Alternative Technologies for Foam Sector – HFO by DuPont

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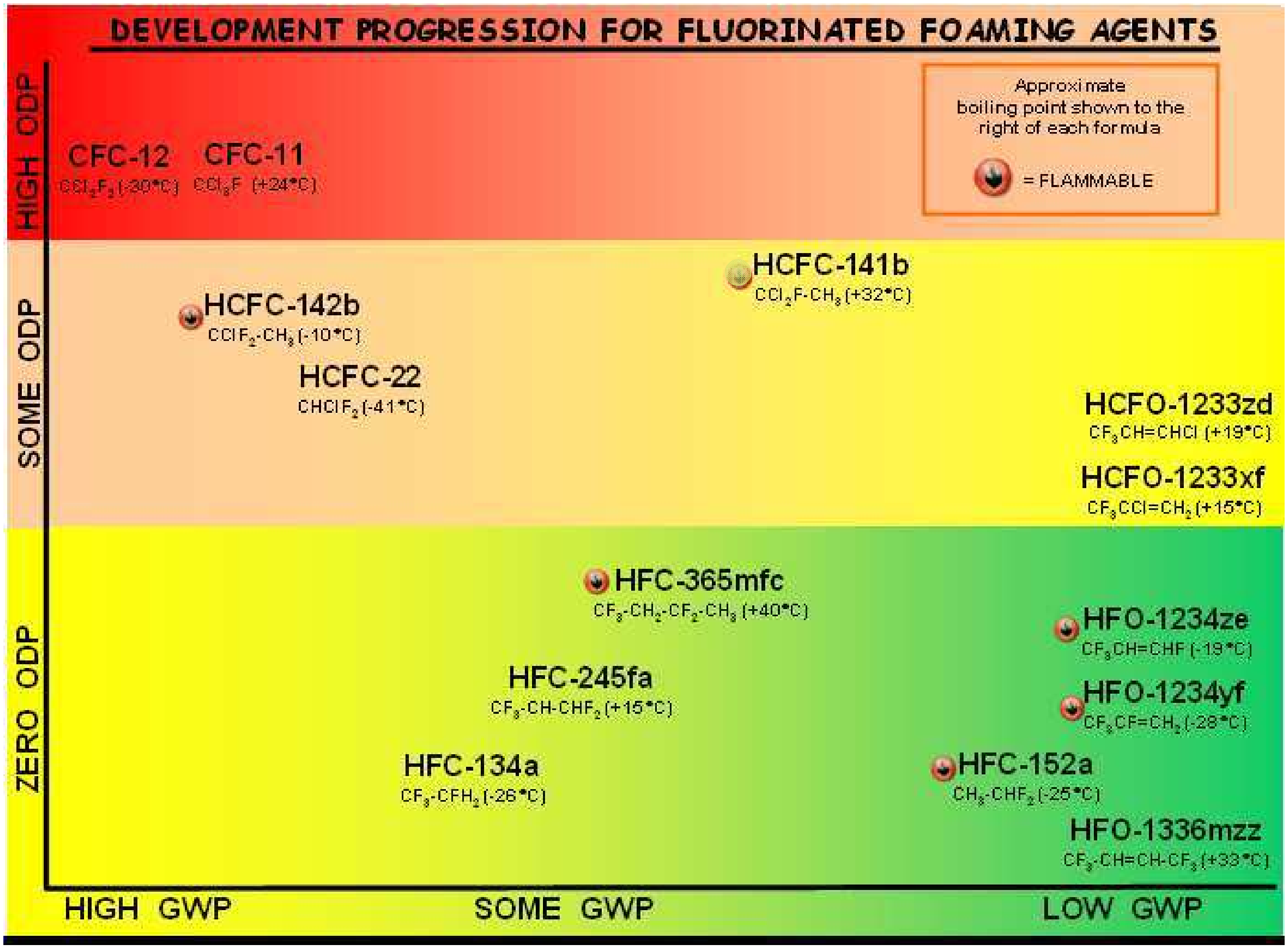
DuPont Next Generation Foaming Agents

- Continually challenged to reduce environmental footprint
  - minimize global warming impact
  - maintain/improve all previous environmental & performance characteristics
  - deliver competitive products in timely manner

- Evaluating hydrofluoro-olefins (HFO) family

Overview of fluorinated foaming agents



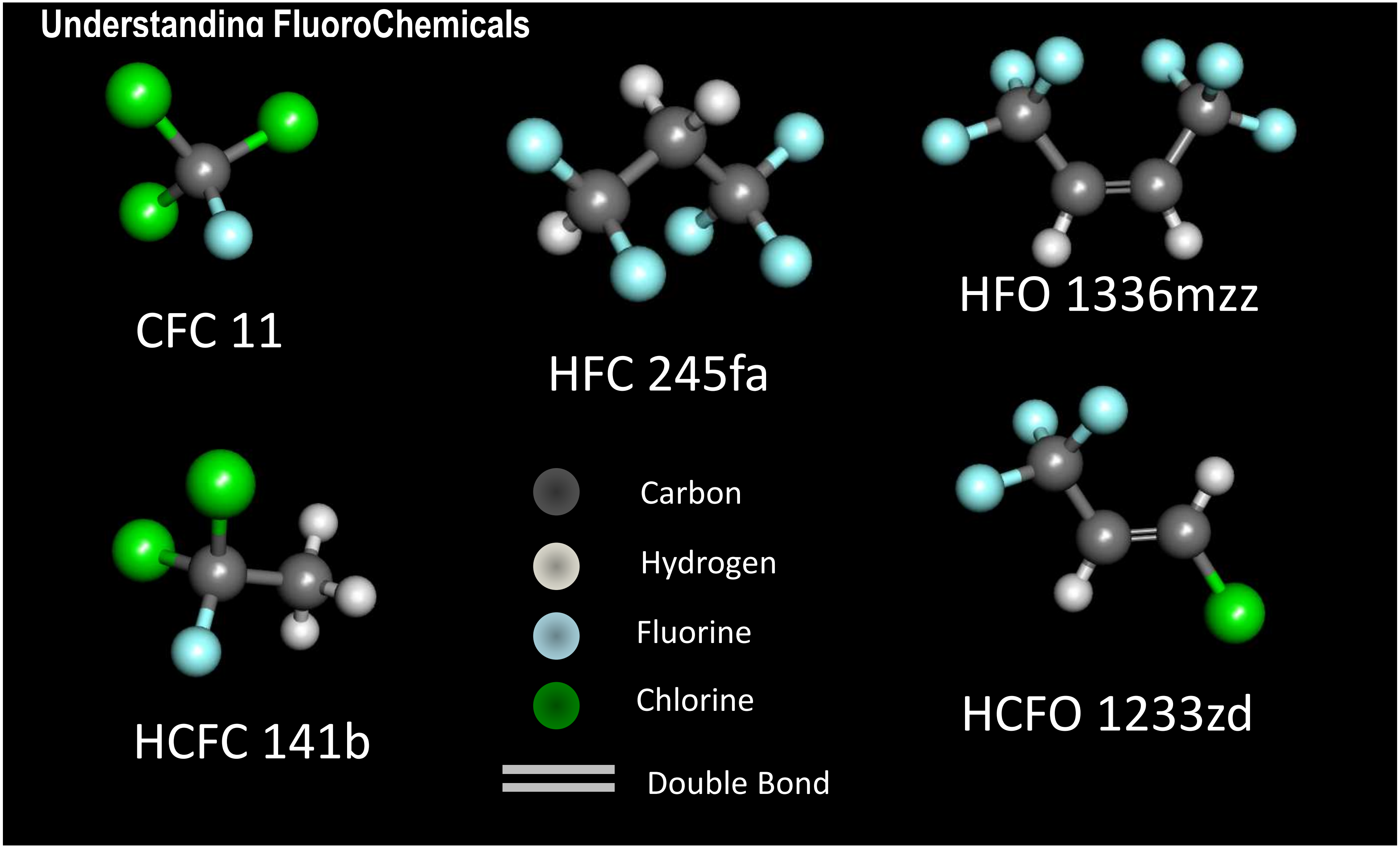
Options for PU foams

Scouting low GWP hydrofluoro-olefins can present quite a challenge identifying functional candidates among a large number of possibilities

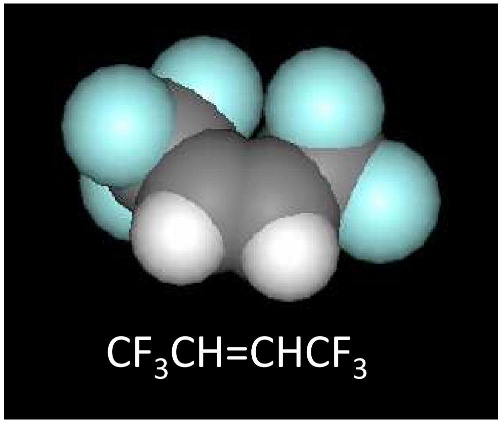
Property	3-Carbon Series						4-Carbon Series		5-Carbon Series	
	HFO 1243zf	HFO 1234yf	HFO 1234ze-E	HFO 1225ye-Z	HCFO 1233xf	HCFO 1233zd-Z	HFO 1345zfc	HFO 1336mzz-Z	HFO 1447fz	HFO 1438mzz-E
Formula	$CF_3CH{=}CH_2$	$CF_3CF{=}CH_2$	$CF_3CH{=}CHF$	$CF_3CF{=}CHF$	$CF_3CCl{=}CH_2$	$CF_3CH{=}CHCl$	$CF_3CF_2CH{=}CH_2$	$CF_3CH{=}CHCF_3$	$CF_3CF_2CF_2CH{=}CH_2$	$CF_3CH{=}CHCF_2CF_3$
ODP	None	None	None	None	ODP[1]	ODP[1]	None	None	None	None
GWP	Low	Low	Low	Low	Low	Low	Low	Low	Low	Low
Boiling Point (°C)	-22	-28	-19	-20	14-15	19	5	32	32	29
Molecular Weight	96	114	114	132	131	131	146	164	196	214
Toxicity		Acceptable	Acceptable	Disqualified for toxicity				Acceptable		
Flammable		Yes	Slight	No	No	No		No		

1. Executive Summary: Scientific Assessment of Ozone Depletion: 2006, 19 pp. World Meteorological Organization, Geneva, Switzerland, 2007. [Reprinted from Scientific Assessment of Ozone Depletion: 2006, Global Ozone Research and Monitoring Project-Report No. 50, 572 pp., World Meteorological Organization, Geneva, Switzerland, 2007.]

Options for PU foams



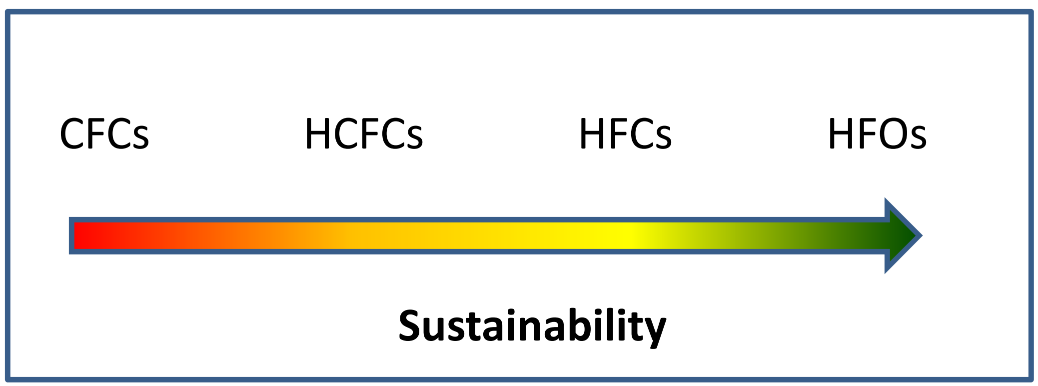
Formacel® 1100: *A Next Generation Foam Expansion Agent*



HFO-1336mzz-Z

- **Ozone Depletion Potential (ODP) = 0 (no chlorine)**
- **Global Warming Potential (GWP) 100 yr ITH = 8.9 (NOAA)**
- **Atmospheric lifetime = 22 days (NOAA)**
- **Nonflammable (ASTM E 681 at 60 °C & 100 °C)**
- **Boiling Point = 33 °C**
- **Vapor Thermal Conductivity k= 10.7 mW/mK @ 25 °C**
- **AEL[a] = 500 ppm 8hr / 12hr**
- **Maximum Incremental Reactivity (MIR) = 0.04 g O_3/g**

a: DuPont Acceptable Exposure Limits (8-12 hr TWA)



COMPARISON OF FORMACEL® 1100 WITH OTHER ZERO ODP FOAM EXPANSION AGENT OPTIONS

Property	Formacel® 1100	HCFC-141b	HFC-245fa	HFC-365mfc	Cyclopentane	Methyl Formate
Molecule Structure	$CF_3CH=CHCF_3$	CCl_2FCH_3	$CF_3CH_2CHF_2$	$CF_3CH_2CF_2CH_3$	$(CH_2)_5$	$CH_3(HCOO)$
Molecular weight	164	117	134	148	70.1	60
Boiling Point (°C)	33	32	15	40	49	32
ODP	0	0.11	0	0	0	0
GWP(100yr ITH)	8.9	725	1030	794	11	<25
VOC	No*	No	No	No	Yes	No
Exposure Limits (ppm)	500**	500	300	1000	600	100
Flammability	No	No	No	Yes	Yes	Yes
Vapor Thermal Conductivity @ 25 °C (mW/mK)	10.7	9.7	12.7	10.5	13	10.7

**Expected based on low MIR Value*

*** DuPont Acceptable Exposure Limits (8-12 hr TWA)*

Challenges for the Appliance Industry

More stringent environmental & energy requirements →

	HCFCs (HCFC-141b)	HFCs (HFC-245fa)	HCs (Hydrocarbons)
ODP	Low	Zero	Zero
GWP	High	High	Low
VOC	No	No	Yes
k-factor	Low	Higher	Much higher

Challenges - meet the requirements of environmental sustainability and energy efficiency while maintaining the cost effectiveness

Recent Lab study – 1336mzz vs HCFC-141b

1336mzz - a zero ODP and low GWP version of HCFC-141b

FEA Property	HCFC-141b	1336mzz
Molecule Structure	CCl_2FCH_3	$CF_3CH=CHCF_3$
Chlorine	Yes	No
ODP	0.11	0
GWP (100 yr ITH)	725	8.9
VOC	No	No*
Exposure Limits (ppm)	500	500
Flammability	No	No
Lambda @ 25 ^{o}C (mW/mK)	9.7	10.7
Boiling Point (^{o}C)	32	33
Molecular Weight	117	164

** Expected based on low MIR value*

HCFC-141b Level Reduction

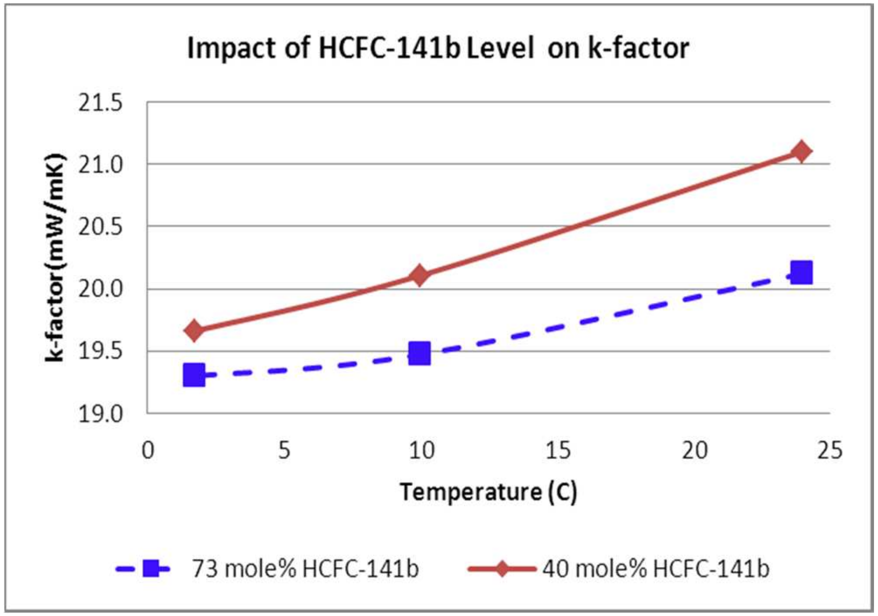
- Same generic appliance formulation
- Reduced HFC-141b level from 73 mole% to 40 mole%

Formulations	73 mole % HCFC-141b	40 mole % HCFC-141b
Foam index	1.2	1.2
Polyol Blend (pbw)	100	100
Additives (pbw)	9.9	9.9
Water (pbw)	1.7	3.8
FEA (pbw)	30	16
Moles of FEA	0.26	0.14
Moles of Water	0.09	0.21
Mole % of FEA	73%	40%

Impact of HCFC-141b Level Reduction

At 40 mole% HCFC141b:

- Reduced FEA usage by 45 wt%
- Worse k-factor at all temperatures



Initial Foam Properties	73 mole % HCFC-141b	40 mole % HCFC-141b
Density (kg/m^3)	28.8	28.2
k-factor (mW/mK) at 24 °C	20.1	21.1
k-factor (mW/mK) at 10 °C	19.5	20.1
k-factor (mW/mK) at 1.7 °C	19.3	19.7
Relative k-factor changes		
k-factor at 24 °C	Control	4.9%
k-factor at 10 °C	Control	3.3%
k-factor at 1.7 °C	Control	1.9%
Relative FEA changes		
FEA (weight)	Control	-45%

Formacel® 1100 Level Reduction

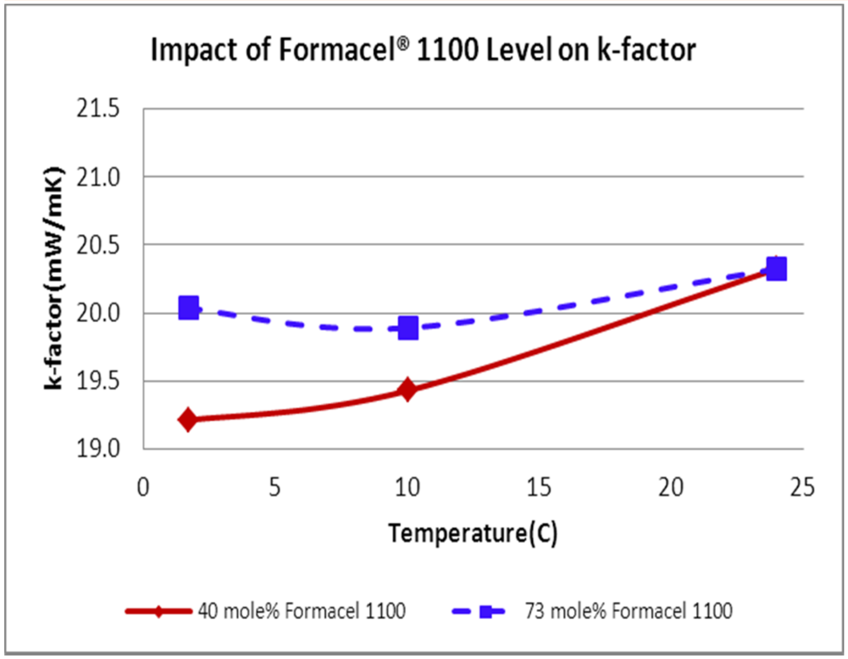
- Generic appliance formulation
- Formacel® 1100 level reduction from 73 mole% to 40 mole%

Formulations	73 mole % Formacel® 1100	40 mole % Formacel® 1100
Foam index	1.2	1.2
Polyol Blend (pbw)	100	100
Additives (pbw)	9.9	9.9
Water (pbw)	1.7	3.8
FEA (pbw)	42	23
Moles of FEA	0.26	0.14
Moles of Water	0.09	0.21
Mole % of FEA	73%	40%

Impact of Formacel® 1100 Level Reduction

At 40 mole% Formacel® 1100:

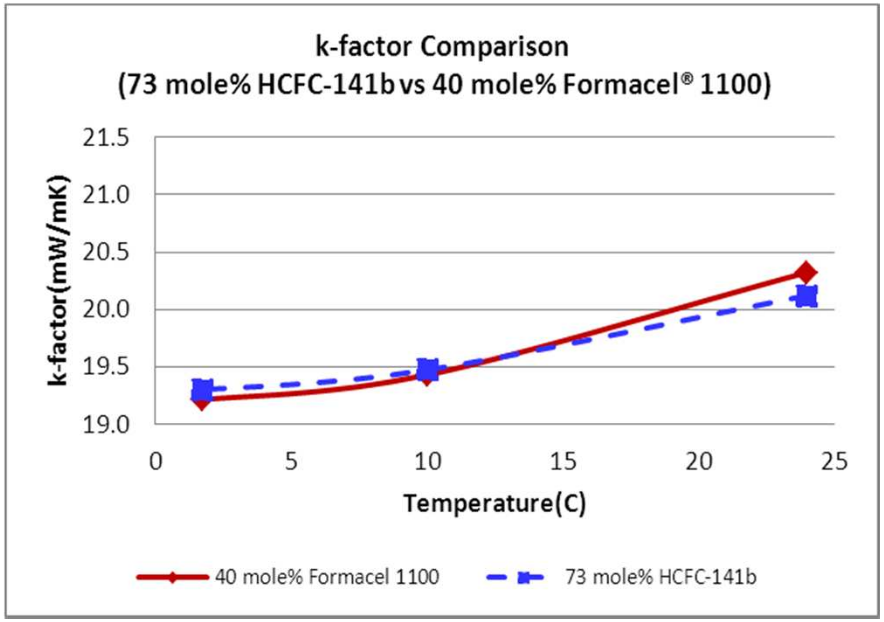
- Reduced FEA usage by 45 wt%
- Improved k-factor at 10C° and 1.7C°
- No impact on k-factor at 24C°



Initial Foam Properties	73 mole % Formacel® 1100	40 mole % Formacel® 1100
Density(kg/m³)	27.0	28.5
k-factor(mW/mK) at 24 °C	20.3	20.3
k-factor (mW/mK) at 10 °C	19.9	19.4
k-factor (mW/mK) at 1.7 °C	20.0	19.2
Relative k-factor changes		
k-factor at 24 °C	Control	0.0%
k-factor at 10 °C	Control	-2.3%
k-factor at 1.7 °C	Control	-4.1%
Relative FEA changes		
FEA (weight)	Control	-45%

Comparison of Formacel® 1100 at 40 mole% vs HCFC-141b at 73 mole%

- **Reduced Formacel® 1100 usage by 23 wt%**
- **Equivalent k-factor performance at all temperatures**



Initial Foam Properties	73 mole % HCFC-141b	40 mole % Formacel® 1100
Density (kg/m³)	28.8	28.5
k-factor (mW/mK) at 24 °C	20.1	20.3
k-factor (mW/mK) at 10 °C	19.5	19.4
k-factor (mW/mK) at 1.7 °C	19.3	19.2
Relative k-factors		
k-factor at 24 °C	Control	1.0%
k-factor at 10 °C	Control	-0.2%
k-factor at 1.7 °C	Control	-0.4%
Relative FEA Changes		
FEA (weight)	Control	-23%

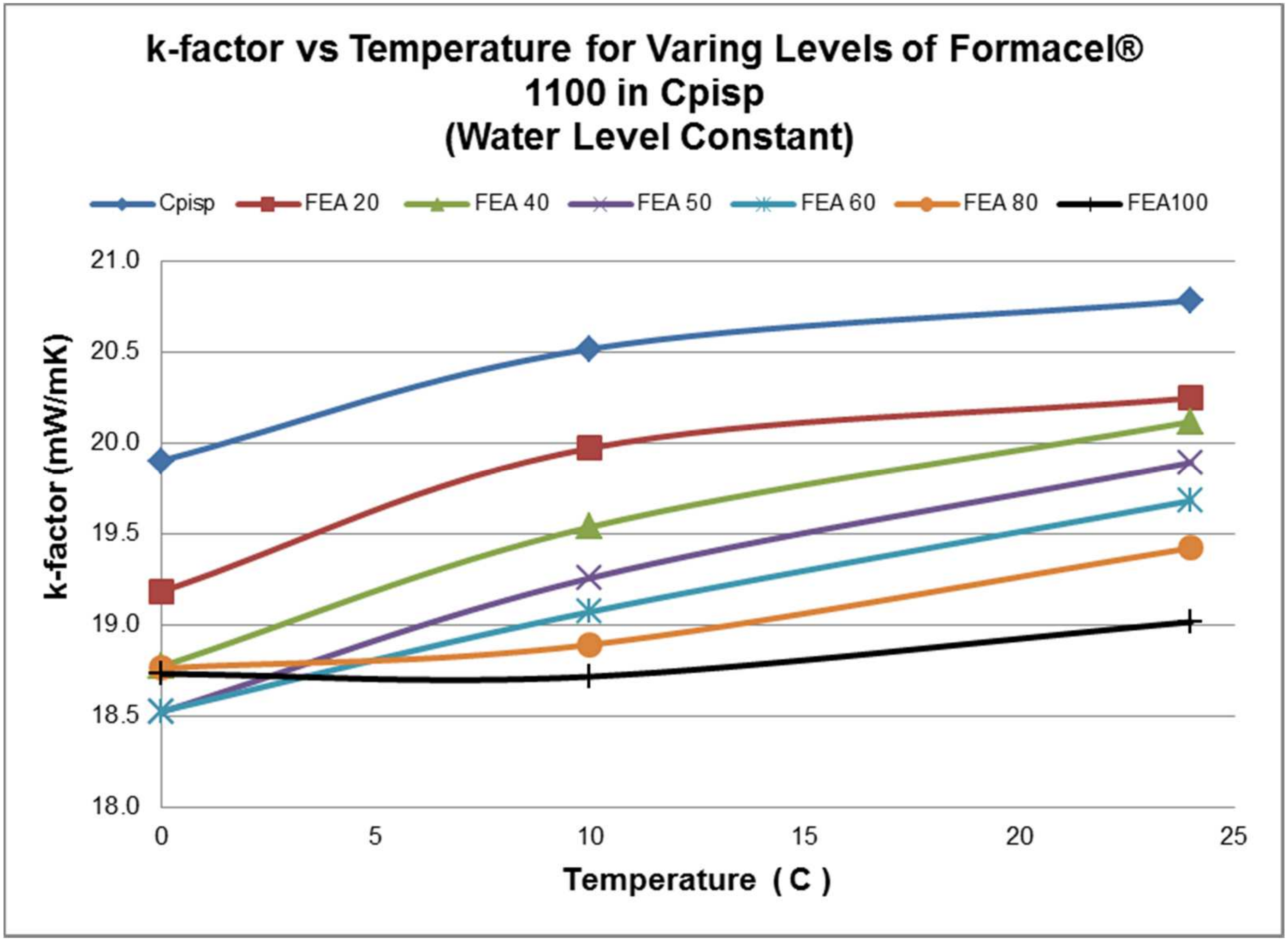
Experimental Work

- **Bench scale experiments by DuPont [1, 2]**
  - ➢ **1336mzz blends improved k-factor**
  - ➢ **1336mzz at reduced level provided equivalent or improved k-factor performance**
- **High pressure machine experiments by Dow Chemical [3]**
  - ➢ **1336mzz was dropped into an appliance formulation using cyclo-/iso-pentane (Cpisp) blend**
  - ➢ **The molar ratio of 1336mzz was varied from 100% to 0% as designated as FEA100, FEA80, FEA60, FEA50, FEA40, FEA20 and FEA zero (100% Cpisp)**
  - ➢ **Several performance advantages were identified**

1. *Loh, G., Creazzo, J., Robin, M.L., "Further Development of FEA-1100 – a Zero ODP and Low GWP Foam Expansion Agent", Proceedings of 2011 Blowing Agents and Foaming Processes, Dusseldorf, Germany*
2. *Loh, G., Creazzo, J., Robin, M.L., "Formacel® 1100: A Zero ODP and Low GWP Foam Expansion Agent", Proceedings of 2012 Polyurethanes Technical Conference, Atlanta, GA, USA*
3. *Rose, M., Altoe, P., Parenti, V., Riccio, R., "Assessment of Formacel® 1100 (FORMACEL®) Blowing Agent in Rigid Polyurethane Insulating Foams for Domestic Appliance", Proceedings of 2012 Polyurethane Technical Conference, Atlanta, GA, USA*

k-factors

- **Reduced k-factor at various Formacel® 1100 levels**
- **Potential k-factor improvement with reduced Formacel® 1100 usage**



Summary of options for PU foam

- **Established HFC's and blends as alternatives for HCFCs available**
  - **Based on 245fa or 365mfc/227ea**
  - **HFO 1336mzz for high performance applications**

- **Future**
  - **HFO's**
  - **like e.g. 1336mzz**
    - **Low GWP**
    - **No ODP**
  - **paradigm change: reduced environmental footprint <u>and</u> improved performance**
  - **improved performance for HC blown foams**
  - **1336mzz capacities in ramp up status**

Acknowledgement:

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Dow Brazil Sudeste Industrial

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Japanese Urethane Foam Association

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