



Surface protection of an organic pigment based on a modification using a mixed-micelle system



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ABSTRACT

The surface of a model red organic pigment, 3,6-bis(4-chlorophenyl)pyrrolo[3,4-c]pyrrole-1,4-dione, was modified using a mixed-micelle system containing different surfactants and polymers to improve the dispersibility of the pigment. It is shown that modifying the surface using a non-ionic surfactant and a mixed-micelle solution leads to good dispersibility of the pigment. The surface-modified pigment particles were additionally encapsulated with a SiO₂ shell to improve the UV/TiO₂ fastness. The influence of the synthesis parameters, such as the temperature and the pH, on the formation of the SiO₂ protective layer around the pigment particles and, consequently, on the UV/TiO₂ protection were investigated. The conditions leading to a compact and uniform protective silica layer over the majority of the pigment particles are discussed in detail.

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1. Introduction

Pigments are defined as colorants that are practically insoluble in most solvents and, specifically, in the media they are incorporated into by dispersion techniques [1]. Depending on the particular application, their structure, morphology and other characteristics, pigments may be classified into various categories. In terms of chemical structure, organic pigments are gradually replacing the more conventional inorganic pigments [2,3]. The properties of organic pigments (color, fastness, dispersibility) are a function of different factors, such as molecular structure, crystal-lattice properties, particle morphology and surface characteristics [1]. The molecular structure and the particle morphology give organic pigments good coloristic properties (a high value of color strength, purity of the shade), while also potentially offering a

poor dispersibility and photochemical fastness (UV stability, TiO₂ stability) [2].

A number of methods have been developed to improve the dispersibility of organic pigments, such as surfactant adsorption [4–9], emulsion polymerization [10–13], polymer and copolymer surfactant adsorption [10,14–19], the super fluid technique [20–22], or phase separation methods [23–26]. Adsorption of surfactants [27], silica [28–30] and other compounds on solid particles may decisively affect the fundamental driving forces such as electrostatic interactions, chemical interactions, hydrophobic lateral interactions, hydrogen bonding, etc. On the other hand, the functions of polymers in a dispersion are mainly to control the rheological behavior and the stability of the dispersion. In comparison, the roles of surfactants are to wet the dry powders, emulsifiers for oil-containing formulations and to provide stability against aggregation [31]. The function of the dispersion, in turn, is mainly to improve the dispersibility of the pigments in the final application.

Both of the aforementioned components, i.e., polymers [32–34] or surfactants [35–37], as well as the dispersions themselves, can be used as pretreating agents for targeted pigment encapsulation. Wu et al. [38] studied the influence of a cationic and anionic

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surfactant surface pretreatment on alumina encapsulation. Yuan et al. [35] investigated the influence of the layer-by-layer adsorption of two different polyelectrolytes on silica-layer formation. They also reported the influence of the addition of a non-ionic surfactant on silica-layer formation.

The UV protection of organic pigments is mostly based on a modification of the surface of the pigment or the encapsulation of pigment particles [32,33,35,39]. Due to its high transparency and thermal stability, silica is normally the encapsulation material of choice. Silica can be synthesized via a sol–gel procedure using waterglass [32,36] or TEOS as precursors [33], using a layer-by-layer technique with pre-prepared SiO₂ nanoparticles [34] or by the dry milling of SiO₂ with organic nanoparticles [40]. Surprisingly, silica has very rarely been used for the encapsulation of organic pigments [37].

The main aim of the present work was to modify the surface of the red organic pigment, 3,6-bis(4-chlorophenyl)pyrrolo[3,4-c]pyrrole-1,4-dione (abbreviated to *p*-Cl-DPP), or C.I. Pigment Red 254, in order to protect it against UV irradiation. As shown in the paper, due to the poor interaction of this pigment with silica, an appropriate surface treatment needs to be developed in order to form a compact, protective silica layer around the individual pigment particles. The crucial problem that is solved is the stabilization of the initial dispersion of organic particles and, in particular, the surface modification of these particles prior to the silica encapsulation. Namely, the selected model pigment *p*-Cl-DPP has an extremely incompatible surface composition for functionalization with other materials. However, we show that an appropriate mixture of ionic and non-ionic surfactants is a very good compromise for solving both problems simultaneously. Using the present approach the inherently sensitive organic pigments can be protected quite efficiently against an external chemical attack, as demonstrated in this investigation.

2. Materials and methods

2.1. Materials

The red pigment *p*-Cl-DPP (C.I. Pigment Red 254) was obtained from Clariant, Switzerland; according to the manufacturer it is without impurities, it is crystalline and corresponds to the α -polymorphic modification [42], see Fig. 1.

The cetyl trimethylammonium bromide (CTAB), poly(diallyldimethylammonium chloride) (PDADMAC) solution (low

molecular weight), hydrochloric acid, butan-1-ol and ethanol were purchased from Sigma Aldrich, Germany, while the ethoxylated alcohol 5-C₁₂/C₁₃(OC₂H₄)₅H (available on the market as Tomadol 23-5 Surfactant) (EA) was obtained from Air Products & Chemicals, USA. Potassium waterglass (solid content 28.6%, consisting of 20.4% SiO₂ and 8.2% K₂O) and titanium dioxide – P25 were obtained from Woellner, Germany and Evonik, Germany, respectively.

2.2. Preparation of modified organic pigment particles

The pigment dispersions were prepared by modifying the surfaces of the pigment particles with the appropriate addition of one of four different surfactants: cetyl trimethylammonium bromide (CTAB), ethoxylated alcohol 5 (EA), poly diallyldimethyl ammonium chloride (PDADMAC) and a mixture of cetyl trimethylammonium bromide (CTAB) and ethoxylated alcohol 5 (EA). The sample labels with the corresponding synthesis conditions are presented in Table 1. 100 g of the pigment dispersion was prepared by adding 1 g of organic pigment into water with corresponding amount of modifier, presented in the column 3 in Table 1 (amounts of added modifiers are listed as the modifier concentrations in dispersions).

In the calculation it was assumed that the pigment surface was covered with a monolayer of oil [43]. First, the surfactant or the mixture of surfactants was added to water at room temperature and stirred for 10 min to obtain a solution into which the pigment was added to obtain a dispersion. The dispersion was stirred for 1 h at room temperature and at a stirring rate of 2000 rpm, followed by sonification for 4 min at 40% amplitude using an Ultrasonic Vibra Cell (Sonics & Materials, USA).

2.3. Preparation of the silica-encapsulated pigment particles

The modified pigment particles were additionally encapsulated with silica. The already prepared dispersions of pigment particles (Section 2.2) were heated to temperatures of 70 °C and 90 °C, respectively. Simultaneously, with 0.1 M HCl, the solution of waterglass was added to the pigment dispersion until pH 8 was achieved. Different amounts of waterglass were added to the dispersion of the pigment so as to obtain the following ratios between the SiO₂ and the pigment, i.e., 0.1:1; 0.2:1 and 0.4:1 (Table 2). These ratios theoretically correspond to the formation of 3-nm, 5-nm or 10-nm silica layers on the surface of the pigment particles, assuming a 100% packing density of the silica particles. The prepared mixture was stirred for 30 min at temperature 70 °C or 90 °C, which was followed by filtering and washing.

2.4. Characterization

2.4.1. Morphological studies

The particle size distribution was measured using a Horiba LB-550, Japan. The particle surface charge was measured using a PCD02 particle-charge detector from Muetek, Cleveland Analytical, New Zealand. The silica-encapsulated and pristine pigment particles were dispersed in water and filtered through a copper net for the transmission electron microscopy (TEM) using a Jeol JEM-2100, Japan. An accelerating voltage of 200 kV was used. In order to investigate the compactness of the silica shell by TEM, the encapsulated pigment particles were pre-heated to 600 °C for 1 h in order to eliminate the organic pigment. Nitrogen-adsorption measurements were carried at 77 K using an ASAP 2020 analyzer. The BET (Brunauer, Emmett and Teller) method was used to determine the specific surface area. Thermogravimetric analyses were carried out using an STA 409 PC from Netzsch, Germany. The samples were heated from 25 to 1400 °C in an atmosphere of synthetic air.

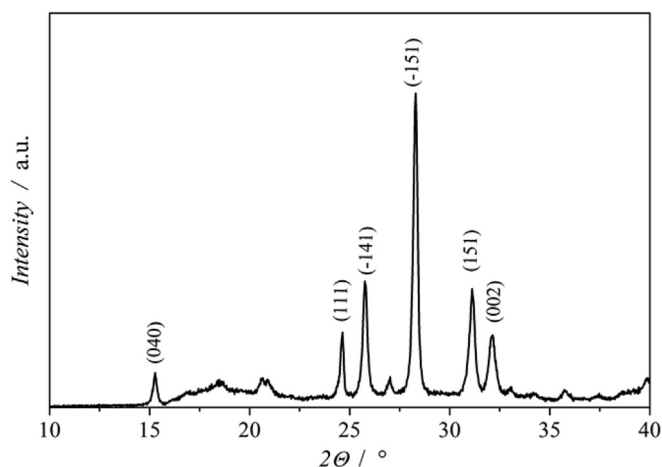


Fig. 1. XRD pattern of *p*-Cl-DPP.

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