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Dear Milena:

This is the scientific report of the COST Phonasum 540 meeting WG3; 26/27 October in Lausanne.

F. Peterka: Perspectives and ISO standards for photocatalytic materials. Recent advances in bacterial inactivation

The recent trends and markets for new photocatalytic products were described regarding the use of photocatalytic materials in cars, catheters, modified TiO₂ tiles. The problems encountered when testing these materials were exposed. The activities of the ISO standardization committee was reviewed and the problems encountered in assessing the photocatalytic bactericide testing of Hydrotec tiles were discussed.

T. Mantyla: Photocatalytic coatings against bio-fouling.

The improvement of surfaces used in the beverage and paper industry was presented (submerged or splash surfaces). The TiO₂ applied by sol-gel, liquid flame and spraying and atomic layer deposition was described. Pertinent bibliography about recent work in this area and the problem with the UV application for the bactericide treatment on these surfaces was described. The role of Ag on surfaces kept in the dark is indicated. The application of TiO₂ + Ag on steel surfaces in the brewery industry was mentioned. The damage to cytoplasmic bacteria by Cu-covered surfaces is presented.

T. Egerton: Electro-activation of illuminated TiO₂ surfaces for bacterial inactivation.

The problem of carrier illumination on TiO₂ surfaces and the necessity of using a bias voltage to improve the charge carrier separation above efficiency of 3% are presented. The description of the reduction of Cryptosporidium oocyst in tap water by photo-electrochemistry with a bias of 1V applied to the TiO₂ electrode. The problem with the dye methylene blue (MB) a cationic species sold as their respective chloride not interacting with the cathode (-) is mentioned. Bicarbonate is shown to decrease the TiO₂ activity under light illumination.

C. McCullagh: The use of photocatalysis in disinfection of drinking water as alternative biocides in cultural heritage applications.

The test results on *Salmonella Enterica* on illuminated TiO₂ and *P. Aeruginosa* were presented. The general trend indicated that in the dark the bactericide abatement did not take place, but with UV-band gap illumination this bactericide effect takes place and was enhanced by light irradiation in the presence of surface-TiO₂. The problem how some bacteria growth on cement was addressed and pertinent bibliography was given. Results were presented on the abatement of *C. Vulgaris* as detected by fluorescence methods.

P. Lukes: Mechanism of bacterial killing by AOT's

An up to date review was presented about the mechanism of the destruction of *E. coli* (gram negative bacteria) and for gram positive bacteria species. The intracellular mechanism of bacterial destruction was shown to proceed with the disruption of the cell bilayer membranes by the highly oxidative radicals generated by the TiO₂ upon light excitation in aqueous media. The damage of the membrane layers increases the permeability to H₂O₂, TiO₂ affecting the core DNA. The peptide bond is referred as the strongest bond in the protein material of the different bacterial bilayers (peptoglycan layer). The nature of the groups being more susceptible to attack was described for the two types of bacteria as mentioned above. Recent bibliography was provided to back the proposed mechanisms of bacterial destruction. The ROS internal bacterial mechanism and related features were discussed.

C. Pulgarin: Parameters influencing the inactivation of *E coli* by TiO₂ photocatalysis.

The common parameters affecting the rate and efficiency of bacterial destruction of *E. coli* in TiO₂ suspension upon light irradiation were discussed. The abatement of *E coli* was defined to be completed if a suspension of *E coli* irradiated for a certain time does not show bacterial re-growth within 48 hours. This is the time usually needed for the consumption of the water after treatment. Additives in water were shown to be favorable or unfavorable for the photocatalytic destruction of *E coli* under solar light depending of the nature and concentration of the chemical species involved in each case and type of water. Photosensitized effects of chemical species in natural waters were presented in their favorable action on the abatement of *E coli* in natural processes and the residual effects of photocatalytic processed were discussed in disinfection processes.

P. Fernandez: Inactivation of *Fungi* by TiO₂ photocatalysis.

Work was presented that is important the field of phytophysiology and associated sicknesses. *Fussarium equiseti* was presented as the most resistant Fungi to TiO₂ photocatalytic abatement treatment starting with a concentration of 10³ CFU/L. It takes about 10 hours to abate totally the Fungi by photocatalytic means. With UV light the abatement of Fungi proceeds but it is not so effective as when TiO₂ is present. The TiO₂ is adsorbed in the wall membranes of Fungi and also of *Fussarium oxysporum*. The allowed limit *Fungi* in tap water is 1 CFU/100 ml equal to the limit allowed for bacteria in EU countries. The TiO₂ suspension changes their pH during the abatement of Fungi from 5.8 to 4.5 probably due to the highly oxidative reaction described below since the TiO₂ hole oxidation reaction $h^+ + H_2O \rightarrow H^+ + OH^0$ is important in trans-membrane and cross film processes.

V. Nadtochenko: TiO₂ photocatalytic damage to *E coli* cell walls.

The systematic study of the damage of phospholipids, polysaccharide and peptoglycan bilayer membranes found in *E coli* during the presence of TiO₂ during the photocatalytic degradation under solar light illumination was described. Also the *E coli* cell inactivation in periods close to 30 min was shown in detail. The methods to follow the membrane damage were IR, AFM and spectroscopy in the UV-Visible region. The introduction of double bonds in the cell wall membranes was taken as a measure of the degree of peroxidation of *E coli* cell wall membranes. The decomposition of the membranes in the initial irradiation period was observed to lead to toxic products that were subsequently degraded within longer irradiation times. Tetra-nitromethane was used as probe to test the mechanism involving the highly oxidative species generated on the TiO₂ under illumination leading to membrane cell degradation.

U. Lavrencic/I. Doska: Photocatalytic and bactericide coatings in Slovenia.

Low and high temperature coatings of TiO₂ prepared by sol-gel methods were described on glass surfaces. Surfactants were used to introduce more a more structured surface, higher surface area and increased porosity on the TiO₂ crystalline coating on the glass surface. Results were presented involving surfactants as Pluronic F-127, Brij 56 and TritonX-100. SiO₂ layers on the glass applied before the TiO₂ film were also tried to avoid the diffusion of Na-ion in the glass during the thermal period associated with the TiO₂ film preparation on this substrate. DMPO in EPR studies was described as been able to detect the radicals in TiO₂ photocatalytic processes and differentiate between OH^o and HO^o radicals.

R. Dillert: TiO₂ recent developments and applications.

Several recent reports were presented focusing on the possible toxicity of TiO₂ nano-crystalline powders on human health and possible associated effects on specific structures and organs. This topic is of topical interest due a growing concern of the toxicity associated to nano-materials effects on human health. Recent reports on this subject were presented. Some workers found that the reactive O-species (ROS) had some effect on brain cells, specifically on brain microglia and had damaged the brain neurona. Other report showed that there was no effect of TiO₂ on the growth of mammalian cells. The situation seems to be controversial and needs further exploration.

R. Hayden: Irish research on bactericide surfaces.

This report addressed the preparation of a new kind of TiO₂ having 3 times higher pore size than of anatase without the urea additive calcining only at 200 °C. Ti-isopropoxide was mixed in a 1:1 ratio with urea and subsequently calcined at this relatively low temperature. The TiO₂ was tested against control samples during the photo-induced discoloration of rhodamine. Bactericide surfaces were discussed in terms of these new TiO₂ film preparations pointing out to the beneficial addition of other bacteriostatic metallic agents like Ag-ions and Z- ions and their incorporation into the TiO₂ films.

J. Kiwi: TiO₂ self-cleaning textiles under light irradiation and Ag-bactericide textile performance in the dark.

The techniques to activate natural and artificial fibers or the combination of both were described. The details of plasma and vacuum-UV activation were cited in relation to the activation of tissues of different origin. Coating techniques with sol-gel and powders or combination of both led to self-cleaning effects when irradiated with lamps of different intensities. Techniques to measure quantitatively the self-cleaning effect on textiles were discussed and the characterization of the TiO₂-clusters on the textiles presented. There is no standardization of the norms to make the self-cleaning performance acceptable to the market for large-scale consumer products like sacks or shirts. Silver loaded surfaces on activated surfaces or not were discussed and tested in the abatement in the dark of *E coli* on artificial fibers and natural fibers (cotton textiles).

O. Prieto: Functional applications of TiO₂

The results from photo-degradation experiments in liquid and gaseous phase were reported. The photo-degradation of phenol and coloured effluents with TiO₂ P25 were carried out using a Taguchi's Parameter Design Method. In gaseous phase, the innovative fluidized bed photoreactor has been used for degradation of TCE and toluene. The TiO₂ sepiolite photocatalyst was presented and its particular performance during the degradation of TCE. The sepiolite enhanced the adsorption of TCE to provide more contact with TiO₂ possibly accelerating the degradation kinetics of TCE. In the study of photodegradation of toluene, the deactivation of a photocatalyst has been observed. Benzoic acids and benzaldehyde were detected as degradation products of toluene. A new research based on prepared self-cleaning and antibacterial buildings materials, that is funded by a national project were presented. The details of FP7 including a priority No4 "Nanosciences and nanomaterials. New products and research" and priority N^o6 "Environment" were addressed for information purposes

N. Bengtsson: Applications of TiO₂ to construction materials

The effects of TiO₂ on the cement microstructure were reported. The effect of Cl-anion and of the CO₂ adsorption on the structural changes of cement containing and not containing TiO₂ was presented. The penetration of Cl-anion on building blocks was analyzed quantitatively within a 2-year period. The Cl-anion penetration did not affect the cement microstructure. The TiO₂ doped cement was tested on the degradation of methanol and acetone. Also CO₂ from kitchen outlets and next to the highway was investigated in relation to the alteration of the cement microstructure.

General Discussion

The points discussed were:

- The need to correlate WG3 work in the textile, construction and health field with the guidelines under discussion in the WG2 working group of Phonasum 540.
- To carry out industrial related research without the interference of industrialists.

- The necessity to invite more specialists and outside groups to achieve the objectives of WG2 in the project.
- Focus 2 or 3 research projects with the participation of different groups of WG2.
- The necessity to try the bactericide surfaces on other bacteria than *E coli*. Health related bacteria of hospitals like Staphylococcus Aureous.
- To increase the bactericide action in tiles of TiO₂ by the addition of Ag and Cu.
- The need to work on the improved TiO₂ deposition on stainless steel plates as used widely in hospitals. To measure bacterial abatement in the solid –gas interface.

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