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HFO-Stable Polyurethane Catalyst Solutions

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Performance Products

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Huntsman Performance Products

- Over 350 products
- 15+ chemical process technologies
- Over 900 customers
- Approximately 2 billion pounds of annual production capacity through many different chemistries
- 2020 revenues of USD 1 billion
- 10 manufacturing locations
- Approximately 800 associates worldwide

Key Products and Markets

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- **AMINES**: Leading global producer of specialty amines used in gas treating, fuel and lube additives, PU additives, coatings, adhesives and composites.
- **MALEIC ANHYDRIDE**: Largest global producer and supplier into markets such as unsaturated polyester resins (UPR), food, lube additives, and coatings.
- **CARBONATES:** One of the largest global producers of alkylene carbonates and the only producer in the US; used for high purity applications in electronics and as electrolyte solvents for lithium-ion batteries.

ADVANCED TECHNOLOGY
Battery, Electronics

COATINGS, ADHESIVES & COMPOSITES

CONSTRUCTION
UPR, Industrial Applications

FUELS & LUBRICANTS
Fuels , Lubes, Metalworking

GAS TREATING
Gas Processing Chemicals & Licensing

PU ADDITIVES
Amine Catalyst Technology

HPP Polyurethane Additives R&D

What we do

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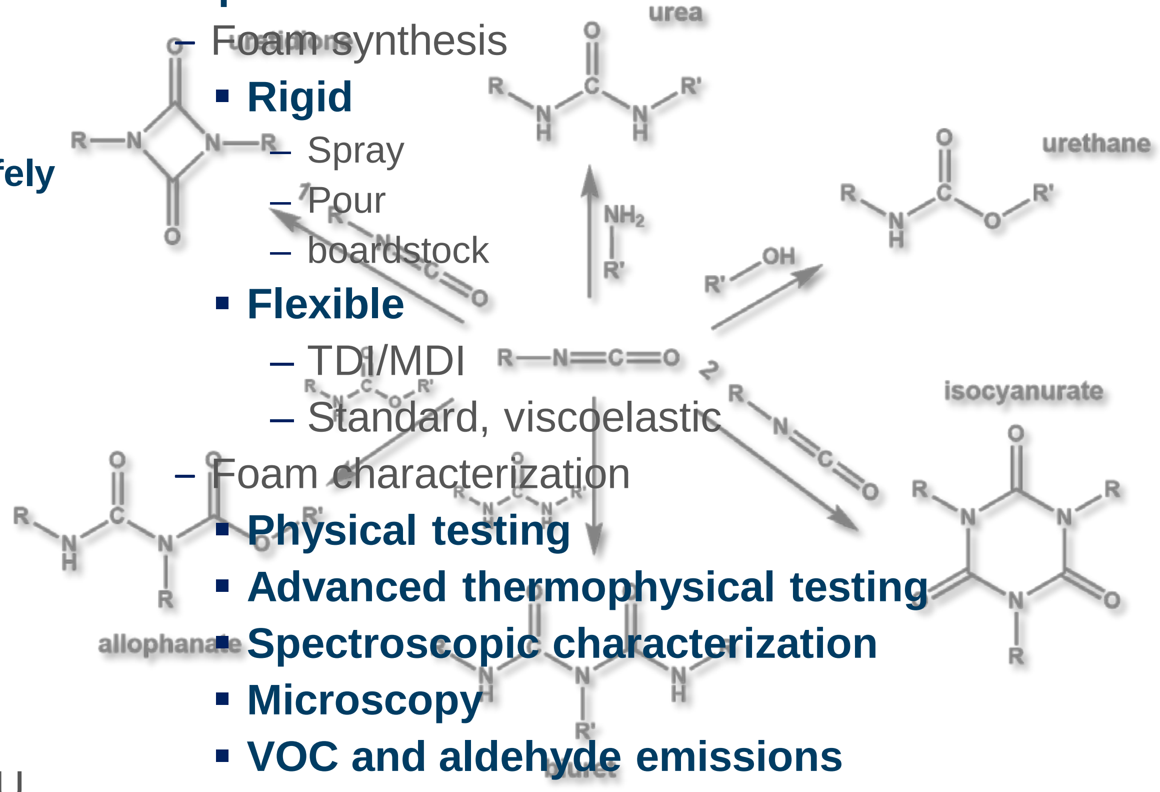
- **Technical support**
  - Customers
    - **Respond quickly to customer issues/inquiries**
      - Samples, blends, foam troubleshooting, on-site visits
    - **Train customers/co-workers to use our products correctly and safely**
  - Plant issues
    - **New product scale-up, product quality troubleshooting, training**
  - Interfacial cooperation with marketing and sales
- **Development**
  - Investigation of new applications for existing products
  - Market expansion of niche products
  - Market-driven development and/or testing
    - **New blends**
    - **Emissions testing**
- **Research**
  - Strive to understand structure/property relationships between PU additives and foams
  - Fundamental investigations of new molecules or new phenomena
    - **Synthesis, spectroscopic characterization, foam testing, etc.**



- **Capabilities**
  - Foam synthesis
    - **Rigid**
      - Spray
      - Pour
      - boardstock
    - **Flexible**
      - TDI/MDI
      - Standard, viscoelastic
  - Foam characterization
    - **Physical testing**
    - **Advanced thermophysical testing**
    - **Spectroscopic characterization**
    - **Microscopy**
    - **VOC and aldehyde emissions**
  - Small molecule synthesis
    - **New catalysts**
    - **new additives**

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R&D Approach – How we do it

Strategy and areas of focus

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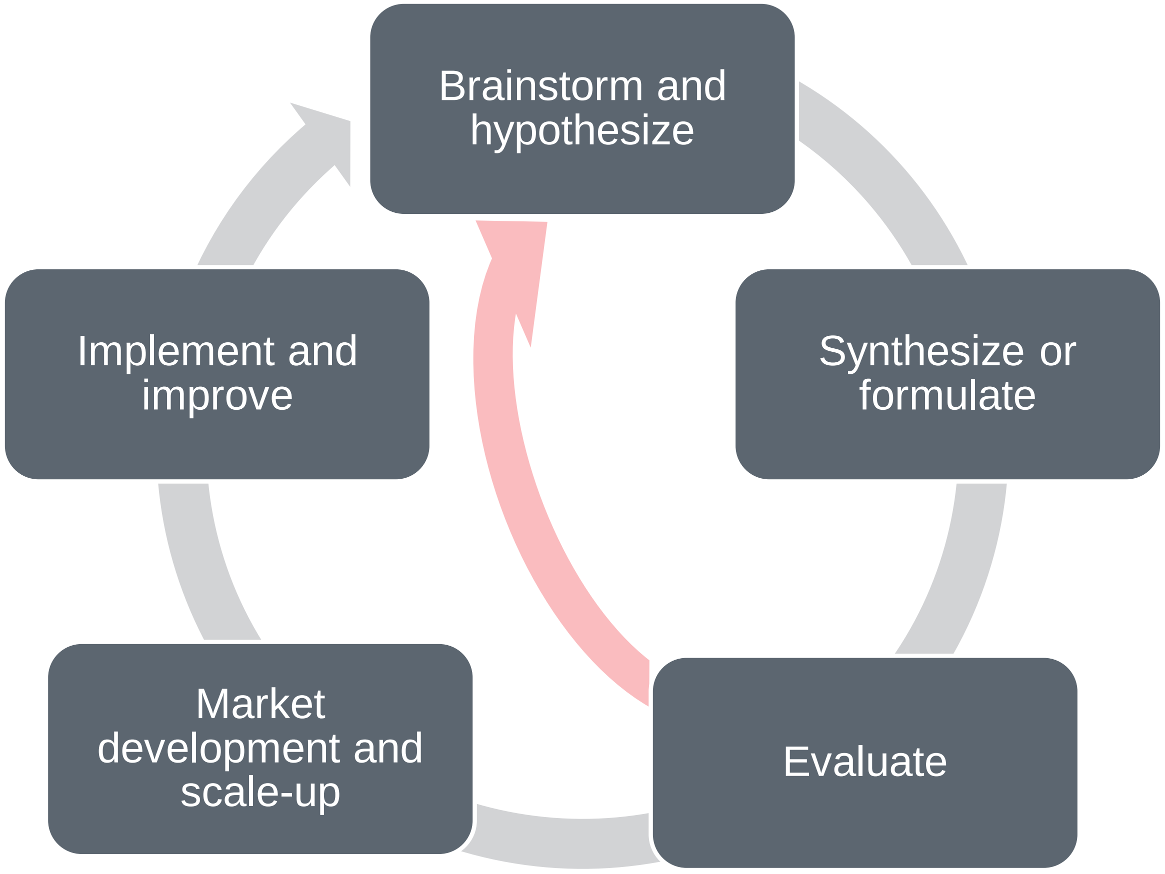
Low-emission catalysts
- Lower odor and VOCs
- React into the foam (non-fugitive)

Expanding chemistry portfolio
- New tools for customers
- New, differentiated molecules



Aldehyde reduction strategies
- Regulatory pressure to reduce aldehydes
- Reduce aldehydes during and after foaming

HFO-stable spray-foam catalysts
- New blowing agents not stable
- Future market growth

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Polyurethane Foam

Macroscopic, microscopic, and atomic levels

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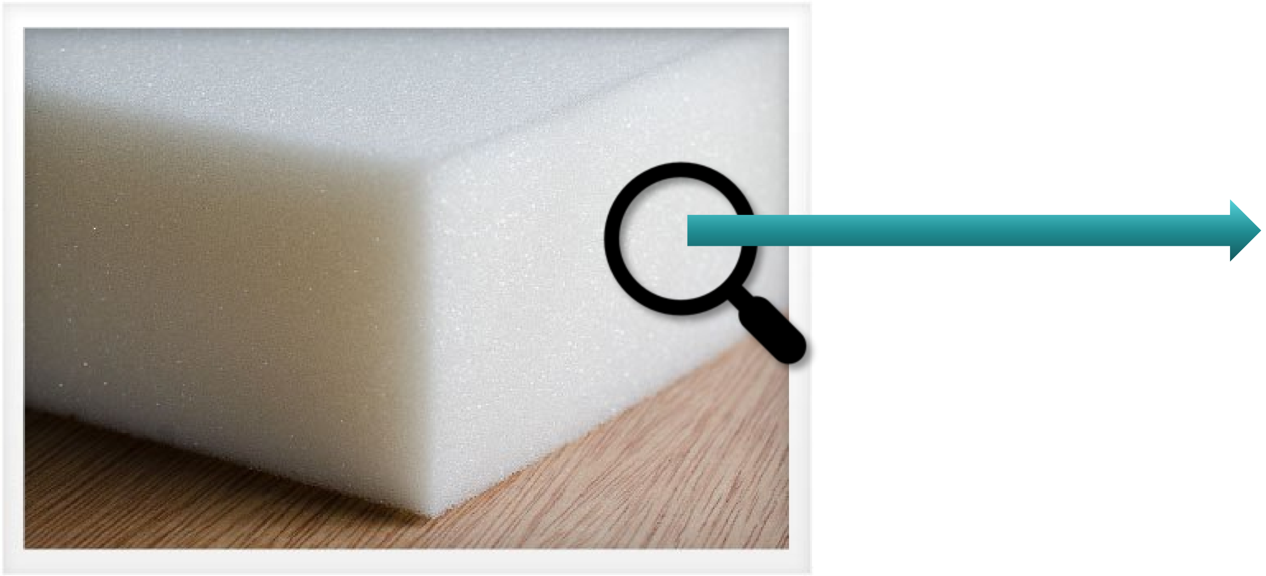

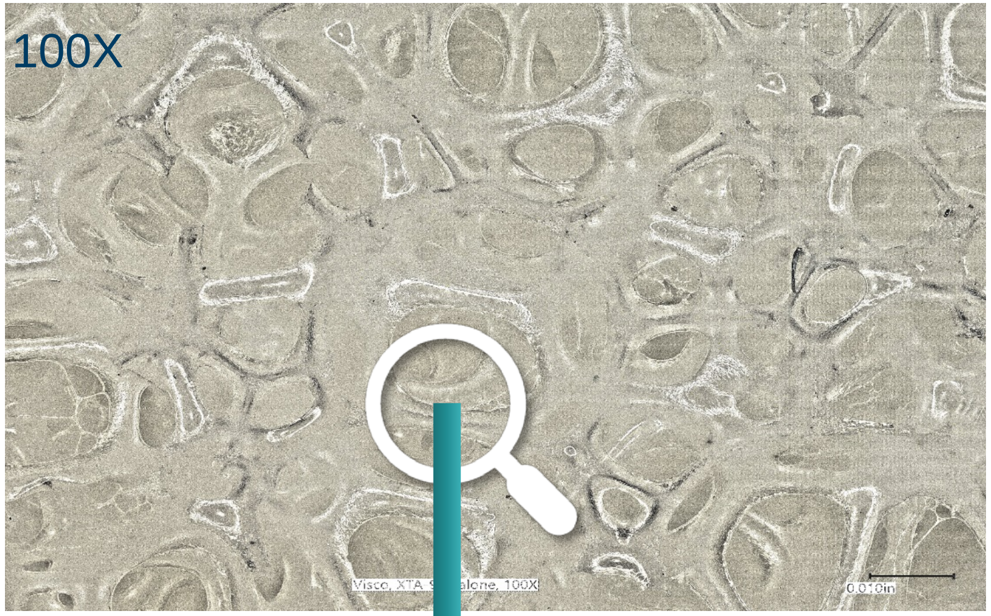

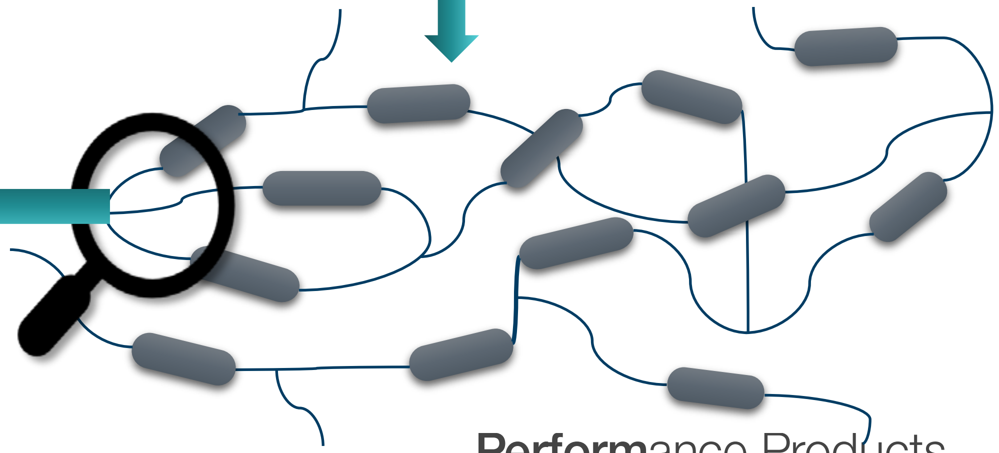

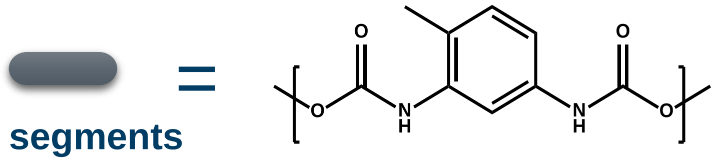

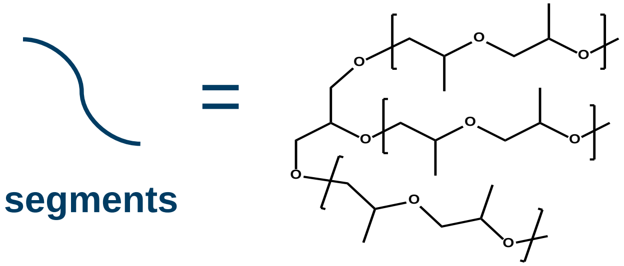

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Polyurethane Foam Chemistry

Foam formation reactions

- Polyurethane foam formation is a balancing act between two reactions
  - Isocyanates reacting with water to produce CO_2 and a urea linkage
    - **"Blowing" reaction**
    - **Generates CO_2 gas that contributes to foaming**
    - **Also builds molecular weight**
  - Isocyanates reacting with polyols to form a polymer
    - **"Gelling" reaction**
    - **Needed to build strength to support rapidly expanding foam**
- These reactions happen in concert with each other
  - Too much blowing results in large splits or blow-holes, resulting in possible foam collapse
  - Too much gelling and the foam will be too closed, resulting in shrinkage and/or foam collapse
- How are these reactions controlled?
  - Catalysts!

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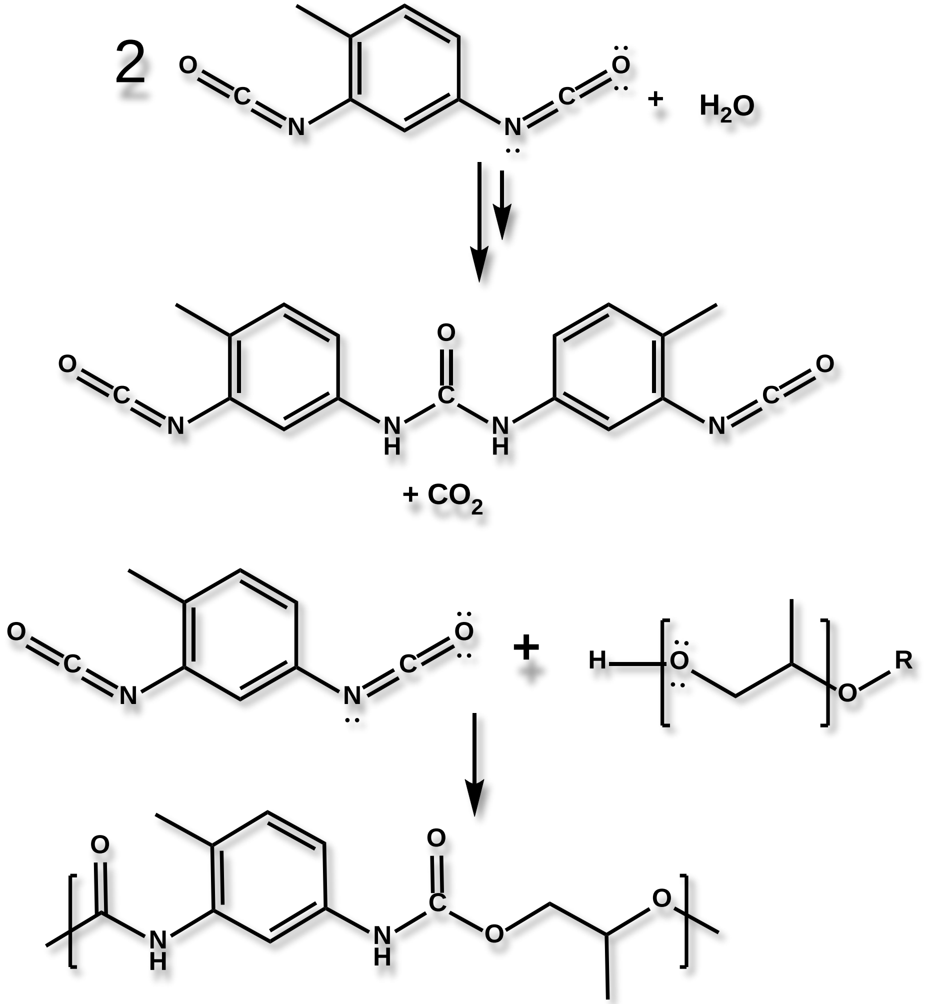

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JEFFCAT® Polyurethane Catalysts

The tuning knobs of the foam formation process

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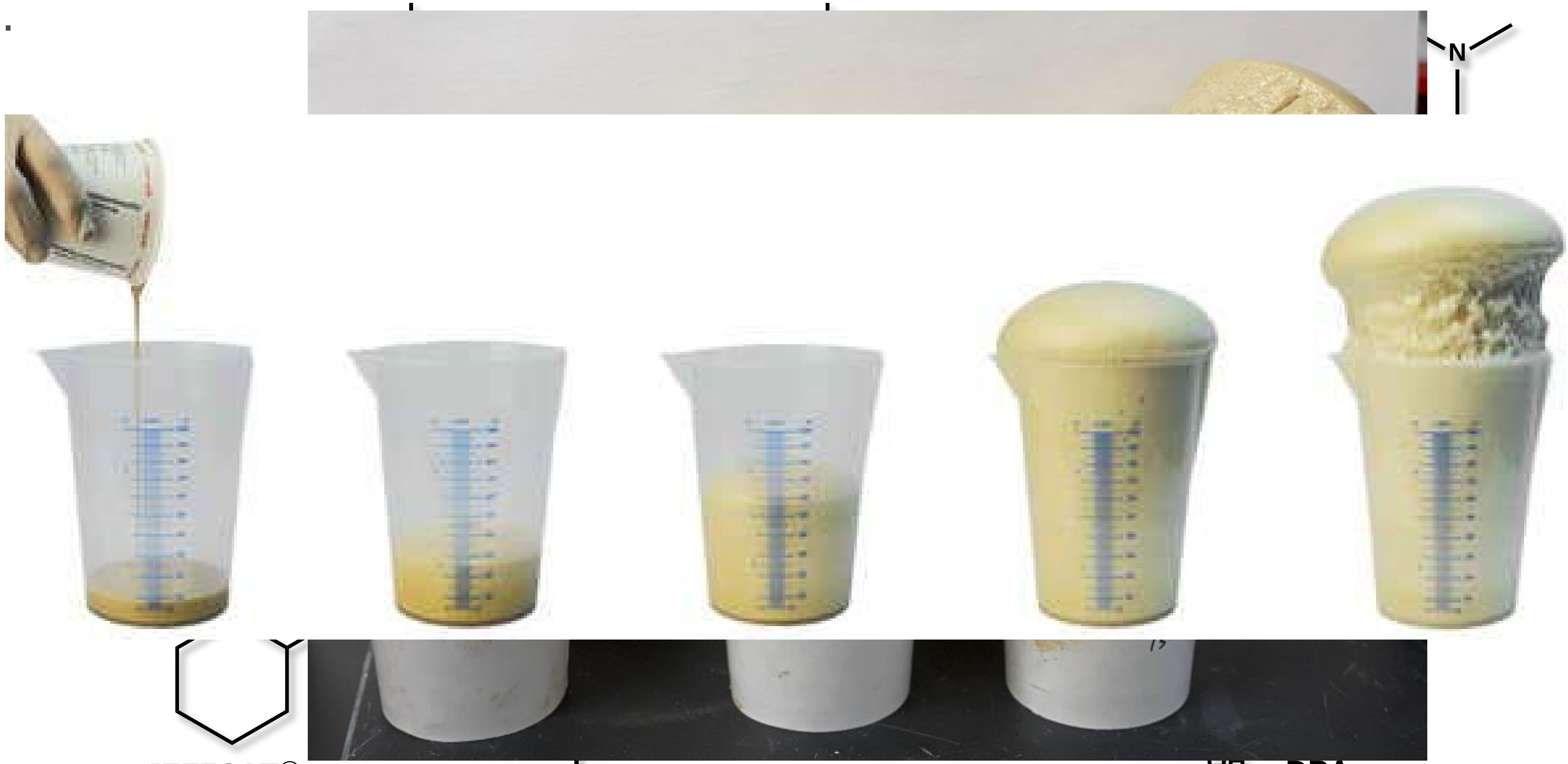
- Why are there so many JEFFCAT® catalysts???
- JEFFCAT® catalysts are a small part of foam formulations but have a drastic effect on foam processing and properties.

- Factors affecting catalyst function
  - Acid blocking
  - Alkalinity
  - Amine equivalent weight
  - Atom arrangement
  - End group
  - Mobility
  - Molecular structure
  - Nucelophilicity
  - Number of active centers
  - Solubility
  - Steric Hindrance
  - Volatility



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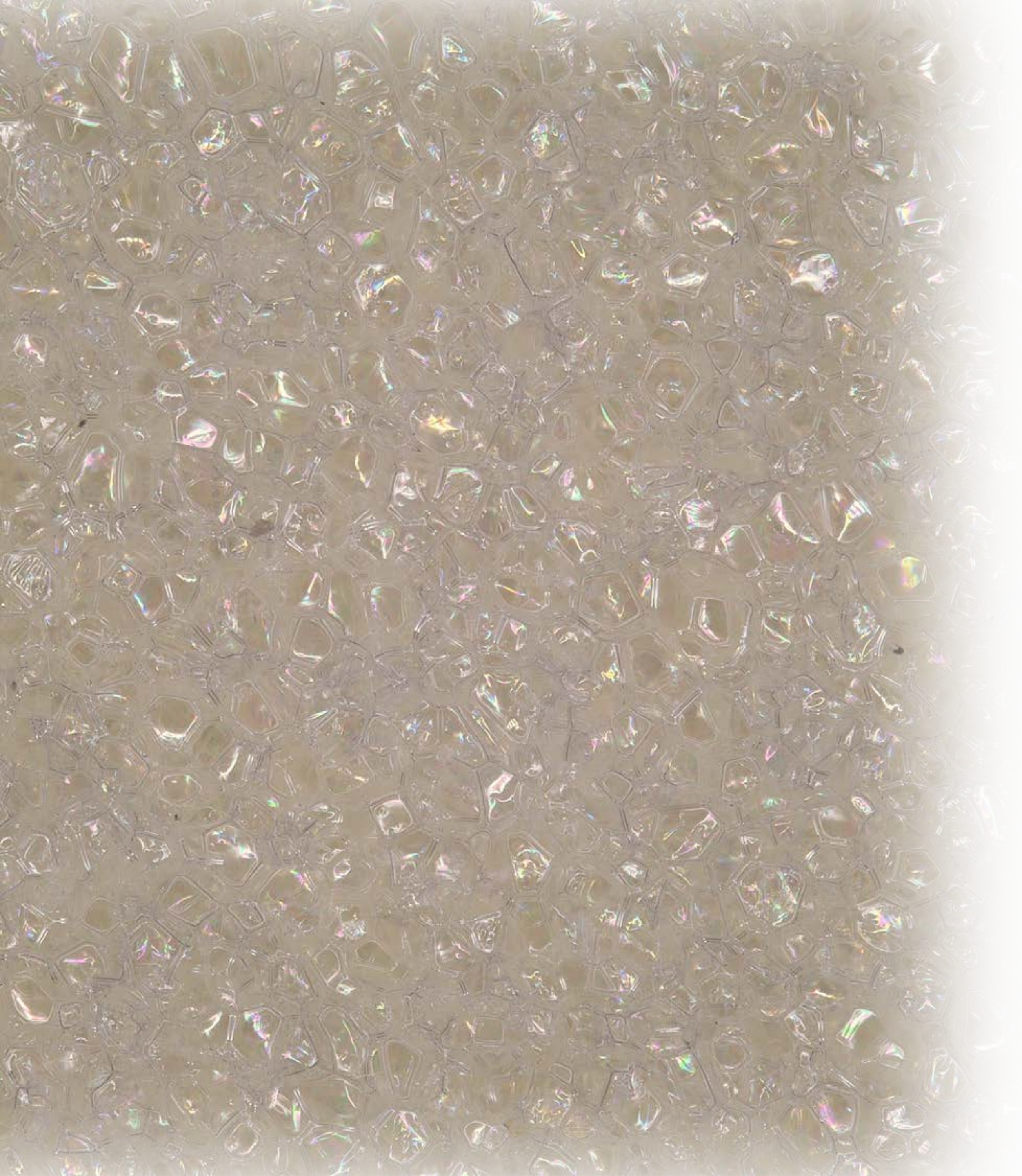

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HFO-Stable Catalyst R&D

Background, Synthesis of New Concepts, and Evaluation Process

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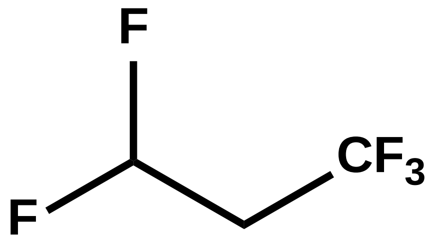
HFO Chemistry in Polyol Resin Blends

Reactivity differences in blowing agents



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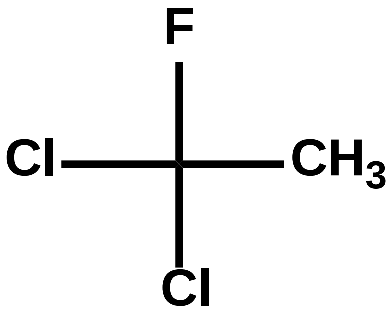

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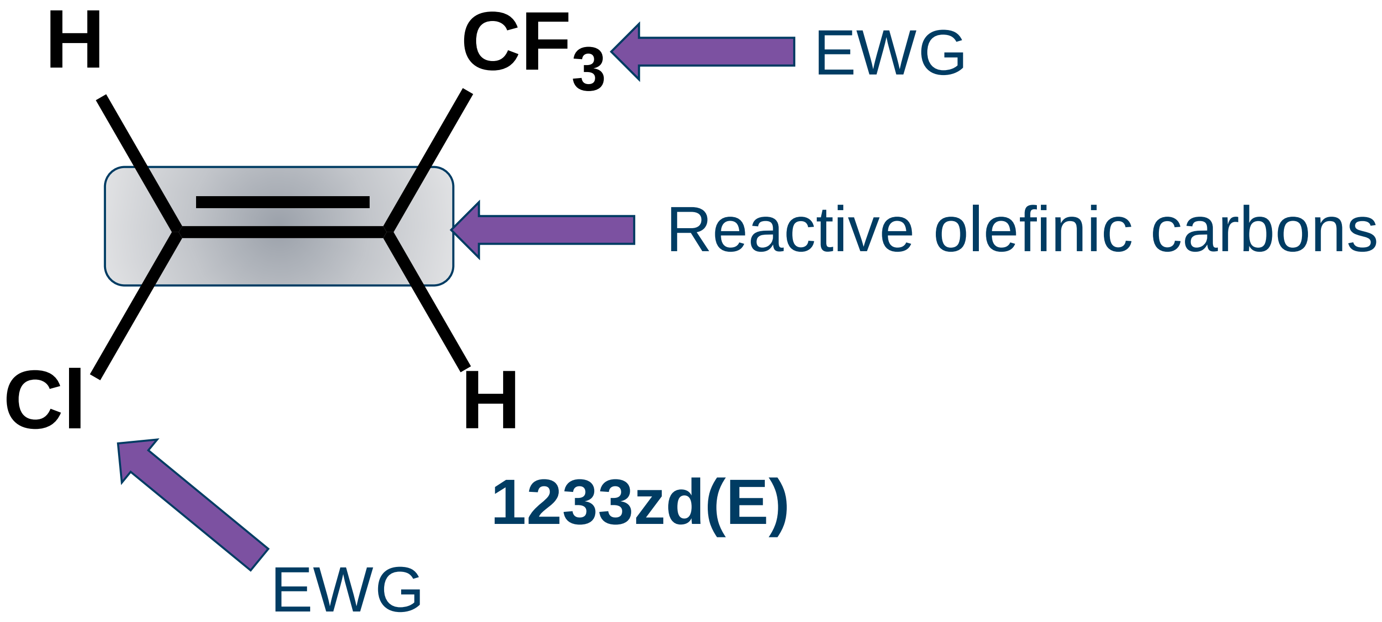
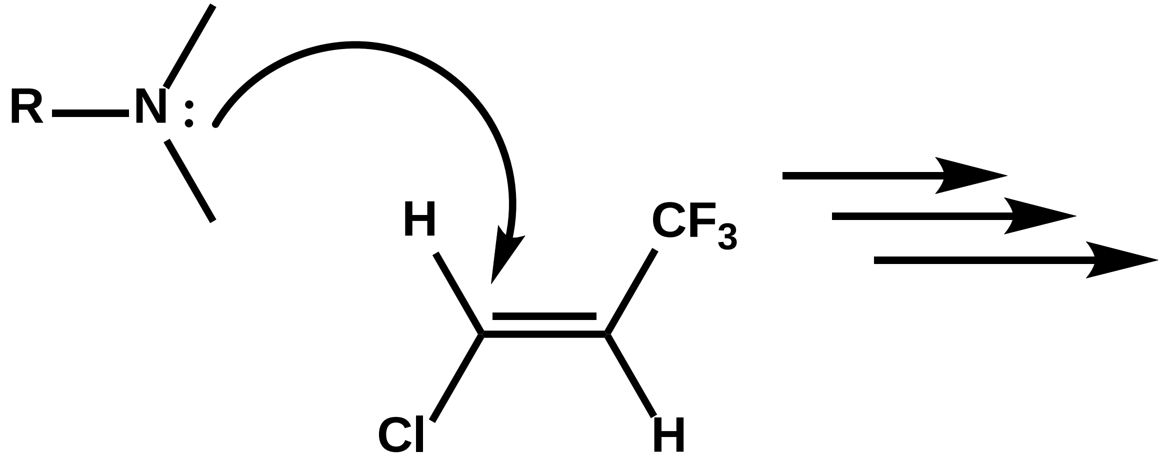


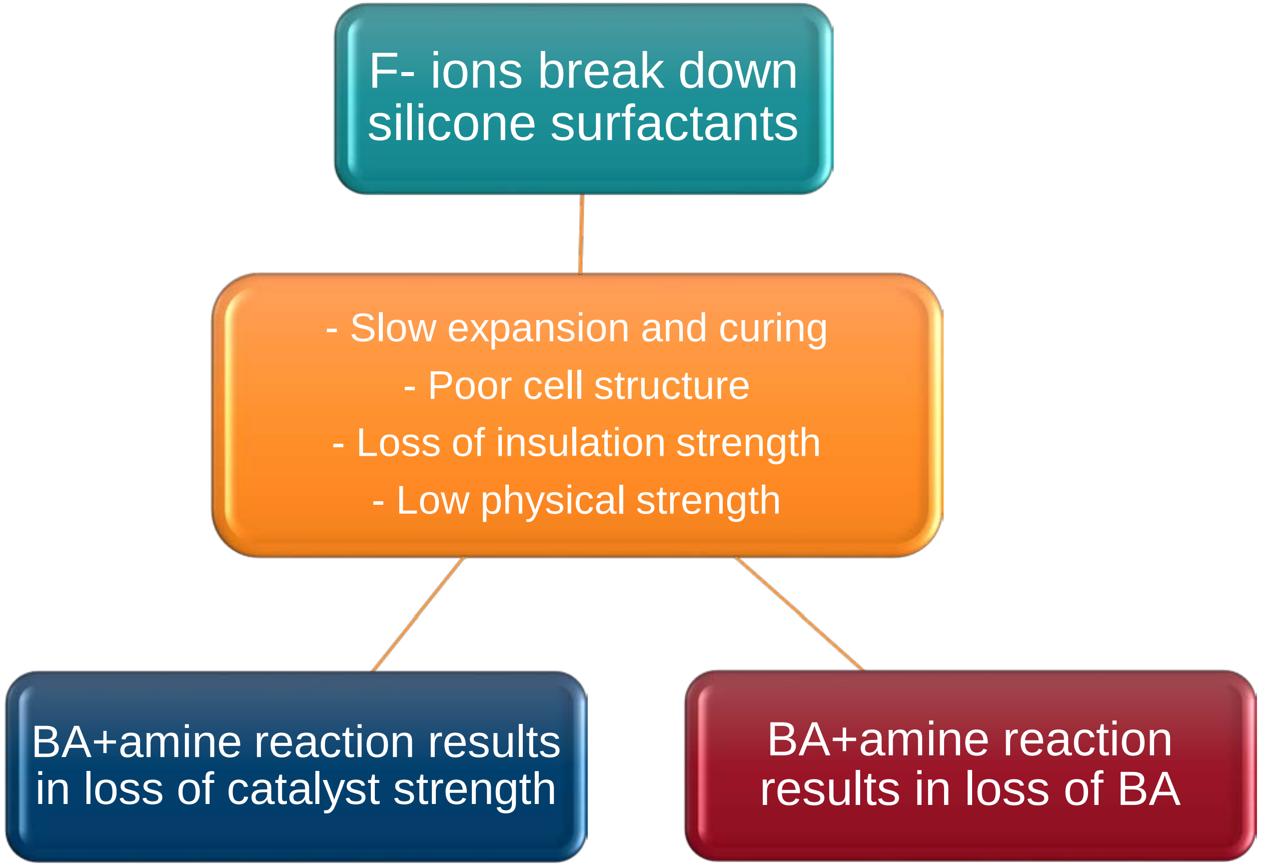
1233zd(E)

- Previous generation blowing agents have halogen electron-withdrawing groups (EWGs) but no olefinic (reactive) moieties, generally resulting in stability
- New low-GWP blowing agents have both, making them unstable nucleophilic species (such as amine catalysts)

HFO Chemistry in Polyol Resin Blends

Amine-promoted degradation



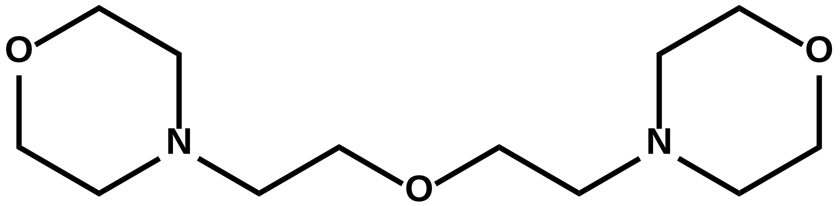


- Traditional amine catalysts contain highly nucleophilic methylamino groups that react with the olefinic bonds in the HFO blowing agents, forming by-products that are neither catalytic or blowing
- Solutions are required which provide fast front-end catalysis and are stable with HFO blowing agents

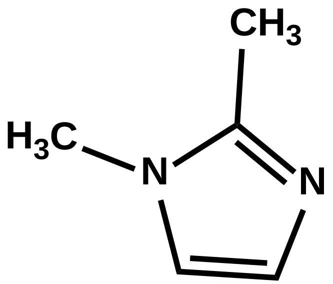
HFO-Stable Catalyst Solutions

Developing a platform of solutions

- Commercial products
  - JEFFCAT® H-1 catalyst – blend of JEFFCAT® DMDEE and 1,2-dimethylimidazole
    - **Very stable blend of gel and blow catalysts, optimized for spray foam**
  - JEFFCAT® DMDEE catalyst
    - **Completely stable with HFO due to reduced activity of amines**
    - **Part of almost every HFO-based catalyst solution**
  - JEFFCAT® H-73 catalyst (in commercialization process)
    - **1,2-dimethylimidazole in EG (offset to known products)**
    - **Gelling compliment to DMDEE, gives boost to adhesion**
    - **Do not over-use or density loss/over-gelling can occur**
- Most formulations blend these products, possibly in conjunction with catalytic polyols and minimal amounts of other products
- Faster catalysts are needed to boost adhesion and cold-weather performance without affecting stability
- Existing chemistry is lacking in performance and diversity - inventive new chemistry required



JEFFCAT® DMDEE



1,2-dimethylimidazole

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HFO Chemistry in Polyol Resin Blends

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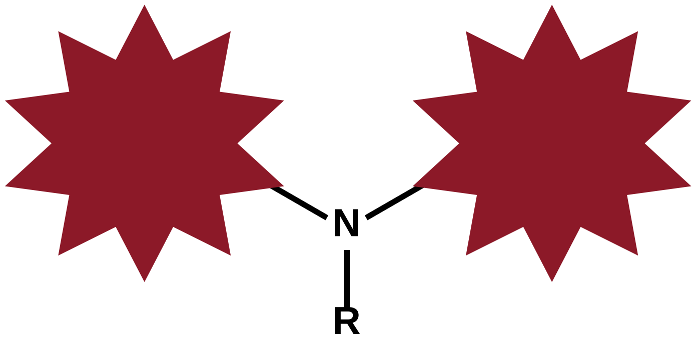
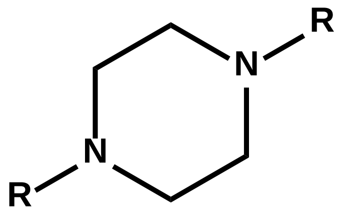
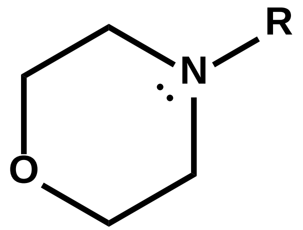
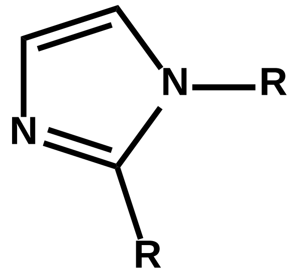
Deactivated amine solutions

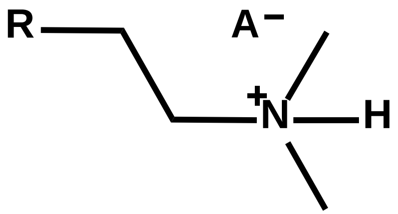
- Known strategies to improve stability – pros and cons
  - Sterically hindered amines
    - **Stability depends on size of groups**
    - **Slower catalysis**
  - Electronically deactivated amines
    - **Very stable**
    - **Sometimes slow**
    - **Limited choices and availability**
  - Acid-blocked amines
    - **Provides some reactivity of parent amine**
    - **Needs front-end thermal kick to unblock acid**
    - **Increase in corrosivity**
- Effective solution will combine strengths and minimize weaknesses
- Catalyst program has synthesized and investigated many options











Evaluation of HFO-stable Candidate Catalysts

Stability, Speed, and Cream

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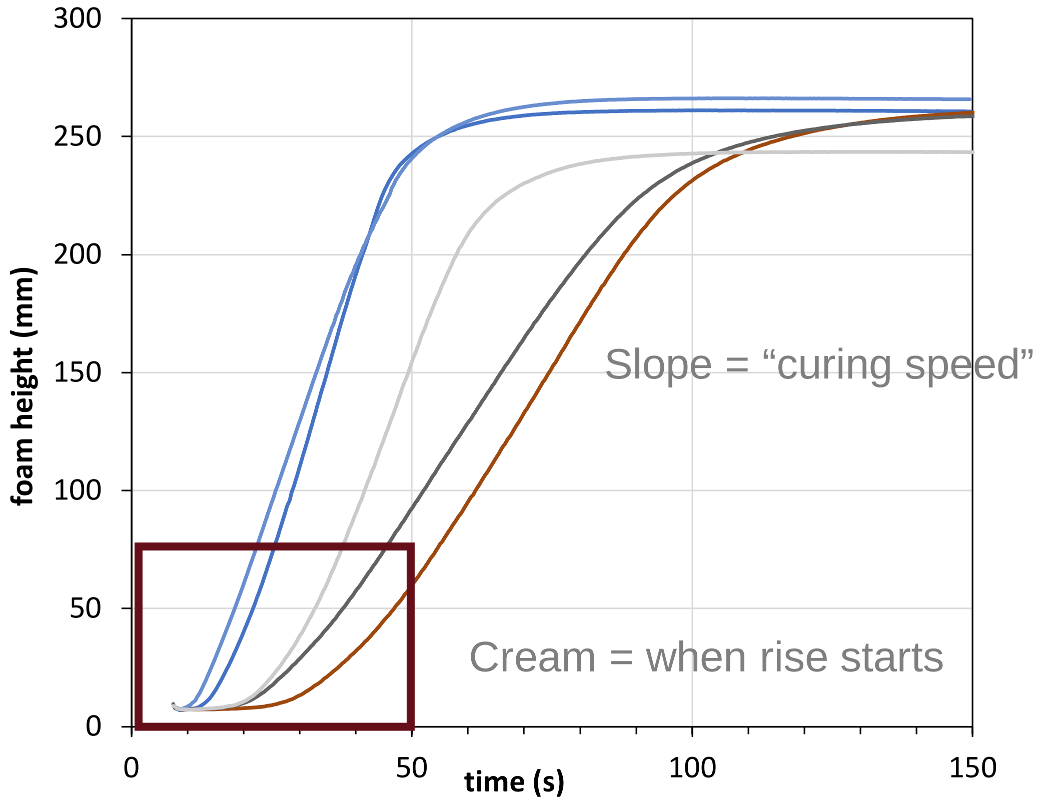
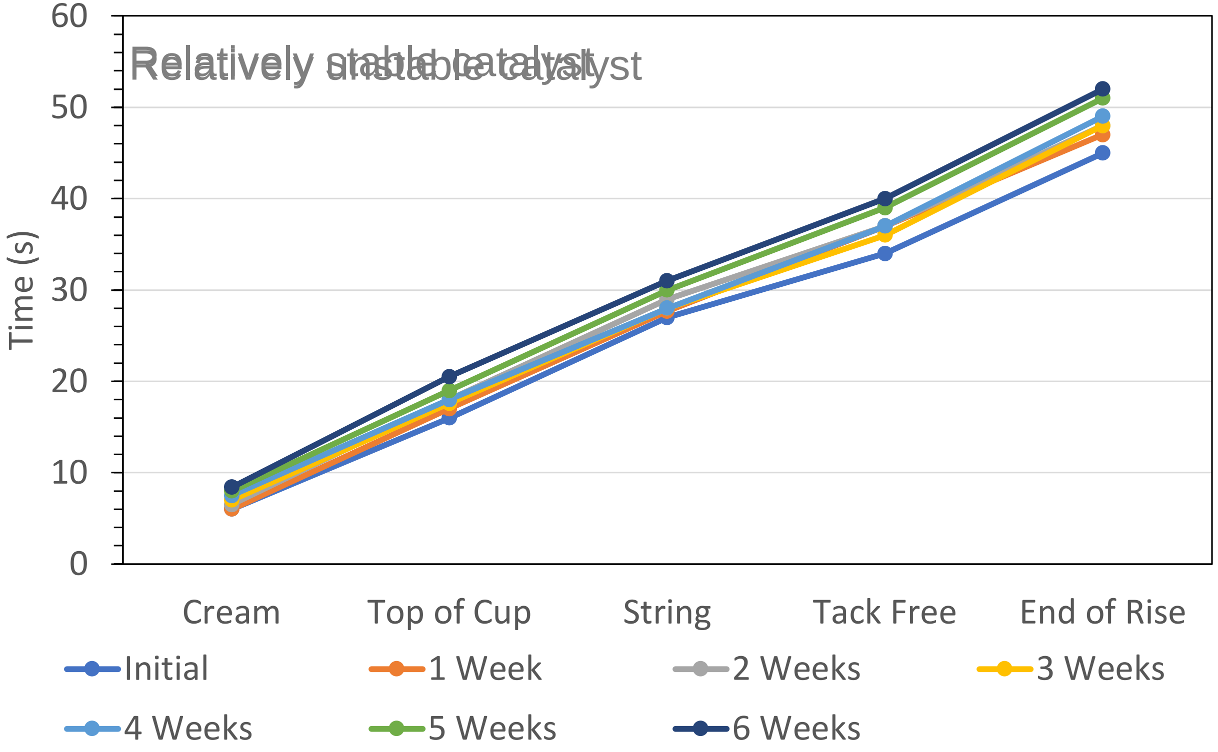
- FOAMAT® used to evaluate speed and cream time; accelerated storage stability testing used to evaluate catalyst compatibility



Rate-of-rise studies use 1% catalyst in polyol

Stability studies use 5% catalyst in B-side, 50ºC storage



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Evaluation of HFO-stable Candidate Catalysts

Stability, Speed, and Cream

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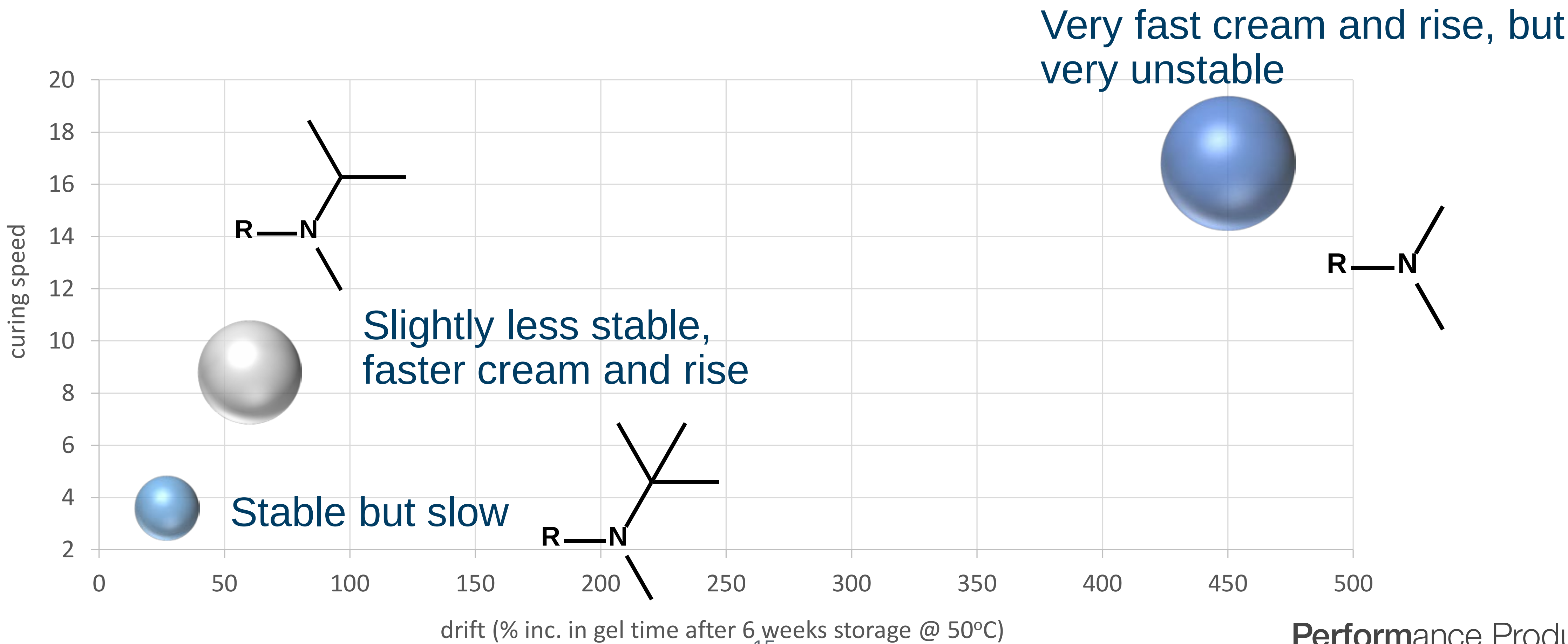
- Combination of all three parameters onto one “bubble” graph



Evaluation of HFO-stable Candidate Catalysts

Stability, Speed, and Cream

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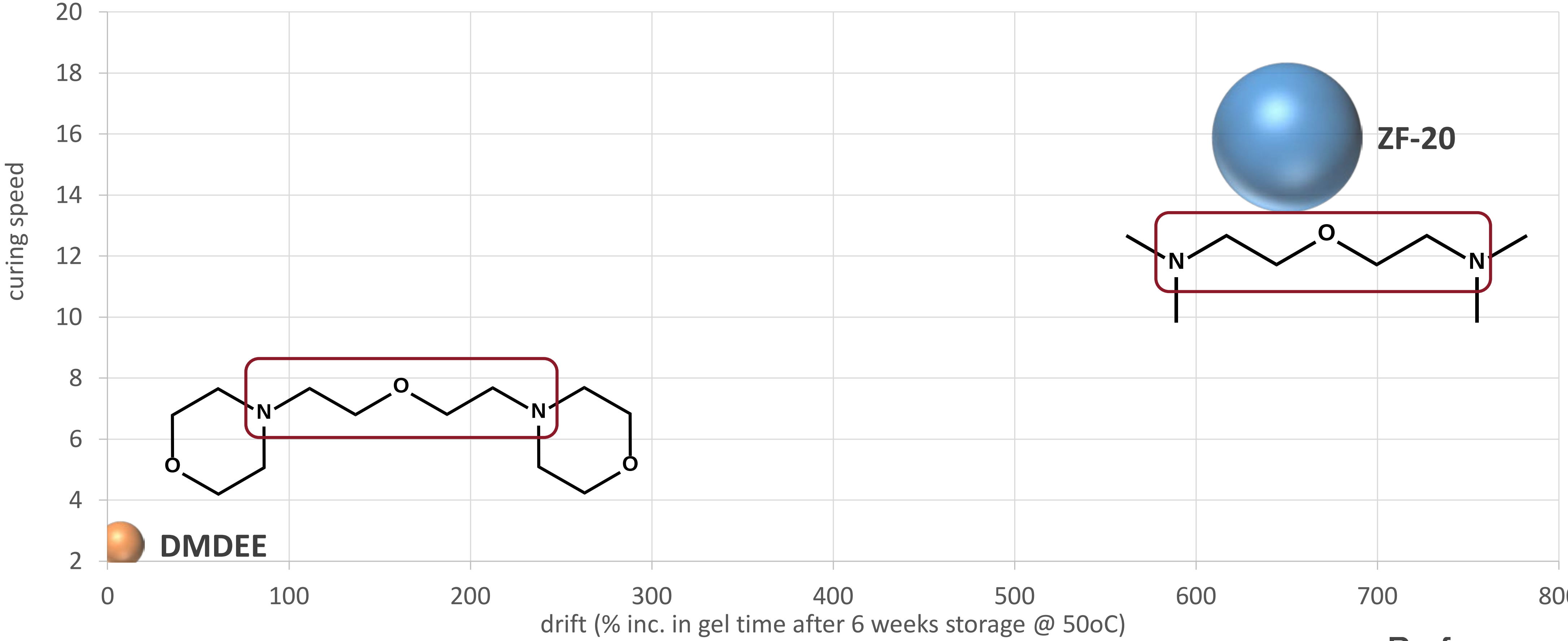
- Electronic effects (morpholine groups add stability but remove speed)



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Evaluation of HFO-stable Candidate Catalysts

Many catalysts, small window of optimal performance

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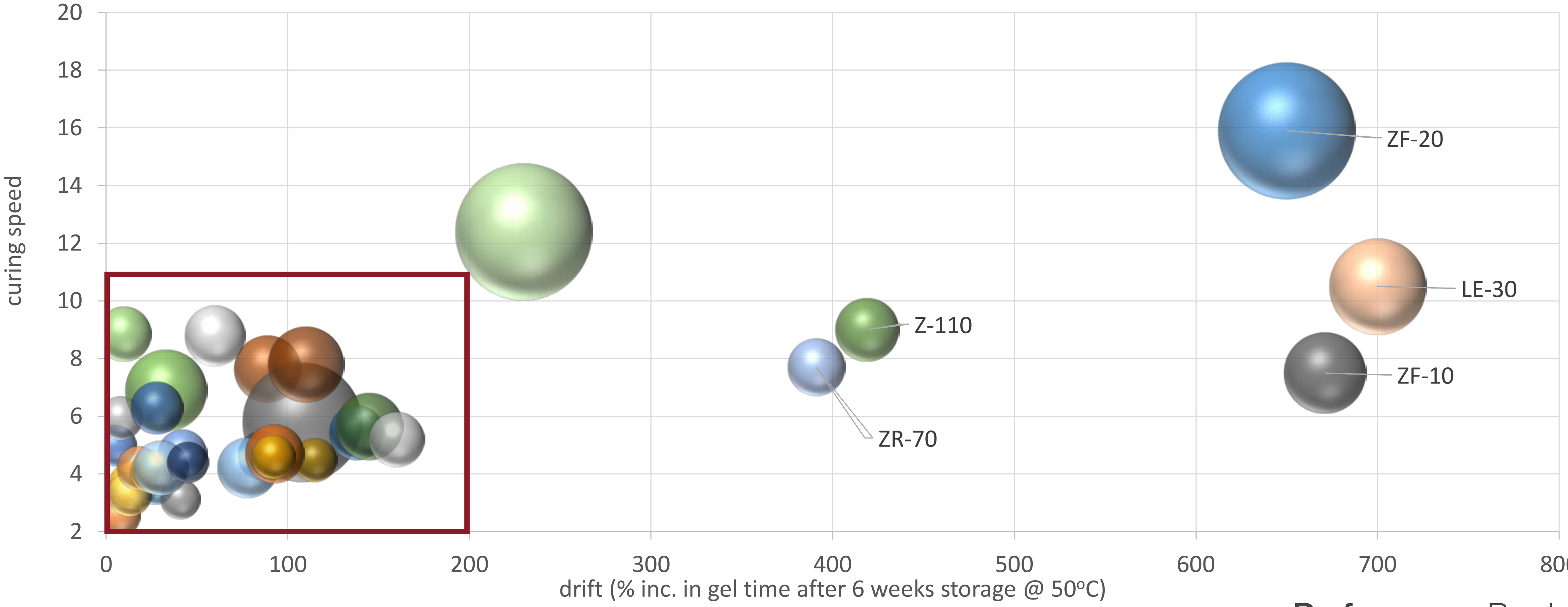
- Traditional catalysts are fast but too unstable



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Evaluation of HFO-stable Candidate Catalysts

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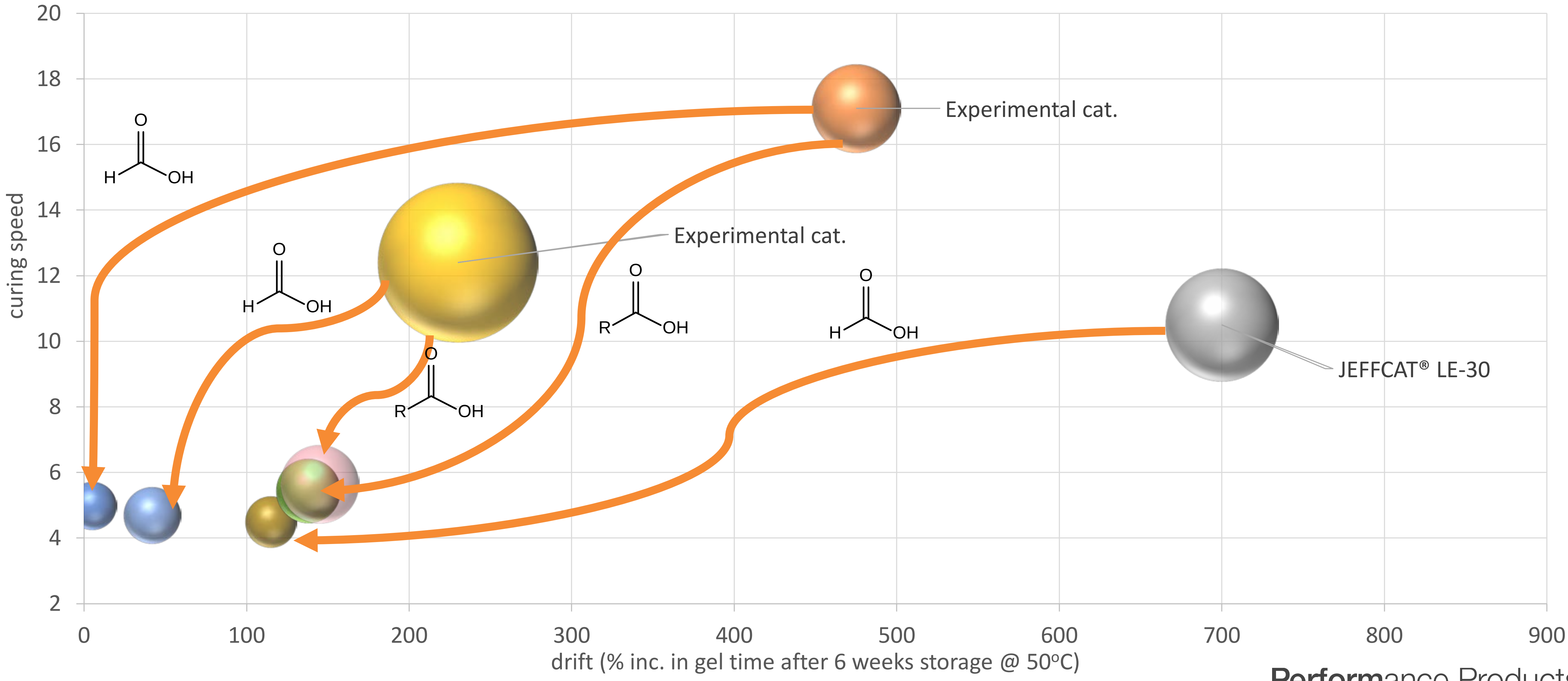
Acid Blocking



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Evaluation of HFO-stable Candidate Catalysts

Acid-blocked products - not adequate solution

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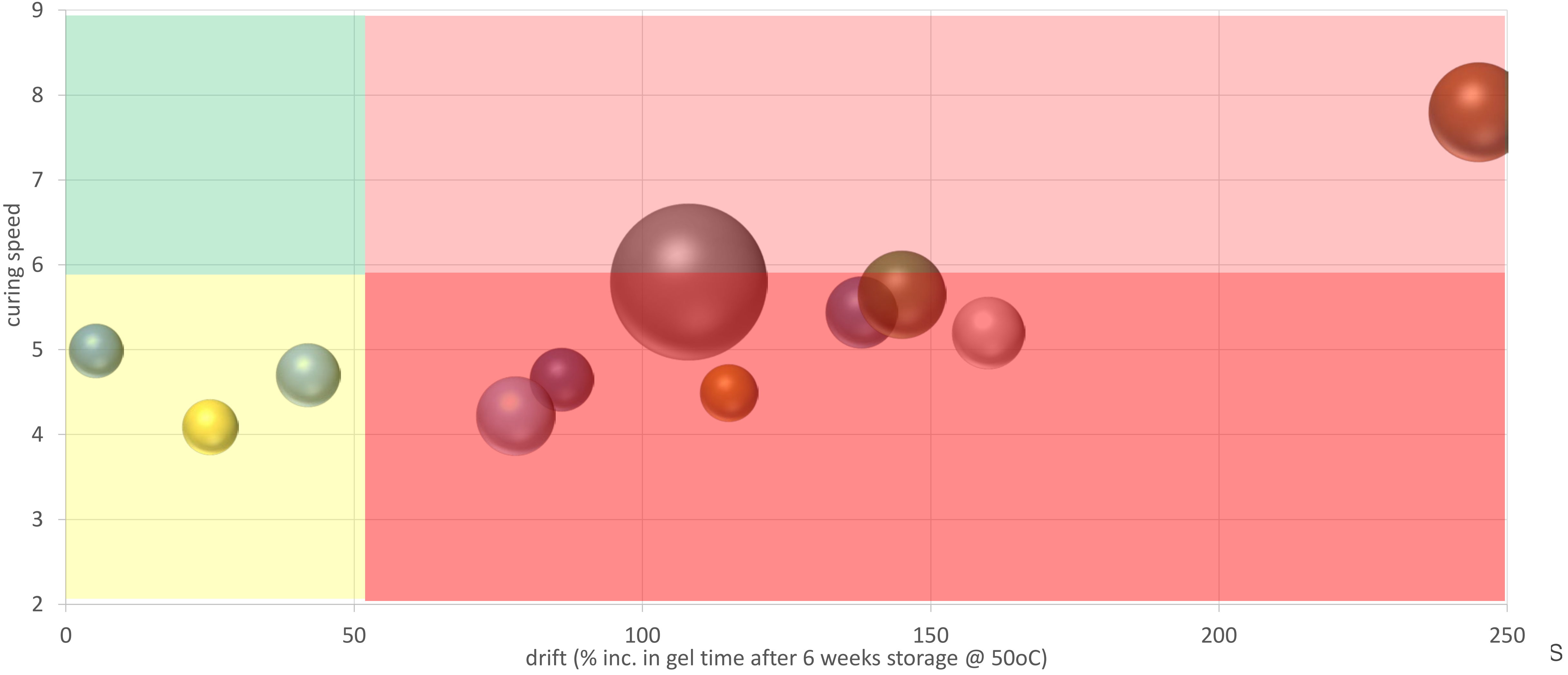

Evaluation of HFO-stable Candidate Catalysts

Molecular modifications towards new products

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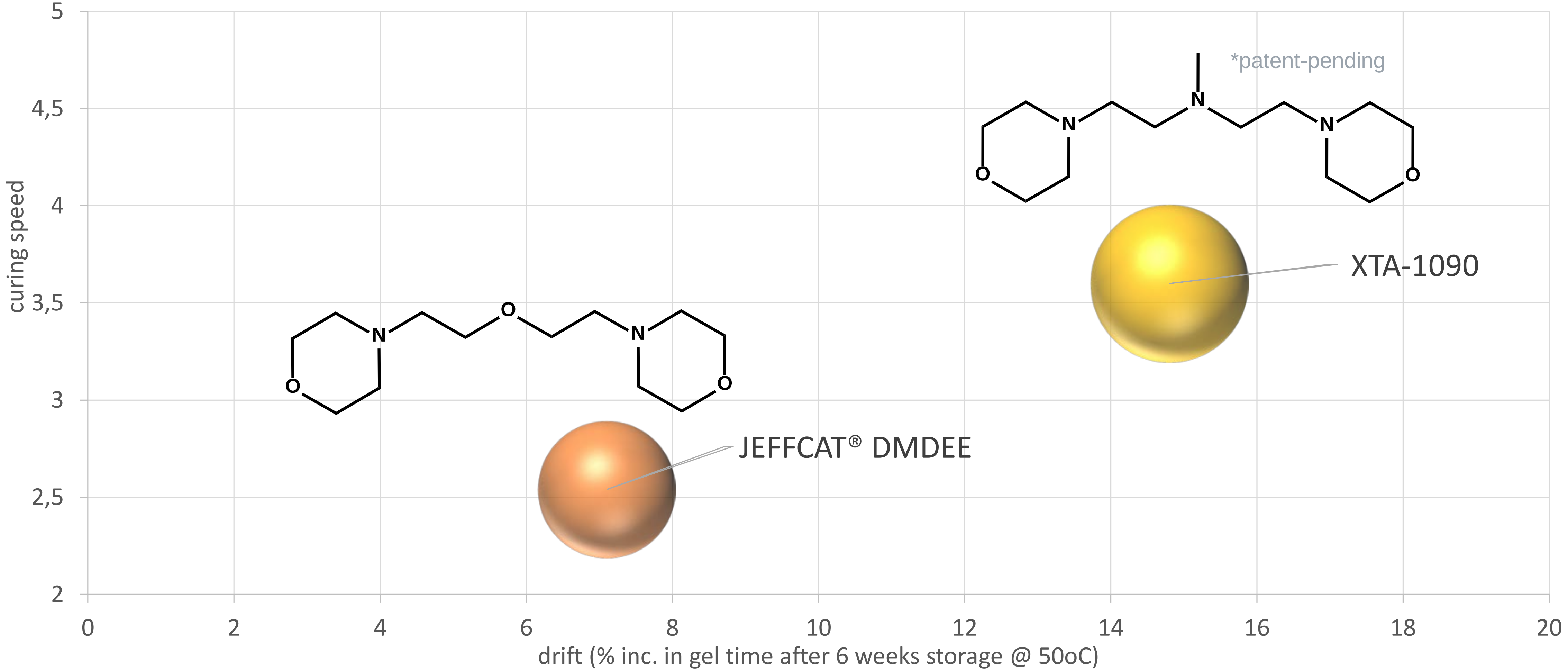

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XTA-1090

Next-generation DMDEE

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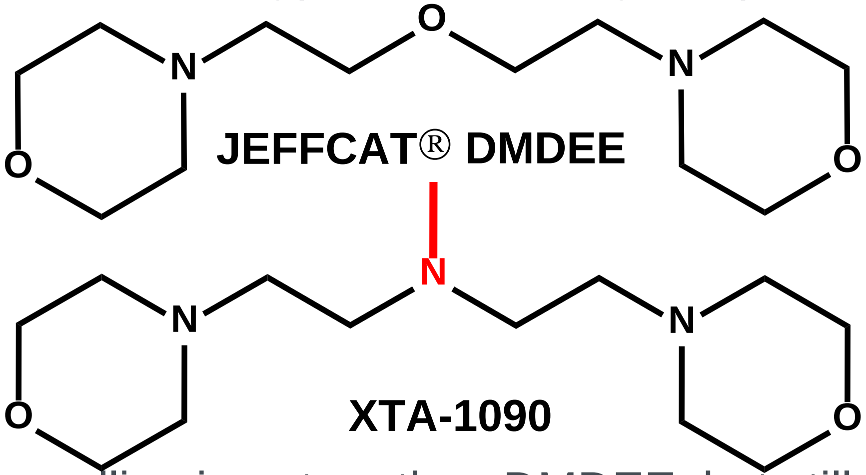
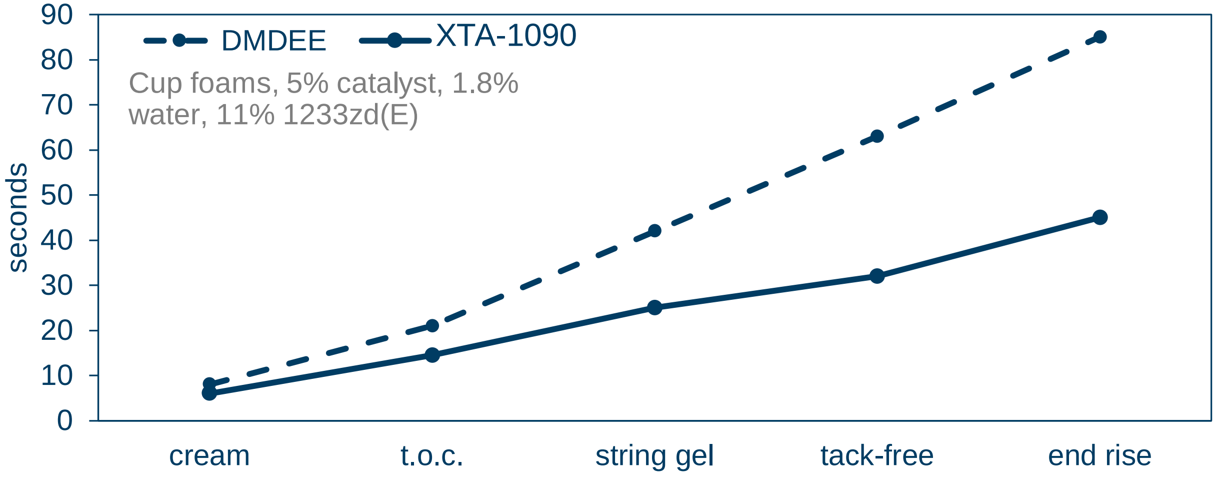
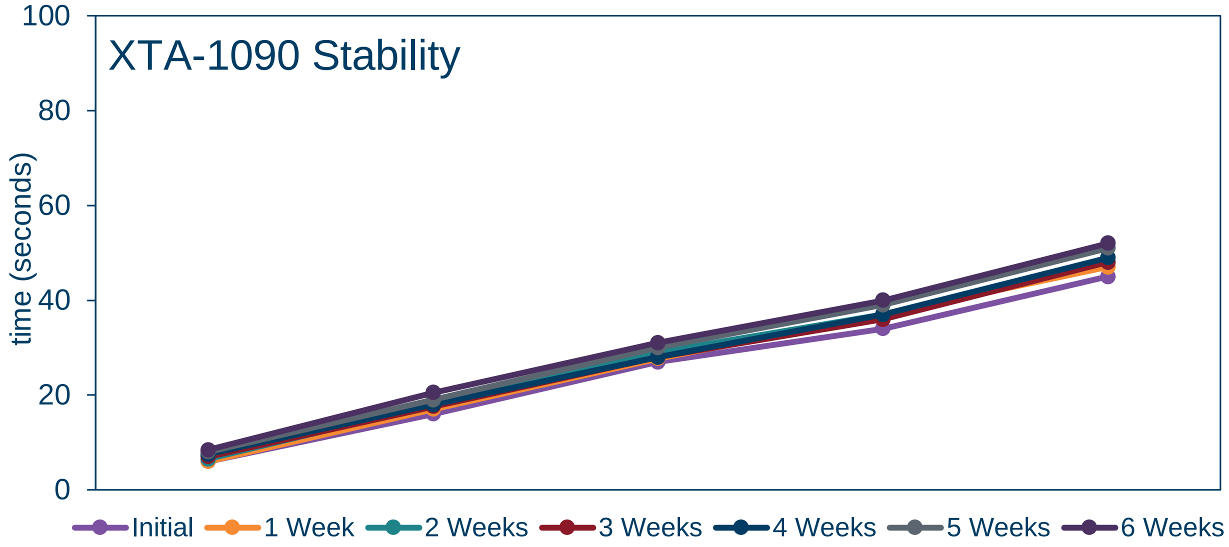
- Faster DMDEE-type, stabilized by morpholine groups



- More gelling in nature than DMDEE, but still leans heavily towards blowing
  - DMDEE gel/blow ratio = 49.4
  - XTA-1090 gel/blow ratio = 14.0
- Faster front-end and 2X faster tack-free time
- Excellent stability with HFO
- Equally low in emission due to high MW
- Stable with Sn/Bi co-catalysts





50ºC storage of B-side

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DMDEE, DMI, and XTA-1090 in Pour-in-Place Foams

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Comparison with DMDEE/DMI blend

System	Cup density (pcf)	Tube density (pcf)	Flow number
4% DMDEE + 0.5% DMI)	1.6877	2.7013	1.60
3.0% XTA-1090	1.6684	2.6587	1.59

- HFO-blown appliance foams need good flowability and good adhesion to optimize k-factor, and must use stable catalysts
- JEFFCAT® DMDEE and H-73 can be blended to provide this combination of properties
- Exploring the use of XTA-1090 as a replacement for this combination
  - One catalyst instead of two
  - DMI is expensive
  - Flow test shows equivalent flow at lower overall catalyst usage
  - Looking for more advanced PiP formulators to give feedback on this material as a catalyst for HFO pour-in-place systems

*for the flow test, gel time of the control is measured and matched with the required amount of XTA-1090. Cup density and tube density are then taken for each, and the ratio gives the flow number

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HFO-Stable Catalysts for Spray Foam

Promising experimental

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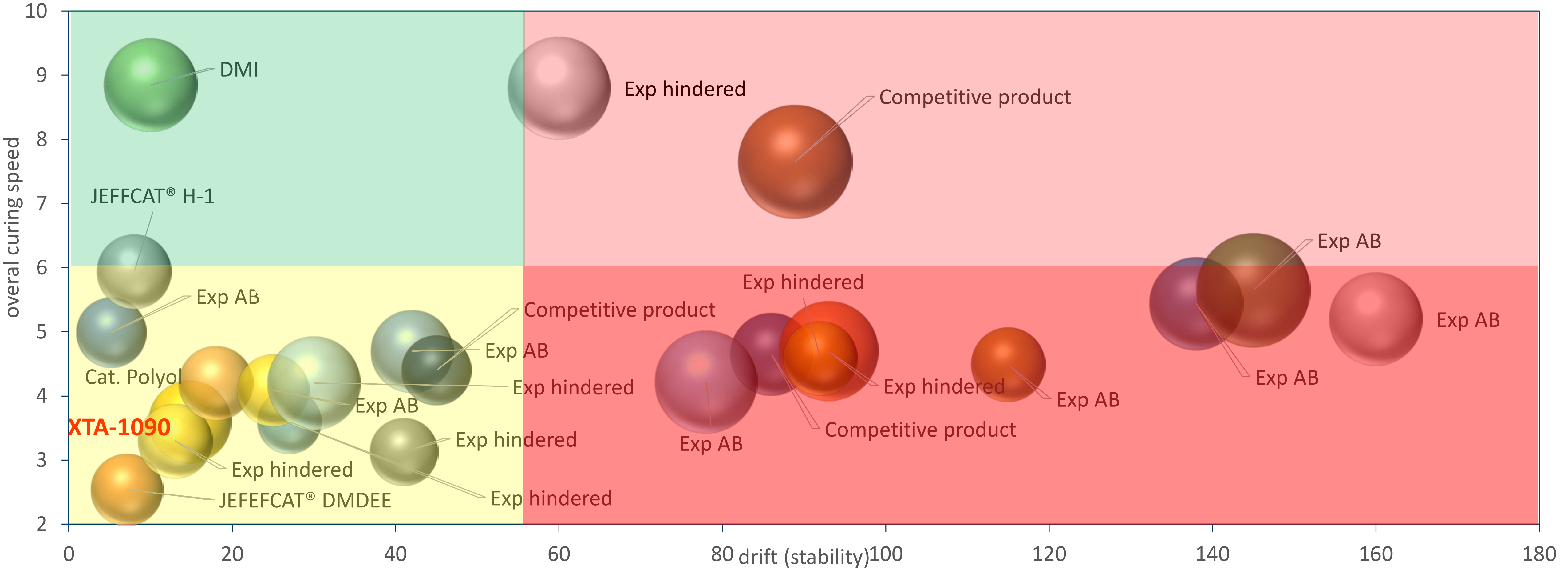
- Stable, fast amine, with no acid blocking is ideal situation



Conclusions, Path Forward

New catalysts on the way to compliment industry standards and add to toolbox

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- Formulation with HFO blowing agents in challenging
  - Smaller toolbox of catalysts to work with
- JEFFCAT® DMDEE, JEFFCAT® H-73 and JEFFCAT® H-1 catalysts are existing tools to help create stable HFO formulations
- Formulators need more tools in their kits to create effective HFO systems
  - New tools = new molecules
    - **Long development timeline, but effective solutions possible**
- Must consider the optimal combination of stability and speed in HFO formulations
- Working on multiple new products to help with this market

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