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Enhancement of the light-scattering ability of coatings by using hollow pigments

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Abstract: The light-scattering properties of coatings based on monodisperse polymeric spheres of two different diameters (ca 0.5 and 1 μm) were evaluated from reflectance measurements as a function of the wavelength from 400 to 700 nm. Some of these plastic pigments were hollow and it was noted that these particles gave coatings with a greater light-scattering ability than coatings based on solid particles of a similar size. It was possible to estimate the contribution of the internal pores to the scattering ability of the coating layers by saturating the layers with an oil of a refractive index similar to that of the polymeric pigment particles. A simple model accounting for the scattering provided by the internal pores of the hollow particles is suggested. The agreement between the experimental results and the prediction of the model is fair. It was noted that the light scattering coefficient of the coatings increased when the external diameter of their constituent hollow particles increased from ca 0.5 to 1 μm.

Key words: Coating – optical scattering – pigment – plastic pigment – porosity

Introduction

A pigmented coating layer is required, in most instances, to exhibit a high light-scattering efficiency and a good hiding power, for instance, when opacity is a critical function of the layer. Coatings subject to these requirements are used in paint technology and for paper coating applications. Extensive analyses of the scattering and absorption properties of such layers have been performed over the years, cf e.g. [1, 2]. In the case of paper coatings, the scattering properties are strongly dependent on the pore structure of the layer. These porous layers are mainly based on pigments such as kaolin or calcium carbonate which have rather small light absorption coefficients in the visible wavelength region.

One characteristic of this type of porous layer is that the size of the particles constituting the layer is of the same order of magnitude as the wavelength of light. As a consequence, the light-scattering coefficient (s) may vary quite markedly with the wavelength. It is also well-known that the maximum light-scattering coefficient for a given pigment is obtained at a certain particle size [3, 4]. The porous coating may, however, also be regarded as a solid matrix containing voids which then constitute the scattering sites. The scattering efficiency of the layer can then be related to void or pore size [5–7]. Provided that the refractive index of the pigment is constant, the particle size or the void (pore) size thus governs the light-scattering properties of these types of coatings. Borch and Lepoutre [6] have shown that the Mie-theory can be used to estimate the optimum particle (or pore) size for maximum light scattering. It is however difficult to predict the light-scattering coefficient of these close-packed systems in absolute terms, in the first place due to the effects of multiple scattering and interference. On the other hand, the wavelength dependence of the s-value can be used to obtain an estimate of the average pore size of the layer, as shown by Gate [8].

In an earlier work [9], the extent to which the particle (or pore) size controlled the scattering properties in the visible range and extending into the ultraviolet region was investigated by means of model coatings. These model coatings were based on solid polystyrene spheres with diameters between 140 and 650 nm. Some experiments were also performed using kaolin fractions with narrow particle size distributions. The results indicated that, for a pigmented coating of a given porosity, the maximum light-scattering ability was obtained when the pore diameter was approximately one-half of the wavelength. It was furthermore noted that for pore diameters smaller than this value the *s*-values could be quite uniquely related to the specific area of the particles and to the ratio between the pore diameter and the wavelength of light. The aim of this work is to extend the results obtained with the model coatings by using hollow plastic particles. With such pigments, the porosity of the coating layer and the pore size can be changed without varying the outer dimensions of the pigment particles and the corresponding effects on the light scattering ability of the layers can be investigated. A further aim of this work was therefore to estimate the contribution of the internal pores of these pigments to the scattering ability of the coating layers. Coatings based on solid plastic pigments were used as a reference.

It is known that hollow pigments of this type can have a positive effect on the optical properties of paper when they are incorporated into the coating layer [10, 11]. Both types of plastic pigments used here (solid and hollow) have a refractive index close to that of a conventional coating grade of kaolin (ca 1.6).

Experimental

Materials

The homogeneous polystyrene (PS) spheres used here were kindly supplied by Dow Rheinmünster GmbH, Germany. The diameter of the particles was, according to the manufacturer, 0.45 μm. The solid pigment is denoted PS-1. The hollow plastic pigments based on a styrene-acrylate copolymer were kindly supplied by Rohm and Haas, France. Two grades of the hollow pigment, differing in particle size, were used. According to the manufacturer, the diameters of these particles were 0.5 and ca 1 μm. These pigments are denoted HP-1 and HP-2 respectively. According to the manufacturer, the thickness of the polymeric shell of the hollow pigments was ca 0.1 μm. The particle sizes were also measured using a Zetasizer 3 and a Master Sizer (both from Malvern Instruments Ltd., England). The diameters obtained from those measurements were 0.41, 0.52 and 1.10 μm for PS-1, HP-1 and HP-2, respectively.

Electrophoretic mobility

The electrophoretic mobility of the plastic pigment particles was determined with a Zetasizer 3, Malvern Instruments Ltd, England. The particles were dispersed in a 0.01 M NaCl-solution. The electrophoretic mobility of the particles (expressed as the *z*-potential) was measured at different pH's. The particle concentration during the measurements was $1.7 \times 10^{-3}\%$.

Preparation of coating films

Coatings were drawn down on polyester film (Mylar, DuPont) using a laboratory coater (K-coater, RK Print-Coat Instruments Ltd, England). The polymer dispersions contained 0.5% poly(vinyl alcohol) to ensure sufficient adhesion between the particles. The grammage of the dry coatings was varied in a controlled manner between ca 10 and 25 g/m^2. The layers exhibited no fluorescence when exposed to ultraviolet radiation.

Light-scattering coefficient

Reflectances of the coatings on the polyester film with white and black backings were measured at wavelengths between 400 and 700 nm using an Elrepho 2000-instrument. The light-scattering coefficient (*s*) was calculated according to the Kubelka-Munk theory [12]. The *s*-values of the coatings were also evaluated from reflectance measurements with a black backing assuming the light absorption coefficient to be zero. Both techniques for determining the *s*-value gave similar results.

Porosity

The porosity of the coating layers corresponding to the pores between the spherical particles

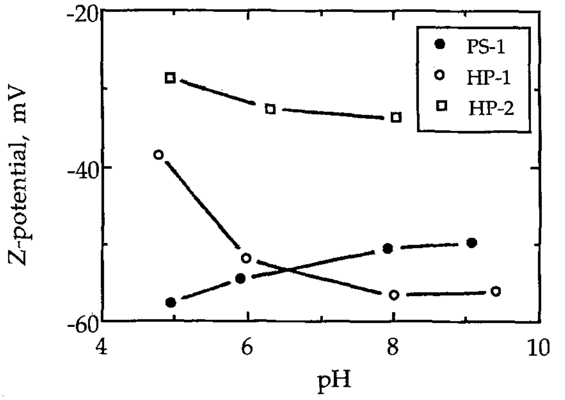

Fig. 1. The *z*-potential of PS-1, HP-1 and HP-2 as a function of pH.

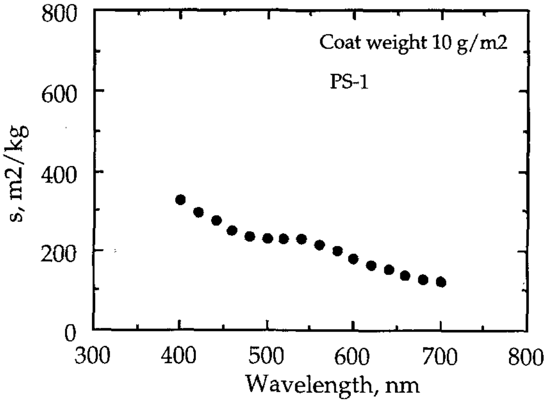

Fig. 2. The light-scattering coefficient (*s*) of coatings based on PS-1 vs the wavelength.

was determined by oil absorption [13]. The density of the mineral oil used was 0.826 g/cm^3. The porosity determined in this way is termed "external porosity".

Results

The electrophoretic mobility of the particles

Figure 1 shows the *z*-potential of the three different particles as a function of pH. The particles were anionic over a rather wide pH-range and the larger hollow pigment particles were less negative than the other two plastic pigments.

The porosity of the coatings

Earlier work has indicated that the almost monodisperse spherical pigment particles in the dry coatings arrange themselves in a close-packed state. Scanning electron micrographs suggested that there are highly ordered regions in the close-packed structure [9] which perhaps can be characterized as being a mixture of cubic and rhombohedral packing, cf [14]. The porosity of such structures formed by homogeneous particles should be independent of the particle size. Alince and Lepoutre [7] found that the mean porosity of coatings based on polystyrene particles of different sizes was approximately 0.33, which corresponds to the voids between the particles.

From the oil absorption capacity of the coatings, the external porosity of the coating layers was evaluated. For coatings based on the solid PS-1, the external porosity was 0.308 and for the layers based on HP-1 and HP-2 the values were 0.336 and 0.362 respectively. These values are fairly close to the value 0.33 reported by Alince and Lepoutre [7] indicating that the particles arrange themselves in a fairly close-packed state. When the hollow pigments are used, the pores inside the particles also contribute to the scattering ability. Since the thickness of the polymeric shell is known (0.1 μm) this internal porosity can be calculated. The total porosity (the sum of the internal and external porosities) of the layers based on the hollow pigments was 0.480 for HP-1 and 0.688 for HP-2. The contribution of the internal pores is thus significant.

The light-scattering ability of the coatings

Figure 2 shows the light-scattering coefficient of coatings based on PS-1 as a function of the wavelength (λ). The grammage (coat weight) of the coating layer was ca 10 g/m^2. The effect of the coat weight on the scattering coefficient was not very pronounced, although a slight decrease in the *s*-value was observed as the coat weight increased. In general, the light-scattering coefficient decreased as the wavelength increased from 400 to 700 nm. Lindblad et al. [9] showed that, for coatings based on solid polymeric particles with diameters in the range 0.14 to 0.65 μm, the *s*-value in this wavelength region increased in general when the particle diameter (or the pore size) increased. This increase in the *s*-value was however less

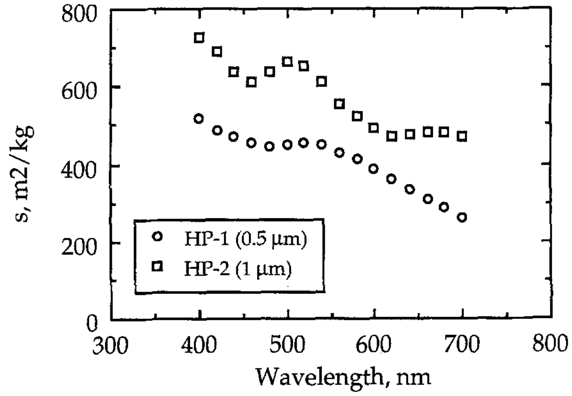

Fig. 3. The light-scattering coefficient (s) of coatings (grammage ca 10 g/m^2) based on the hollow pigments HP-1 and HP-2 vs the wavelength. The particle diameters were 0.5 and ca 1 μm, respectively.

pronounced in the higher particle size region. Since the porosity of the coatings remained constant (the films being based on almost mondisperse spherical particles), the importance of the particle or the pore size for the scattering ability of the coatings was thus illustrated.

The maximum noted in the $s(\lambda)$-curve was reproducible, but difficult to account for. It may reflect deficiencies in the Kubelka-Munk theory, cf [15], or it may be due to interference phenomena occurring in these ordered structures, cf [16]. A detailed investigation of the significance of these irregularities will not however be attempted here.

Figure 3 shows the light-scattering ability of the coatings based on the hollow pigments HP-1 and HP-2 versus the wavelength. The grammage of the coatings was ca 10 g/m^2. Lower s-values were obtained when the wavelength increased and the coating based on the smaller particles exhibited a lower light-scattering efficiency. Note, however, that the wavelength dependence of s for coatings based on the large HP-2 particles was not very pronounced. The most interesting feature of the curves shown in Fig. 3 is that the light-scattering coefficient values were very high. The s-values for a coating based on homogeneous pigment particles of a similar size (cf. Fig. 2) were significantly lower. This difference in scattering ability must be attributed to the scattering provided by the internal pores of the particles. For a coating layer based on a commercial coating grade of kaolin the s-value is much lower and of the order of 100–150 m^2/kg [9].

Figure 4 shows that when the hollow pigments HP-1 and HP-2 are mixed, the $s(\lambda)$-curves gradually changes from that for coatings based on one pigment into that for the other. In principle, it is thus possible to control the scattering ability of the coatings in this manner. The fact that the order of the particle structure decreases as pigments of different sizes are mixed apparently has no marked effect on the scattering coefficient.

The light-scattering ability of coatings immersed in oil

When the coatings based on PS-1 were immersed in a suitable mineral oil having a refractive index matching that of the polymeric spheres, they became transparent. Reflectance measurements on these oil-saturated coatings yielded a very low value of the light-scattering coefficient.

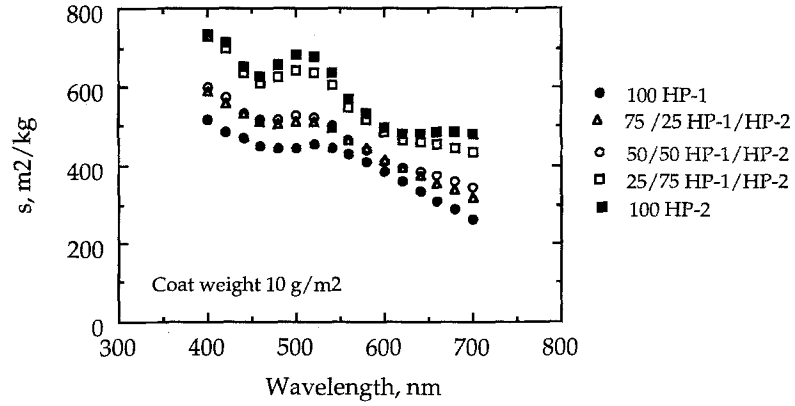

Fig. 4. The light-scattering coefficient (s) of coatings based on blends of the hollow pigments HP-1 and HP-2 vs the wavelength.

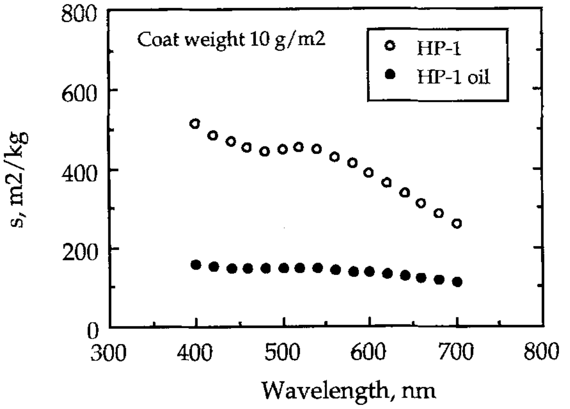

Fig. 5. The light scattering of coatings based on HP-1 (coat weight 10 g/m^2) vs the wavelength of light before and after saturation with the mineral oil.

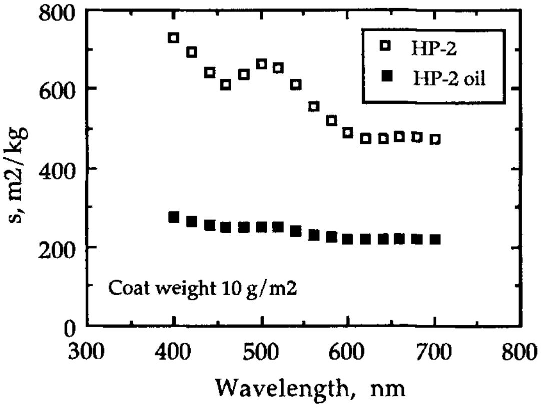

Fig. 6. Same as Fig. 5 but for coatings based on HP-2.

When the coatings based on the hollow pigments were immersed in the oil, they did not however become transparent. These coatings still scattered light, and this is strong confirmation that the scattering is indeed associated with internal pores in the particles, not accessible to the oil. Figures 5 and 6 show the light-scattering coefficients of the coatings before and after saturation with the oil. The grammage of the coating films was, as before, ca 10 g/m^2.

As can be seen in the graphs the internal pores make a significant contribution to the scattering of these layers. The larger pores of the HP-2 particles appear to be more effective in scattering light than the smaller ones of the HP-1 particles. The internal porosity of the coatings was however also higher in the case of the larger particles. The wavelength dependence of the s-value associated with the internal pores is not very marked, which perhaps can be attributed to the fact that the internal pores are rather large. It is thus possible to separate the light scattering associated with the internal pores from that due to the external pores between the particles. It can also be noted, when comparing Figs. 2 and 5 that, if the s-values for the coating based on HP-1 saturated with oil are subtracted from the corresponding s-values for the coating not exposed to the oil, the resulting $s(\lambda)$-relation is quite similar to that obtained for the coatings based on PS-1. This appears to be reasonable since PS-1 and HP-1 have rather similar outer diameters.

By subtracting the s-values for the coatings immersed in oil from the corresponding s-values for the coatings not exposed to the oil, an estimate of the scattering contribution from the external pores can be obtained. The difference in this contribution between oil-immersed coatings based on HP-1 and HP-2 was markedly smaller than the difference in the light scattering efficiency of the coatings not immersed in oil, (cf. Fig. 3). This would indicate that the higher s-values for the coating based on the large HP-2 particles compared to those of the coating based on HP-1 could to a significant extent be attributed to the internal pores and porosity and not primarily (or only) to the larger external pores (or larger outer particle diameter). This may not be unrealistic since large particles in themselves are not expected to provide a very efficient light scattering.

Discussion

With pigment particles of the size common in paper coating applications, the scattering ability is strongly connected to the particle size and the magnitude of the wavelength of light. This is evident from the results presented here and from data presented by others, e.g. [7]. When routes to optimizing the light-scattering ability are sought for, the particle size is one very important factor. From an optical point of view, the use of monodisperse particles is an advantage since it enables all scattering sites (particles or pores) to be equally effective. The use of monodisperse particles as coating pigments is however (as is well-known) restricted by other requirements with regard to the pigment.

The use of hollow spheres as pigments leads to an improvement in scattering efficiency over that achieved with homogeneous plastic pigments of similar size and refractive index. This is evidently attributed to the internal voids of the particles and the increased porosity of the coatings. Although it is difficult to predict the effect of the pore size on the light-scattering coefficient in absolute terms, a simple way to rationalize the effect of the internal voids is presented here.

For layers based on homogeneous (solid) spherical particles with a uniform size, the diameters of the pores between the particles should be equal and can be estimated by the hydraulic pore diameter (d) given by Graton and Fraser [14]:

$$d = 2\varepsilon D/3(1-\varepsilon)\,, \qquad (1)$$

where ε is the porosity of the film and D the particle diameter. Lindblad et al. [9], who investigated the scattering properties of coatings based on homogeneous spherical particles with different diameters and thus different specific surfaces A, noted that the ratio s/A was a unique approximately linear function of d/λ (if $d/\lambda < 0.5$) irrespective of particle size and wavelength. For $d/\lambda < 0.5$, the slope of the line was steep, indicating the pronounced wavelength dependence of the scattering ability, but above this value the results indicated a significantly smaller increase in s/A with increasing values of d/λ.

The findings reported by Lindblad et al. [9] can be modeled as outlined in Fig. 7, although this is quite a crude description. This model describes the scattering ability of coatings based on homogeneous polystyrene particles when the pores between the spheres are considered to be the scattering sites. It is now assumed that this model also can be used to estimate the scattering ability of the coatings based on the hollow particles. The light-scattering coefficient of these coatings may then be evaluated by accounting for the additional specific area of the particles provided by the internal pores. With such a model, the wavelength dependence of the scattering coefficient of the coatings is similar for solid and for hollow spheres when their outer diameters are the same. For the hollow particles used here, this may not be unrealistic, since the internal pores are comparatively large and in such a case the corresponding wavelength dependence is not very pronounced, cf. Figs. 5 and 6 and also Lindblad et al. [9]. In a way, this assumption resembles the findings reported by Fineman et al. [17], who noted an almost linear relation between s for filled paper structures and the specific area of the pores with a diameter greater than 0.2 μm. The dimensions of the pores were in that case determined by mercury porosimetry.

Figure 8 compares the experimental values of the light-scattering coefficient for the hollow spheres with diameter 0.5 μm with the values

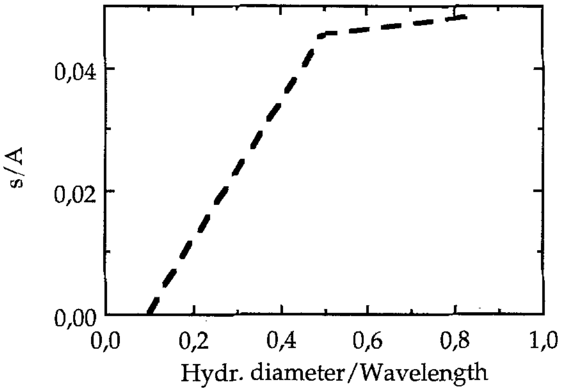

Fig. 7. Schematic representation of the relation between s/A and d/λ for coatings based on homogeneous polystyrene particles.

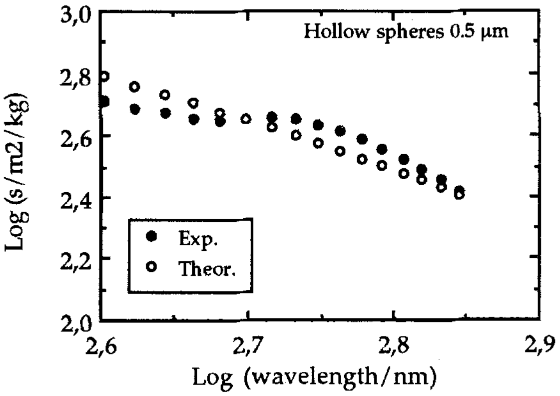

Fig. 8. The light-scattering coefficient (s) vs the wavelength of light for the coating based on the hollow particles and the corresponding prediction of the model. The diameter of the spheres was 0.5 μm.

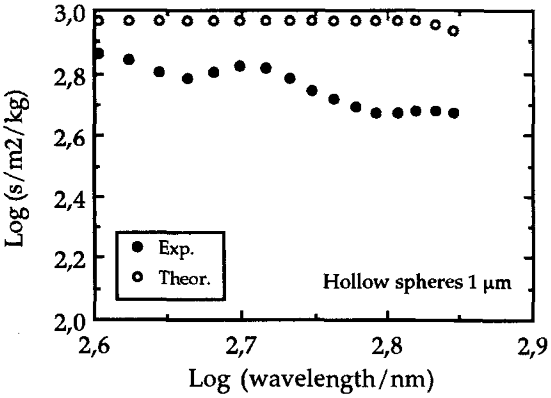

Fig. 9. Same as Fig. 8 but for coatings based on hollow particles with a diameter of ca 1 μm.

predicted by the model. This graph is constructed from Fig. 7 assuming that the specific surface now consists of one contribution for the outer surface of the hollow particle and one from the inner surface. The agreement between the two curves is satisfactory considering the simplicity of the model. This result supports in a sense the assumption that the surface area associated with the internal pores of the hollow particles is an important factor giving these pigments a greater scattering ability than solid plastic particles.

The experimental values of s for the coating based on the larger hollow spheres (ca 1 μm) are compared with the prediction of the model in Fig. 9. The agreement between the experimental result and the model prediction is less satisfactory for these larger particles. To some extent, this is naturally related to the crudeness of the model used, especially at large hydraulic diameters, cf. Fig. 7. There is, in fact, little data available for d/λ-values larger than 0.5 cf. [9].

The scattering ability of coatings of the types considered here can clearly be considerably enhanced and also controlled by the use of monodisperse hollow pigment particles. This is another illustration of the importance of the pore structure for the light-scattering properties of coatings, and the surface area associated with interior voids in the particles appears to an important factor contributing to the improvement in light scattering. In practice, it may be difficult to take full advantage of the scattering ability of the hollow particles since there are also other demands on coating pigments which make it difficult to use monodisperse particles. Compromises have to be made, but it is important to assess the potential for achieving high scattering coefficients using specialty pigments.

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