

SCIENTIFIC REPORT

2nd Meeting of Working Group 2

Photocatalytical Applications, Standardization and Testing Methods

Hotel Vltava, Řež u Prahy, Czech Republic, 19-20 April 2007

Following Scientific Report from the 2nd WG2 meeting was written by Dr. John Colreavy (CREST). Full presentations given at the meeting are available through authorized access on the website of COST Action 540 (www.cost540.com) and will be also sent to all active participants of the meeting on CD-ROM during May 2007. Meeting was opened by Dr. Ondrej Kunc, head of Czech Normalization Institute (responsible for standards). During the meeting representatives and experts from COST Action 540 European countries gave brief survey about actual situation regarding photocatalytic applications and testing towards industrial applications in their countries. Dr. Gerard Riviere, president of CEN/STAR, informed about CEN and possibilities to propose CEN photocatalytic standards. There were also invited experts in the field of photocatalysis and ISO methods from Japan (Dr. Koji Takeuchi, Mr. Tatsuya Imura, Mr. Shig Kato) and Taiwan (Prof. Antony S.-T. Chiang) in the meeting. In summary, approx. 60 participants from academia and industry attended Prague's meeting incl. 31 COST540 MC, WG members and invited experts.

Dr. Frantisek Peterka
Chair of COST540

Day 1, 19th April 2007

Prof. Günther Rupprechter (Vienna University of Technology, Vienna, Austria)

Photocatalytic Materials and Applications in Austria

The first presentation outlined 1) Spin-coated TiO₂ thin-films, 2) TiO₂ nanomaterials prepared by MOCVD and hydrothermal processing, 3) double-face[“] TiO₂ nanoparticles, 4) potential industrial applications 5) standardisation and testing. Prof. Rupprechter described photo-electrochemical measurements to examine photocurrent vs. wavelength measurements and degradation concluding IPCE (Incident-Photon-to-Current Conversion Efficiency) depends on wavelength, light intensity and sample morphology. With degradation, mass transfer limitation occurs due to the fast reaction on the surface of the photocatalyst. The Phonas project was also described, outlining anatase nanoparticles on various substrates, such as glass and topo-selective masking of nanoparticles. Standardisation in Austria is looking at furniture, air treatment and water treatment, however no national standards yet validated in Austria.

Dr. Benoit Kartheuser (CEntre de Ressources TEchnologique en CHimie (CERTECH), Belgium)

Survey of Belgium's Activity on Photocatalysis

Active groups in Belgium are: *Universities* - Antwerpen, Gent, Liège, Namur; *Research Centers* - Belgian Road Research Center (BRRC), Coatings Research Institute (CoRI), Centre Scientifique et Technique de la construction (CSTC), Belgium Building Research Institute (BBRI), Centre Technologique en Chimie (CERTECH); *Industry* - Acerlor Mittal, Codume.

Mesoporous nanotubes were described from Antwerpen, the University of Gent are exploring the breakdown of ethanol; CMI are examining self-cleaning glass through the FP6 project 3-NMP 505952, BRRC; CoRI and CSTC/BBRI are exploring building materials, in particular tiles and outlining the test method following the proposed ISO standard "Fine ceramics (advanced ceramics, advanced technical ceramics) – Test method for air purification performance of photocatalytic materials – Part 1: Removal of nitric oxide", ISO TC 206/SC N. A system to develop accelerated algal growth was also described. Arcelor's activities in air purification, self-cleaning and anti-microbial systems were outlined, describing the modelling tools employed.

Prof. José C. Conesa (Inst. de Catálisis y Petroleoquímica (CSIC), Madrid, Spain)

Photocatalytic Technologies and Expertise, Commercial Products and Activities Related to Testing Methods. Situation in Spain

Besides studying air and water purification, over 24 researchers in Spain are examining photocatalytic behaviour in the following areas, Visible light-active solid photocatalysts, Photo-Fenton processes, Use of dyes and organics as photocatalysts (in solution or adsorbed), Thin film growth with physical deposition techniques, insertion in monoliths and microporous solids, advanced spectroscopic studies (XAFS, EPR, NMR, XPS), applications in building materials, H₂ production, incorporating TiO₂ in plastic food containers, selective organic synthesis, photo-electrochemical studies, photovoltaic dye cells. Specifically, the technology centres that are active are, INASMET, S. Sebastián/Donosti (F. Cano functional coatings), CARTIF, Valladolid (O. Prieto building applications, textile industry), LABEIN, Zamudio (Y. de Miguel functional coatings), LEITAT, Terrassa (L. Bautista textile applications), GAIKER, S. Sebastián/Donosti (A.I. Díaz water disinfection), INESCOP, Elda (A.C. Orgilés footwear, rubber). Industrial affiliations are not readily ascertainable. Available information shows emerging commercial activity. Ecosystem Environmental Services S.A. Barcelona, produces photoreactors for water cleaning (TiO₂ or photo-Fenton), with designs made in cooperation with PSA and other labs. Beissier S.A. (Erretería; acquired by STO AG) will shortly commercialise StoClimasan (a self-cleaning painting containing vis-active TiO₂), in Spain. Other commercial activities include, textile and shoe industries, materials for buildings and water supply services.

Dr. Ralf Dillert (Gottfried Wilhelm Leibniz Universität, Hannover, Germany)

Photocatalytic Companies in Germany

Commercialisation of PC products is strong in Germany using Japanese technology. The following companies were mentioned, **Pigments** –Degussa, Kronos, and Sachtleben, **Self-cleaning surfaces** – Nano-X, Pilkington, Saint-Gobain, **Coatings**: Genthe-X, Gpn-GmbH, Iridia-Titam; **Indoor-Air applications** – Alpina (Alpina Air Clean), STO (Climasan Color), Caparol (Thermosan) Window profiles- Profine, **Roof tiles**- Erlus.(Elrus-lotus); **Paper** – Vitan-Papier (product of Japanese EIN Engineering), **Air-conditioning** -DAIKAN. Dr Dillert stated that active research was underway at Siemens, BMW, Daimler-Crysler, Hella, Pilkington active.

Dr. Andrijana Sever Škapin (Slov. National Building and Civil Engineering Inst., Ljubljana, Slovenia)

Recent photocatalytic R&D activities in Slovenia

Research centres that are active are, University of Nova Gorica, University of Ljubljana, Slovenian National Building and Civil Engineering Institute - ZAG Ljubljana, National Institute of Chemistry, Ljubljana, Jožef Stefan Institute, Ljubljana. Active companies are JUB, d.d. – coatings, HELIOS, d.d. – coatings, TONDACH Slovenija, d.o.o. – roofing tiles, SIPA Kobarid, d.o.o. – easy-cleaning surfaces. The approaches to testing for PC and superhydrophilic activity were outlined as discoloration of an organic pigment, determination of quantum yields, system liquid-solid: monitoring of degradation of a dye in aqueous solutions by UV-VIS, system liquid-solid: monitoring of degradation of various POPs in a novel Carberry type photoreactor, combination of two AOPs: Photocatalytic Ozonation, testing of anti-bacterial activity, developing of some other new methods. Detailed experimental setups were outlined. Details on the Eureka project E!3969 - CLEANTILE (2007-2009): *Development of Self-Cleaning Clay Roofing Tiles*, were given.

Dr. Christos Trapalis (Institute of Materials Science, NCSR Demokritos, Attikis, Greece)

Photocatalytic Research and Applications in Greece

Research groups active in PC studies are, University of Patras (Prof. P. Lianos, Prof. X. Verykios, Dr. E. Stathatos...), Technical University of Crete (Prof. D. Mantzavinos,...), University of Ioannina (Prof. T. Albanis,...), Aristotle University of Thessaloniki (Prof. I. Poulis,...), and NCSR Demokritos (Dr. P. Falaras, Dr. C. Trapalis,...). Active industry in Greece was described as follows, TITAN S.A. – Cement, PHILKERAM JOHNSON S.A. – Ceramic Tiles, INDUSTRIAL MINERALS Ltd – Cement Ground, MONOTHERM S.A. – Self Cleaning Glass (Small glass pieces for construction applications), EPILECTOS S.A., Textile and Fabric, PYROGENESIS S.A. – Thermal Deposition of Inorganic Coatings on Metals, for Construction Applications. NCSR research with Titan was described. The aim was the development of visible Light Active Powders by Anion Doping (N, F -TiO₂) using a combination of Sol-Gel and Flame Spray Pyrolysis (FSP). N-doping was achieved with ammonia gas or urea wet chemistry. The work on antibacterial Self-Cleaning Tiles based on TiO₂ Coatings with PHILKERAM JOHNSON S.A was also described. Other research interests, using soft-chemistry routes, were presented. Photocatalytic materials being, visible Light Active Nanoparticles and Thin Coatings (TiO₂-xN_x, TiO₂-xF_x, TiO₂-xS_x...), antibacterial Composite Materials (AgSiO₂, CuSiO₂, AgTiO₂...), Hollow Nanospheres (TiO₂), Magnetic Materials, Nanocomposite Magnetic Materials (metaloxides, metals), Bimetallic Magnetic Nanoparticles (FePt, CoPt), Functionalized Inorganic Nano-Pigments and Carbon Nanotubes (CNT) and Magnetic Clay Nanocomposites and Hollow Clay Microspheres.

Dr. John Colreavy (CREST Centre Director; Focas Institute, Dublin Institute of Technology, Ireland)

Review of Research in the Republic of Ireland on Photocatalytic Materials

The research activity was outlined in Ireland consisting mainly of nationally-funded and FP6-funded research in PC development for hygiene control (Dr. Sureah Pillai, Dr Hugh Hayden - CREST), water purification (Dr. Kevin McGuigan Royal College of Surgeons) and optical signal processing enhancement (Prof. Martyn E Pemble, Tyndall National Institute, University College Cork). Prof. Pemble's work involves coloured oxide-derived semiconductor (SC) nanostructures for visible light photocatalysis, Photocatalytic inorganic-organic hybrid nanostructures, Nanocomposites SC-SC, Metal-SC and other strategies for improved charger carrier separations, Engineering of photocatalytic wave guides (thin film technologies). Prof. Pemble a participant of

EU Project PHOTOCOAT, No. GRD1-2001-40791 (established and held by MEP at the University of Salford, UK), with partners, Uni Salford, Uni Strathclyde, Uni Westfalian, Uni Duisberg-Essen, Fraunhofer Dresden, St Gobain, Pilkington, EADS, Thysson-Krupp, EMPA, DACS, Galileo-Avionica).

Prof. Claudio Minero (Università di Torino, Torino, Italy)

Standardisation: The Needs

Standardisation must answer the question from the market to include final user expectation, and to reflect producer/seller advertising/market penetration requirements. Also, the suitability of a product for use requirements (efficacy, chemical durability, mechanical properties) and assessment for the type of application (materials, goods, substrates). In particular, it was emphasized that common to all tests is the principle that standard tests have to avoid discrimination, which is a preferential evaluation for some materials depending on the test conditions. The efficacy, chemical durability and by-products of materials must be addressed. The standard test method for goods must use simple and affordable instrumentation, define standard chemical analysis specifying substrates, conditions and detection methods. Prof. Minero stated that if one is following species such as OH[•] or by-products one must ensure that all of the species catalysed are being detected.

Comment: Frantisek Pererka stated that consideration of the latter point would be presented in the discussion on ISO methods.

Comment: José Conesa stated that EPSR analysis can be an accurate method for tracking OH[•] generation, although concentration cannot be reliably measured.

Prof. Tapio Mäntylä (Tampere University of Technology, Finland)

Standardization – Photocatalytic Research in Finland

So far there has not been any official activities for standardization within the PC field in Finland. Also the different research groups have tested photocatalytic activity by testing the degradation of stearic acid films and methylene blue, bacterial destruction or photocatalysis induced hydrophilicity. Depending on the intended application one could, measure the change in concentration of an impurity, measure the anti bacterial effects, observe the fouling behaviour of a surface, measure the colour change of an organic colorant, observe/measure the change of contact angle of a water droplet on the surface, measure the formation of reaction products from the decomposition of organic compounds. Using 2-propanol and acetaldehyde-toluene as model compounds, the efficacy of Kemira pigments against competitors was examined. CO₂ or intermediary compounds generation, such as acetone can be followed. Ongoing research at Tampere University was detailed as, advanced surface modification for cleaner paper machine, improving the cleanability of process surfaces in the beverage industry, titania modification and titania composite (TiO₂ + Ag etc) coatings by ALD, Sol-gel process and thermal spray techniques (LFS). Prof. Mantyla described the research activities of Kemira (powders) Millidyne (sol-gel manufacture), Beneq Oy (Nanopowders).

Comment: José Conesa commented that the humidity levels have a significant influence on the degradation of toluene.

Prof. Carlos J. Tavares (Prof. Adélio Mendes FEUP Portugal)

Photocatalytic Research and Technologies in Portugal

LEPE started recently doing research on NO_x photo-oxidation based on paint films, dye-sensitised solar cells (DSC), self-cleaning surfaces and organic volatiles photo-oxidation. Prof. Mendes

described the development and study of paint coatings additives, for photocatalytic oxidation of NO_x. The collaboration in the BRITE-URAM project with Germany, Italy and CIEMAT PSA-Almeria in Spain was also outlined. The work of on photocatalytic TiO₂ thin films deposited by dc reactive sputtering was described. The removal of coffee stains from titania-treated textiles was presented.

Question: John Colreavy enquired into the retention of mechanical properties.

Comment: John Kiwi stated that the mechanical properties actually improve.

Dr. Beata Tryba (Szczecin University of Technology, Poland)

Photocatalysis in Poland

Active research centres in Poland were identified as, Cracow University of Technology, fundamentals of catalysis, Preparation of nanocrystalline TiO₂ by sol-gel method, Testing of TiO₂ in gas-phase oxidation, Photoelectrochemical oxidation on TiO₂, Warsaw University of Technology-Testing of TiO₂ photocatalytic material for water purification, Adam Mickiewicz University, Poznań University of Economics-Testing of photocatalysts for water purification; Wrocław University of Technology-The photocatalytic hydrogen generation by water splitting; Gdańsk University of Technology -Testing of TiO₂ for decomposition of toxins; Technical University of Lublin-Testing of TiO₂ for water purification.

Dr. Florin Dan Vasiliu (National Institute of Materials Physics, Bucharest–Magurele, Romania)

Characterisation and Photocatalytic Activity of Some Undoped and Doped TiO₂ Materials

Various undoped TiO₂ and cation (Fe, Eu) and anion (N)-doped TiO₂ systems, nanoparticles, and aerogel films were synthesized by various methods (high energy ball milling, hydrothermal, supercritical drying, sol-gel, pulsed laser deposition, reactive magnetron sputtering). X-ray diffraction, electron microscopy, XPS, Raman spectroscopy, EXAFS, XANES, Mössbauer spectroscopy were used to study the structure, morphology and substitution in the nanosized samples. Important red shifts (20-35 nm) had been registered for some systems and the N-doped TiO₂ films prepared by reactive magnetron sputtering; these materials have super-hydrophilic characteristics, offering the possibility to use a wider range of photon energies (including visible light) for photoactivation of the catalytic and hydrophilic properties. Photocatalytic activities of doped TiO₂ nanosystems have been tested by measuring the degradation rate of the salicylic acid used as reference organic TiO₂ material and by photocatalytic oxidation of styrene. Their photoreactivity is higher or comparable with the Degussa powder's activity, making them attractive as efficient photocatalysts in the wastewater depollution.

Dr. Cathy McCullagh (The Robert Gordon University,UK)

Modification of TiO₂ Following Exposure to Laser Sources

The influence of laser treatment was outlined and in particular the effects of treatment on properties such as surface area, band gap and anatase/rutile ratio demonstrated. Conclusions were, that the crystalline phase changes in TiO₂ following laser treatment together with generating Ti³⁺ sites. The conversion of anatase to rutile forms could be followed using this method. Photocatalytic activity of TiO₂ is marginally affected by crystal phase of the material. Dr. McCullagh stated that work on standardisation undertaken by Dr. Andrew Mills in the UK and was reported on his website.

Dr. Shigekazu Kato (Vice chairman of International Committee Photocatalysis Industrial Association Japan)

State of Art of photocatalytic Applications in Japan

The value of the Japanese market was estimated as being €300M with 3,000 companies involved. The European market value was estimated as being €100M. The patent versus publication ratios, contrasted starkly between Europe and Japan. The history of the evolution of PC was presented from the early work of Honda-Fujishima published in Nature in 1972, up to the first mass production of self-cleaning glass in Japan in 2004. The delay in market uptake was discussed and attributed to; credibility for consumers, standardisation, cultural changes and safety concerns. Recent commercial successes were outlined as Self Cleaning (Housing Exteriors, TENT canopies, Glass Window), Air Purification (Odor Decomposition, VOC Decomposition) and water purification. The reasons for the market drive for research in PC in Japan were described as follows, Consciousness of the Environment, Mind Shift from “Application R&D” to “Innovation R&D”, Mind Shift to “Growing seed technology originated in Japan”, Tendency to maintain clean surroundings. Photographic data was presented showing many applications in Japan and Europe, in particular showing the application of anti-bacterial coatings applied by High Volume Low Pressure (HVLP).

Dr. Koji Takeuchi (Research Institute for Environmental Management Technology (Emtech), National Institute of Advanced Industrial Science & Technology (AIST) Tsukuba, Japan)

Status of ISO Standardization in Photocatalytic Field Initiated by Japan

The urgent need for standardization is due to rapid commercialization in Japan, Asia and Europe and a subsequent strong demand for protection of consumers, by prompt standardization. Sales in PC products in Japan have risen from €150M in 1999 to €300M in 2003. It was decided to modify an existing standard rather than adopt a new one due to the urgency. The ISO/TC206 fine ceramics: scope was defined as ‘ Standardization in the field of fine ceramic materials and products in all forms: powders, monoliths, coatings and composites, intended for specific functional applications including mechanical, thermal, chemical, electrical, magnetic, optical and combinations thereof. The term “fine ceramics” is defined as “a highly engineered, high performance, predominantly nonmetallic, inorganic material having specific functional attributes”. The following timeline was presented regarding proposals NO_x – 2003 JIS/2004 ISO; VOC – 2005 JIS/2006 ISO; Malodorous substances 2006JIS/2007ISO; Antibacterial – 2005JIS/2005ISO; Antifungal – 2006JIS/2007ISO; Water – 2006JIS/2006ISO. The timing of each stage was presented as follows, 2003-10-03 Proposal, 2004-05-13 WD, 2005-04-01 CD, 2006-05-02 DIS, 2007-03-16 to be published. The national experts in the relevant WG 37 were from China, Germany, Indonesia, Italy, Korea, Japan, Malaysia, UK, USA.

Prof. Anthony Shiaw-Tseh Chiang (President of Taiwan Photocatalyst Industry Association TPIA, Taiwan)

Current Status on Photocatalytic Application and Testing Methods in Taiwan

The association was established in 2004. It was stated that the SARS outbreak triggered the interest in hygiene and anti-bacterial solutions. Certification protocols and labels were established in February 2005, followed by two testing standards announced in September 2005 and another to follow in 2007. Descriptions were given of the standard methodologies and the balancing pro’s and con’s presented. Details of the standards are, TPIA-A1: NO_x mineralization for photocatalytic activity in air; TPIA-B1: Antibacterial test based on *Escherichia coli* or *Staphylococcus aureus* and TPIA-T1-1: Super-hydrophilic & easy clean test announced as a new standard for January 2007.

Photographic evidence was presented of in-service performance of photocatalytic (PC) coatings on glass facades, facade tiles, stainless steel cladding and automotive paintwork. The standardization development was critical to gain the trust and confidence of the market and the public. Architects and real estate developers see the new technologies as a niche advantage in their offer. Variations in humidity affect the PC effect. Cleaning of the substrate is vital prior to application and the resultant film thickness achieved is about 50nm.

Question: It was asked why the solution was yellow?

Answer: The solution was buffered to a natural pH, hence the yellow colouration.

Dr. Gérard Rivière (President of CEN-STAR)

Standardization as Tool to Diffuse Research Results and to Promote Innovation in Europe – Introduction of CEN, CEN/STAR, ISO-CEN Relation

Dr Riviere revisited the Nice Treaty TITLE XVI INDUSTRY ART. 157 ‘fostering better exploitation of the industrial potential of policies of innovation, research and technological development’ to understand the need for and commitment to encourage standardisation within the community. It was stated that standards are a convenient and effective way of disseminating research results in addition to patents and papers. The means by which the EU supports research was detailed and the commitment to “pre-normative” and “co-normative” research relevant to improving the quality of standards and their implementation.” (Ref. Council Decision 1982/2006/CE 18 December 2006) cited. Norms and standards increase safety and allow interoperability, increase understanding and information transfer, promote competitiveness of industry and increases competition, are the basis for agreement on the design, manufacture, performance and testing of products, services, or operations, and are greatly dependent on the input from R&D. COST *Lighting in the XXIst Century* COST Action 221 was cited as a model for effective CEN-STAR interaction with researchers. The importance of instruments such as the Technology Platforms as well as cost actions for supporting the development of norms and standards was emphasized. CEN standardization means that adoption by the national standardization bodies of member states has occurred.

Dr. Koji Takeuchi (Research Institute for Environmental Management Technology (Emtech), National Institute of Advanced Industrial Science & Technology (AIST) Tsukuba, Japan)

Development of Test Methods for Photocatalytic Air Purification Materials as JIS and ISO Standardization Activity

It was stated that the test method should, be accurate and reliable, be simple and easy-handling, use common not special instruments, give results in short-time or real time, be capable of being used in the field, provide information for various performances, be low cost and be safe (without using toxic gas, ...). Large-scale field trails showed that performance was dependent on UV, [NO_x] and place, long term durability was good (>3yrs), automatic neutralization occurred with particulate matter and self-cleaning effect was manifest. The ISO/DIS 22197-1 method was described. Nitric oxide (NO) was chosen as a model as it is one of the most common, important air pollutants, has simpler chemistry, less intermediates (NO, NO₂, NO₃⁻), enables evaluation of both oxidation and sustaining powers due to build-up of oxidation product (nitrate). NO is the primary pollutant emitted from combustion sources and enables testing both species by producing NO₂. Model VOC were, (NO_x), HCHO, CH₃CHO, Benzene, Toluene, NH₃, (CH₃)₃N, H₂S and CH₃SH. Findings on VOC degradation were; plexiglas reactors can be used without adsorption problems, conversion to CO₂ is good for CH₃CHO, but not for toluene, indoor level analysis of reactants and CO₂ is very difficult, some materials (e.g., paper) produce CO₂ under illumination, (*CO₂ formation is not always the best index*) higher toluene concentrations cause irreversible change of surfaces and

materials containing adsorbents make the tests very difficult. Three methods were explored, gas-bag, continuous flow chamber and the small chamber method. Test method A was identified as a cost effective, rapid means to test available to most labs.

Comments: John Kiwi stated that the plastic bag (possibly Tedlar) had a cut-off below 400nm.

Question: John Colreavy asked if inherently mesoporous TiO₂ films could be used to instead of a binder supporting TiO₂ nanoparticles. Why choose toluene and have lower vapour pressure VOC's such as glycols been examined.

Answer: Toluene replaced benzene and the vapour pressure of the glycols are too low to facilitate effective detection and quantification.

Dr. Tatsuya Imura (chairman of Standardization Committee of Photocatalysis Industrial Association Japan)

Development of ISO Standard for Self-cleaning of Photocatalytic Materials

Dr. Imura described the efforts undertaken to establish a JIS SC standard for self-cleaning glass. Membership is as follows. TOTO. LTD, Toshiba Lighting and Technology Corp., Nippon Soda Co, LTD, Nippon Sheet Glass Co., LTD, Sekisui Jushi Technical Research, Matsushita Electric Works Ltd, Bau Corp., Toyota Central Research and Development Labs. Inc, Kawasaki Heavy Industries Ltd. The technical membership is, National Institute of Advanced Industrial Science and Technology (AIST), Building Research Institute, Hokkaido Industrial Research Institute, Tsukuba Building Test Laboratory, with the Japan Fine Ceramics Association as Secretariat. Three performance prediction tests were developed and examined in light of data collated from environmental exposure programmes in the field. Test 1 involved evaluating the degradation of Oleic Acid on the PC substrate under specified irradiation. Test 2 involved simply following the decay of the contact angle with UV-irradiation time. Test 3 involved monitoring the degradation of methylene blue with UV-irradiation time. Test 1 was selected on the basis of manifesting the best correlation with field-exposure data. The irradiation was specified as, black light fluorescent lamp which has a peak wavelength of 352nm, and emits light with a half band width of 40nm (a fluorescent lamp which uses BaSi₂O₅:Pb as the phosphor, and uses a visible light absorbing glass tube). The evaluation indices were agreed as being, contact angle after 12, 24, 48 hours and the final (steady-state) contact angle.

Dr. Pavel STAHEL (Advex Instruments s.r.o., spin-off company of Masaryk University, Brno, Czech Republic), Dr. Frantisek Peterka (NANOPIN, Czech Republic)

Introduction of Evaluation System Designed for ISO Self Cleaning Method, Practical Demonstration

A cost-effective device was presented that allows accurate and rapid determination of surface-free-energy through contact-angle measurements. The development of the software was aimed at the self-cleaning performance evaluation according to the ISO standard ISO TC 206/SC. In 2000, the first version of SEE System was developed at Department of Physical Electronic, Faculty of Science, MU Brno (St'ahel, Navrátil, Buršíková, Janča.), in 2006 modification for ISO photocatalytical self cleaning performance standard was made. System for ISO testing will be commercially available in second half 2007 by contacting NANOPIN. With both softwares device seems to be excellent handy multifunctional device for surface investigation for reasonable price for each laboratory.

Day 2, 20th April 2007

Dr. Gérard Rivière (President of CEN-STAR)

Information about CEN System and Possibility to Propose CEN Photocatalytic Standards, Harmonizing CEN with ISO

The rationale for a common strategy on norms and standards was reiterated from the previous day. Increase safety and allow interoperability, increase understanding and information transfer, promote competitiveness of industry and increases competition. They form the basis for agreement on the design, manufacture, performance and testing of products, services, or operations and are highly dependent on input from R&D. The values and principles are based on, transparent, consensus-based working forum open to all interested parties; standstill national commitment, binding decision and national transposition with withdrawal of conflicting standards (EN!); freely agreed, voluntarily applied and verifiable compliance, coherent set of specifications and a state of the art, 3 or 5-yearly review. The actual process was described as, Proposal (NSO, European Federations, Industry, European commission, EFTA...); Review proposal (technical committee); Acceptance and Working Group CEN WG; Draft Standard (prEN); Circulation for comments; Technical committee CEN TC; Maastrich weighted vote by National Standards Bodies; EU Publication and national transposition. The duration was identified as three years. Interaction with CEN could be achieved through the development of a CEN workshop adopting the following steps; business plan (scope. objectives. price. schedule); kick-off; drafting using electronic tools; adoption of the documents through partners' consensus; CEN workshop agreement published by CEN national members; check validity after 3 years minimum.

Comment: One can propose a new standard or propose a review.

Comment: Frantisek Peterka suggested that the COST Action 540 group approach an existing standard rather than make a new standard, such as in Japan. Dr. Riviere emphasized that there must be support from NSO, Industry federations etc. to justify attention.

Dr. Ralf Dillert (Gottfried Wilhelm Leibniz Universität, Hannover, Germany)

Photodegradation of Methylene Blue in Water: A Standard Method to Determine the Activity of Photocatalytic Coatings?

On national (DIN) and international (ISO) levels, the determination of the photonic efficiency of the light-driven decolorisation of methylene blue solutions (MB), in contact with a photocatalyst, was explored as a standard method for testing and comparison of photocatalytic coatings. The aim was to ascertain that the photocatalytic reaction of MB, was a simple and robust method which meets the requirements of non-specialised laboratories in industry. Conclusions provided were as follows, no inhibition by reaction products was detected. A standard protocol has to define materials with a low capability to adsorb MB, the initial concentration of MB and the light intensity has to be fixed in a standard protocol, the quantum efficiency is strongly influenced by the ratio between dark and illuminated time intervals, this influence can be explained by assuming a transport limitation by diffusion. There was good correlation between the MB test and exterior performance. However, the presenter closed with the question, is it really possible to compare different samples?

Question: One participant suggested that photon efficiency was not linear with area exposed. It was also suggested that the head-space gas-phase kinetics, could be affected by area. Degradation products are difficult to detect?

Comment: Frantisek Peterka stated that the method should be appropriate to the effect being evaluated e.g. self-cleaning, hydrophilicity, anti-microbial.

Dr. Jaromir Jirkovsky (J. Heyrovsky Institute of Physical Chemistry AS CR & NANOPIN, Czech Republic)

Fundamental Approach to Photoactivity Tests

Comparative photoactivity tests were undertaken looking at, suspensions of powder photocatalysts compared to a standard TiO₂, P25 (Degussa), photoactive coatings compared to a standard TiO₂ layer, model substances, chlorinated compounds (4-chlorophenol, dichloroacetic acid) and organic dyes (methylene blue, orange II). Quantum yield determination was undertaken using, colloidal solutions Q- TiO₂ particles, suspensions of powder photocatalysts, thin films showing interference. A novel approach employing integration sphere spectrometry was presented. Questions to be answered were identified as, how many and which model substances, how many and which pH values and how many and which irradiation wavelengths to use? The following conclusions were drawn; for comparative tests, there were difficulties in keeping identical irradiation condition in different laboratories. For quantum yield determination the issues were, should one not get the same values in different laboratories, a novel concept involved employing integration sphere spectrometry, absorption determination undertaken of suspensions scattering light, absorption determination of thin films show interference and photocatalytic degradation occurred under identical irradiation conditions. Model substances were, chlorinated compounds (4-chlorophenol, dichloroacetic acid) and organic dyes (methylene blue, orange II). Questions left to be answered were, how many and which pH values, and how many and which irradiation wavelengths?

Dr. Martina Bergant (University of Nova Gorica, Slovenia)

Testing Methods for Determination of Anti-Bacterial Activities of Different Coatings

The development of anti-microbial coatings in collaboration with HELIOS paints was presented. The 'drop-test' method and photo-reactor used, was described. High-T sol-gel TiO₂ films are more effective than TiO₂ low-T sol-gel films due to higher crystallinity. Fe-doping decreases antibacterial activity of high temperature sol-gel TiO₂ films in near UV spectrum. An increase in annealing temperature from 400 to 600°C improves antibacterial properties of TiO₂ and Au/TiO₂ nanocomposites. Gold deposition decreases anti-bacterial activity. The synthetic route to low and high temperature TiO₂ was presented.

Question: John Colreavy asked what happens to the bio-film and has scrub-resistance or solvent double-rubs been undertaken.

Answer: No data was available on chemical, mechanical or biofilm growth.

Question: Will all of this effort encourage bacteria that are resistant in the future?

Comment: Carlos Conesa stated that gold could block the pores and prevent adsorption of bacteria.

Dr. Carlos J. Tavares (Department of Physics, University of Minho, Guimarães, Portugal)

Strain Analysis of Photocatalytic TiO₂ Thin Films on Polymer Substrates

Titania thin films were deposited on polymer sheets by DC magnetron sputtering at room temperature. Polymer substrates were reported to have found their way in the semiconductor industry as a base layer for sensor and actuator applications. The optimum performance of these systems may be affected by dirt adsorbed on their surfaces, which can also originate mechanisms for the degradation of the polymer under layer. The photocatalytic behaviour of the titania coatings was determined by combined ultra-violet irradiation and absorption measurements of industrial dyes (pollutant) in the presence of this catalyst. In order to assess the mechanical behaviour of the as-deposited films, the film/substrate composite system was loaded uni-directionally using a tensile testing machine. Conclusions presented were, that the films developed a photocatalytic efficiency by degrading common textile industry dyes via UV light irradiation. Stress-Strain analysis is

essential for assessing the mechanical behaviour of the coatings on large-scale industrial applications.

Question: Was the scratch resistance measured before and after exposure?

Answer: No data was available.

Comment: Pencil hardness could be done to assess the adhesion and wear potential. How long had the film been irradiated?

Comment: Rutherford backscattering shows films are a little over-stoichiometric.

Comment: Carlos Conesa suggests that there is peroxide present.

Prof. Adélio Mendes (University of Porto, Portugal)

Photocatalysis of NO_x using Paint Films

The use paint coatings for NO_x photo-oxidation was presented. Contribution to decreasing the pollution related with NO_x is a motivation. Emphasis was on exterior paints: responding to the collaboration with the paint company CIN SA. The motivation was, limits until 2010: 250 kt/year for Portugal and 847 kt/year for Spain. Portugal exceeds 8% this value and Spain exceeds 81%. The findings were, a 98% conversion with, a 1 ppm NO air stream, 80% RH, 3 mg/cm TiO₂ from Degussa (P25) in a paint film 200 μm thick (wet thickness), 2.3 s residence time, 8 W/m² UV power radiation and 30°C. 98% conversion is equivalent to a 9 mmol/m² day NO abatement. The catalytic activity of the paint film increases during certain periods, stabilizing afterwards. The photo-oxidation produces NO₂ (not desirable) besides HNO₃ and HNO₂. RH seems to have an optimum value.

Question: If nitric acid is a by-product then would the calcium carbonate not dissolve.

Answer: One can substitute with barium sulphate. Optimum size of TiO₂ is 20nm.

Question: John Colreavy asked if mechanical properties are acceptable if the cPVC is exceeded.

Answer: Exterior paints only were developed.

Comment: The presenter stated that the TiO₂ can be encapsulated to protect the binder from the effects of the catalyst. However, a stronger UV source is then needed.

Dr. Alexander Riss (Vienna University of Technology, Vienna, Austria)

Na-induced Changes in the Photoluminescence of TiO₂-based Materials

Synthesis of titanate nanostructures were undertaken. Structural and spectroscopic similarity to TiO₂ presented. H⁺/Na⁺ exchange with simultaneous morphology transformation. High PL emission yield decreased surface charge transfer. The question asked was whether this is a simple screening method for catalytic activity. Titanate nanotubes were described as a well-defined model system for surface studies on TiO₂ nanostructures. Electronic properties were similar to TiO₂ anatase. Tubes collapse after annealing at 600°C and transforms into anatase nanorods. Two independent and persistent charge separation channels and particle morphology influences charge trapping.

Dr. Pilar Fernández Ibáñez (CIEMAT – Plataforma Solar de Almería, Spain)

Experience and Capabilities of the PSA Pilot Plant Testing

The objective of the CIEMAT project is to establish the necessary scientific and technical background for developing technologies required for application of solar radiation to chemical processes with environmental impact, especially, the usage of solar energy and ultraviolet spectrum for the destruction of toxic compounds, chemical wastes and micro-organism's in aqueous phase. The objectives of the SOLARDETOX Project (1997-2000), which was financially supported by EU-DGXII (Brite Euram Program), was described as the creation of an Industrial Consortium to

develop the overall solar technology to make possible the manufacturing and set-up of plants for the treatment of hazardous water contaminants using solar photocatalysis. The CADOX EU Project (2003-2006) was outlined as industrial scale coupling of oxidative pre-treatment (Solar Photo-Fenton & Ozone) and immobilised biomass activated sludge biotreatment. The AQUACAT and SOLWATER projects were financed by EU under the INCO-DEV program during (2003-2006). The objective was the development of a completely autonomous solar system, chemical-free, for drinking water disinfection and, additionally, elimination of potential organic pollutants at trace level.

Question: Sol-gel to produce particles, was this a combination of sol-gel and something else.

Answer: Not sure as others did the work.

Dr. John Kiwi (EPFL Lausanne, Switzerland)

Photocatalytic Applications in the Textile and Construction Fields

Dr. Kiwi gave an informal overview of PC treatment of fabrics for an aerospace company. A 184nm UV lamp used. 240nm UV will sterilise water. Plasma treatment produces carboxyl carbonyl radicals, COO[•], etc. Fiber-type wool and polyamide needs to be taken into account. Rutile TiO₂ can be achieved at 100°C by sol-gel on fibers. The presence of moisture was cited as important to the production of OH[•]. The presenter invited emails from the attendees, if further discussion was needed.

Panel Discussion

Dr. Frantisek Peterka emphasized that the COST action means cooperation. Therefore, the group must engage with ISO as the expert group in the EU, as the standardization train is moving. The invited experts from Japan and CEN – STAR, were then invited to give their impressions.

Dr. Takeuchi was happy to know standardisation is going on. It is time consuming but necessary for industry movement. More industry involvement is required. Speed is of the essence. The strategy should be to make an imperfect standard quickly, then modify as we know more. ISO has a five-year review. We can review year by year.

Dr. Anthony Shiao-Tseh Chiang stated that Taiwan is a small country, so following is the next strategy for them. He suggested that it is vital to know what the target is and who the customer is. Denox would be sold to Government bodies as it is too expensive for market forces alone. However, Government bodies need a standard to assist with tender bids. In particular, the consumer needs standardization. Each company has its own standard internally, to assess efficacy of e.g. effluent treatment. Indoor and outdoor scenarios are different. It is important to note that the commercial offers are not always reliable, and can be even damaging to the technology, hence the urgency for international standardization.

A discussion was raised on the validity of the Methylene Blue test. A question was raised on the mass transfer effects and if mixing would change the result. Dr. Dillert stated that most of the test methods presented over the two days were too complex and too expensive and therefore not suitable for industry. Mixing would reduce simplicity. Dr. John Kiwi stated that one can measure mass and charge transfer effects separately. However, he emphasized that the community must hurry as there are no standards in Europe. Further discussion prompted the comment that only the measurement of colour reduction was required and not total loss. A test time of 3 hours was suggested as being too long, with preference being for less than an hour. It was pointed out that the paints industry

routinely run accelerated exposure tests lasting up to 1,000 hours before releasing new products. Dr. Dillert stated that there must be a standard even if it is imperfect.

Dr. Frantisek Peterka stated that ISO will be approved in slow and bureaucratic steps. He urged that everyone should join national organizations. It was pointed out that the ISO standard in preparation is an evolution of a Ceramics standard. Dr. Peterka stated that he had access to the ISO draft and that many questions were unanswered. General concerns were expressed as to the PC expertise involved in the ISO process. Dr. Peterka stated that it had been decided during the MC meeting, that a small group would meet to decide on the actions to provide expert support from the Phonasum COST Action group going forward.

Written by

A handwritten signature in black ink, appearing to read "John Colreavy". The signature is written in a cursive style with a large initial 'J' and 'C'.

Dr J Colreavy
