Cleanability and Antimicrobial Efficacy of a Titanium Dioxide Coating

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NSF International / The Toxicology Group, L.L.C.

Smart Coatings 2005

Presentation Outline

- Brief introduction to NSF International and The Toxicology Group, L.L.C
- Experimental Design
  - Cleanability assessment
  - Antimicrobial efficacy
- Results
- Future Experimentation

NSF Mission

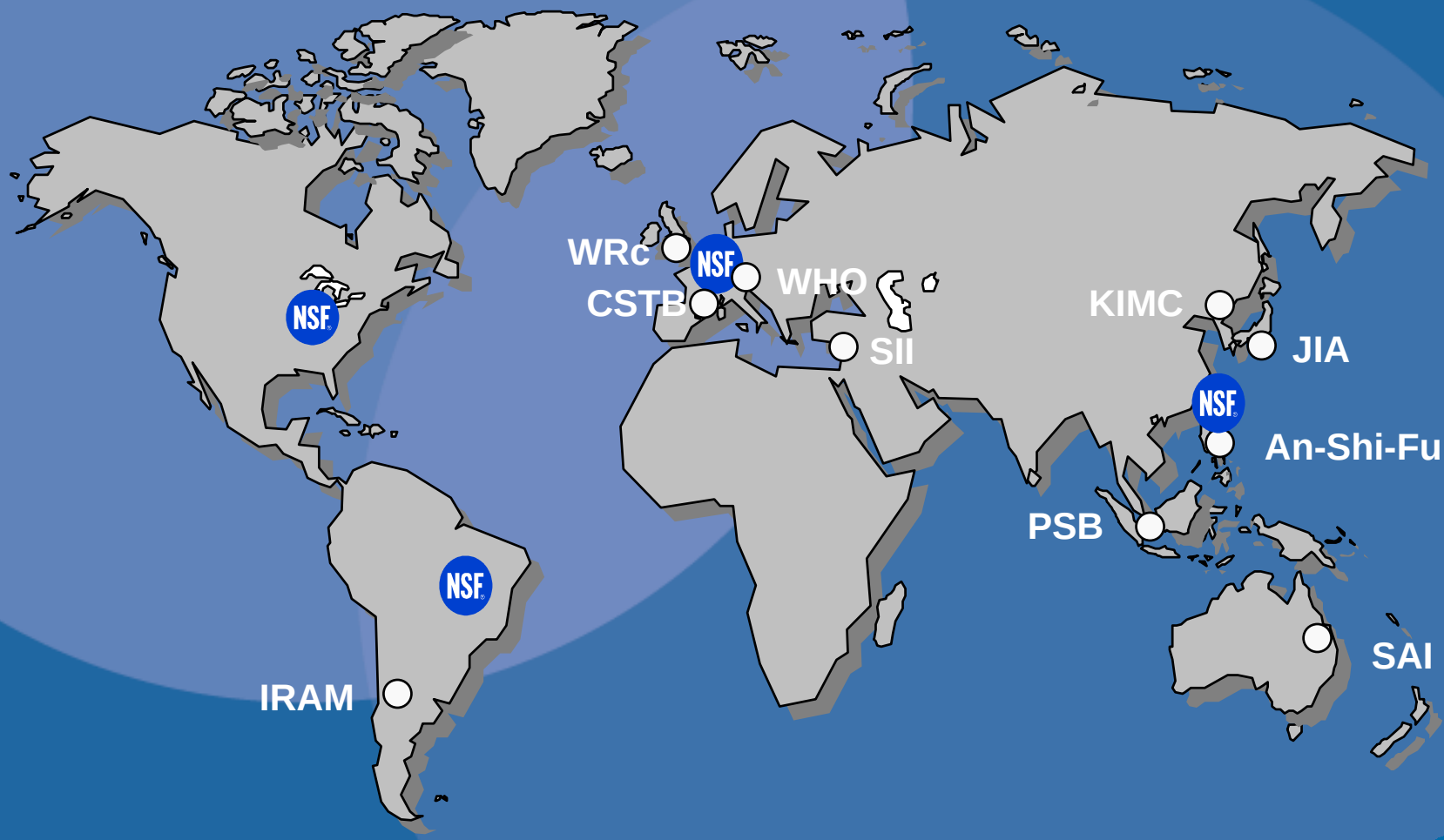
NSF International, an independent, not-for-profit non-governmental organization, is dedicated to being the leading global provider of public health and safety-based risk management solutions while serving the interests of all stakeholders.

NSF Is The Global Leader In Public Health And Safety

- Serving over 4,000 companies and 8,000 plants across 80 different countries
- Registering over 3,500 quality and environmental systems
- Conducting over 20,000 audits a year
- On-site Laboratories: Microbiology, Chemistry, Engineering

NSF Offers A Multiplicity Of Public Health And Safety-Based Services

A Global Network Of Partners



Recognized By The World Health Organization

- Collaborating Centre for:
  - Water Safety and Treatment
    - Drinking Water Quality Guidelines
    - Recreational Water Safety Guidelines
  - Food Safety
  - Indoor Environment

International Accreditations

U.S. **Canada**

The Toxicology Group, LLC.

As a leader in toxicological assessments, evaluations, laboratory testing, and consulting, NSF is addressing clients business and technical needs cost effectively.

Who We Are…

- A Wholly Owned Company of NSF International
- Formed in direct response to client's requests, based on 50 year history of evaluating chemical formulations, performing laboratory analyses, and determining potential toxicological concerns.
- Focus redefined based on need and broad spectrum of technical expertise available in-house.
- Scope of Services includes technology development including due diligence, regulatory guidance, toxicological evaluations, and laboratory services to Industrial, Commercial, and Governmental Sectors.

Project Funding

- Prizmalite Industries, Inc. contracted The Toxicology Group, L.L.C. to perform an independent, third party assessment of their product's (TioxoClean®) ability to "self clean" various organic compounds
- Experimentation occurred in 2004

TioxoClean®

- Aqueous, amorphous, titania, film-former that holds nano particles (as small as 6 nm) of anatase TiO_2 in a stable suspension
- High surface area of titanium dioxide particle
- Rate of photocatalytic oxidation is enhanced by increased surface area
- Antimicrobial mode of action may be the targeting of the cellular membrane by the hydroxyl radicals, thus increasing permeability, disrupting metabolism, waste excretion and membrane stability

Experimental Design

Cleanability – Selection of Dyes

- Four organic soils utilized as the challenge agents
- Red dye #2, Red dye #220, Blue dye #440, and 3 in 1 oil (in order of theoretical ease of cleaning)
- Dyes selected on visualization and potential susceptibility to photocatalytic oxidation
- Dyes were applied to test and control plates in a "cross" manner
  - two 1" x 6" lines

Cleanability – Plate Setup and Exposure

- 6” x 6” glass plates were obtained for the following groups
  - Experimental Group 1 = TioxoClean®
  - Experimental Group 2 = Competitor’s TiO_2 product
  - Control Group = No Coating
- All experimentation performed in triplicate
- Three exposure scenarios were examined
  - Artificial Ultraviolet – 35 $\mu W/cm^2$ @ 254 nm
    - American Ultraviolet Co. Model CE-15-4BL equipped with a 350 nm blacklight (model 350BL)
    - 12” exposure distance from light source
  - Natural Indoor UV - 1 $\mu W/cm^2$ @ 254 nm
  - Natural Outdoor UV - 1 mW/cm^2 @ 254 nm
    - (Fujishima et al, 1999)

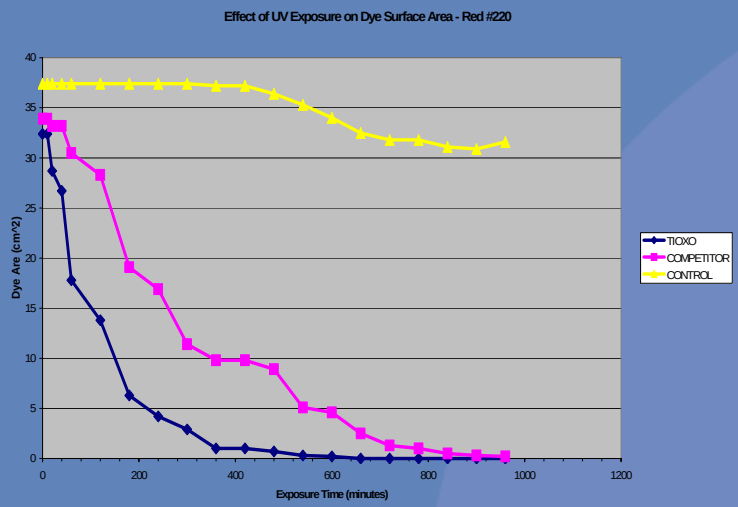
Cleanability – Exposure Protocol

- Recorded weight of plates, opacity and dye surface area at the following exposure time points:
  - Time 0, 10 min, 20 min, 40 min, 60 min, and hourly from 2 hr through 16 hr
- Opacity was measured as follows:
  - Used Orbeco-Hellige Color Disc No. 611-11
  - Mean opacity of the triplicate plates was calculated for each treatment group
- Dye surface area was calculated as follows:
  - Individual areas of the two dye lines were calculated and averaged
  - Mean area of the triplicate plates was then calculated for each treatment group

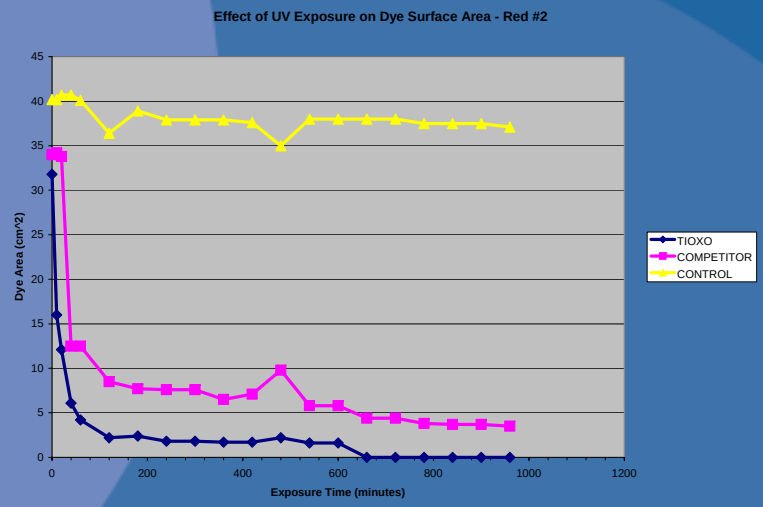
Cleanability Results

Self Cleanability - Artificial UV

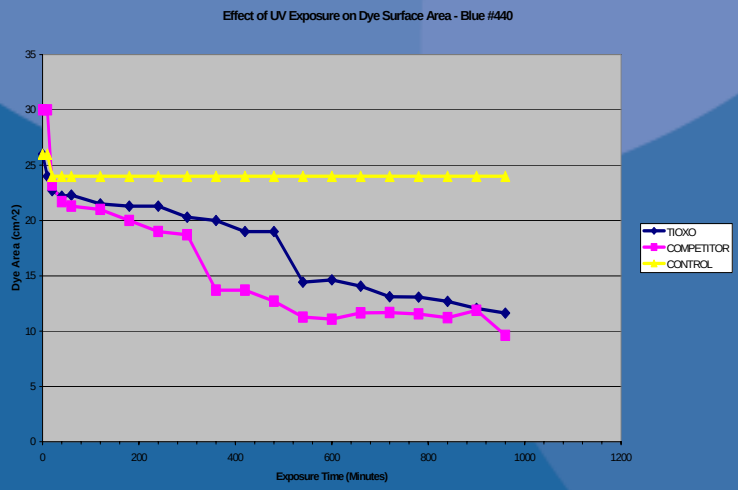
Red #220



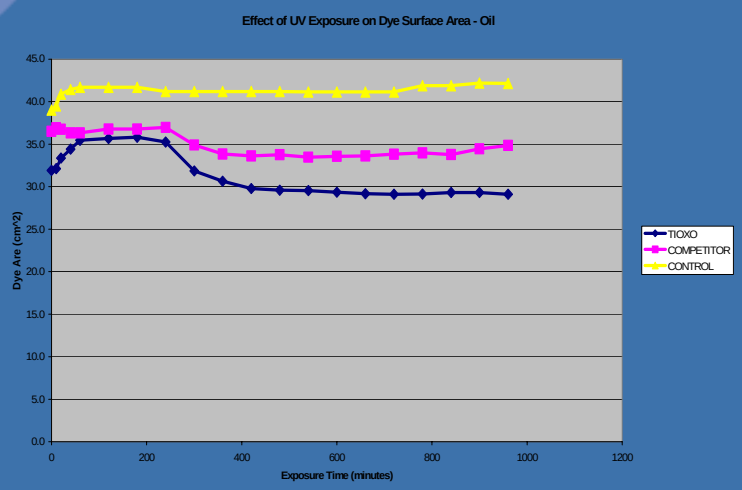
Red #2



Blue #440

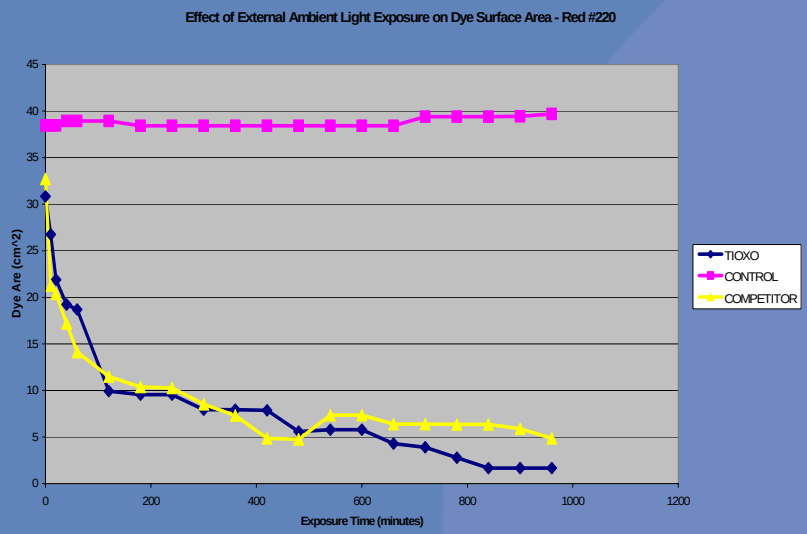


3 in 1 Oil

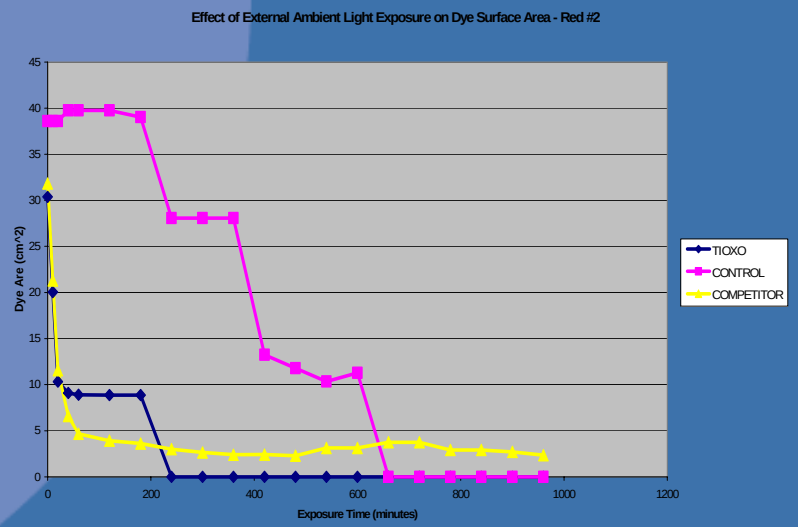


Self Cleanability - External UV

Red #220

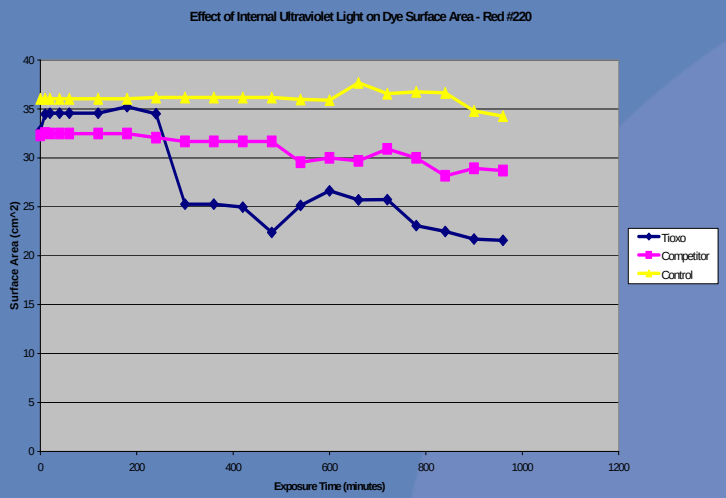


Red #2

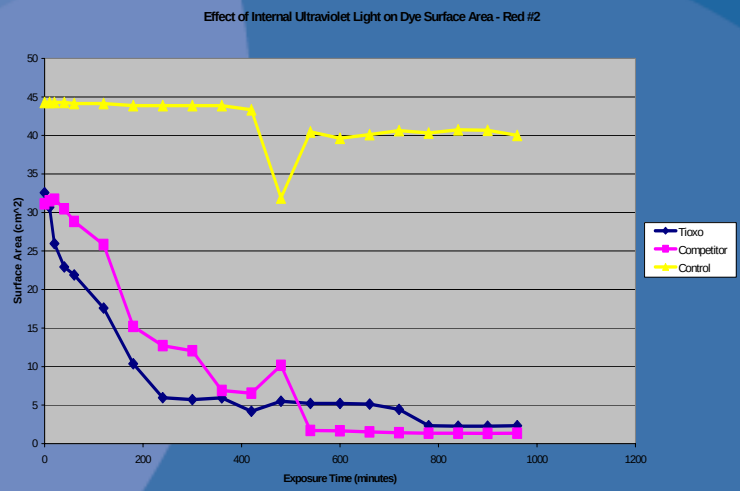


Self Cleanability - Indoor UV

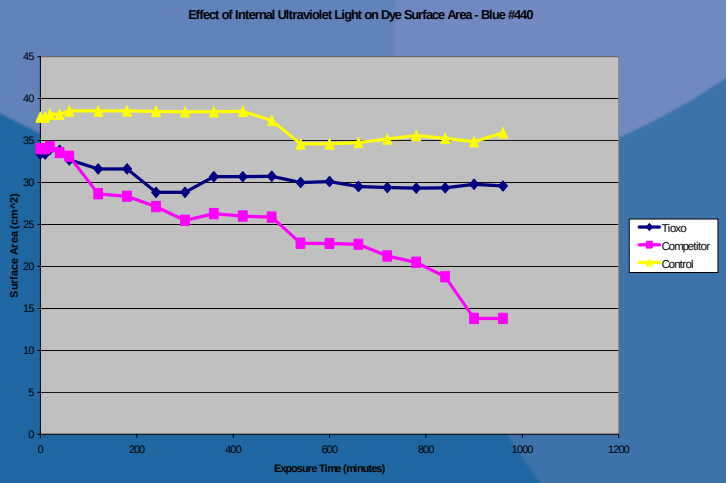
Red #220



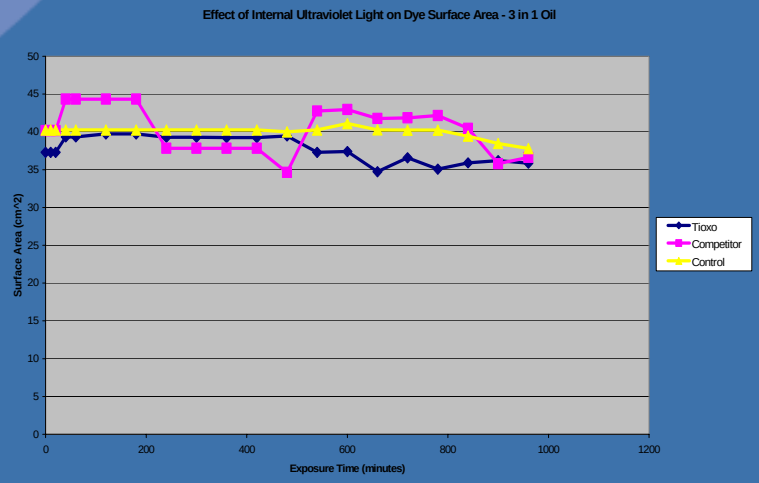
Red #2



Blue #440



3 in 1 Oil



Cleanability Study Results

- Removal efficiencies ranked in the following order of greatest to least (easiest to most recalcitrant):

  Red #2 ← Red #220 ← Blue #440 ← 3-in-1 Oil
- TioxoClean® coated plates displayed a greater rate of removal of both Red #2 and Red #220 compared to Product A under each UV light treatment.
- Product A possessed a more efficient cleanability rate when Blue #440 was utilized as the challenge dye.

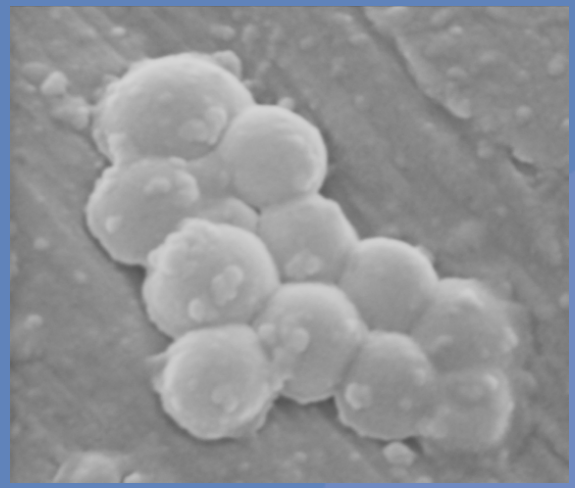
Cleanability Study Results

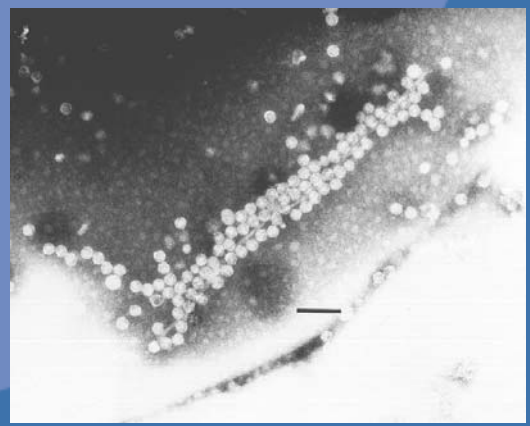
- Red #2:
  - TioxoClean® coating under indoor UV conditions yielded the highest rate of cleanability (0.172 cm^2/min), followed by outdoor UV (0.127 cm^2/min) and artificial UV (0.048 cm^2/min).
- Red #220:
  - TioxoClean® coating under artificial UV conditions yielded the highest rate of cleanability (0.049 cm^2/min), followed by outdoor UV (0.035 cm^2/min) and indoor UV (0.012 cm^2/min).
- For Blue #440:
  - Product A coating proved more effective than the TioxoClean® coating in both outdoor and indoor UV conditions (0.021 and 0.022 cm^2/min, respectively).

Cleanability Study Conclusions

- **3-in-1 Oil:**
  - **No significant difference between the removal efficiencies for either photocatalytic coating under both the outdoor and indoor UV conditions.**
  - **Both treatments did display cleanability rates that were slightly enhanced when compared to the negative control group.**

Antimicrobial Efficacy





- *S. aureus* image - http://www.iuk.edu/faculty/cchauret/Microphotographs.htm
- *E. coli* image – http://www.ars.usda.gov/isi/index.htm
- MS2 coliphage image - http://www.ncbi.nlm.nih.gov/ICTVdb/WIntkey/Images/089-30.htm

Organism Description

- *Escherichia coli*
  - Gram negative bacterium (1 x 3 µm)
  - Member of coliform group – enteric, lactose fermenting bacteria, facultative anaerobe
  - Structure – LPS, Outer membrane
  - Endotoxin production
  - Flagellated (motile)
  - Infectious dose varies by strain
  - Route of infection - oral

Organism Description

- *Staphylococcus aureus*
  - Gram positive bacterium (1 µm)
  - Cluster forming
  - Thick peptidoglycan layer in cell wall
  - Enterotoxin production (staphyloenterotoxemia) at cell level of 10^5 CFU/mL (1.0 ug of toxin)
  - Non-motile
  - Route of infection - oral

Organism Description

- *MS2 Coliphage*
  - RNA virus; 27 nm in diameter
  - Icosahedral shape
  - Genus of the family *Leviviradae*
  - Surrogate for polio and rotavirus in EPA Water Purifier Guide standard
  - Used as challenge organism for ANSI/NSF Standard 55 “Ultraviolet Microbiological Water Treatment Systems”
  - *E. coli* ATCC 15597 is bacterial host

Efficacy Protocol

- JIS Z2801:2000
- Organisms utilized:
  - *Staphylococcus aureus* ATCC 6538
  - *Escherichia coli* ATCC 8739
  - MS2 Coliphage ATCC 15597
- Bacteria were pre-enriched for 24 hr on TSA slants; harvested and washed via centrifugation and stock density was estimated using Acridine Orange Direct Counting
- Target challenge concentration 1 x 10^4 cfu(pfu)/mL (minimum 1 x 10^3 cfu(pfu)/mL) added to plates

Efficacy Protocol

- Prior to inoculation, plates were sterilized via immersion in 70% ethanol
- Sterile foil (40 x 40 mm) utilized to temporarily cover amended challenge organism and disperse the culture uniformly across plate surface; foil was removed 60 seconds after application
- Exposure scenarios (performed at RT ~ 22°C)
  - Artificial UV light – same conditions and UV light source as cleanability studies
  - Natural indoor light
- Exposure duration = 1 hour

Efficacy Protocol

- Exposures performed in triplicate
- Following exposures, plates were aseptically transferred to stomacher bags containing 10 mL of sterile phosphate buffered water and organisms were eluted
- For the bacterial challenges, eluent suspensions were pour plated with SPCA and incubated for 24 hr at 35°C
- For the phage challenge, eluent suspensions were processed via the top agar overlay method and incubated for 24 hr at 35°C

- Plates containing between 25 and 250 colonies/plaques were enumerated

Efficacy Protocol

- The following experimental coatings were evaluated:
  - TioxoClean® coated
  - TioxoClean® coated + 0.1% Nickel
  - Competitor coated

- 6” x 6” plates were utilized

Efficacy Results

Effectiveness Against *E. coli* ATCC 8739 After 1 Hour UV Exposure

Coating Type	Log Reduction (Indoor)	Log Reduction (Artificial)	Percent Reduction (Indoor)	Percent Reduction (Artificial)
Competitor	0.00	0.08	0.00%	17.65%
TioxoClean®	0.68	3.57	78.95%	99.97%
TioxoClean® + 0.1% Ni	0.38	3.40	58.54%	99.96%

Effectiveness Against *S. aureus* ATCC 6538 After 1 Hour UV Exposure

Coating Type	Log Reduction (Indoor)	Log Reduction (Artificial)	Percent Reduction (Indoor)	Percent Reduction (Artificial)
Competitor	0.0	0.0	0.00%	0.00%
TioxoClean®	0.51	2.38	69.23%	99.51%
TioxoClean® + 0.1% Ni	1.11	2.81	92.31%	99.85%

Effectiveness Against MS2 Coliphage ATCC 15597 After 1 Hour UV Exposure

Coating Type	Log Reduction (Indoor)	Log Reduction (Artificial)	Percent Reduction (Indoor)	Percent Reduction (Artificial)
Competitor	1.83	0.70	98.51%	80.17%
TioxoClean®	1.05	0.81	91.02%	84.43%
TioxoClean® + 0.1% Ni	3.40	1.59	99.96%	97.44%

Efficacy Study Conclusions

- TioxoClean® is more effective against the gram negative and gram positive surrogates than Product A
- *E. coli* is more susceptible to photocatalytic oxidation kill compared to *S. aureus*
- Addition of 0.1% Ni enhances kill of gram positive surrogate
- Effect of 0.1% Ni on virus inactivation needs to be investigated further

Future Experimentation

- Antibacterial properties
  - Foodborne pathogens
    - i.e. *Listeria*, *Salmonella*, *Campylobacter*, *E. coli* 0157:H7
- Antifungal properties
  - Hospital environments
    - i.e. *Candida*, *Trichophyton*
  - Environmental / Residential
    - i.e. *Aspergillus*, *Penicillium*, *Stachybotrys*
- Antiviral properties
  - Hospital environments
    - i.e. HIV, Herpes, Hepatitis
  - Environmental
    - i.e. Norovirus, West Nile, Avian Flu, Coronavirus

Future Experimentation

- Investigate affect of increased microbial load
- Exposure time variation on existing studies
- Longevity analysis
- Application studies
  - Water disinfection
  - Direct food contact surfaces
  - Air abatement systems

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