# 2009 BFRL Project Description

## Project Title: Photoreactivity of Narrow Band Gap Metal Oxide Nanostructures

6/3/2008

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**BFRL Program:** Service Life Prediction of Nanostructured Polymeric Materials

**Objective:** To measure and quantify the fundamental properties and mechanisms controlling the photoreactivity of nanostructured narrow band gap metal oxide (NBMOs) and its effect on the service life of polymeric materials.

**Problem:**

***What is the problem?*** No quantitative, scientifically-based measurement science tools currently exist for measuring photoreactivity of nanostructured $TiO_2$ and other narrow band gap metal oxides (NBMOs), which are the types of materials necessary for the production of electrons and other excited species that are capable of causing the rapid destruction of organic materials with which they come into contact. High volumes of nano-$TiO_2$ and zinc oxide (ZnO) are utilized each year as fillers and UV absorbers for building materials such as paints, sealants and bulk plastics. Recently, these materials have found wide-scale application in self-cleaning and self-disinfecting surfaces and components. A common issue shared by these applications is that their service life and durability is affected by the photoreactivity of these nanomaterials. The photoreactivity of nanostructured $TiO_2$ can range from low (photostable) to high (reactive). At both ends of the photoreactivity spectrum, there is a need to develop rapid and reliable measurement science for measuring photoreactivity and identifying properties that contribute to photoreactivity. With the recent increased interest in nanomaterials, there are no scientifically-based standardized photoreactivity testing protocols available for the many new nanoparticle products on the market.

***Why is it hard to solve?*** NBMOs come in wide range of chemistries and phases, but many are not commercially viable for nanocomposite systems. However, nano-$TiO_2$ is a metal oxide commonly used in the polymers and coatings industry, which makes it a good candidate for initial studies. $TiO_2$ is a complex material with a wide range of photoreactivity, multiple crystal phases, and different physical forms (powders, vapor-deposited films, single crystals). Increased interest in nanosized $TiO_2$ ($\leq$ 100 nm) has produced additional variations in crystal phases and forms, and has cast doubt on conventional methods of photoreactivity measurement, which were

intended for particles > 250 nm. Each industry utilizing $TiO_2$ has developed its own test methods for assessing photoreactivity, and there are no linkages between the different tests.

***How is it solved today, and by whom?*** The photoreactivity of NBMOs, particularly $TiO_2$, have been extensively studied for many years, but there has been no coordinated, systematic, practical, scientifically-based approach, as is currently being developed within BFRL, to connect fundamental properties to end-use performance. Academic research, both in the U.S. and internationally, has emphasized synthesis of novel nanoscale metal oxides using simplistic end-use application demonstrations. Other government agencies in the U.S. and abroad have focused on novel metal oxide materials as standard reference materials, particularly for use in the semiconductor industry. In industry, specific product-based tests have been developed that are, at best, qualitative/ semi-quantitative or "trial and error" methods. In the development of $TiO_2$ products and characterization of photoreactivity, Japan and Europe are more advanced than the U.S. and many of these products have come to the U.S. However, there is a lack of standards to characterize and evaluate the materials used in these products.

***Why NIST?*** BFRL has the in-house knowledge and expertise in NBMOs and characterization of their performance, durability, and service life (a BFRL building materials core competency), and strong relationships with nanomaterial and end-user industries needed to solve the measurement science problem for NBMOs ($TiO_2$ initially) photoreactivity. By developing photoreactivity measurement tools, we can create critical solution-enabling tools for the manufacture of $TiO_2$ nanomaterials and their end-use in polymeric materials.

**Approach:**

***What is the new technical idea?*** Measurement science tools for NBMO ($TiO_2$) photoreactivity will be developed with a focus on electron paramagnetic resonance (EPR) methods. When irradiated with ultraviolet (UV) radiation, electrons and hole (positive charge) are generated in the $TiO_2$, migrate to the surface and react with surface species to generate various free radical species. EPR, which measures unpaired electron species such as free radicals, will be used to elucidate the mechanisms involved in the UV response of $TiO_2$. EPR analysis will be carried out on $TiO_2$ in the solid state (dry powder) as well as in liquid suspensions with spin traps. Since different spin traps target specific radical species, the use of a well-chosen set of spin traps in EPR studies allows for a comprehensive understanding of the specific radicals generated for a given material. This knowledge could allow the optimum $TiO_2$ to be selected for an end-application. Correlations can also be drawn between specific particle characteristics (size and size distribution, surface physical and chemical properties, crystal phase, etc.) and the nature/quantity of free radicals generated.

EPR analyses will also be used to rank photoreactivity on the basis of the nature/quantity of free radicals generated. Rankings obtained by EPR will be compared to rankings obtained by chemical assays, which are widely used by industry to obtain quantitative assessments of photoreactivity. Although chemical assays are less robust than EPR measurements, they are more easily carried out in an industrial setting where access to EPR instruments is non-existent or limited. In both types of liquid suspensions used in the spin trap and chemical assays, $TiO_2$ agglomeration occurs, which in turn influences the measurement. Light scattering techniques will be used to measure agglomerate size and distribution, so that agglomeration effects can be determined.

End-application performance tests, which are used by industry to qualitatively assess their products, will utilize polymeric coatings filled with selected $TiO_2$ specimens exposed to UV radiation, temperature and moisture on the SPHERE. The durability and performance of the $TiO_2$-filled polymeric coating will be correlated to the photoreactivity of the $TiO_2$ pigments as determined by EPR measurements.

***Why can we succeed now?*** This project can succeed now because of the growing demand from end-users, particularly from metal oxide nanomaterial manufacturers and the coatings industry; advancements in EPR instrumentation, supporting computational simulation in spectra interpretation, and nanoparticle characterization; and the availability of technical staff with the required combination of expertise and experience.

***What is the research plan?*** This project has three main thrusts: (1) development of EPR measurement protocols, (2) Correlation of EPR measurements with chemical assay methods used in industry, and (3) performance testing of pigmented polymeric systems. These photoreactivity measurements will be developed to yield specific information on each of the three primary processes in a photocatalytic reaction, which are (1) photo-induced charge carrier generation in the NBMOs, (2) interfacial charge transfer to surface species on the surface of the NBMOs, and (3) reaction of charge carriers and activated species with adsorbed materials on the NBMO surface. Information obtained from these tools will contribute toward a more comprehensive understanding of the entire photocatalytic process, which will aid in the elucidation of physical and chemical mechanisms in photoreactivity and lead to enabling ASTM type standard protocols.

EPR protocols will be developed to measure charge carrier generation mechanisms and kinetics in solid state (dry powder) $TiO_2$, and interfacial charge transfer reactions via $TiO_2$ liquid suspensions with spin traps. These measurements will provide fundamental information on the inherent photoreactivity of a given $TiO_2$, which is a function of $TiO_2$ properties (particle size, surface coating, crystal phase). Samples studied will include $TiO_2$ SRMs, which will be obtained via collaboration with NIST's Ceramics Division, as well as commercial products. Analysis of the well-characterized and homogeneous SRMs will provide baseline measurements that the measurements on commercial products can be benchmarked against. A database of $TiO_2$ photoreactivity measured via EPR (solid state and with select spin traps) will be compiled and made available to industry for product selection and development purposes. The influence of $TiO_2$ properties (particle size, surface coating, crystal phase) on photoreactivity will be studied via (1) use of carefully selected subsets of the commercial products where one parameter is varied, (2) fractionation of $TiO_2$ products to obtain specific, narrow size distributions, and (3) collaboration with $TiO_2$ producers to obtain model systems.

EPR results can also be used to rank materials according to photoreactivity. These rankings will be compared to $TiO_2$ photoreactivity rankings measured by chemical assay methods used in industry, which utilize methyl viologen, horseradish peroxidase and isopropyl alcohol as probe molecules. This research will provide critical knowledge to industry as to which chemical assays are most closely linked to fundamental photoreactivity measurements and are hence most reliable in assessing performance.

To test how well photoreactivity measurements correlate to end-use performance, UV weathering performance of polymeric coatings containing select $TiO_2$ samples will be evaluated.

Coatings will be exposed to UV radiation and analyzed via EPR, as well as via spectroscopic (ATR and photoacoustic FT-IR) and mechanical (bulk and microscale) measurements. Coating properties measured during UV exposure will be correlated with the photoreactivity of the $TiO_2$ pigments determined from the EPR spin trap and solid state studies.

**Recent Results:** In FY08, major **output**s include:

- 1 meeting proceeding
  - "Effects of Pigment and its Dispersion on UV Degradation of Epoxy and Acrylic Urethane Polymer Systems" S. Watson, A. Forster, I. Tseng, L. Sung, J. Lucas, and A. Forster, *Nanophase and Nanocomposite Materials V*, edited by S. Komarneni, K. Kaneko, J.C. Parker, and P. O'Brien (Mater. Res. Soc. Symp. Proc. **Volume 1056E**, Warrendale, PA, 2008), 05-HH03-67.
- 2 book chapters (peer-reviewed, in press)
  - "Investigating Pigment Photoreactivity for Coatings Applications: Methods Development", from Service Life Prediction for Polymeric Materials: Global Perspectives, Eds: J. Martin, R. Rynz, J. Chin, R. Dickie, Springer Press, 2008.
  - "Assessment of Spectrophotometric Assay Methods on Nanostructured Pigments", S. Watson, A. Forster, I. Tseng, L.Sung, ACS Symposium Series: Nanotechnology Applications in Coatings, Vol 1008, Eds: R. Fernando, L. Sung, Oxford Press, 2008.
- 2 meeting presentations (1 invited)
  - "Effects of Pigment and its Dispersion on UV Degradation of Epoxy and Acrylic Urethane Polymeric Systems" MRS Symposium HH: Nanophase and Nanocomposite Materials V, MRS Fall Meeting November 26-30, 2007, Boston, Massachusetts.
  - "Photoreactivity Measurements of Nanostructured Pigments" Federation of Societies for Coatings Technology Advancement in Coatings Series-Nanotechnology in Coatings: Emerging Applications, March 26-28, 2008, Orlando FL.

Major **outcomes** include the development of quantitative measurement science tools:

- EPR protocols for measuring photoreactivity of dry particles and suspensions of $TiO_2$ (e.g., nitroxide spin trap techniques in aqueous $TiO_2$ suspensions and solid state analysis of dry $TiO_2$ specimens)
- EPR protocols for measuring photoreactivity of $TiO_2$ in cured pigmented polymeric films
- New knowledge on correlation between surface morphology of $TiO_2$ and UV-degradation performance of $TiO_2$ pigmented coatings containing $TiO_2$ of varying photoreactivity and volume content.

**Standards and Codes:** Collaboration with NIST's Ceramics Division (852, Vincent Hackley) on the development of a nano-$TiO_2$ reference material. $TiO_2$ photoreactivity measurements from this project will be used as an informational value measurement.