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DEVELOPMENT PROGRAM UPDATE FOR LOW GWP FOAM EXPANSION AGENT

W H I T E P A P E R

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ABSTRACT

Polyurethane foams are widely employed for thermal insulation in the appliance and construction industries. Foam expansion agents (FEAs or blowing agents) are critical for providing the insulation performance of these foams. CFC-11 and HCFC-141b were once the FEAs of choice, but their use is being phased out due to their ozone depletion potential (ODP). The current zero ODP FEAs include hydrofluorocarbons (HFCs) and hydrocarbons, but these agents face further challenges. Both HFCs and hydrocarbons are characterized by increased thermal conductivities compared to both the HCFCs and CFCs, resulting in inferior insulation performance, and HFCs such as HFC-245fa and HFC-365mfc have global warming potentials (GWPs) near 1,000. In addition, the low boiling point of HFC-245fa and the flammability of hydrocarbons and HFC-365mfc present significant challenges to processing and handling. With the increased focus on global warming potential and energy efficiency, the industry is looking for a foam expansion agent that is environmentally sustainable with superior insulation performance.

DuPont Fluoroproducts introduces a novel foam expansion agent, FEA-1100, for polyurethane foams. FEA-1100 has zero ODP and low GWP. It is also non-flammable and a stable liquid at ambient temperature. This paper discusses the properties and characteristics of FEA-1100 for PUR applications such as appliance, pour-in place, spray and PIR boardstock. We will discuss recent results in toxicity evaluation, material compatibility, and foam properties, particularly insulation performance.

INTRODUCTION

In recent years concerns over climate change have intensified, and as a result the industry is seeking foam expansion agents not only characterized by zero ODP, but also by lower global warming potentials (GWPs) compared to those of the HFCs. In addition, the increased demand for energy efficiency also requires the FEAs to have low vapor thermal conductivity to produce foams with superior insulation performance. Taking these requirements into consideration, DuPont Fluoroproducts has developed a novel "Fourth-Generation" foam expansion agent FEA-1100. We report here further application studies on FEA-1100, including material compatibility and the performance of FEA-1100 with the major types of polyols employed for the manufacture of polyurethane foams. The results indicate that in addition to being characterized by improved environmental properties, FEA-1100 also provides superior insulation performance in foam applications. Data obtained to date also suggest that FEA-1100 can serve as a "drop-in" to replace other types of liquid FEAs with low conversion costs.

PROPERTIES OF FEA-1100

FEA-1100 has an excellent environmental profile. It is characterized by zero ozone depletion potential and low global warming potential. Recent estimates indicate that FEA-1100 has a short atmospheric lifetime of approximately 16 days.

FEA-1100 has low vapor thermal conductivity, providing excellent insulation performance.

FEA-1100 is non-flammable in standard ASTM tests. Testing according to ASTM E 681 Standard Test Method for Concentration Limits of Flammability of Chemicals (Vapors and Gases) indicated non-flammability at temperatures of 60°C and at 100°C. The non-flammability enables the safe use of FEA-1100 in a broad range of applications.

FEA-1100 is a stable liquid at room temperature, with a boiling point > 25°C. This eliminates the handling and processing issues associated with the use of lower boiling FEAs such as HFC-245fa, allowing optimal FEA level in formulations to provide desired foam properties.

Table 1 lists the properties of FEA-1100 and other FEAs. As shown in **Table 1**, the previous FEA transition sacrificed some desirable characteristics (low vapor thermal conductivity, high boiling point, and nonflammability) in exchange for improved environmental properties. FEA-1100 provides improved environmental properties while maintaining the desired characteristics of low vapor thermal conductivity, non-flammability and a boiling point above 25°C.

Table 1: Properties of Foam Expansion Agents

	CFC-11	HCFC-141b	HFC-245fa	HFC-365mfc	Isopentane	FE-1100
ODP	1	0.12	0	0	0	0
GWP (100 year ITH)	4750	725	1020	782	11	5
e gas 25°C mW/mK	8.4	9.7	12.7	10.5	13.3	10.7
Flash Point	non	none	none	-25.0°C	-51°C	none
bp °C	23.9	32.1	15.3	40.0	27.9	>25

TOXICITY ASSESSMENT

Toxicological testing performed to date indicates that FEA-1100 can be safely used in foam expansion applications. **Table 2** summarizes these toxicity assessments. Further toxicological testing is underway to evaluate the risks of longer term exposure.

Table 2: FEA-1100 Toxicological Assessments

Test	Results
ALC and LC-50	Very low acute toxicity
Skin Irritation	Non-irritating
Mutagenicity-Ames	Non-mutagenic
Chromosomal Aberration	No genetic material damage when tested in bacterial and mammalian cell cultures
Cardiac Sensitization	Favorable cardiac sensitization potential profile
28 day repeated inhalation	Favorable repeated inhalation profile

COMPATIBILITY WITH METALS

Compatibility tests for FEA-1100 with metals were performed in sealed tubes. Metal coupons (copper, brass, carbon steel, stainless steel and aluminum) were immersed in FEA-1100 and heated in an oven for 14 days at 100°C (212°F), and changes in weight and appearance of the metal coupons were recorded. The liquid solutions were also evaluated for appearance and decomposition products such as fluoride. As shown in **Table 3**, FEA-1100 is compatible with metals commonly employed in polyurethane foam processing. While these simple exposure tests help screen effects on materials of construction, the final materials selection should include testing more specific to the application.

Table 3: Metal Compatibility—2 Weeks Exposure to FEA-1100 at 100°C (212°F)

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

COMPATIBILITY WITH PLASTICS

Plastics compatibility tests were performed by exposing plastic materials to FEA-1100 at room temperature for two weeks. Weight, volume and hardness before and after the exposure were measured. Observations of changes are summarized in **Table 4**, which indicates that FEA-1100 is compatible with commonly employed plastics. As always, verifying compatibility using actually fabricated parts under end-user conditions is advised as the performance of plastics is affected by polymer variations, compounding agents, fillers and molding processes.

Table 4: Plastic Compatibility – 2 Weeks Exposure to FEA-1100 at Room Temperature

Symbol	Material	Brand	% Weight Change	% Volume Change	% Hardness Change
ABS	Acrylonitrile-butadiene-styrene	Cyclocac®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 Chloride	Bakelite®	0.0%	0.0%	0.0%
PTFE	Fluorocarbon(PTFE)	Teflon®	1.1%	0.3%	-17.2%
ETFE	Fluorocarbon(ETFE)	Tefzel®	0.7%	0.0%	12.9%
	Lonomer	Suryln®	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%

COMPATIBILITY WITH ELASTOMERS

Elastomeric materials were exposed to FEA-1100 at room temperature for 2 weeks, and changes in volume, weight and hardness were measured before and after the exposure. **Table 5** provides a summary of results which indicate that FEA-1100 is compatible with commonly employed elastomers. While these simple exposure tests help screen effects on materials of construction, final materials selection should include testing more specific to the application.

Table 5: Elastomer Compatibility—2 Weeks Exposure to FEA-1100 at Room Temperature

Symbol	Material	Brand	% Weight Change	% Volume Change	% Hardness Change
NR	Natural Rubber	Natural Rubber	4.4%	1.9%	0.0%
CR	Polychloroprene	Neoprene®W	0.8%	0.1%	0.0%
NBR	Acrylonitrile Butadiene	BUNA N	15.3%	2.6%	-13.6%
CSM	Chlorosulfonated Polyethylene	Hypalon 40®	0.2%	0.8%	-1.3%
FFKM	Fluoroelastomer	Kalrez®	7.9%	-3.4%	-2.9%
T	Polysulfide	THIOKOL FA®	0.3%	6.7%	-6.1%
IIR	Isobutylene Isoprene	Butyl Rubber	0.3%	13.1%	-13.3%
EPDM	Hydrocarbon (Ethylene-Propylene Terpolymer)	Nordel®	1.4%	5.5%	-7.1%

SOLUBILITY IN POLYOLS

One of the important considerations in using a new FEA in polyurethane (PUR) and polyisocyanurate (PIR) foams is its solubility with the foam system polyols. The solubility of FEA-1100 in polyols was tested at 21°C and at 50°C using commercially available polyols from several manufacturers. FEA-1100 was added to the polyols in 5% by weight increments, shaken to mix, and allowed to settle at test temperatures. The addition of FEA-1100 was repeated until the FEA-1100 weight percent reached 50% or until FEA-1100 no longer dissolved in the polyol and formed a separate layer. The maximum weight % of FEA in polyols for a single phase mixture is listed in **Table 6**, which demonstrates that FEA-1100 exhibits good solubility in a wide range of polyols.

Table 6: FEA-1100 Solubility in Polyols

Polyol Type	OH# (mg KOH/g)	Weight % in Polyols for Single Phase Mixture (21°C)	Weight % in Polyols for Single Phase Mixture (50°C)
Polyethers			
Amine	391–800	5–50+	40–50+
Sucrose/amine	400–499	50+	50+
Sucrose/glycol	440	50+	50+
Sucrose/glycerine	280–520	50+	50+
Sorbitol	490	50+	50+
Mannich-base	300–390	5–50+	29–50+
Polyesters			
	240–307	5–30	23–35

VAPOR PRESSURE IN POLYOLS

FEA-1100 vapor pressure tests in various polyols were performed at 50°C since FEA-1100 has very low vapor pressure at room temperature. The vapor pressure of FEA-1100 increases with its concentration in polyols and reaches a maximum as the solubility limit is approached. As shown in **Figure 1**, FEA-1100 vapor pressure at 50°C is well below the typical drum pressure rating of 22 psig. Good solubility and low vapor pressure allow higher FEA-1100 levels to be employed in formulations providing optimal foam properties.

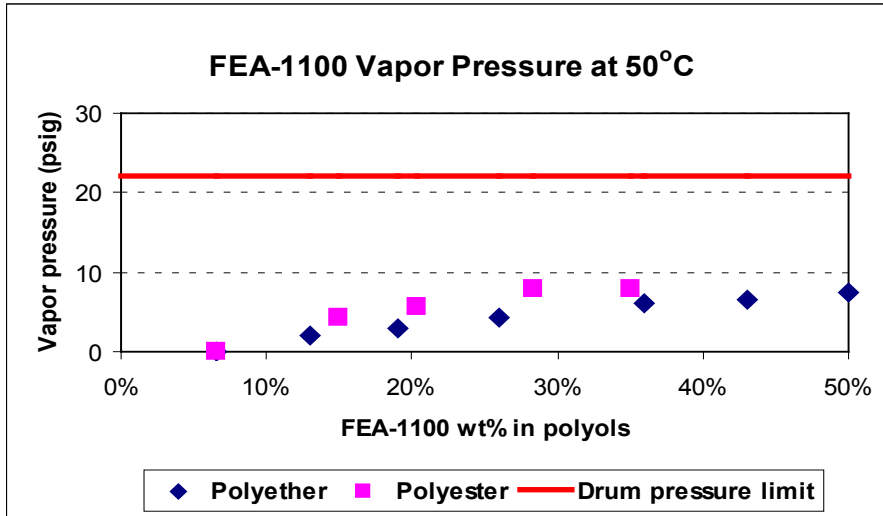


Figure 1. FEA-1100 Vapor Pressure in Polyether and Polyester Polyols

FEA-1100 IN MANNICH-BASE POLYETHER FOR SPRAY FOAM APPLICATION

Mannich-base polyether polyols are typically employed in spray foam applications. In these tests, the effect of the FEA level was evaluated in a spray foam formulation optimized for HFC-245fa. Equimolar quantities of FEAs and water (CO₂) were used for comparison. FEA-1100 was first substituted for HFC-245fa in the formulation using low levels of HFC-245fa. The FEA levels were then increased to high levels as typically employed in HCFC-141b formulations. Foams produced using high and low FEA levels were analyzed for R-value and density. The foam formulation and properties are listed in **Table 7**.

Figure 2 shows the effect of FEA level on R-values. FEA-1100 provided superior R-values compared to HFC-245fa at low FEA levels, however, this improvement becomes much more pronounced as the FEA level increases. Since the level of HFC-245fa in formulations is limited by its low boiling point, FEA-1100 can significantly improve foam R-values through the use of a higher level of FEA.

Table 7: Effect of FEA Level in Spray Foam Formulation

Ingredients (pbw)	HFC-245fa (low FEA level)	FEA-1100 (low FEA level)	HFC-245fa (high FEA level)*	FEA-1100 (high FEA level)
Mannich polyol	50	50	50	50
Polyester polyol	50	50	50	50
Surfactant	0.25	0.25	0.25	0.25
Flame retardant and additives	24.50	24.50	24.50	24.50
Catalysts	1.22	1.22	1.22	1.22
FEA (moles)	0.045	0.045	0.179	0.179
Water (moles)	0.169	0.169	0.035	0.035
Total moles (FEA + water)	0.214	0.214	0.214	0.214
Isocyanate	138	138	97	97
Reaction Profile				
Cream time(s)	8	8	7	7
Rise time(s)	70	67	85	71
Tack free time(s)	70	70	90	85
Foam Initial Properties				
Foam index	1.1	1.1	1.1	1.1
Sample density (pcf)	2.6	2.6	2.5	2.8
Initial R-value (ft**2-h-F/Btu-in) @ 75°F	6.1	6.2	7.2	7.7

*Vapor pressure may exceed drum pressure rating



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