Self-Opacifying Aluminum Phosphate Particles for Paint Film Pigmentation

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Introduction

Titanium dioxide is the most common white pigment due to its strong ability to backscatter visible light, which is in turn dependent on its refractive index. Substitutes for titanium dioxide have been sought, but the refractive indexes of both the anatase and rutile forms of this oxide are much higher than those of any other white powder, for structural reasons.

Although many efforts to replace TiO₂ have been made, currently there is not a competitive replacement. Other solids (barite, kaoline, CaCO₃) are used as extenders replacing part of the white pigment and aiming at the preservation of the optical properties of the finished products (paints, coatings, paper) but at significantly lower prices.

It is known that the inclusion of closed pores of sub-micrometric dimensions within film pigments causes an increase in their light scattering ability. It was shown that the addition of microvoids offers greater hiding efficiency than does an increase in the prime pigment content within the film.

A theoretical study on pigmented microvoid coatings was made by Kerker, Cooke, and Ross. Models are presented for three void types: (1) voids within the pigment particles; (2) voids in between pigment particles and resin matrix; and (3) voids within the resin. There is synergism between particle and microvoid scattering, within the pigmented resin films. Microvoid effect does not seem to differ significantly among the three models studied, but the authors are very cautious about their results. They indicate the need for further studies, including pigment polydispersion and the effect of polychromatic visible light, which are certainly relevant in real systems.

In spite of the three possibilities presented by Kerker et al., there are still only a few processes for making void filled films.

Closed-pore formation within the resin was described by Rankin in the process of making a thermoset film, by reaction of epoxy resin particles on a substrate. The irregular shapes of the particles allow the retention of interstitial air bubbles within the film. However, the films thus obtained present some problems: the irregular surface is responsible for a low film brightness, and the coalescence or collapse of bubbles during the reaction reduces the number of closed pores.

Studies on the thermal stability of microvoid coatings prepared from thermoplastic and alkyd resins using a solvent-non-solvent technique were done by Ramiaia and Funke.

Processes in which void formation occurs within a resin filled with solids are also scarce. An example of a study on voids trapped between pigment particles or at the pigment-resin interface is given by Fishman, Kurtze, and Bierwagen. This study evaluates the consequences of void formation on organic coatings, when PVC exceeds a critical concentration.

On the other hand, there are many publications which describe the synthesis of hollow particles, but most discuss polymeric spheroidal particles, which are used as paint and paper whiteners. Only a few examples of inorganic hollow particles available exist in the literature.

The introduction of hollow polymeric particles in the coatings industry led many paint manufacturers to successfully use this technology to lower their total raw materials costs, while maintaining the quality of their formulation. This trend has accelerated recently due to increased prices for titanium dioxide, improvements in hollow polymer pigment technology, and the move towards pricing paint by volume rather than by weight.
weight. Fasano\textsuperscript{3} studied the application of hollow opaque polymer particles in paints without losing mechanical resistance; Hermenway, Latimer, and Young described similar studies obtaining improved gloss and opacity\textsuperscript{8} in paper coatings. Ramig and Ramig studied the effect of plastic pigment composition on latex paint performance as a novel approach to microvoid hiding.\textsuperscript{19} Improved scrub resistance can be obtained using microvoid coatings under particular conditions.\textsuperscript{11} The making of polymer particles for microvoid coatings is described in the open literature as well as in the patent literature.\textsuperscript{12,18}

Braun's review on white pigment technology stresses the importance of void hiding by three mechanisms: (1) voids which scatter light; (2) very small voids, which reduce the refractive index of the binder/air combination; this process increases the light scattering ability from any pigments; and (3) foams which scatter light at the air/polymer interfaces. The author also lists some commercially available hollow plastic pigments.\textsuperscript{13} Rennei and Rigdahl\textsuperscript{15} confirm that the scattering ability of some coatings can be considerably enhanced and also controlled by the use of monodisperse hollow pigment particles. This enhancement is positively or negatively affected by many factors, and some compromises may have to be made.

There are also some examples of hollow inorganic pigments: Kawahashi, Persson, and Matijevic obtained zirconia\textsuperscript{22} and yttria\textsuperscript{24} hollow spheres by deposition of zirconium compounds on cat-ionic and anionic polystyrene lattices followed by calcination. Kaneko et al.\textsuperscript{23} presents a procedure to make microporous silica microballoons, for use in adsorption studies. Roth and Köbrich\textsuperscript{26} also produced hollow spheres by a sophisticated apparatus which involves electrodeposition, heating, and spinning. Other studies have reported on inorganic materials.\textsuperscript{26,27} Theoretical studies on the optical properties of coatings containing hollow pigments\textsuperscript{29} are available. The appearance and growth of voids within solids under several conditions were studied\textsuperscript{27,28}; a more specific study was done by Strawbridge and Hallett on the application of Mie theory to hollow latex spheres\textsuperscript{29}; the scattering by low-refractive index dielectric spheres and cylinders was compared with rigorous calculations for hollow particles by Jazbi and Wickrasinghe.\textsuperscript{30}

Past work from this laboratory described making hollow particles of amorphous phosphate and polyphosphate compounds, and their use as white pigments.\textsuperscript{31-33}

According to our previous studies, closed pores are formed within non-crystalline, hydrated aluminum phosphate and polyphosphate particles under heating. This is due to the simultaneous occurrence of two phenomena: (1) solid matrix softening; and (2) release of low molecular weight, volatile components from the matrix. When the hydrated particles are heated, water vapor is released and bubbles are formed and kept within the particles provided the viscosity of the matrix is neither too high or too low.

More recently, we found that polymer films prepared with transparent, unheated, dense amorphous aluminum phosphate particles could also be highly opaque. This result was at first rather surprising, but we found that these particles underwent some morphological transformation during polymer film formation. Voids were formed within these particles and they account for film opacification.

In this work we describe the characterization and evaluation of amorphous aluminum phosphate as a white pigment in self-opacifying polymer films. Also, a morphogenetic mode is proposed for the formation of voids within particles dispersed in a polymer film, leading to self-opacification.

**Experimental**

Aluminum phosphates were precipitated by admixture of aqueous solutions of aluminum nitrate, sodium dihydrogen phosphate, and ammonium hydroxide. After centrifugation, washing, drying, and milling the precipitate, we obtained white powders with different chemical compositions depending on the initial concentration of the