FEIPUR 2018

Rigid Technical Seminar

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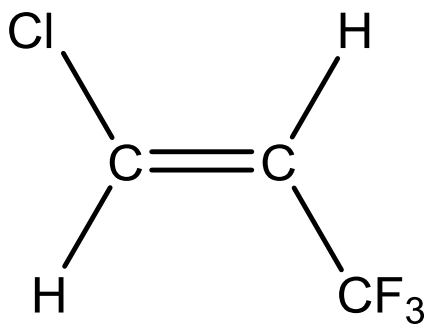
4th generation blowing agents: Chances and Challenges with HFOs

Alternative Blowing Agents for HCFC-141b Replacement

Blowing Agent	Advantages	Disadvantages
Water + Isocyanate (CO_2)	Availability, low price, non-flammable	Bad thermal insulation, high MDI consumption, formulation challenges
Hydrocarbons	Good thermal insulation, low price, availability	Highly flammable, high investment costs
HFCs	Good thermal insulation, non-flammable	Limited availability (regulated, phase-out due to high GWP), high price
HFOs	**Good thermal insulation, low GWP/ODP, non-flammable**	**High price, formulation challenges, chemical degradation possible**
Methylal	Low price, good insulation value	Flammable, formulation challenges
Methyl Formate	Low price, good insulation value	Flammable, formulation challenges

4th Generation Blowing Agents: HFO-1233zd(E)



HFO-1233zd(E)

- Chemical name: trans-1-chloro-3,3,3-trifluoropropene; 1233zd(E)
- Two suppliers on the market:
  - Honeywell: Solstice LBA ("Liquid Blowing Agent")
  - ARKEMA INNOVATIVE CHEMISTRY: Forane FBA 1233zd
- Non-flammable, BP = 19 °C, molecular weight = 130.5 g/mol
- Low Global Warming Potential (GWP), zero Ozone Depletion Potential (ODP)
- Good thermal insulation properties
- Can cause system stability issues due to catalyst/surfactant reactions
- More soluble in some polyols than 245fa - may impart plasticization effect
- Globally good availability

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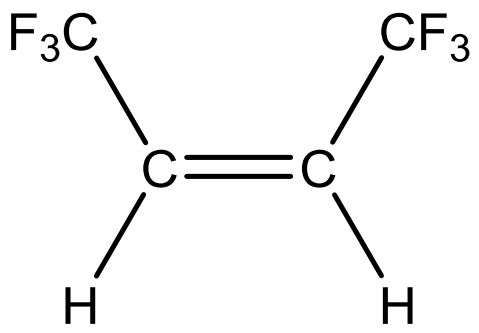
4th Generation Blowing Agents: HFO-1336mzz



HFO-1336mzz-Z

- Chemical name: (Z)-1,1,1,4,4,4-Hexafluoro-2-butene 1336mzz-Z
- Supplier: Chemours™ Opteon 1100 (formerly known as Formacel FEA-1100)
- Non-flammable, BP = 33 °C, molecular weight = 164 g/mol
- Low Global Warming Potential (GWP), zero Ozone Depletion Potential (ODP)
- Good thermal insulation properties
- Stable in PU polyol side; but higher cost-in-use compared to HFO-1233zd(E)
- Good solubility in polyol - may impart plasticization effect
- Availability still limited, but supplier is working intensely on production capacities

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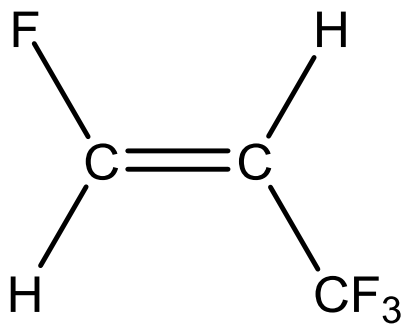
4th Generation Blowing Agents: HFO-1234ze



HFO-1234ze

- Chemical name: 1,3,3,3-Tetrafluoropropene; 1234ze
- Supplier: Honeywell Solstice GBA („Gaseous Blowing Agent“)
- Non-flammable, BP = -19 °C, molecular weight = 114 g/mol
- Low Global Warming Potential (GWP), zero Ozone Depletion Potential (ODP)
- Good thermal insulation properties
- Severe system stability issues in PU resin side
- Good solubility in polyol - may impart plasticization effect
- Globally available
- Application in OCF and other pressurized PU applications

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4th Generation Blowing Agents: Opteon 1150

?

Opteon 1150

- Chemical name: ? (not yet published)
- Supplier: Chemours™ Opteon 1150
- Non-flammable, BP = 7.5 °C
- Low Global Warming Potential (GWP), zero Ozone Depletion Potential (ODP)
- Good thermal insulation properties (slightly worse than Opteon 1100; 11.5 vs. 10.7)
- Can be used separately or in blends with other blowing agents
- Can improve low temperature* insulation performance, if used as co-blowing agent
- Not yet available on the market, limited information so far

* at -5 - 15 °C, low use level (~3 pphp)

4th Generation Blowing Agents: Pros & Cons

Most common options at the moment: Honeywell Solstice LBA & Chemours™ Opteon 1100

Both molecules are established in technical applications and on the market globally and will probably play the major role in the future as 141b replacement.

Summary of advantages:

- Low thermal conductivity
- In general good compatibility with most resins
- Environmental-friendly
- Not flammable

+

Some possible issues:

−

- High solubility → Can act as plasticizer + high use level
- Formulation challenges with Opteon 1100: In some cases compatibility is limited/High selectivity for surfactants
- Formulation challenges with Solstice LBA: Shelf life issues
- Relatively high molecular weight (→ high use level) combined with high price leads to high costs
  (but this must always be seen in comparison to 245fa, which is also a heavy molecule and quite expensive)

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4th Generation Blowing Agents - Relevant Insulation Applications

Appliance

- In most cases formulated systems
- Shelf life (typical range 0-6 months)
- System solubility & flowability
- Thermal insulation properties (λ-value)

Panels (PUR & PIR)

- In many cases formulated systems but tendency decreasing towards self formulation
- Shelf life (typical range 0-6 months)
- FR performance
- Thermal insulation properties (initial & aged λ-value)

Closed Cell Spray Foam

- In most cases formulated systems
- Shelf life (typical range 6-12 months)
- Dimensional stability
- FR performance
- Thermal insulation properties (λ-value)

4th Generation Blowing Agents – Differences In Formulation & Application

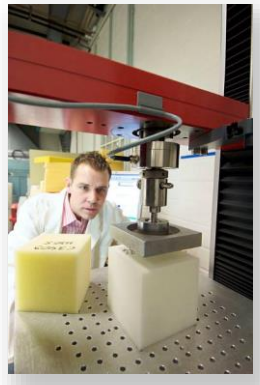
Polyol-Side Stability

- Formulation
  - system miscibility & compatibility upon change of blowing agent
  - potential additive variation to meet application & properties
- Storage & Transportation
  - shelf-life should fit application needs

Application

- Different boiling-point
  - Heat-reaction differences
  - Different reaction-profile
- Flammability during application
- Sprayability
- Different viscosity

Foam Properties

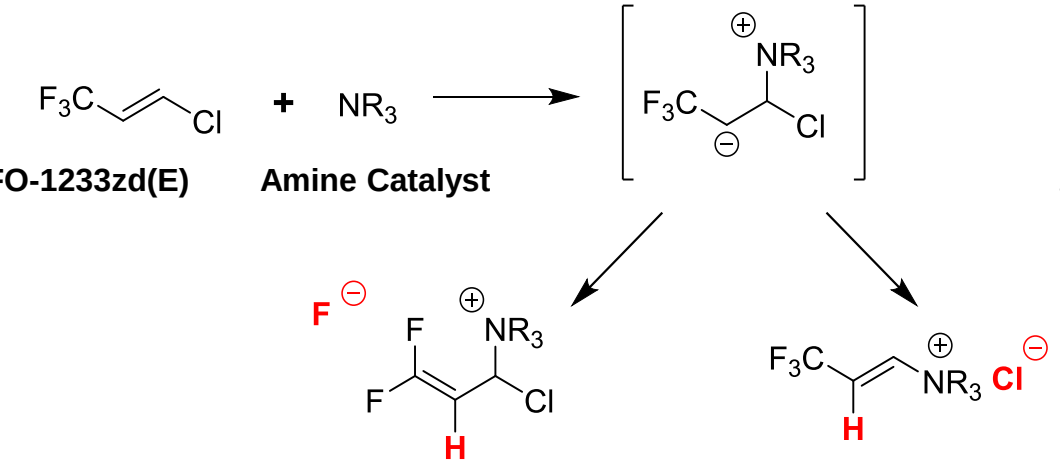


- Foam appearance (e.g. surface, cells, foam defects, collapse)
- Dimensional stability (e.g. shrinkage, post expansion)
- Foam adhesion
- FR properties
- Thermal conductivity
- Lambda aging

4th Generation Blowing Agents: HFO-1233zd
HFO Degradation Mechanism

- **Polyol blend formulation is the key step to succesful HFO application in all cases.**
  The biggest challenge for HFO-1233zd applications is the polyol-side shelf life stability
- Wrong polyol-side formulation may lead to HFO & silicone surfactant degradation over time

HFO-1233zd Degradation
(proposed mechanism):



→ *but, multiple other pathways possible…*

- **Potential aging consequences:**

  Processing issues due to blocking of catalysts (decreasing reactivity) and decomposition of silicone surfactant

  (coarse cells or even foam collapse)

  → deterioration of foam performance (insulation efficiency) upon storage of system blend

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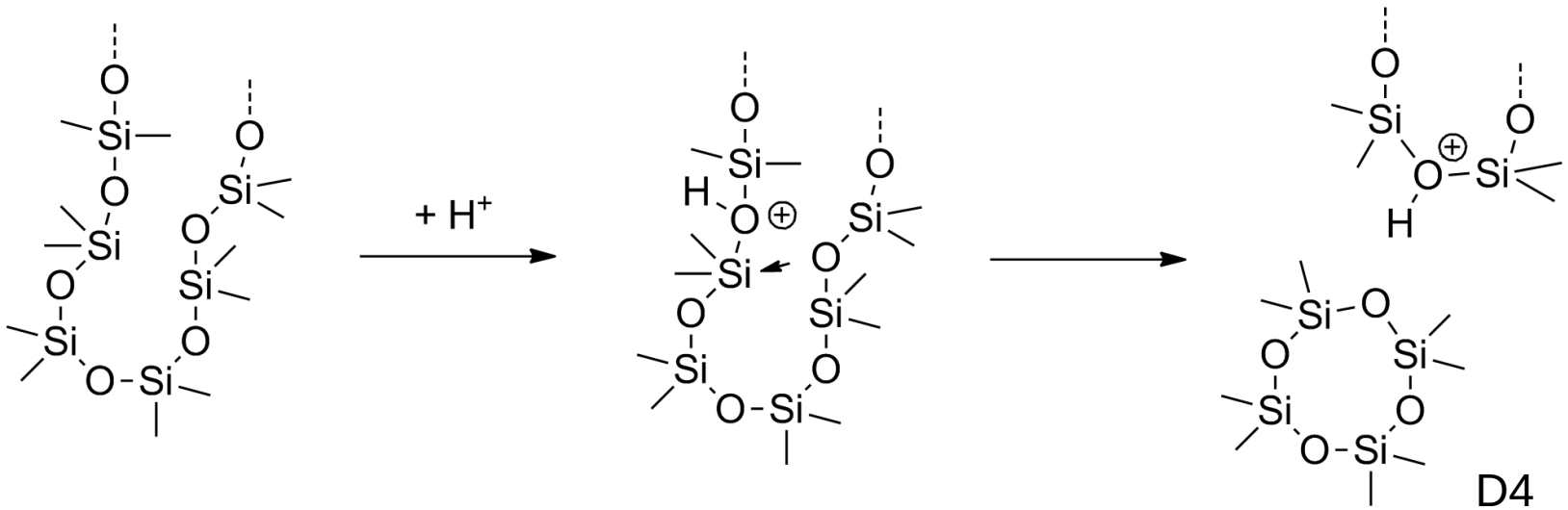
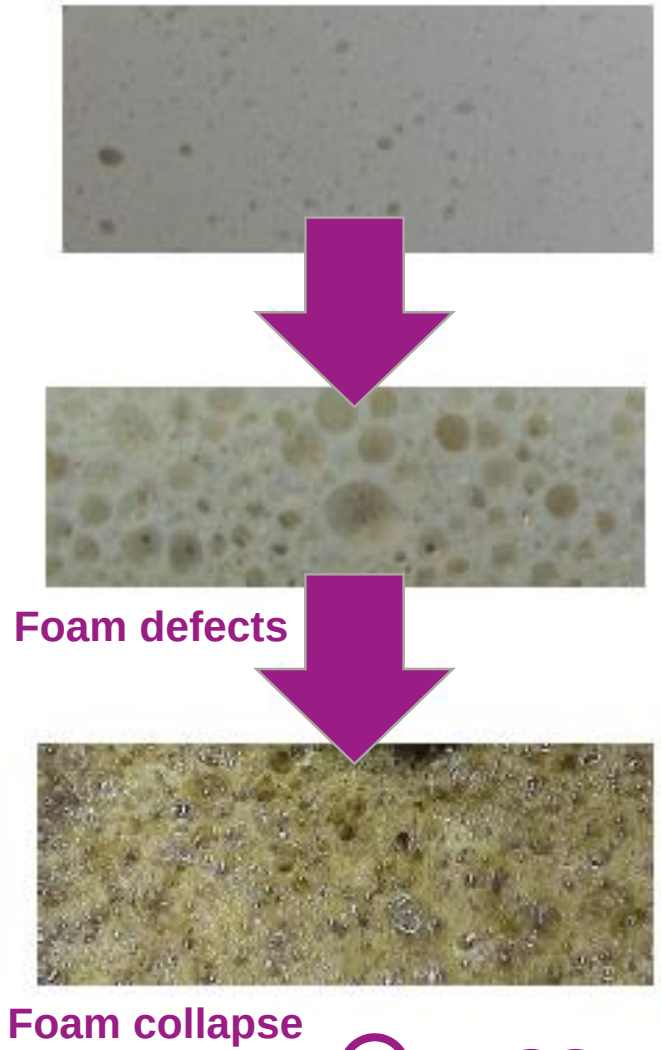
4th Generation Blowing Agents: HFO-1233zd
Surfactant Degradation Mechanism

- Acids (e.g. H^+ or $NR_4^+F^-$) catalyze the cleavage of Si-O-Si bonds within the siloxane chain
- Breakdown of the siloxane backbone results in loss of stabilization potency
- Degradation products are lower molecular weight siloxanes, esp. cyclic compounds like octamethyl cyclotetrasiloxane “D4”

“back-biting”





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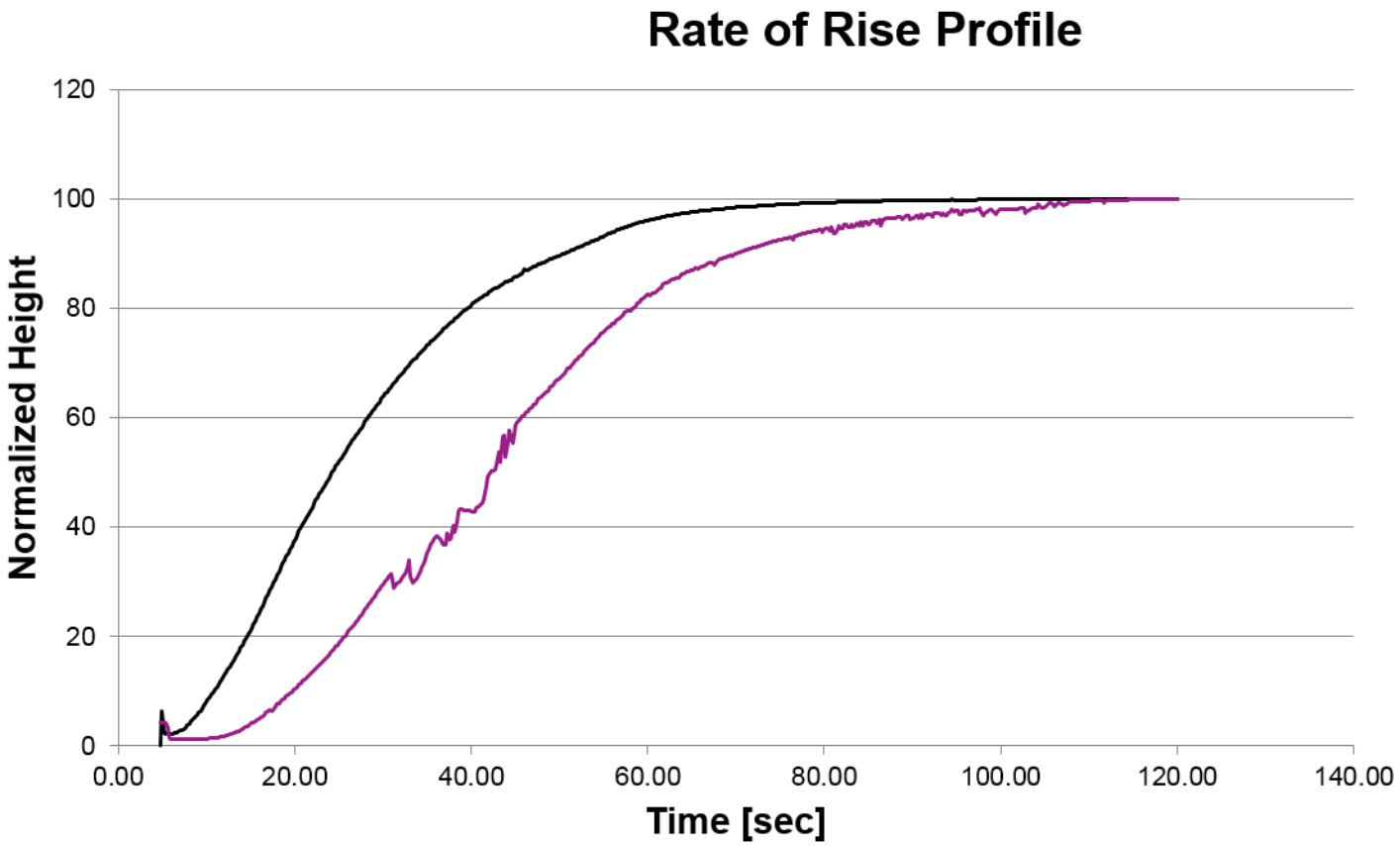
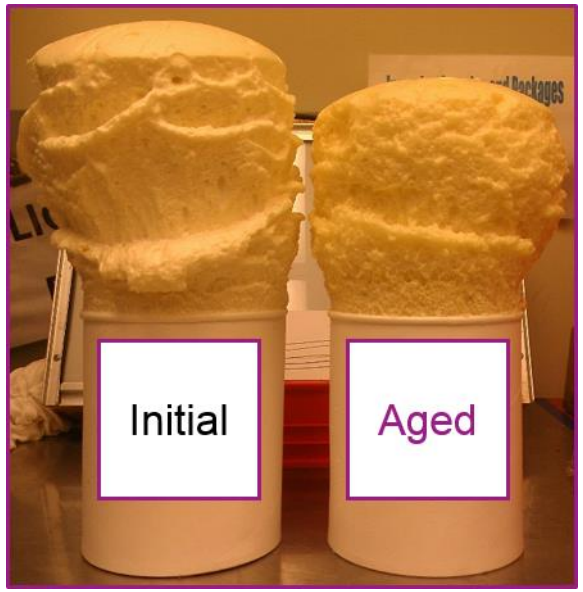
4th Generation Blowing Agents: HFO-1233zd
Influence of Aging on System Reactivity





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4th Generation Blowing Agents: HFO-1233zd Strategies to Avoid Shelf Life Problems

1. Low storage temperature, short storage time or do not use fully formulated system, but blend system daily (day tank) (or use third line to dose blowing agent)

2. If only coarse cell problems occur:

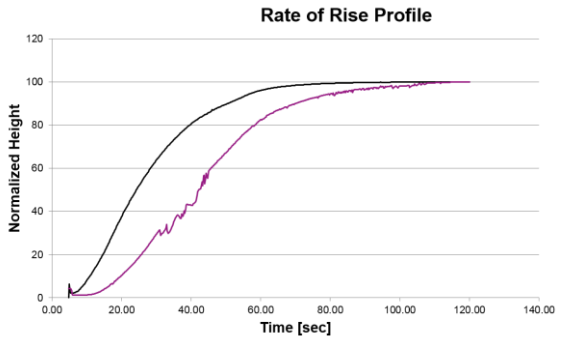
   → Use more surfactant

   → Use more resistant surfactant

   If a system is aged and coarse cells occur, sometimes adding additional surfactant can bring the system back to good quality

3. If reactivity shift occurs and/or the above mentioned measures did not work/are not helpful:

   → Use different catalyst package

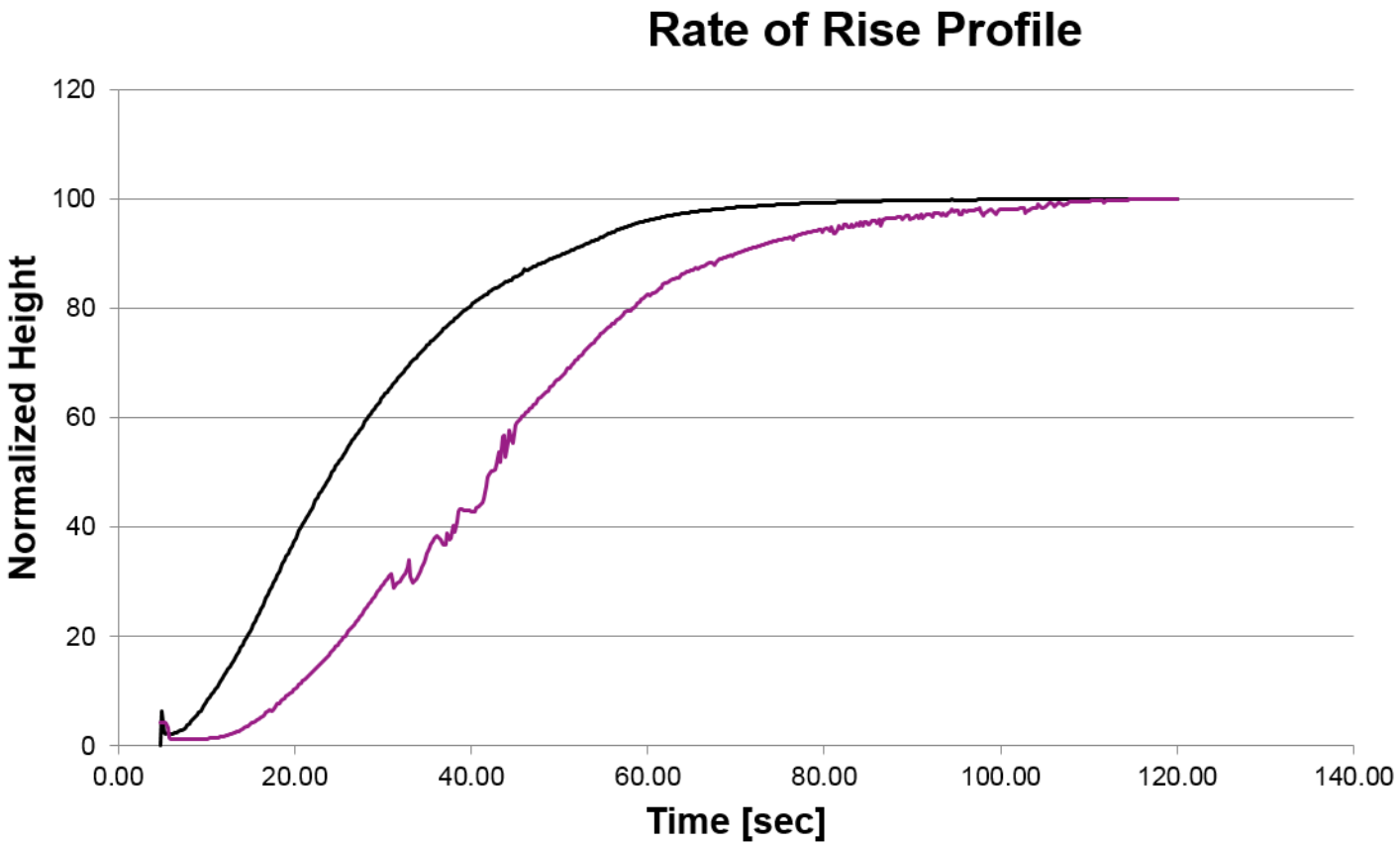


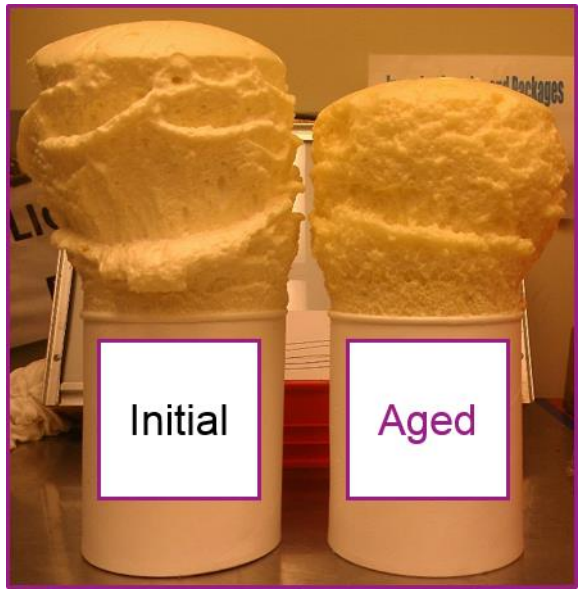
4. Try co-blowing approach to lower HFO-1233zd concentration (e.g. blending with pentanes, more water...)

   But be careful: More water sometimes accelerates the degradation process

5. Work on the polyol composition (ask your system house and/or work with the HFO supplier!)

4th Generation Blowing Agents: HFO-1233zd
Influence of Aging on System Reactivity





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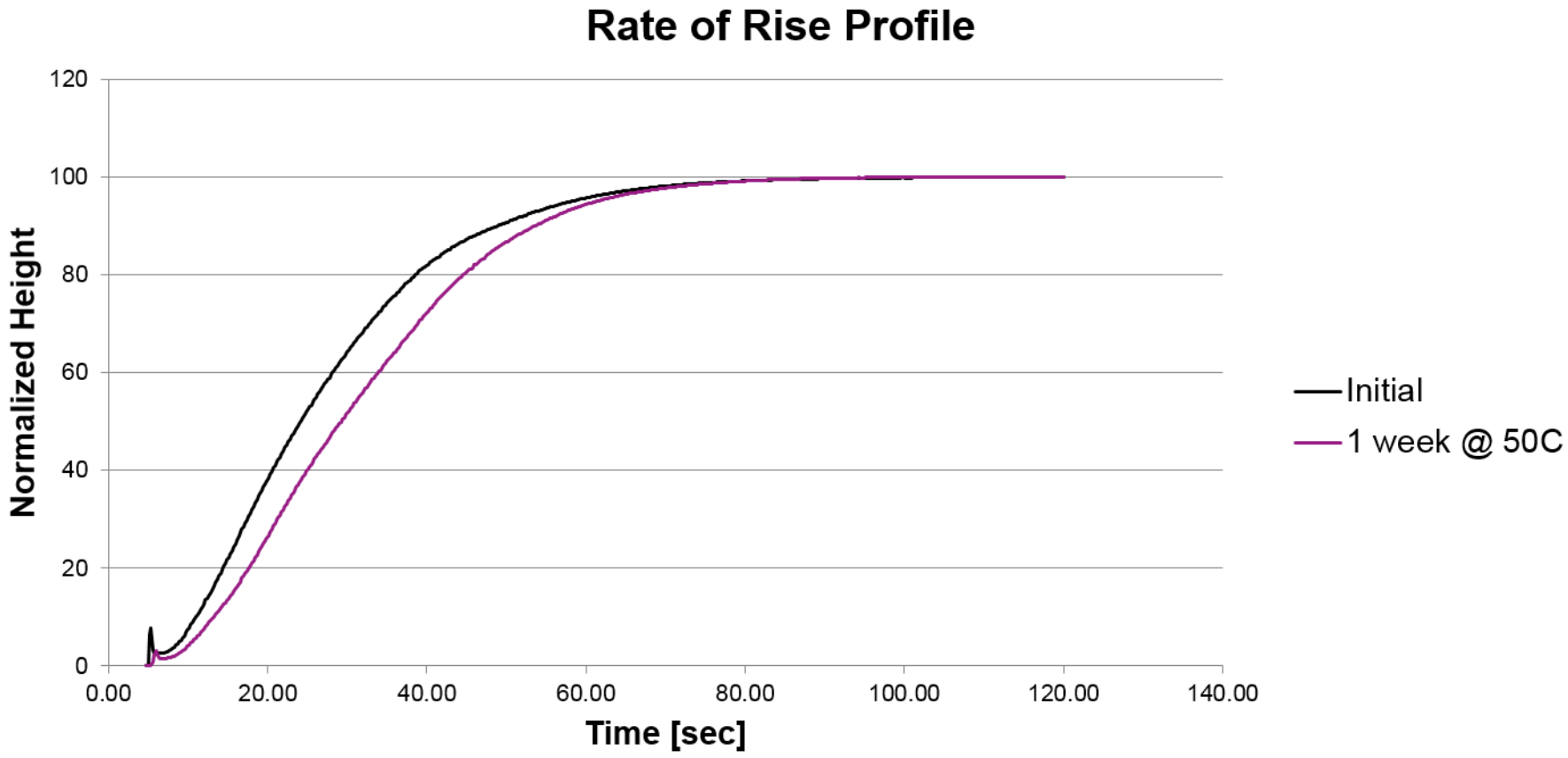
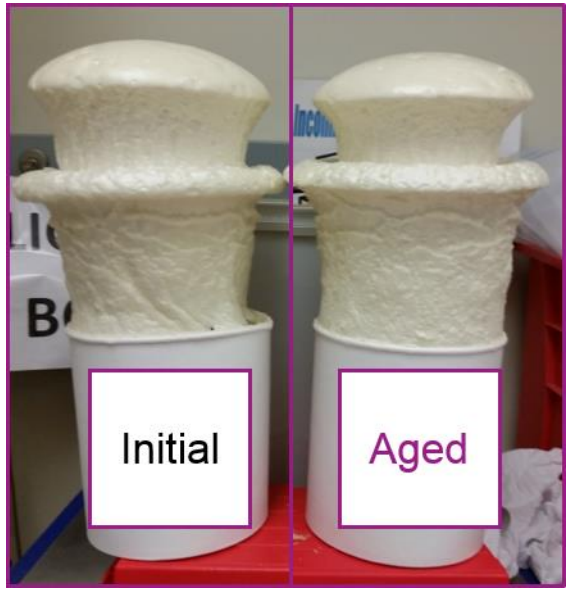
4th Generation Blowing Agents: HFO-1233zd
Influence of Aging on System Reactivity





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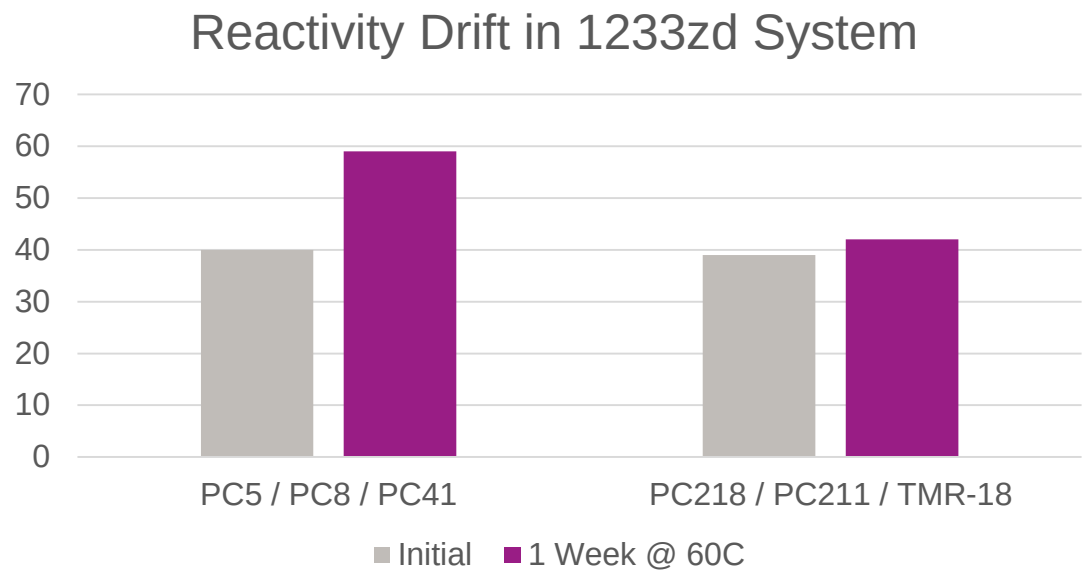
Optimizing the Catalyst Package for Appliance and Discontinuous PUR Panel Formulations Blown With HFO-1233zd

POLYCAT® 218, POLYCAT® 211, and DABCO® TMR-18 containing Appliance/Panel PUR formulation exhibit significantly improve stability with HFO-1233zd blowing agent in stability studies

Processing: Improved front end reactivity with balanced reaction profile yields and improvement in flow-ability without effecting post expansion and de-mold times

Initial Foams containing HFO-1233zd€	PC5/PC8/PC41	PC218/PC211/TMR-18
Min fill density (pcf)	2,00	1,95
Core density (pcf)	1,88	1,83
3 min post expansion (in)	0,0670	0,0790
K-factor	0,128	0,124
K-factor Δ (top-bottom)	0,007	0,001



Thermal Properties: Improving the front end reactivity also produces finer cell structure, yielding an improvement in thermal properties with a tighter gradient.

Physical Properties: Using a catalyst package of PC218 / PC211 / TMR-18 yields no change in physical properties with a reduction in core density.

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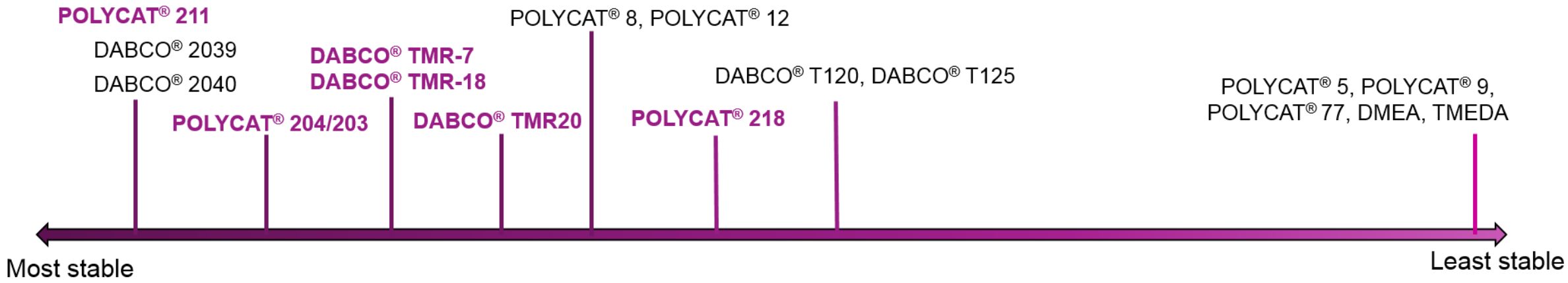
Catalyst Stability in HFO-1233zd-Blown Formulations



- Appliance & Disconti panel formulations containing HFO-1233zd have unique formulating challenges
  - Water / HFO Concentration
  - Resin side alkalinity
  - Reactivity Times
  - Processing Conditions
- Due to higher reactivity times, more stable catalysts are required.

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Additives for HFO-Blown Appliance & Discontinuous Panel Formulations

Relatively short to medium storage time requirements in appliance, medium storage requirement demand in discontinuous panel applications

Surfactant recommendations	
Surfactant	**Remarks**
TEGOSTAB® B 84205	Good choice for HFO blown formulations with sufficient compatibility; resulting in low lamda values
TEGOSTAB® B 8491	Balanced performance and high stability against chemical degradation
TEGOSTAB® 84210	Recommended for HFO blown systems with challenging compatibility; good FR properties

→ Recommended as high resistancy surfactant.

Alternative for panels:

B 8485

Catalyst recommendations		
Blow Catalyst	**Gel Catalysts**	**Cure Catalysts**
POLYCAT® 218	POLYCAT® 211	DABCO® TMR 2
		DABCO® TMR 3 (delayed action)

For HFO-1336mzz a standard catalyst package is working fine in many cases (e.g. PC5/PC 8/PC 41).

Additives for HFO-Blown Continuous Panel Formulations

Surfactant recommendations	
Surfactant	**Remarks**
TEGOSTAB® B 84501	Mitigates formulation challenges with HFOs
TEGOSTAB® B 84512	Well-balanced performance, supports foam flow

Catalyst Recommentations		
Blow Catalyst	**Gel Catalysts**	**Trimerization Catalysts**
POLYCAT® 5	POLYCAT® 36	DABCO® TMR 12
DABCO® BL 11	POLYCAT® 34	KOSMOS® 70 LO
		KOSMOS® 45 MEG

As in most cases the blowing agent is streamed directly into the mixing head (no fully blended system, no shelf life issues), standard catalysts are being used.

Additives for HFO-Blown Spray Foam Formulations

Surfactant recommendations	
Surfactant	**Remarks**
TEGOSTAB® B 84711	Suitable for HFO blown systems with high solubility demand; strong FR support
TEGOSTAB® B 84715	Dedicated for HFO-1336mzz blown systems
TEGOSTAB® B 84704	Creates smooth foam surface and a very regular cell structure

Catalyst recommendations for HFO-1233zd	
Catalyst	**Remarks**
POLYCAT® 218	Blow catalyst
POLYCAT® 203	Gel catalyst
DABCO® MB 20	Cure Catalyst (Bismuth based)
DABCO® 2040	Gel Catalyst

For HFO-1336mzz a standard catalyst package is working fine in many cases (e.g. PC5/PC 8/PC 41).


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