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Green Chemistry
&
Green Engineering
at
Yale

Designing Safer Chemicals and Systems

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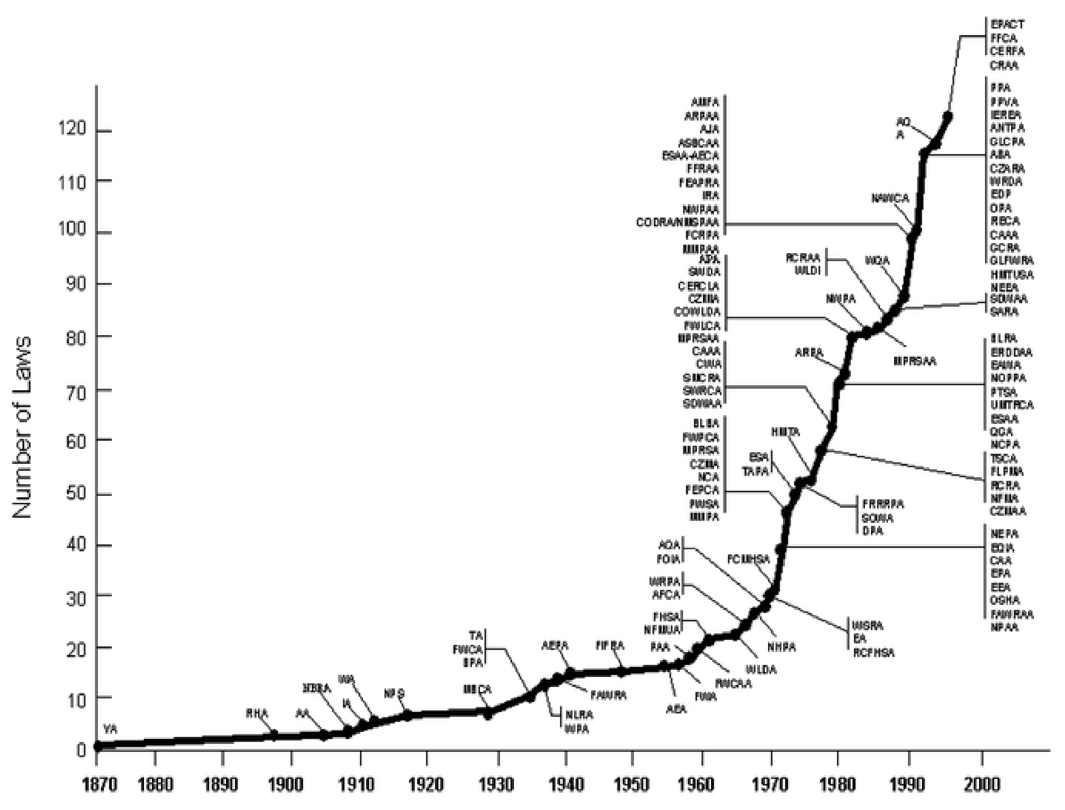
Yale University

Advance the science Prepare the next generation Catalyze implementation Raise Awareness

Environmental Regulation Growth



Source: J. A. Cusumano, New Technology for the Environment, Chemtech, 1992, 22(8), 482–489

P. T. Anastas, Meeting the Challenges of Sustainability through Green Chemistry, Journal of Green Chemistry, 2003, 5(2), G29-G34.

U.S. Dept. of Commerce Report on Manufacturing 2003

MANUFACTURING IN AMERICA

A Comprehensive Strategy to Address the Challenges to U.S. Manufacturers

U.S. Department of Commerce

the cost is for compliance with envi[illegible] mental regulations; the remainder [illegible] compliance with workplace safet[illegible] product safety requirements, a[illegible] or the time spent filling out go[illegible] paperwork and keeping recor[illegible]

One measure of the [illegible] cost of compliance is th[illegible] ment of managing regula[illegible] and the consequent drai[illegible] ues which that effort repres[illegible] budget outlays for regula[illegible] activities have almost [illegible] in the past 13 years, from $13.7 [illegible] in 1990 to $26.9 billion in 2003 in real terms.[14] Those costs cover all regulatory activities, from trade and customs, to consumer safety, to securities laws. They do not include the cost to the private sector of compliance, which can be many times greater.

From a manufacturer's perspective, particularly that of a small or medium-sized business, the most common compliance costs are related to environmental regulation, workplace safety, and tax compliance/employment rules. The Small Business Administration's Office of Advocacy has conducted the most comprehensive study of those costs.[15] The study found that the total cost of complying with regulations in those areas in 1997 amounted to $147 billion annually, or a cost per employee of $7,904. Of the individual categories that made up that total, environmental compliance costs took the largest share. Environmental costs accounted for nearly 50 percent of the total: $69 billion in 1997, or a cost per employee of $3,691.[16]

Significantly, the cost of compliance with such rules falls hardest on businesses with fewer than 20 employees. According to the SBA study, small manufacturing businesses reported that compliance with workplace rules amounted to a cost of $16,920 per employee. For larger firms, that cost dropped by more than half, to $7,454 per employee.[17]

Further, taken together, all compliance costs appear to have increased significantly since the SBA's study of 1997 data. According to a recent NAM study, the total burden of environmental, economic, workplace, and tax compliance is $160 billion on manufacturers alone, equivalent to [illegible] 12-percent excise tax on manufacturin[illegible] This reflects an increase of [illegible] over the last five years. [illegible] regulatory compliance costs a[illegible] than income in the manufac[illegible] which implies a loss of co[illegible] or, at a minimum, a negative o[illegible] benefits of the extraordinary pro[illegible] gains and efforts by manufactu[illegible] costs under their direct control.

Rising Energy Costs

Another point of concern for manufacurers is the rising cost of energy, particularly natural gas. Manufacturers depend on affordable, reliable energy. Industry uses more than one-third of all the energy consumed in the United States, the majority of which is natural gas and petroleum, followed by electricity. In all sectors, energy prices have a significant effect on operations and product prices.

Manufacturers uniformly criticized the failure to enact the legislative aspects of a comprehensive and coherent energy plan that would increase America's energy independence while yielding energy prices that would help ensure manufacturers' long-term competitiveness. Don Wainwright of Wainwright Industries put it in straightforward terms at a roundtable in St. Louis, Mo., explaining that manufacturing is "one of the biggest users of energy." He emphasized that, in his view, the biggest challenge facing his industry is "energy policy, which is before the Senate right now."

As it stands, America "faces the most serious energy shortage since the oil embargoes of the 1970s," directly attributable

MANUFACTURING IN AMERICA 43

- "The total federal budget outlays for regulatory compliance activities have almost doubled in the past 13 years, from $13.7billion in 1990 to $26.9 billion in 2003 in real terms."
- "The total burden…is $160 billion on manufacturers alone."

Economics of Regulation

- US industry expenditures on environmental controls (i.e., compliance with regulation, waste treatment, etc.) is approximately:
    - $200 billion per year (USD)
    - $550 million per day (USD)
    - $22,900,000 per hour (USD)
    - $380,000 per minute (USD)

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EPA Enforcement Actions

- In December 2005, EPA announced a fine for Teflon maker DuPont of $16.5M
  - for two decades' worth of covering up company studies that showed it was polluting drinking water and newborn babies with an indestructible chemical that causes cancer, birth defects and other serious health problems in animals.
  - The chemical is in the blood of over 95 percent of Americans.
- This fine is the largest administrative fine the EPA has ever levied under toxic chemicals law.
- The fine is less than half of one percent of DuPont’s after-tax annual profits from the Teflon product when averaged over the 20-year cover-up.

Environmental Realities

United States Environmental Protection Agency

- Toxics Release Inventory (TRI)
- 4.25 billion lbs. of toxic chemicals were released directly to air, land, and water in 2006 (latest year data released)

- Only 650 of toxic chemicals and toxic chemical categories out of 78,000 in commerce are tracked by TRI

Historic Approach

- Identify, quantify, measure, monitor, review and assess environmental problems.
- Consideration and balance of costs versus benefits of environmental protection
- Regulatory framework as the driver to change

New Approach

- Innovation based
- Solutions oriented
- Advancing competitiveness
- Intrinsic versus circumstantial
- Systematic sustainability

Environmental Management Goals to Support Mission

1 **Direct Mission Support**

Provide direct mission support by integrating environmental considerations into programs and projects.

2 **Proactive Risk Mitigation**

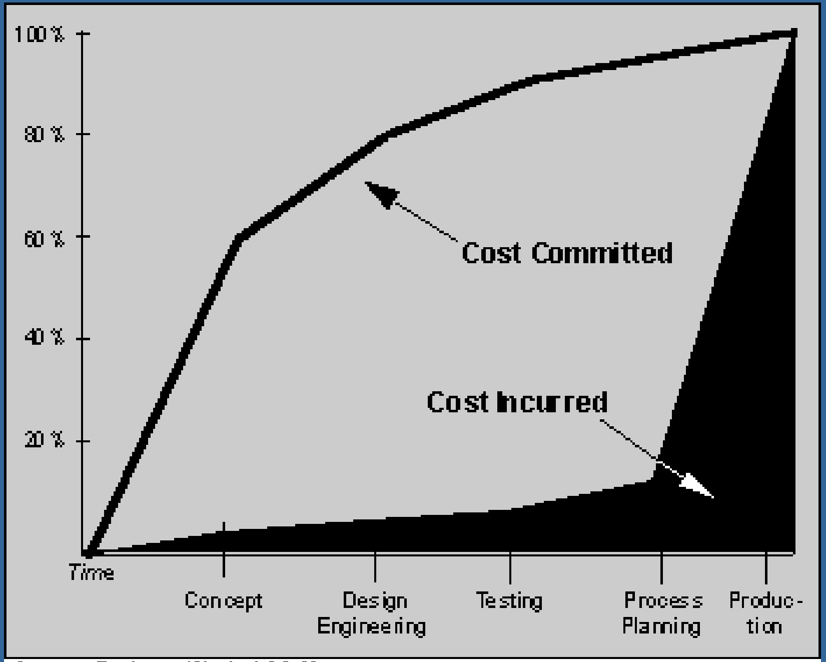
Proactively reduce NASA’s exposure to institutional, programmatic and operational risk.

3 **Protect Mission Resources**

Pursue environmental initiatives designed to restore, protect and enhance mission resources.

Impacts of Design Decisions

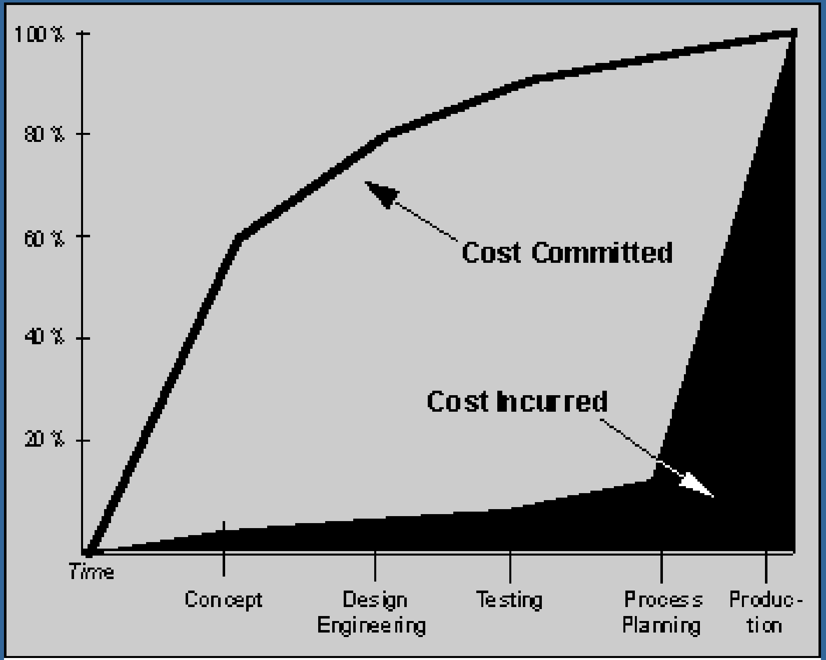
- For a typical product, 70% of the cost of development, manufacture and use is determined in its design phase.
- **Analogous for environmental impacts**



Source: Business Week 4-30-90

Impacts of Design Decisions

- Engaging in upfront product design can:
  - increase efficiency
  - reduce waste of materials and energy
  - reduce costs
  - impart new performance and capabilities
  - incorporate “inherently benign”



Source: Business Week 4-30-90

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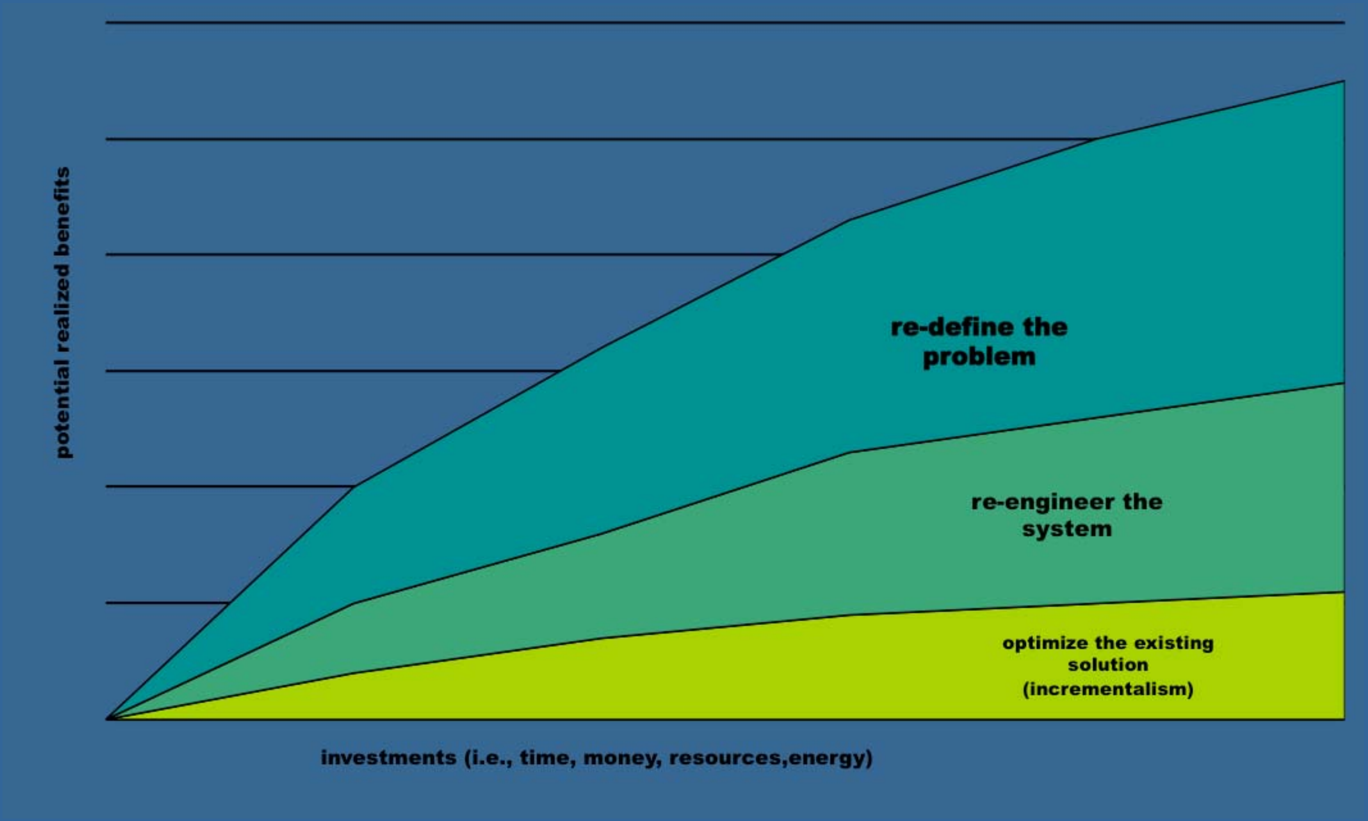
Not just how you design but what you design

Schematic of potential benefits vs. investments



Why “Leap-Frog” Innovation?

- Incremental improvement is hard to justify financially; principles of sustainability applied to product improvements may not readily pay for themselves.
- Sustainability generally considered to be “the right thing to do”, but is there also a good business case?

Sustainability

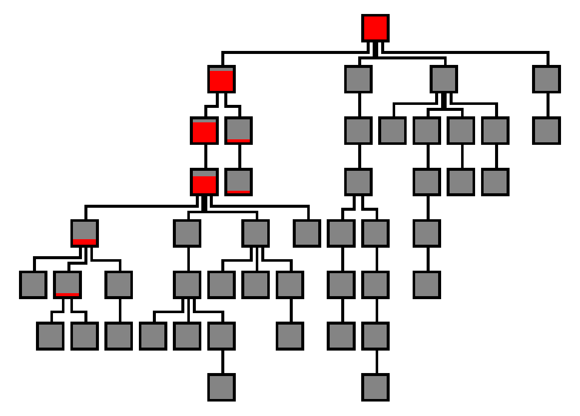
“Sustainability” without innovation is….unsustainable.

“Innovation” without sustainability is….unsustainable.

Fundamental Issues

- Inherency

- Life cycle foundation
- Holistic or so-called "systems thinking"
- Resiliency



Principles of Green Chemistry and Green Engineering

Chemistry

- Prevention
- Atom economy
- Less hazardous synthesis
- Safer chemicals
- Safer solvents
- Energy efficiency
- Renewables
- Reduce derivatives
- Catalysis
- Design for degradation
- Real-time analysis
- Inherently safer chemistry

Engineering

- Inherent rather than circumstantial
- Prevention rather than treatment
- Design for separation
- Maximize mass, energy, space & time efficiency
- Output-pulled
- Conserve complexity
- Durability rather than immortality
- Minimize excess
- Minimize material diversity
- Integrate material & energy flows
- Design for afterlife
- Renewable rather than depleting

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Plastics and polymers

- Design next generation polymers to minimize toxic additives (i.e., flame retardants, plasticizers, and thermal stabilizers).
- These polymers can be made from bio-based, renewable materials and controlled to be durable for reuse, developed to be self-healing, or degradable for beneficial disposition.

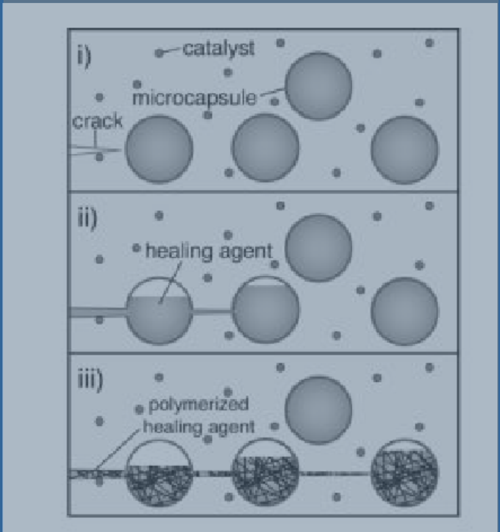


Figure 1. The self-healing concept.

Smart and Obedient Materials

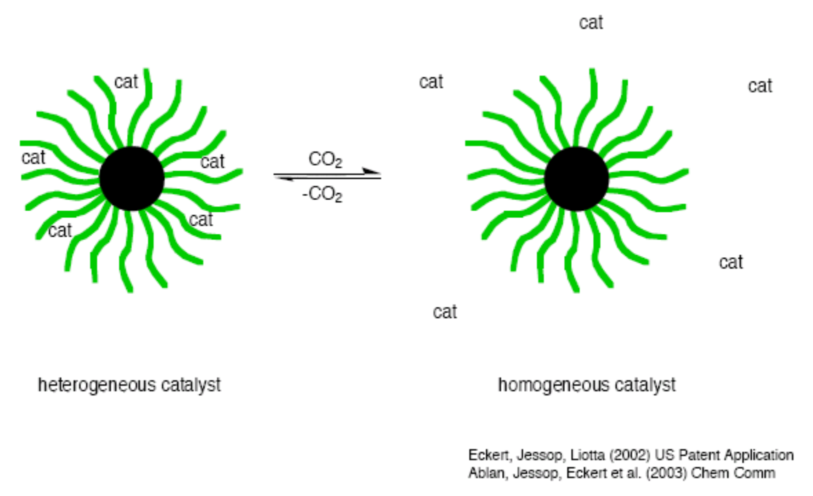
- **A “smart” solvent or catalyst** is one that will automatically change its nature when circumstances require it to do so.
- **An “obedient” solvent or catalyst** is one that will reversibly change its nature when triggered to do so by the operator.

The “trigger” could be:

  - a temperature rise
  - application of a gas
  - irradiation with light

The change in a solvent could be:

  - fluorophobic/fluorophilic
  - protic/aprotic
  - polar/nonpolar
  - volatile/nonvolatile



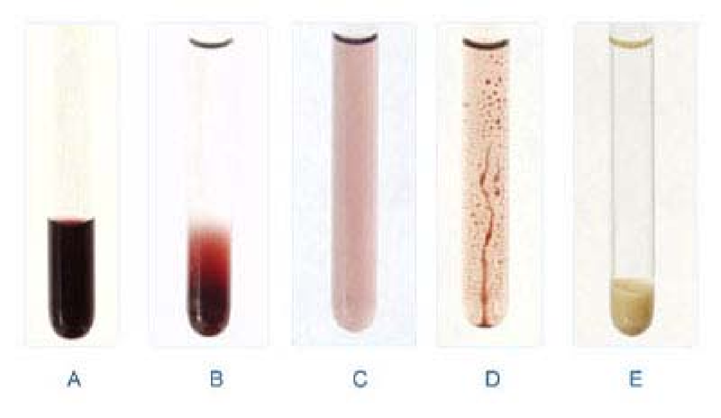
Eckert, Jessop, Liotta (2002) US Patent Application
Ablan, Jessop, Eckert et al. (2003) Chem Comm

The change in a catalyst could be:

  - homogeneous/heterogeneous

Self-Separating materials

- Up-front design allows products to self-separate using intrinsic physical/chemical properties such as solubility, volatility, etc.

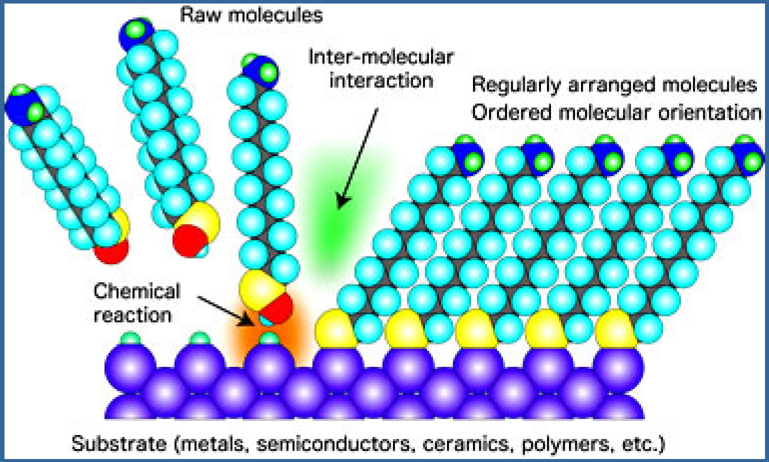


The catalyst is soluble in one of the reagents and remains soluble when the other reagent is added. As the reaction goes on, and the product builds up, the catalyst precipitates from the mixture as oil. This oil—liquid clathrate—remains to be an active catalyst, as the reagents are able to penetrate into it. When all the reagents are converted into products, the oily catalyst turns into a sticky solid, which can be easily separated and recycled.

"A Recyclable Catalyst that Precipitates at the End of the Reaction." Dioumaev, VK, and RM Bullock. July 31, 2003. Nature 424(6948):530-531

Self-Assembly / Direct Metal Deposition

- Rather than melting, machining, mass removal/reduction processes, create systems where molecules assemble and materials “grow” into the desired shape



Risk characterization

Risk = f(Hazard, Exposure)

Risk = f(Hazard, Dose, Time)

National Academy of Sciences, 1983.

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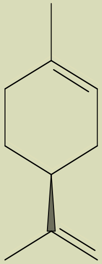
Circumstantial vs. Inherent

- Circumstantial
  - Use
  - Exposure
  - Handling
  - Treatment
  - Protection
  - Recycling
  - Costly

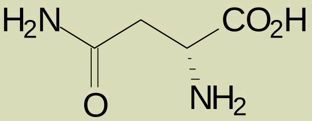
- Inherent
  - Molecular design for reduced toxicity
  - Reduced ability to manifest hazard
  - Inherent safety from accidents or terrorism
  - Increased potential profitability

Molecular Formulas: Function and Toxicity



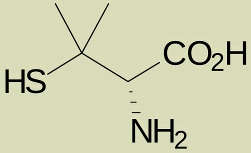
lemon

orange



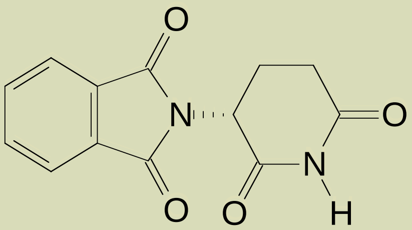
sweet

bitter



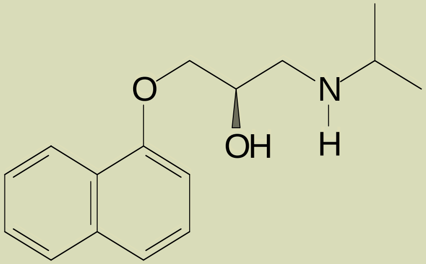
anti-arthritis

toxic



sedativum

teratogenic



contraceptive

β-blocker

Molecular Formulas: Function and Toxicity

Molecular formula (C_3H_6O)			
Name	Acetone	Methyl vinyl ether	Allyl alcohol
Toxicity LD-50	9.0 g/kg (oral-rat)	4.9 g/kg (oral-rat)	0.06 g/kg (oral-rat)

Biomimicry

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Types of inherent hazards

- **Physical** - explosivity, flammability, particulate-biological interactions, reactivity, corrosives
- **Toxicological** - acute, chronic toxicity, carcinogenicity, ecotoxicity
- **Global** - stratospheric ozone depletion, global climate change, global toxics dispersion, resource depletion

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Structural Design and Hazard Minimization

- Hazard is simply one of the many physical/chemical properties possessed by a substance that is a direct reflection of its molecular/material structure.
- Through molecular/material structural design, properties can be changed and hazard can be minimized.

Hazard and Physical-Chemical Properties

- Hazard types
  - Toxicological/Eco-toxicological
    - Carcinogenicity
    - Reproductive
    - Developmental
    - Neurological
    - Global warming potential
    - Ozone depleting potential
    - Bioaccumulation
    - Persistence
  - Physical
    - Explosivity
    - Flammability
    - Corrosivity

- Phys/Chem Properties
  - Water solubility
  - Log Kow
  - Volatility
  - Molar volume
  - Aspect ratio
  - Radical formation
  - Nucleophilicity
  - Electrophilicity
  - pH/pKa
  - Surface area
  - Reducing potential
  - Oxidizing potential
  - Polarizability

Designing Safer Chemicals

- Toxicology has evolved from a descriptive science to a mechanistic science.
- Efforts are emerging to develop predictive toxicology.
- Green Chemistry uses all the tools of molecular level understanding of toxicology – not only as a way of characterizing problems - but as the basis of a molecular design framework.
- Preventive Toxicology

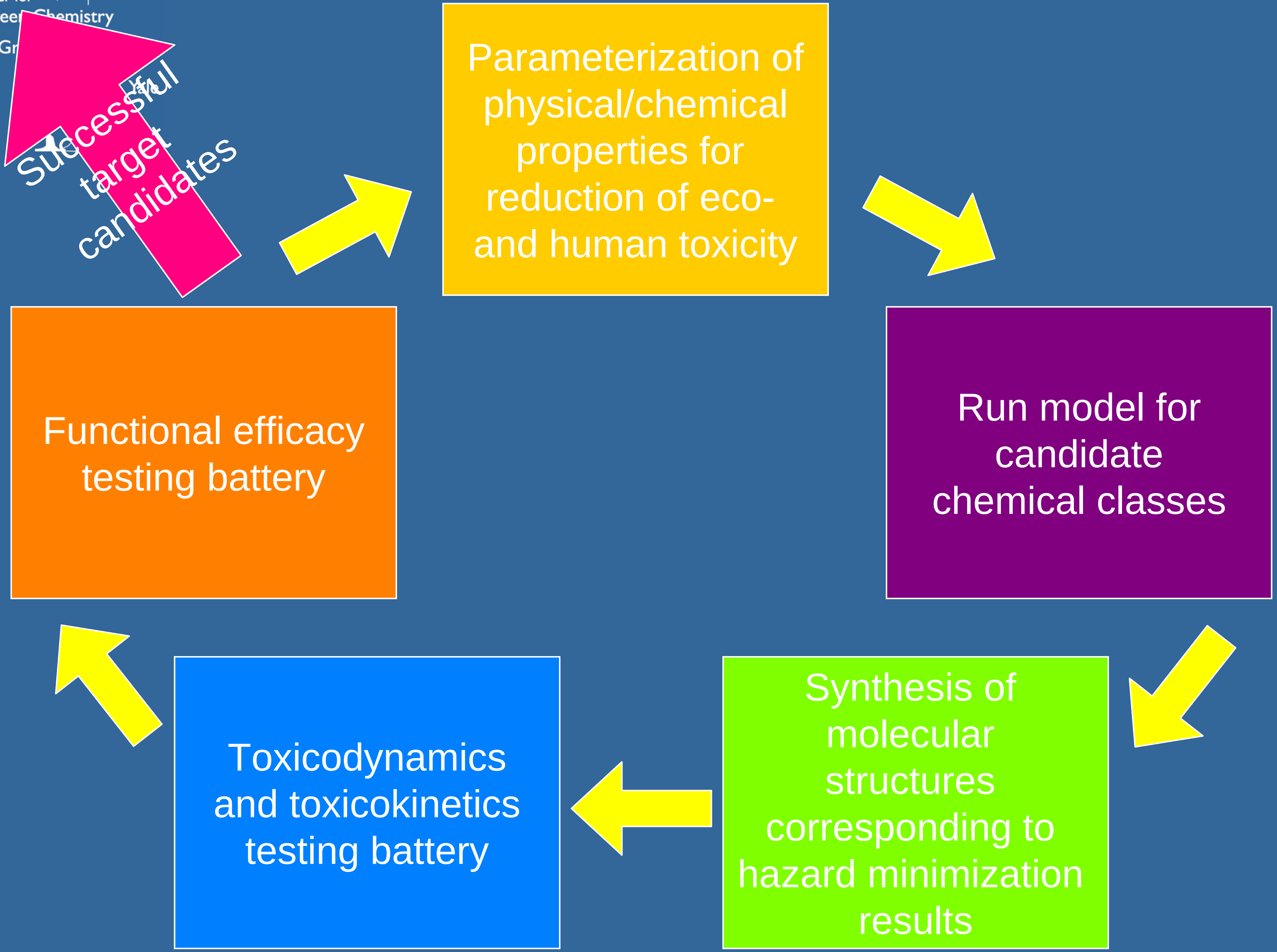
Pharmaceuticals vs Industrial Chemicals

- Pharmaceuticals
  - Designed to be biologically active
  - Performance criteria include reduced toxicity
  - Produced in relatively small volumes
  - Well defined use scenarios

- Industrial chemicals
  - No intentional biological activity
  - Performance is generally separate from toxicity
  - Can be produced in multi-billion pound quantities
  - Extremely diverse use scenarios

Minimization of Hazard through Molecular Design

1. Modification or termination of biological pathway of action.
2. Changing reactive functional groups
3. Reducing or eliminating bioavailability
4. Reduction of need for associated hazardous substances
5. Design for End-of-Useful product life



Parameterization of physical/chemical properties for reduction of eco- and human toxicity

Run model for candidate chemical classes

Synthesis of molecular structures corresponding to hazard minimization results

Toxicodynamics and toxicokinetics testing battery

Functional efficacy testing battery

Successful target candidates

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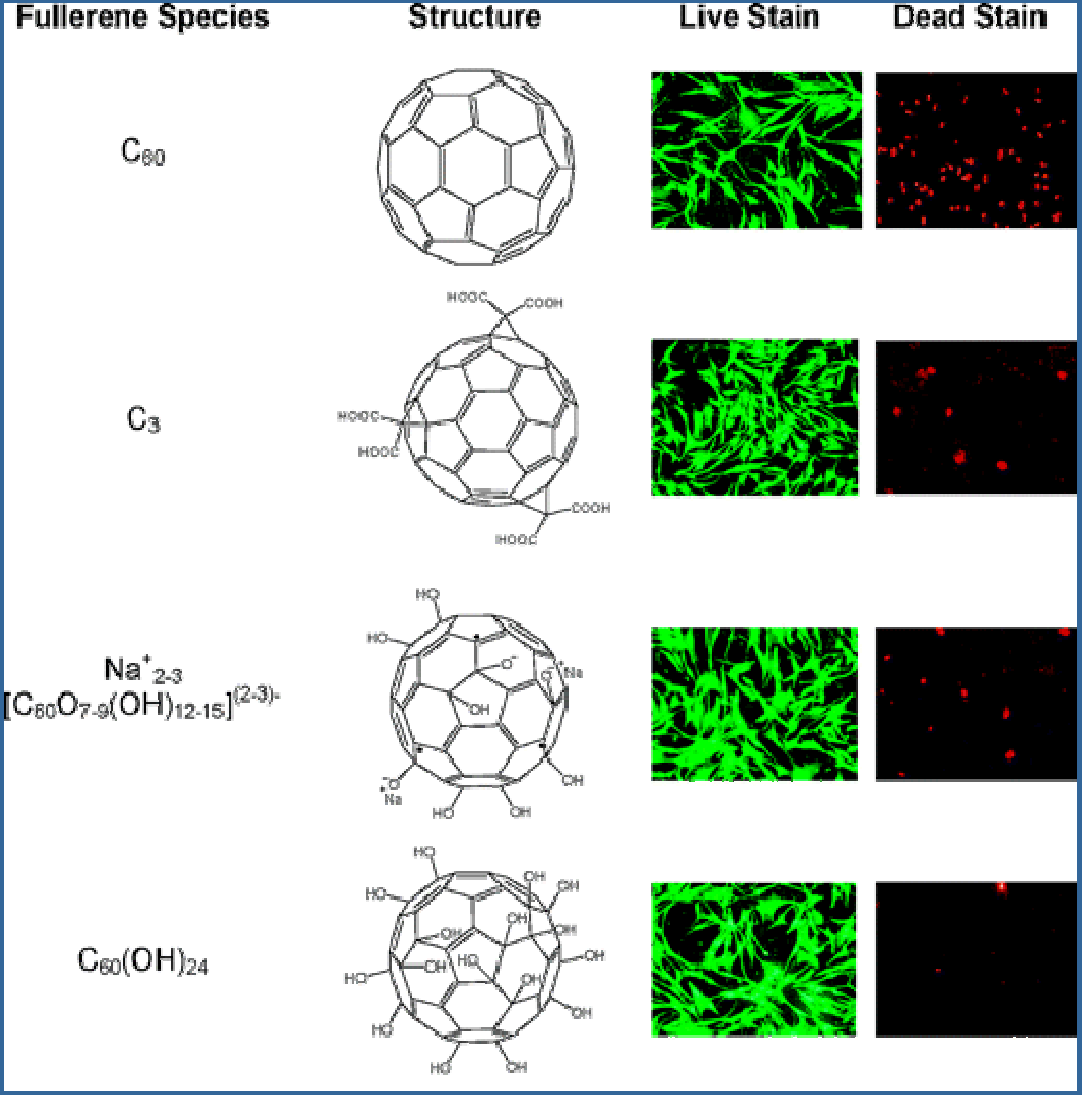
Case Study:
Nanoscience and nanotechnology

Risk Assessment

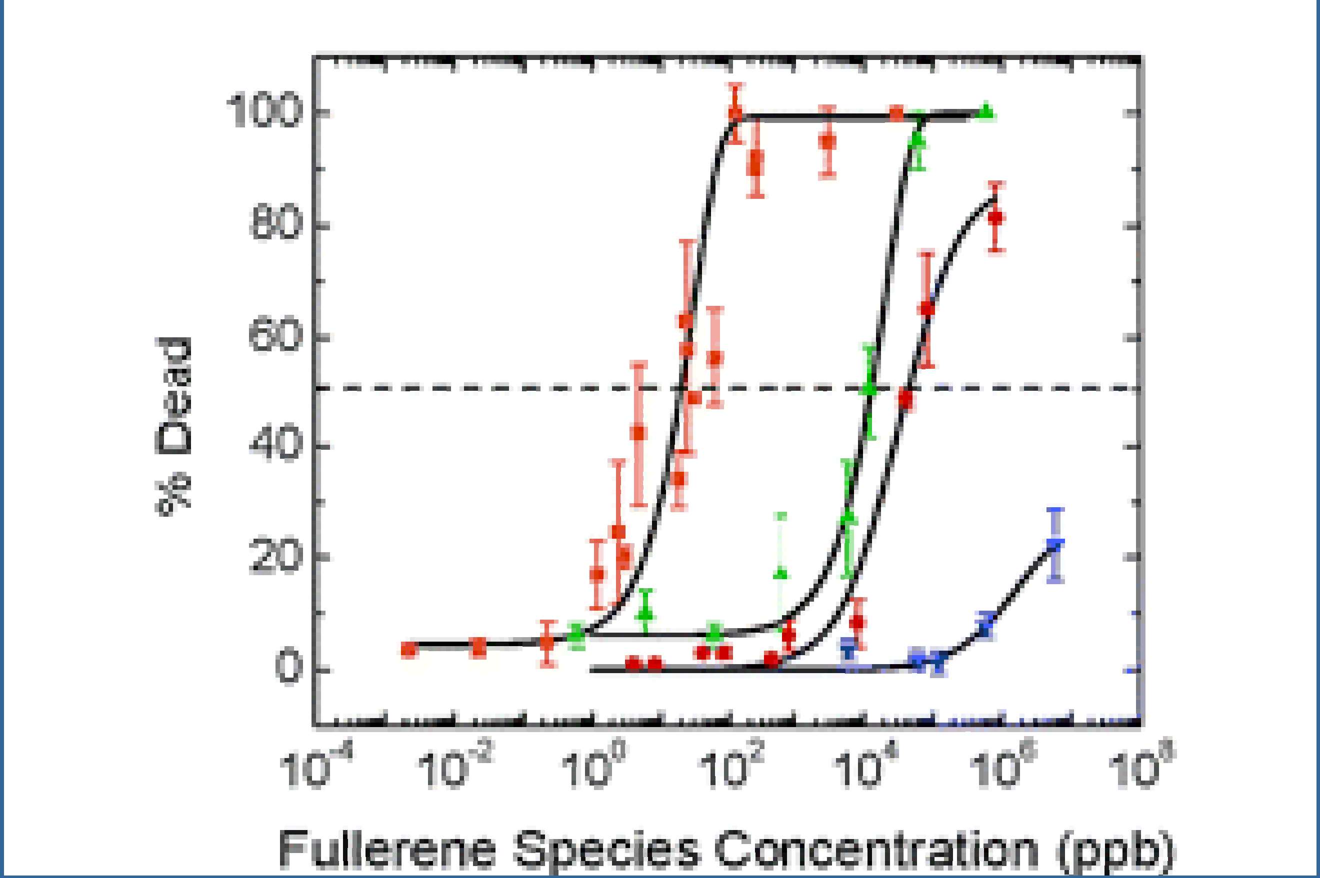
“The lack of toxicological data on engineered nanoparticles does not allow for adequate risk assessment.”

Oberdorster, G., et. al., Environ. Health Perspect., 113, 823-839, 2005



Differences in the structure and cellular activity of nano-C60, C3, Na+2-3[C60O7-9(OH)12-15](2-3)-, and C60(OH)24.

Sayes, C.M., et al., Nanoletters, 4(10), 1881-1887, 2004.



The differential cytotoxicity of nano-C60 (--) as compared to C3 (--), Na+2-3[C60O7-9(OH)12-15](2-3)-(--), and C60(OH)24 (--) in human dermal fibroblasts. Cells were exposed to toxicant for 48 h.

Sayes, C.M., et al., Nanoletters, **4**(10), 1881-1887, 2004.

Case Study:
Precision cleaning of oxygen systems

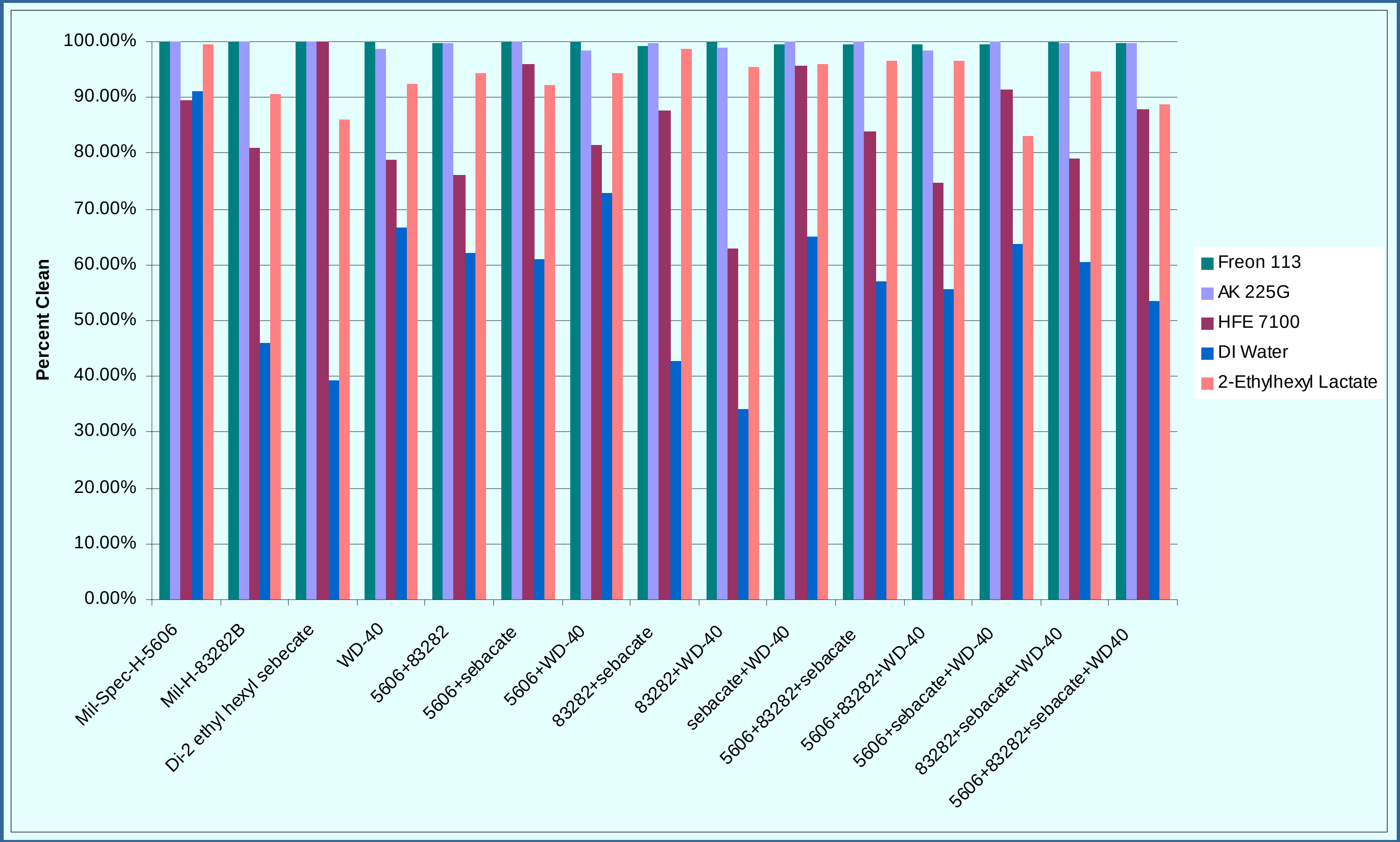
Background

- Most solvents are Ozone Depleting Substances (ODS)
  - Class I ODS (CFC 113, 1,1,1 Trichloroethane)
    - Phased out in 1990s
  - Class II ODS (HCFC 141b, HCFC 225g)
    - Scheduled to be phased out
  - Need Green solvent

Green Solvent Properties

- Performance Criteria
    - Acceptable cleanliness
    - Non-accumulating in environment
    - Non ozone depleting
    - Low toxicity
    - Compatible in oxygen environment

No flow data


100.00%
90.00%
80.00%
70.00%
60.00%
50.00%
40.00%
30.00%
20.00%
10.00%
0.00%
Percent Clean
Mil-Spec-H-5606
Mil-H-83282B
Di-2 ethyl hexyl sebecate
WD-40
5606+83282
5606+sebacate
5606+WD-40
83282+sebacate
83282+WD-40
sebacate+WD-40
5606+83282+sebacate
5606+83282+WD-40
5606+sebacate+WD-40
83282+sebacate+WD-40
5606+83282+sebacate+WD40
Freon 113
AK 225G
HFE 7100
DI Water
2-Ethylhexyl Lactate

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Improvements

- Examine effect of energy addition on cleaning performance
  - Flow experiments
  - Elevated temperature

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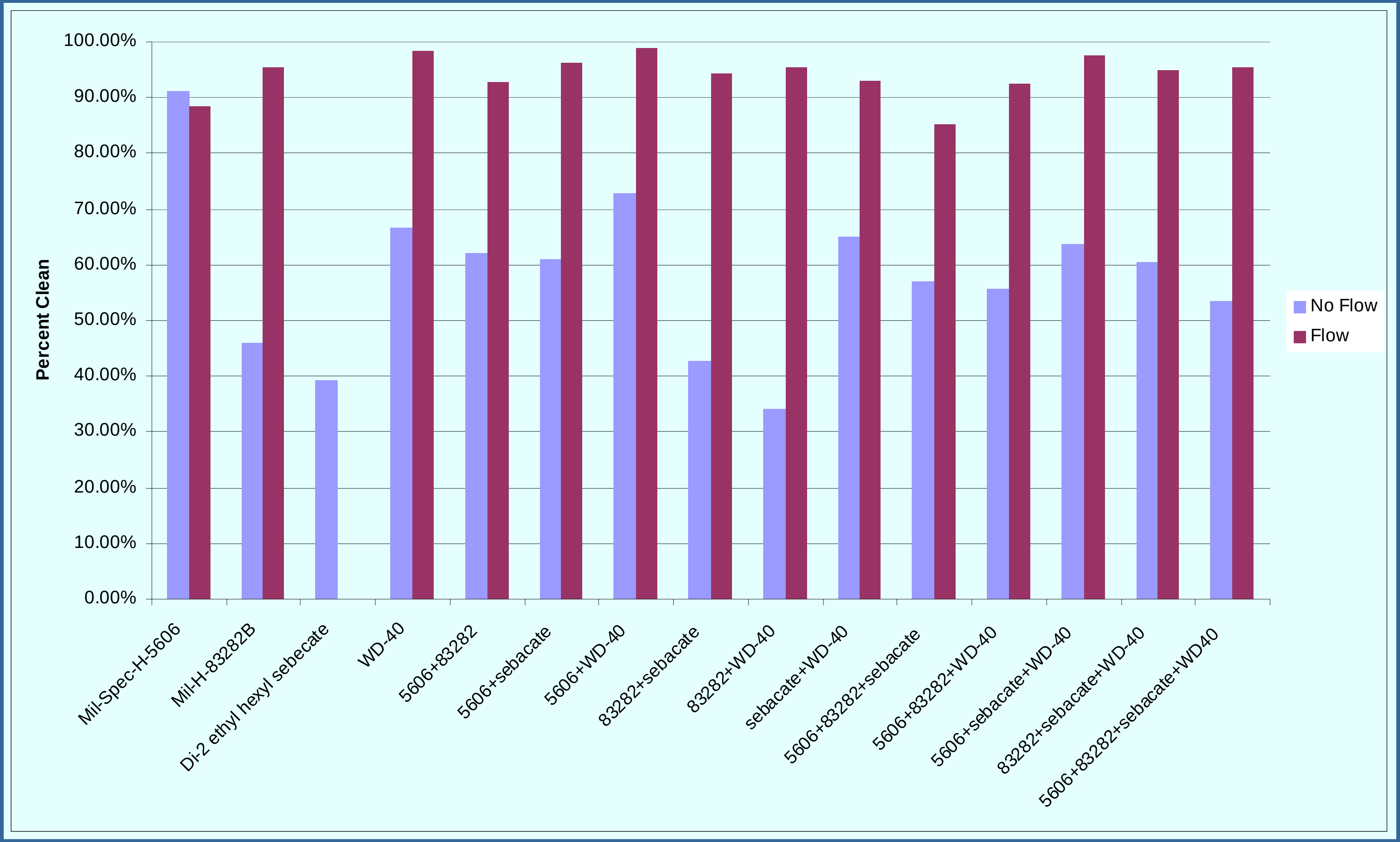
DI Water Flow vs. No Flow



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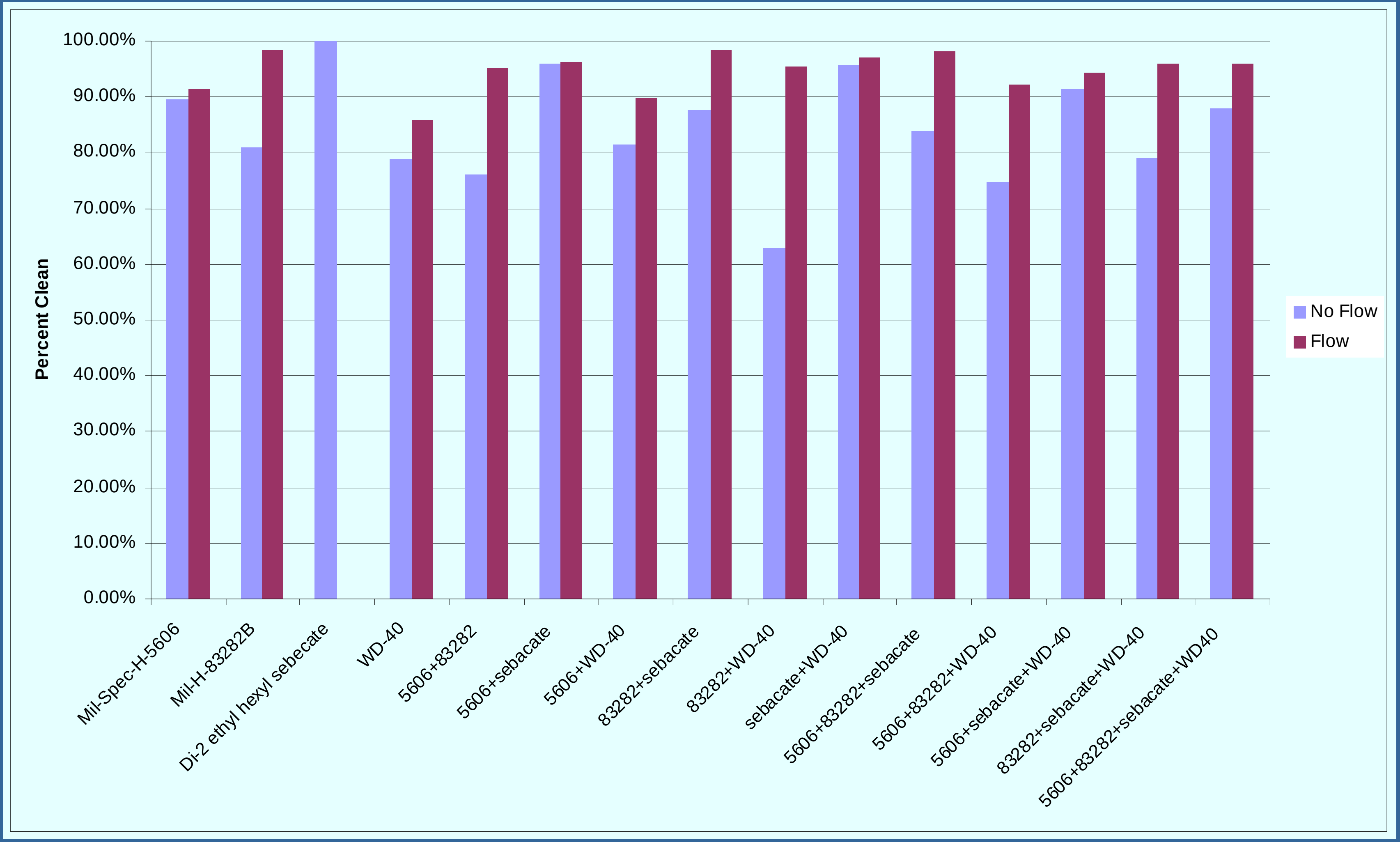
HFE 7100 Flow vs. No Flow



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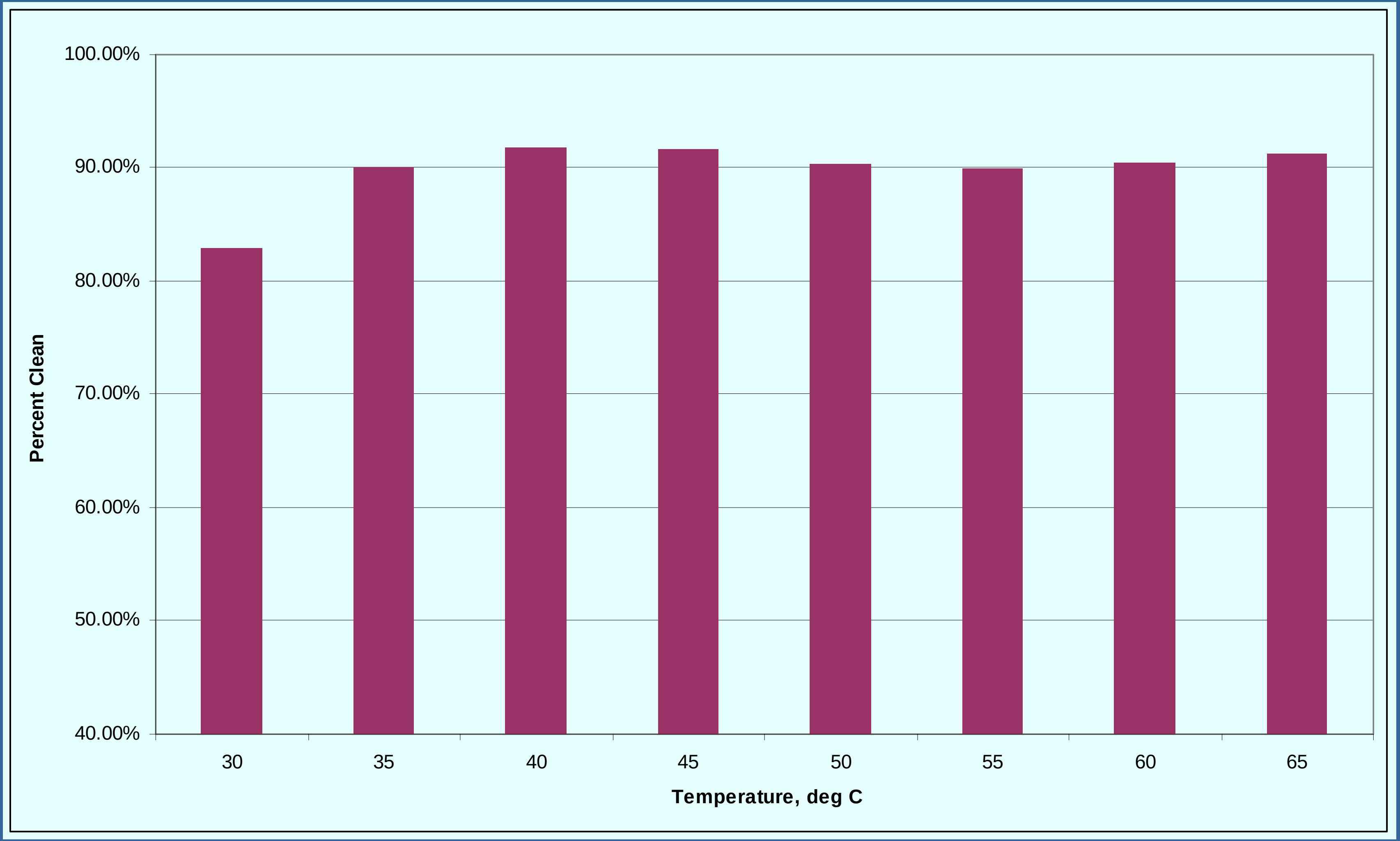
HFE 7100 Temperature



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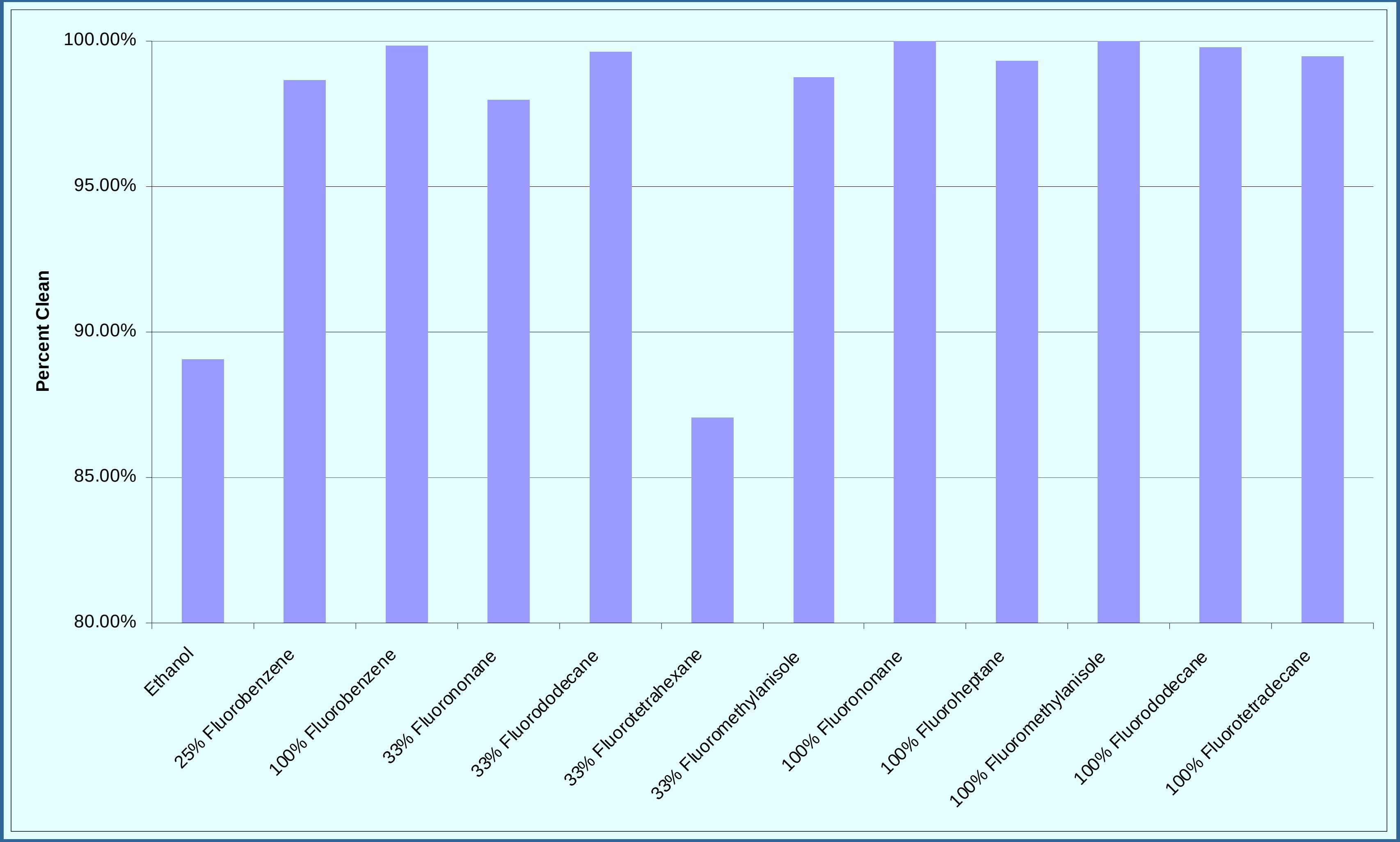
Perfluorinated Solvents



Perfluorinated Solvents

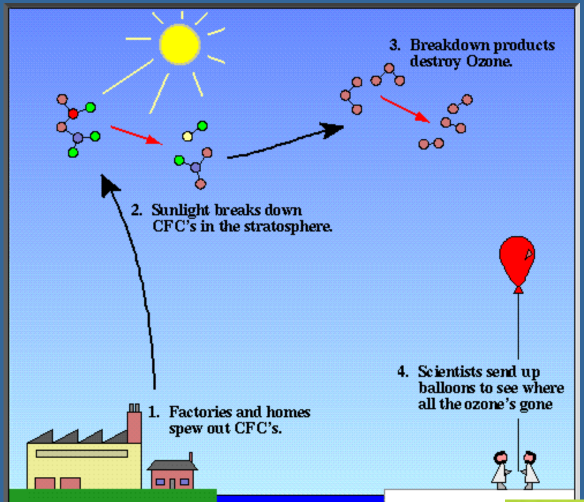
PERFORMANCE

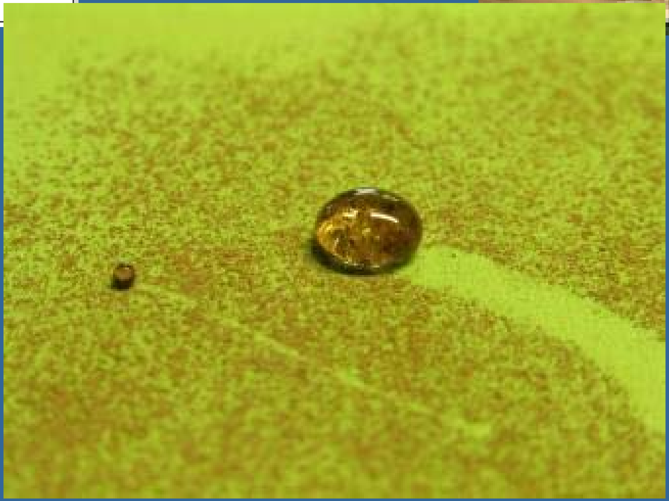
- Finding the balance between:
  - Reduced flammability
  - Improved cleaning
  - Minimized environmental persistence
  - Increased cost effectiveness
  - Enhanced ability for recycle, reuse

Perfluorinated Solvents

- Correlation of physical –chemical properties with performance criteria as affected by:
  - Chain length
  - Degree of fluorination
  - Position of fluorination
- Laboratory evaluation → parameterization and modeling

What if…





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Leap-frog ideas can create structural problems…

BUILD A BETTER LIFE BY STEALING OFFICE SUPPLIES Dogbert's Big Book of Business 101

A necessary caveat: How do we know our frog is jumping in the right direction?

Some frogs are poisonous…..

Sustainability is a process of continuous improvement, we can't forget to check to make sure we're actually improving.