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A review of polymeric dispersant stabilisation of titania pigment

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ABSTRACT

A review of past and present published works examining the interaction of polymeric dispersants with titania pigment particles is presented. Titania is the most important white pigments currently used in the world and its suspension properties are very important for consumer industries such as paints, papermaking and plastics; if aggregates are present, the end-use properties including gloss, opacity and storage stability will be highly affected. As polymeric dispersants are generally used to disperse titania pigment particles, it is very important to understand the interactions between the pigment particles and polymeric dispersants of varying functionality. Although, in principle, the adsorption of polymers onto titania pigment and influences on pigment dispersion and stabilisation are fairly known, it is nevertheless hardly possible to forecast the behaviour of a given polymeric dispersant in advance, unless to have a broad knowledge of the interaction occurring between pigment and dispersants and effect of dispersant structure upon adsorption. While only titania pigment is discussed, the issues raised may also apply to other mineral oxides such as alumina or zirconia.

Contents

1. Introduction

Titania is the most important white pigments currently used in the world, with a total annual production capacity about five million tons [1]. Today, titania is such an important industrial product which is often considered to be an indicator for economic growth [2]. Titania pigment is used widely in paint, papermaking, plastic, cosmetic and pharmaceutical industries due to its outstanding physicochemical properties. Paint industry is the most important titania pigment consumer using nearly 60% of the global pigment consumption [3]. The regulations in paint formulations restricting the use of organic solvents have seen the rapid development of water-based products. However, complete dispersion of pigments in water-based paints is fraught with difficulty; if aggregates are present, the end-use properties including gloss, opacity, tint strength, colour distribution and storage stability will be highly affected. The pigment dispersion is also effective on coatings durability during outdoor exposure [4]. Incomplete dispersion of pigment particles causes uneven colouring and the optimum effect of the pigments is not fully

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utilised. As polymeric dispersants are generally used to disperse titania pigment particles [5], it is very important to understand the interactions between the pigment particles and polymeric dispersants of varying functionality.

Extensive research has been performed on the interaction of polymeric dispersants with titania pigment particles [6–11]. The type and density of polymer functional groups play a major role in the pigment–polymer adsorption mechanism and stabilisation forces arising from the interfacial behaviour. A few studies have been undertaken aiming to investigate the effect of polymer functional groups on the pigment–polymer adsorption behaviour [12–15], and very few did practically link the results to the particle dispersion properties [16]. Furthermore, although the interactions between some industrially common dispersants and titania pigment have been studied [17–20], systematic plans to highlight the role of different dispersant functional groups have not been made rather than a few examples (such as [11]).

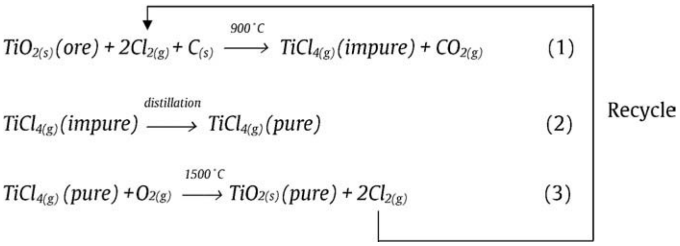
This paper presents a review of the past and recently published works related to interaction of polymeric dispersant with titania pigment. Although, in principle, the adsorption of polymers onto titania pigment and influences on pigment dispersion and stabilisation are fairly known, it is nevertheless hardly possible to forecast the behaviour of a given polymeric dispersant in advance, unless to have a broad knowledge of the interaction occurring between pigment and dispersants and effect of dispersant structure upon adsorption. While only titania pigment is discussed, the issues raised may also apply to other mineral oxides such as alumina or zirconia.

2. Titania pigment

Titania, or titanium dioxide, exists in a number of crystalline forms, the most important of which are anatase and rutile [21,22]. Titania is derived from ilmenite or leucoxene ores and titania pigment is manufactured by using either the sulphate or the chloride process [21]. The type of process used is dependent upon economic and environmental factors. For example, the chloride process produces much less and safer waste material than the older sulphate process. On the other hand, the chloride process is more expensive than the sulphate process at small scale operations [23].

In the sulphate process, the titanium raw material is dissolved in sulphuric acid. It is then precipitated from the resulting solution as titanium oxyhydrate, washed free of impurities, calcined and surface treated. Suitable titanium bearing raw materials must be soluble in sulphuric acid and include ilmenite and concentrated TiO_2 slags. The sulphate process is used to produce titania pigment in the anatase form which is used in papers, ceramics and inks. Details of the sulphate process can be found in literature [21,22].

In the chloride process, the titanium raw material is chlorinated to form titanium tetrachloride. Commercial titania pigment is primarily manufactured by the chloride process [24]. The chemical reactions in the chloride process are summarised in Eqs. (1) to (3) [24]. The chloride process involves the reaction of chlorine with synthetic rutile to form volatile titanium tetrachloride (Eq. (1)). After removal of impurity salts and further fractional distillation, the pure titanium tetrachloride is reacted with oxygen at high temperature to produce titania (Eqs. (2) and (3)). The un-reacted chlorine is then re-cycled to the process.



$$TiO_{2(s)}(ore) + 2Cl_{2(g)} + C_{(s)} \xrightarrow{900\,^{\circ}C} TiCl_{4(g)}(impure) + CO_{2(g)} \tag{1}$$

$$TiCl_{4(g)}(impure) \xrightarrow{distillation} TiCl_{4(g)}(pure) \tag{2}$$

$$TiCl_{4(g)}(pure) + O_{2(g)} \xrightarrow{1500\,^{\circ}C} TiO_{2(s)}(pure) + 2Cl_{2(g)} \tag{3}$$

Aluminium trichloride ($AlCl_3$) is added in small amounts, usually up to 5 mol% [25], to the reaction sequence at the oxidation step (Eq. (3)). At this stage, the aluminium trichloride undergoes oxidation to produce aluminium-doped titania pigment. Aluminium is added to titania pigments for a number of reasons including (a) to increase the rate of converting anatase to rutile during the base pigment formation [23,24]; (b) to reduce pigment aggregation [24]; (c) to regulate the crystal growth [23]; (d) to enhance photochemical stability by introducing defects into the rutile lattice which act as traps for photogenerated charges with TiO_2 [26,27]; and finally, (e) to improve pigment dispersability [28].

The raw pigment produced via either sulphate or chloride process is then slurried and coated with a thin layer of inorganic oxides such as alumina or silica followed by alumina in order to optimise pigment application performance including the reduction of photo-catalytic activity and the improvement of dispersion and gloss properties [29]. The thickness of the inorganic layer is very thin, in order of nanometres, particularly when compared to the pigment particle as shown in Fig. 1.

The surface composition of titania pigment controls the electrochemical properties including zeta potential and isoelectric point (iep), as well as the rheological properties such as dispersion and aggregation. Therefore, impurities at the surface or surface modifications will alter these properties accordingly. The presence of aluminium at the surface is thought to provide better particle dispersion [28]. It has been shown that the strong adsorption on polymeric dispersants on rutile came from the aluminium treatment of its surface [30]. Generally, the average surface area of untreated titania pigment is 6–9 m^2/g. However, because of increased surface roughness, the inorganic coatings may double the pigment surface area when compared to that reported for untreated pigment [21]. The surface characterisation of the pigment sample is therefore very important. After the inorganic coating is applied, the coated pigment in aqueous slurry or dry form may be treated with organic reagents, usually a polyol or amine, to modify the dispersion properties depending upon the final application [21,22].

2.1. Surface properties

The surface of titania pigment after manufacturing is not simply titanium and oxygen. While pigment particles grow, partially soluble components are accumulated on their surface [24]. These components may be either impurities present in the ore that are not removed in the purification process, or additives such as aluminium designed to control crystal structure and growth, as well as regulate agglomeration. The presence of aluminium on the surface is thought to give a better dispersion because alumina has a lower Hamaker constant than titania, 2.75×10^{-20}J compared to 6.0×10^{-20}J, respectively, and therefore decreases the effect of the van der Waals attractive forces [28].

Due to the presence of dopant at the surface, a heterogenous surface will be formed with the iep values shifted to account for the characteristics of the dopant [31] depending upon the concentrations of the surface species involved. For example, if the aluminium dopant was present on the surface in the form of alumina (α-Al_2O_3), the iep value would be increased to be similar to the iep value of alumina, depending on its surface coverage [32]. For example, an iep value of 7.8 has been reported for an industrial titania pigment (with alumina type coating), compared to the iep values around 4–5 for titania [16,28].

There is some dispute with regard to the distribution of dopants such as aluminium within titania pigment particles. Several authors claimed that dopants reside to a greater degree at the surface as opposed to the bulk [21] while others, in contrast, proposed that the majority of the dopant is held in the bulk of the pigment [33]. A study on the surface and bulk properties of the aluminium-doped titania pigment has shown that aluminium at low concentration was