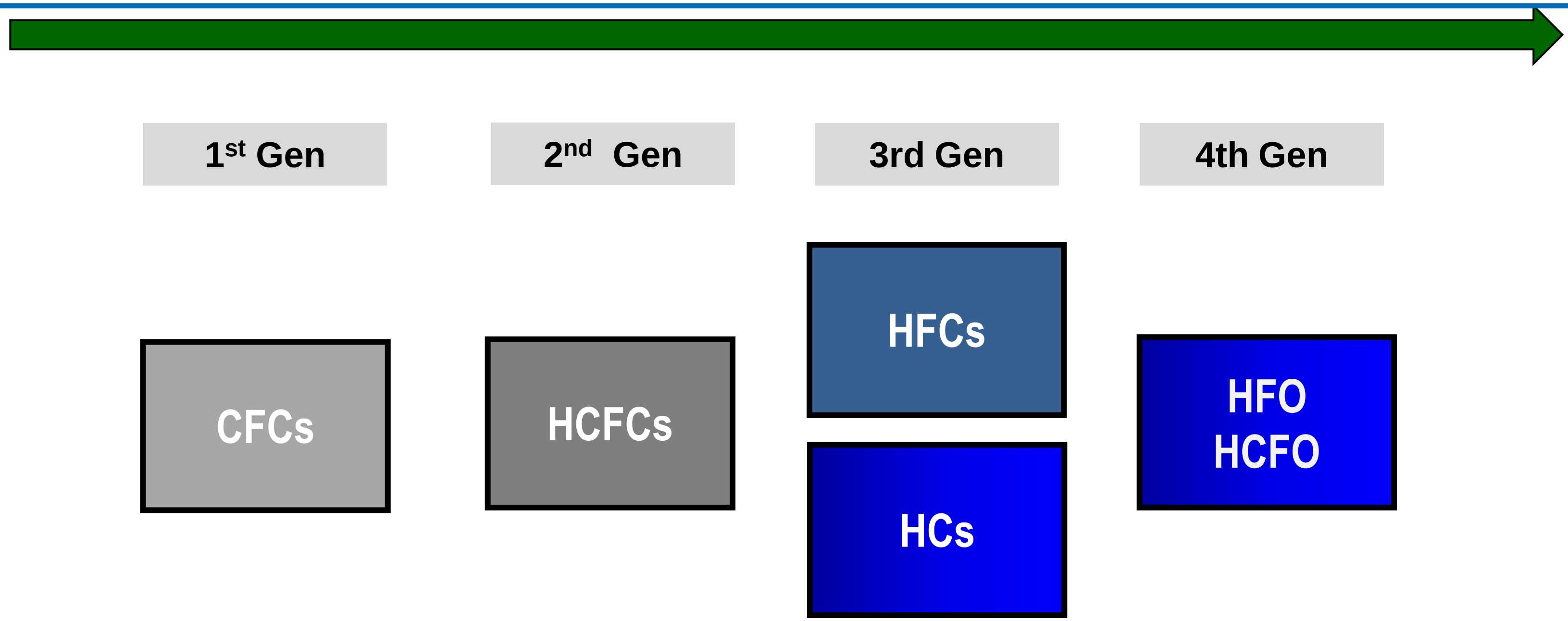
Formacel®1100 – a Foam Expansion Agent with Unique Characteristics for Polyurethane Foam Applications

Trend of Foam Expansion Agent (Blowing Agent) Transition

More stringent environmental & energy requirements



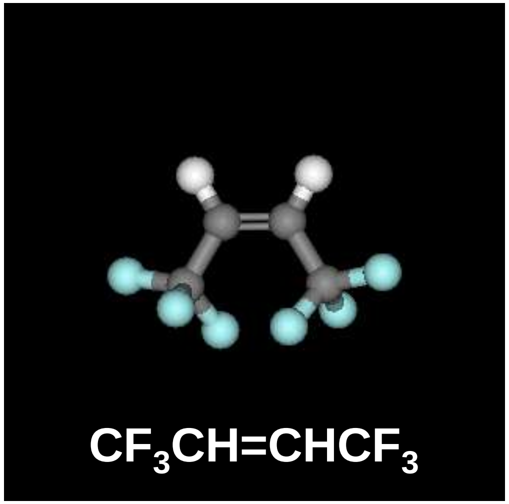
Industry Needs for the 4th Generation Solutions

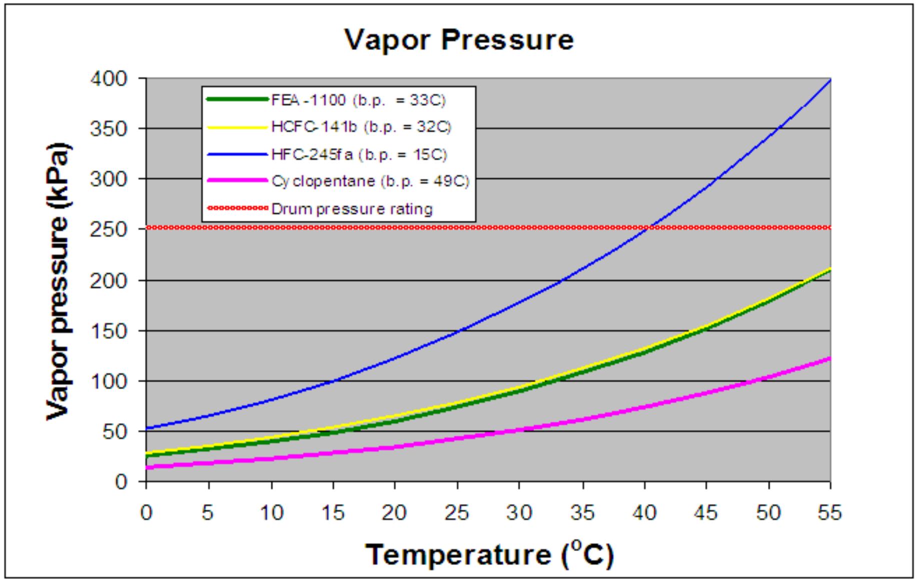
- Environmental Sustainability
- Energy Efficiency
- Cost

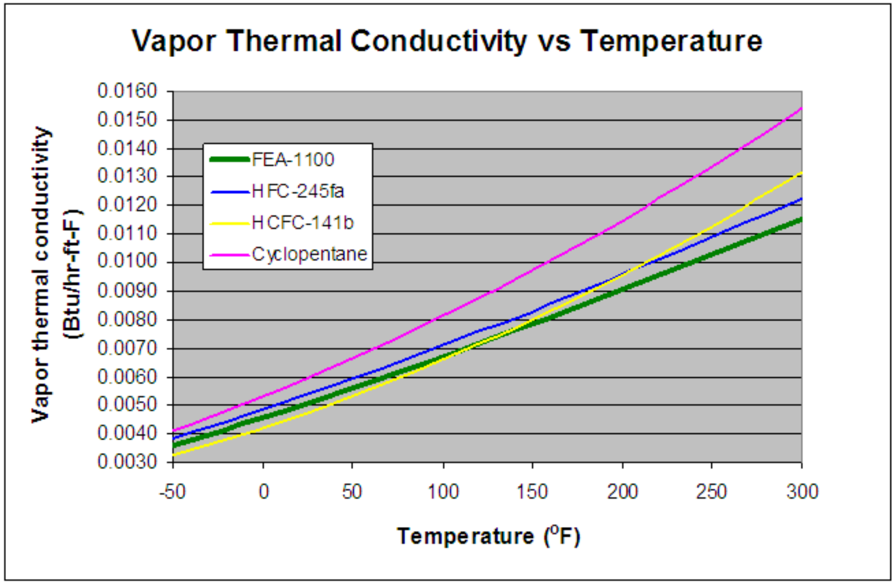
Formacel® 1100 – A Sustainable & Balanced Option

- ODP : 0 (No Chlorine)
- GWP 100 yr ITH : 2 (AR 5)
- Atmosphere Lifetime: 22 days (NOAA)
- VOC: None*

*Expected based on low MIR or POCP value

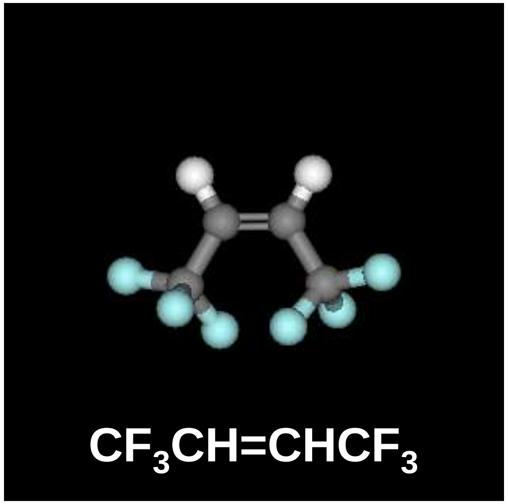






HFO-1336mzz-Z – Excellent Environmental Profile

- ODP : Zero
- GWP $_{100\ yr\ ITH}$: 2 (AR5)
- Atmosphere Lifetime: 22 days (NOAA)
- VOC: None*
- Non flammable
- Stability
- Low thermal conductivity (10.7)



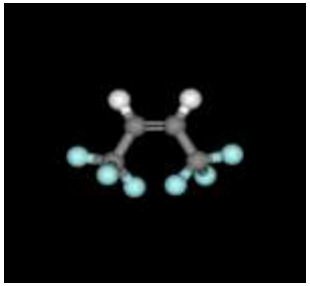
HFO-1336mzz-Z is a Zero ODP and low GWP version HCFC-141b

Foam Expansion Agent	MIR (g O_3/g)
HFO-1336mzz-Z	**0.04**
Methyl Formate	0.06
HFO-1234ze	0.1
HFO-1234yf	0.28
n-Pentane	1.31
Isopentane	1.45
Cyclopentane	2.39
Ethane	**0.28**

**Expected based on low Maximum Incremental Reactivity*

Formacel® 1100 – Unique Properties

- **Environmental sustainability**
- **Cost**
- **Energy efficiency**



Property	Formacel® 1100	HCFC-141b	HCFO-1233zd	HFC-245fa	Cyclopentane
Molecule Structure	$CF_3CH{=}CHCF_3$	CCl_2FCH_3	$CHCl{=}CHCF_3$	$CF_3CH_2CHF_2$	$(CH_2)_5$
ODP	0	**0.11**	**0.0003**	0	0
GWP(100yr ITH)	2 [1]	**782** [1]	1[1]	**858**[1]	11
VOC	No [2]	No	No	No	Yes
Exposure Limits (ppm)	500[3]	500	800	300	600
Flammability	No	No	No	No	**Yes**
Boiling Point (C)	33	32	**19**	**15**	49
Molecular weight	**164**	117	130	134	70.1
Lambda @ 25 C (mW/mK)	10.7	9.7	10.2[4]	12.7	**13**

[1] GWP 100 YR (AR 5) 100
[2] Expected based on low MIR Value MIR
[3] AEL is DuPont Acceptable Exposure Limits (8-12 hr TWA)
[4] Honeywell Solstice™ Liquid Blowing Agent Technical Information Table 1 Vapor Thermal Conductivity(mW/mK) at 20C

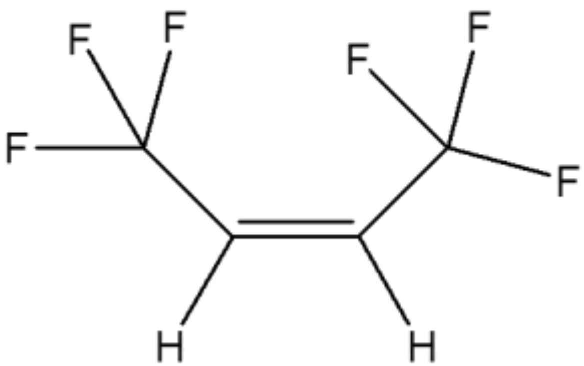
What is the unique characteristics of Formacel®1100 compared to other commercially available FEAs ?

Customer Evaluations

- Drop-in performance for various applications (HCFC and HFCs)
- Physical stability (up to 9 months)
- Chemical stability (up to 9 months)
- Insulation performance (initial & aged k-factors)
- Energy efficiency (appliance test)
- Other foam properties (dimensional stability, mechanical properties..)
- Use in blends to balance insulation performance & cost

Unique Characteristics for Ambient Temperature Applications

- Unique chemical stability
- Less molar usage with improved insulation performance
- Improved foam properties



Formacel®1100 (HFO-1336mzz-Z , $CF_3CH=CHCF_3$)

Construction Applications

Unique Chemical Stability in Foam Systems (DuPont Lab)

No reactivity or density increase after 6 month storage at 50^{o}C

Formacel®1100 Stability in Polyether System - 6 Month Storage at 50° C

Days at 50 °C in Oven	Cream time (seconds)	Tack free (seconds)	Ratio (Tack free /Cream time)	Foam density (pcf)
0	25	90	3.6	2.1
4	20	90	4.5	2.2
21	21	110	5.2	2.2
53	23	100	4.3	2.4
89	25	75	3.0	2.6
122	27	120	4.4	2.6
150	28	100	3.6	2.2
187	28	100	3.6	1.9

Formacel®1100 Stability in Polyester System - 6 Month Storage at 50° C

Days at 50 °C in Oven	Cream time (seconds)	Tack free (seconds)	Ratio(Tack free /Cream time)	Foam density (pcf)
0	25	90	3.6	2.5
15	30	110	3.7	2.4
47	20	130	6.5	2.3
83	25	135	5.4	2.6
116	27	120	4.4	2.2
144	30	100	3.3	2.4
181	30	100	3.3	2.2

Unique Chemical Stability in Foam Systems (Customer Confirmation)

Similar chemical stability compared to HFC-245fa after 6 months at room temperature

	HFC-245fa (Initial)	HFC-245fa (6 months)	Formacel® 1100 (Initial)	Formacel® 1100 (6 Months)
Cream Time (s) (Visual)	0.9	**1.3**	0.9	**1.3**
Gel Time (s) (Visual)	5.5	**5.3**	5.5	**5.4**
Tack Free (s) (Visual)	10.5	**9.6**	10.2	**10.5**
Density (kg/m^3) (ASTM D1622)	33.32	**37.8**	35.24	**37.16**
% closed cell (ASTM D6226)	88.65	**91.1**	89.24	**90.38**

Less Molar Usage - Customer Demonstration (Spray Foam)

Equal-weight substitution: 18-29 mole% less FEA usage with improved insulation performance

	HCFC-141b	Formacel®1100 in HCFC-141b formulation	HFC-245fa	Formacel®1100 in HFC-245fa formulation
pbw based on 100 pbw Polyol				
FEA	**19.0**	**19.0**	**9.0**	**9.0**
H_2O	0.3	0.3	1.8	1.8
Foam Properties				
Foam density (kg/m^3)	43.4	38.5	44.2	45.6
Initial k-factor at 23 ^oC (mW/mK)	20.1	19.3	23.0	22.6
Relative k-factor	**Control**	**-4%**	**Control**	**-2%**
Closed cell %	93%	94%	98%	99%
Molecular weight	117	164	134	164
Relative Formacel®1100 reduction vs equimolar substitution	**Control**	**-29%**	**Control**	**-18%**

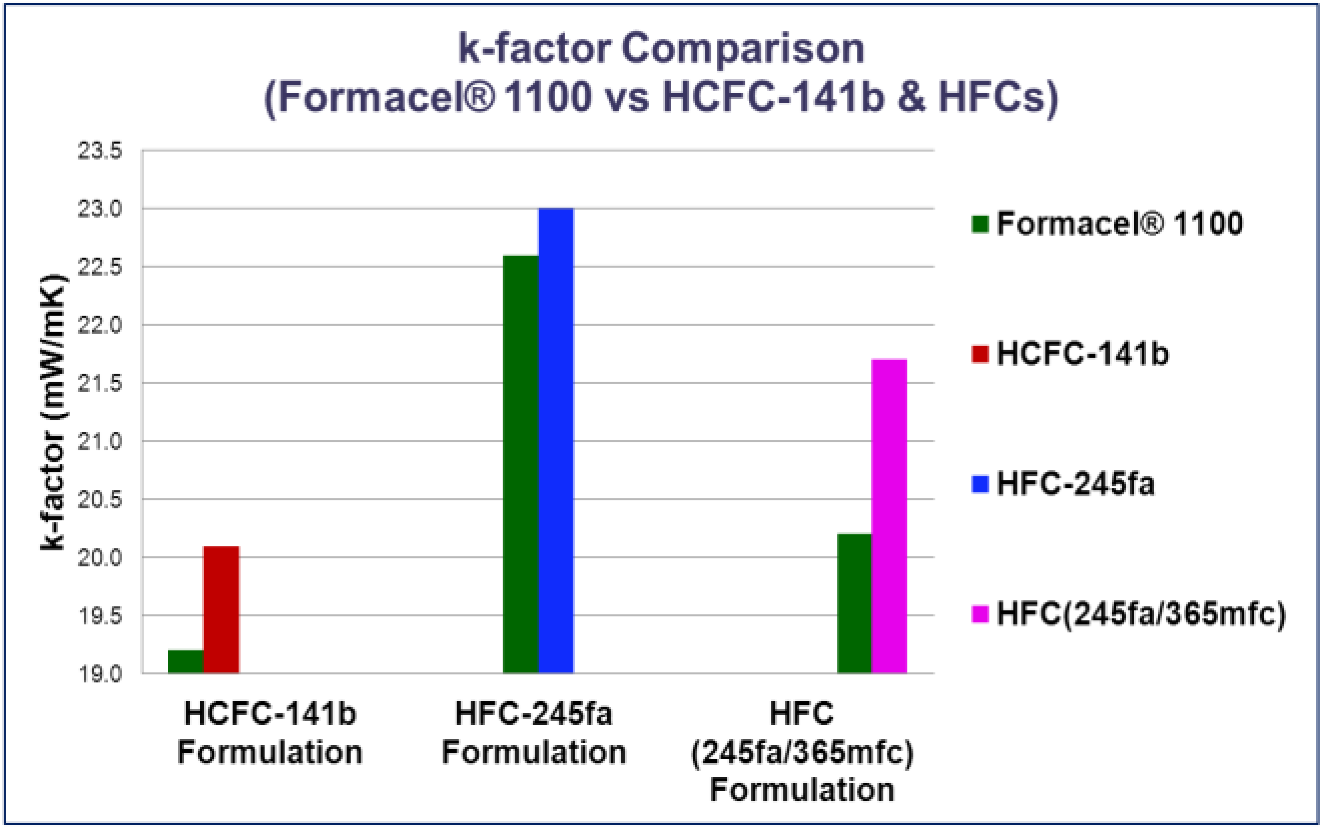
Less Molar Usage - Customer Evaluation (Panel Foams)

Equal-weight substitution : 14-40 mole% less FEA usage with improved insulation performance

	HCFC-141b	HFC-245fa	HFC-365mfc	Formacel®1100
Foam density (kg/m^3)	40.1	40.3	40.2	39.8
Core density (kg/m^3)	37.6	39.0	38.7	38.4
k-factor at 23 ^{o}C (mW/mK) – initial	20.5	20.8	21.2	19.9
Relative k-factor vs HCFC-141b-initial	**Control**	**1%**	**3%**	**-3%**
k-factor at 23 ^{o}C (mW/mK) - 28 days	23.1	22.3	22.9	21.3
Relative k-factor vs HCFC-141b-28 days	**Control**	**-3%**	**-1%**	**-8%**
Closed cell %	0.9	0.9	0.9	0.9
Molecular weight	117	134	148	164
Relative Formacel®1100 reduction vs equimolar substitution	**Control**	**-14%**	**-26%**	**-40%**

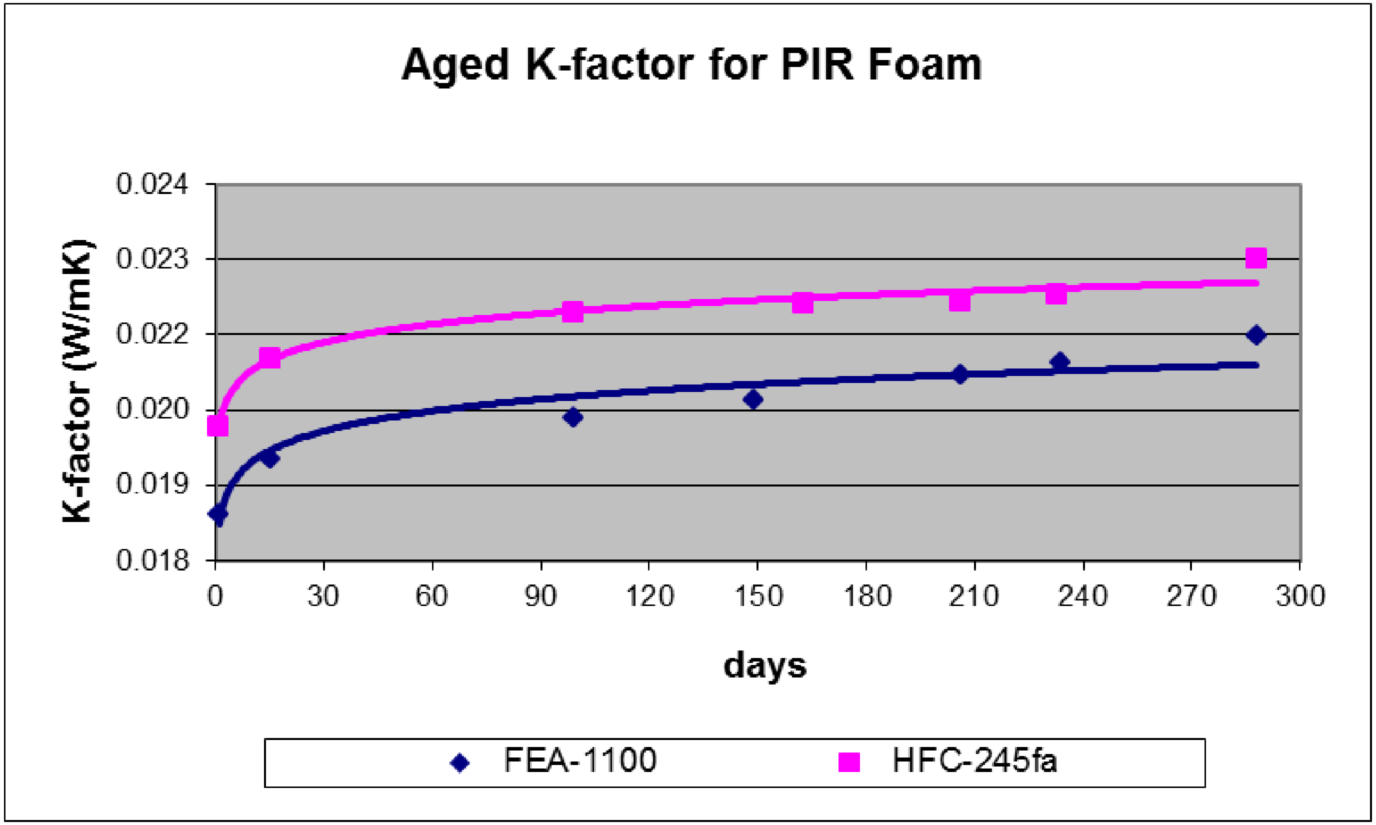
Improved k-factors in Various Foam Systems (Customer Evaluation)

Formacel® 1100 demonstrated 7%-16% k-factor improvement in various spay foam tests



Foam Properties with Aging (DuPont Lab)

Superior insulation performance maintains with aging



Spray Foam Properties with Aging (Customer Foams)

Superior insulation performance after aging

Aged k-factor after 5 Years (32 kg/m³ Spray Foam)		
	HCFC-141b	**Formacel® 1100**
Initial	18.5 mW/m°K	18.6 mW/m°K
4 years (23C) 4	26.9 mW/m°K	24.3 mW/m°K
5 years (23C) 5	27.1 mW/m°K	24.6 mW/m°K

Unique Characteristics for Cold Temperature Applications

- **Blends - less Formacel®1100 usage and better cold temperature insulation**
- **Drop-in to HC systems with reduced foam cost**
- **Good liner compatibility**

Formacel®1100 –H2O Blend (DuPont Lab)
Formacel®1100

Formacel®1100 blends reduce k-factors and FEA usage

Formulation	Formacel®1100 (0.21 Moles)	Formacel®1100-H2O Blend (0.14 Moles)
Polyols and additives (pbw*)	109.9	109.9
Water (pbw)	**2.5**	**3.8**
Formacel®1100 (pbw)	**34.6**	**23.0**
Moles of H_2O	0.14	0.21
Moles of Formacel®1100	0.21	0.14
Isocyanate	169	191
Foam index	1.1	1.1
Initial Foam Properties		
Density (kg/m^3)	28.7	27.9
K-factor (mW/mK) at 24 °C	20.6	20.4
K-factor (mW/mK) at 10 °C	19.6	19.2
K-factor (mW/mK) at 1.7°C	19.4	18.7
Relative k-factor Changes		
K-factor (mW/mK) at 24 °C	**Control**	**-1.1%**
K-factor (mW/mK) at 10 °C	**Control**	**-2.3%**
K-factor (mW/mK) at 1.7 °C	**Control**	**-3.7%**
Relative FEA Changes		
Formacel®1100 (pbw)	**Control**	**-34%**

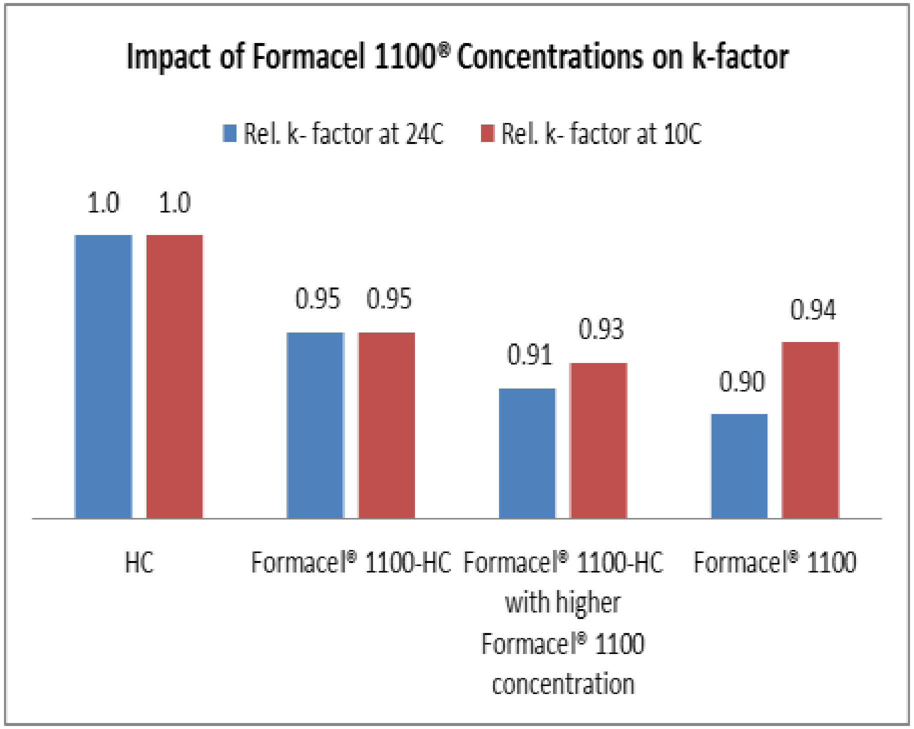
Formacel®1100 –H2O Blend (Customer Evaluation)
Formacel®1100

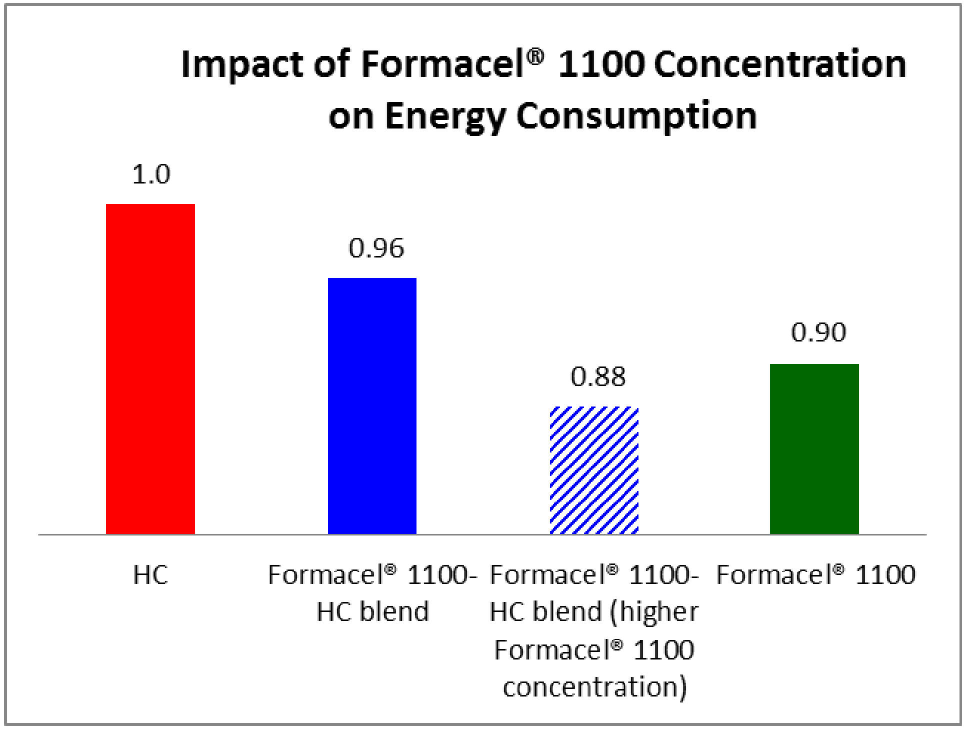
5.4% lower k-factor at 1.7C and 19 % less FEA usage

Ingredients	75 mole % Formacel® 1100	54 mole % Formacel® 1100 (Formacel®1100-H2O Blend)
Polyol and Additive(pbw)	100	100
Water (pbw)	**1.31**	**2.81**
Formacel®1100 (pbw)	**36.8**	**29.9**
Initial Foam Properties		
Density(kg/m^3)	31.7	29.4
k-factor(mW/mK) at 24 °C	19.3	19.3
k-factor (mW/mK) at 1.7 °C	18.6	17.6
Relative k-factor Changes		
k-factor(mW/mK) at 24 °C	**Control**	**0.0%**
k-factor (mW/mK) at 1.7 °C	**Control**	**-5.4%**
Relative FEA Changes		
Formacel®1100 (pbw)	**Control**	**-19%**

Formacel® 1100 – HC blends (Whirlpool Trial)

Lowest k-factor and energy consumption

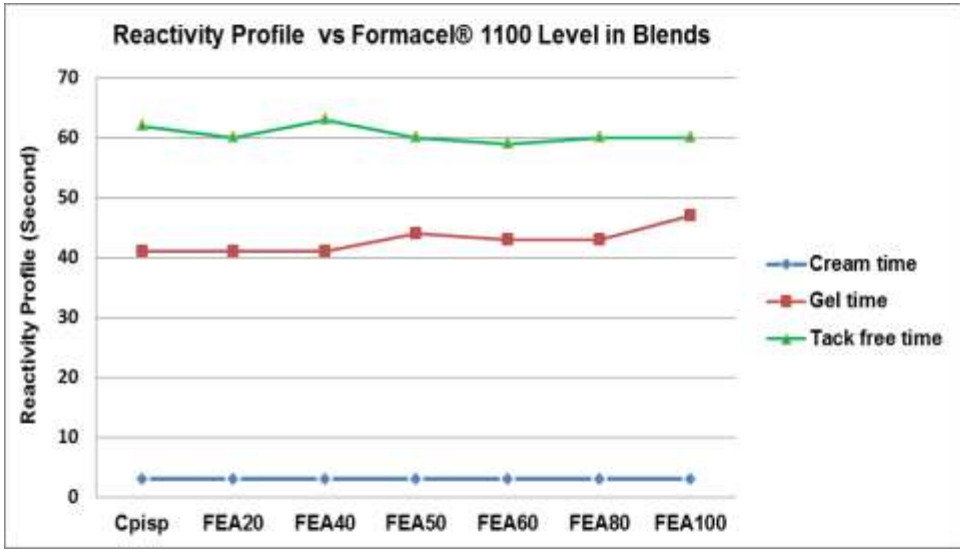


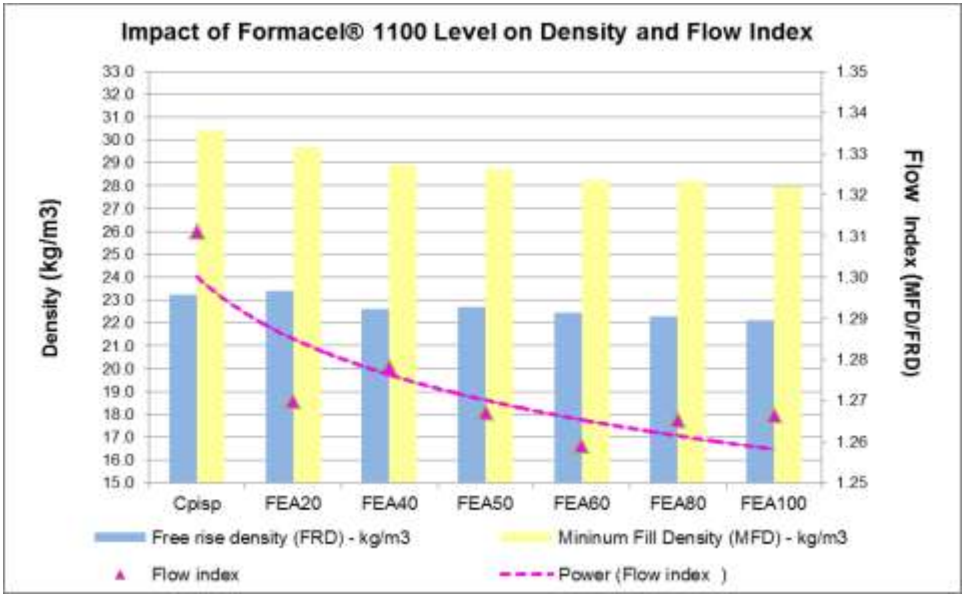


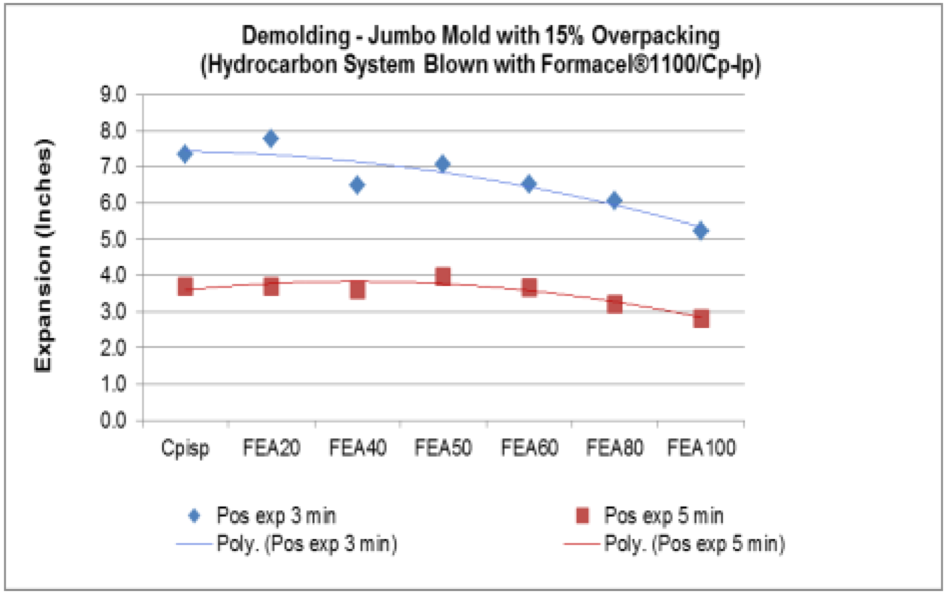
* Thomas,G., Altoe,P, Loh, G., Torio, A.,"Formacel® 1100: A Zero ODP and Low GWP Foam Expansion Agent for the Appliance Industry", Proceedings of 2013 Polyurethane Technical Conference, Phoenix, AZ, USA

Foam Processing (Dow Lab)

Potential drop – in with reduced foam cost and demold time







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Foam Processing (Whirlpool Production Line Test)

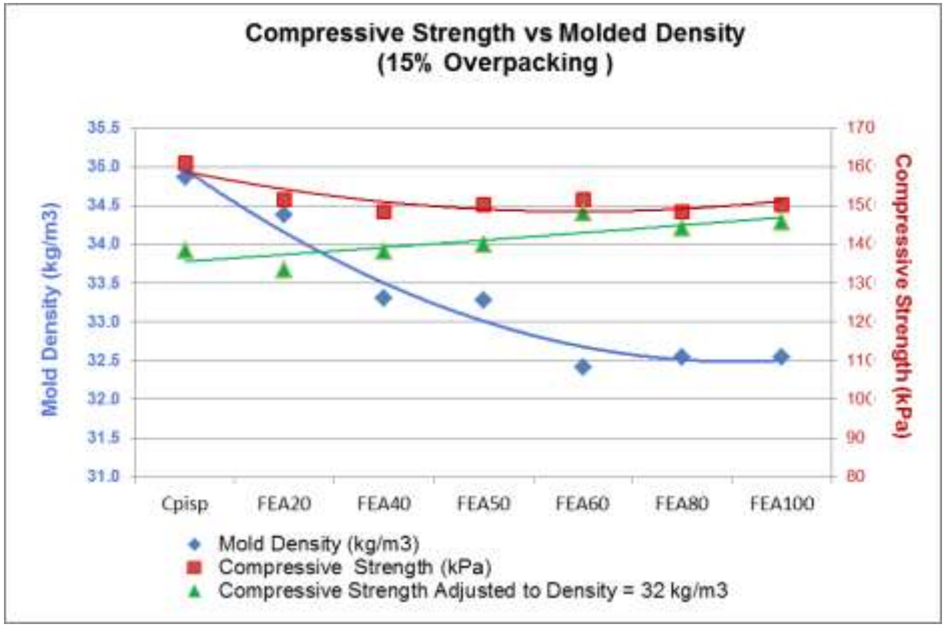
- **Formacel® 1100 was dropped into a commercial HC process/formulation without modification/optimization**
- **Refrigerators were built using Formacel® 1100 & Formacel® 1100-HC blend without process or productivity issue**
- **Reduced 4 - 6% foam shot weight (improved foam cost effectiveness)**

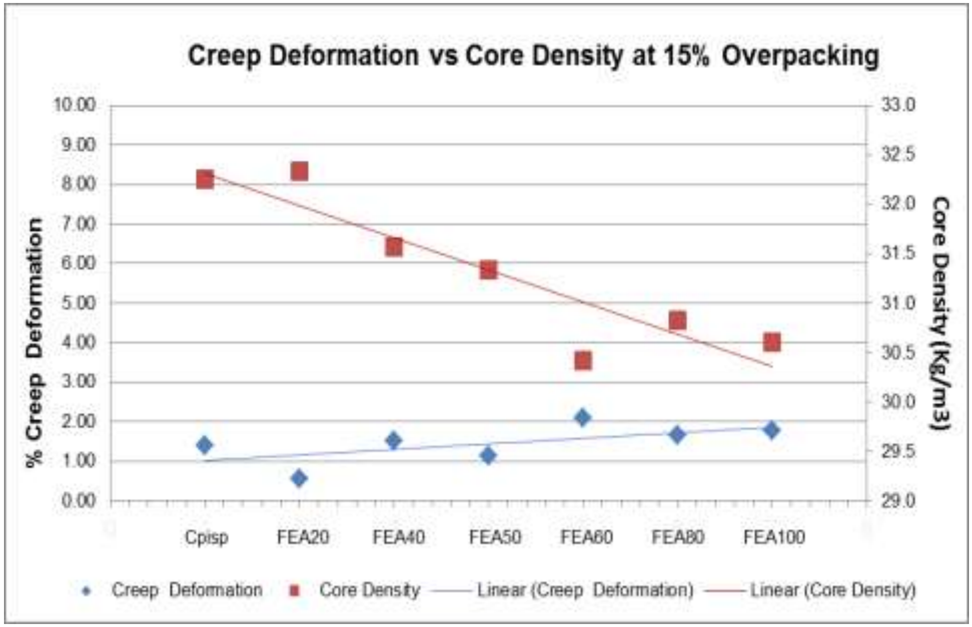
	HC	Formacel ®1100 -HC blend	Formacel® 1100
Total output rate (g/sec)	1255	1255	1255
Injection pressure (kg/cm²)	140 - 150	140 - 150	140 - 150
Mold/fixture temperature (ºC)	40 - 50	40 - 50	40 - 50
Chemical material temperature (ºC)	20 - 23	20 - 23	20 - 23
Demold time	Control	Identical	Identical
Gel time	Control	Within 10%	Within 10%
Foam flow	Control	Better	Much better
Foam shot weight	Control	**-4%**	**-6%**

* Thomas,G., Altoe,P, Loh, G., Torio, A.,"Formacel® 1100: A Zero ODP and Low GWP Foam Expansion Agent for the Appliance Industry", Proceedings of 2013 Polyurethane Technical Conference, Phoenix, AZ, USA

Foam Properties (Dow Lab)

- Comparable compressive strength and creep deformation at reduced density
- Potential density reduction without negative impact on foam properties





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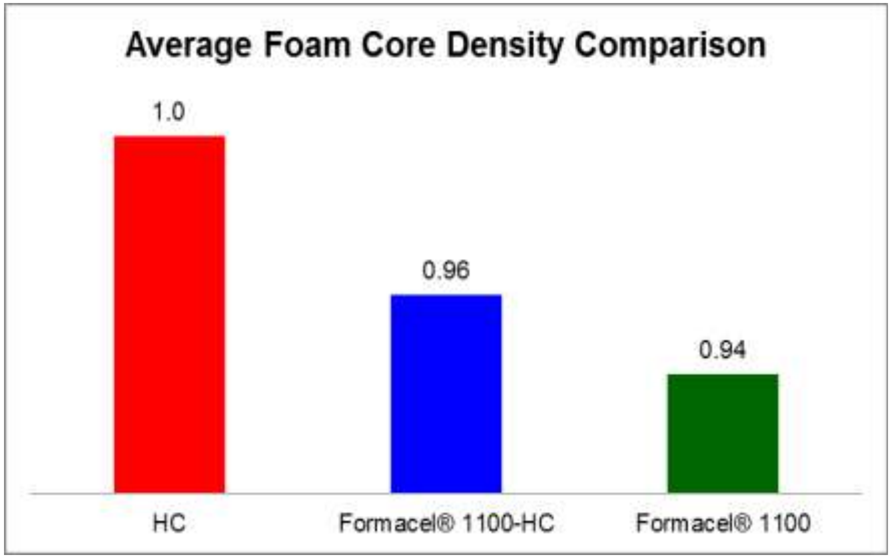
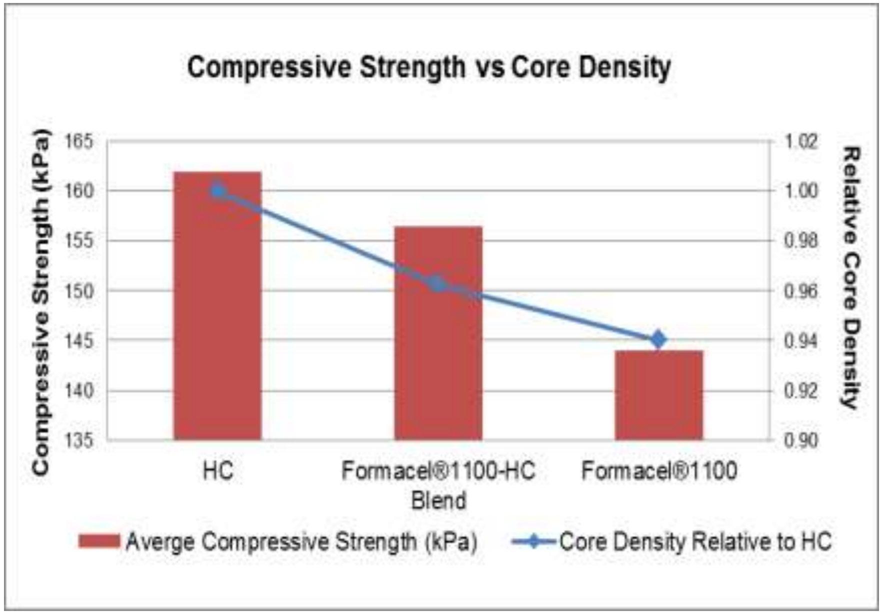
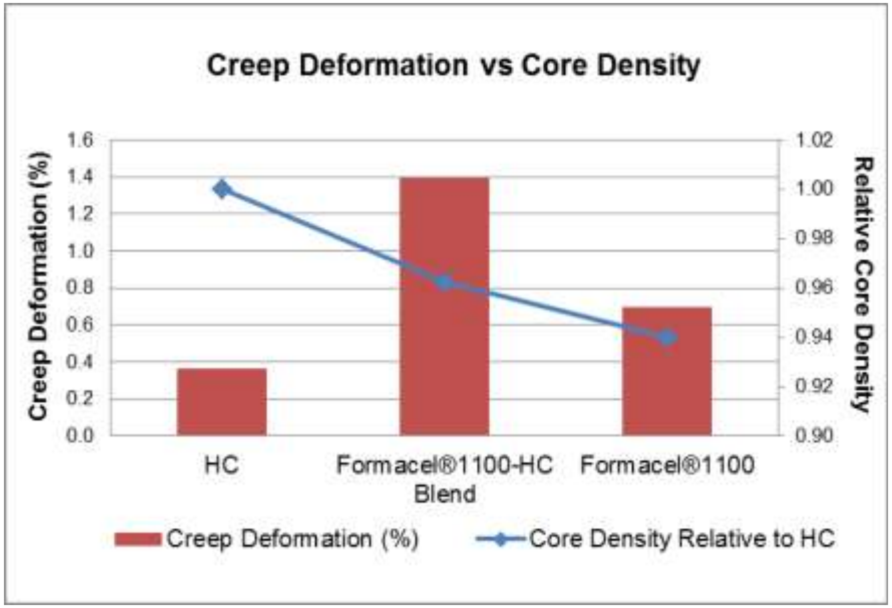
Foam Properties (Whirlpool Trial)

Less foam usage without negative impact on foam properties







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Material Compatibility – Plastics (DuPont Lab)

Formacel-1100 is compatible with commonly used plastics

Changes after 2 weeks at room temperature in Formacel®1100

Symbol	Material	Brand	% Weight Change	% Volume Change	% Hardness Change
ABS	Acrylonitrile-butadiene-styrene	Cycolac®EX58	-0.1%	-0.6%	0.0%
HIPS	High Impact Polystyrene		0.3%	-0.4%	-2.9%
PET	Poly(ethylene terephthalate)	Rynite®	0.0%	0.7%	-1.2%
PS	Polystyrene	Styron®	-0.4%	0.9%	0.0%
PVC	Polyvinyl Choloride	Bakelite®	0.0%	0.0%	0.0%
CPVC	Chlorinated Polyvinyl Choloride		0.0%	-0.3%	0.0%
PTFE	Fluorocabon(PTFE)	Teflon ®	1.1%	0.3%	-17.2%
ETFE	Fluorocabon(ETFE)	Tefzel®	0.7%	0.0%	12.9%
	Ionomer	Surlyn®	0.3%	0.0%	1.9%
POM	Acetal	Delrin®	0.1%	-1.2%	-1.3%
PC	Polycarbonate	Tuffak®	0.0%	-0.6%	0.0%
PEEK	Polyetheretherketone	Victrex®	0.0%	0.2%	0.0%
	Polyarylate	Arylon®	0.2%	-0.2%	-4.4%
LCP	Polyester	Xydar ®	0.0%	-0.4%	-1.5%
	Nylon 6/6	Zytel® 101	0.4%	-0.5%	3.1%
PEI	Polyetherimide	Ultem®	-0.1%	0.0%	0.0%
	Polyaryl sulfone	Radel®	-0.2%	0.3%	0.0%
PVDF	Poly(vinylidene fluoride)	Kynar®	0.1%	-0.3%	0.0%
PP	Polypropylene	Tenite®	0.3%	-0.5%	0.0%
	LCP	Zenite	-0.1%	-0.9%	0.0%
HDPE	High Density Polyethylene	Alathon ®	0.0%	0.3%	3.3%
	Phenolic	Duzez®	0.0%	-0.1%	1.2%

Liner Compatibility(Whirlpool Trial)

- High impact polystyrene (HIPS) used in the refrigerator model
- Thermal cycle test
  - Refrigerators were heated to 50˚C for 10 hours then cooled to -23˚C for an additional 10 hours
  - The cycle was repeated for 8 days
- Comparable performance for refrigerators using Formacel 1100® & Formacel 1100®-HC blend
  - No visual defects such as blistering or cracking
  - Comparable to HC baseline

Unique Characteristics for High Temperature Applications

- Typical Applications
  - Pipelines and tanks
  - Water heaters
- Unique characteristics of Formacel®1100
  - No chlorine in molecule –no HCl corrosion
  - Good chemical stability for high temperature insulation
  - Good insulation performance

Chemical Stability for High Temperature Insulation – a Study by F.V.V. de Sousa [5]

- Observations
  - Increased halide content (not related to flame retardant) at 120°C
  - Increased metal corrosion caused by foams aqueous extracts at 120°C
- Recommendations
  - Control raw materials used for foams production - mainly the Cl concentration
  - Control the pH of the metal/foam interface

[F.V.V. de Sousa "Characterization of corrosive agents in polyurethane foams for thermal insulation of pipelines" Electrochimica Acta 52 (2007)

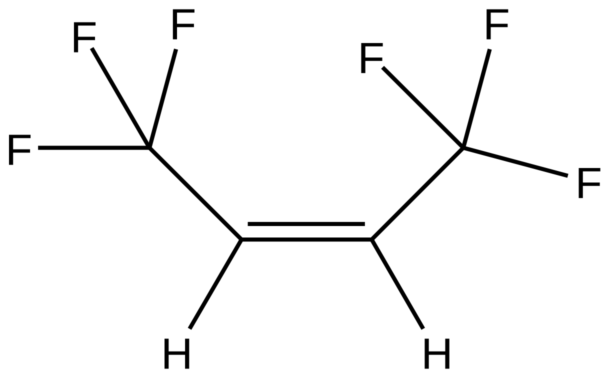
Table 2
Chemical analysis of the foams aqueous extracts obtained at 80 and 120 °C

Commercial foams	$T = 80\,°C$					$T = 120\,°C$				
	pH	k (μS/cm)	F^- (ppm)	Cl^- (ppm)	PO_4^{-3} (ppm)	pH	k (μS/cm)	F^- (ppm)	Cl^- (ppm)	PO_4^{-3} (ppm)
HCFC with FR	6.12	60.8	0.3	4.0	<0.5	3.30	293.0	5.7	30.4	<0.5
HCFC without FR	6.15	69.4	0.2	3.0	<0.5	3.31	277.0	5.2	26.3	<0.5
CFC with FR	6.23	44.0	0.2	4.0	<0.5	7.59	99.5	0.7	23.5	<0.5
CFC without FR	6.58	25.7	0.4	9.0	<0.5	7.57	70.0	0.4	15.1	<0.5
CO_2 with FR	8.75	87.8	0.7	8.0	18.4	9.01	186.0	0.3	10.0	23.1
CO_2 without FR	8.86	108.0	1.9	10.0	<0.5	9.02	191.0	0.2	12.0	3.4

k: Conductivity, FR: flame retardant.

Chemical Stability of Formacel®1100

- Formacel®1100 ($CF_3CH=CHCF_3$) contains no Cl to contribute to HCl corrosion
- F forms the **strongest** carbon halogen (C-X) bond
- CF_3 groups in $CF_3CH=CHCF_3$ help stabilize the molecule by increasing bond strengths (high bond dissociation energies) on adjacent carbon atoms CF_3



Formacel®1100 (HFO-1336mzz-Z , $CF_3CH=CHCF_3$)

Bond Dissociation Energies of Ethanes

D^o(C-X)(Kcalmol^{-1})				
X	CH_3CH_2-X	CH_3CF_2-X	CF_3CH_2-X	CF_3CF_2-X
H	100.1	99.5	106.7	102.7
F	107.9	124.8	109.4	126.8
Cl	83.7	-	-	82.7
Br	69.5	68.6	-	68.7
I	55.3	52.1	56.3	52.3

Metal Compatibility Test at 100 °C(DuPont Lab)

Formacel®1100 showed good metal compatibility after 2 weeks of exposure at 100 °C

Metal Coupons	Metal Coupon Weight	Metal Coupon Appearance	FEA Solution Appearance	FEA Solution Analysis
Stainless Steel	No weight change	No sign of corrosion	Clear	No fluoride detected **
Carbon Steel	No weight change	No sign of corrosion	Clear	No fluoride detected **
Copper	No weight change	No sign of corrosion	Clear	No fluoride detected **
Brass	No weight change	No sign of corrosion	Clear	No fluoride detected **
Aluminum	No weight change	No sign of corrosion	Clear	No fluoride detected **

** Detection limit = 0.5 ppm

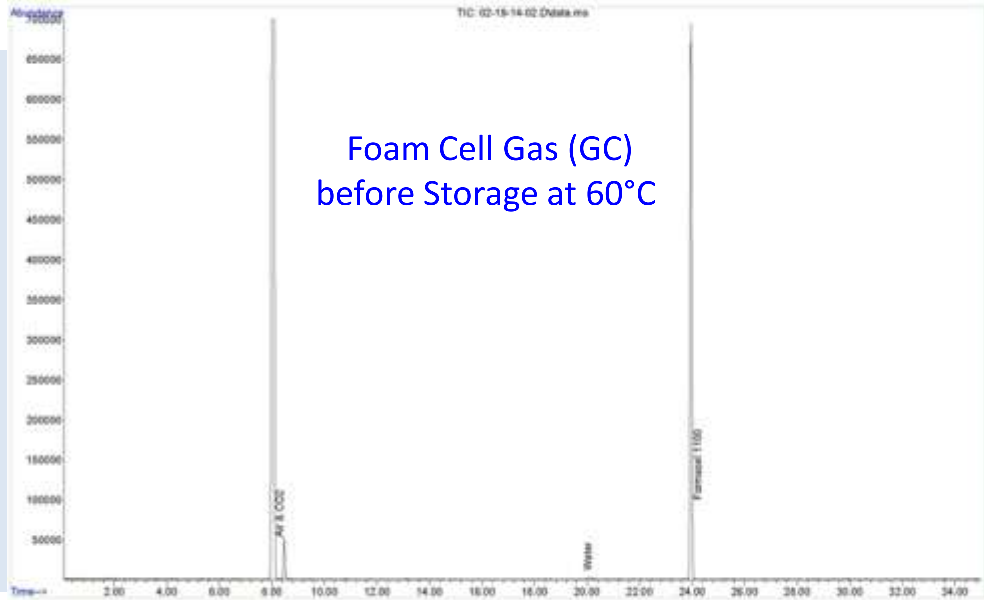
Formacel®1100 for High Temperature Application (DuPont Lab)

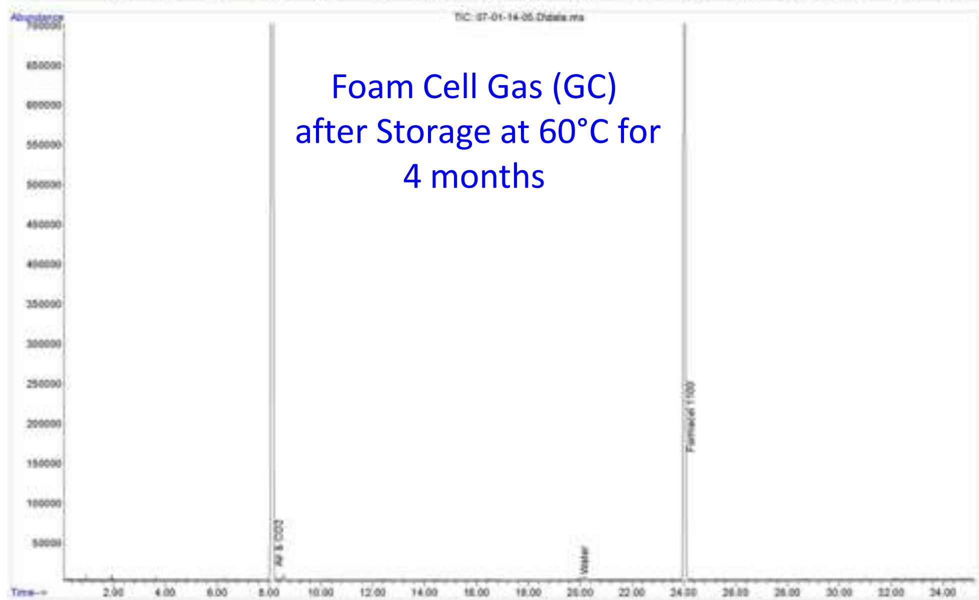
- Sealed tube test - carbon steel, copper and aluminum coupons immersed in HFO-1336mzz-Z (Formacel®1100) or HFC-245fa
- Aging at 250 ˚C for 7 days
- Negligible concentrations of fluoride ions based on ion chromatography analysis

		Without Air or Moisture Contamination		With Air and Moisture Contamination	
		HFC-245fa	HFO-1336mzz-Z (Formacel®1100)	HFC-245fa	HFO-1336mzz-Z (Formacel®1100)
Air	mm Hg	n/a	n/a	7.6	7.6
H2O	ppm	n/a	n/a	200	200
F-	**ppm**	**8**	**8**	**20**	**11**

Water Heater Application - Chemical Stability (DuPont Lab Study)

- Stored in a 60˚C oven for 4 months
- Foam cell gas was analyzed by GC at regular time intervals
- No additional peaks were detected (no degradation)

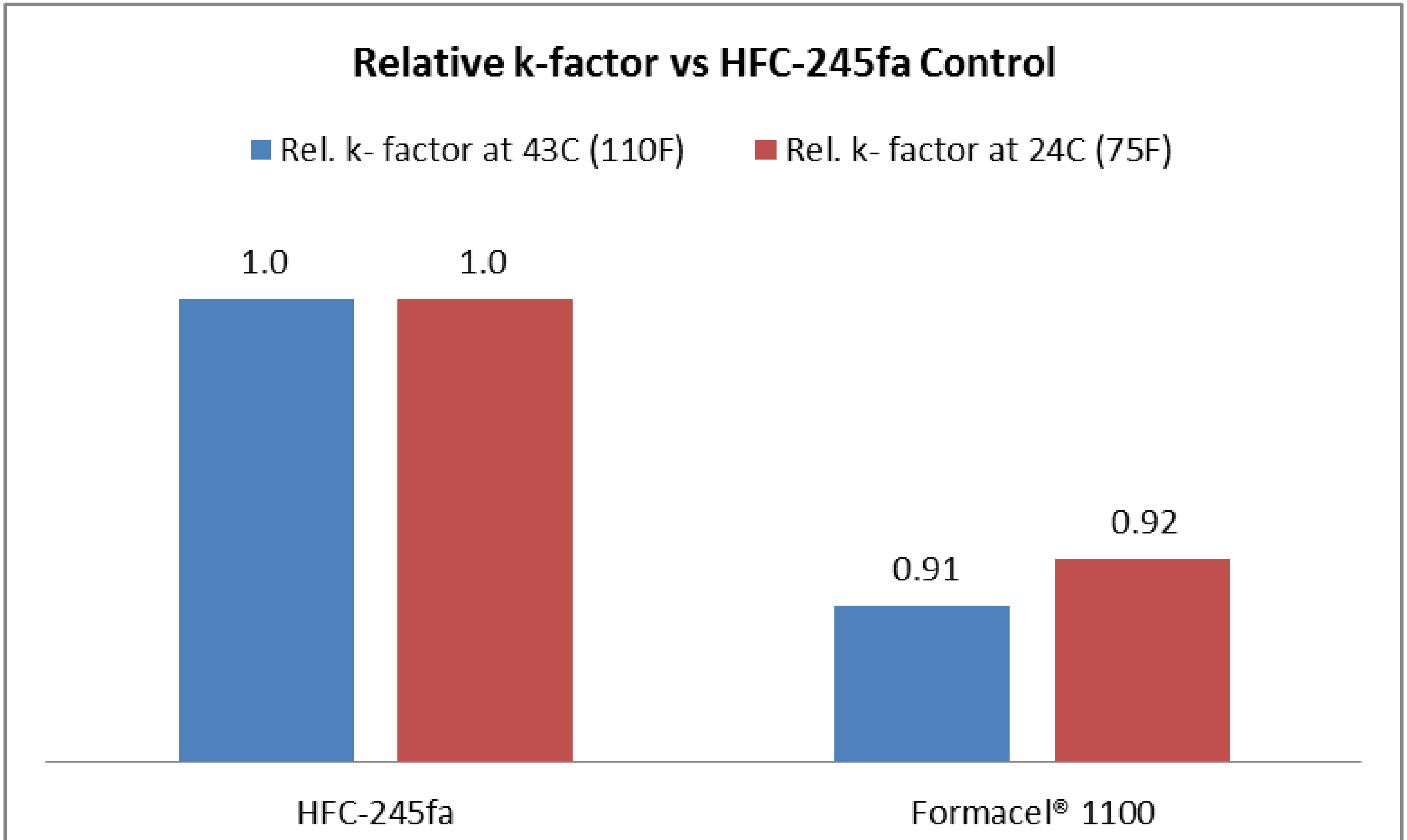




B-side Ingredients	Weight% (pbw)
Sucrose-based Polyol	45
Amine -based Polyol (TDA)	35
Aromatic Polyester	20
Silicon Type Surfactant	2.7
Amine-based Catalysts	3.9
Formacel®1100	**40.2**
Water	1.4
Isocyanate	142
Foam index	1.2

Water Heater Application – k-factors(Customer Evaluation)

8-9% k-factor improvement at 43°C and 24°C



Formacel®1100 Commercialization Status

- Customer Evaluation
  - Continued global interests for Formacel®1100
  - Customer feedback from global evaluation indicates significant improvement in performance vs. incumbent products
  - Samples are available for global customer evaluation
- Commercialization status
  - Semi-commercial plant : next weeks
  - Full-Scale production: 2H 2016
- Global regulatory approval status:
  - Approved : Asia (Japan, Korea, India) , Europe, US and Canada
  - In Progress: China, Australia

Summary

- Lab study and customer data revealed several unique characteristics of Formacel®1100
- Significant performance and cost benefits have been derived from these characteristics These unique characteristics of Formacel®1100 also indicate the great potential for Formacel®1100 optimization
- DuPont is in the process to commercialize Formacel®1100