

Additives and Catalysts VOC Low-Emission Automotive Polyurethanes

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A photograph of a young child with dark hair, smiling and resting their chin on their arms, which are crossed over the top of a car seat. The background is a blurred view of a car's interior.

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

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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



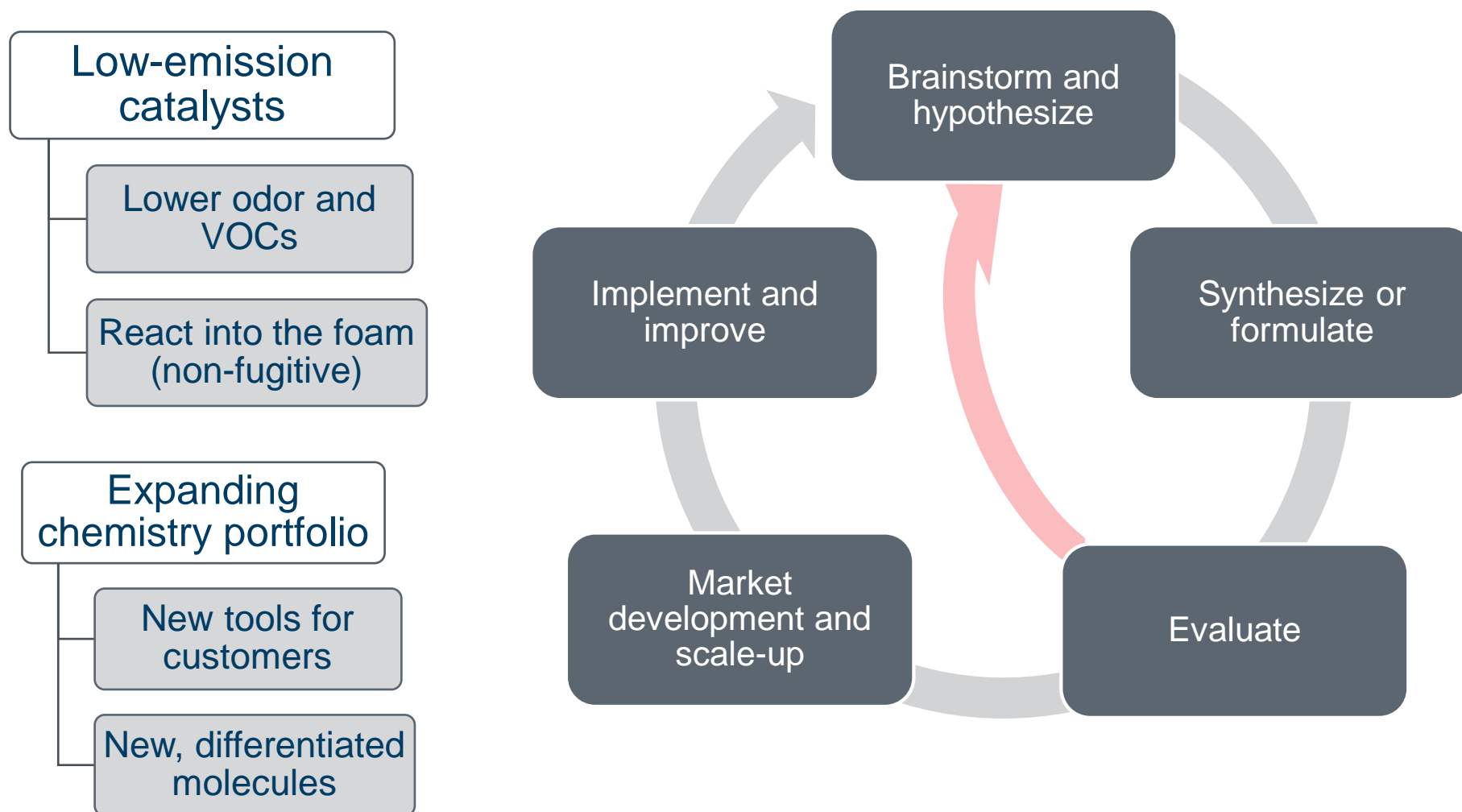
GAS TREATING
Gas Processing Chemicals
& Licensing



PU ADDITIVES
Amine Catalyst Technology

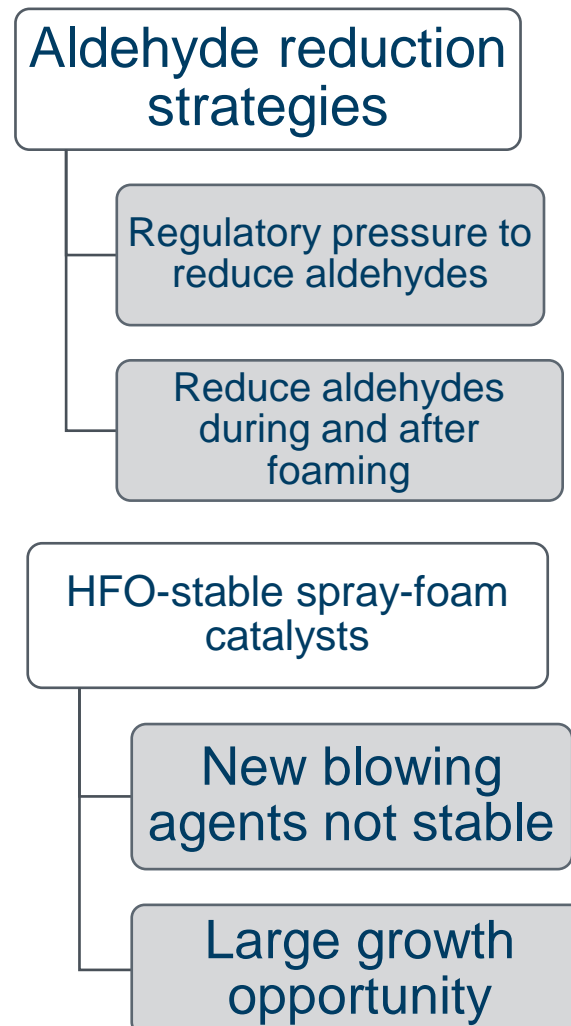
R&D Approach – How we do it

Strategy and areas of focus



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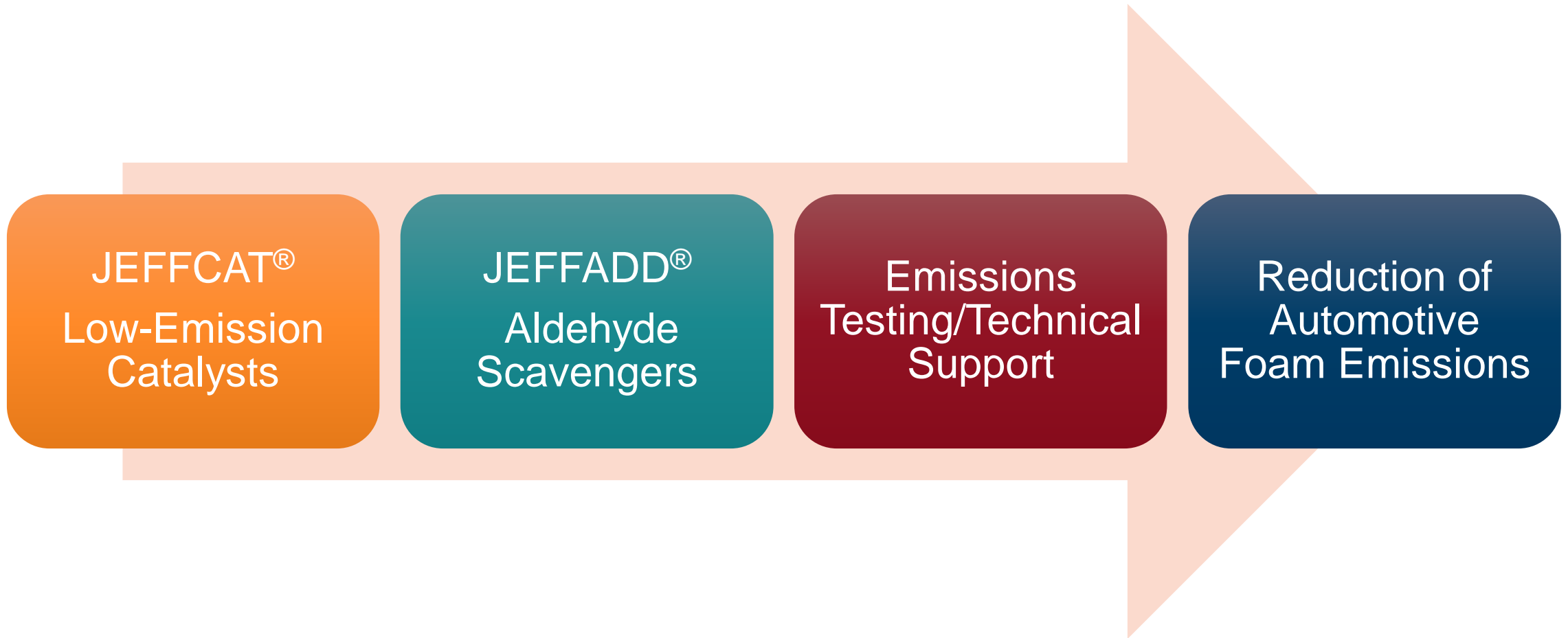
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VOC Reduction Strategies

HPP Polyurethane Additives: A portfolio of innovative solutions



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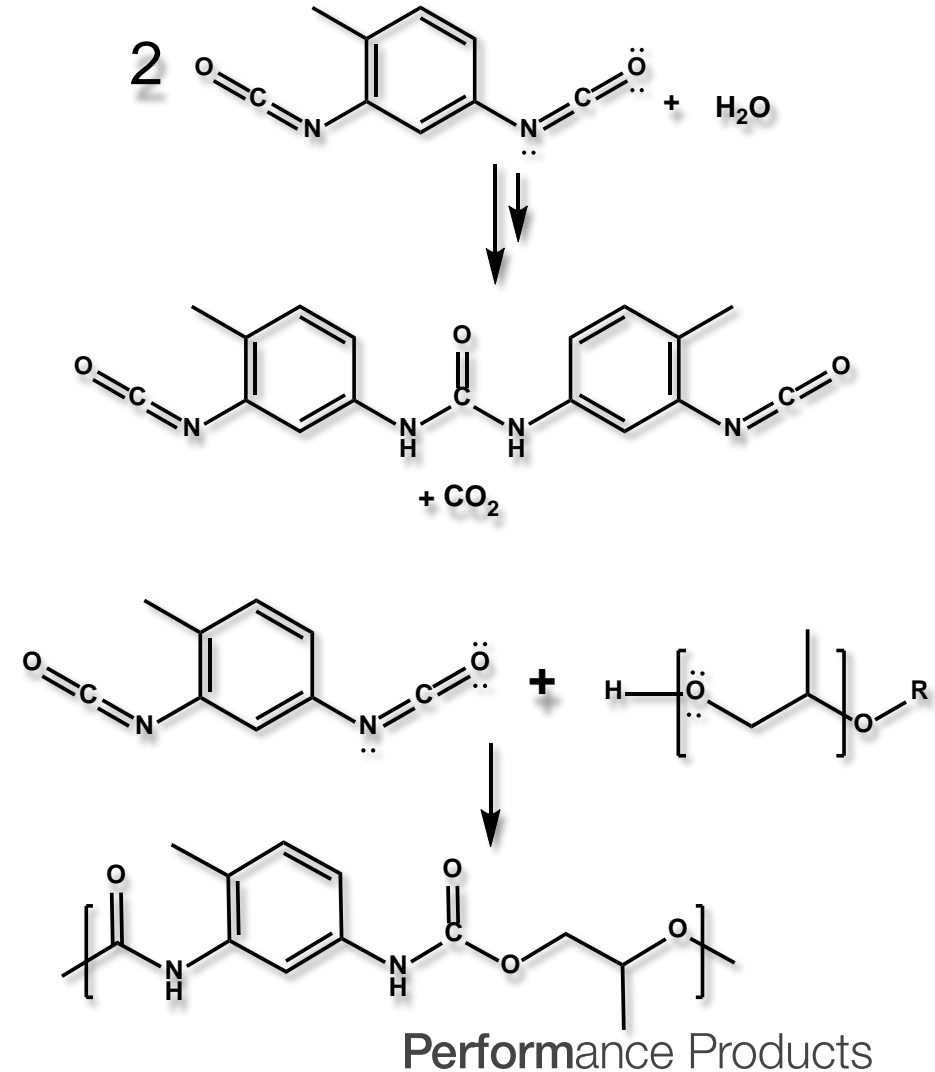
Polyurethane Foam Chemistry

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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JEFFCAT® Catalyst Portfolio

Blow / Gel balancing

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Newer Catalysts

JEFFCAT® H-73

JEFFCAT® LE-30

JEFFCAT® LE-220

JEFFCAT® LE-225

JEFFCAT® LE-340

Delayed-Action Catalysts

JEFFCAT® LED-103

JEFFCAT® LED-104

JEFFCAT® LED-204

JEFFCAT® ZF-54

Sn, Pb, & Hg salts

JEFFCAT® TD-33A

JEFFCAT® Z-80

JEFFCAT® DMCHA

JEFFCAT® ZR-40

Gelling

JEFFCAT® ZR-50

JEFFCAT® Z-130

JEFFCAT® DPA

JEFFCAT® DMEA

JEFFCAT® Z-110

JEFFCAT® ZR-70

JEFFCAT® PMDETA

JEFFCAT® ZF-10

JEFFCAT® LE-30

JEFFCAT® ZF-20

JEFFCAT® DMDEE

Formulated Catalyst Blends

JEFFCAT® H-1

JEFFCAT® LE-310

JEFFCAT® LE-355

JEFFCAT® Z-131

JEFFCAT® ZF-53

Back-End Cure Catalysts

JEFFCAT® TR-52

JEFFCAT® TR-90

Blowing

*blue = non-reactive/emissive

*green = reactive/non-emissive

*yellow = only low-emission under certain test conditions

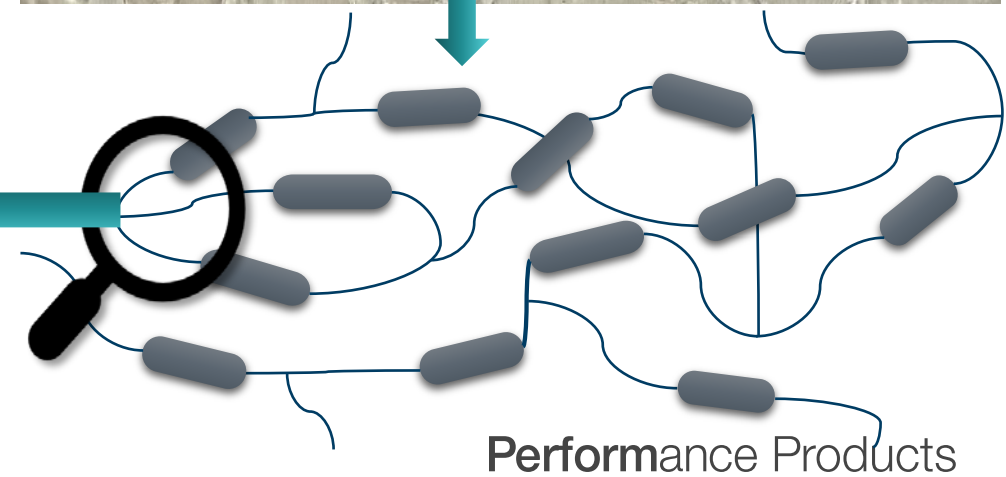
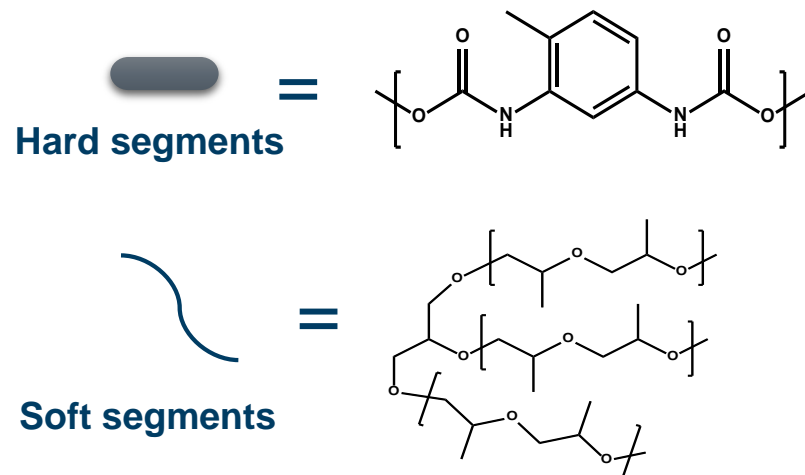
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Polyurethane Foam

Macroscopic, microscopic, and atomic levels

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JEFFCAT® Polyurethane Catalysts

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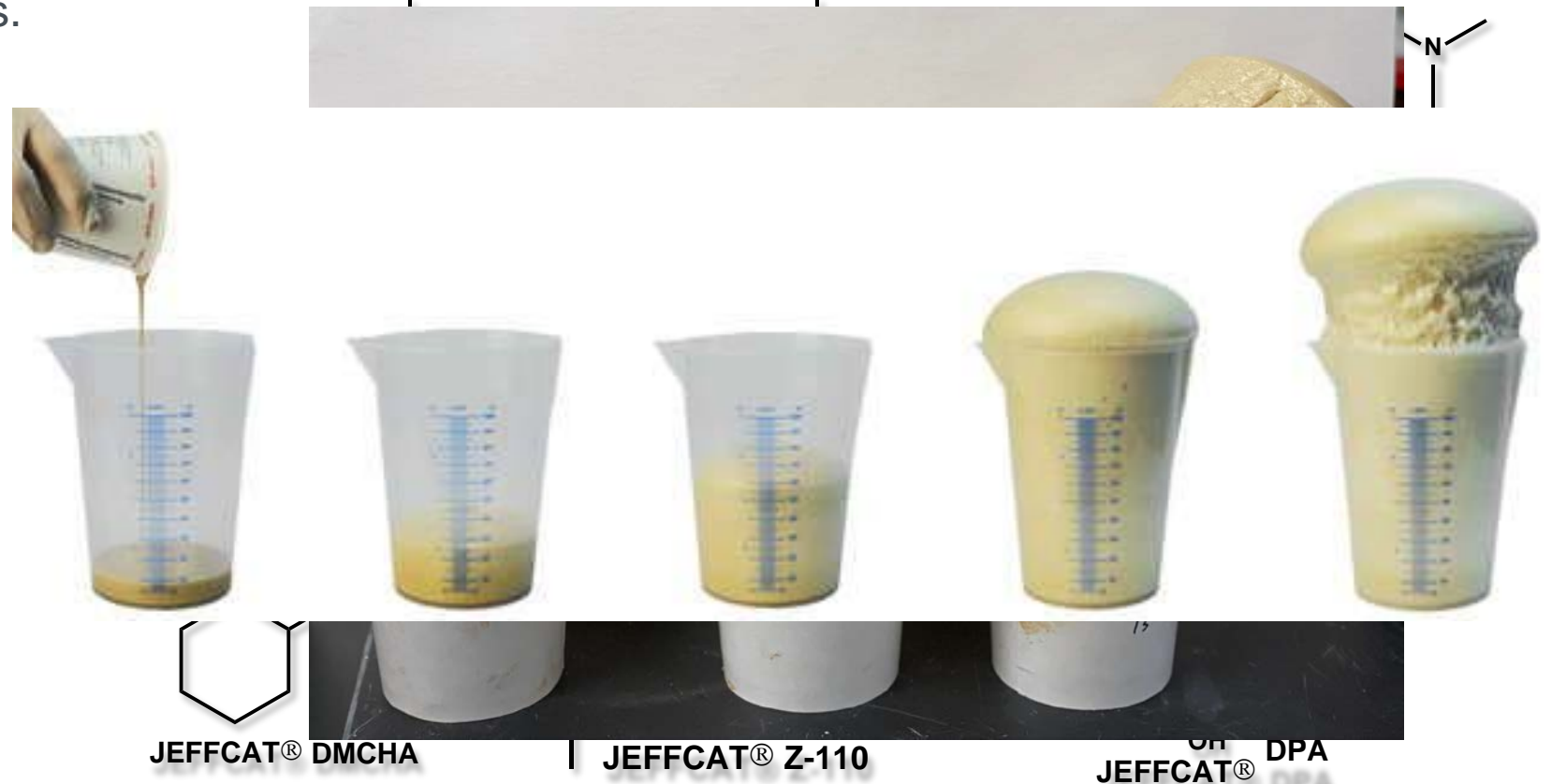
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The tuning knobs of the foam formation process

- 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
- Nucleophilicity
- Number of active centers
- Solubility
- Steric Hindrance
- Volatility



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PU Foam Emissions

Background and Solutions

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Polyurethane Foam Formulations

Typical components in flexible foams and emissive considerations



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Component	Parts	Function
Isocyanate (TDI or MDI)	30 - 50	Reacts (A-side)
Base polyol	80 - 100	Reacts, controls physical properties
Secondary polyol	0 - 30	Addnl. physical properties
Silicone surfactant	0.5 - 1.5	Stabilizes foam and controls cell size
Tin catalyst	0.0 - 0.8	Promotes gelling reaction, synergy with amines
JEFFCAT® amine catalysts	0.5 – 2.0	Blowing and gelling reactions, synergy with tin
Auxiliary blowing agent	0 - 7	Density control, cooling, softness
Water	2 - 5	Blowing, urea reaction
Other additives	0 - 5	chain extenders, flame retardants, pigments, fillers

- **Formulations vary greatly depending on the specific type of foam, the machinery used, the desired physical properties, and the manufacturer's experience**

- **Flexible foam uses**

- Automotive
 - **Seats, arm rests, head rests, chair backs, etc.**
 - **Can be molded or slab foam**
- Furniture and Bedding
 - **Mattresses, sofa cushions, etc.**
 - **Standard or viscoelastic grades**
- Carpet underlay

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▪ Emissions from each component:

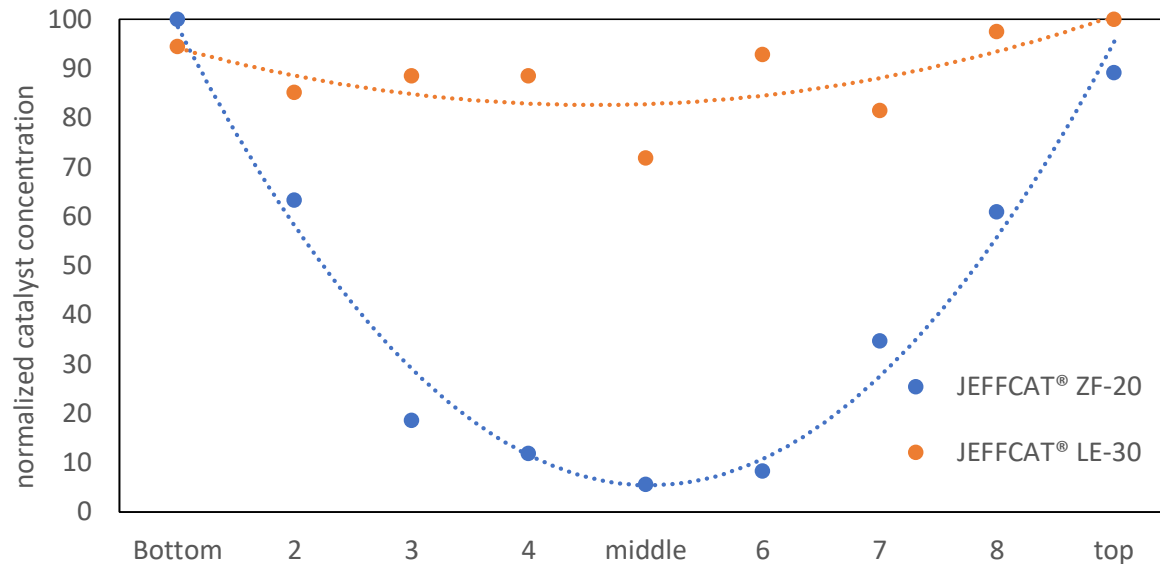
- Production impurities or foam reaction by-products such as MDA or TDA
- Low MW glycols and aldehydes from alkoxylation process
- Aldehydes and low MW silicones
- Carboxylates like 2-ethylhexanoic acid
- Non-reactive amines and aldehydes
- Antioxidant by-products and flame retardants commonly observed

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Polyurethane Catalyst Emissions

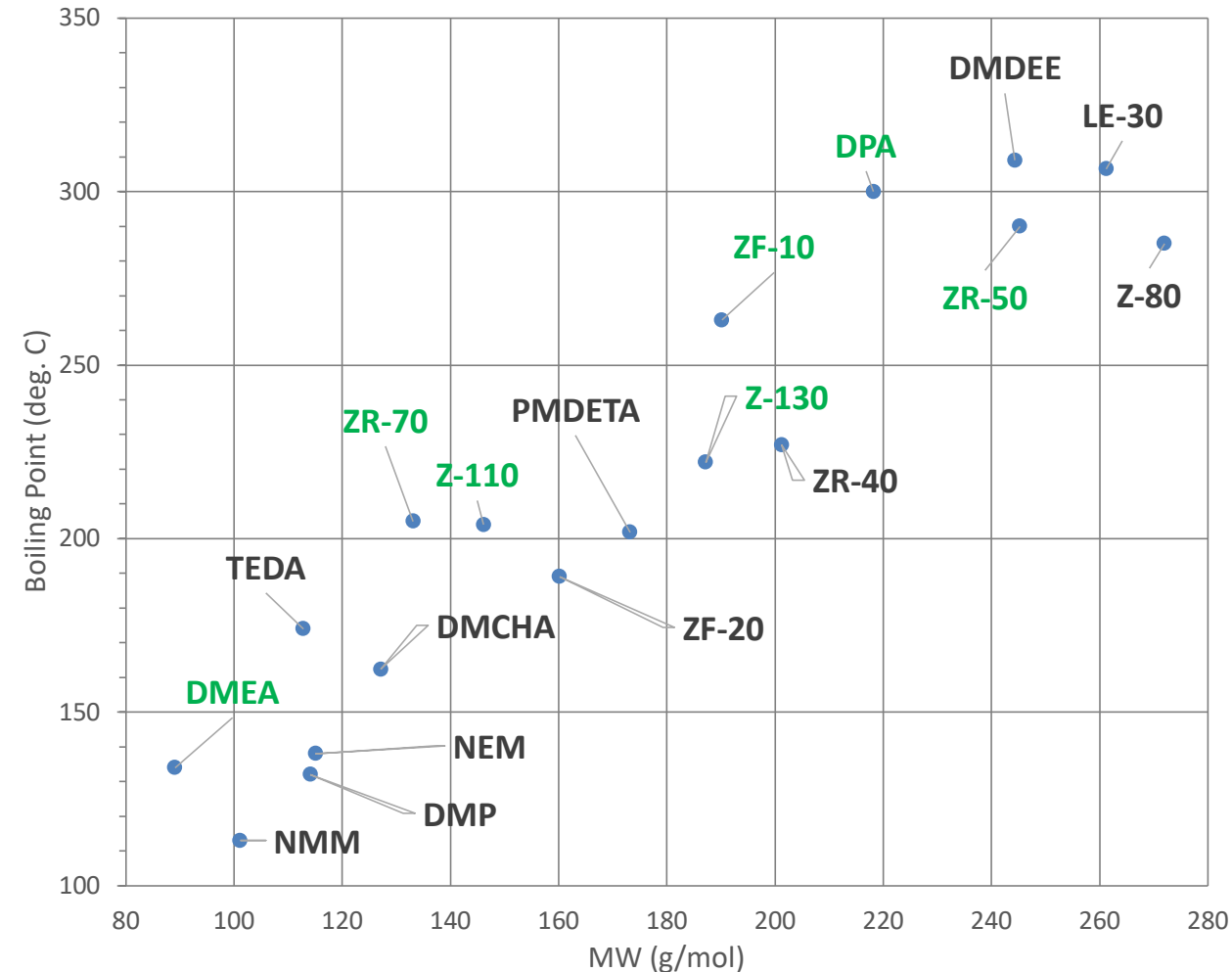
Catalyst volatility implications

- Catalyst volatility *can* play a role in emissions and odor
 - Lower MW = lower boiling point and higher vapor pressure
 - Volatile catalysts migrate to the surfaces of the foam (can influence surface cure) – makes odor worse at surface
 - Less volatile catalysts migrate less
 - Reactive catalysts are not thought to migrate



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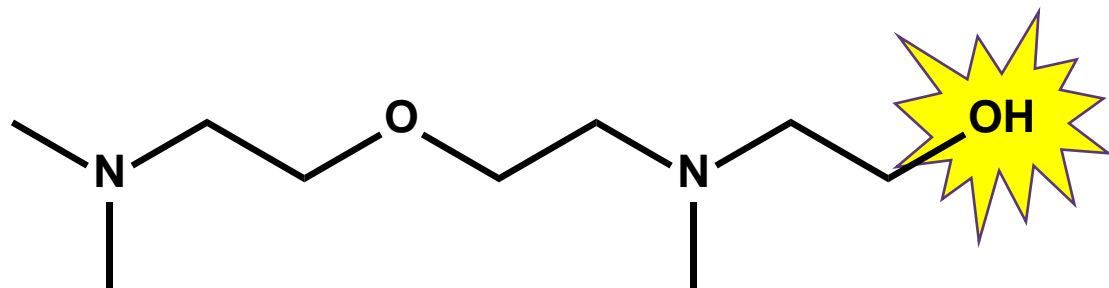
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JEFFCAT® ZF-10

Reactive vs. non-reactive emissions data



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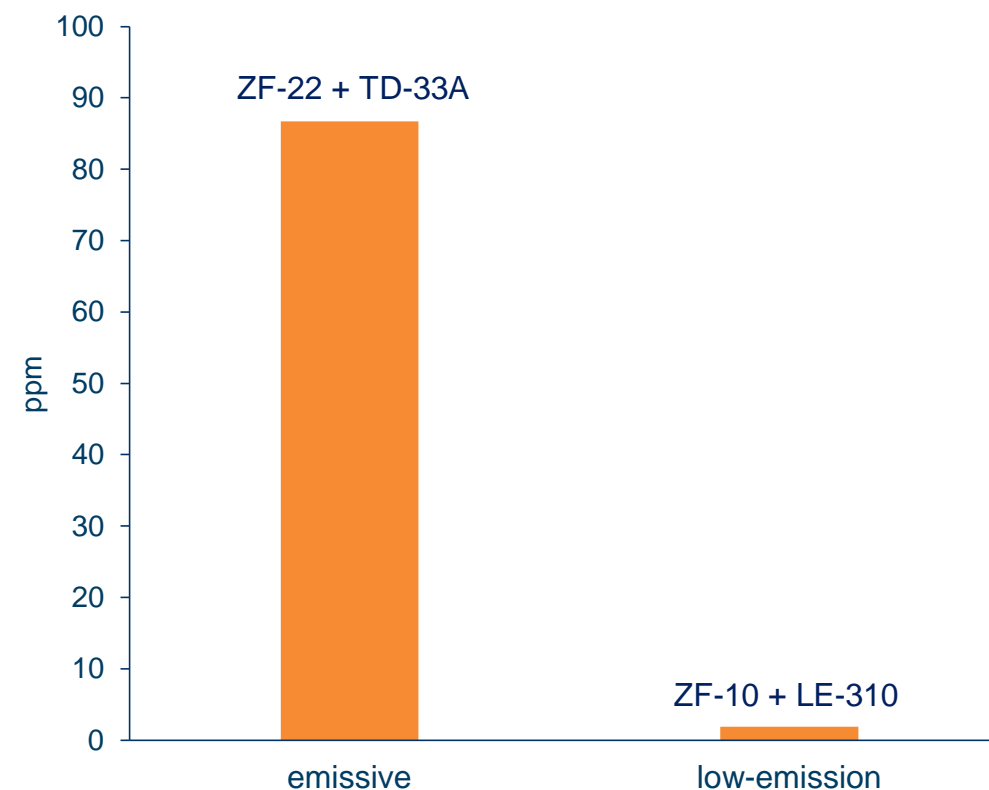
Typical Physical Properties

Boiling point, °C (°F)	255 (491)
Flash point, PMCC, °C (°F)	118 (245)
pH	11
Specific gravity, 20/20°C	0.95
Vapor pressure, mmHg, 20°C (68°F)	< 0.1
Viscosity, cSt, 25°C (77°F)	13
Water solubility (%)	> 10

- Flexible Foam

Amine catalyst emissions

- Lower absolute levels due to lower catalyst use rate



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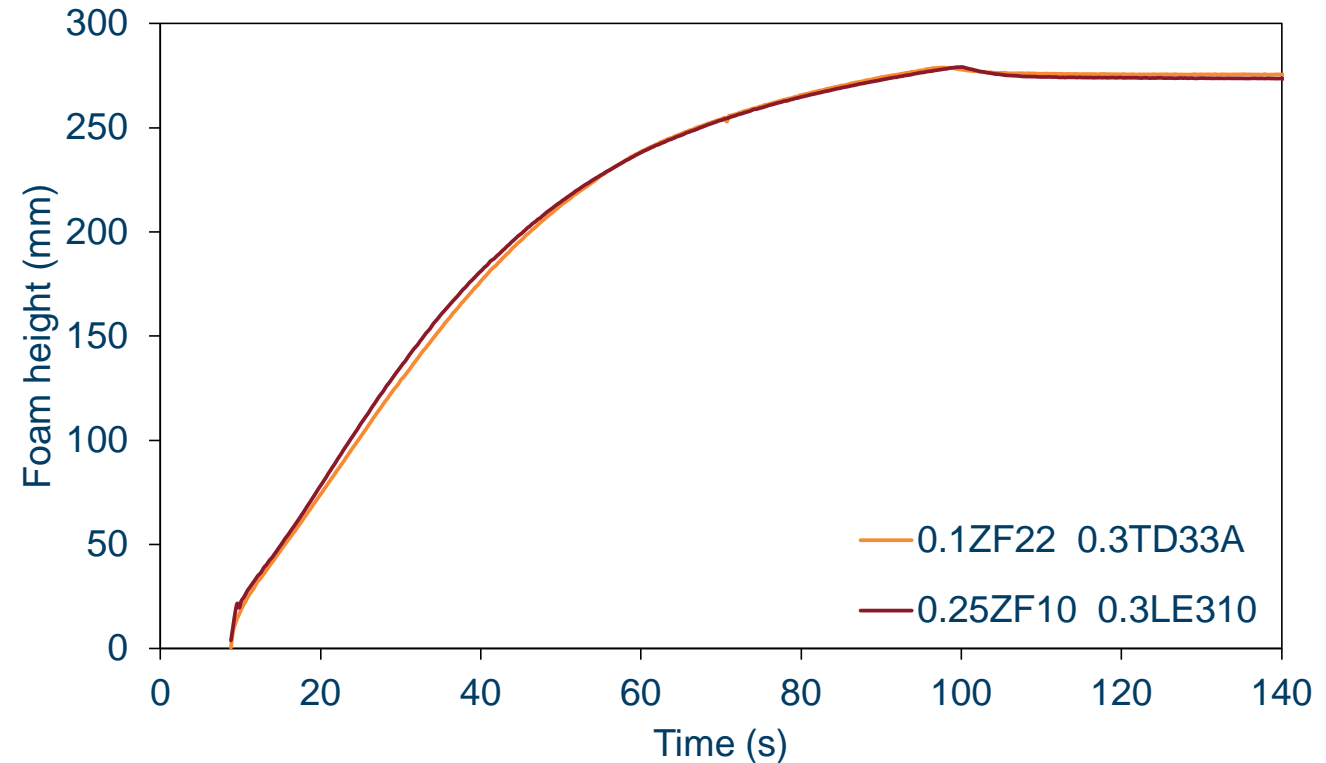
Reactive, Low-Emission Gel-Biased Catalysts

JEFFCAT® LE-310, ZR-50, Z-81

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- JEFFCAT® LE-310 catalyst designed to be a close “drop-in” for JEFFCAT® TD-33A (or equivalent)
 - Combination with JEFFCAT® ZF-10 allows for almost exact reaction profile matching with standard emissive catalyst system that many formulators use
- JEFFCAT® DPA catalyst is another industry standard
 - Slower than JEFFCAT® LE-310, but more processing latitude
- Other LE gelling catalyst options
 - JEFFCAT® ZR-50, JEFFCAT® Z-131



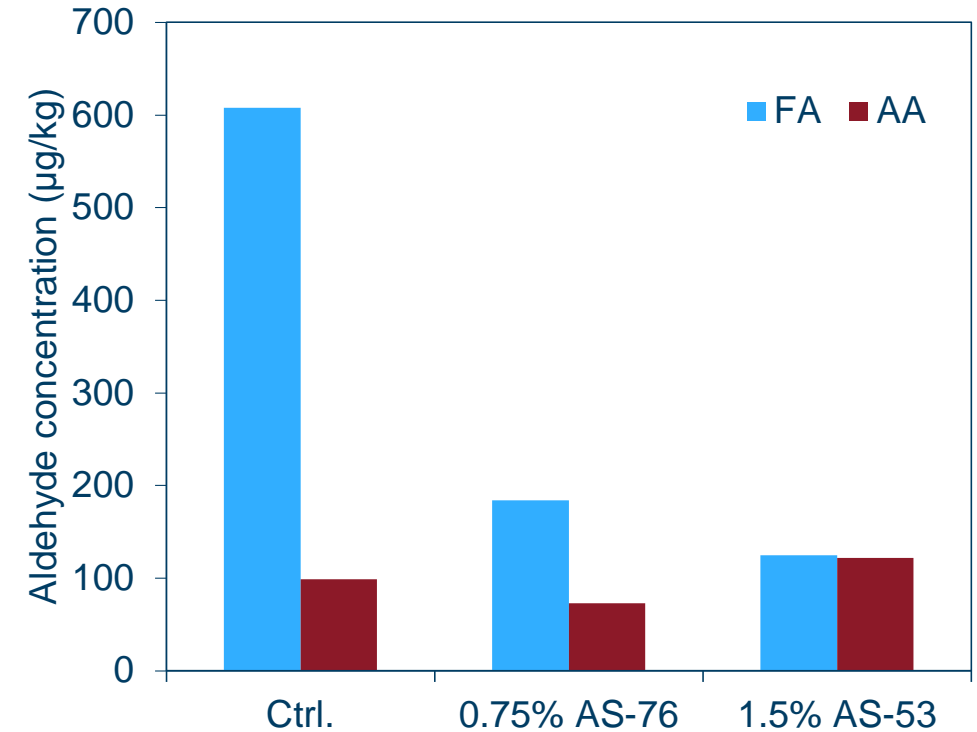
JEFFADD® AS-76 and AS-53

High-performance aldehyde scavengers



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- JEFFADD® AS-76
 - Patented technology based on a partially neutralized, reactive polyamine¹
 - Water-based system with no flammability concerns
 - Does not contribute to emissions (VDA-278)
 - Low usage rate of 0.75-1.0%
- JEFFADD® AS-53
 - Water-free and acid-free system for more sensitive polyol blends
 - Enhanced long-term stability in polyol formulations
 - **No phase separation**
 - **Optimal for systems that must be stored for long periods or without temperature control**



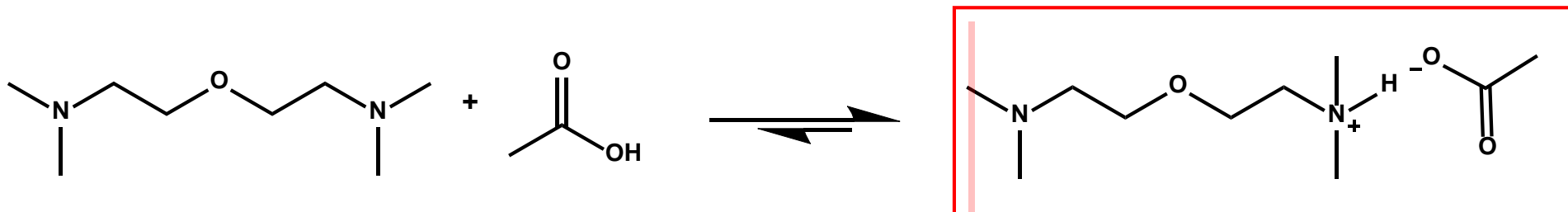
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Delayed Action Catalysts

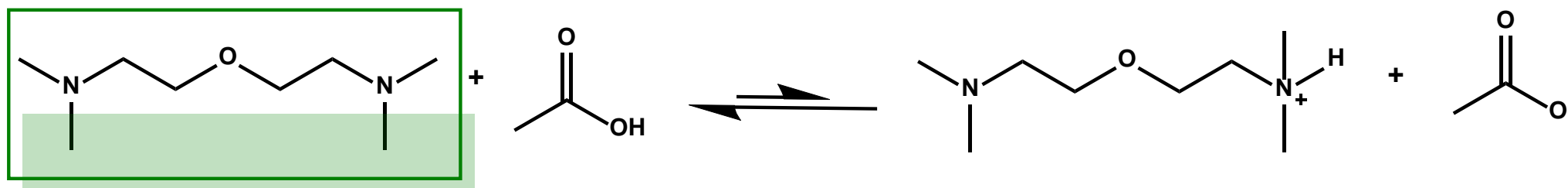
Background and Chemistry

- Sometimes foam formation needs to be “delayed”
 - Filling cavities or molds
 - But, once the delay is achieved, reactivity needs to take off rapidly for quick de-mold times

At lower T, the "blocked" catalyst salt complex dominates



As T increases, equilibrium shifts to free catalyst and acid species

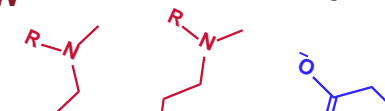


Low-Emission Delayed Action Catalysts

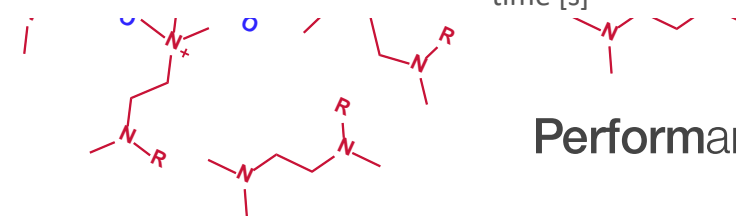
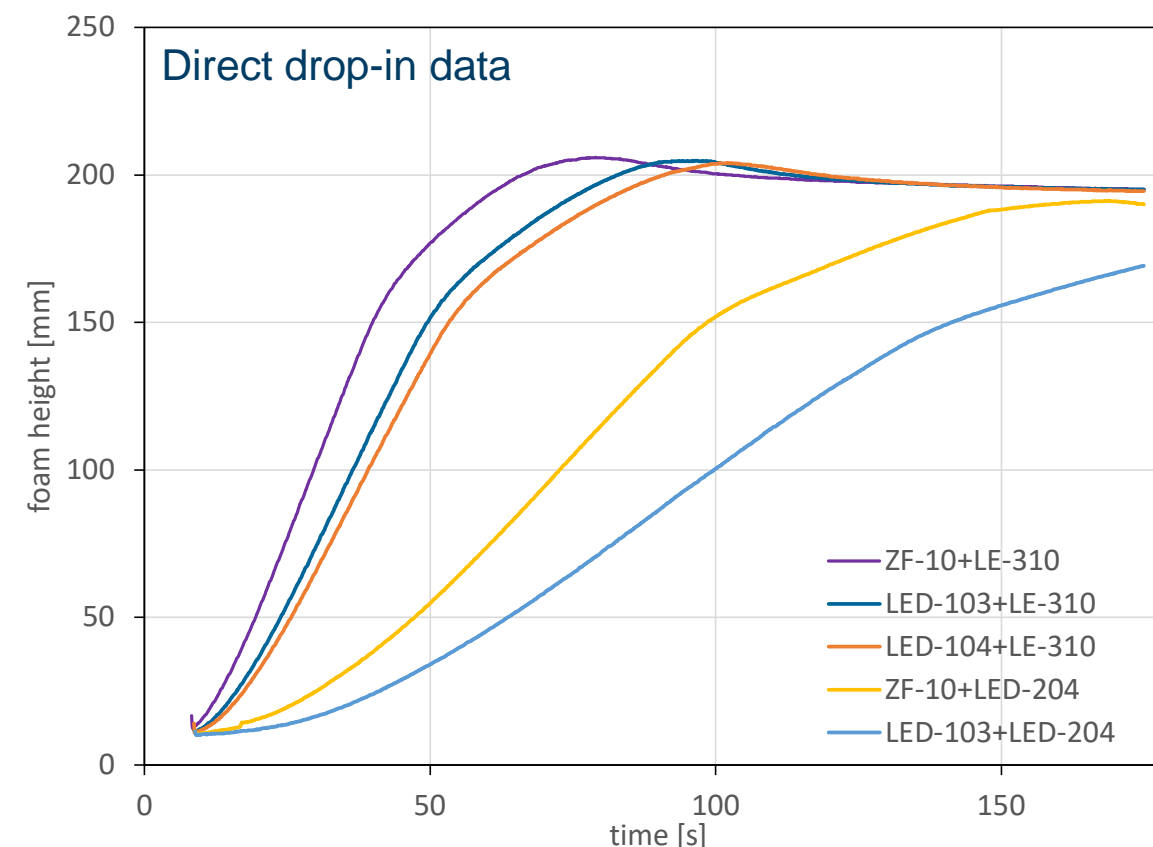
Amine catalysts pre-reacted with a zero-emission polymeric acid for improved flow

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- JEFFCAT® LED-103
 - Industry standard LE blowing catalyst with a blocking level of 19%
- JEFFCAT® LED-204
 - Industry standard gelling catalyst with 50% blocking level
 - Significant delay when dropped in for JEFFCAT® LE-310
- **New Product:** JEFFCAT® LED-104
 - Industry standard LE blowing catalyst with higher blocking level of 50%
 - Stronger slow-down on front end of creaming reaction to keep viscosity ultra-low and promote flowability
- No contributions to emissions
- Polymeric acid shown to lower aldehyde levels in amine catalysts¹
- Improvements in physical properties²



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(1) US Pat. 9856344
(2) Eur. Pat. EP2106415B1

JEFFCAT® LE-340

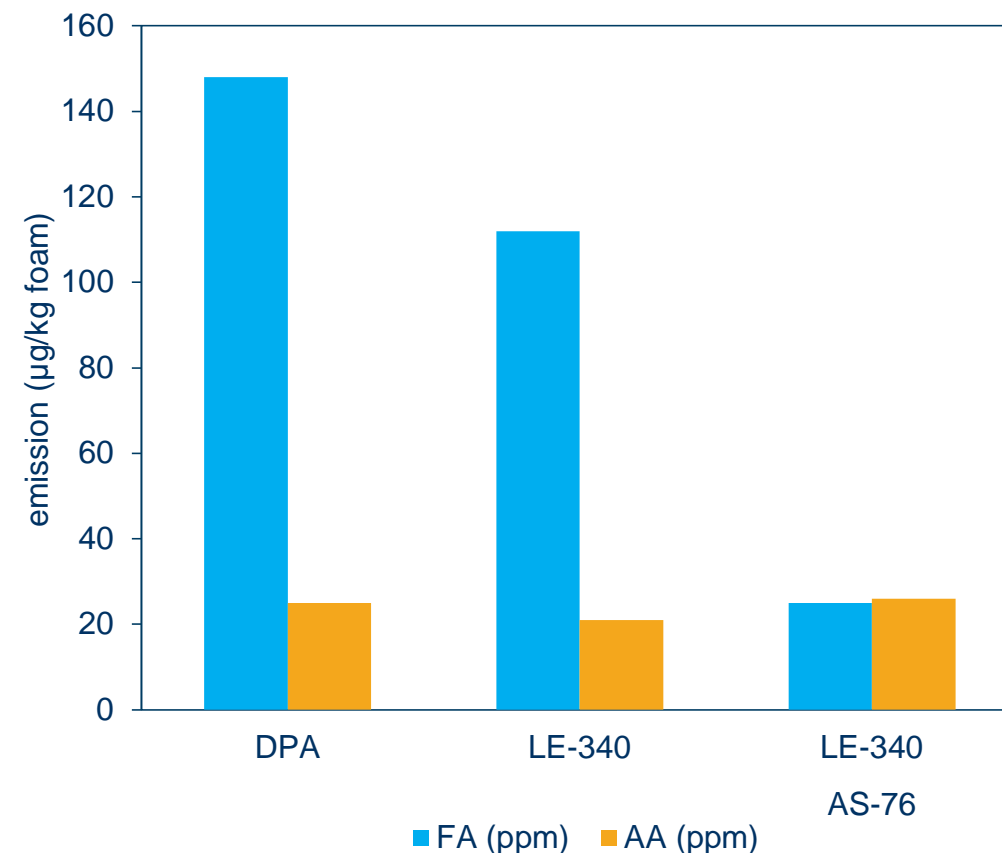
Low-odor gel catalyst

- Low-emission, low odor gel catalyst, 99% pure
- Paired with JEFFCAT® ZF-10 and JEFFADD® AS-76 for excellent low-emission, low-odor catalyst package
 - Excellent
- Reduces or eliminates amine odor in freshly cut foam
- Consistently < 50 ppm formaldehyde content in neat amine (not a spec)
- Designed for HR molded and polyether slabstock foams
- Typically used at 0.5-1.0 pbw in B-side

Typical Properties	Value
Flash point (closed cup)	135°C
Viscosity, 25°C	140
Density, 20°C	0.92 g/mL
Hydroxyl value	514 mgKOH/g

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VDA-276-type chamber test

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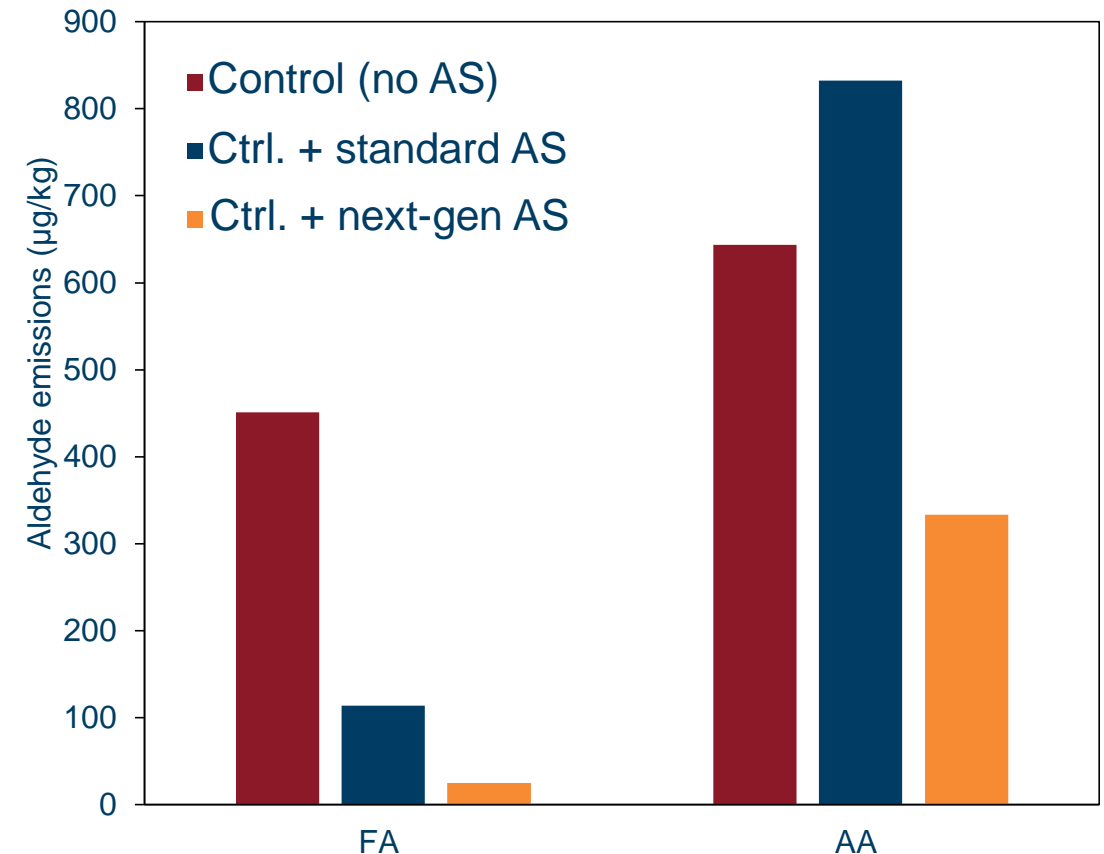
Next-Generation Aldehyde Scavengers

Focusing on acetaldehyde and matching reactivity



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- Existing AS technology is established – it will take a significant improvement in one or two areas to create a new product
- Many amine-based aldehyde scavengers alter the reactivity of the system, which is not optimal and requires reformulation
 - Focus on keeping reactivity the same with next gen
- Acetaldehyde less reactive than formaldehyde, more difficult to scavenge
 - Requires different chemistry
 - Solution will require multiple mechanisms of scavenging in one product
- Promising new results indicate ultra-efficient formaldehyde scavenging *and* lower acetaldehyde



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Conclusions

Keeping the pipeline full of low-VOC solutions

- Low-VOC amines and additives are core to advancing automotive foam technology
- HPP continues to develop solutions and improve on industry standards
 - Established low-emission catalysts
 - **JEFFCAT® ZF-10 (blowing)**
 - **JEFFCAT® LE-310 (gelling)**
 - New low-emission catalysts
 - **JEFFCAT® LE-340**
 - New delayed action catalysts
 - **JEFFCAT® LED-104**
 - New aldehyde scavenging technology
 - **JEFFADD® AS-76**
 - **Next-gen scavengers to tackle acetaldehyde emissions**



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