EFFECTIVE REFRACTIVE INDEX AND THE POROSITY OF COATED PAPER

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This note is based on: Elton, N.J. & Preston, J.S. Polarised light reflectometry for studies of paper coating structure II: Application to coating structure, gloss and porosity. Tappi Journal, August 2006, 10-16. (2006)

1. INTRODUCTION

As described in Surfoptic Technical Paper no. 2 (TP2), the ***effective refractive index*** of a surface composed of several components is linear combination of the individual refractive indices of each component (e.g. Meeten, 1986 & Fig 1):

$$n_{eff} = \sum_{1}^{m} v_i n_i \qquad (1)$$

Where n_i is the refractive index of the ith component and v_i its volume fraction.

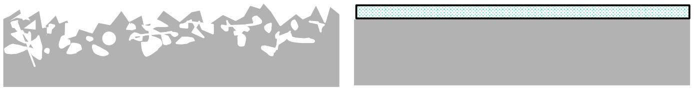


Figure 1 illustrating the idea of an effective medium. The microrough-porous surface on the left can be modelled as a smooth surface with an effective refractive index being some mixture of air and specimen material.

The effective refractive index depends on the relative proportions of the components and also how they are structured physically. An open, porous, microrough coating, will have a lower refractive index than one of identical composition which is more closed and less porous – this is because the more porous sample has more air present in the structure which lowers the refractive index.

Typical paper coating colours comprise mineral pigment, binder and minor quantities of other additives such as flow modifiers. When consolidated, the dry coating also contains air. Typically, the refractive index of the mineral pigment and the binder are rather similar (e.g. kaolin ~ 1.5, calcite ~ 1.66, latex ~

1.5). Thus, according to (1), variations in binder-pigment ratio do not have a dramatic effect on the effective refractive index unless the variations are very large. The refractive index of air, however, is unity. Therefore, small variations in void fraction at the surface of the coating can produce relatively large changes in refractive index. So, for microporous coatings, it is expected that effective refractive index should be a good measure of surface porosity, while being relatively insensitive to other changes in composition.

This note describes some experiments on coated paper showing that effective refractive index as measured by reflectometry does indeed relate surface porosity and is a summary of work previously published (Elton & Preston, 2006).

2. PAPERS STUDIED

The coatings used in this study contained a number of mineral types, including platey, blocky, fine and coarse kaolins, precipitated calcium carbonates (PCCs) and ground calcium carbonates (GCCs). Coatings with each mineral sample were formulated with between 9 and 12 wt% (expressed on clay), of a carboxylated styrene-butadiene latex binder, DL950TM (Dow Chemical, Horgen, Switzerland). 3 wt% of a commercial starch derivative was also present. Coatings were applied to a commercial 80 gm^{-2} woodfree base-paper at a speed of 1000 m min^{-1} using a pilot scale coater fitted with a roll applicator blade metering device (Valmet AutobladeTM). Coat weights of 14 gm^{-2} were applied to both sides of the paper and the coated papers were then passed through an 11 nip supercalender (Kleinwefers AG, Germany) at a speed of 800 m min^{-1}, a temperature of 100°C, and a linear pressure of 300 kN m^{-1}. Most of the samples had been characterised in detail as part of earlier studies (e.g. Preston *et al*., 2001).

3. MEASUREMENTS

Reflectometric measurements were made using the Surfoptic SIRS 75 Imaging Reflectometer. Other characterization (notably mercury intrusion porosimetry and tack rise measurements) was carried out as desribed as described in Preston *et al*., 2001.

4. RESULTS

Because refractive index is determined by composition and structure, it is expected that the effective refractive index measured by reflectometry should relate to surface porosity. For a range of samples of similar coating chemistry (i.e. similar formulation and pigment type), differences in effective refractive index between samples are expected to relate directly to differences in particle packing and hence void fraction at the coating surface.

Mercury porosimetry is the usual technique for measuring the pore size and volume of paper coatings. The method was applied to the range of coated papers available for this study and the relations between effective refractive index and porosimetry pore size and pore volume are shown in Figures 1a and 1b).

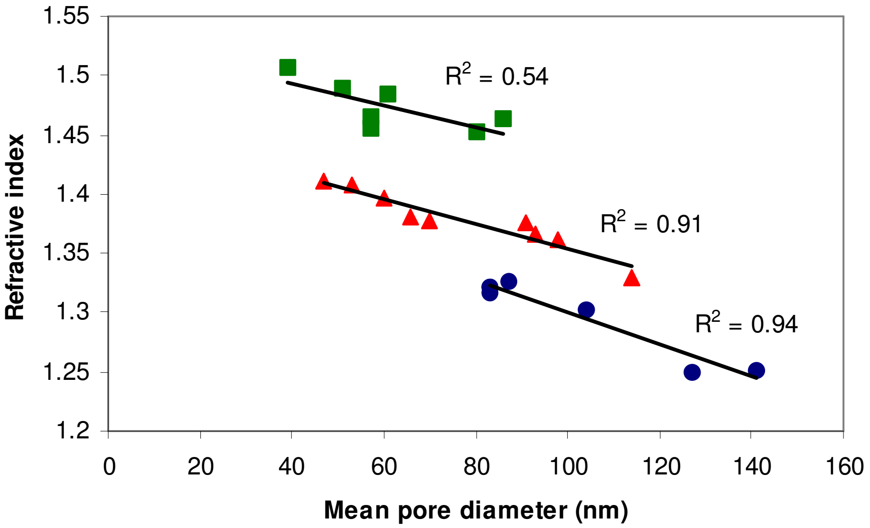


Figure 1a Refractive index versus mean pore diameter (determined by mercury porosimetry) for a range of paper coatings containing various pigment types.

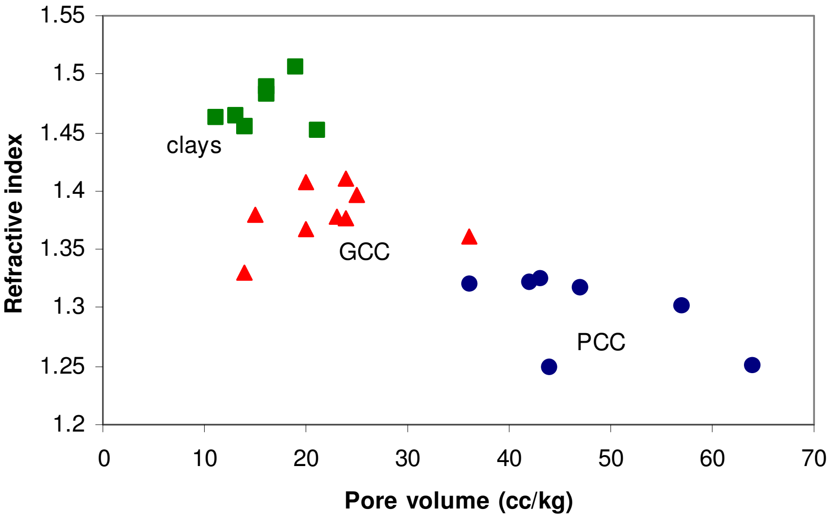


Figure 1b Refractive index versus pore volume for the same coatings.

Within a given pigment type, refractive index correlates well with mean pore diameter (Figure 1a). Data for pore volume (Figure 1b) are more scattered, but across the range of pigments used there is a general trend of refractive index decreasing as pore volume increases (as might be expected). However, within a given pigment group, there is often little correlation between refractive index and pore volume; or indeed, in the case of clays, an apparent anticorrelation.

One reason for the scatter on the pore volume measurements is simply experimental error in determining the pore volume by mercury porosimetry, which can be relatively large. However, mercury porosimetry and optical reflectometry also sample different regions of the coating layer. Reflectometry is very surface sensitive for opaque or scattering surfaces: the interaction volume is expected to be of the order of the microroughness, and recent studies on multilayer coating bear this out (Hiorns, *et al.* 2005). Mercury porosimetry on the other hand is (largely) a bulk measurement technique and the measured pore volume is characteristic of the whole coating layer including interface regions.

In many cases, the surface of the coating layer may be expected to have a different structure to that of the bulk. Differences may be due to coating colour – base sheet interactions, drying and subsequent calendering. If the surface is relatively dense and closed compared with the bulk, surface porosity may not necessarily be expected to correlate with bulk porosity. This idea is supported by the data shown in Figure 2 which shows the relation between porosimetry pore diameter and volume. Overall there is a trend of increasing volume with pore size, but within pigment groups, notably the clays and GCCs, there is poor correlation. This lack of correlation is interpreted as meaning that the surfaces through which the mercury are intruded do not have the same pore structure as the bulk. The well known "ink-well" model of pore structure is an example of a structure which would have no obvious correlation between pore diameter and volume determined by mercury porosimetry

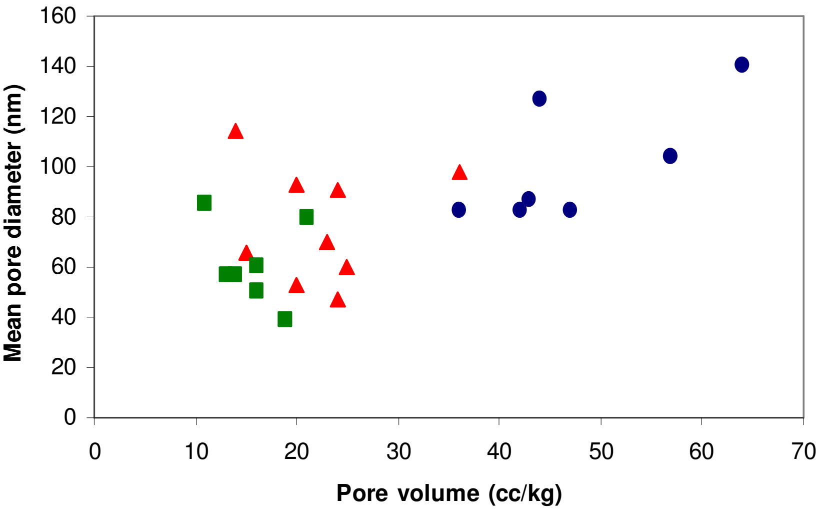
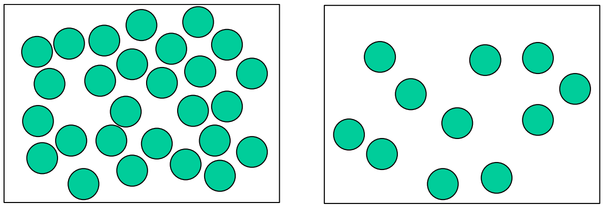


Figure 2 Pore diameter vs. pore volume as measured by mercury porosimetry for the same coatings. Compare with Figure 2b.

In Figure 1a, the three pigment groups obviously form distinct classes. While the correlation between effective refractive index and pore diameter within each group is strong and linear, it is possible that for a given pore diameter (as determined by mercury porosimetry) clays, GCCs and PCCs each have distinctly different effective refractive indexes. Because refractive index relates to surface void fraction (not strictly pore diameter), we expect that the surface pore density is also of importance.



Schematic illustrating two porous surfaces (viewed from above – pores in green). The pore diameter is the same for both surfaces. But the surface on the left has a much higher surface pore density. This surface will imbibe ink vehicle much faster.

The importance of surface pore density (number of pores per unit area) has been highlighted in earlier work on ink setting (Preston *et al.* 2001). For a single pore, ink imbibition rate increases with increasing pore diameter. However, in a coating with many pores, the surface pore density is also crucial in determining the overall imbibition rate. For a given pore diameter, the more pores per unit there are, the faster the overall fluid imbibition. Clays tend to have relatively low surface pore densities owing to the size, shape and packing of platy particles at the surface, while PCCs can have relatively high pore densities owing to their open packing properties. Thus in Figure 2a, the fact that PCCs are expected to have the highest pore densities explains why they have the lowest effective refractive index (for a given pore diameter).

For coatings with approximately equal surface pore diameters, we expect ink setting rate to be strongly correlated with the surface pore density. The higher the pore density, the faster the ink vehicle imbibition and the faster the ink immobilisation. The effective refractive index is a measure of surface porosity, but for a given pore diameter (and basically similar surface chemical composition), variations in effective refractive index should relate to variations in surface pore density.

Figure 3 shows the correlation between ink tack rise (as measured using the SeGan ISIT) and effective refractive index for coatings having similar pore diameters (around 80 nm) as measured by mercury porosimetry. Across the range of pigments, the correlation is fair and lends further supports to the ideas presented above. Generally, however, effective refractive index does not correlate well with ink setting rate.

Despite this limitation, it is clear that refractive index can provide useful information about coating porosity, especially when used in comparative studies. Recent work indicates that mapping of refractive index over the surface of a coated paper can be useful in interpreting origins of gloss and print mottle (Preston *et al.* 2005; Preston *et a.l*, 2007).

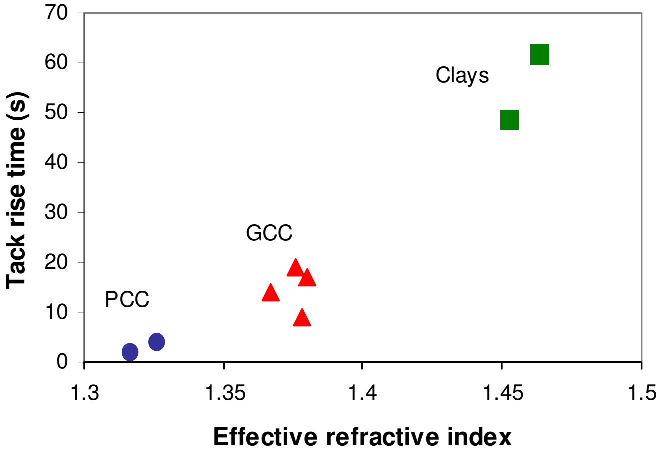


Figure 3 Tack rise versus effective refractive index for pigment coatings having a pore diameter around 80 nm as measured by mercury porosimetry.

CONCLUSIONS

The correlations observed between effective refractive index and pore diameter and volume measured by mercury porosimetry support the expectation that refractive index is strongly related to surface void fraction for microporous materials like coated paper. Because effective refractive index is a surface measurement, it does not (in general) correlate well with bulk measurements of pore volume. To predict ink setting rates, it would be necessary to know both pore diameter and pore number density. The effective refractive index therefore only contains part of the information necessary to understand ink setting rates. However, measurement of effective refractive index is quick and easy, and allows useful comparison between coatings. It should also be useful in comparing point-to-point variations in porosity over a coating surface.

ACKNOWLEDGMENTS

We wish to thank Dr Len Gate (Surfoptic) and Dr Tony Hiorns (Imerys) for valuable input. Thanks are also due to Imerys Minerals Ltd and Surfoptic Ltd for permission to publish this work.

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