 Electron micrograph of 55% PVC paint surface showing presence of discrete bumps (cf profile in figure 8). Such features are very deleterious for gloss.

Scale bar is 100 µm.

Surface structure around and above the CPVC

An interesting feature of the gloss data at high angles of incidence is the significant increase above the CPVC. At first this observation seems counterintuitive because roughness might be expected to continue increasing or reach a plateau beyond the CPVC as the binder recedes from the surface particles. However, this gloss rise above the CPVC is well known and has been discussed previously by Colling et al (1968) and Guillaume (1969) who suggested using the inflection point as a method of determining the CPVC. Previous authors did not reach definite conclusions on the mechanism for gloss increase. Guillaume noted that optical microscopy indicated that the surface above the CPVC was 'finer' in appearance. Colling et al, suggested, by reference to Mie theory, that the size and spacing of scattering centres in the surface become progressively smaller above the CPVC, thus leading to a decrease in scattering efficiency and increase in specular gloss.

As shown by figures 2a and c, refractive index increases above the CPVC while microroughness falls. The discrete macroroughness seems to peak at the CPVC as illustrated by the data in figure 7. Together these changes largely account for the trend in gloss (Figure 6) and demonstrate that the surface above the CPVC has lower microroughness roughness amplitude than at the CPVC, and also has lower surface void fraction (from the point of view of the scattered light).

Figure 11 shows high magnification electron micrographs of the paint surface close to the CPVC and above the CPVC. Binder is clearly visible at the surface at the CPVC, and qualitatively the surface appears rougher than that above the CPVC which fits with the gloss, refractive index and microroughness data. The surface above the CPVC also appears to have more, or better dispersed, titanium dioxide (but this may simply be that the particles are more 'visible' with no excess binder present). The differences in the appearance of the surface for paint formulated at the CPVC and above are consistent with the conclusions from reflectometry. Measurements of rms roughness on three paints around the CPVC (Figure 12) by atomic force microscopy (AFM) indicate that the surface above the CPVC is physically smoother than that at the CPVC.

The changes in roughness and refractive index above the CPVC are related to particle packing behaviour upon drying. It is suggested that at the CPVC, particles are partially embedded in binder, and that this state is one of maximum particle disorder at the surface. At higher PVC levels, the binder cements particles together at contact points, and film-formation during the drying process may exert additional forces between particles that lead to re-orientation (of platey particles) relative to the surface plane and a small, but general, compaction of the surface. It is also possible that above the CPVC, in later stages of drying, some migration of fines or binder takes place towards the surface. Such a process may contribute to a reduction in microroughness and increase in refractive index. However, measurements on drying paint films (See Applications Note AN9 – Elton and Legrix 2008), suggests that the structural differences are already present from the earliest stages of consolidation.

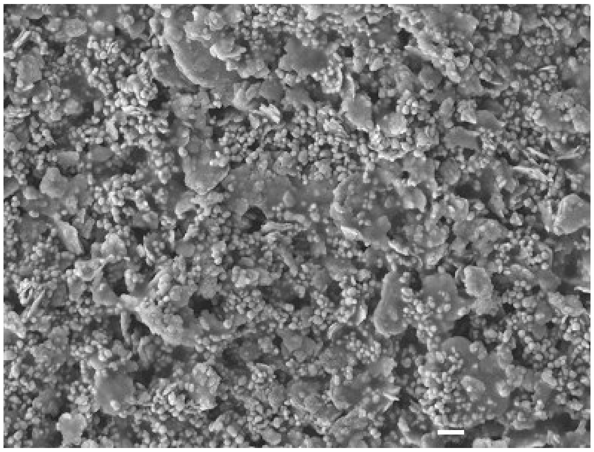


Figure 11a Electron micrograph of paint near the CPVC. Scale bar is 1 µm.

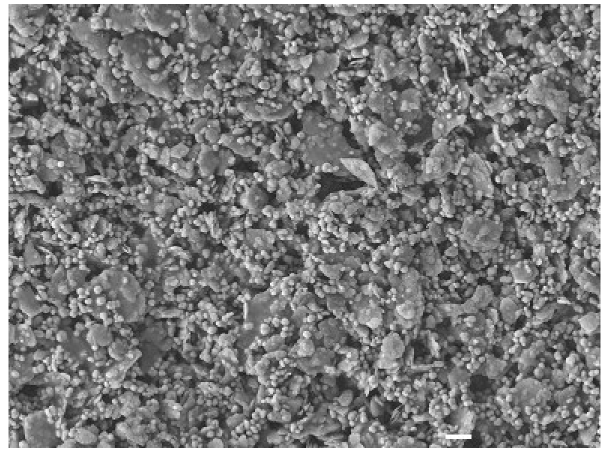


Figure 11b Electron micrograph of paint above the CPVC. Scale bar is 1 µm.

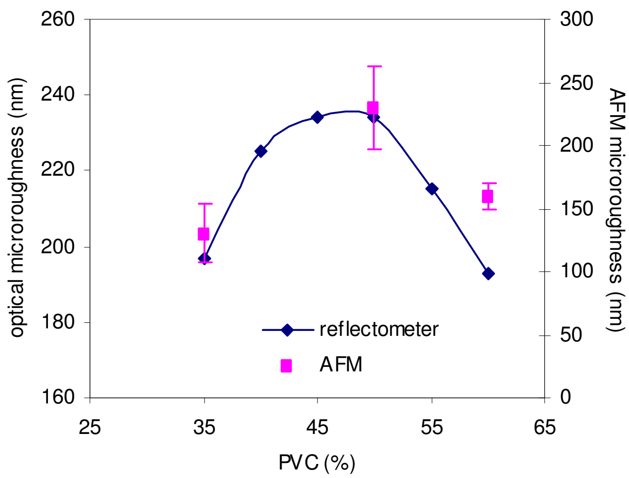


Figure 12 AFM measurements of rms roughness for paints around the CPVC. The AFM data show a decrease in roughness above the CPVC.

Conclusions

Direct measurements of effective refractive index and microroughness by reflectometry are helpful in understanding the gloss properties of paint over a range of pigment volume concentrations. More detailed analysis such as gloss modelling and examining the angular distribution of scattered light can reveal further useful information about the surface structure. The data show that the gloss is controlled by surface roughness and refractive index, and minimum gloss at the CPVC corresponds to a state of greatest roughness and lowest refractive index. An overall reduction in gloss for all formulations is explained by the presence of discrete regions of macroroughness. The conclusions are supported by SEM imaging.

Acknowledgements

The authors wish to thank Michèle Julian for preparation of the paint samples, Gary Sleeman for the electron microscopy and Dr Roger Wygant for the AFM data.

References

Al-Turaif H and Lepoutre P 2000 Evolution of surface structure and chemistry of pigmented coatings during drying. *Prog. Org. Coat.* **38** 43–52

Elton N J and Legrix A 2008 Reflectometry of Drying Paint. Surfoptic Applications Note no.9 (AN9)

Azzam, R M A & Bashara, N M 1989 *Ellipsometry and Polarized Light* (North Holland, New York).

Bennett, H E 1963 Specular reflectance of aluminized ground glass and the height distribution of surface irregularities. *J. Opt. Soc. Am.* **53**, 1389-1394.

Bierwagen G, Fishman R, Storsved T, Johnson J (1999) Recent studies of particle packing in organic coatings. *Prog. Org. Coat.* **35** 1–9.

Braun J H 1991 Gloss of paint films and the mechanism of pigment involvement. *J. Coat. Tech.* **63**, 43-51.

Colling J H, Craker, W E and Dunderdale J 1968 An investigation into the relationship between the nature of surface defects and gloss. *J. Oil Chem. Assoc.* **51**, 524-546.

Gate L F and Preston J S 1995 The specular reflection and surface-structure of emulsion paint films. *JOCCA-Surface Coatings International* **78** (8) 321-330.

Guillaume, G 1969 CPVC determination with a goniophotometer. *Paint. Technol.* **33** (1), 16-21.

Schaake R C F, v de Heijkant J A M and Huisman HF (1988) CPVC relationships iii. The real CPVC and its relationship to young's modulus, magnetic moment, abrasive wear and gloss. *Prog. Org. Coat.*, **16** (1988) 265 - 276 265

Simpson L A 1978 Factors controlling gloss of paint films. *Prog. Org. Coat.* **6**, 1-30.

Appendix – simplified paint formulations

	PVC								
Ingredient	20%	25%	30%	35%	40%	45%	50%	55%	60%
TiO_2 pigment	22.80	22.35	21.92	21.50	21.03	21.03	21.03	21.03	21.03
Kaolin pigment	0.00	3.54	6.95	10.23	13.34	13.34	13.34	13.34	13.34
Dispersants	0.82	0.89	0.96	1.03	1.10	1.10	1.10	1.10	1.10
Water	21.46	22.41	23.31	24.18	25.24	25.24	25.24	25.24	25.24
Vinyl Acetate Ethylene binder	54.92	50.81	46.86	43.06	39.29	39.29	39.29	39.29	39.29
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00