



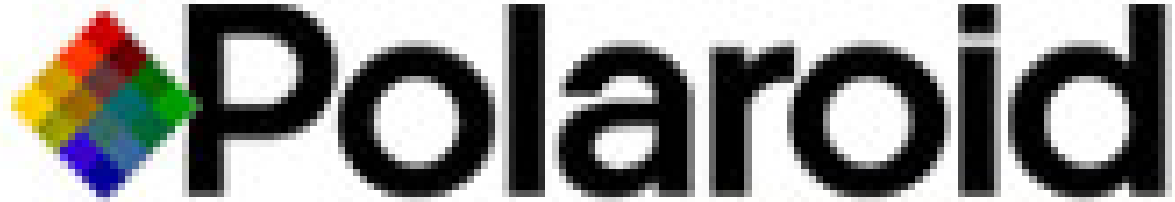
# Introduction to Green Chemistry

John C. Warner

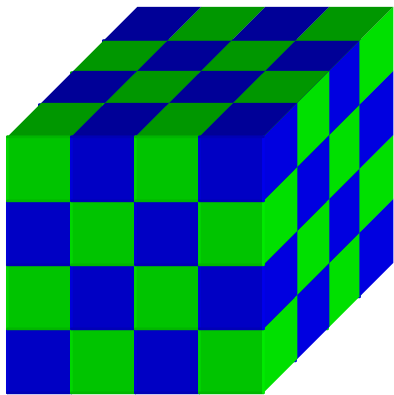
Professor, Plastics Engineering and  
Community Health and Sustainability

Director, Center for Green Chemistry

University of Massachusetts Lowell



## Noncovalent Derivatization



← nanometers →

"Process and Composition for Use in Photographic Materials Containing Hydroquinones. Continuation in Part." Taylor, Lloyd D.; Warner, John. C., US Patent 5,338,644. August 16, **1994**.

"Process and Composition for Use in Photographic Materials Containing Hydroquinones." Taylor, Lloyd D.; Warner, John. C., US Patent 5,177,262. January 5, **1993**.

"Copolymeric Mordants and Photographic Products and Processes Containing Same." Grasshoff, J. Michael; Taylor, Lloyd D.; Warner, John C., US Patent 5,395,731. March 7, **1995**.



# EPA Approval

Low Volume Exemption  
Premanufacturing Notification

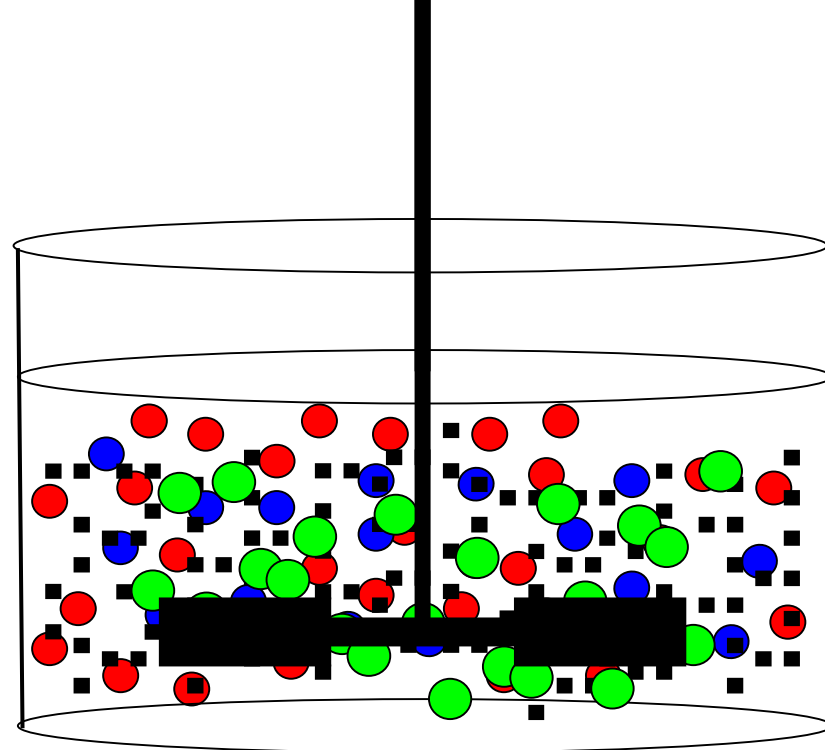
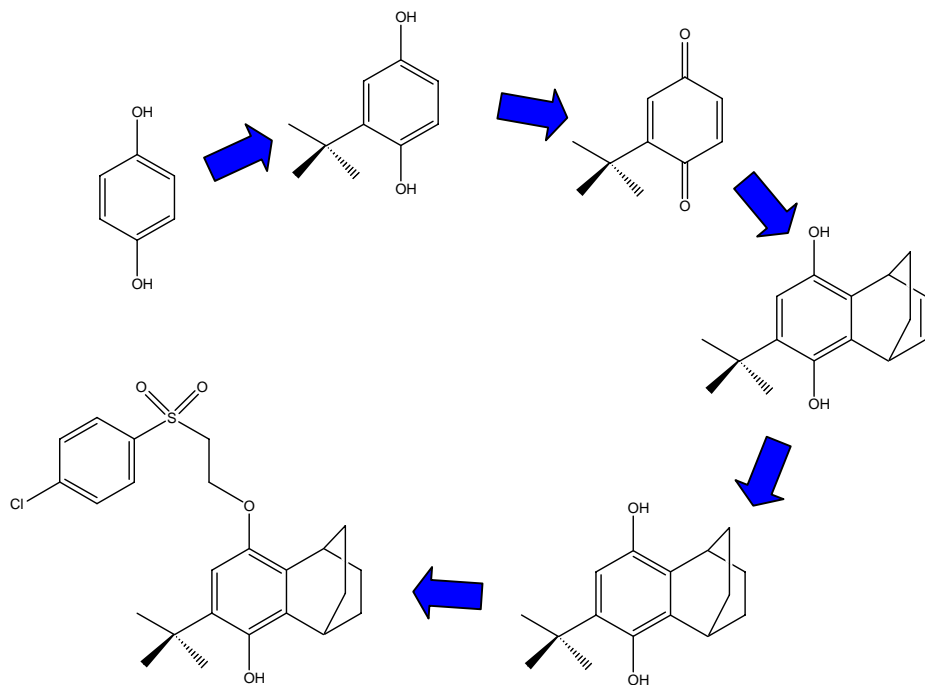
*Small particles?*

*Molecular Complexes?*



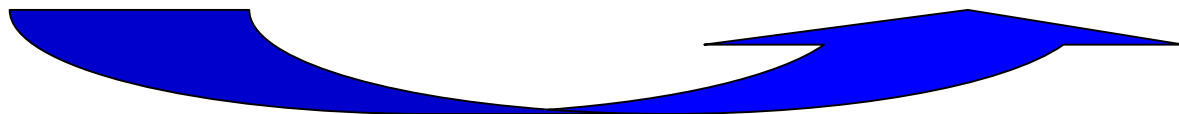
Paul Anastas





**Old Technology**  
 Several Solvents  
 High Energies  
 Hazardous Reagents

**New Technology**  
 Aqueous Conditions  
 Low Energies  
 Non-hazardous Reagents



## Presidential Green Chemistry Challenge



### The Presidential Green Chemistry Challenge

## Awards Opportunities

**T**he Pollution Prevention Act of 1990 established a national policy to prevent or reduce pollution at its source whenever feasible. The Pollution Prevention Act also provided an opportunity to expand beyond traditional EPA programs and devise creative strategies to protect human health and the environment. Green chemistry, or the design of chemical products and processes that reduce or eliminate the use and generation of hazardous substances, is a highly effective approach to pollution prevention. Green Chemistry applies innovative scientific solutions to real-world environmental situations, all through voluntary partnership programs. In order to successfully effect the technical and behavioral changes necessary to accomplish wide-spread pollution prevention through green chemistry, the benefits of the approach must be clearly demonstrated and communicated.

#### **OBJECTIVE:**

The Presidential Green Chemistry Challenge seeks to recognize outstanding accomplishments in green chemistry through an annual awards program in order to demonstrate the scientific, environmental, and economic benefits that green chemistry technologies offer.

#### **BACKGROUND:**

The Presidential Green Chemistry Challenge was implemented as a voluntary EPA Design for the Environment (DfE) partnership with the chemical community. DfE partnerships encourage changes that both promote economic development and benefit industry by identifying cost-effective ways to prevent pollution.

#### **DESCRIPTION:**

The Presidential Green Chemistry Challenge Awards Program is an opportunity for individuals, groups, and organizations to compete for annual awards in recognition of innovations in cleaner, cheaper, smarter chemistry. The Challenge Awards Program provides national recognition for outstanding chemical technologies that incorporate the principles of green chemistry into chemical design, manufacture, and use, and that have been or can be utilized by industry to achieve its pollution prevention goals.

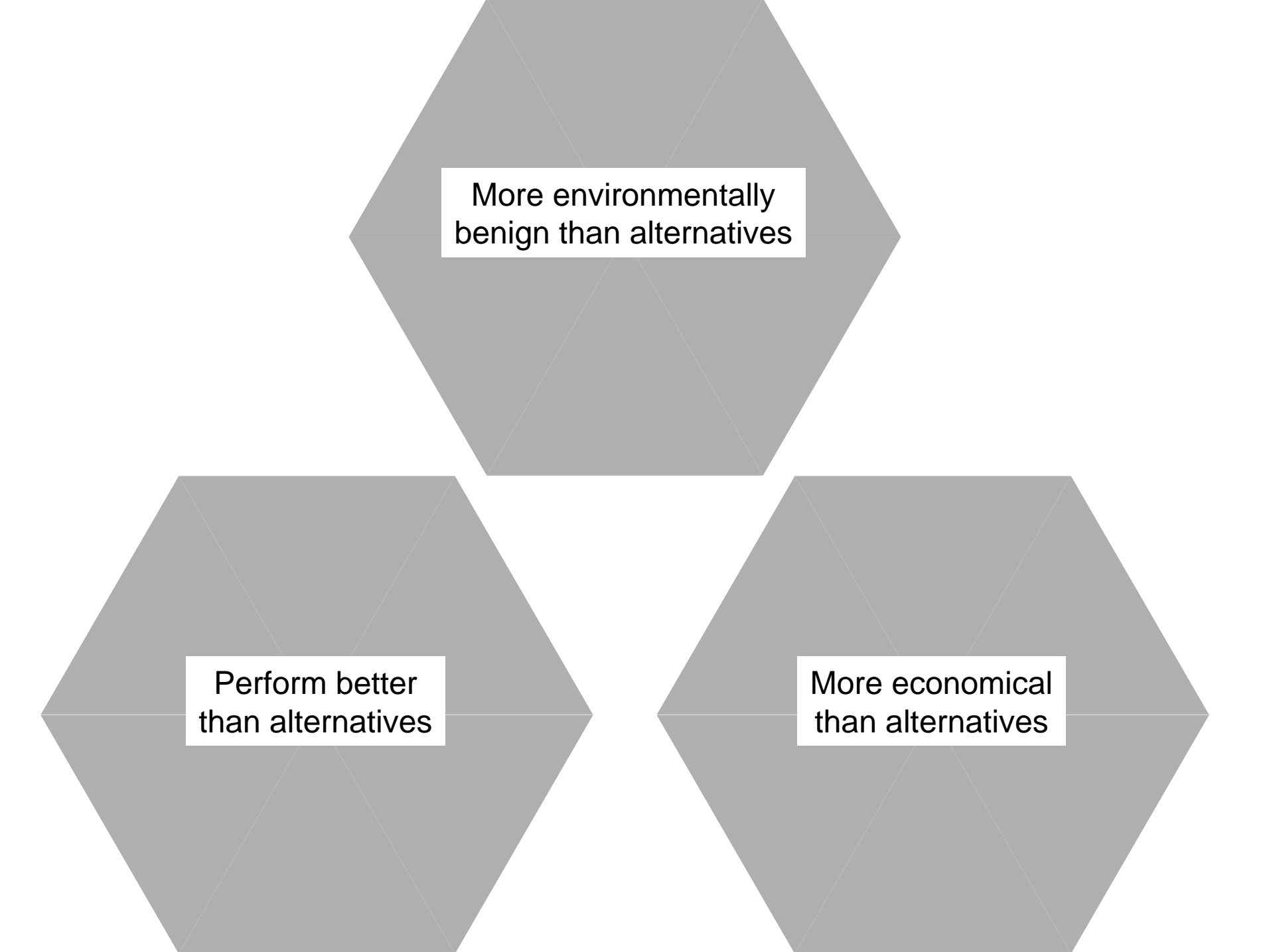
Nominations received for the awards are judged by an independent panel of technical experts convened by the American Chemical Society. Typically, five awards are given annually to industry and government sponsors, an academic investigator, and a small business. Individual projects selected for support may be funded by EPA, NSF, or jointly by both agencies. This is at the option of the agencies, not the grantee.



Printed on paper that contains at least 50 percent postconsumer fiber



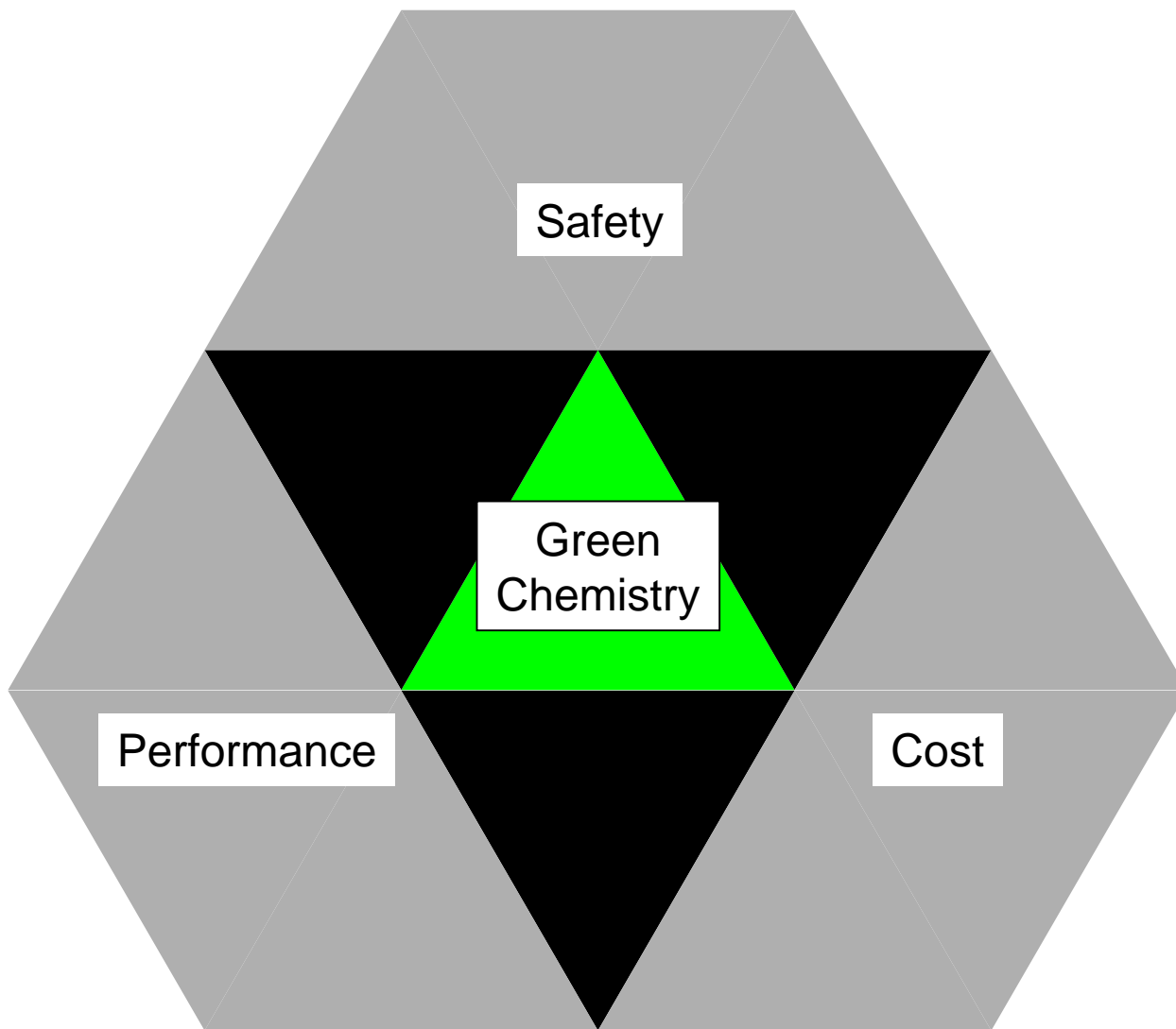
	<b>1996</b>	<b>1997</b>	<b>1998</b>	<b>1999</b>	<b>2000</b>	
Academic	Mark Holzapple	Joseph DeSimone	Barry Trost Karen Draths John Frost	Terry Collins	Chi Hue Wong	
Small Business	Donlar Corporation	Legacy Systems	PYROCOOL Technologies	Biofine	RevTech	Ede
Alternative Synthetic Pathway	Pharmacia	BHC Company	Flexsys America	Lilly Research Laboratories	Roche Colorado	C
Alternative Solvents and Reaction Conditions	Dow	Imation	Argonne National Labs	Nalco Chemical Company	Bayer Corporation	N
Designing Safer Chemicals	Rohm and Haas	Albright and Wilson Associates	Rohm and Haas	Dow AgroSciences	Dow AgroSciences	



More environmentally  
benign than alternatives

Perform better  
than alternatives

More economical  
than alternatives



Safety

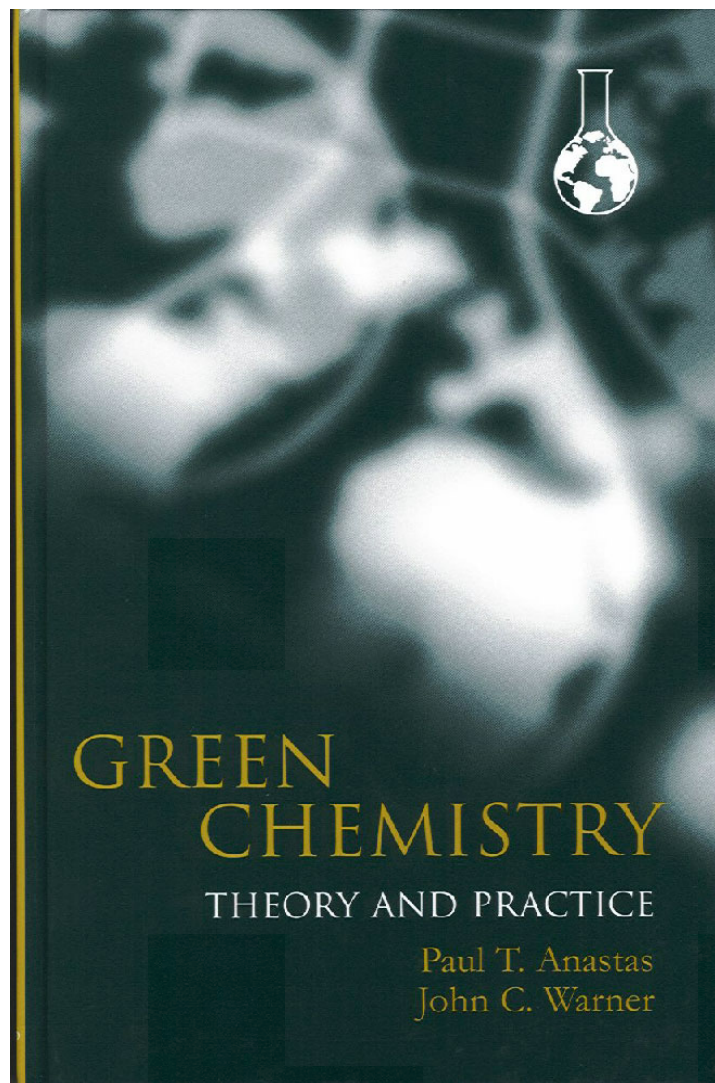
Green  
Chemistry

Performance

Cost



Green Chemistry is the *design* of chemical products and processes that reduce or eliminate the *use and/or generation* of hazardous substances.




# The Twelve Principles of Green Chemistry

- 1. Prevention.** It is better to prevent waste than to treat or clean up waste after it is formed.
- 2. Atom Economy.** Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product.
- 3. Less Hazardous Chemical Synthesis.** Whenever practicable, synthetic methodologies should be designed to use and generate substances that possess little or no toxicity to human health and the environment.
- 4. Designing Safer Chemicals.** Chemical products should be designed to preserve efficacy of the function while reducing toxicity.
- 5. Safer Solvents and Auxiliaries** The use of auxiliary substances (solvents, separation agents, etc.) should be made unnecessary whenever possible and, when used, innocuous.
- 6. Design for Energy Efficiency** Energy requirements should be recognized for their environmental and economic impacts and should be conducted at ambient temperature and pressure.
- 7. Use of Renewable Feedstocks** A raw material or feedstock should be renewable rather than depleting whenever technically practicable.
- 8. Reduce Derivatives** Unnecessary derivatization (blocking group, protection/deprotection, temporary modification of physical/chemical properties) should be avoided whenever possible.
- 9. Catalysis** Catalytic reagents (as opposed to stoichiometric reagents) are superior to stoichiometric reagents.
- 10. Design for Degradation** Chemical products should be designed so that at the end of their function they do not persist in the environment and degrade into innocuous degradation products.
- 11. Real-time Analysis for Pollution Prevention** Analytical methods should be developed to allow for real-time monitoring and control of the chemical process to minimize the amount of hazardous substances released, explosions, and fires.
- 12. Inherently Safer Chemistry for Accident Prevention** Substances and the form of a substance used in a chemical process should be chosen to minimize the potential for chemical accidents, including releases, explosions, and fires.

Risk = Hazard x Exposure



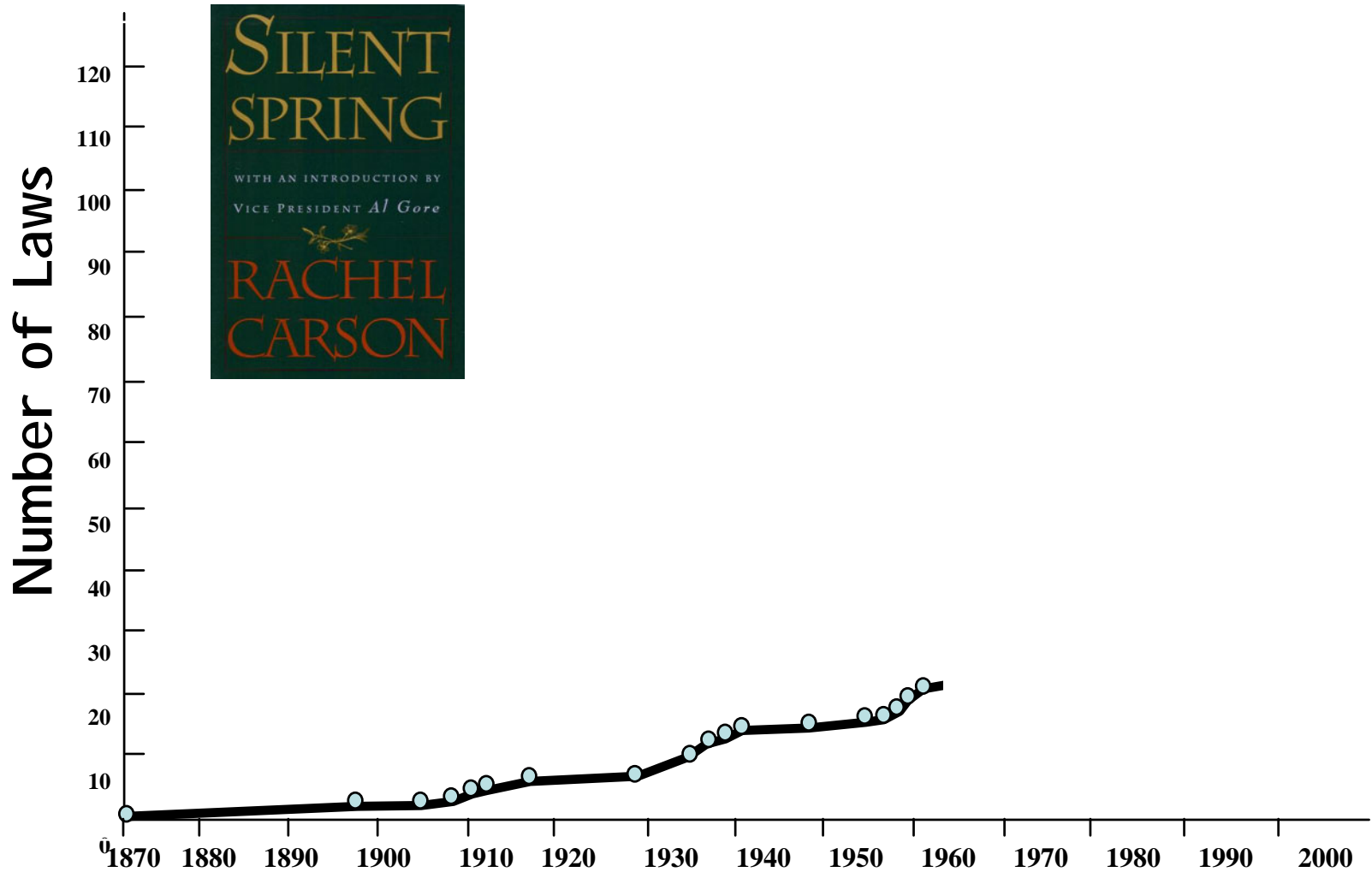


The background of the slide is a dense, overlapping collage of US dollar bills. Visible denominations include \$100, \$50, and \$20 bills. Several stacks of \$100 bills are bound with blue rubber bands, with labels indicating 'Hundreds' and '\$10,000'. The overall image conveys a sense of significant financial cost.

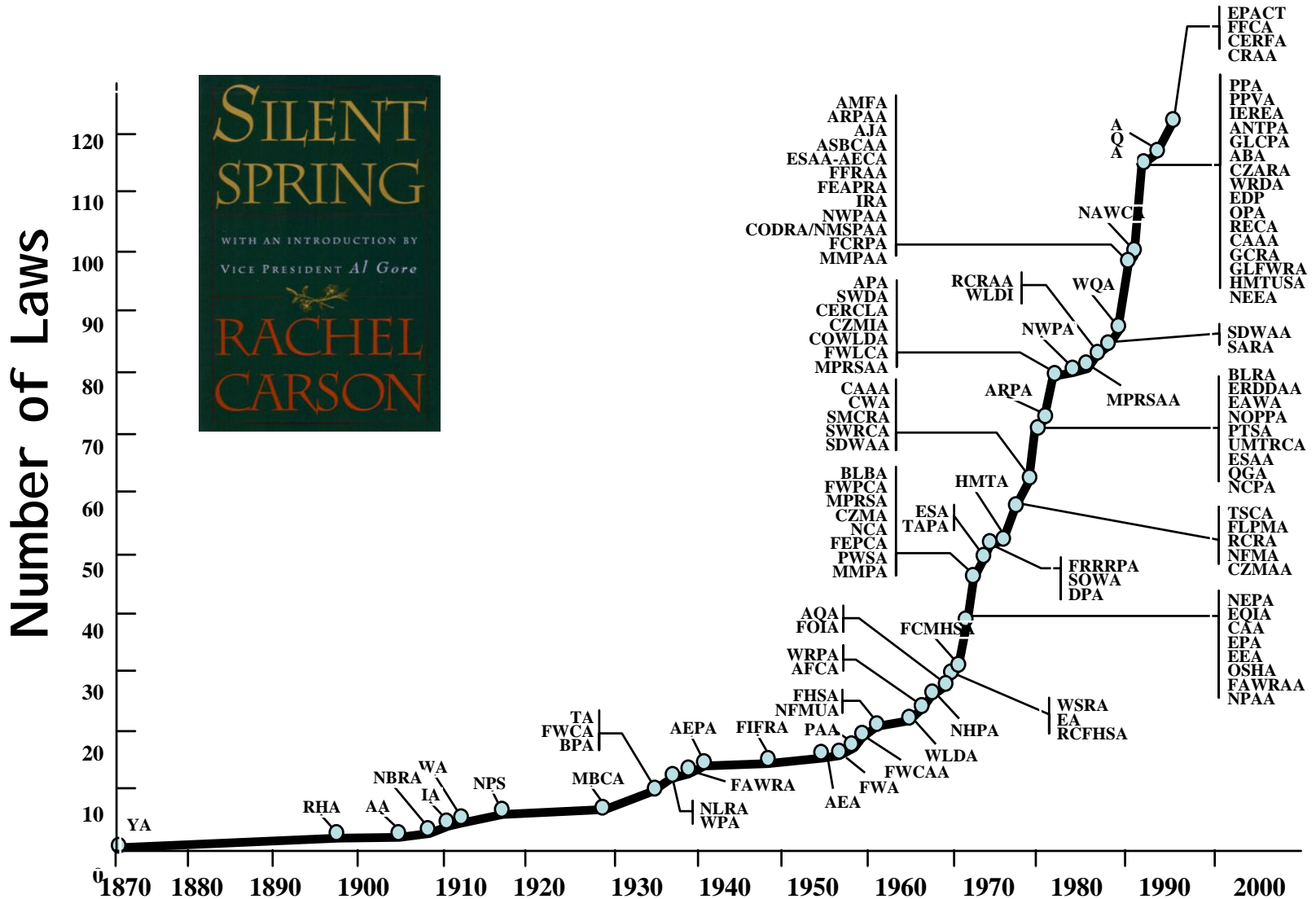
## The cost of using hazardous materials:

- Storage
- Transportation
- Treatment
- Disposal
- Regulatory Costs
- Liability
- Worker Health and Safety
- Corporate Reputation
- Community Relations
- New Employee Recruitment

# Environmental Regulations



# Environmental Regulations





Carbon-Carbon Bonds  
Oxidations  
Reductions  
Hydroxylations  
Polymer Syntheses

Traditional Processes



WI-8000 &  
WI-3000



Traditional Processes

ML-900 &  
ML-500



Green Alternatives

# Green Chemistry Research and Development Act of 2005



# Integrating Research

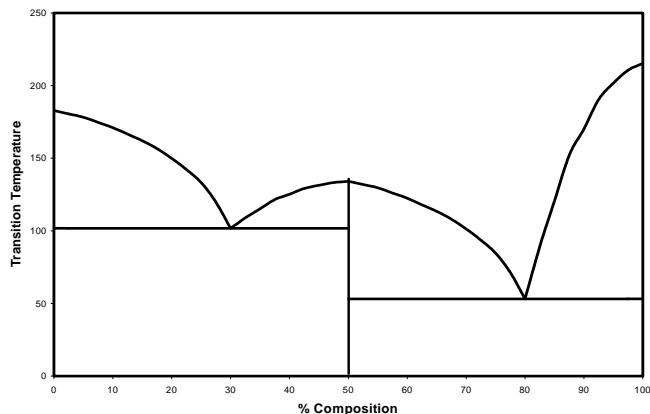
# Center for Green Chemistry

## NonCovalent Derivatization

### Publications

- "Noncovalent Derivatives of Hydroquinone: Complexes with Trigonal Planar Tris-(N,N-Dialkyl)trimesamides" Cannon, Amy S.; Foxman, Bruce M.; Guarrera, Donna J.; Warner, John C. *Crystal Growth and Design* **2005**, 5(2), 407-411.
- "Synthesis of Tetrahedral Carboxamide Hydrogen Bond Acceptors" Cannon, Amy S.; Jian, Tian Ying, Wang, Jun; Warner, John C. *Organic Prep. And Proc. Int.* **2004** 36(4), 353-359.
- "Synthesis of Phenylenebis(methylene)-3-carbamoylpyridinium Bromides" Zhou, Feng; Wang, Chi-Hua; Warner, John C. *Organic Prep. And Proc. Int.* **2004**, 36(2), 173-177.
- "Noncovalent Derivatization: Green Chemistry Applications of Crystal Engineering." Cannon, Amy S.; Warner, John C. *Crystal Growth and Design* **2002**, 2(4) 255-257.
- "Non-Covalent Derivatives of Hydroquinone: Bis-(N,N-Dialkyl)Bicyclo[2.2.2]octane-1,4-dicarboxamide Complexes." Foxman, Bruce M.; Guarrera, Pai, Ramdas; Tassa, Carlos; Donna J.; Warner, John C. *Crystal Engineering* **1999** 2(1), 55.
- "Environmentally Benign Synthesis Using Crystal Engineering: Steric Accommodation in Non-Covalent Derivatives of Hydroquinones." Foxman, Bruce M.; Guarrera, Donna J.; Taylor, Lloyd D.; Warner, John C. *Crystal Engineering*. **1998**, 1, 109.
- "Pollution Prevention via Molecular Recognition and Self Assembly: Non-Covalent Derivatization." Warner, John C., in "Green Chemistry: Frontiers in Benign Chemical Synthesis and Processes." Anastas, P. and Williamson, T. Eds., Oxford University Press, London. pp 336 - 346. **1998**.
- "Non-Covalent Derivatization: Diffusion Control via Molecular Recognition and Self Assembly". Guarrera, D. J.; Kingsley, E.; Taylor, L. D.; Warner, John C. *Proceedings of the IS&T's 50th Annual Conference. The Physics and Chemistry of Imaging Systems*, 537, **1997**.
- "Molecular Self-Assembly in the Solid State. The Combined Use of Solid State NMR and Differential Scanning Calorimetry for the Determination of Phase Constitution." Guarrera, D.; Taylor, L. D.; Warner, John. C. *Chemistry of Materials* **1994**, 6, 1293.
- "Process and Composition for Use in Photographic Materials Containing Hydroquinones. Continuation in Part." Taylor, Lloyd D.; Warner, John. C., US Patent 5,338,644. August 16, **1994**.
- "Process and Composition for Use in Photographic Materials Containing Hydroquinones." Taylor, Lloyd D.; Warner, John. C., US Patent 5,177,262. January 5, **1993**.
- "Structural Elucidation of Solid State Phenol-Amide Complexes." Guarrera, Donna. J., Taylor, Lloyd D., Warner, John C., *Proceedings of the 22nd NATAS Conference*, 496 **1993**.
- "Aromatic-Aromatic Interactions in Molecular Recognition: A Family of Artificial Receptors for Thymine that Shows Both Face-To-Face and Edge-To-Face Orientations." Muehldorf, A. V.; Van Engen, D.; Warner, J. C.; Hamilton, A. D., *J. Am. Chem. Soc.*, **1988**, 110, 6561.

### Entropic Control in Materials Design



# Center for Green Chemistry

## Bioinspired Polymers



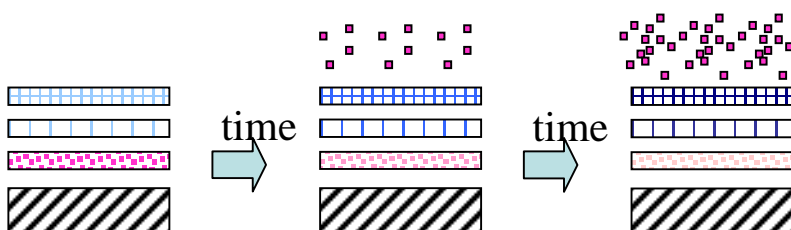
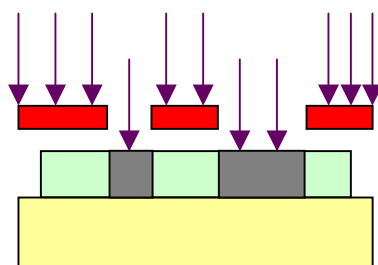
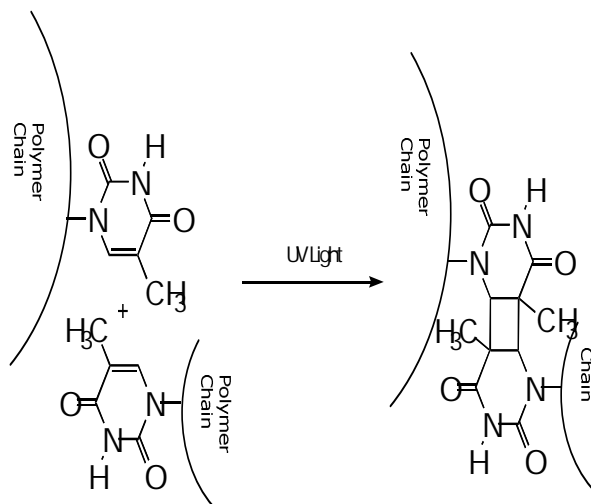
February 12 2005

### Features

SCIENCE NEWS

### Chemistry au Naturel

Chemists aim to mimic natural systems with the hope of developing more-efficient chemical processes that are also less harmful to the environment.



"Spectroscopic and Microscopic Analysis of Photocrosslinked Vinylbenzylthymine (VBT) Copolymers for Photoresist Applications" Trakhtenberg, Sofia; Warner, John C.; Nagarajana, Ramaswamy; Bruno, Ferdinando F.; Samuelson, Lynne A.; Kumar, Jayant *Chem. Mater.* **2005** Submitted for publication.

"Effect of Dye Additives on Photodimerization of Thymine Pendant Groups in Water-Soluble Photoresist Polymers" Yu, Catherine; Trakhtenberg, Sofia; Cain, Timothy E.; Warner, John C. *Journal of Polymers and the Environment.* **2005** Submitted for publication.

"(4-Vinylbenzyl)cinnamate: A Useful Monomer for Water-Soluble Photopolymers" Cannon, Amy S.; Warner, John C., *J. Macr. Sci.* **2005**. In Press

"Methylene Blue Adsorption on Thymine Based Polyvinylphenylsulfonate Films" Kiarie, Cecilia; Bianchini, Jason; Trakhtenberg, Sofia; Warner, John C. *J. Macr. Sci.* **2005**. In Press

"Enzymatic Reversal of Polymeric Thymine Photocrosslinking with E. coli DNA Photolyase" Whitfield, Justin; Morelli, Alessandra and Warner, John C., *J. Macr. Sci.* **2005**. In Press

"Photocrosslinked Immobilization of Polyelectrolytes for Enzymatic Construction of Conductive Nanocomposites" Trakhtenberg, Sofia; Hangun-Balkir, Yelda; Warner, John C.; Bruno, Ferdinando; Kumar, Jayant; Nagarajan, Ramaswamy; Samuelson, Lynne A. *J. Am. Chem. Soc.* **2005** 127, 9100-9104

"Photoreactive Polymers and Devices for use in Hair Treatments", Cannon, Amy S.; Raudys, Jennifer; Undurti, Arundhati; Warner, John C. *PCT Int. Appl.* **2004**, 23pp WO 2004058187.

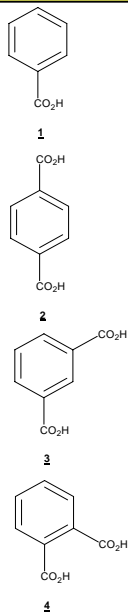
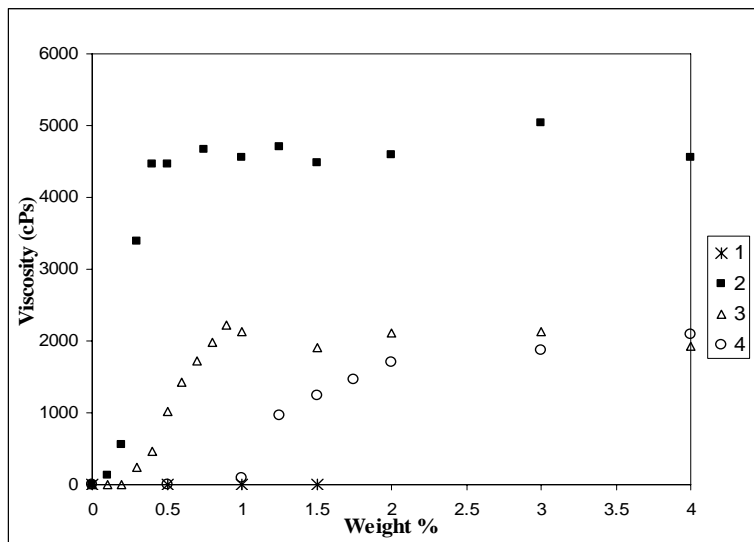
"Methods of solubilizing and recycling biodegradable polymers containing photoreactive moieties using irradiation", Warner, John C.; Morelli, Alessandra; Ku, Man-Ching U.S. Pat. Appl. Publ. **2003**, 4 pp. US 2003224497.

"Thymine-Containing Styrene Polymers as Environmentally Benign Photoresists" Lloyd-Kindstrand, Lisa; Warner, John C. *Biopolymers*, **2002**, 8, 165-174.

# Center for Green Chemistry

## Ambient Metal Oxide Semiconductors

Titanium Dioxide Film Formation: Pre-formed TiO<sub>2</sub>



"The Low Temperature Processing of Titanium Dioxide Films by the Addition of Trimesic Acid" Cannon, Amy S.; Guarrera, Donna J.; Morelli, Alessandra; Pressler, Whitney; Warner, John C. *J. Sol Gel Sci.* **2005**. In Press

"Structure Activity Relationship of Organic Acids in Titanium Dioxide Nanoparticle Dispersions" Cannon, Amy S.; Jian, Tian Ying, Wang, Jun; Warner, John C. *Chem. Mater.* **2004** 16, 5138-5140..

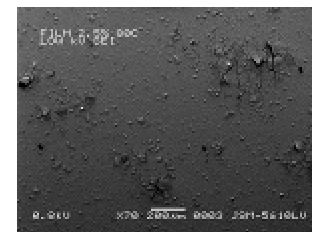
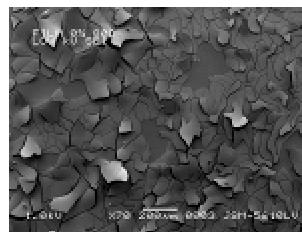
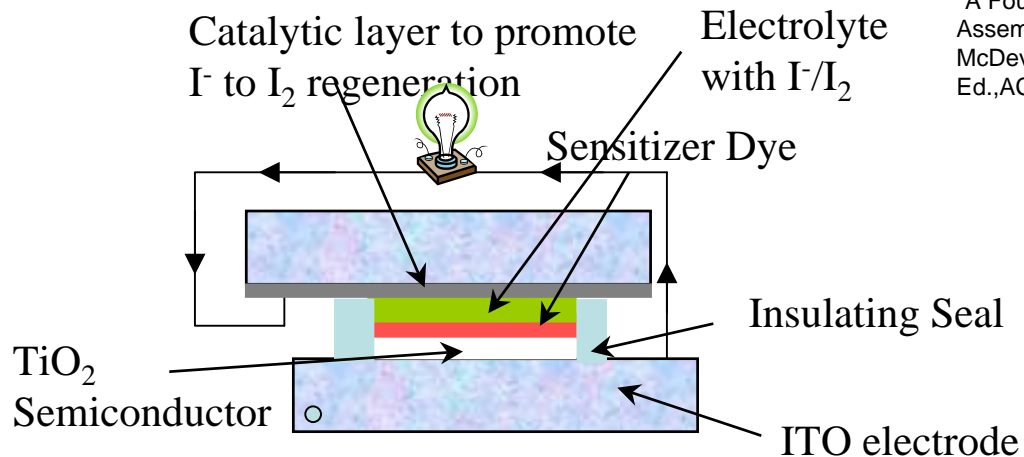
"Metal Oxide Films", Morelli, Alessandra; Warner, John C. *PCT Int. Appl.* **2003**, 14pp. WO 2003008079.

"Green Chemistry Considerations in the Construction of Solar Energy Devices" Cannon, Amy S.; Warner, John C. *6th Annual Green Chemistry and Engineering Conference Proceedings*, Washington, DC, **2002**.

"Photocatalysis of Electron Transfer Reactions by C60 Adducts." Hamann, Thomas W.; Bussandri, Alejandro P.; Van Willigen, Hans; Najah, Samira; Warner, John C. *Proceedings – Electrochemical Society* **2000**, (*Fullerenes: Volume 8: Elctrichemistry and Photochemistry*), 289-298.

"Lithographically patterned superconductor bolometer detectors for visible and near-infrared radiation incorporating wavelength-selective light-absorbing elements." Eames, Sara J.; Yoo, J. Seung-Jin; Warner, John C.; Neikirk, Dean P.; McDevitt, John Thomas. *Proc. SPIE-Int. Soc. Opt. Eng.*, **3790**(*Engineered Nanostructural Films and Materials*), 160-168, **1999**.

"A Four Color Optical Sensor: Wavelength-Selective Dye/Superconductor Assemblies"; Eames, S.; Savoy, S.; Wells, C.; Zhao, J.; Warner, J. C.; McDevitt, J. in *Spectroscopy of Superconducting Materials*, E. Faulques, Ed., ACS Books, US, **1999**, 278-2



Thank You