

Application of spray techniques for new photocatalytic gradient coatings on plastics

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Available online 2 September 2005

Abstract

Transparent coating systems applicable on plastics surfaces by a spray technique are presented. The coatings are based on highly photocatalytically active nanoscaled titania powders, surface modified with silanes containing organic or fluoro-organic side chains. The modification allows for the introduction of the particles in organic inorganic hybrid NANOMER® coating systems. In the wet film—due to the evaporation of the solvents—a decompatabilisation of the coated particles to the matrix results in a self-organising gradient layer formation with an up-concentration of the active particles at the interface layer between coating and air. After activation by irradiation with artificial or natural UV-light, highly active transparent photocatalytic coatings for a great variety of materials are obtained.

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Keywords: Photocatalysis; Polymers; Gradient coatings; Titanium dioxide; Nanoparticles

1. Introduction

In 1972 Fujishima and Honda [1] described the effects of the irradiation of titania by UV-light. The development of a high oxidative potential of illuminated TiO₂, especially the anatase modification, was described as the photocatalytic effect. The effect is caused by the formation of an electron-hole pair in the semiconducting material if the photon energy exceeds the band gap, so for anatase wavelengths less than 388 nm are needed. Due to the diffusion of hole and electron to the surface, an oxidation potential of 3.2 eV is obtained. On the surface aggressive species such as hydroxyl- or hydroperoxidyl-radicals are generated from moisture and atmospheric oxygen. These species easily attack and destroy organic substances in their vicinity. The effect is described in greater detail elsewhere [2,3].

This photocatalytic principle found at first mainly applications concerning the decomposition of organic contaminants and was discussed as an advanced oxidation technique for the treatment of water and air [4–6]. Later on

it was discovered that illuminated titania also exhibited superhydrophilic properties, which were exploited for various applications with an emphasis on the self-cleaning, anti-fogging and antimicrobial effects [7].

A direct application of photocatalytically titania on organic materials like plastics, e.g. PC or PET, leads to a degradation of the substrates, resulting in the delamination of the coatings. To inhibit substrate degradation, it is necessary to provide a barrier layer between the photocatalyst and the polymeric substrate. Double- or multilayer systems have been developed, which do not allow a single-step application, thus being time consuming and causing additional costs compared to single layer coatings.

To circumvent this problem at INM a single-step coating system was developed, which does not depend on the separate application of a barrier layer. This approach is based on experimental results achieved in the nineties of the last century at INM when the self-organising gradient formation in sol-gel materials was discovered. Suitably surface modified nano particles in organic–inorganic hybrid coating matrices will enrich at the interface between coating and air during the drying of the applied wet film, leading to the formation of a gradient in the particle concentration [8]. This principle was adapted to titania particles allowing for

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the formation of photocatalytically active gradient coatings [9]. The organic–inorganic matrix systems can be tailored to special requirements and are well known at INM (e.g. NANOMER®-coatings). Besides their functionality they have the advantage of easy application methods like spray coating, dip coating and flow coating.

The work presented refers to first results of the adaptation of these coating systems on plastic materials applied by spray coating.

2. Experimental

2.1. Synthesis of anatase nanoparticles by a reflux process

162.45 g 1-pentanol were mixed at room temperature with 107.51 g titanium tetraisopropylate in a round-bottomed flask under heavy stirring. After 2 min mixing time 7.458 g of a 37 wt.% hydrochloric acid were added dropwise while continuing the agitation. Ten minutes later 7.973 g water were added in the same way. During the addition of the water, the solution turned opaque. When amorphous particles or a white precipitate was observed, the continuation of the process did not yield redispersible nanoparticles. The solution was stirred for another 20 min and the flask afterwards was transferred into a heating bath preheated to 135 °C. The mixture was held at boiling temperature under reflux conditions for 16 h. The reaction mixture was centrifuged (Megafuge 2.0 R by Heraeus, 500 ml PP-centrifugation vessels at 4000 rpm for 30 min), the liquid phase was disposed. The solid paste was transferred into a round-bottomed flask and dried using a rotary evaporator at 40 °C bath temperature and reduced pressure. Further drying could be executed in an evacuated drying chamber over night at 40 °C. About 14 g of a slightly yellowish powder was obtained. The powder was completely redispersible in toluene up to approx. 20 wt.% of nano titania with a particle size of 4–6 nm (Fig. 1).

2.2. Surface modification of the anatase nanoparticles obtained by the reflux process

1.007 g of the dry titania nanoparticles obtained from the reflux process were dispersed in 9.075 g of dry toluene by ultrasonic agitation for 15 min. This sol was centrifuged at 8000 rpm in 45 ml PP centrifuge vessels (Dow-Corning) using a Hermle Z323K centrifuge in order to remove agglomerates. The solids were discarded and the sol was transferred in a round bottom flask, mixed with 0.234 g 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl-1,1,1-triethoxysilane (FTS) and stirred in the dark for 16 h. Afterwards the solvents were evaporated using a rotary evaporator at 40 °C bath temperature and reduced pressure to obtain a dry powder. Further drying could be executed in an evacuated drying chamber over night at 40 °C.

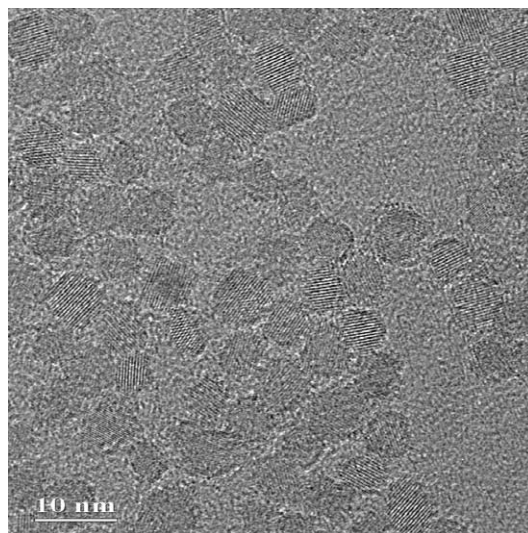


Fig. 1. TEM microphotograph of anatase particles.

2.3. Preparation of the coating materials

2.3.1. Binder

36.6 g methyltriethoxysilane (MTEOS), 11.59 g tetraethoxysilane (TEOS) and 20.4 g Levasil 300/30 (an aqueous silica sol, Bayer AG) were mixed and stirred vigorously. 0.43 g of 32 wt.% HCl were quickly added in one step. The reaction is exothermic and the mixture was stirred for 30 min until the sol was cooled down to room temperature. The resulting sol was diluted with 72 g isopropanol (other diluents have been used as well, as described in the “results” part). The diluted sol was filtrated using a 0.8 µm filtration membrane. This “binder” sol was stable in a refrigerator for at least 2 months.

2.3.2. Composite coating material

For the preparation of the photocatalytic coatings 150 mg FTS modified TiO₂-particles were suspended in 12 g of dry MEK (methyl ethyl ketone) under sonification. This mixture was added to 50 g of the binder sol and treated in an ultrasonic bath until a completely transparent suspension was obtained.

2.3.3. Coating procedure

The application of the coatings on PVC was done by spray coating and also by dip coating, spin coating or flow coating. For optimal adhesion a pre-treatment of the plastic substrates with primers (e.g. a prehydrolyzed solution of aminopropyltrimethoxysilane in 1-butanol [10]), Ar/O₂-RF-plasma or surface flame impingement (SurASil 600, SurA Chemicals, Jena, Germany) was used. After the application, the wet film was allowed to pre-dry at room temperature before the coated substrates were transferred into an oven for at least 1 h at 110 °C. The optimal thickness of these coatings was recognised to be around 1–2 µm, the viscosity of the coating sols could be adjusted by the addition of diluents like isopropanol. The photocatalytic coatings could

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