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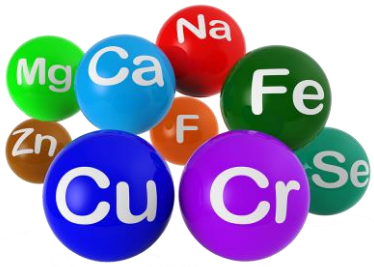

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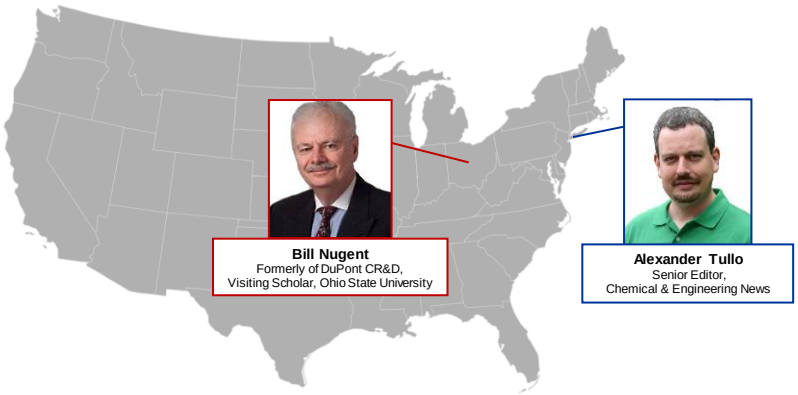

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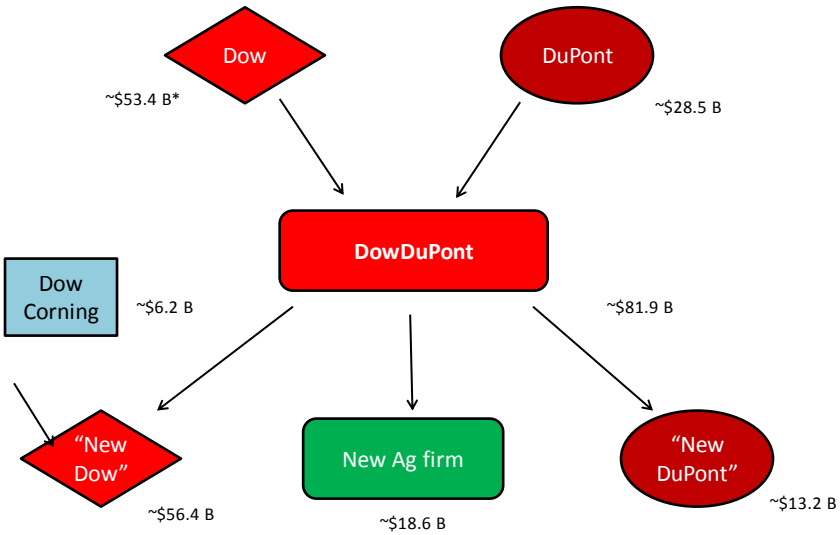
The Dow/DuPont Deal at a Glance

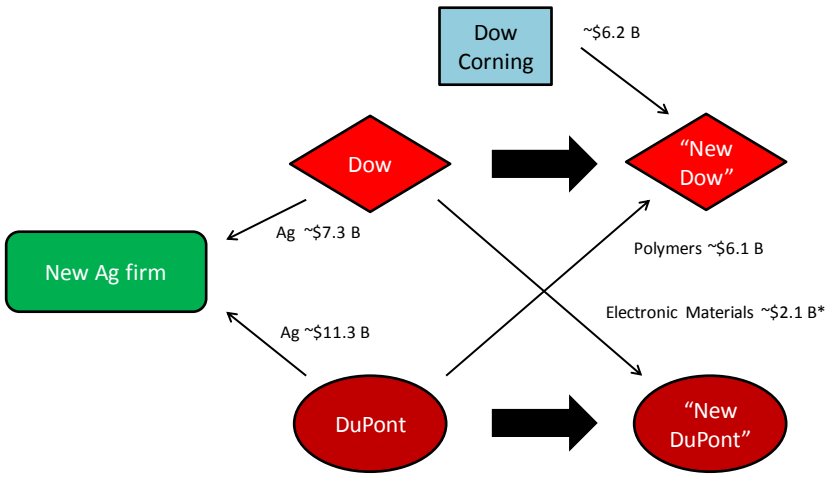


* C&EN estimates based on 2014 revenue figures.

11

Dow/DuPont is no big deal

…it's many smaller deals



* C&EN estimate.

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Effect on R&D

- **DowDuPont** will cut combined R&D spending by $300M, as part of $3B in cost cutting
- **DuPont** to "reorganize" Central R&D into "Science & Innovation" as part of separate, $700 million restructuring
- ~200 layoffs at CR&D (unofficially)
- **DuPont** to spend $1.6B - $1.7B on R&D in 2016, a decline from $1.9B in 2015
- **Dow** spent $1.6B on R&D in 2015

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DuPont Experimental Station

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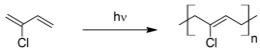
Prehistory of CRD

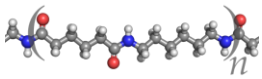
- During the 1930's, Chemicals Dept. had demonstrated the value of exploratory research.

  - **neoprene (1930)**



  - **Teflon® (1938)**

  - **nylon (1939)**



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- The tradition waned during WWII.
- In 1957 DuPont formalized commitment to basic research by establishing CRD.

Rationale Behind CRD

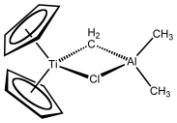
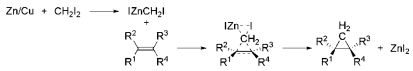
Mission:

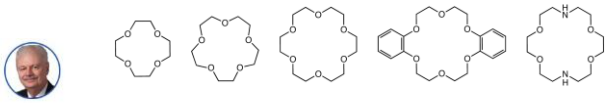
- Do excellent science in areas of company interest
- "Technology push" vs. "market pull"
- "Discover the next nylon"

Intangibles:

- Stable of "in-house consultants"
- Recruiting tool
- Promote university relations

Contributions to Organic Synthesis

- The Tebbe reagent 
- The Simmons-Smith Reagent 
- Fluorination of alcohols with DAST (Middleton)
- N-Heterocyclic carbene ligands (Arduengo)
- Crown ethers* (1987 Nobel Prize to Pedersen)



*discovered in Elastomers Dept.

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Some Commercial Successes

Research	Application
Potassium titanyl phosphate (KTP)	Laser frequency doubling
Group transfer polymerization	Ink jet inks; automotive finishes
Hyperbaric crystallization of ultra-high molecular weight polyethylene.	Hylamer® polyethylene for hip and knee replacement
Catalysts for manufacture of hydrochlorofluorocarbons (HCFCs)	Suva® non-ozone depleting refrigerants
Novel fluorescent labels for DNA	Qualicon® technology (identifies bacteria for food safety)
Ureas and uracils with herbicidal activity	Establishment of DuPont agrichemical business (later, sulfonylurea herbicides)

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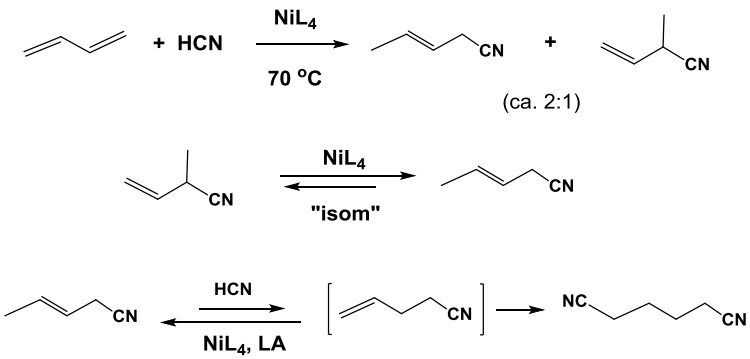
Hydrocyanation of Butadiene



NiL_4 = nickel triarylphosphite complex, LA = Lewis acid additive.

Technology is now practiced on 2 billion pound per year scale.

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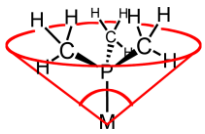
Hydrocyanation: Scientific Advances



- Tolman's introduction of **ligand cone angles** to quantititate steric effects in catalysis
- Also the systematic understanding of electronic effects
- First cyclic representation of a catalytic process using 16 and 18 electron complexes

20

Why Did It Work So Well?

- **Serendipity** – the encouragement to pursue unexpected experimental results
- **Critical Mass** – both in terms of business opportunities and breadth of expertise
- **The Scientists** – intentional recruitment of "academic" personality types

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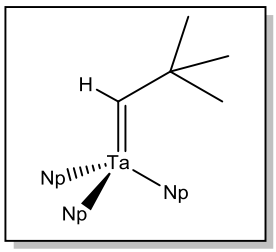
The First Alkylidene Complex



Np = neopentyl

Tantalum alkylidene complex containing Ta=C double bond.

Antecedent to first well defined olefin metathesis catalysts.

This work eventually led to the 2005 Nobel Prize in Chemistry.

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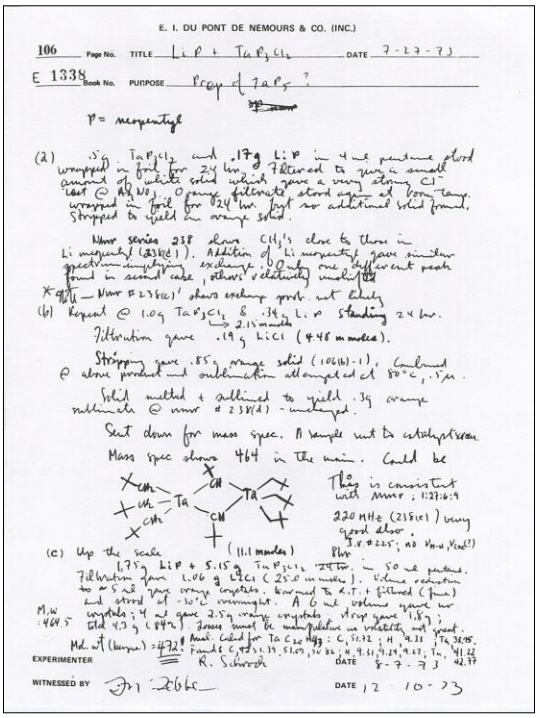

E. I. DU PONT DE NEMOURS & CO. (INC.)

106 Page No. TITLE Li P + TaP_3Cl_2 DATE 7-27-73

E 1338 Book No. PURPOSE Prep of TaP_5 ?

P = mesityl

(a) .5g TaP_3Cl_2 and .17g Li P in 4 ml pentane stirred wrapped in foil for 24 hr. Filtered to give a small amount of white solid which gave a very strong Cl^- test @ $AgNO_3$. Orange filtrate stirred again at room temp. wrapped in foil for 24 hr. but no additional solid formed. Stripped to yield an orange solid.

Nmr series 238 shows CH$_3$'s close to those in Li mesityl (238(c)). Addition of Li mesityl gave similar spectrum - implying exchange. Bound one different peak found in second case, others identical - unclear.

* q/H — Nmr #238(c)' shows exchange prob. not likely

(b) Repeat @ 1.0g TaP_3Cl_2 & .34g Li P standing 24 hr. → 2.15 mmoles

Filtration gave .19g LiCl (4.48 mmoles).

Stripping gave .85g orange solid (1.06(b)-1). Combined @ above product and sublimation attempted at 80°C, .1 μm.

Solid melted + sublimed to yield .3g orange sublimate @ nmr #238(d) - unchanged.

Sent down for mass spec. A sample sent to catalyst screen.

Mass spec shows 464 in the main. Could be

This is consistent with nmr; 1:27:6:9

220 MHz (238(c)) very good also.

I.R. #225; no $\nu_{M-H}, \nu_{C=C}$(?)

8hr

(11.1 mmoles)

(c) Up the scale

1.75g Li P + 5.15g TaP_3Cl_2 24 hr. in 50 ml pentane. Filtration gave 1.06 g LiCl (25.0 mmoles). Volume reduction to ~5 ml gave orange crystals. Warmed to R.T. + filtered (fine) and stored at -30°C overnight. A 6 ml volume gave no crystals; 4 ml gave 2.5g orange crystals. Strip gave 1.8g; total 4.3 g (84%). Losses must be manipulative as volatility not great.

M.W. : 464.5

Mol. wt (barrier) = 472! Anal. Calcd for $TaC_{20}H_{33}$: C, 51.72; H, 9.33; Ta, 38.95. Found: C, 49.51, 51.39, 51.09, 50.86; H, 9.31, 9.24, 9.22; Ta, 41.22, 42.77

EXPERIMENTER R. Schrock DATE 8-7-73

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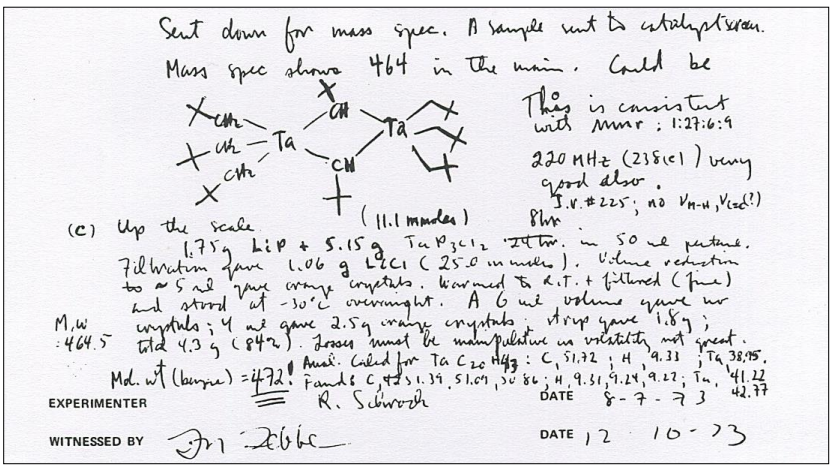
Birth of Alkylidene Chemistry



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EXPERIMENTER R. Schrock DATE 8-7-73

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The Benefits of "Critical Mass"

- Bert Ciganek discovers potential non-addictive pain killer
- T.V. RajanBabu attempts innovative synthesis of Ciganek compound using TASF (discovered by Bill Middleton)
- The reaction fails producing instead oligomers. Owen Webster suspects this involves novel polymerization mechanism
- He encourages Dotsevi Sogah to apply to polymerization under practical conditions

25

Group Transfer Polymerization

- In some runs the reaction resulted in useful polymerization but results were erratic
- Bill Farnham explains the results in terms of trace hydrolysis and formation of bifluoride anion

GTP was the first completely new polymerization process to be identified in two decades and is now used to manufacture printer inks and automotive finishes.

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The Scientists

- CRD employed scientists with an academic bent who would be equally at home in a university chemistry department.
- Publication was encouraged as a useful objective in its own right.
- Visiting scientists from universities spent sabbaticals in CRD.

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CRD Alumni in Academia

Material Science
Dotsevi Sogah (Cornell)
Michael Ward (NYU)
Arthur Sleight (Oregon State)
Joel S. Miller (Utah)
Galen Stucky (UC San Diego)
E. Bryan Coughlin (U. Mass.)
Zhibin Guan (UC Irvine)
Stephen Craig (Duke)
Anand Jagota (Lehigh)
Paul Smith (ETH)
Bruce Parkinson (Colorado St.)

Organic Chemistry
T.-V. RajanBabu (Ohio State)
Douglass Taber (Delaware)
James Becker (Ben-Gurion U.)
Shlomo Rozen (Tel-Aviv U.)

Biochemistry
William DeGrado (Penn)
George Lorimer (Maryland)
Jim Lear (Penn)

Organometallic Chemistry
R. Tom Baker (Ottawa)
Pam Shapiro (Idaho)
Richard Schrock (MIT)
Bo Arduengo (Alabama)
SonBinh Nguyen (Northwestern)
Tracy Hanna (Texas Christian)
Todd Marder (Durham)
William Crowe (LSU)
Giambattista Consiglio (ETH)
David Milstein (Weizmann Inst.)

Physical Chemistry
V. Ramamurthy (Miami)
David Dixon (Alabama)

Analytical Chemistry
Bruce Chase (Delaware)
Charles McEwen (U. of Sciences)

Inorganic Chemistry
Mas Subramanian (Oregon State)
James Mayer (Yale)

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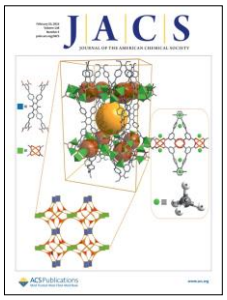
A Metric for Exploratory Research?

Hypothesis: A company's commitment to exploratory chemical research will be reflected by the number of papers it publishes in JACS in a given year



Advantages of the metric

- Easy to measure
- Provides a standard of quality

Potential limitations

- Alternative journals continually appear
- Page budgets have increased over time

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What the Data Shows

Publication in JACS was common among US companies in the 1950s but gradually diminished.

Six elite companies maintained a commitment to exploratory chemistry research into the 21st Century.

- AT&T/Lucent Technologies
- Eastman Kodak
- Merck
- Exxon
- IBM
- DuPont

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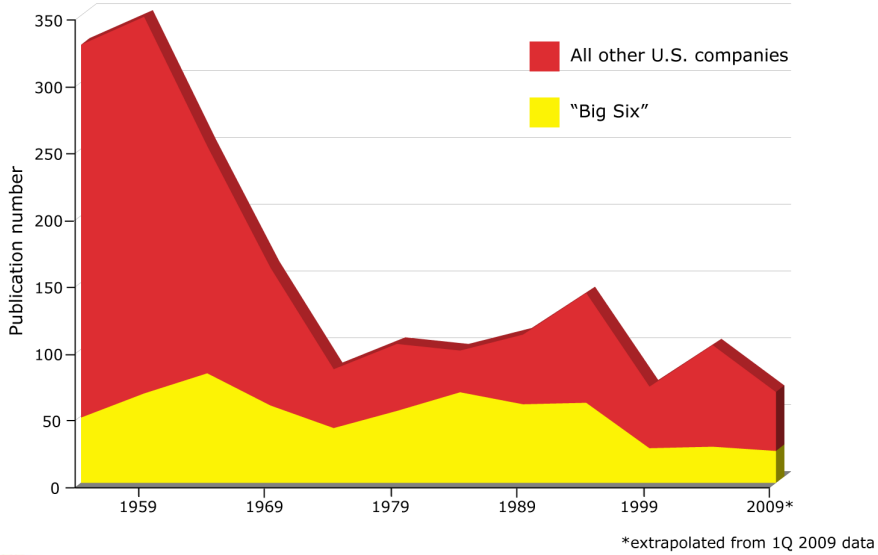
JACS Papers from US Companies



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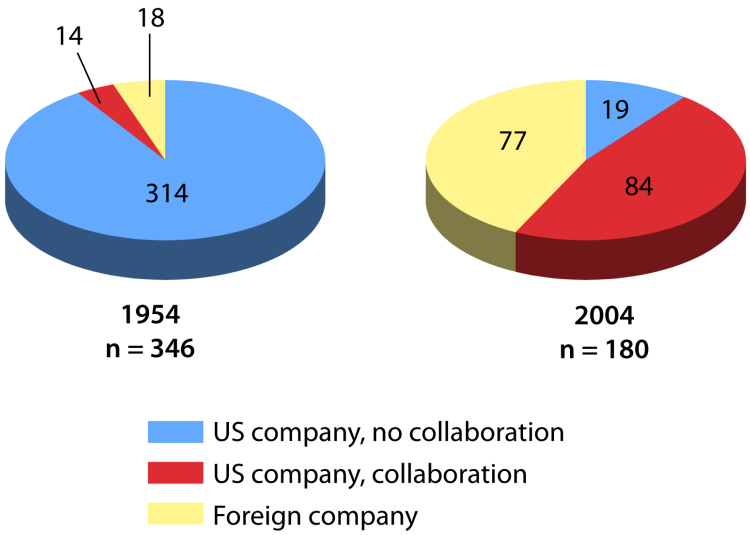
Industrial Publications in *JACS*



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The 1990s – Changing Business Needs

- Shorter investment timeline
- Diminished opportunities (Perception that the "low hanging fruit" had been harvested)
- Concept of "risk management"
- "Technology push" no longer viable

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"Apex Research"

- In 1998, DuPont undertook a transformational change in long-term discovery research.
- All proposals required to contain a technical and business case.
- Proposals were evaluated by a group of senior business leaders.

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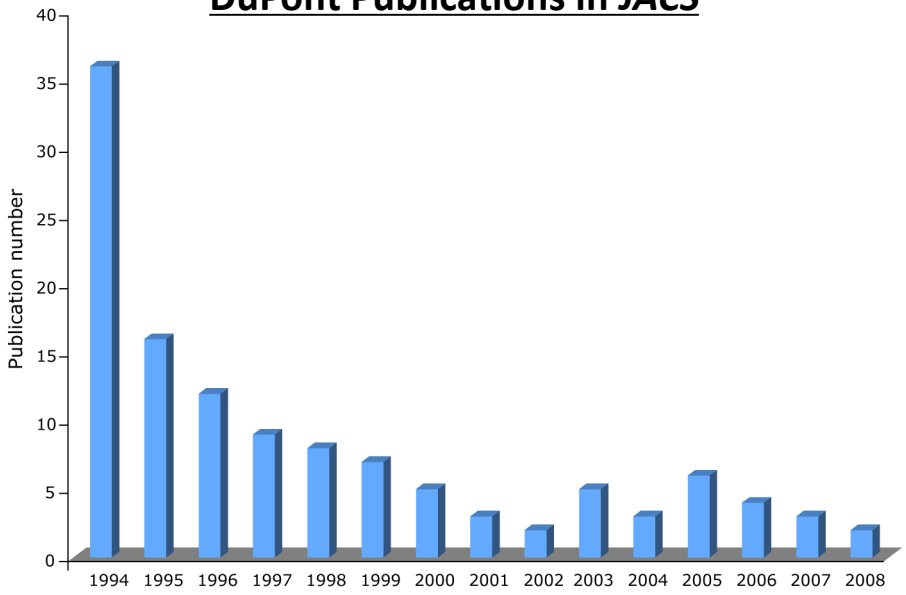
DuPont Publications in *JACS*



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The End of Exploratory Chemistry

- In 2011 for the first time in the history of the department, no JACS papers were published from CRD
- Although CRD was closed in 2016, its original mission was abandoned years ago
- US industry will be increasingly dependent on the universities for breakthrough science

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Audience Survey Question

ANSWER THE QUESTION ON BLUE SCREEN IN ONE MOMENT

In the future, what will be the most important source of novel chemistry-based technologies for the US industry:

- Start-up companies funded by venture capital
- Colleges and universities
- In-licensed technology from non-US corporations
- In house discovery in existing US companies

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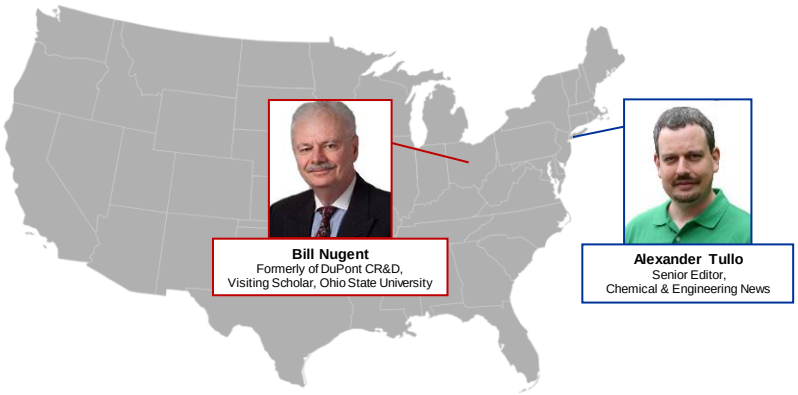

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Chemistry of Hello: Lithium Ion Batteries

Challenges and Opportunities for Personal Electronics Applications

Dee Strand, Chief Scientific Officer, Wildcat Discovery Technologies

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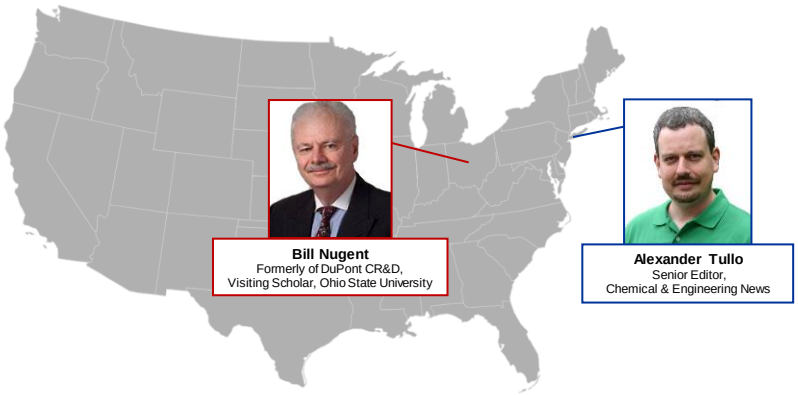

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