

Transparent Photocatalytic Coatings on Glass and Plastics

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Abstract

Self organising gradient coatings for a variety of substrate materials were developed. The coatings are highly photocatalytically active and are transparent. The coatings show self cleaning properties and exhibit long term stability in weathering experiments.

Keywords: photocatalysis, coatings, plastics, titanium dioxide

1. Introduction

In the 1970s the effects of the irradiation of titania by UV-light were independently described by groups in France [1] and Japan [2]. The development of a high oxidative potential of irradiated TiO₂ (anatase modification) was described as the photocatalytic effect. The effect is caused by the formation of excitons in the semiconducting material if the energy of the incident photons exceeds the band gap energy. In the case of anatase wavelengths less than 388 nm are needed for excitation. Thus an oxidation potential of 3.2 eV is obtained. On the surface aggressive radicals are generated from moisture and atmospheric oxygen by charge transfer from the excited semiconductor. These species easily attack and destroy organic substances in their vicinity. The effect is described in greater detail elsewhere [3].

A direct application of photocatalytically active 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 the 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 one-step coating system was developed. First results from the application of this techniques were presented at ICCG-5 [4].

The work presented refers to new results of the adaptation of these coating systems on plastic or glass surfaces.

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 under heavy stirring. After 2 min mixing time 7.458 g of a 37 wt% hydrochloric acid were added dropwise while continuing the agitation.

10 min later 7.973 g water were added in the same way. The solution was stirred for another 20 min and the vessel afterwards was transferred into a heating bath preheated to 135°C. The mixture was held at boiling temperature under reflux conditions for 16 hours. 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 dried using a rotary evaporator at 40°C bath temperature under reduced pressure. About 14 g of a slightly yellowish powder were obtained. The powder was completely redispersible in toluene a particle size of 4-6 nm.

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

1.007 g of the dry titania nanoparticles were dispersed in 9.075 g of dry toluene. This sol was 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 hours. Afterwards the solvents were removed using a rotary evaporator at 40°C bath temperature under reduced pressure to obtain a dry powder.

2.3 Preparation of the coating materials

36.6 g methyltriethoxysilane (MTEOS), 11.59 g tetraethoxysilane (TEOS) and 20.4 g Levasil 300/30 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. 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.

150 mg FTS modified TiO₂-particles were suspended in 12 g of dry MEK (methylethylketone) 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.

2.4 Coating procedure

The application of the coatings on plastics was done by spray-, float- spin- or dip coating. For optimal adhesion a pre-treatment of the plastic substrates with primers, Ar/O₂-RF-plasma or surface flame impingement (SurASil 600, SurA Chemicals, Jena, Germany) was often necessary. On glass substrates only an intensive cleaning involving an alkaline step was necessary.

After the application, the wet film was allowed to pre-dry at room temperature before the coated substrates were transferred into an oven. Plastics substrates were dried for at least 1 h at 110°C. Coatings on glass were cured at 450°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 easily be activated by irradiation with UV-light (e.g. from a low pressure Hg-lamp) or direct sunlight.

3. Results and Discussion

The described coating compositions were successfully applied on glass, on transparent plastics such as PMMA or PC, on soft and hard PVC, on previously coated materials such as steel painted with automotive urethane varnish or aluminium with a polyester based powder coating.

In any case a colourless coating was obtained which either retained the transparent properties of the base materials, or in case of opaque materials retained the original colour of the substrate.

The cured coatings on plastics showed hydrophobic behaviour due to the enriched fluoro organic titania particles in the interface between surface and air. The coatings cured above 400°C e.g. on glass showed contact angles of about 40-50° after curing. Either coatings obtained superhydrophilic properties after irradiation with artificial UV-light (Atlas CPS+ suntester) after 3 to 5 hours or after exposure to direct sunlight for 2 to 5 days. In any case contact angles against water of 10° and less were measured.

The low contact angles were also determined after storing the material in the dark for up to 5 days. Longer dark storage resulted in contact angles above 20°. Subsequent irradiation re-established the superhydrophilicity within several hours under natural sunlight.

The long term stability of the coatings is determined by both exposure to outdoor weather as well as by accelerated weathering. Samples on PMMA were exposed in a Xenon Weather-O-Meter for 5000 hours (68W/m² at 300-400nm, 2 h cycles with 12 min water spray in each cycle) while obtaining photocatalytic activity and good coating quality.

Samples of coatings on white PVC were exposed to the outdoor weather since July 2003 and still show superhydrophilic properties. The results of a soiling experiment are shown in fig.1. After 6 months of outdoor exposure, a coated (right column) and an uncoated (left column) PVC sample were soiled with copier toner powder as shown in the top row. After 24 h the samples were sprayed with water using a spray bottle intended for home gardening application (approx. 500ml for 2 samples of 30 x 6 cm²). On the coated sample the water almost completely removed the toner powder from the surface, whereas the uncoated surface withheld most of the toner particles (bottom row).

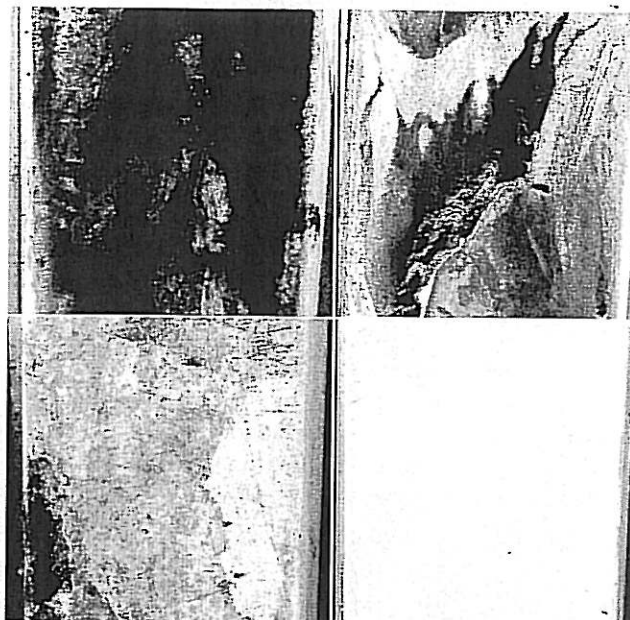


Fig. 1. Soiling experiment on white hard PVC Right column (a, c) photocatalytically coated, left column (b, d) not coated. a, b: after soiling with copier toner, c, d: after spraying with water.

4. Conclusion

The presented technique for the preparation of photocatalytic gradient coatings based on nanoparticulate titania opens up a new way for the manufacture of highly photocatalytically active surfaces on temperature sensitive materials. The small particle size of the titania used together with the presented surface modification of the nanoparticles enables the introduction into coating systems in a very simple way to form transparent photocatalytic coatings on various substrates.

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