Green Chemistry and Commercial Applications

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BBC NEWS
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EPA Is Reconsidering
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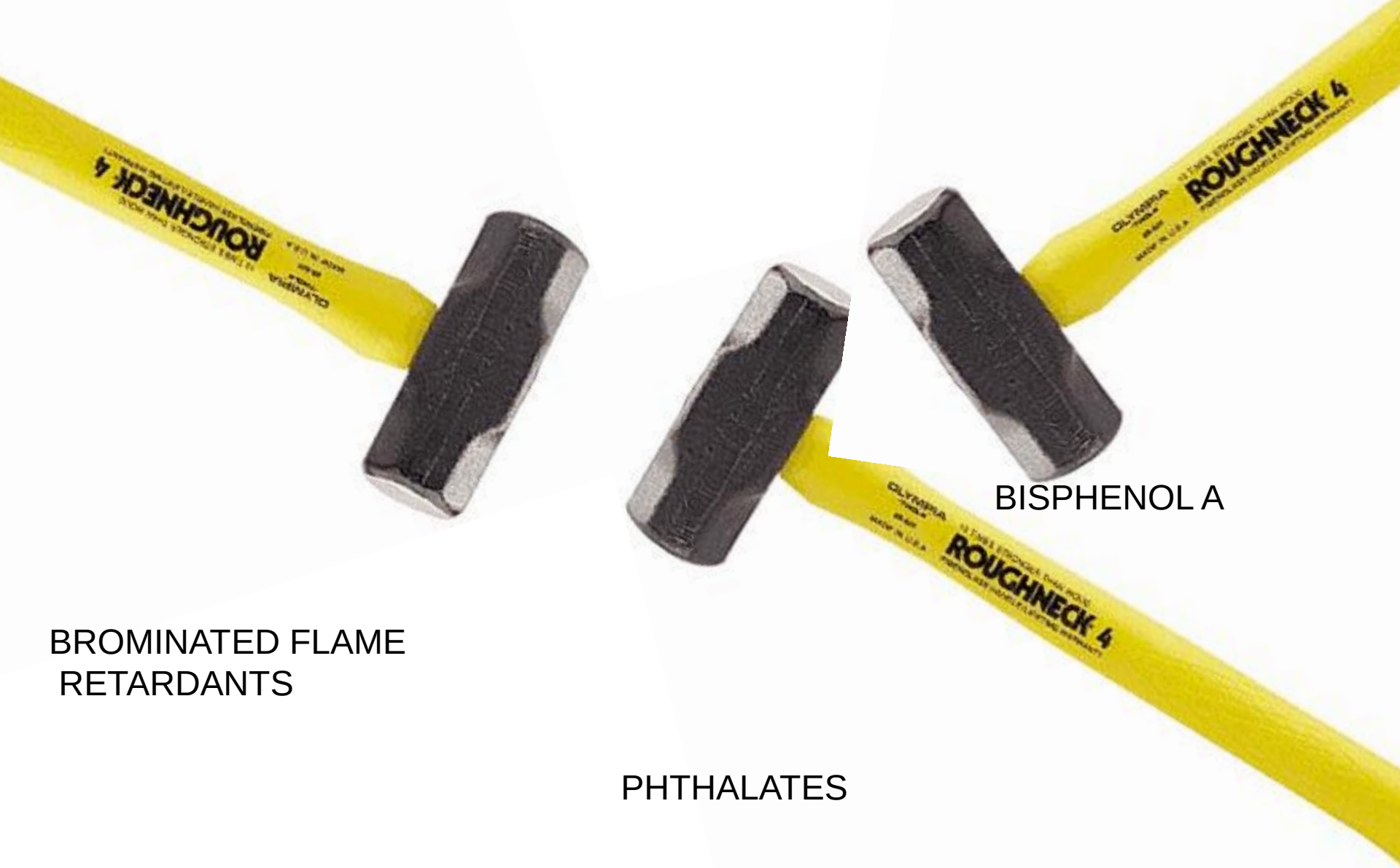
The New York Times
Child obesity is link
to chemicals in plastic
TIME
The Poisoning of America
The Japan Times
Oceans awash in toxic seas of plastic
THE WALL STREET JOURNAL.
Yes, Bisphenol-A Does Enter the Body from Plastic Bottles
CNN.com
erious contaminati
from Africa's m
USA TODAY
5,000 evacuated after
hazardous Pa. acid spill
Chicago Tribune
Chicago's Toxic Air
THE SUNDAY TIMES
Household Dust Contains Highly Toxic Chemicals


WHACK A MOLE!



BISPHENOL A

BROMINATED FLAME
RETARDANTS

PHTHALATES

Asking the Right Questions

Why would a chemist make a hazardous material?

How do we train chemists?

UMASS Boston – 1980-1984

Professor J.-P. Anselme

- "N-Nitrosamines from the Reaction of N-Chlorodialkylamines with Sodium Nitrite." Nakajima, M.; Warner, J. C.; Anselme, J.-P. *J. Chem. Soc., Chem. Commun.,* **1984**, 451.
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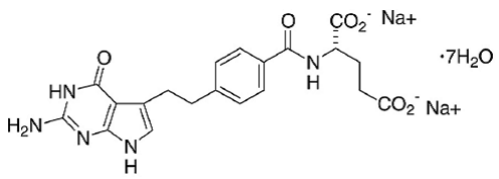
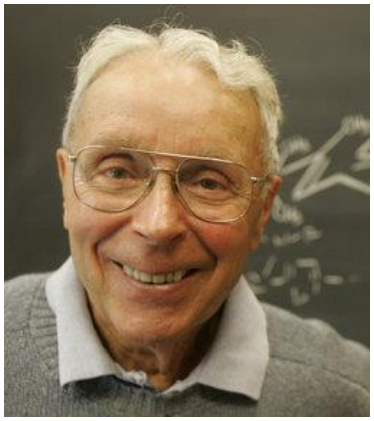
Princeton University – 1984-1988



Lilly

VET TES EN NOV TAM TVM



Professor E. C. Taylor

- "Diels-Alder Reactions of Bicyclic 1,2,4-Triazines: The Conversion of Pyrimido[4,5-*e*]-1,2,4-triazines to Pyrido[2,3-*d*]pyrimidines." Taylor, E. C.; McDaniel, K. F.; Warner, J. C. *Tetrahedron Lett.*, **1987**, *28*, 1977.
- "Synthesis and Structural Confirmation of 5,6-Cyclopenteno-5-deazapterin." Taylor, E. C.;Warner, J. C., *Heterocycles*, **1987**, *26*, 2673.
- "Heterodienophilic Intramolecular Diels-Alder Reactions of 1,2,4-Triazines. Synthesis of Novel Polycyclic Condensed Pyrazines and Lumazines." Taylor, E. C.; Pont, J. L.; Warner, J. C., *Tetrahedron.*; **1987**, *43*, 5159, **1988**, *44*, 1825.
- "Intramolecular Diels-Alder Reactions of 6-Azalumazines and 6-Azapterins. A Facile Route to 6,7-Annulated-5-deazapteridines." Taylor, E. C.; Warner, J. C.; Pont, J. L., *J. Org. Chem.*, **1988**, *53*, 800.
- "Diels-Alder Reactions of 7-Azalumazines. Synthesis of Condensed Lumazines and 8-Deazalumazines" Taylor, E. C.; Warner, J. C.; Pont, J. L., *J. Org. Chem.*, **1988**, *53*, 3568.
- "Diels-Alder Reactions of 6-Azapterins. An Alternate Strategy for the Synthesis of 5,10 Dideaza-5,6,7,8-tetrahydrofolic Acid (DDATHF)." Taylor, E. C.; Harrington, P. M.; Warner, J. C., *Heterocycles*, **1988**, *27*, 1925.
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- "Competitive Intramolecular Diels-Alder Reaction and Intramolecular Coplanar Cycloamination of 3-(3-Butynylthio)-1,2,4-triazin-5-ones." Taylor, E. C.; Pont, J. L.; Van Engen, D.; Warner, J. C., *J. Org. Chem.*, **1988**, *53*, 5093.
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- "New Synthetic Studies on Deazafolates." Taylor, E. C.; Chang, Z. Y.; Harrington, P. M.; Hamby, J. M.; Papadopoulou, M.; Warner, J. C.; Wong, G. S. K.; Yoon, C. M.; Shih, C., *Chem. Biol. Pteridines, 1989 Proc. Int. Symp. Pteridines Folic Acid Deriv.*, 9th, Meeting Date 1989, 987. Ed. by: Curtius, H.-C.; Ghisla, S.; Blau, N. de Gruyter: Berlin, Fed. Rep. Ger. **1990**.
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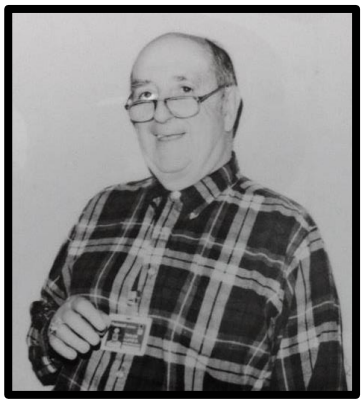
Polaroid Corporation – 1988-1997



Lloyd D. Taylor

Edwin Land

- "Thermographic Recording Films." Dombrowski, Edward J.; Jones, Robert L.; Warner, John C.; Yang, Jiyue US Patent 5,750,463. Filed April 22, 1997. Published May 12, 1998.
- "Acid-Catalyzed Thermal Decomposition of Secondary Acid Generator and Formation of Second Acid; Copper Compound and Reactive Material Used to Decompose Superacid Precursor" Marshall, John L.; Baker, Rita Shon S.; Takiff, Larry C.; Telfer, Stephen J.; Warner, John C. US Patent 5,741,630. Filed April 25, 1994. Published April 21, 1998.
- "Copolymers having pendant functional thymine groups" Grasshoff, J. Michael; Taylor, Lloyd D.; Warner, John C. US Patent 5,708,106. Filed May 3, 1996. Published January 13, 1998.
- "Photograph Development" Guarrera, Donna J.; Mattucci, Neil C.; Mehta, Avinash C.; Taylor, Lloyd D.; Warner, John C. US Patent 5,705,312. Filed Nov. 25, 1996. Published January 6, 1998.
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- "Images by Exposure to Actinic Radiation; Solvent Removal of Non-Exposed Areas" Grasshoff, J. Michael; Taylor, Lloyd D.; Warner, John C. US Patent 5,616,451. Filed May 24, 1995. Published April 1, 1997.
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- "Low-Volatility, Substituted 2-Phenyl-4,6-bis[Halomethyl]-1,3,5-triazine for Lithographic Printing Plates." Fitzgerald, Maurice J.; Kearney, Frederick R.; Liang, Rong-Chang; Schwarzel, William C.; Guarrera, Donna, J.; Hardin, John M.; Warner, John C. PCT Int. Appl. WO 1996034315. Filed April 19, 1996. Published October 31, 1996. CA 2189459. Filed April 19, 1996. Published October 31, 1996. DE 69609136. Filed April 19, 1996. Published August 10, 2000. EP 0767932. Filed April 19, 1996. Published April 16, 1997.
- "Low-Volatility, Substituted 2-Phenyl-4,6-bis[Halomethyl]-1,3,5-triazine for Lithographic Printing Plate Preparation" Fitzgerald, Maurice J.; Kearney, Frederick R.; Liang, Rong-Chang; Schwarzel, William C.; Guarrera, Donna, J.; Hardin, John M.; Warner, John C. US Patent 5,561,029. Filed April 28, 1995. Published October 1, 1996.
- "Vinylbenzyl Thymine Monomers and Polymers and Products Prepared from Same" Grasshoff, J. Michael; Taylor, Lloyd D.; Warner, John C. PCT Int. Appl. WO 1995031755. Filed May 10, 1995. Published November 23, 1995. CA 2185144. Filed May 10, 1995. Published November 23, 1995. EP 0759193. Filed May 10, 1995. Published February 26, 1997. DE 69504652. Filed May 10, 1995. Published October 15, 1998.
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- "Imaging Medium and Process." Fehervari, Agota F.; Gaudiana, Russell A.; Kolb, Eric S.; Mehta, Parag G.; Taylor, Lloyd D.; Warner, John C. US Patent 5,424,268. Filed May 13, 1994. Published June 13, 1995.
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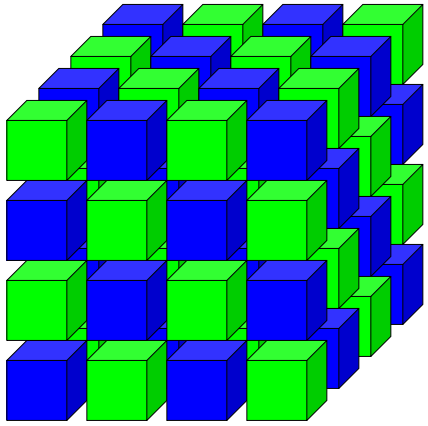
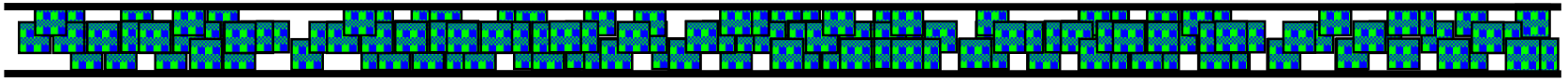
- "Process and Composition for Use in Photographic Materials Containing Hydroquinones." Taylor, Lloyd D.; Warner, John C. US Patent 5,338,644. Filed December 23, 1992. Published August 16, 1994.
- "Process and Composition for Use in Photographic Materials Containing Hydroquinones." Taylor, Lloyd D.; Warner, John C. US Patent 5,177,262. Filed July 19, 1991, Published January 5, 1993. EP 0523470. Filed July 3, 1992, Published February 3, 1993. CA 2070450. Filed June 4, 1992, Published January 20, 1993. DE 69218312. Filed July 3, 1992, Published April 24, 1997. JP 06230540. Filed July 16, 1992.

Non Covalent Derivatization





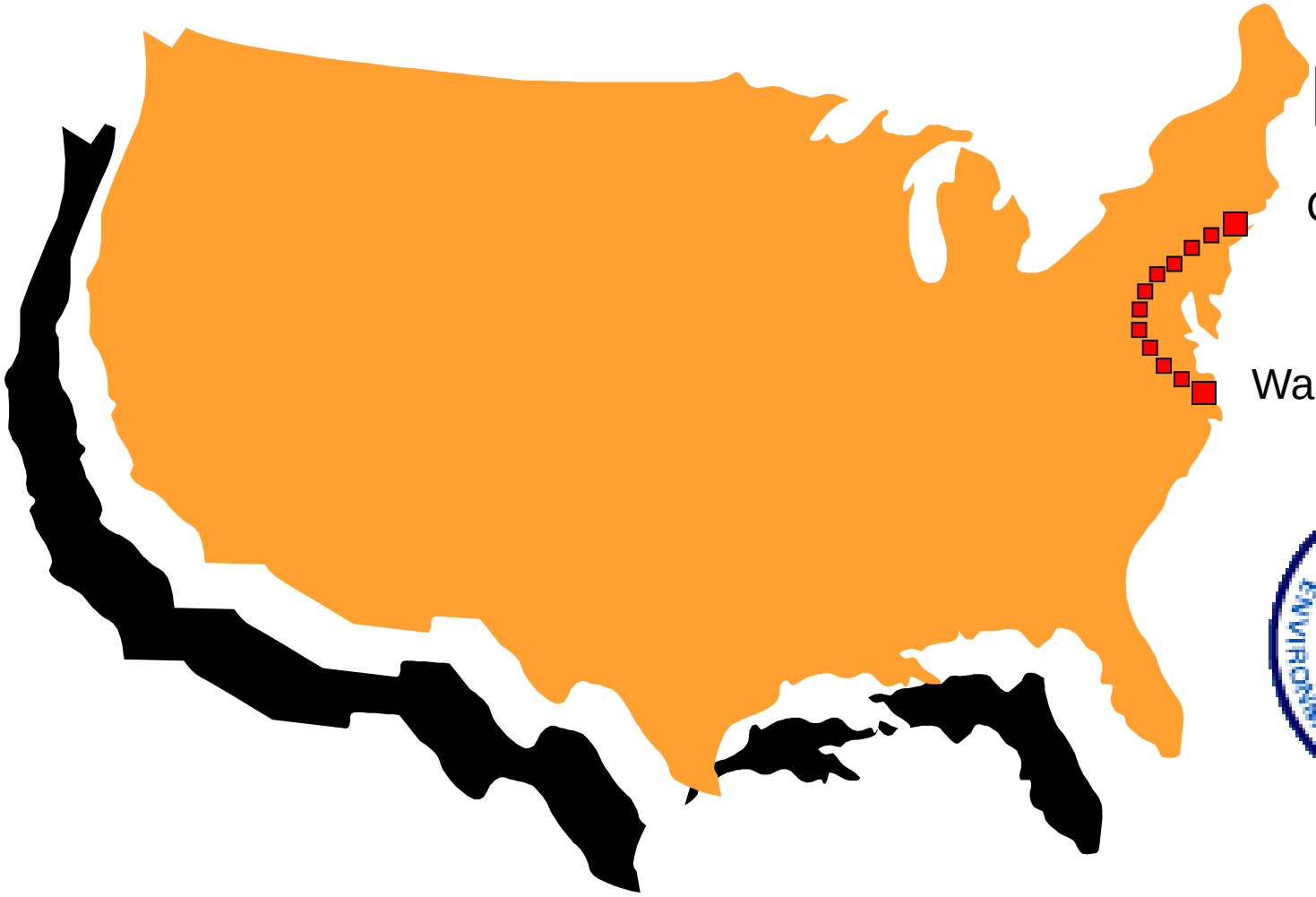
EPA Approval

Low **V**olume **E**xemption

Pre**M**anufacturing **N**otification

"Small particles"?

"Molecular Complexes"?



Polaroid

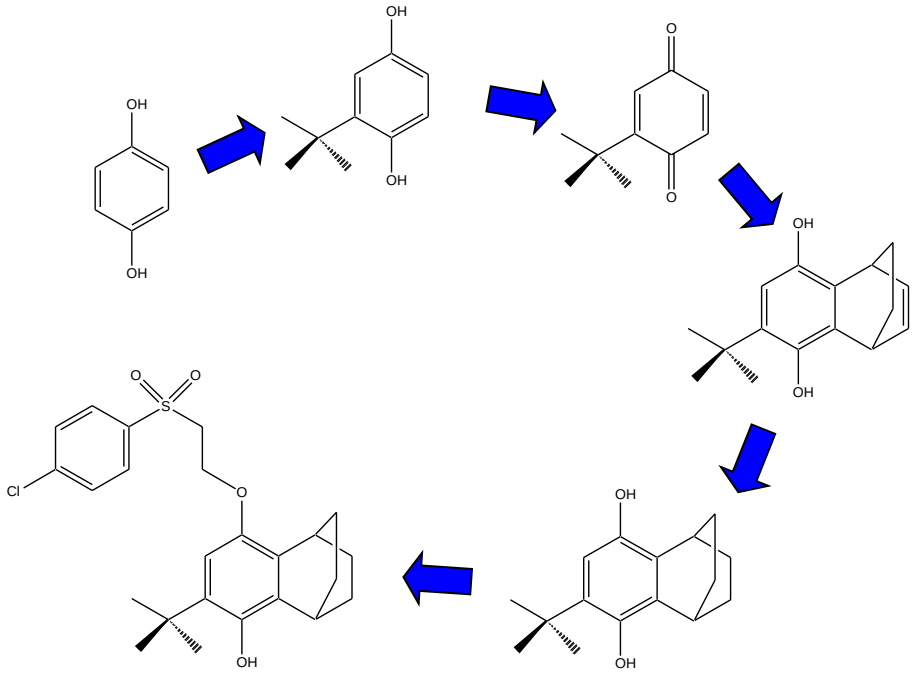
Cambridge, MA

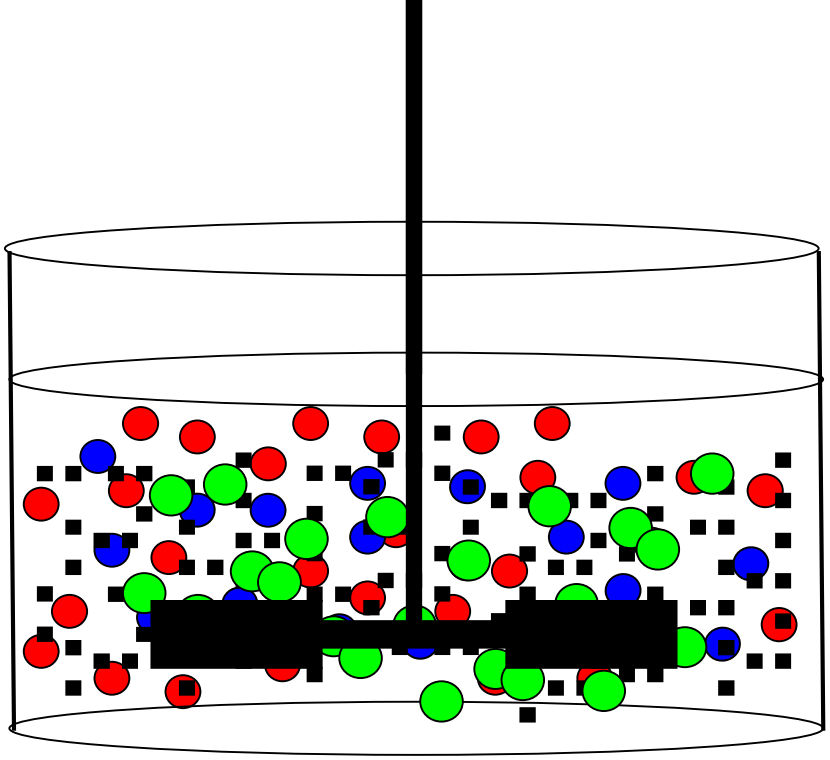
Washington, DC

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

Paul Anastas

Office of Pollution Prevention and Toxics





Old Technology
Several Solvents
High Energies
Hazardous Reagents

New Technology
Aqueous Conditions
Low Energies
Non-hazardous Reagents

Every Year: (United States)

Chemistry and Chemical Engineering Graduates

15,000 Undergraduate Degrees

3,000 Masters Degrees

3,000 Doctoral Degrees

50.9 % Women Undergraduate Degrees (2004)

To get a degree in Chemistry…

No universities require any demonstration of knowledge regarding toxicity or environmental impact!

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 minimized. Synthetic methods 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 and economically practical.

8. Reduce Derivatives. Unnecessary derivatization (blocking group, protection/deprotection, temporary modification of physical/chemical processes) should be avoided whenever possible .

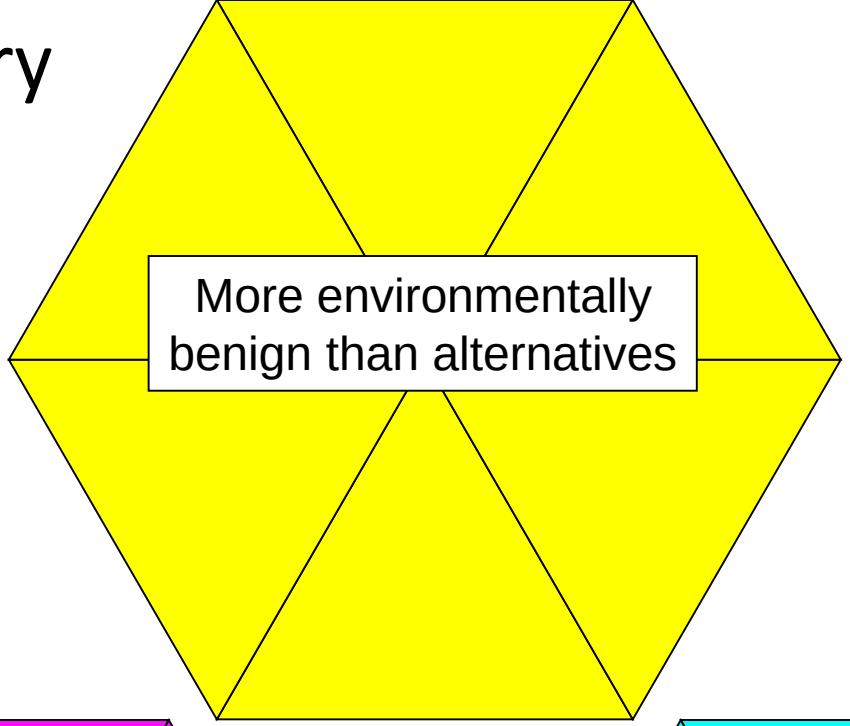
9. Catalysis. Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.

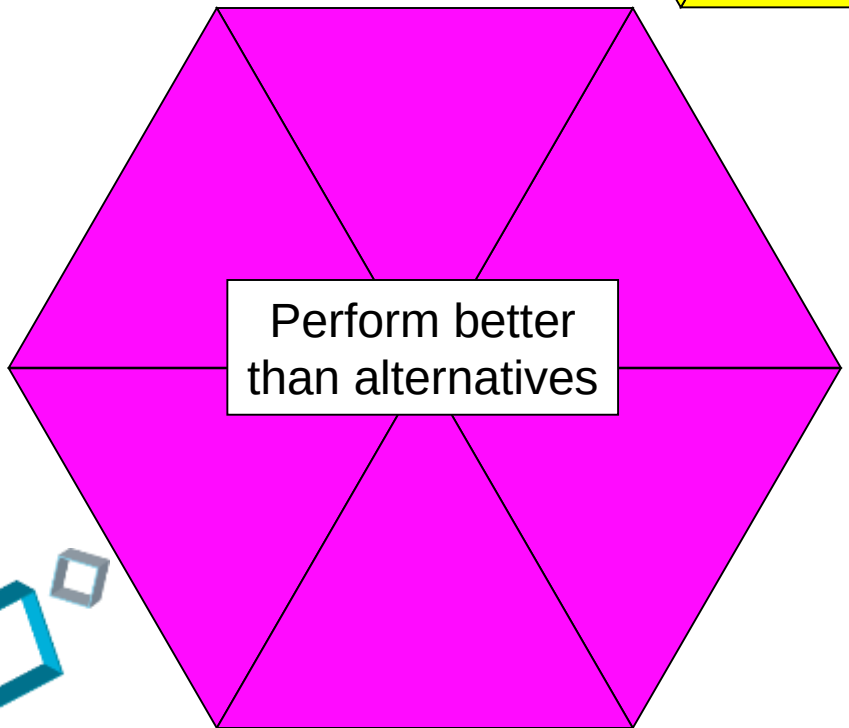
10. Design for Degradation. Chemical products should be designed so that at the end of their function they do not persist in the environment and instead break down into innocuous degradation products.

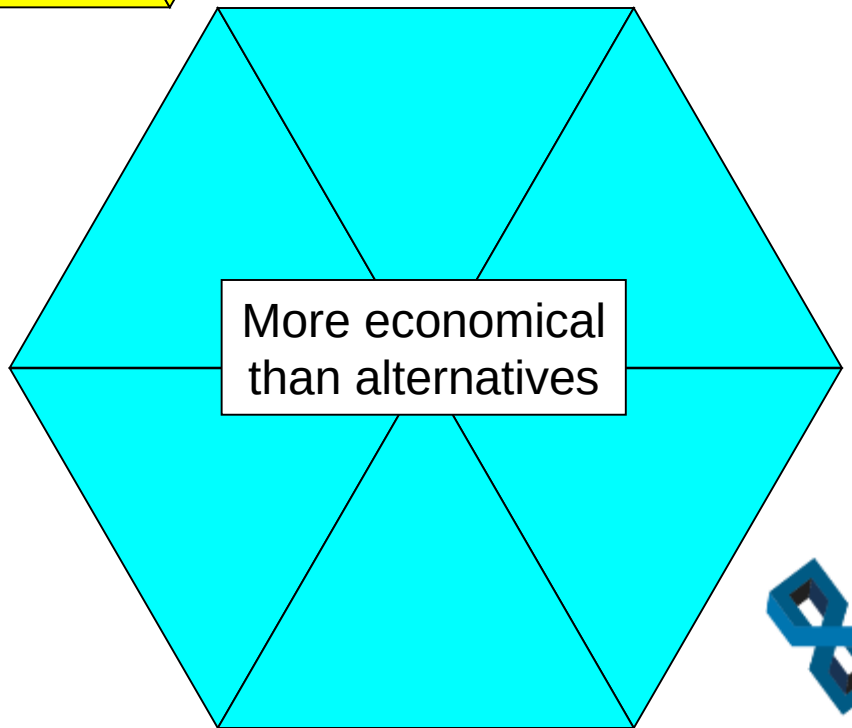
11. Real-time Analysis for Pollution Prevention. Analytical methodologies need to be further developed to allow for real-time in-process monitoring and control prior to the formation of hazardous substances.

12. Inherently Safer Chemistry for Accident Prevention. Substance and the form of a substance used in a chemical process should be chosen so as to minimize the potential for chemical accidents, including releases, explosions, and fires.

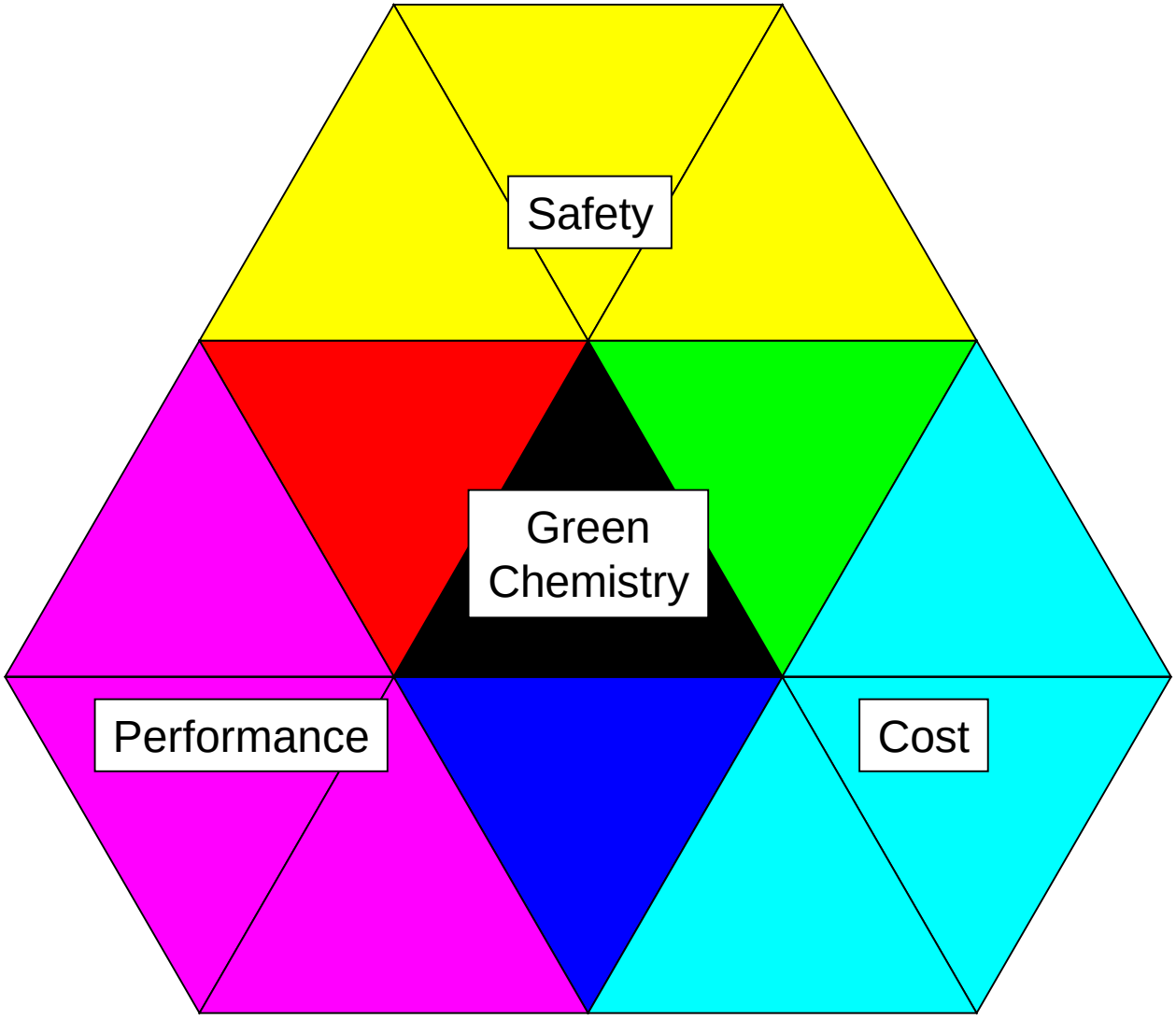
Green Chemistry







Green Chemistry



UMASS – 1996-2007

1997 Assistant Professor
1998 Associate Professor (Tenure)
1999 Director of Biochemistry
2000 Full Professor
2001 Chair Chemistry Department
2001 Director Green Chemistry PhD Program
2004 Professor Plastics Engineering (UML)

PHOTO BY ROB SHERMAN

INCUBATOR The University of Massachusetts, Boston, houses the first Ph.D. program in green chemistry.

GREEN CHEMISTRY EARNS A PH.D.

The University of Massachusetts, Boston, now offers a Ph.D. track in green chemistry

SINCE LAST FALL, THE UNIVERSITY of Massachusetts, Boston (UMB), has been accepting students into a new program called the green chemistry Ph.D. track. It is offered by the department of environmental sciences but administered by the department of chemistry.

The first of its kind in the world, the program is the brainchild of its director, UMB chemistry professor John C. Warner. Students in the program, he explains, will be trained much like other Ph.D. chemistry students, although their education will emphasize skills to design materials and processes that have minimal impact on human health and the environment. Areas of concentration include environmentally benign synthesis, environmental monitoring and detection, biodegradation, and bioremediation.

What makes the program different from anything else available so far, Warner says, is the requirement of courses in toxicology, environmental law and policy, environmental fate and transport, and industrial chemistry. Through these courses, he explains, "we broaden the students' understanding of environmental realities—such as what makes a molecule toxic, what laws have been established to govern synthetic procedures, and what happens in the environment—which conventional chemistry programs don't teach."

Terrence J. Collins, a chemistry professor at Carnegie Mellon University, notes that "we do not live in a sustainable civilization, sustainability meaning that what we do every day can be carried on to the indefinite future without causing damage." Collins was a recipient of the 1999 Presidential Green Chemistry Challenge Academic Award. The UMB program, he tells C&EN, is one way to call attention to the fact that "a sustainable civilization needs the intimate engagement of chemistry."

The UMB program "is timely, as there has been a distinct shift in focus in chemistry," says Janet Scott, deputy director of the Centre for Green Chemistry at Monash University, in Australia. "Even those who might not consider themselves 'green chemists' are beginning to focus on issues of sustainability and the design of benign products and processes to prevent pollution at the source. The chemical industry is beginning to demand a wider knowledge of and attention to issues of sustainability."

Mary Kirchhoff, assistant director of the Green Chemistry Institute, in Washington, D.C., agrees that the time is right for a green chemistry Ph.D. program. It might have been met with skepticism 10 years ago, when the term "green chemistry" first surfaced, she tells C&EN. Warner is the ideal person to lead such a program, she adds. "He's got the research credentials, the teaching credentials, the commitment to students, and the passion."

Particularly in organic synthesis, formal green chemistry training will force chemists to change how they think.

"One of the things that makes organic synthesis so exciting is that, if you draw a molecule, there are probably an infinite number of synthetic pathways that you can follow to make that molecule," Warner says. Traditionally, the focus has been on maximizing yields and stereoselectivities. Considerations of environmental and toxicological impact rarely come into play.

"IF ONE STEP in a synthetic sequence requires a hazardous reagent that's regulated by the federal government, that sequence could be more expensive than an alternative route that might give less yield," Warner explains. Regulatory and environmental realities often decide the economic viability of a synthetic route, he adds.

Chemists usually learn of such considerations when they're working for a company, Warner says. "Industry would like people to come in with some understanding of these issues, because there's economic benefit if processes designed in labs do not have to be reworked to satisfy regulatory requirements."

A green chemistry Ph.D. would be a big plus for chemists interested in process development, notes Berkeley Cue, vice president of pharmaceutical sciences at Pfizer Global Research & Development, Groton, Conn. "What we try to incorporate into the design of manufacturing processes—such as safety, efficient use of raw materials, minimal use of solvents, and online analysis—are aligned to the concepts that Warner and people like him are teaching," he explains. "We just didn't call it green chemistry. We called it process development."

Amy Cannon is the first student enrolled in UMB's green chemistry Ph.D. program. She's working on constructing solar energy devices in a more environmentally benign manner. Currently, she explains, producing solar cells consumes so much energy that a solar panel has to operate for years before it generates as much energy as was used to make it.

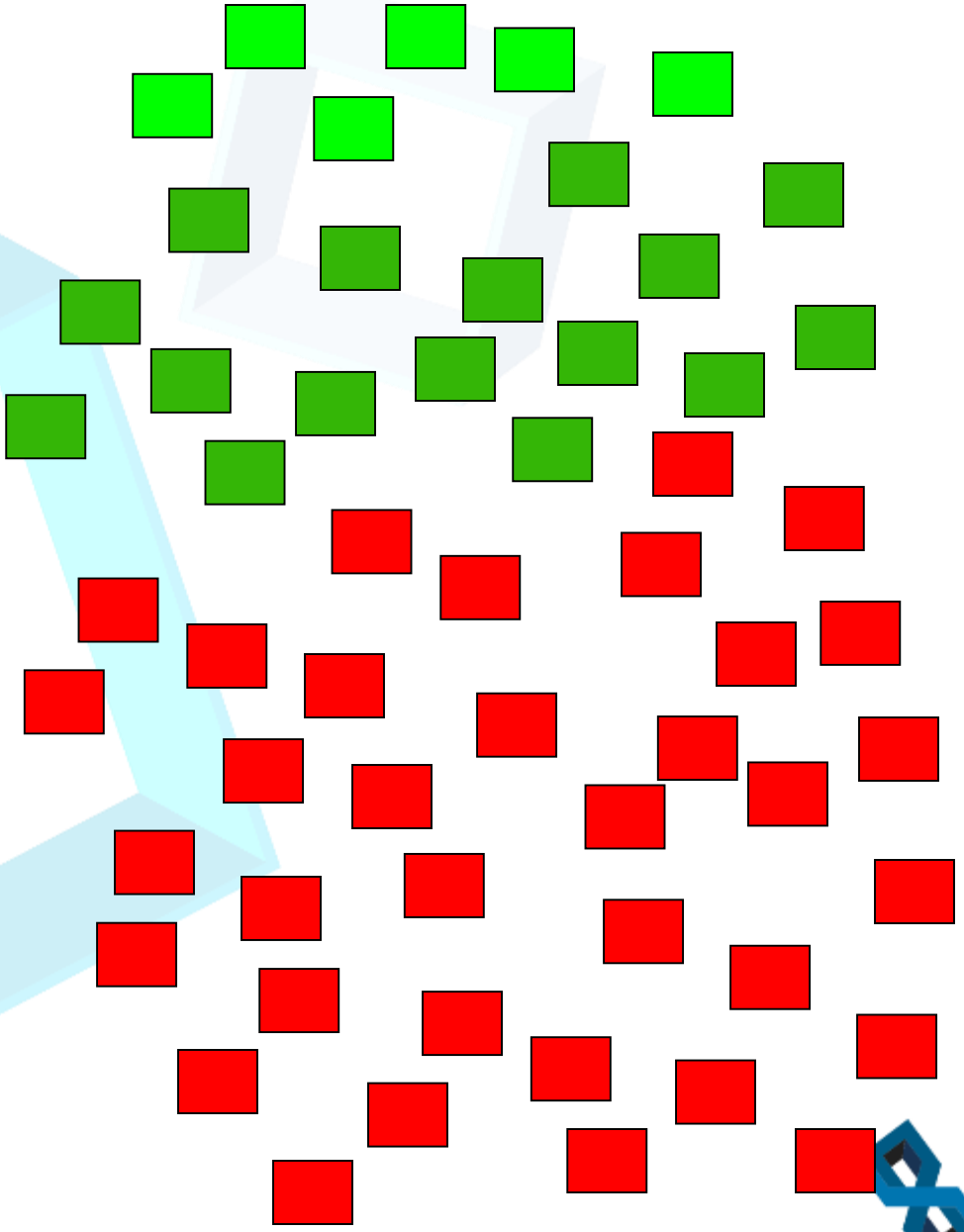
"Alternative energy is one of the most important areas in terms of sustainability," Cannon tells C&EN. Having just completed her master's degree under Warner's guidance, Cannon is passionate about green chemistry. "What could be better than this," she asks, "given that my big goal in life is to help save the world by doing what I can where I am?"—MAUREEN ROUHI

Of all the products and processes…

Maybe 10% are benign…

Maybe 25% have alternatives available…

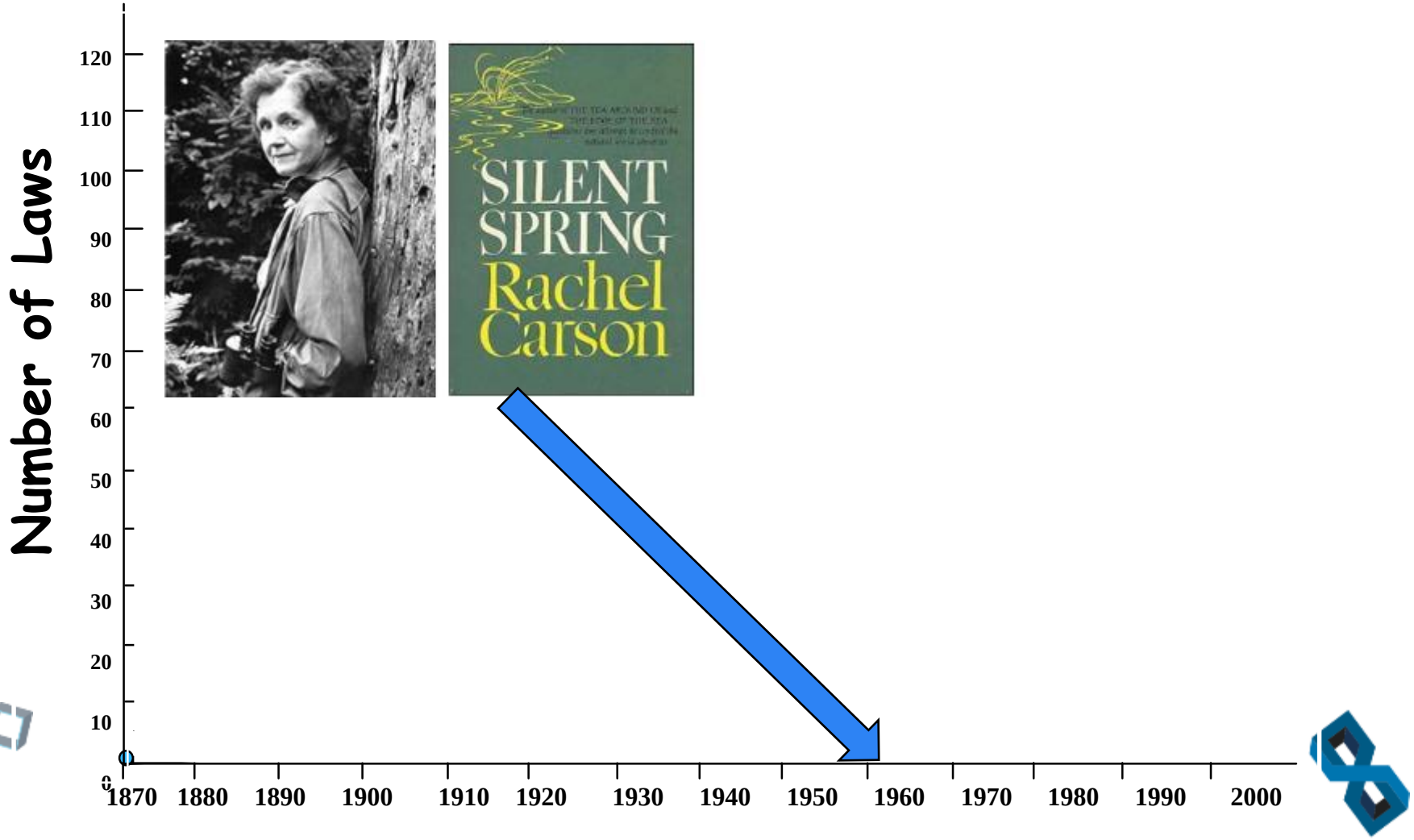
65% Still have to be invented!



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

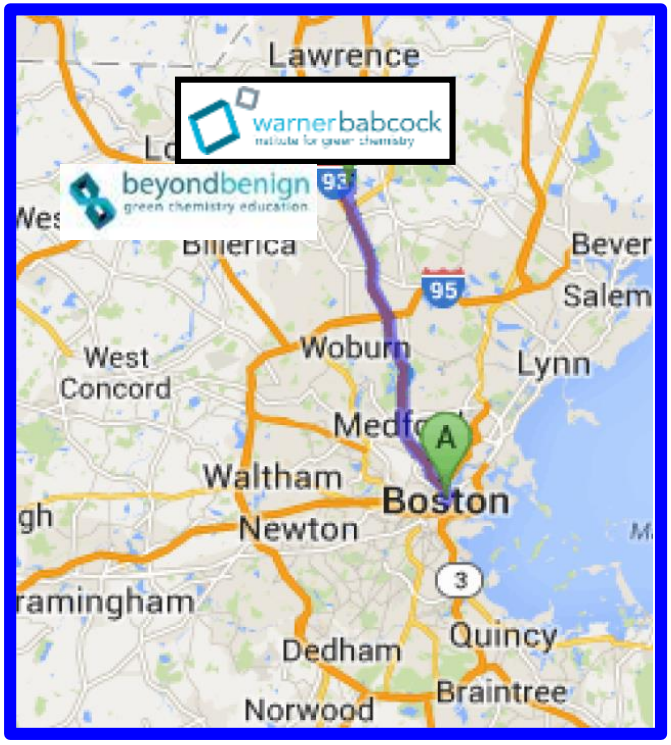


WBI - 2007 ->

John Warner Amy Cannon

Jim Babcock

Joe Pont, CEO



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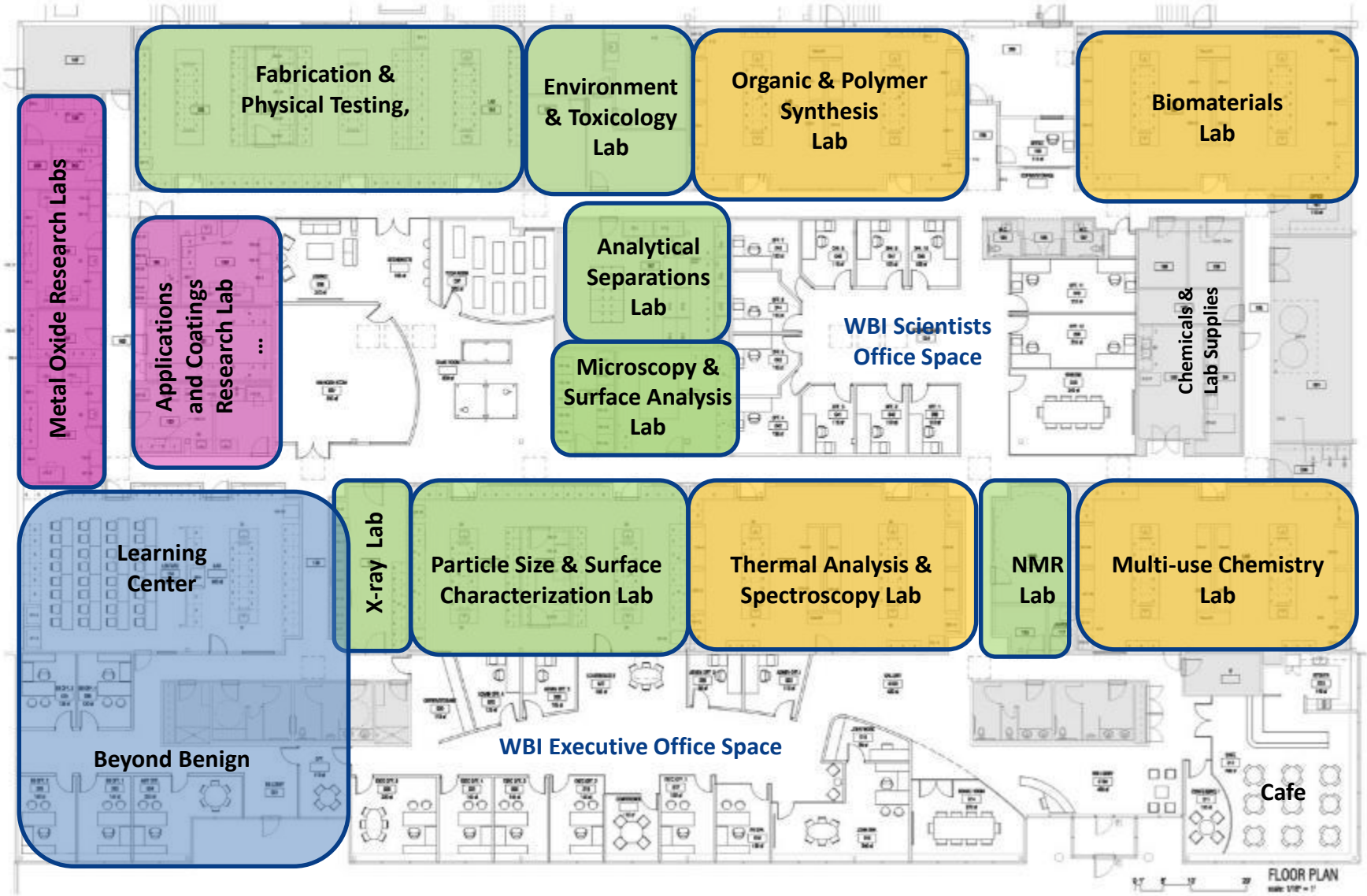
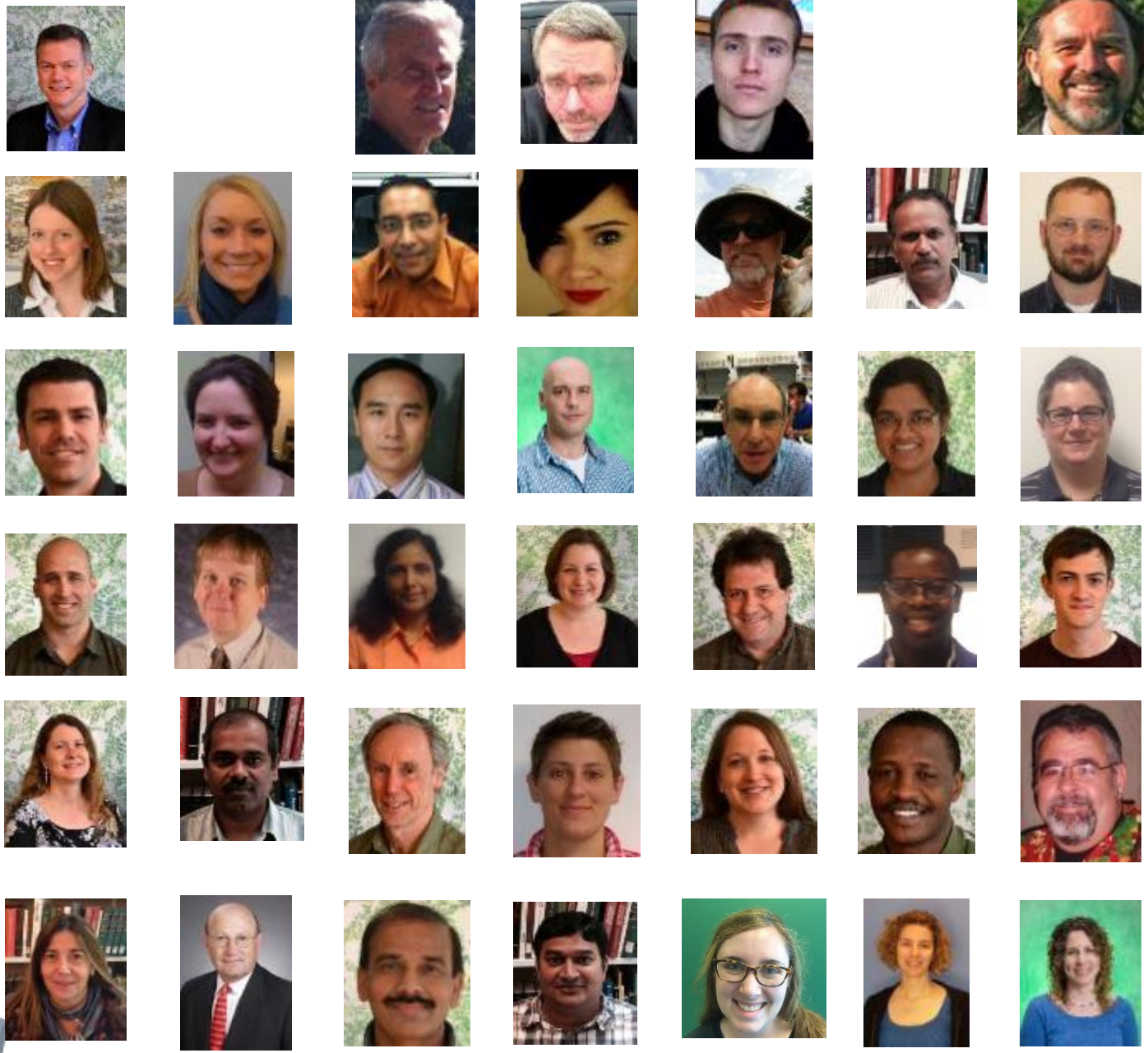
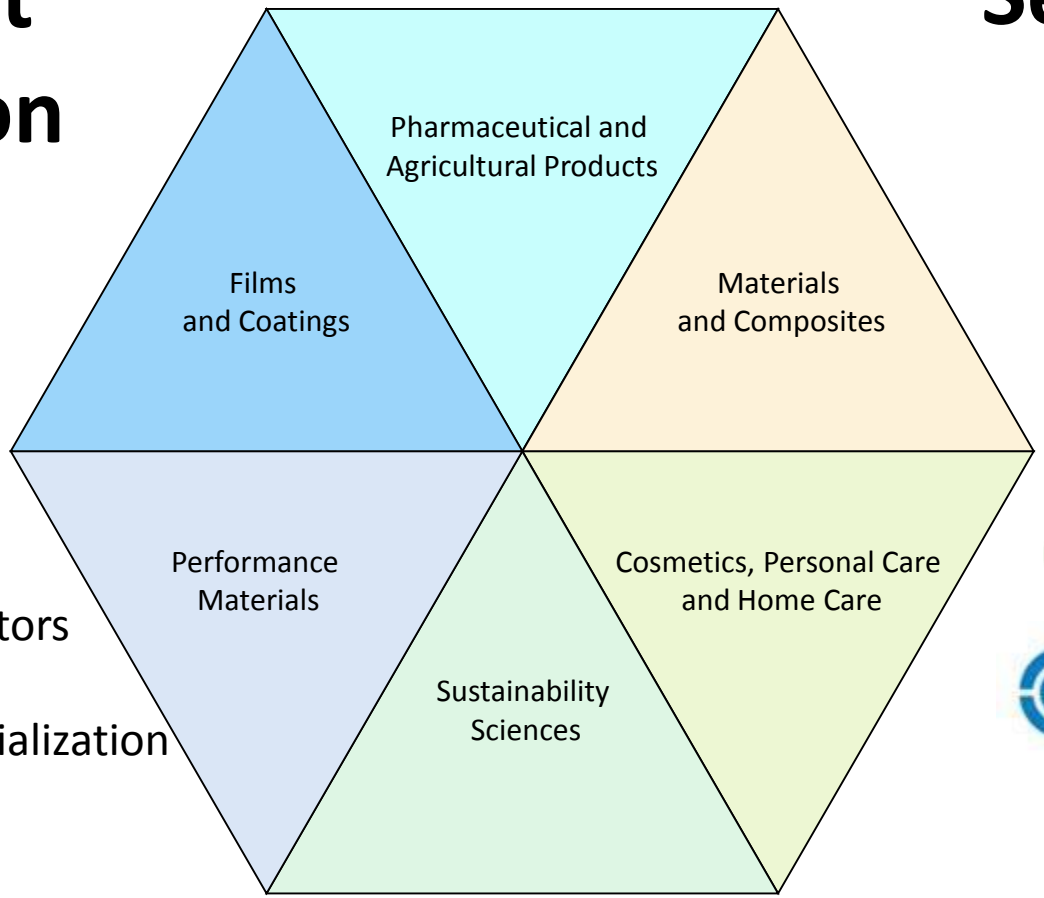

Fabrication & Physical Testing,
Environment & Toxicology Lab
Organic & Polymer Synthesis Lab
Biomaterials Lab
Metal Oxide Research Labs
Applications and Coatings Research Lab
...
Analytical Separations Lab
Microscopy & Surface Analysis Lab
WBI Scientists Office Space
Chemicals & Lab Supplies
Learning Center
X-ray Lab
Particle Size & Surface Characterization Lab
Thermal Analysis & Spectroscopy Lab
NMR Lab
Multi-use Chemistry Lab
Beyond Benign
WBI Executive Office Space
Cafe
FLOOR PLAN



warnerbabcock
institute for green chemistry

Contract Invention

Self-Funded Invention



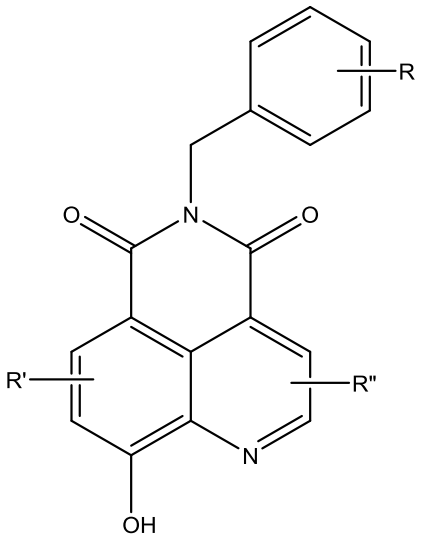
Invent for collaborators

Help with commercialization

COLLABORATIVE AGGREGATES LLC

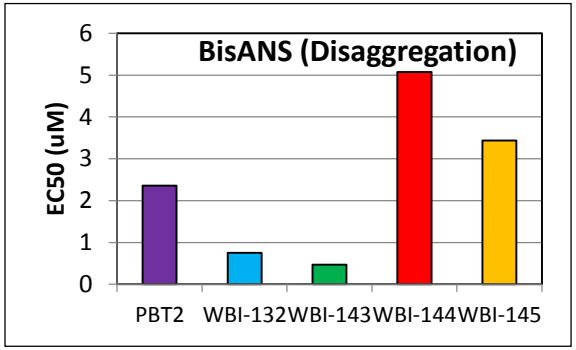
COLLABORATIVE MEDICINAL DEVELOPMENT LLC

Alzheimer's Disease Therapeutic

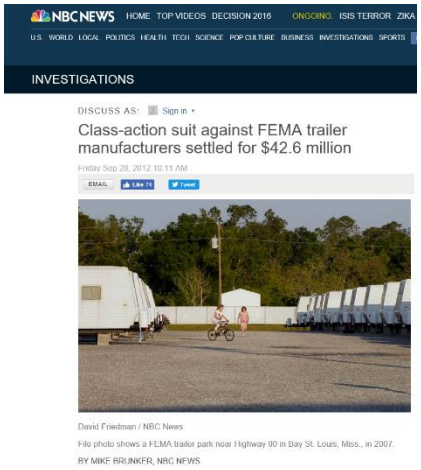


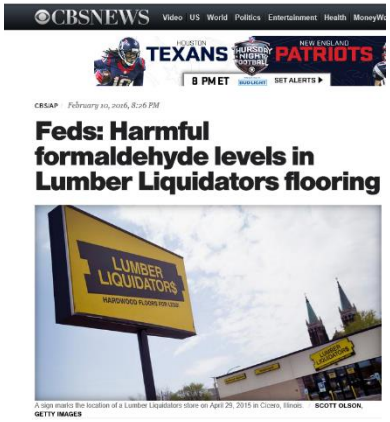
Cthulhunol

"Dihydro-6-Azaphenalene Derivatives for the Treatment of CNS, Oncological Diseases and Related Disorders" Warner, John C.; Nguyen, Dieu; Gladding, Jeffery A.; Cheruku, Srinivasa R.; Loebelenz, Jean R.; Norman, James J.; Thota, Sambaiah; Lee, John W.; Rosenfeld, Craig. US Pat. Appl. US 20140094487. Filed September 27, 2013. Published April 3, 2014. PCT Int. Appl. WO 2014052906. Filed September 27, 2013. Published April 3, 2014. CA 2886749. Filed September 27, 2013. Published April 3, 2014.



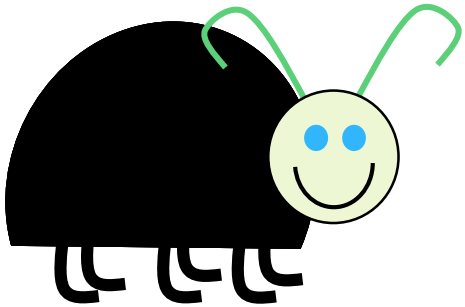
Formaldehyde Free Wood Composites

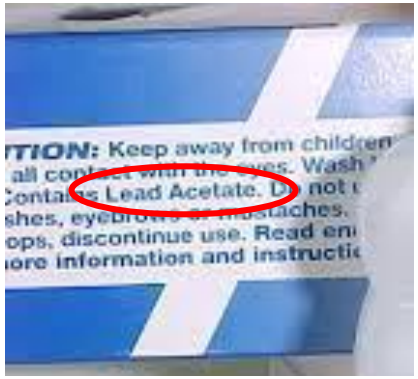


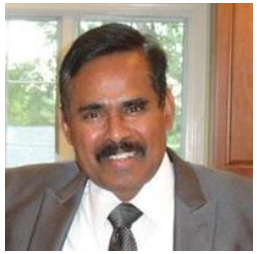


“Lignocellulosic Compositions and Methods of Making Same” Warner, John C.; Whitfield, Justin R.; Gladding, Jeffery A.; Allen, Richard M., US Patent Filed May 26, 2015

Hair Color Restoration







Manickam Sugumaran
UMASS Boston

"Formulation and Processes for Hair Coloring" Warner, John C.; Muollo, Laura; Stewart, Amie US Patent Appl. 20160184197. Filed September 9, 2014. Published June 30, 2016. Appl. WO 2015057254. Filed January 25, 2015. Published April 23, 2015. US Patent 8,828,100. Filed Oct. 14, 2013. Published September 9, 2014.

Ocean Plastics Recycling and Reclamation

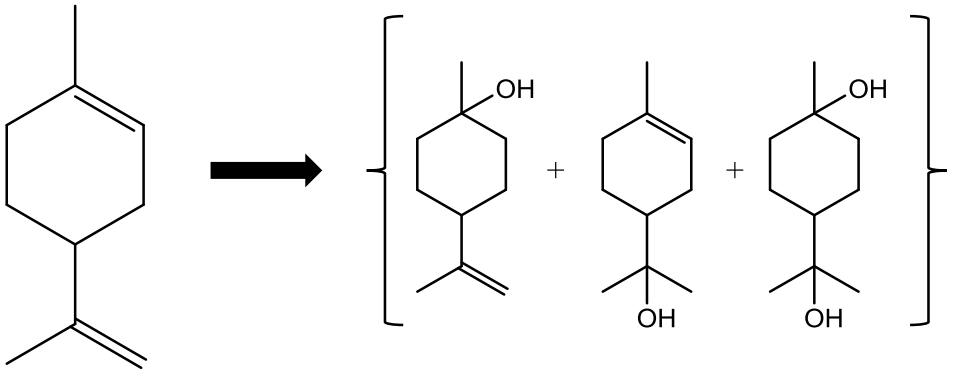
June 29, 2015

United Nations

warnerbabcock
institute for green chemistry

adidas

Electronics Recycling and Reclamation



$LiCoO_2$

"**Method for the recovery of lithium cobalt oxide from lithium ion batteries**" Poe, Sarah L.; Paradise, Christopher L.; Muollo, Laura R.; Pal, Reshma; Warner, John C.; Korzenski, Michael B. US Pat. Appl. US 20140306162. Filed June 19, 2012. Published October 16, 2014.

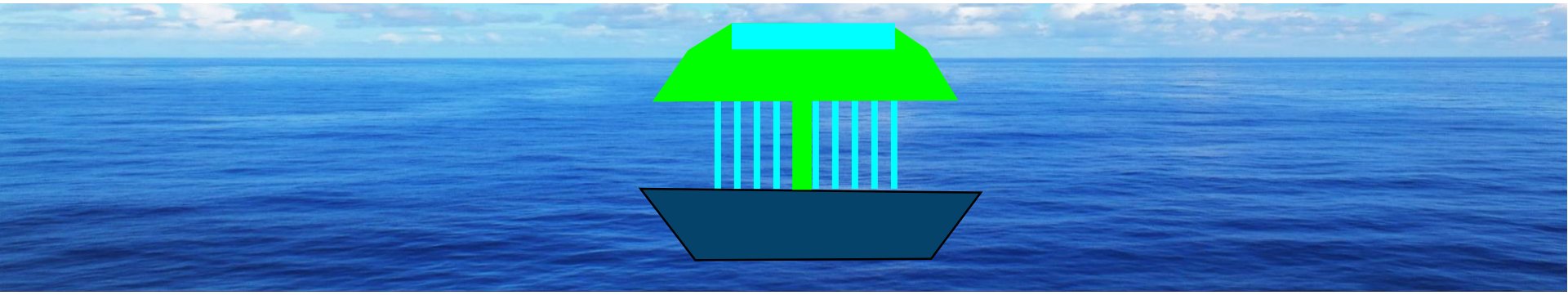
"**Sustainable process for reclaiming precious metals and base metals from electronic waste**" Korzenski, Michael B.; Jiang, Ping; Norman, James; Warner, John C.; Ingalls, Laura; Gnanamgari, Dinakar; Strickler, Fred; Mendum, Ted. US Pat. Appl. US 20130336857. Filed August 19, 2011. Published December 19, 2013.

"**Sustainable process for reclaiming precious metals and base metals from electronic waste**" Korzenski, Michael B.; Jiang, Ping; Norman, James; Warner, John C.; Ingalls, Laura; Gnanamgari, Dinakar; Strickler, Fred; Mendum, Ted. PCT Int. Appl. WO 2012024603. Filed August 19, 2011. Published February 23, 2013. CN 103249849. Filed August 19, 2011. Published August 14, 2013. EP 2606158. Filed August 19, 2011. Published June 26, 2013.

"**Non-fluoride containing composition for removal of polymers and other organic material from a surface**" Korzenski, Michael B.; Jiang, Ping; Warner, John C.; Mendum, Ted; Lugus, Michelle; Whitfield, Justin; Vanbenschoten, Helen; Payne, Makonnen PCT Int. Appl. WO 2010091045. Filed Feb 3, 2010. Published August 12, 2010.

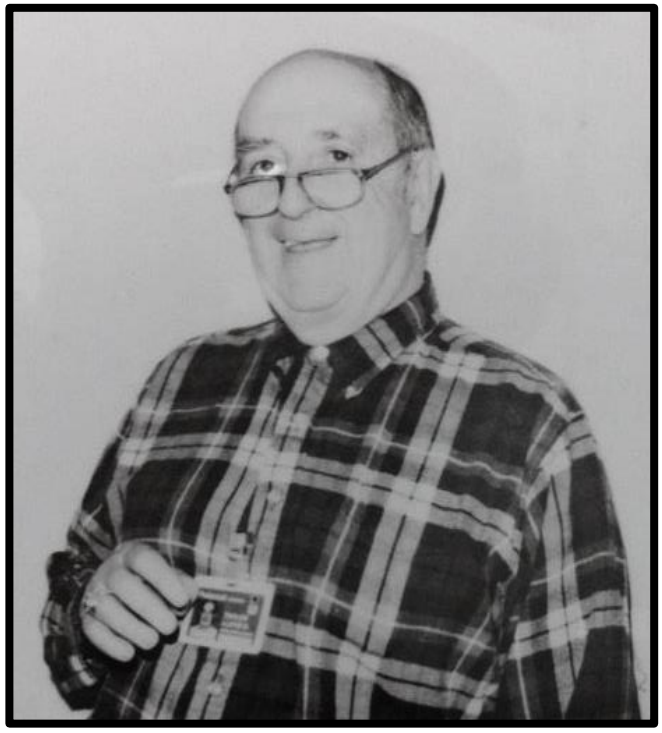
Water Harvesting Technologies

Hydrophobic ⇌ Hydrophilic



Polaroid Corporation – 1988-1997

Edwin Land



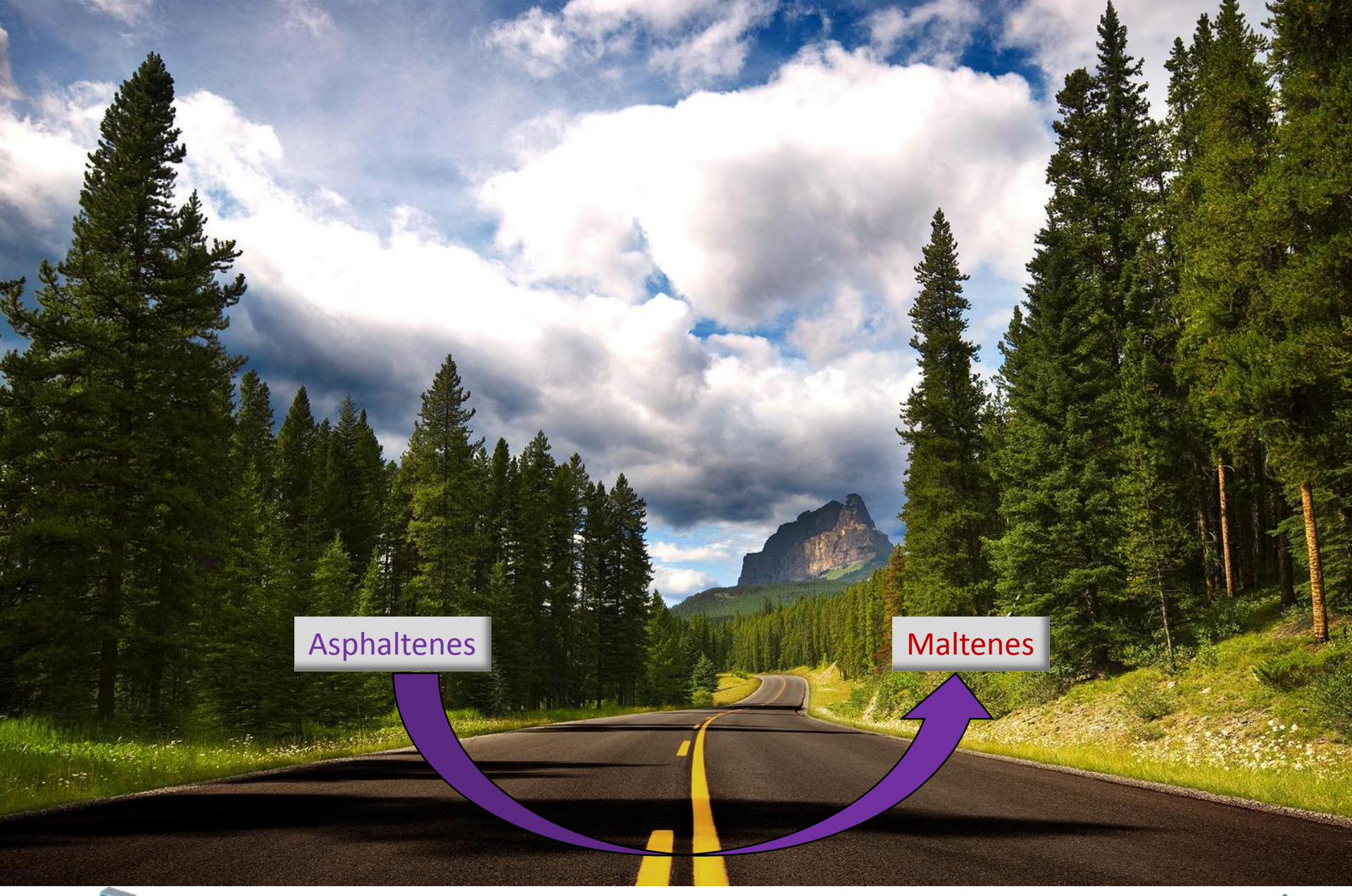
Lloyd D. Taylor

This is world's oldest known photograph made in 1825

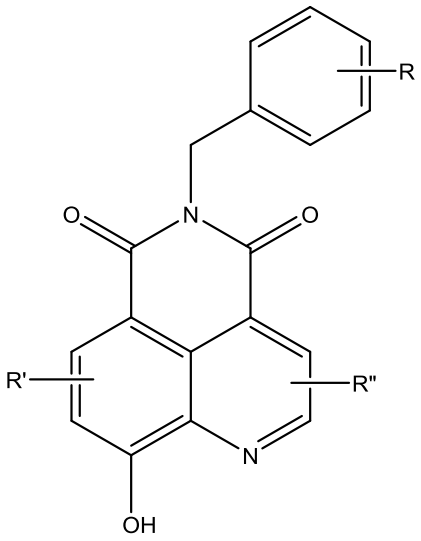
It was made by
Joseph Nicéphore Niépce

He exposed a metal sheet coated with a material to light in a camera for 8 hours. The areas irradiated by light washed off!

The material was ASPHALT!


Asphaltenes
Maltenes

Alzheimer's Disease Therapeutic



Cthulhunol

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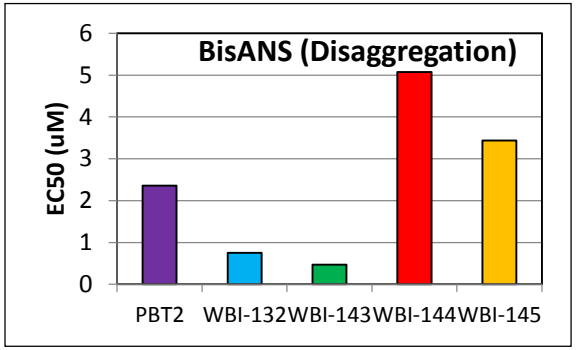
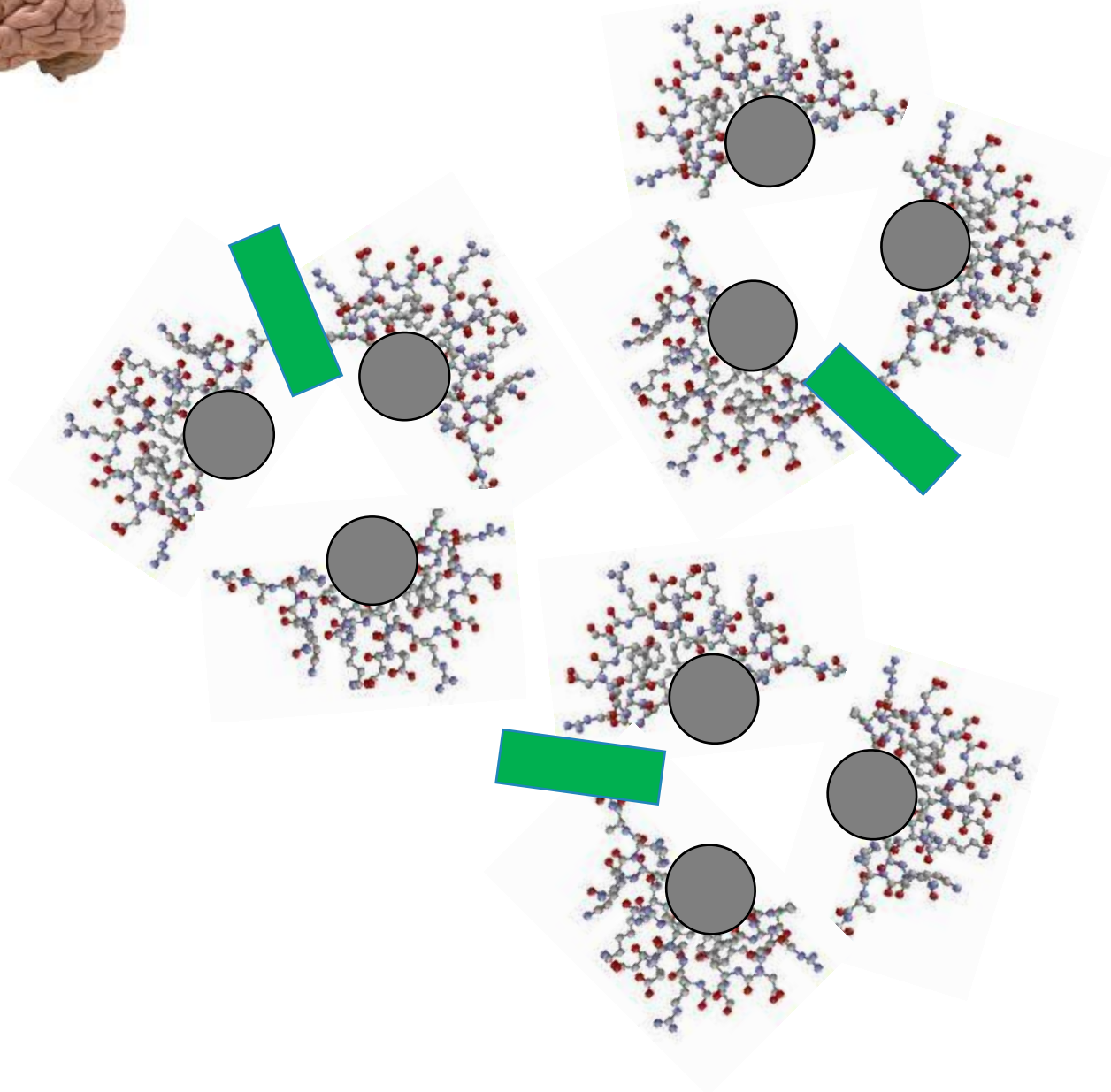
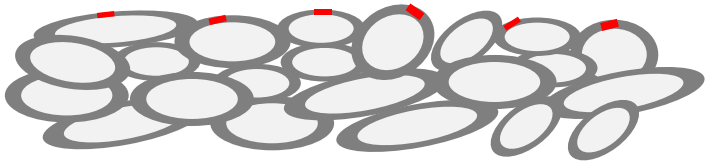
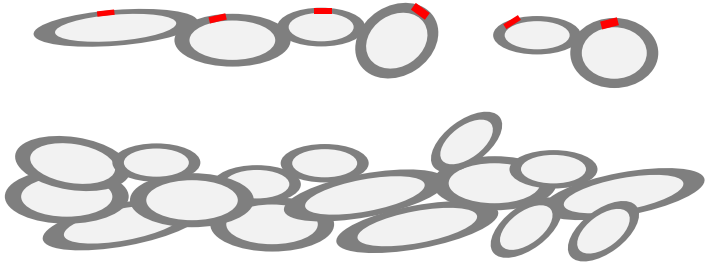




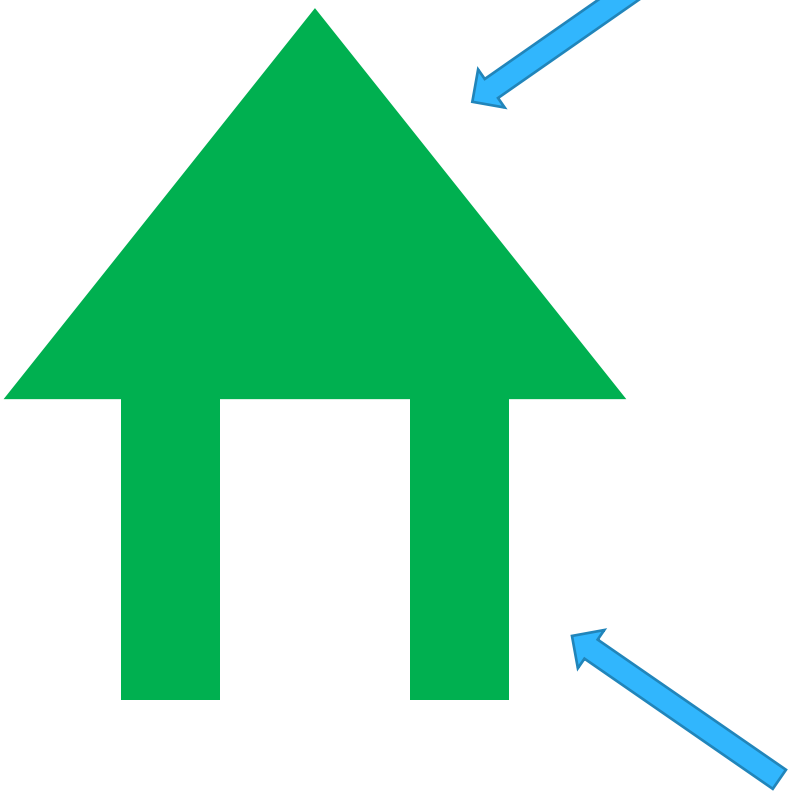
Sunlight and air damage asphalt.



To repair this damage, the top layer is removed and replaced.



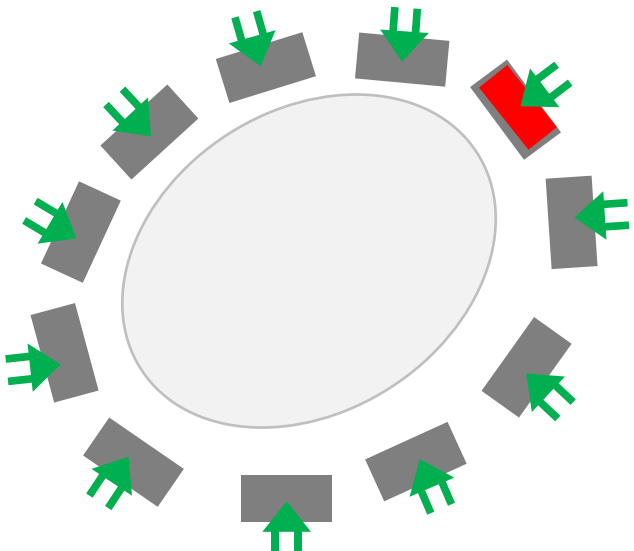
Asphalt Compatiblizer Group



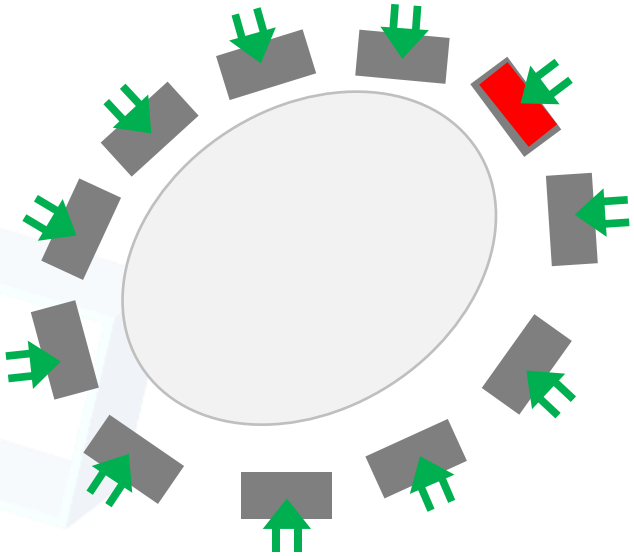
Aggregate Binding Group

There is only a small amount of oxidized asphalt, but because it is localized it hurts the performance.

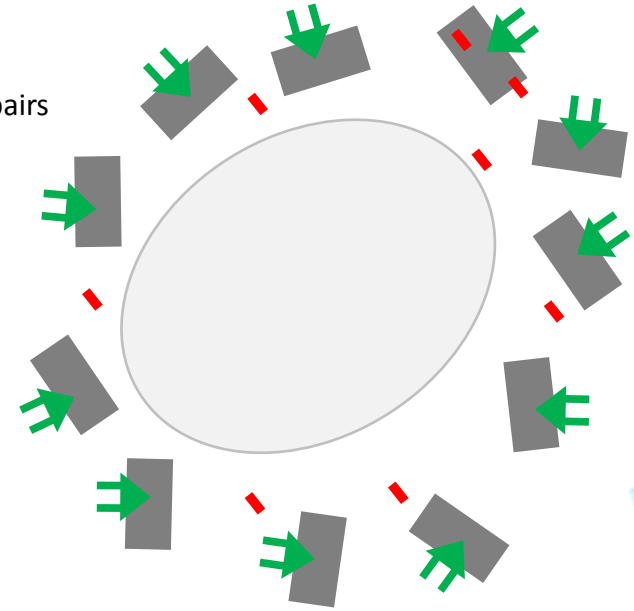
Delta-S is a dynamic rheology modifier.



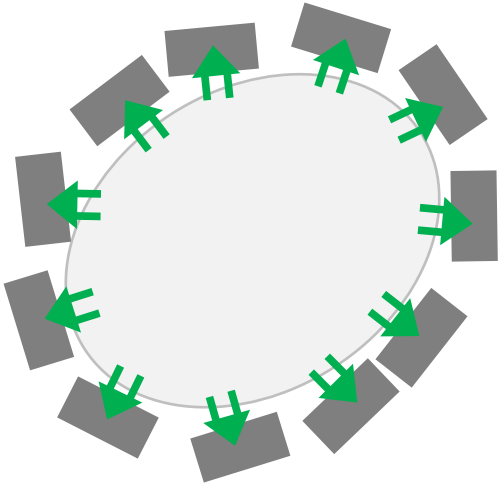
It first helps lift of the damaged asphalt from the aggregate



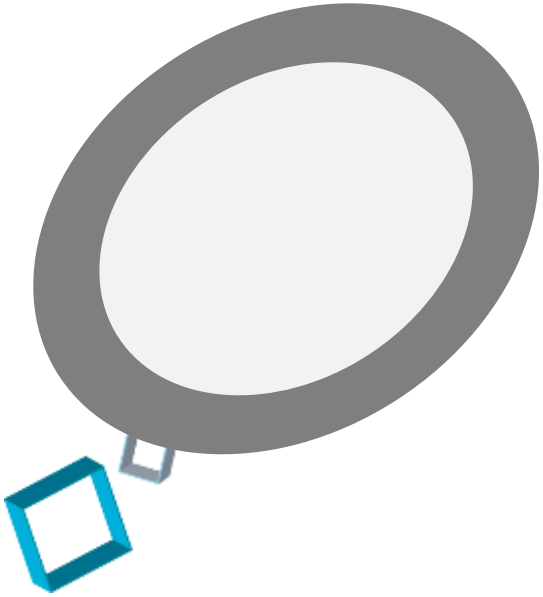
It then distributes and repairs the oxidative damage.

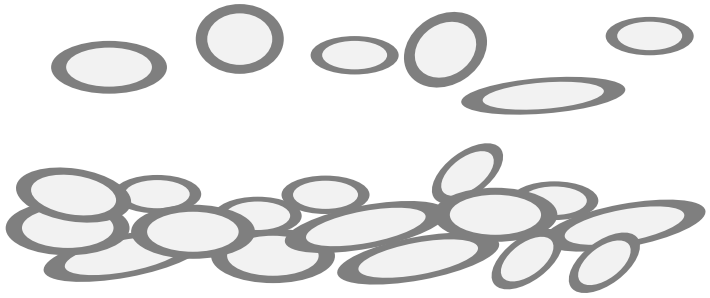


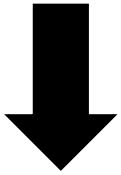
If this is all that Delta-S did, the material would remain soft and never harden.

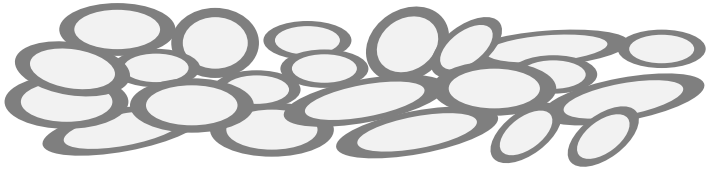


But the dynamic rheology modifier then reverses behavior and helps re-establish the bonding of the asphalt to the aggregate.









The aggregate is returned to its original state, but now has Delta-S built in to add added future stability.

Construction Materials: Asphalt Paving

Monday, November 25, 2013

17°F

> 60% Recycled Material

“Asphalt Binder Additive Compositions and Related Materials” Warner, John C., Muollo, Laura R.; Walker, Rowan L., Bianchini, J. R. PCT Int. Appl. WO 2015070180. Filed November 10, 2014. Published May 14, 2015.

COLLABORATIVE AGGREGATES LLC

Delta-S

EcoSeal

Innovation & Creativity

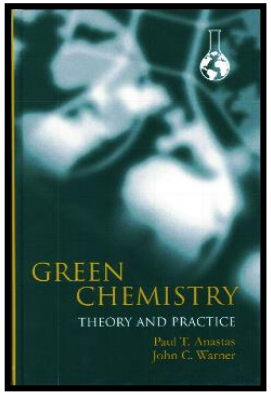
We are successful not **IN SPITE** of green chemistry

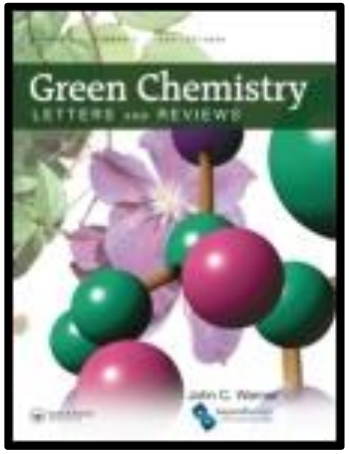
But **BECAUSE** of green chemistry

warnerbabcock
institute for green chemistry

beyondbenign

warnerbabcock
institute for green chemistry





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