Progress in Organic Coatings 77 (2014) 1619–1628

Contents lists available at ScienceDirect

Progress in Organic Coatings

journal homepage: www.elsevier.com/locate/porgcoat

Theoretical analysis of light scattering properties of encapsulated rutile titanium dioxide pigments in dependent light scattering regime

J.-C. Auger[a,*], Daragh McLoughlin[b]

[a] Expert Capability Group, RD&I AkzoNobel, Shanghai, China
[b] Decorative Paints, RD&I AkzoNobel, UK

ARTICLE INFO

Article history:
Received 28 January 2014
Received in revised form 22 April 2014
Accepted 2 May 2014
Available online 15 July 2014

Keywords:
Dependent scattering
Multiple scattering
White coating
Opacity
Hiding power
Rutile titanium dioxide

ABSTRACT

Using numerical simulation, we study and compare the optical properties of model systems representing three types of scatterer: (a) standard TiO_2 pigments, (b) standard TiO_2 pigments encapsulated by a hard polymer shell and (c) standard TiO_2 pigments encapsulated by a layer of air and a polymer shell. Calculations are performed taking into account multiple and dependent light scattering regimes. Assuming an equivalent amount of TiO_2 in each system, results show that a standard TiO_2 pigment particle encapsulated by air could be a better opacifier than a standard un-encapsulated TiO_2 pigment because the presence of air could provide: (a) additional volume to the existing particle to scatter light; (b) better redistribution of the scattered field in the backward hemisphere; (c) a scattering cross-section less affected by crowding and (d) spacing effects due to the presence of the thin hard polymer shell which is required to encapsulate the air layer. Nonetheless, results also suggest that such benefits could probably not be exploited in real paint systems as encapsulated TiO_2 would only be more efficient than standard TiO_2 in a range of pigment volume filling fractions (PVC) that would not generate enough scattering efficiency to yield complete hiding as required by international standards.

1. Introduction

Rutile titanium dioxide (TiO_2) is by far the most effective white pigment that is used to provide opacity in architectural coatings. However it is also the most expensive. The search for an alternative scattering system that would bring either enhanced scattering efficiency for the same price or identical hiding property at a lower cost, has been a major area of research for the coating industry since the middle of the 20th century.

Among several designed strategies, one promising approach consists of encapsulating the TiO_2 pigment into a hard polymer shell. The presence of a thick polymer shell provides a steric barrier, which prevents TiO_2 particles from clustering and consequently limits the decrease of the scattering efficiency due to crowding effects. Such composite particles are nowadays commercially available from Dow Chemical under the name of Zeno™.

Another postulated approach, which has been proposed since the early 1960s, involves the encapsulation of TiO_2 pigments within an air void, bounded by a hard polymer shell. The presence of the surrounding air layer is assumed to enhance the rutile titanium scattering efficiency because of the increase of the refractive index contrast between the pigment and its direct surrounding medium. Ross and Kerker [1,2] realized the first theoretical studies of the optical properties of such composite scatterers at the beginning of the 1970s. Using Mie theory, they calculated the scattering efficiency of a spherical particle of rutile titanium dioxide placed at the center of spherical air bubble embedded into an infinite polymeric medium. They found that such a system could never scatter light with better efficiency than the combination of the isolated TiO_2 pigment and the equivalent volume of air directly embedded into the resin. A slightly more realistic study, assumed that the pigment is stuck at the internal face of the polymer shell surrounding the air void, reached an equivalent conclusion [3]. Also, the effect of displacing the pigment on the internal face of the air shell was found to only have minor influence on opacity, because: (i) when the size of the inclusion is much smaller than the dimension of the air bubble, the scattering characteristics of the composite object are mainly driven by the air bubble properties; (ii) When it is comparable to the dimension of the air bubble, the maximum distance at which the particle can be shifted off center is too small to significantly modify the overall light scattering properties of the composite particle.

However, it is difficult to apply the conclusions of those studies to real paint systems since they were conducted with the assumption of independent scattering, which only holds in the limit of

* Corresponding author. Tel.: +86 21 5707 9349; fax: +86 21 3353 8505.
E-mail address: jean-claude.auger@akzonobel.com (J.-C. Auger).

http://dx.doi.org/10.1016/j.porgcoat.2014.05.005
0300-9440/

infinitely diluted medium. Thus, any possible extrapolation of these conclusions to the case of non-isolated particles, which represents the realistic light propagation regime in paint films, was uncertain. Today, there remains uncertainty as to what is the practical capacity of these composite particles to efficiently substitute standard TiO_2 pigments. This question becomes even more important now as attempts are being made to synthetize such particles [4].

Consequently, the objective of this work is twofold: (a) To determine, via the use of numerical simulation the scattering efficiencies of these composite particles in the context of multiple scattering and to compare their opacifying capabilities with standard TiO_2 pigments; (b) to provide a fundamental understanding of the effect of the air layer and polymer shells on the light scattering properties of those particles.

To reach those objectives, the article is organized as follows: in the first section we briefly recall the origins of opacity and several key parameters that can influence it in a paint film. We also use a semi empirical approach to demonstrate the limitation of the extrapolation of independent scattering properties trends to dense medium. In a second section, we examine the optical properties of various homogeneous and complex structured pigments in diluted media where the approximation of independent scattering holds. In the last section we compare the optical properties of different scatterers taking into account multiple scattering interactions and we analyze the effect of the air layer around the TiO_2 pigments. Finally we discuss the possibility of using such encapsulated pigments in real paint systems and we conclude on the nature of the fundamental mechanisms, which govern the light scattering processes of these particles.

2. Preliminary discussion

2.1. Origins of opacity

Opacity describes the ability of a paint film to hide or obliterate a given substrate. At a microscopic scale, and for non-absorbing medium, the opacity of white paint originates from the multiple scattering interactions of light with either white pigments such as rutile titanium dioxide, hollow opaque polymer or air voids trapped within the paint film (when formulating above the Critical Pigment Volume Concentration (CPVC)). The higher the proportion of the total scattered field redistributed in the back hemisphere at each scattering event, the better is the opacity. The effectiveness of the backscattering interaction between the incoming light and the randomly dispersed pigments is generally quantified by the magnitude of the pigment scattering efficiency (having unit of Length^{-1}), defined as:

$$S(\phi) = n(\phi) b_{sca}(\phi) \tag{1}$$

where ϕ is the pigment volume-filling fraction, $n(\phi)$ and $b_{sca}(\phi)$ represent the number of particle by unit volume (unit of length^{-3}) and the backscattering coefficient of the scattering centers (unit of length^2) present in the paint film. The latter can be expressed in terms of the particles' scattering cross-section and the particles' asymmetry parameter (denoted C_{sca}, (unit of length^2) and g (unit less) respectively) such that:

$$b_{sca}(\phi) = C_{sca}(\phi)[1 - g(\phi)] \tag{2}$$

where g ranges from -1 for total backwards scattering, to +1 for complete forward scattering and the value of 0 represent isotropic scattering. Inspection of Eqs. (1) and (2) shows that optimum scattering efficiency is reached when the following conditions simultaneously occur: (a) the number of particles by unit volume is a maximum, (b) the magnitude of the scattering interaction, which is given by the value of the scattering cross-section, is a maximum and (c) the angular re-distribution of the scattered light in the backward hemisphere is maximum (asymmetry parameter g being a minimum).

Consequently, a strong scattering interaction alone does not, a priori lead to good hiding especially if most of the incoming light is scattered in the forward hemisphere. On the other hand, a large angular distribution of the scattered light in the backward hemisphere cannot provide good hiding if the overall scattering interaction is too weak because only a small proportion of the incoming light is scattered. Finally, at a constant back scattering coefficient and constant PVC, the smaller the particle, the higher is the opacifying power.

2.2. Validity of the extrapolation of independent light scattering trends to dense media

We consider two different white pigments, labeled A and B, such that the scattering efficiency of A is greater than the scattering efficiency of B in an infinitely diluted system, i.e. $S_A(\phi) > S_B(\phi)$ when $\phi \ll 1$. In a first approximation it is possible to represent the variation of the pigments' cattering efficiencies as a function of the PVC by a simple Polynomial function such that:

$$S(\phi) = B^I_{sca}\phi - \gamma\phi^2 \tag{3}$$

where $B^I_{sca} = b_{sca}/v$ is the independent scattering efficiency by unit volume v of the particle and γ is mostly a positive number, which represents the magnitude of the crowding effect such that the larger the value of γ, the higher the magnitude of dependent scattering phenomenon. The polynomial function has no zero order, because the scattering efficiency must vanish in absence of pigments, i.e. $S(0) = 0$. Also, in the limit of infinitely diluted systems, where independent scattering assumption holds, $\phi \to 0$ and Eq. (3) simplifies to the well-known relation of proportionality between S and ϕ.

Now, Eq. (4) below, derived from Eq. (3) and our initial assumption, describes in terms of physical quantities and semi empirical parameters the condition under which the scattering efficiency of pigment B can become superior to the scattering efficiency of pigment A. That is:

$$S_B(\phi) > S_A(\phi), \quad \text{at } \phi > \phi_t \Rightarrow \left\{ \frac{B^{I(A)}_{sca} - B^{I(B)}_{sca}}{\gamma_A - \gamma_B} < \phi_t < \phi \right. \tag{4}$$

where ϕ_t, represents the threshold PVC at which the change, due to the presence of non negligible dependent light scattering effect, may occur. This simple relationship shows that, when the evaluation of ϕ_t is either not physical ($\phi_t > 1$) or non compatible with realistic range of PVC found in paint formulation, the inequality $S_A(\phi) > S_B(\phi)$ holds even in dense medium as shown in Fig. 1. However, it also indicates that pigment B could develop higher scattering efficiency than A if the magnitude of dependent light scattering effect is much larger for A than for B (i.e. $\gamma_A \gg \gamma_B$). Such an example is given in Fig. 2. Moreover, if $B^{I,(A)}_{sca}$ and $B^{I,(B)}_{sca}$ have relatively similar values, then γ_A needs only to be slightly higher than γ_B.

3. Light scattering properties in independent scattering regime

3.1. Theoretical formalism

We consider an incident electromagnetic plane wave, of wavelength λ_0 which impinges on a spherical dielectric particle of radius r_1 and complex index of refraction n_1. The particle, which is embedded in a continuous and non-absorbing medium of index of refraction n_0, can enclose a spherical dielectric inclusion, concentric or not, characterized by a radius r_2 and complex index of