Green Chemistry: The Missing Elements

John C. Warner

President and Chief Technology Officer Warner Babcock Institute for Green Chemistry, LLC

President Beyond Benign



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JohnWarnerOrg







BROMINATED FLAME RETARDANTS

KOUCHNEOK 4

PHTHALATES

ROUGHNEC

BISPHENOLA

ROUGHNEOK &

Asking the Right Questions

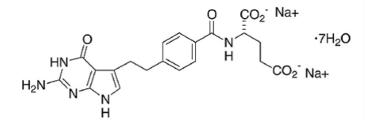
Why would a chemist make a hazardous material?

How do we train chemists?



Confidential - Warner Babcock Institute for Green Chemistry, LLC

Princeton University – 1984-1988







Professor E. C. Taylor

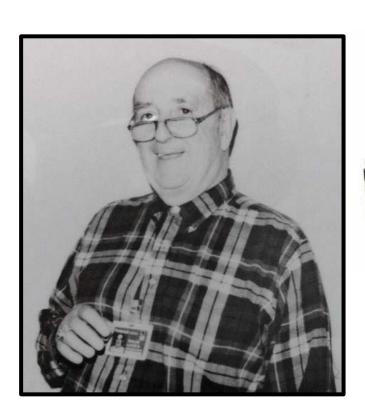


Natalie Warner [1932 – 2002]









POLARCID LAND CAMERA

Lloyd D. Taylor





Edwin Land







For over 180 years of "Modern Chemistry"...



Heat things under high temperature

Runs reactions at "room" temperature

Apply high pressures

Runs reactions at ambient pressure

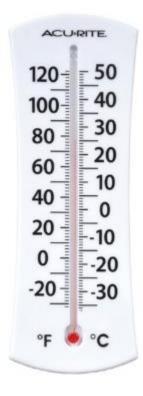
Use organic solvents

Uses water as a solvent





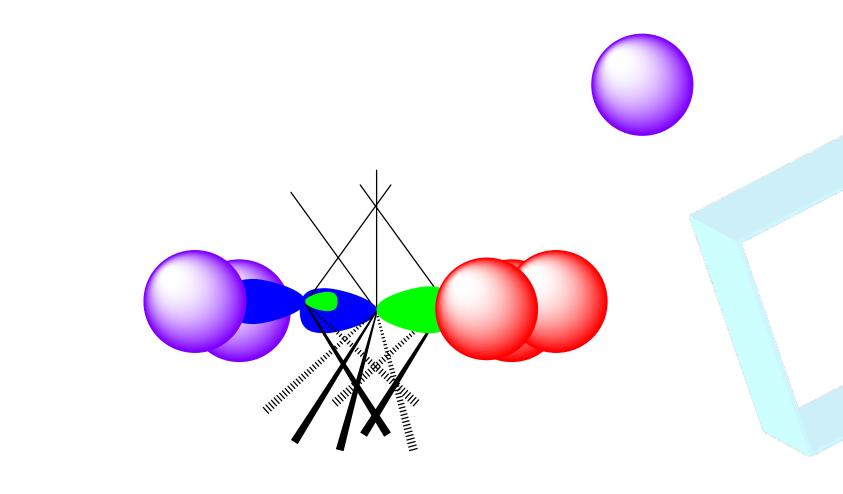
A thermometer is a molecular speedometer...







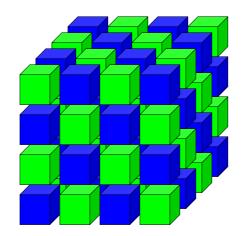








Non Covalent Derivatization













EPA Approval Low Volume Exemption PreManufacturing Notification

"Small particles"?

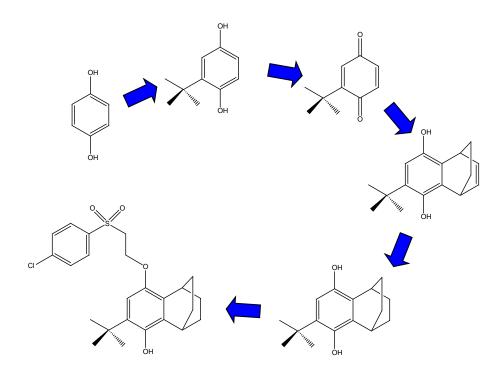
"Molecular Complexes"?

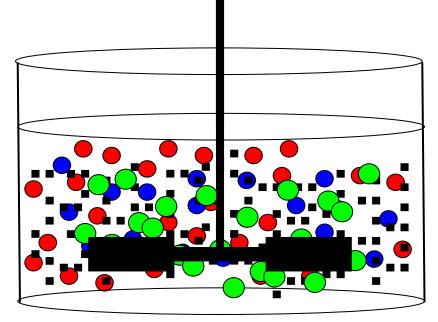










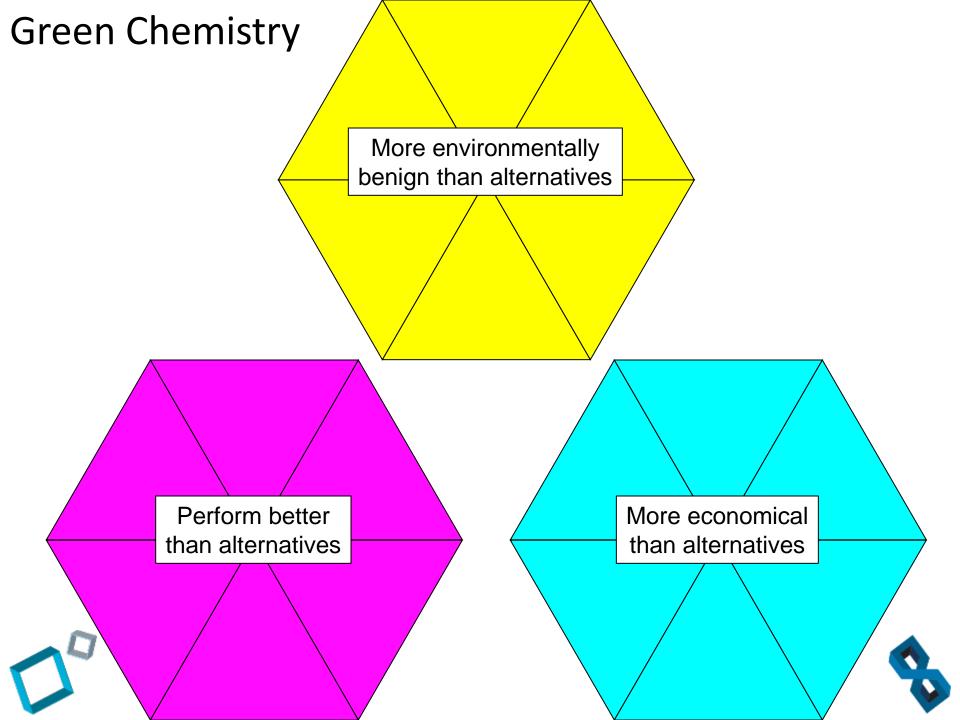


Old Technology Several Solvents High Energies Hazardous Reagents

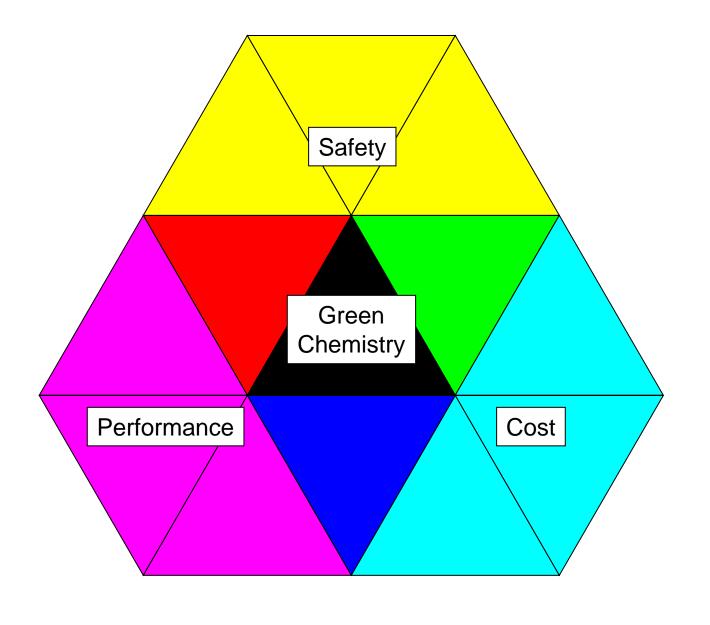
New Technology

Aqueous Conditions Low Energies Non-hazardous Reagents





Green Chemistry







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.

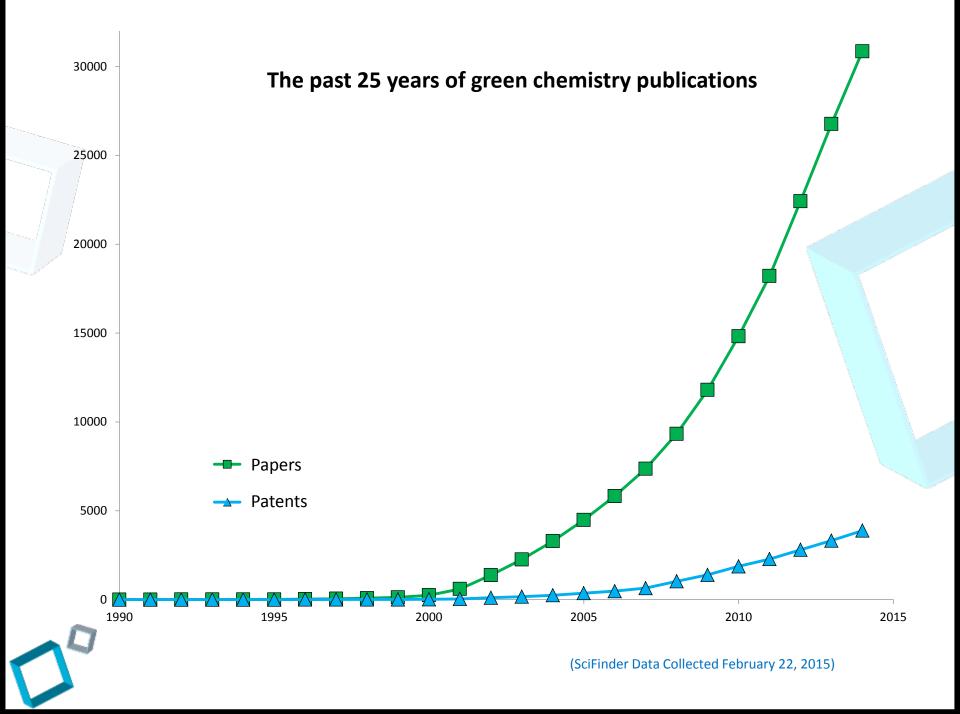
8. Reduce Derivatives. Unnecessary derivatization (blocking group, protection/deprotection, temporary modification of physical/chemical processes) should be avoided whenever possible .

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 inprocess 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.



Presidential Green **Chemistry Challenge**

Awards Opportunities The Follution Prevention Act of 1990 established a national policy to prevent or reduce volution at its source whenever feasible. The Pollution Prevention Act also provided an The 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 Pollution at its source whenever feasible. The Pollution Prevention Act also provided an opportunity to expand beyond traditional EPA programs and device creative strategies of chemical model. opportunity to expand beyond traditional EPA programs and devise creative strategies of protect hum an 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 substances, is a substances of the substanc Protect hum an health and the environment. Green chemistry, or the design of chemical Products and processes that reduce or eliminate the use and generation of hazardous aubitances, is a highly effective approach to pollution Prevention. Green Chemistry applies innovative sciencific ucts and processes that reduce or eliminate the use and generation of hazardous substances, is highly effective approach to pollution prevention. Green Chemistry applies innovative sciencific solutions to real-world environmental situations, all through voluntary partnership processes. highly effective approach to pollution prevention. Green Chemistry applies innovative scientific solutions to real-world environmental situations, all through voluntary pattership programs. In order to successfully effect the technical and behavioral changes necessary to accomplish solutions to real-world environmental situations, all through voluntary Partnership Programs. In order to successfully effect the sechaical and behavioral changes necessary to accomplish with mental velocities research on the order chemistry, the benefits of the approach man 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.

the remaining areas community Challenge seeks to recognize outstand-Challenge seeks to recognize outstand-ing scomplishments in green chemistry ing accompositions in green community through an annual awards program in order to demonstrate the scientific. environmental and economic benefits environmentas ana economic veneros that green chemistry technologies offer.

BACKGROUND:

The Presidential Green Chemistry Challenge The Presidential Green Chemistry the residential Green Chemistry Challenge was implemented as a volum-Cnuttinge was impremented as a volum tary EPA Design for the Environment min the second second second (DE) partnership with the chemical tene, paranennip with the constant community. Die partnership encours age changes that both promote economic development and benefit industry by identifying cost-effective ways to prevent pollution.

The Presidential Green Chemistry The Presidential Unter Commenty Challenge Awards Program is an oppor-tunity for individuals, groups, and organizations to compete for annual awards in recognition of innovations in awaras in recognition or innovations in cleanes, cheaper, imarer chemistry: The CL.I. A. . cleaner, cheaper, imaner chemistry: 1 Challenge Awards Program provides Chattenge Awards Program Provides national recognition for outstanding chemical technologies that incorporat the principles of green chemicity into chemical designs manufactures and use and chat have have a result to static chemical design, manufacture, and use, and that have been or can be utilized by and that have been or can be united by industry to achieve its pollution preven-

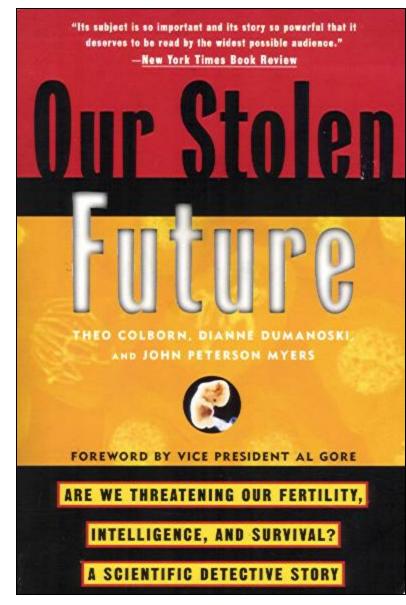
Nominations received for the awards are judged by an independent panel of Judged by an independent panet of echnical experts convened by the American Chemical Society: "Tpically, five awards are given annually to industry and government sponsors, an ty and government pointors an academic investigator, and a small busi-tors, for Li, to the total busiacademic investigators and a small busi-ness. For this program. Individual Projects selected for supporting by funded by PRA, NSR or joindly by both supercise. This is seen for certing of the agencies. This is at the option of the agencies, not the grantee. See Printed on paper that contacts at least to Jackar postonaumer that

ANNUL ENGE

	1996	1997	1998	1999	
Academic	Mark Holzapple	Joseph DeSimone	Barry Trost Karen Draths John Frost	Terry Collins	Chi ł
Small Business	Donlar Corporation	Legacy Systems	PYROCOOL Technologies	Biofine	R
Alternative Synthetic Pathway	Pharmacia	BHC Company	Flexsys America	Lilly Research Laboratories	Roch
Alternative Solvents and Reaction Conditions	Dow	Imation	Argonne National Labs	Nalco Chemical Company	Bayer
Designing Safer Chemicals	Rohm and Haas	Albright and Wilson Associates	Rohm and Haas	Dow AgroSciences	Dow A









I have synthesized over 2500 compounds!!!!!





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!





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)





EDUCATION



GREEN CHEMISTRY EARNS A PH.D.

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

Sity 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 realitiessuch 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 profes-

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

mal 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 regulared by the federal government, that sequence could be more expensive than an alternative route that might give less yield," Warmer 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 Cae, 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 completedher 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 ROUH

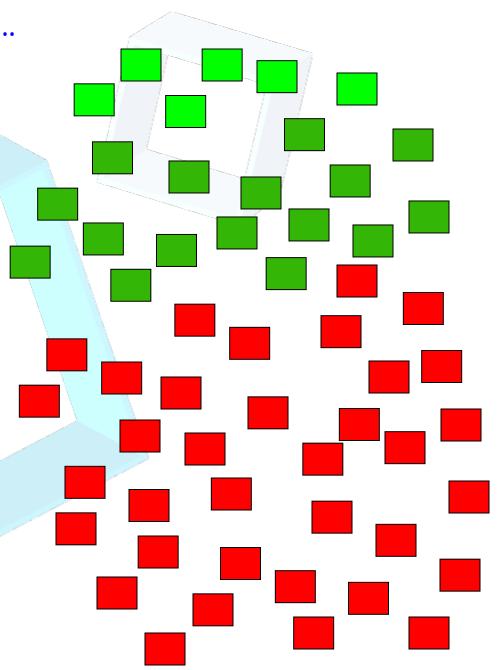


Of all the products and processes...

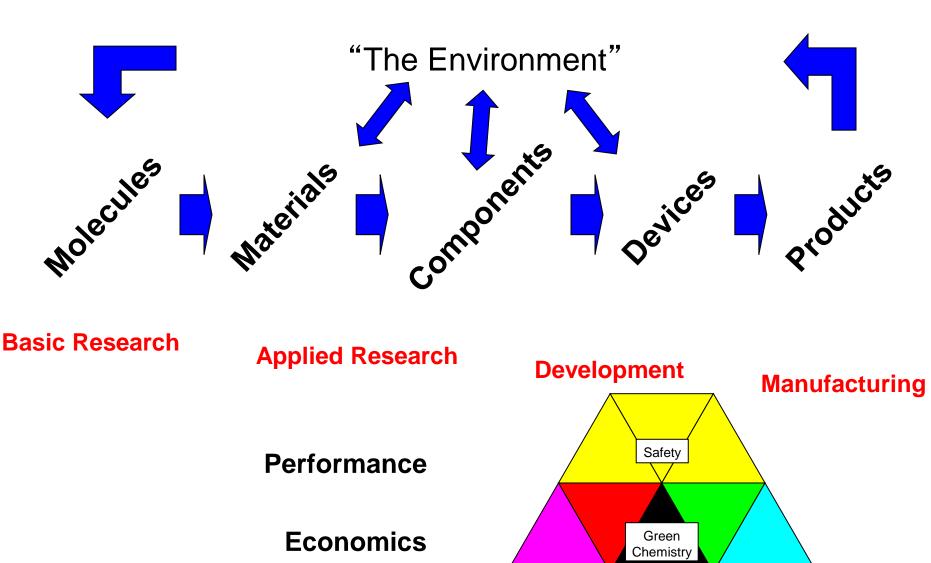
Maybe 10% are benign...

Maybe 25% have alternatives available...

65% Still have to be invented!



Where do products come from?



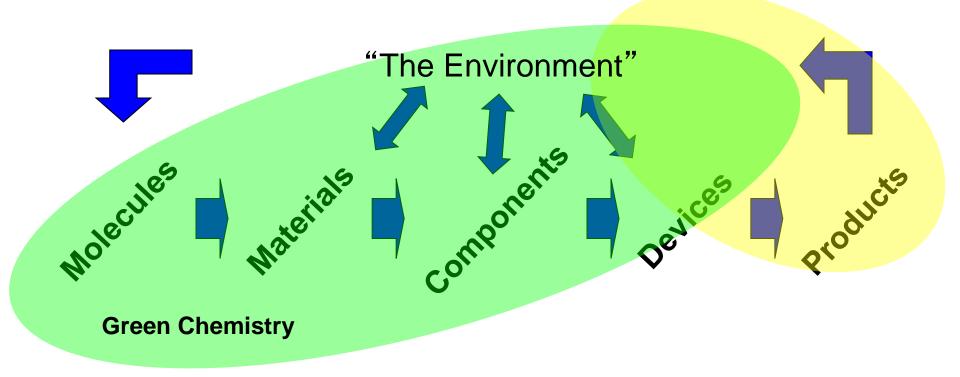
Performance

Cost



Social Implications

Chemicals Policy









Chemists have ALWAYS cared about Human Health and the Environment.









Risk = Exposure x Hazard





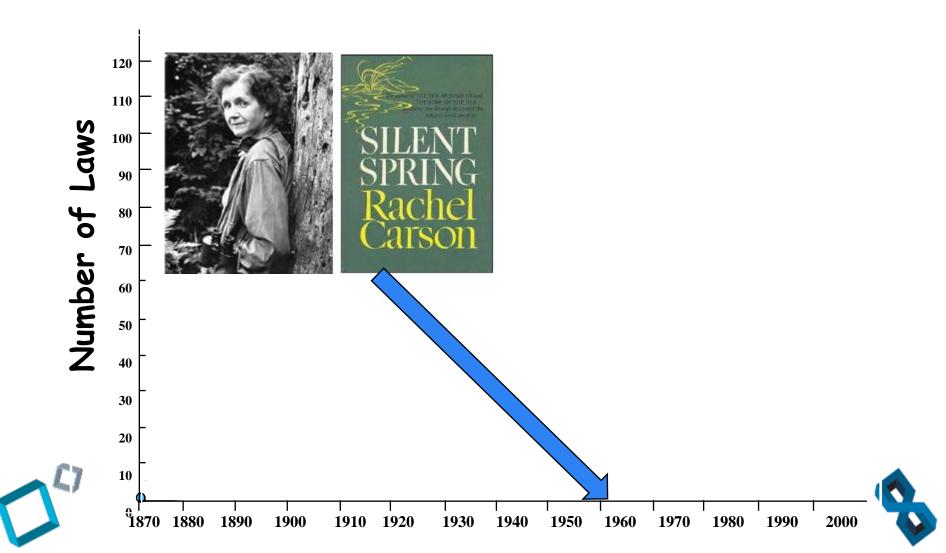
The cost of using hazardous materials:

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





Environmental Regulations





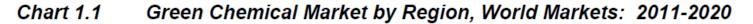


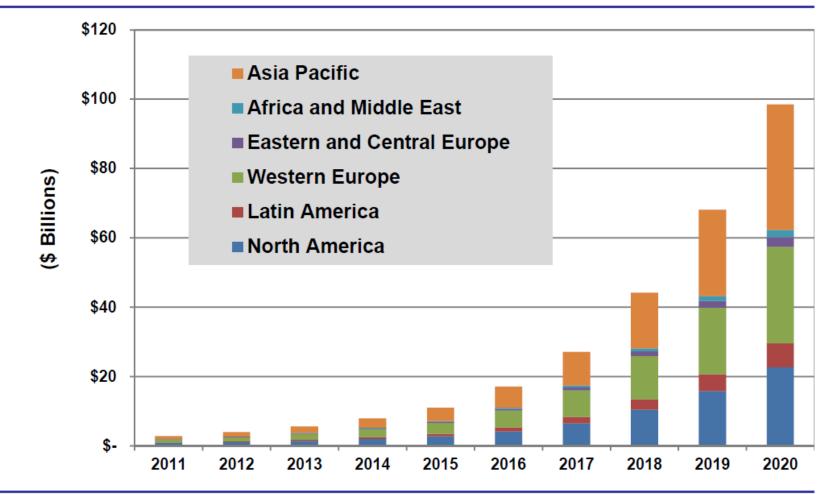
Green Alternatives





Traditional Processes





(Source: Pike Research)





2007 onward...





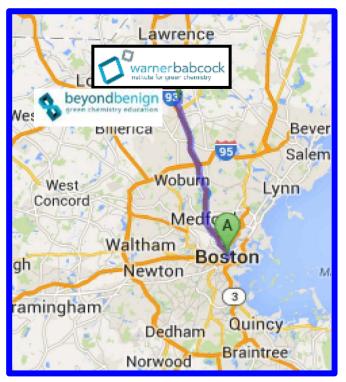




James & Jim Babcock

Joe Pont, CEO

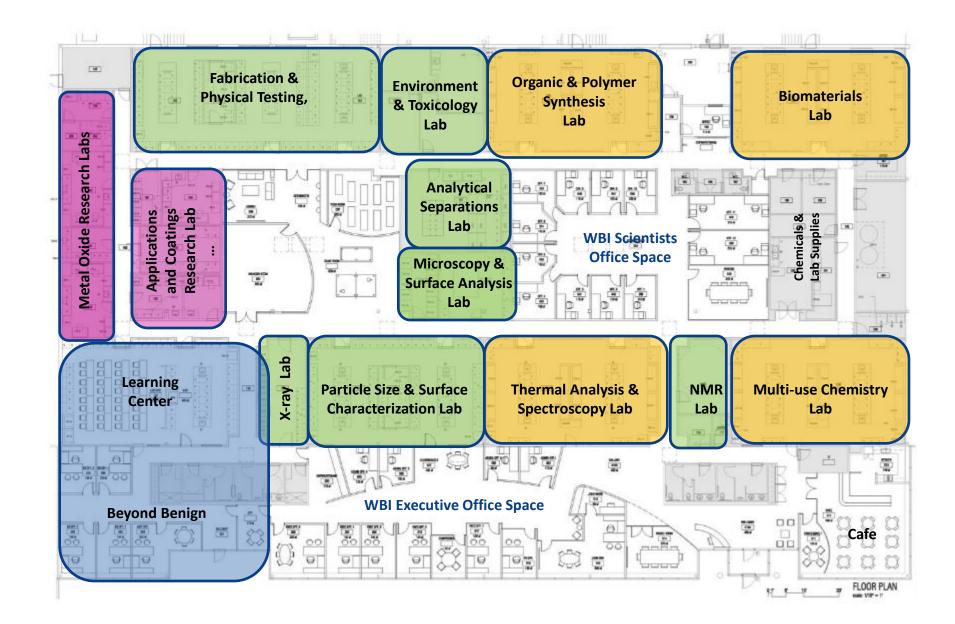
John Warner Amy Cannon





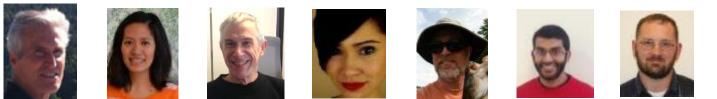
100 Research Drive Wilmington, MA 01887











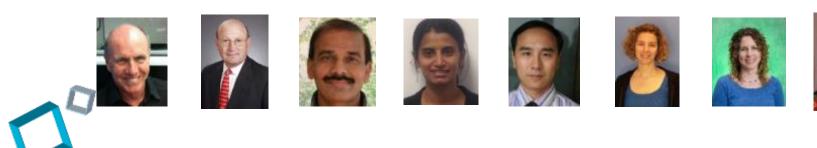








































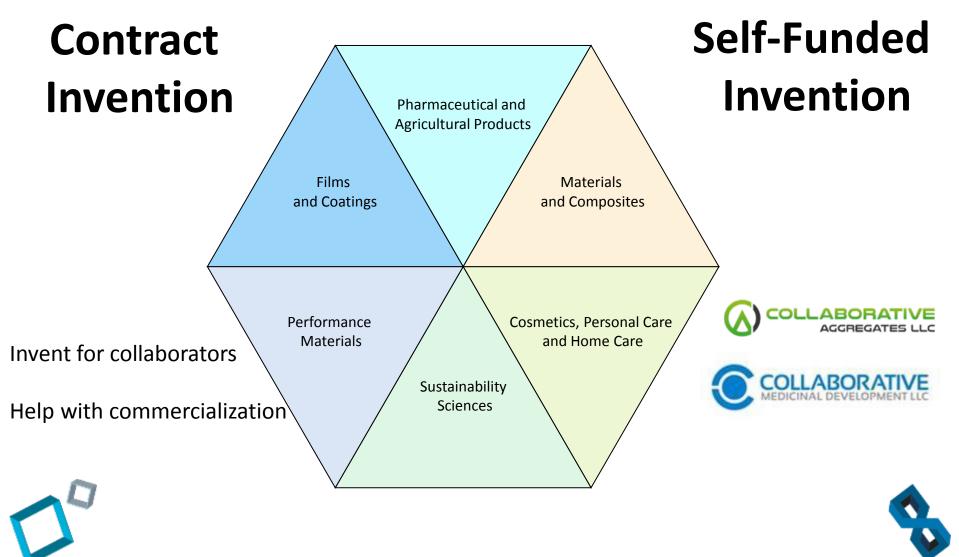


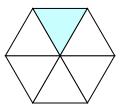




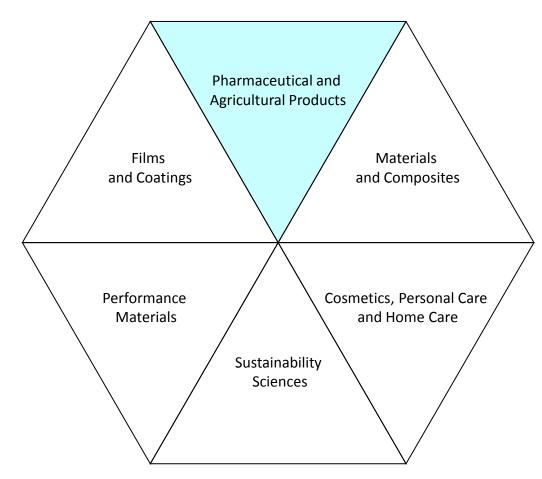








Pharmaceuticals and Agricultural Products





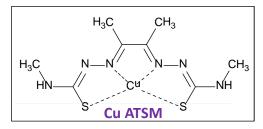
Parkinson's/ALS Disease Therapeutic





Tuest (1)







develop therapy for Parkinson's disease

11 October 2013



INCINE + ABOUT THE POUNDATION + FUNCED GRAVITS

PARKINSON'S FUNDED GRANT

Lead Optimization for a Parkinson's Disease Therapeutic

ORANT ABSTRACT

Objective/Rationale

Cull(atom) has the potential to delay disease progression in Devision's disease, based on extensive pre-clinical model data. Cull(atom) has been shown to significantly improve motor function in standard models of Positionaris disease. The observed motor improvement correlates with preservation of dispaminergic neurons in the brain and biomarities of neuronal health and function.

Project Description

Cull(atm) is spainingly soluble and requires formulation for oral administration prior to extensing human clinical development, Procepta will private two parallel approaches to develop a proprietary out formulation (1) Procepta will userk with the Warner Babcock Institute for Green Chemistry to develop a proprietary formulation of Cull(atm) incorporating GRAS (Greenally Regarded As Eafe) excipients; and (2) Procypta will evaluate the solubility of proprietary Cull(atm) analogue. The utility of these formulations will be evaluated using standard solubility and bioavailability seasys and efficacy will be compared to the parent formulation in the MPTP toxic lesion pre-clinical model of Parkinson's disease.

Relevance to Diagnosis/Treatment of Parkinson's Disease.

Cull(strm) has the potential to delay disease progression is Barkinnon's disease. Successful dinical development of an optimized formulation of Cull(strm) would provide Parkinson's disease patients, an diagnosis, the opportunity to delay the progression of their disease and mointain their quality of life for a much exceeded period of time. In patients with more advanced Barkinnon's disease, condeministration of Cull(strm) with symptomatic therspectics would delay further disease progression and halt the debilitating motor and coopsitive detarination.

Anticipated Outcome:

On successful completion of The Nichael J. Fax Foundation project, Procypra will have development. The optimized formulation of Califyrian justifiable for human clinical development. The optimized formulation will be advanced into formal IND-directed taxicology tradies in preparation for the commencement of clinical trade.

INTERIM PROGRESS REPORT

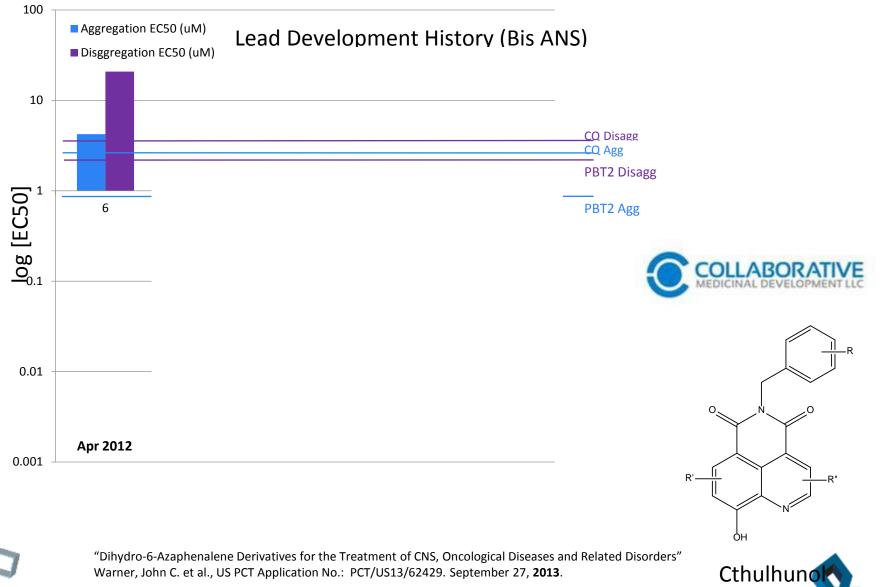
At this interim point in the program, a number of variant candidates of the parent drug

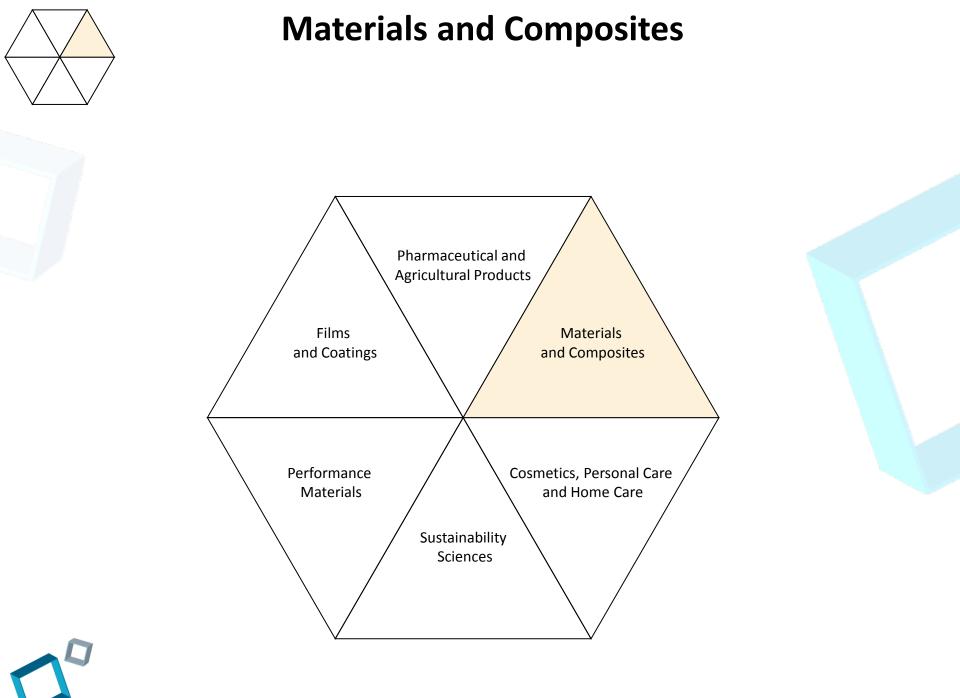


"Non-Covalent Derivatives of Metal Complexes and Methods of Treatment" Warner, John C., Cheruku. Srinivasa R.; *US Pat Application* No. 61/932,348 January 28, **2014**. "Copper (II) bis(N-alkyl-hydrazinecarbothioamide) Complexes as Non-Covalent Derivatives for the Treatment of CNS Conditions" Warner, John C., Cheruku. Srinivasa R.; *US Pat Application* No. 61/902,682 November 11, **2013**.



Alzheimer's Disease Therapeutic





Maltenes undergo photo-oxidation to Asphaltenes making the pavement dryer and more brittle.

Maltenes

Asphaltenes

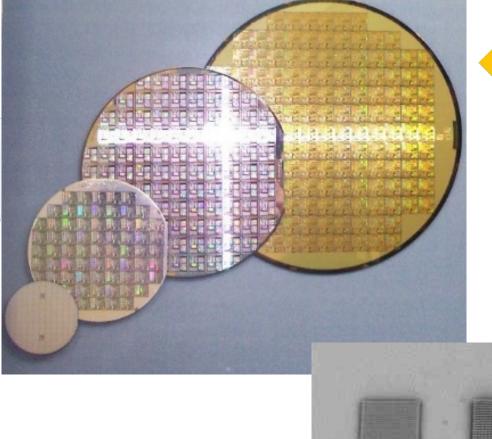


This is world's oldest known photograph made in 1825

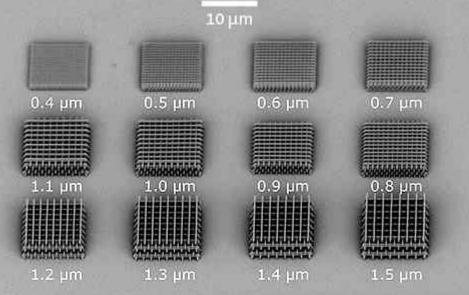
It was made by Joseph Nicéphore Niépce



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



Polaroid



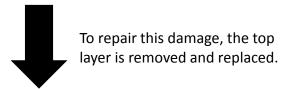
JCW's Patents Involving Photo-imaging Systems at the time

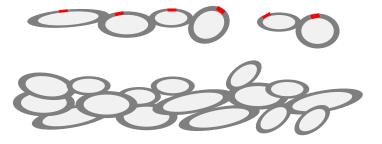
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- 11. "Process for Fixing an Image, and Medium for Use Therein" Ehret, Anne; Marshall, John L.; Baker, Rita Shon S.; Takiff, Larry C.; Telfer, Stephen J.; Warner, John C. US Patent 5,582,956. Filed April 28, 1994. Published December 10, 1996.
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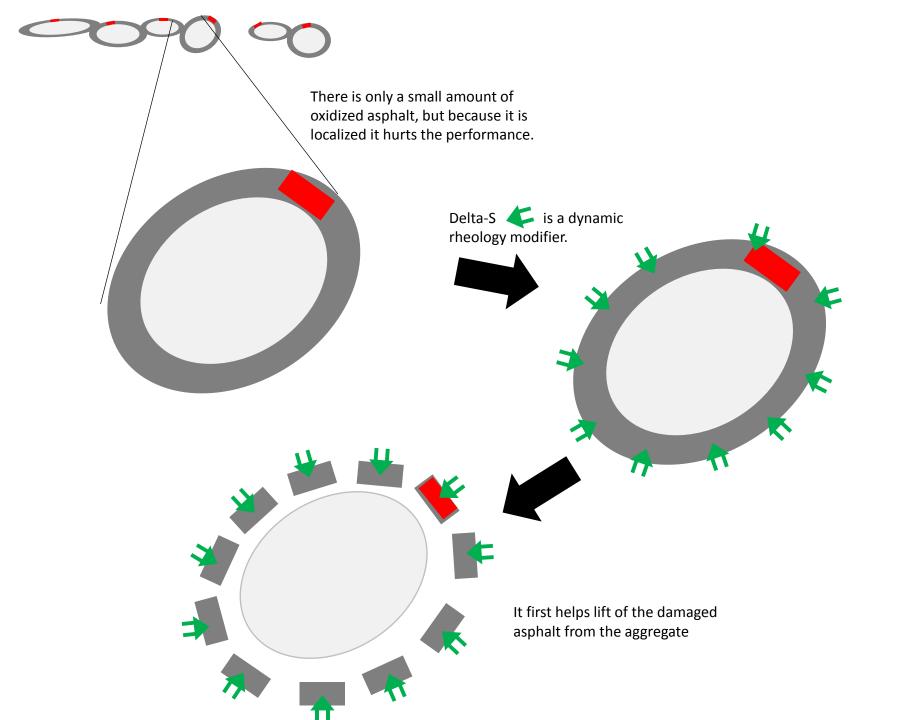


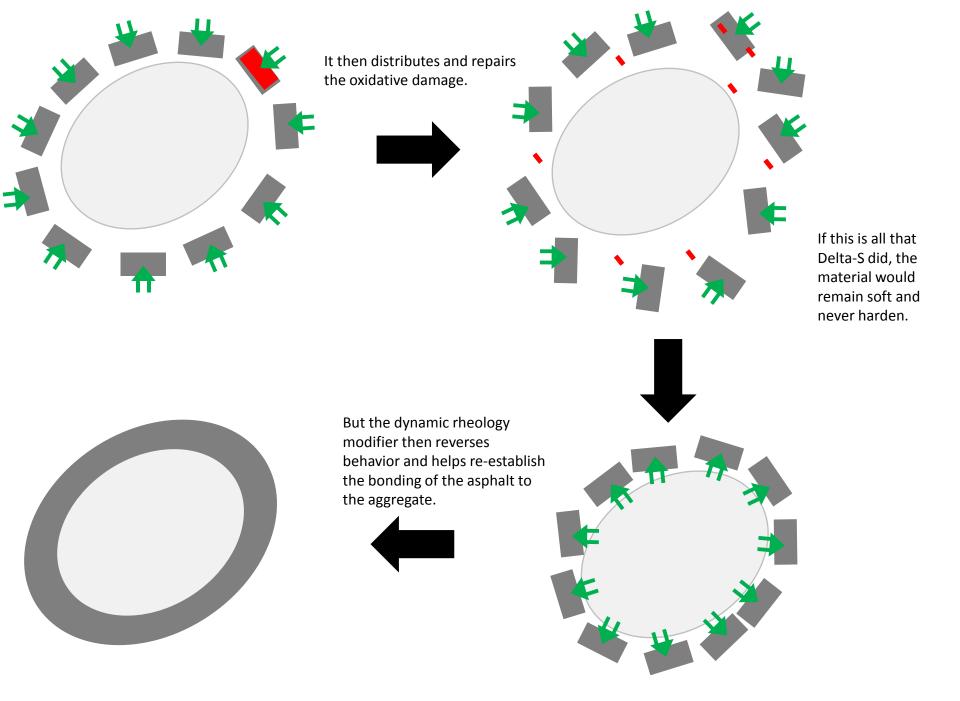
Sunlight and air damage asphalt.

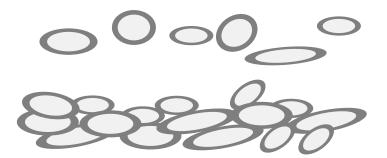














The aggregate is returned to its original state, but now has Delta-S built in to add added future stability.



Construction Materials: Asphalt Paving



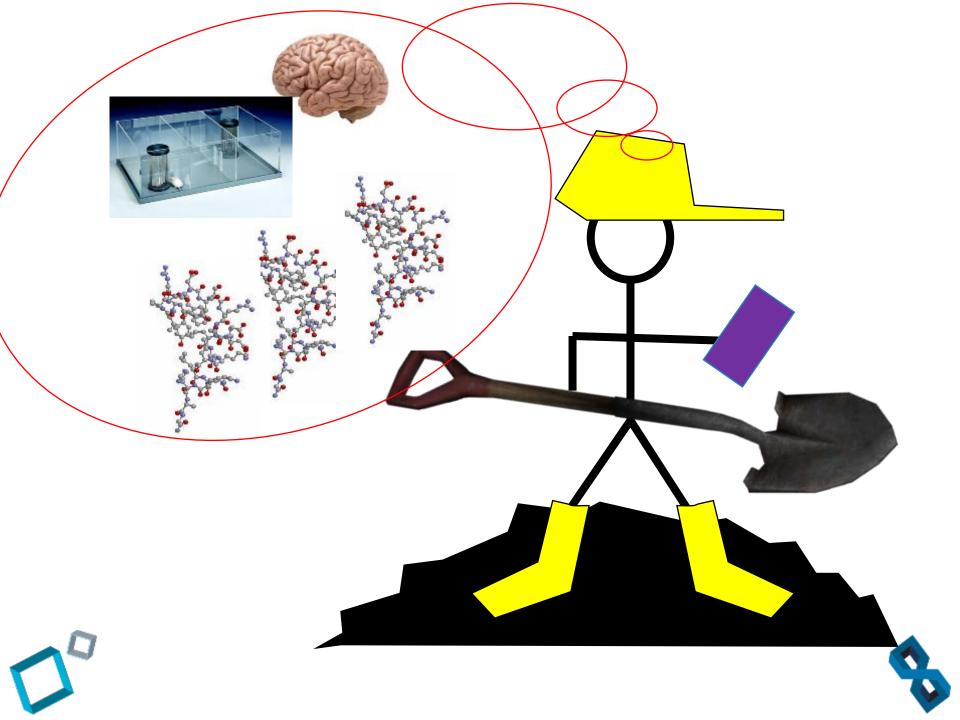






Delta-S "Asphalt Binder Additive Compositions and Related Materials" Warner, John C., Muollo, Laura R.; Walker, Rowan L., Bianchini, J. R. PCT Int. Appl. WO 2015070180. May 14, **2015**. "Composition to Rejuvenate Asphalt" Warner, John C., Muollo, Laura R., Walker, Rowan L. *US Pat Application* No. 61/902,706, November 11, **2013**.

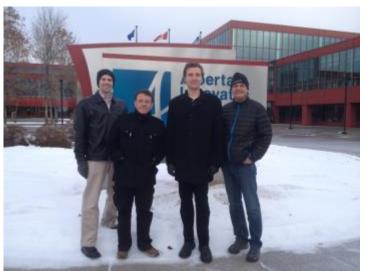




Formaldehyde Free Wood Composites















"Lignocellulosic Compositions and Methods of Making Same" Warner, John C. et al. US Patent Filed

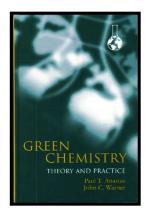


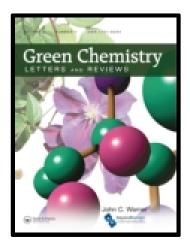




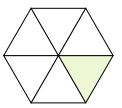
john.warner@warnerbabcock.com

JohnWarnerOrg

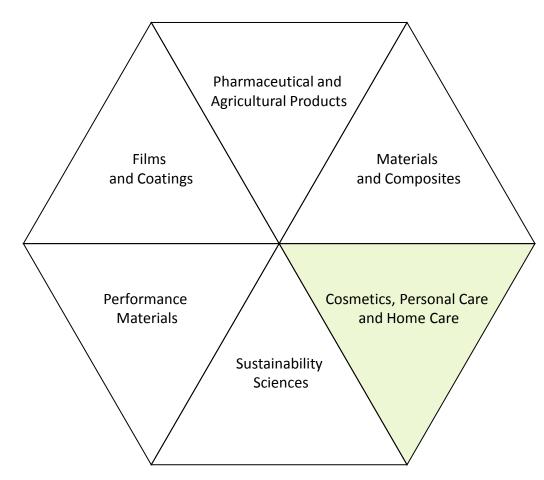






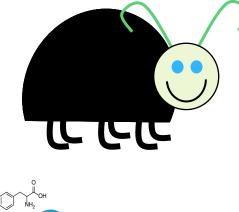


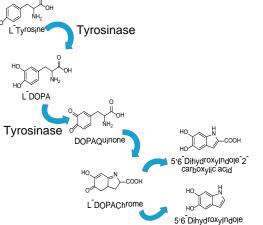
Cosmetics, Personal Care and Home Care

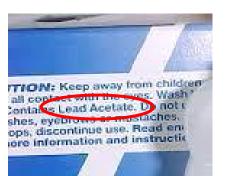




Hair Color Restoration









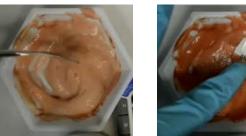






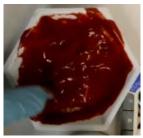
"Formulation and Processes for Hair Coloring" Warner, John C.; Muollo, Laura; Stewart, Amie. US Patent 8,828,100. Filed Oct. 14, 2013. Published September 9, 2014.



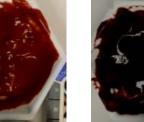




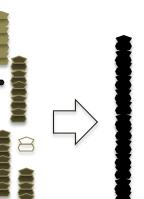




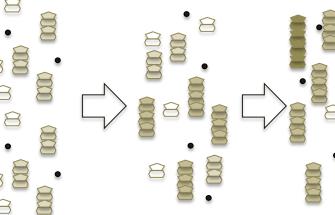


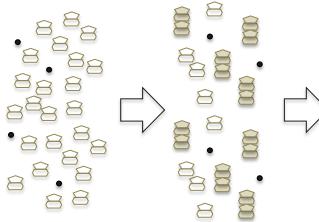


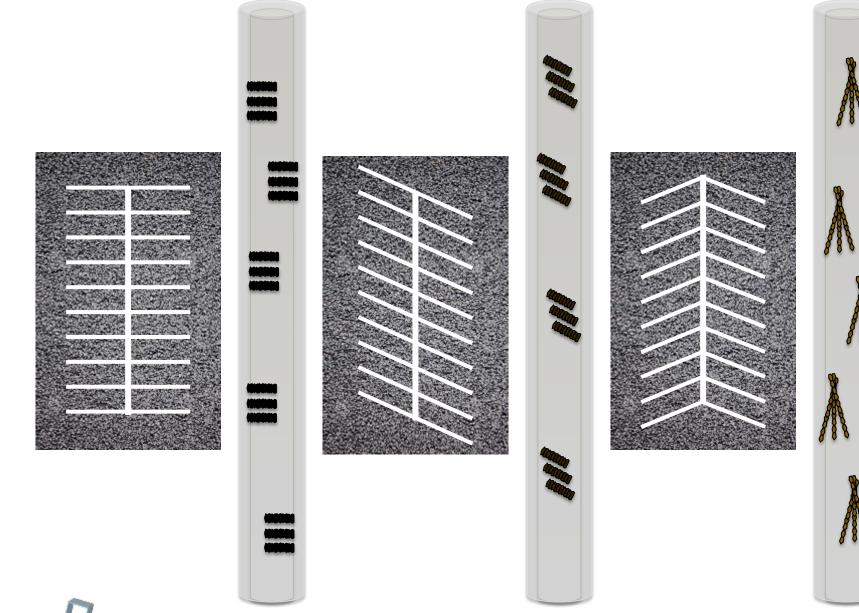
















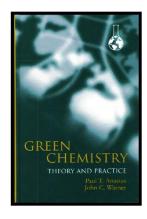


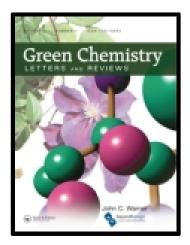




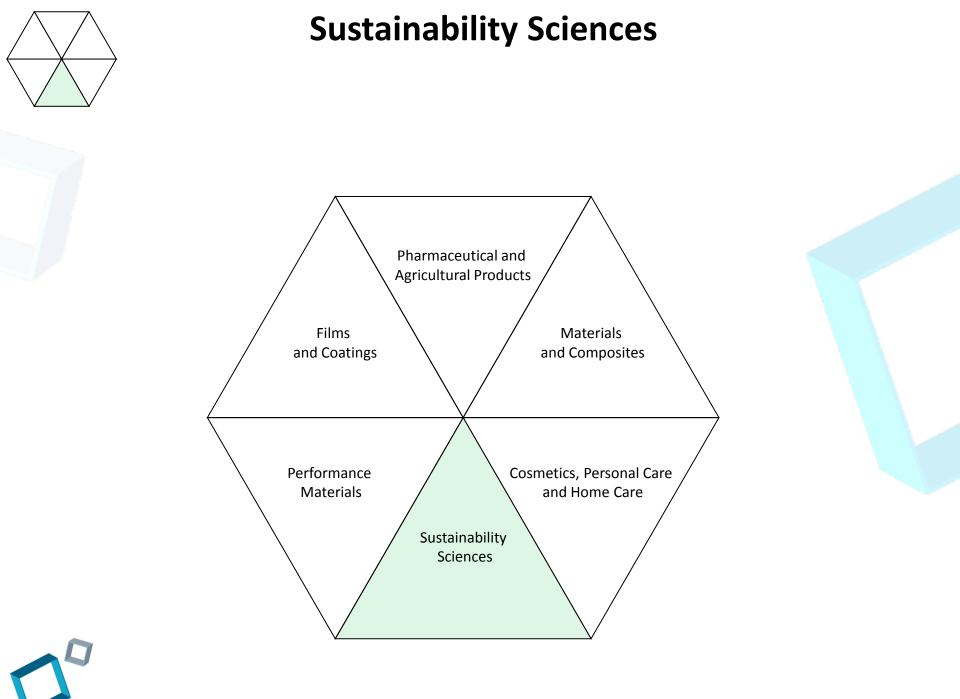
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Ocean Plastics Recycling and Reclamation



June 29, 2015

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