

## Research on the synthesis and applicability of surface modified nanoscaled metal oxide particles as curing catalysers for UV-print-colours and lacquers

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### Abstract

In the BMBF joint research project – NANOCURE – New Curing Methods for Print-Colours, Glues and Lacquers (prom. ref. : 13N9115) - a new class of nanoscaled photo initiators for radical polymerization processes in the printing industry is to be investigated. A possible mechanism for the reaction of  $\text{TiO}_2$  with acrylates, which is already described in literature is presented. Different methods of manufacturing  $\text{TiO}_2$  nanoparticles in the lower nanometric size range and their subsequent processing are described, the method is of special interest as it may lead to a possible integrated production process of UV-printing inks. The TEM analysis shows the homogeneous arrangement of  $\text{TiO}_2$  nanoparticles in an acrylic matrix, which is a necessary requirement for successful polymerization process. IR-spectroscopy is used to show the effect of  $\text{TiO}_2$ -nanoparticles as UV photocatalytic polymerization initiators.

### Introduction

UV radiation curing polymerization methods are allowing a rapid upward trend in printing industry. The average growth ratio per year was about 5-8 % in the recent past. Besides the many advantages of the coating materials used for this application there is one problem which has attracted attention - especially in the field of food packaging - the migration of sometimes toxic byproducts of organic photo-catalysts [1, 2] into food.

Since October 2006 a new class of nanoscaled photo initiators for radical polymerization processes in the printing industry has been investigated.

Within the scope of the project's total objectives INM deals with several work packages. These include the improvement of material's basic properties according to crystalline and amorphous modified or unmodified metal oxides (especially  $\text{TiO}_2$ ), the tailor-made surface modification of these particles regarding their compatibility to the binder matrix (especially acrylates), as well as studies on the curing kinetics and conversion rate of polymerization in the laboratory scale. Characterization methods of these materials and coatings include material science methods and application oriented tests. Up-scaling of material synthesis in the pilot plant stage is also planned.

The technical objectives are that the new photoinitiators exhibit a good radiation energy conversion performance, that they are harmless towards the environment and human health and that they can be produced in a cost efficient way.

### Photocatalytic process and polymerisation

The formal photocatalytic process of an inorganic photo catalyst [3] such as  $\text{TiO}_2$  [4] and an acrylate monomer can be described as follows: UV-radiation exposure leads to excited states of  $\text{Ti}^{4+}$  in  $\text{TiO}_2$ , thereby promoting an electron of the valence band (VB) to the conduction band (CB) leaving an electron defect ("hole")

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in the VB. If the HOMO (= Highest Occupied Molecular Orbital) of the acrylate monomer is located above the VB of the excited  $\text{TiO}_2$ , an acrylate electron is pumped into the defect centre created. Formally the acrylate is oxidized due to the electron loss and forms an acrylic radical, whereas the  $\text{Ti}^{4+}$  becomes reduced to  $\text{Ti}^{3+}$  (colour: dark blue / grey) due to the electron assimilation. This can be optically tracked by a temporarily grey colour of the acrylate coating. The acrylate radical itself can start the intended free radical polymerization process. In order to propagate the reaction,  $\text{Ti}^{3+}$  again has to be oxidized to  $\text{Ti}^{4+}$ . This aforementioned process is electrochemically favoured because the standard redox potential of the reaction  $\text{Ti}^{4+} + e^- \rightarrow \text{Ti}^{3+}$  is  $E_0 = +0.1$  V, as  $\text{Ti}^{3+}$  is a strong reductive species which is easily oxidized. Therefore an electron acceptor must be offered. This task can be optionally fulfilled by doping the  $\text{TiO}_2$  basic structure or modifying the  $\text{TiO}_2$  particle's surface.

At a critical diameter size which, for  $\text{TiO}_2$  is 10 nm, the quantum dot effect becomes decisive for the particle's charge carrier dynamics. With decreasing particle size, the band gap of a semiconductor is broadened and its absorption is shifted to shorter wavelengths (blue shift). The shift of the absorption edge corresponds to higher redox potentials, as the VB is shifted to lower and the CB to higher energies.

In order to enable the  $\text{TiO}_2$  particles to work as a photo initiator of a polymerization reaction, recombination of the charge carriers (excited electron and hole) must

be delayed. In large particles, volume recombination prevails over the surface recombination thus leading to a low photocatalytic activity. Surface recombination is intensified by decreasing the particle size. However at a certain size recombination of electrons and holes occurs faster than the desired charge transfer with species which are adsorbed at the particle's surface. Finally the quantum efficiency of a photocatalytic reaction is given by the ratio of simultaneously running competition reactions: On the one hand the competition between charge carrier recombination and trapping (stabilization) of charge carriers and on the other hand the competition between recombination of trapped charge carriers and boundary surface-charge transfer can occur [5]. Known methods to increase the quantum efficiency are the doping of the  $\text{TiO}_2$  with metal ions [6, 7] or double semiconductor systems and sensitizing with dyes [8, 9]. These methods lead to an electron injection into the  $\text{TiO}_2$ -particle.

In addition to this, the compatibility of  $\text{TiO}_2$ -nanoparticles with the acrylic matrix is of prime importance for the project's success in order to get a homogeneous distribution of particles in the system leading to a homogeneous distribution of polymerization initiating radicals.

#### **$\text{TiO}_2$ synthesis and modification – $\text{TiO}_2$ dispersion in print acrylate mixtures and print process**

Four different methods, based on refluxing under water separator technique for



the synthesis and modification of  $\text{TiO}_2$  were investigated. A number of Ti-precursors, solvents and hydrolyzing educts were examined. The surface modifiers were added during the synthesis process or applied after the manufacturing of  $\text{TiO}_2$ . A third method used an autoclave to produce surface modified  $\text{TiO}_2$ -nanoparticles. Modifiers used included aliphatic alcohols, UV-dye sensitizers, molecules with cumulative double-bondings or aromatic parts and silanes with organic network forming groups like acrylates or epoxides. Besides modification with N or S containing surface modifiers, structure doping with pentavalent ions was also tested.

In all three manufacturing processes the end product is a powder. For application in the printing process the powders have to be dispersed in an acrylate monomer mixture, consisting of a highly viscous, fast reacting acrylate combined with a low viscosity, but slowly reacting acrylate for reactive dilution in order to get a printable ink. A number of methods were attempted to disperse the dry nano-powder homogeneously in the acrylate matrix (different stirring systems, triple roller, disc mill), but the best results have been observed by using solvents such as toluene to pre-disperse the particles. Due to the application under radiation conditions in printing industry, the use of a solvent as a dilution aid has to be avoided. So the solvent must be removed from the acrylate monomer matrix under vacuum. In the production process this would be an additional time and cost factor.

As a result, a fourth synthesis method, in which the particles were synthesized in an acrylic thinner matrix, was developed. In this method a master batch of particles was produced in a thinner acrylate which easily can be mixed with the fast curing highly viscous acrylates. The thinner acrylate matrix has to be compatible with the hydrolyzing component, while the reaction rate of the Ti-precursor and optionally the modifier has to be adapted to the changed reaction medium. The acrylic thinner matrix also should not gel or polymerize during the production process of the nanoparticles. Most of the produced particles were very small or in some cases amorphous. Nevertheless they show improved performance compared to the  $\text{TiO}_2$ -particles produced ex-situ. For amorphous particles this is not obvious at first sight, but it can be explained by the Anderson localization of electrons in amorphous materials [10, 11]. Figure 1 shows a TEM micrograph of crystalline  $\text{TiO}_2$ -particles produced in a thinner acrylate matrix.

Application of the print acrylate mixtures including the nanoscaled initiators was performed with a manual roller printing unit ("Little Joe - Model H") on PVC foil provided by a project partner. Curing was carried out with an IST-UV-Minicure lab machine ("Type M-25-1-Tr-SS"). The irradiated intensity ( $100 \text{ mW/cm}^2$  and  $200 \text{ mW/cm}^2$ ) as well as the conveyor belt speed (20 m/min up to 70 m/min) were varied. The dry-coat thickness measured after the curing process averaged between 2 and 8  $\mu\text{m}$  (measured with TENCOR P-10, surface profiler), depending on the

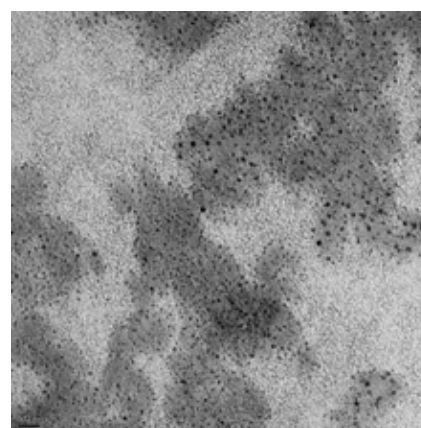


Figure 1: TEM micrograph of crystalline  $\text{TiO}_2$ -particles prepared in acrylic matrix.

- Light grey = background noise
- Dark grey patterns = dried acrylic matrix on TEM net
- Black structures =  $\text{TiO}_2$ -nanoparticles of about 1 to 4 nm diameter homogeneously distributed in the acrylic matrix

composition and viscosity of the applied acrylic matrix.

### Performance of the particles produced in thinner acrylate

The curing properties of the used acrylates and their mixtures with and without photopolymerization catalytic particles were investigated by IR-spectroscopy to assess the efficiency of the produced  $\text{TiO}_2$ . For this purpose the diminishment of the C=C-double bonding peak area (several peaks from  $1650$  to  $1550\text{ cm}^{-1}$ ) is related to the fixed C=O bonding peak area (at  $1730\text{ cm}^{-1}$ ). The ratio [C=C : C=O] therefore should become smaller for increasing C=C-double bond conversion.

For application in the printing industry 65 to 75 % polymerization is required fingerprint dry, in order to avoid the gluing of printed papers or foils in a stack. This can be calculated from the IR-spectra, using the start and end ratios of the peak areas. Figure 2 shows the required numbers of curing cycles in order to get a fingerprint dry coating using an acrylate without initiator, and one with  $\text{TiO}_2$ , manufactured in an autoclave and one with  $\text{TiO}_2$  manufactured in acrylate. Finally it was shown, that particles which were prepared directly in thinner acrylates have the most significant acceleration effect on the polymerization process.

The polymerization behaviour can also be observed if a mixture of different acrylates is used.

Cross cut / tape test on PVC foil showed an excellent adhesion of the coating ma-

Ratio  $\text{C=C} : \text{C=O}$

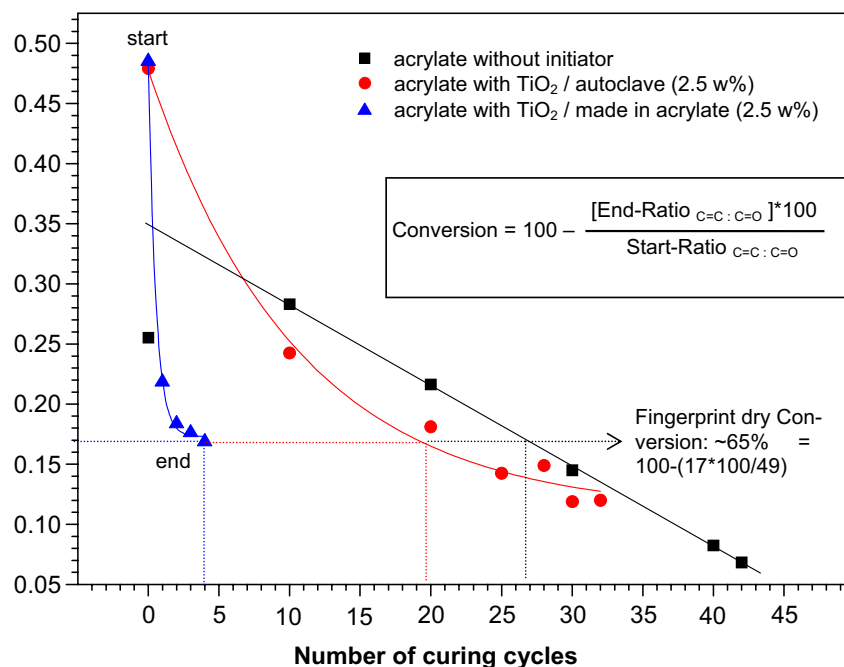


Figure 2: Needed number of cycles to get a fingerprint dry coating on PVC-foil.

terial leading to the conclusion that any possible bad influence of the nanoparticles on the adhesion is too weak to be noticed. The acrylate mixtures with  $\text{TiO}_2$  are transparent and most of them show a slight yellow color.

### Outlook

Further investigations into upscaling of the synthesis process are well underway and are being optimized. In cooperation with the other project partners, pigmented acrylates will be tested in the next step, because the acrylates will be finally used as printing colours. The long term stability of the material also must be investigated and optimized.



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