Studying the Use of Photocatalytic Coatings to Increase Building/Structure Sustainability and Cleanliness at NASA Stennis Space Center:

Overview of Photocatalysis, Photocatalytic Surface Materials Studies, and Demonstration of Self-Cleaning Materials for Space and Terrestrial Based Applications

Presented by
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CSC/NASA Stennis Space Center
March 22, 2013
Built in 1963 to support the Apollo space program

- 13,800 Acre Fee Area
- 125,000 Acre Buffer Zone

Home to the Nation’s largest rocket engine testing facility
Stennis Space Center (SSC)

A unique Federal City hosting the NASA Shared Services Center and more than 30 federal, state, academic and private organizations, as well as numerous technology-based companies.
Resident Agencies at SSC

**Department of Defense**
- Commander, Naval Meteorology & Oceanography Command
- Naval Oceanographic Office
- Naval Research Laboratory
- Naval Small Craft Instruction and Technical Training School
- Navy Special Boat Team 22
- Navy Human Resources Service Center Southeast

**Department of Commerce**
- NOAA, NWS, National Data Buoy Center
- NOAA National Marine Fisheries Service
- NOAA National Coastal Data Development Center

**Environmental Protection Agency**
- Environmental Chemistry Laboratory
- Gulf of Mexico Program

**Department of Interior**
- U.S. Geological Survey, Hydrologic Instrumentation Facility

**Department of Energy**
- Strategic Petroleum Reserve National Aeronautics and Space Administration

**Mississippi State University**
- Northern Gulf Institute

**University of Southern Mississippi - College of Science and Technology**
- Dept. of Marine Science

**Major Contractors**
- Pratt and Whitney Rocketdyne
- Jacobs Technology Inc. – Facilities Operations
- Lockheed Martin IS & GS – Civil - Test Operations Contract
  - A2 Research
- ASRC Research and Technology Solutions (ARTS)
- Paragon Systems Inc.
- Science Applications International Corporation
- Science Systems and Applications Inc.

**Commercial Companies**
- Pratt and Whitney Rocketdyne
- Lockheed Martin IS & GS Defense Systems
- Rolls Royce North America

**State of Mississippi**
- Mississippi Enterprise for Technology
- Enterprise for Innovative Geospatial Solutions

**State of Louisiana**
- Louisiana Technology Transfer Office, Louisiana Business & Technology Center/LSU

**Center for Higher Learning**
- Mississippi State University
- University of Southern Mississippi
- University of Mississippi
- University of New Orleans
- Pearl River Community College
A1- Test Stand: Shuttle Program

Space Shuttle Main Engine (SSME) Testing
A2 Test Stand Apollo Program:
Saturn S-II-T booster testing

And now J2-X
A-3 Test Stand

Stennis Space Center

- 300 feet tall
- Open steel frame structure
- 19-acre site
- Can withstand up to 1 million pounds of thrust
- Able to simulate altitudes of up to 100,000 feet by generating steam to create a vacuum

National Aeronautics and Space Administration
Aerojet AJ26 Engine Test: 
Aerojet, Orbital Science Corporation and NASA
E Complex:
Commercial Rocket Engine Testing Program
SSC Resources

NASA Information Technology Services Contractor

- Historically, operated world-class optics and calibration laboratory
- Experience in:
  - Calibration/validation and modeling expertise
  - Systems Engineering
  - Remote Sensing
  - Chemical and Biological Defense Technologies Experience
  - Instrumentation (Electronics and Optical)
Ground based remote sensing
Brief Overview of Photocatalysis
Photocatalysis: Development of Technology

- Research into photocatalytic technology has been progressing for over three decades
- Early 1990s
  - Japanese and European companies initiate research into photocatalytic technology
- 1996
  - Specific focus on the technology with the first large-scale application: the construction of a church in Rome (Jubilee Church)
- 2000
  - Europe and Japan research into the benefits of photocatalytic technology
- Currently, photocatalytic technology continues to improve, and with time development is becoming more efficient and effective
What is Photocatalysis?

**Photo**: phenomenon induced by the light, having specifically a wavelength around 320-400 nm (artificial or natural sunlight)

**Catalyst**: a material that induces a reaction but is not consumed or transformed by it. The catalyst remains constantly available.

*In this case, the catalyst is made with nano-particles of titanium oxide (TiO₂)*
UV Light and Photocatalysis: How it Works

- UV radiation
  - Decomposes many organic and inorganic compounds
  - Slow, natural process

- Photocatalyst
  - Certain materials act as a catalyst for this decomposition process when exposed to UV radiation

- Photocatalytic agents are activated when exposed to ultraviolet light (320–400 nm) and water

- RE/DOX reaction occurs at the surface of the catalyst and generates free radicals
  - -OH, hydroxyl radicals and
  - O$_2^-$, superoxide ions
Unique Hydrophilic Properties of TiO₂

• When exposed to UV light, the contact angle of the photocatalyst surface with water is gradually reduced
• After enough exposure, the surface reaches super-hydrophilicity
  – the surface does not repel water at all
  – water cannot exist in the shape of a drop, but spreads flatly on the surface of the substrate
  – water takes the form of a highly uniform thin film, which behaves optically like a clear sheet of glass

• Application: pollution leaves an oily residue
  – Original building materials include photocatalytic material
  – Coupled with gravity and rainfall, the dirt on the walls will wash away, keeping the building exterior clean at all times (making it self-cleaning)
Superhydrophilicity

Before UV Exposure

15 mins UV Exposure

30 mins UV Exposure

45 mins UV Exposure

Source: Pilkington Glass
The Two Principles of Photocatalysis

1. Oxidative/reduction reaction processes—pollutants (and stains) are destroyed
2. Hydrophilicity prevents residue build-up
Commercially Available Photocatalytic Self-Cleaning Materials

- Cement & Concrete Pavers
- Tiles
- Glass
- Spray-on Coatings
  - “Spray-on” coating services
  - “Spray-on” coatings for purchase
- Nanomaterials
  - Nanoparticles for purchase

Commercially available photocatalytic **coatings** were determined to have the greatest potential and widest utility since they could be applied to both existing structures and new construction.
Photocatalytic TiO$_2$ Use and Cost

• **Use**
  – These surfaces are in fairly wide use throughout Japan, and are being marketed in Europe
  – *Many of these products have not yet reached the U.S. market*

• **Cost**
  – The cost to transform the facade of a five-story building into a photocatalytic surface would add approximately 100 euros, $120, when to the cost of traditional cost of paint or plaster
  – Paving a street or sidewalk might be a little more costly-but not excessively
  – The Italian cement products are 30-40% more expensive than regular concrete
  – No significant price difference between regular and enhanced tiles
Real-World Demonstration and Use of Photocatalytic Materials
Jubilee Church, constructed in 2003, had white coating added in the concrete to preserve the whiteness.

Nine years later, the coated concrete is as white as it was when constructed, while other parts of the building have grayed because of atmospheric pollution.

Source: [http://figure-ground.com/jubilee_church/](http://figure-ground.com/jubilee_church/)
Photocatalytic Cement Road Italy

- In a test in 2003, the company coated 75,000 square feet (6,750 square meters) of road surface on the outskirts of Milan with photocatalytic cement
- Nitrogen oxide levels were reduced by up to 60 percent, depending on weather conditions

Source: http://www.concretedecor.net/All_Access/504/CD504_New_Tech2.cfm/
Uncoated tile:

Water droplets form

Dirt and lyme is left after drying

Hydrotect tile:

The water spreads as a thin film on the surface and lifts dirt form the surface. Water droplets form . . .

... which can then be easily removed. Result: a clean surface

Uncoated tile:

Oil and grease detach from the surface.

Hydrotect tile:

No chance for dirt, oil and grease

With Hydrotect, dirt is washed down by the water and can then be easily wiped off.

Comparison of wettability

Ordinary ceramic tile surface

Ceramic tile surface coated with super-hydrophilic photocatalyst

Source: http://www.toto.co.jp/products/hydro/genri_en.htm
Hydrotect Technology - Decomposition

Decomposes various organic substances, which prevents the growth of bacteria, algae, mold, germs, and dirt retention.

Sources:  
http://www.toto.co.jp/products/hydro/genri_en.htm  
http://61.114.182.22/products/hydro/genri_en.htm

Source:  
http://www.toto.co.jp/hydro_e/hydro_e4.htm

Fig. 7 Difference of self-cleaning ability by a rainfall between the super-hydrophilic coated plates and the normal silicone coated plates.
Marunouchi Building in Japan

Covered with Hydrotect photocatalytic tiles to reduce discoloring from pollution

Sources:
Muhammad Ali Center in USA

Source: http://2x4.org/work/25/muhammad-ali-center/
SunClean® Glass vs. Conventional Glass

• The coating’s hydrophilic property makes water droplets spread out, or sheet, across the surface of the glass.

• When rain or a light spray of water hits the window, the water helps to more effectively rinse away loosened dirt.

• This sheeting action helps the window dry quickly with minimal spotting and streaking.

Source: http://corporateportal.ppg.com/NA/Glass/ResidentialGlass/ResidentialBuildersRemodelers/ProductInformation/SunClean/Sheet+Action+Big.htm
Pilkington Glass-Pilkington Activ™

- Only reduces the amount of sunlight passing through by only about 5%
- coating is very tough and would require real abrasion, i.e. scrubbing with steel wool, to remove it
- the surface of the glass is hydrophyllic - rather than beading up (and drying in blotches), water forms a sheet that allows organic dirt particles to flow off and then the glass dries without streaks.

Source: http://www.pilkingtonselfcleaningglass.co.uk/pilkingtonactiv
In MTR stations, commonly touched surfaces have been coated (i.e., escalator handrails, buttons on ticket-issuing machines, and elevator buttons)
Preliminary Photocatalytic Surface Materials Studies at NASA SSC
NASA SSC Capabilities

- **NASA Information Technology Services Contractor (CSC-Computer Science Corporation)**
  - Operates world-class optics and calibration laboratory; including spectroscopy capabilities
  - NASA laboratory facilities, technology and expertise has been utilized to test and validate the performance of these commercial photocatalytic coating products which included specialized expertise in spectroscopy to validate performance of photocatalytic coatings under *in situ* and *in vivo* conditions
  - NASA has previously demonstrated successful photocatalytic properties in previously funded projects (see following page)

- **Dr. Lauren Underwood, (NASA/CSC)**
  - An established background in biology, research and development, strategic planning, and project management, complemented by expertise in proposal and scientific writing, cell and molecular biology, and microscopy.
  - Supported business development between NASA and U.S. Department of Homeland Security, Science and Technology Directorate, Chemical and Biological Division for the successful capture of $250, 000, for NASA SSC, for “Investigating Photocatalytic Materials and Coatings for Protecting Infrastructures against Terrorism Threats Self-Decontaminating Material Research”
Photocatalytic Material Funding Studies at NASA SSC Activities: 5 years

- NASA Stennis Space Center (SSC) Center (CIF) FY12 for “Photocatalytic Coating Use at INFINITY for Space-based Applications”
- Southeast Region Research Initiative (SERRI), FY10-FY11 Department of Energy’s Oak Ridge National Laboratory for the U.S. Department of Homeland Security funded project, Assessing the Potential of Photocatalytic Building Materials for Protecting Infrastructure and Developing Resiliency to Natural and Manmade Disasters
- NASA SSC’s Center Director’s Discretionary Funds (CDDF) FY10 for “Time Series Assessment of Photocatalytic Surface Coatings for Creating Self-Cleaning Sustainable Buildings and Structures”
- NASA Cooperative Agreement Notice (CAN) 2009 Dual Use Technology funding for “Investigating Photocatalytic Materials for creating Building Sustainability and Self-Cleaning Surfaces”
- Department of Homeland Security's Science and Technology Directorate (DHS S & T) , FY08-FY09, Chemical and Biological Division for the following scope of work: Investigating Photocatalytic Materials and Coating for Protecting Infrastructures against Terrorism Threats
On-site Testing and Applications: Preliminary Proof of Concept Studies
Nanocept, Inc.

- Primary business line is the manufacture and production of **photocatalytic coatings** based on advanced materials with an emphasis on TiO₂
- They partner with research institutions, national laboratories, and specialized industries to engage themselves as a strong technology provider in the area of photocatalysis

- Demonstrations
  - Methylene Blue dye
  - Odor absorbing
  - Red/ink dye test
  - Hydrophilicity
Self-Cleaning Reduces Maintenance Costs

Clean marble

Methylene blue application on clean marble

Methylene blue dye after 1 hour in the sun
Odor Absorbing
Red Ink Dye Test
Stain Decomposition Test-Red Food Dye

Far left: hydrotect tile
Middle: plain tile
Right: tioxoguard/tioxoclean coated tile

Far left: hydrotect tile + red food dye
Middle: plain tile + red food dye
Right: tioxoguard/tioxoclean coated tile + red food dye
Quarters placed on tioxoguard/tioxoclean coated tiles
Stain Decomposition Test - Red Food Dye

3hrs later, after all tiles have been exposed to direct sunlight
Superhydrophilicity
Test Application 2006: Before TiO$_2$ Coating Application

Building 2206, SSC
Test Application 2006 On-Site: During
Test Demonstration On-Site: Post-application

Building 2206, SSC
Building 6 Years Later: July 3, 2012

Building 2206, SSC
Spectral Reflectance Measurements

• Purpose: to show that the absorbance curve of the red dye decreases over time
• Method: use three separate spectroradiometers to compare the spectral curves, over time, of the following:
  – Tioxoguard/tioxoclean coated tile
  – Plain uncoated tile
  – Spectralon panel
Stain Decomposition Spectral Reflectance Measurements over Time

Test set-up showing spectral radiometers and tiles

Spectralon reference panel
Stain Decomposition Spectral Reflectance Measurements over Time

Initial set-up with spectral radiometers fiber optics
Left: Tioxoguard/Tioxoclean coated tile + food dye
Right: uncoated tile + food dye

After exposure to sunlight
• Time series transmission spectra are taken to determine photocatalytic reaction rate
• Simple standardized method for rapidly screening photocatalytic coatings
• Crystal Violet dye used to assess degradation capability
• UV simulator black lamp from GE
• Rapid method for evaluating photocatalytic materials function/efficacy
Black Lamp Sample Cleaning and Charging
Crystal Violet Dye: Decomposition Demonstration

Pre-dye application

Post-dye application

1 hour UV exposure

1.5 hour UV exposure
Summary

- Simple method for evaluating photocatalytic reaction rate

- Nanocepts, Inc. and PURETi coating clearly demonstrating photocatalytic activity
  - Small residual pure UV breakdown
  - Results replicated - consistent behavior observed
Photocatalyst: Hydrophilic Properties

• As photocatalytic materials are exposed to UV light, the contact angle of that surface with water is reduced gradually
• After enough UV exposure, the surface reaches super hydrophilicity
  – Water becomes a highly uniform thin film, which behaves optically like a clear sheet of glass
• Coupled with gravity and rainfall or assisted washing, the contamination on surfaces is removed making it self-cleaning
Contact Angle Measurement
Non-hydrophilic

Water forms a droplet
Superhydrophilic Photocatalytic Coating

Contact angle vanishes completely,
Water forms a flat sheet

Non-hydrophilic side-
water forms droplets

Superhydrophilic side-
water forms sheets

Source: http://www.rcboataholic.com/faq/hull_finish.htm
Photocatalytic Surface Materials Studies: Funded Projects
Investigating Commercially Available Photocatalytic Materials and Coatings for Protecting Infrastructures Against Terrorism Threats

Bruce A. Davis (DHS/NASA)
Robert E. Ryan (NASA ITS Contractor)
Lauren W. Underwood (NASA ITS Contractor)

May 29, 2009
Objective

Key objectives:

• Investigate the superhydrophilic properties of photocatalytic materials

• Evaluate the photodecomposition of dyes, organophosphate simulants, and biological materials

Key Conclusions:

• Reasonably cost photocatalytic building materials exist today

  • Under bright illumination conditions, these materials could mitigate chemical and biological toxic material

  • Low light and different illumination environments appear promising, but requires further research

• Organophosphates were decomposed

• The hydrophilic property of the photocatalytic surface permits much easier cleaning of contaminated surfaces. Latency effect of photocatalytic material properties needs investigation
**Chemical Analogue Studies**

**Diazinon** - a known acetylcholinesterase inhibitor and chemical weapon stimulant.
Results: after 6 hours UV exposure, degraded 97–99%.

**Fenamiphos** - pesticide with an extremely long half-life (300 days),
Results: after 6 hours UV exposure, degraded 97–99%.

The majority of the reaction occurred in the first 2 hours (85-90% reduction); UV simulated direct sunlight.
Tests performed in a laboratory experienced in this methodology demonstrated a marked reduction value and antibacterial activity for *E. coli*.

Experiments were conducted under very low light levels (levels were comparable an urban canyon setting)

Under many conditions, the vegetative bacteria *E. coli* readily dies; therefore, experimental designs need to account for factors that affect both culture viability and lethality.
Investigating Photocatalytic Materials for Creating Building Sustainability and Self-Cleaning Surfaces
Main Objectives/Task

- Two commercially available photocatalytic coatings were investigated
  - (1) to characterize their components and structure
  - (2) to assess their ability to maintain exterior surface cleanliness over time, and
  - (3) to study their photocatalytic function in a laboratory setting, using a non-photoreactive dye, so that preliminary scientific information can be documented on these commercially available materials
The following facilities/structures were used for this project:

• The exterior surfaces of B-7001-not including the roof
• The two north faces of B-1200
• Booster rocket display—the side of B-1200
• The Stennis Space Center greeting sight sign (a quarter mile south of the south gate)
• Electronic sign at the south guard gate
• All of the above listed facilities/structures were partially coated with commercially available photocatalytic coatings from the partners (Nanocepts, Inc. and PURETi).
Building Sustainability Results

NASA SSC Welcome Sign:

Photocatalytic coatings for creating green/sustainable buildings and structures
Stennis Space Center
Welcome Sign NASA SSC
South Gate

10/19/2009 1/6/2010

National Aeronautics and Space Administration
Spectral Reflectance Measurements

- Spectral measurements of the exterior surfaces of the following buildings were assessed for this project:
  - The exterior surfaces of B-7100-not including the roof
  - The two north faces of B-1200

- The following surfaces were described and included for surface evaluation in the proposal,
  - Booster rocket display-the the side of B-1200
  - Electronic sign at the south gate
  - Welcome sign at south gate
NIST calibrated spectroradiometers were used to perform outdoor surveys/assessments

Data was captured, saved and then processed
Spectral reflectance measurement set up outside building 1200
Spectral reflectance results

• To date, there is no documented scientific analysis of the spectral variability of reflectance measurements or documentation of optical properties of photocatalytic coatings
• The shape and location of the absorption features demonstrated that the photocatalytically coated surfaces maintain a higher reflectance measurement, over time, as compared to the uncoated surfaces
• These initial findings demonstrate that photocatalytic coatings could provide a viable means to increase building sustainability
• Longer evaluation times, and increased surface area study would further validate these promising results
“Time Series Assessment of Photocatalytic Surface Coatings for Creating Self-Cleaning Sustainable Buildings and Structures”
Photocatalytic coating and service required for application were provided by the following companies:

- Nanocepts, Inc., Coldstream Center, 1500 Bull Lea Road, Suite 201, Lexington, KY 40511, 859-396-4339 [http://www.nanocepts.com/about.htm](http://www.nanocepts.com/about.htm)

and

- PURETi, 2849 Product Drive, Rochester Hills, MI 48309, 248-299-2607 [http://www.pureti.com/about.html](http://www.pureti.com/about.html)

Photocatalytic coatings from both these companies can be readily applied to existing surfaces, have previously demonstrated photocatalytic self-cleaning properties, and are currently being retrofit onto existing structures in the United States.

The following facility/structure was used in this study:

The new Cryogenic Facility (building 3418), on Propellant Blvd. at SSC
Soot on TiO₂ coated glass surfaces and monitoring their decomposition

Soot deposited on microscope slides and exposed to UV lamp to induce photocatalytic activity.

A schematic of the set-up used to take transition measurements.
The microscope slides on the left depict three different thicknesses of soot, 

TC-K^1 (medium thickness),

TC-K^2 (light coating)

TC-K^3 (heavy coating) applied to a Nanocepts, Inc. photocatalytically coated slides (TC-K coating);

Image on the left, the slides are shown after 4 weeks UV light exposure;

Image on the right, the slides are shown after 6 of UV light exposure.

The TC-K^2 slide with the lightest soot deposit demonstrated the greatest amount of decomposition. These results were validated with light transmission measurements.
Discussion and Conclusion

• TiO₂ coated surfaces demonstrated both visually through photographic representation, and quantitatively, through reflectance measurements that they improved upon the current state of cleanliness upon the surfaces that they were applied to.

• TiO₂ has the potential to both maintain and increase building’s sustainability and the overall appearance of cleanliness.

• TiO₂ coated slides degraded soot under UV light compared to soot samples on plain uncoated slides under the same conditions.
  – Degradation of soot by photocatalysis was far more apparent than degradation of soot by UV light alone.
  – This demonstration provides the foundation for a laboratory model that could be used to simulate real world applications for photocatalytic materials.

• Additional research is required to better understand the full potential of TiO₂.
Photocatalytic Coating Use at INFINITY for Space-based Applications:

• **Self-Cleaning Validation Experiment**
  – Various surfaces will be photocatalytically coated at the Infinity Science Center i.e. turnstiles, doors, and/or frequently touched glass surfaces, and then quantitatively examined for their self-cleaning capability
  – Demonstrate anti-germicidal properites

• **Infinity/Innovative Center Indoor Air Quality Exhibit**
  – An air purifying exhibit will be created for display
  – The exhibit will demonstrate the dual use of photocatalytic material technology: TiO$_2$ + new UV LED light source
    • Ultra bright GaN LEDs-commercially available within the past year;
    • Last 10s of 1000s of hours;
    • Resistant to mechanical stress;
    • Critically important for future space missions and terrestrial applications
  – Air quality will be monitored
CIF 2012 Project Tasks: Proof of Concept

- Task 1: conduct experience with ATP meter
- Task 2: conduct experiments with test-cultures
- Task 3: examine cultures under light microscope
- Task 4: apply coatings in spaces where air quality is a known issue; document results before and after applications
**Biological Baseline Studies**

- **Plate 1**: Baseline: inoculated pond water culture
- **Plate 2**: inoculated pond water culture + 20% PURETI Clear solution
- **Plate 3**: inoculated pond water culture + 20% TC-K solution

- Tests performed in a laboratory experienced in this methodology demonstrated a marked reduction value and antibacterial activity for bacteria ground from pond water.
- Experiments were conducted in the dark.
- Under these conditions, the vegetative bacteria does not readily thrive on the cultures that were made incorporating proprietary nanoparticles of TiO$_2$.
Commercially Available ATP Meter
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Infinity: State of Art Science Center

Visitor attraction in Hancock County, MS
Stennis Space Center

Create a Hand-on “Touch Surface” Experiment

Source: http://www.visitinfinity.com/exhibits/great-nations/