

FLUOROCHEMICALS







INTRODUCTION

Energy is critical for the economy. In recent years, concerns about energy costs have increased, and standards for energy efficiency have become more stringent to ensure quality of life and sustain a green environment.

Of the energy we consume today, a significant amount is lost due to poor insulation. Rigid foams, including polyurethane (PUR) foams and polyisocyanurate (PIR) foams, are commonly used for thermal insulation in appliances and in residential and commercial buildings because they help provide higher energy efficiency. Blowing agents are vital components and are responsible for the outstanding thermal performance rigid foams.

Arkema's Forane® FBA 1233zd, trans-1-chloro-3,3,3-trifluoropropene is a non-flammable, liquid blowing agent with a boiling point chose to room temperature. Forane® FBA 1233zd low global warming potential (GWP) blowing agent is designed for most PUR applications, including appliances, pour-in-place, spray, and PIR boardstock. Arkema has granted patents on 1233zd use in Foam applications throughout the world.

PROPERTIES

Arkema evaluated a range of new blowing agents, formerly known as the "AFA series," designed for most polyurethane (PUR) applications, including appliances, pour-in-place (PIP), spray, and polyisocyanurate (PIR) boardstock. The AFA series includes both liquid and gas blowing agents that possess very low GWP and negligible ozone epletion potential. We selected Forane® FBA 1233zd as our choice of a 4th generation, low GWP liquid blowing agent because of its physical, environmental, and toxicology properties, as summarized in Table 1.

TABLE 1 Properties of Forane® FBA 1233zd Blowing Agent		
Chemical Name	trans-1-chloro-3,3,3-trifluoropropene	
CAS Number	102687-65-0	
Formula	CHCl=CH-CF3 (E)	
Molecular Weight (g/mol)	130.5	
Boiling Point (°C)	18.6	
Vapor Thermal Conductivity ¹ at 20°C	9.94	
Liquid Thermal Conductivity ¹ at 20°C	88.35	
Vapor Density ¹ (kg/m³) at 20°C	6.10	
Liquid Density ¹ (g/cm³) at 20°C	1.27	
Vapor Pressure ¹ (mmHg) at 20°C	809	
Vapor Viscosity¹ (cP) at 20°C	0.010	
Liquid Viscosity¹ (cP) at 20°C	0.319	
Surface Tension ¹ (dyne/cm) at 20°C	14.039	
Latent Heat of Vaporization at 1 20°C (kJ/kg)	193.3	
Atmospheric Life ² (day)	26	
GWP ²	1	
ODP ³	~ 0	
Flash Point ⁴ (°C)	None	
Flammability Limit ⁵ (vol. %) LFL/UFL	None/None	
Kauri-Butanol ⁶ (KB) Value	27	

TRANSPORTATION

Based on the properties of Forane® FBA 1233zd blowing agent, Arkema has established the following guidelines for transport (Table 2).

TABLE 2 Transportation Information of Forane® FBA 1233zd Blowing Agent			
UN Number	3163		
Proper shipping name	Liquefied gas, n.o.s		
Technical name	trans-1-chloro-3,3,3-trifluoropropene		
Class	2.2		
Marine pollutant	no		

ENVIRONMENTAL

Forane® FBA 1233zd blowing agent was designed to meet the requirement of a 4th generation, low GWP product. The global warming potential² of Forane® FBA 1233zd blowing agent is 1. Similar to hydrofluorocarbons (HFCs), Forane® FBA 1233zd blowing agent should not be considered a VOC molecule due to its low maximum incremental reactivity (MIR). However, as a member of RESPONSIBLE CARE®, Arkema aims to minimize any releases into the environment. Any disposal or treatment of wastes containing Forane® FBA 1233zd blowing agent should be undertaken within the guidelines set by RESPONSIBLE CARE®.

TOXICITY

Forane® FBA 1233zd blowing agent has been approved for polyurethane foam uses by the U.S. EPA under its SNAP program. As a part of the SNAP requirements, an Occupational Exposure Limit (OEL) has been established for handling the material during foam preparation or manufacturing. A user of a chemical should always read the label and thoroughly review its Material Safety Data Sheet before use.

STABILITY

Forane® FBA 1233zd was studied at 100°C for 15 days, no chemical reaction or degradation was observed. It is therefore considered stable for storage and use.

COMPATIBILITY WITH METALS

The exposure of various metals to Forane® FBA 1233zd blowing agent was evaluated; measuring the weight change or the extent to which the metal coupons have been dissolved determines the corrosivity of Forane® FBA 1233zd blowing agent. The study shows that Forane® FBA 1233zd blowing agent is compatible with stainless steel, carbon steel, copper, brass, aluminum, and other metals commonly used in polyurethane equipment and storage.

The test procedure followed ASTM G31-72 (Reapproved 2004) – Standard Practice for Laboratory Immersion Corrosion Testing of Metals. Three cleaned metal coupons were placed into the test vessel: one completely submersed in the solution, one half submersed in the solution, and one exposed only to the vapor phase. Forane® FBA 1233zd blowing agent was added to the test vessel, which was then sealed and connected to the reflux condenser. Once the temperature reached the boiling point of Forane® FBA 1233zd blowing agent, testing continued for 168 hours, after which the coupons were analyzed for corrosion.

TABLE 3			
Metals Compatibility of Forane® FBA 1233zd Blowing Agent			
METAL	COMPATIBILITY		
Steel	V		
Stainless steel	V		
Magnesium	V		
Aluminum	V		
Zinc	V		
Silver	V		
Copper	V		
Phosphorus bronze	V		
Brass	V		
Tin	V		
Solder	V		
Tin plate	V		
Cadmium plated	V		
Nickel plated	V		

COMPATIBILITY WITH PLASTICS AND ELASTOMERS

Arkema used the following procedures to determine compatibility of Forane® FBA 1233zd blowing agent with plastics and elastomers. Three dog-bone shaped samples were prepared from each of the materials shown in the tables 4 and 5; typical dimensions of the dog-bone were 75 mm \times $4 \text{ mm} \times 2 \text{ mm}$ (length x width x thickness). Each piece was introduced into a test tube filled with Forane® FBA 1233zd blowing agent. The tube was sealed and placed in a water bath kept at a temperature slightly above the boiling point of Forane® FBA 1233zd blowing agent for 5 minutes, 24 hours, or 100 hours. At the end of each designated time period, the elastomer or plastic was removed from the test tube and measured for dimensions and weight. The sample was then subjected to a tensile test with crosshead speed of 50 mm/min and the distance between grips set at 30 mm.

TABLE 4 Plastics Compatibility of Forane® FBA 1233zd Blowing Agent		
PBT (polybutylene terephthalate)	~	
PTFE (polytetrafluoroethylene)	~	
PVC	V	
Zytel® (polylamide 6)	V	

All four plastic substrates tested are compatible with Forane® FBA 1233zd blowing agent.

TABLE 5		
Elastomer Compatibility of Forane® FBA 1233zd Blowing Agent		
ELASTOMER	COMPATIBILITY	
Neoprene	~	
Polyacrylate		
Viton® (Fluoroelastomer)		
EPDM (ethylene propylene diene M-class rubber)	~	
Hypalon® (chlorosulfonated polyethylene)	~	
Natural rubber		
Silicone rubber		
SBR (styrene-butadiene rubber)	~	
NBR (nitrile butadiene rubber)	V	

HFO1233zd blowing agent is compatible with neoprene, EPDM, Hypalon, SBR and NPR. It is not recommended to be in contact with polyacrylate, Viton®, natural rubber, and silicone rubber. Among the compatible elastomers, EPDM is preferred due to its lowest loss of weight after 100 hours of immersion in Forane® FBA 1233zd blowing agent.

STORAGE AND HANDLING

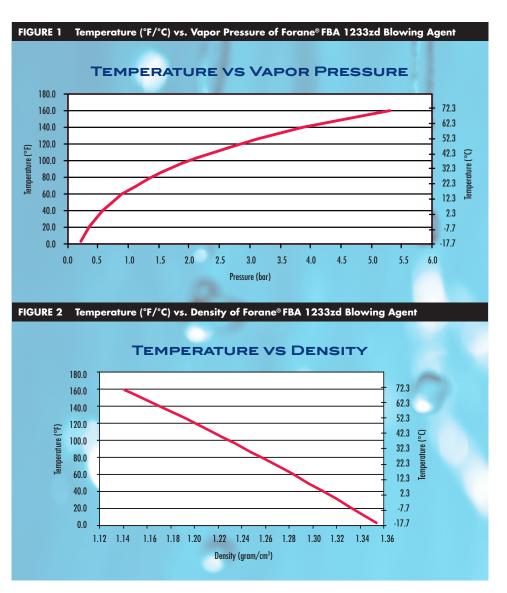
Forane® FBA 1233zd blowing agent should only be stored in an approved cylinder that is in a cool and well ventilated area. If Forane® FBA 1233zd blowing agent needs to be repacked into any vessel different from the original shipping package Arkema's Technical Service Department should be contacted in advance to ensure the new container meets all requirements. The container and its outlet fitting(s) should be protected from physical damage, such as puncturing and denting, and should never be exposed to flame, excessive heat, or direct sunlight. The container valve(s) should be closed if the container is not in use.

Forane® FBA 1233zd blowing agent should not be pressurized in the presence of air and oxygen. If pressurization is necessary, it is recommended that dry nitrogen be used.

If any additional information is needed, please contact the Arkema Inc. Technical Service Department.

TABLE 6			
Vapor Pressure of Forane® FBA 1233zd Blowing Agent at Different Temperatures			
TEMPERATURE	PRESSURE		
(°C)	(bar)		
-15	0.23		
-10	0.30		
-5	0.38		
0	0.48		
5	0.59		
10	0.73		
15	0.89		
20	1.08		
25	1.30		
30	1.55		
35	1.83		
40	2.16		
45	2.53		
50	2.94		
55	3.40		
60	3.92		
65	4.50		
70	5.13		

ensity Forane® FBA 1233zd Blowing Agent Different Temperatures		
TEMPERATURE	DENSITY	
(°C)	(gram/cm³)	
-15	1.35	
-10	1.34	
-5	1.33	
0	1.32	
5	1.31	
10	1.30	
15	1.28	
20	1.27	
25	1.26	
30	1.25	
35	1.24	
40	1.22	
45	1.21	
50	1.20	
55	1.18	
60	1.17	
65	1.16	
70	1.14	



APPLICATION

Forane® FBA 1233zd blowing agent is a cost effective and comprehensive solution to meet stricter energy standards with low environmental impact. It has been tested in applications such as, but not limited to, appliance, pour-in-place, panels, and spray foam using existing equipment and tooling and requiring no modifications to the current foam process. Foams blown with Forane® FBA 1233zd blowing agent typically have very good insulation and other properties.

MISCIBILITY

Table 8 (next page) lists the various polyols and isocyanates examined for miscibility with Forane® FBA 1233zd blowing agent. Blends were prepared by adding a predetermined weight of polyol to a 125ml (~4 oz.) clear Boston Round bottle with Taperseal lined cap. Forane® FBA 1233zd blowing agent was then added to the appropriate weight of polyol to obtain 5, 10, 15, 20, 25 or 30 weight percent of blowing agent, i.e. one bottle for each polyol and weight percent level of blowing agent. Weights of both components were adjusted in order to maintain a similar volume and headspace in each bottle. Bottles were immediately capped and placed on a roller mixer for several minutes until thoroughly mixed. The blends were allowed to stand for 24 hours before being reweighed to ensure no loss of blowing agent. Visual observations were made of the blend condition, i.e., stable solution (clear), stable emulsion (cloudy, but not separated), or if the material showed signs of separation. Observations were repeated after one week at room temperature.

TABLE 8 Miscibility Forane® FBA 1233zd Blowing Agent in Polyols and	OH value* Viscosity** Maximum wt%***		
	OH value	Viscosity	Maximum wt%
Glycerine based polyether polyols			
GP-700 Glycerine/Propylene Oxide 700 MW	230-250	250	30
GP-725 Glycerine/PO 700 MW with 25% Ethylene Oxide (or EO) cap	230-250	250	30
GP-4000 Glycerine/PO 4000 MW	39-42	700	30
GP-4520 Glycerine/PO 4500 MW with 20% EO cap	34-38	890	30
Amine based polyether polyols			
TEAP-265 Triethanol Amine/PO 265 MW	625-645	470	30
EDAP-770 Ethylene Diamine/PO 290 MW	757-783	56,000	30
AD-310 Aromatic Amine/DEG 580 MW	310	2400	30
Sucrose based polyether polyols			
SG-360 Sucrose/Glycerine 730 MW	360	3500	30
SD-361 Sucrose/DEG 690 MW	360	2500	30
SG-522 Sucrose/Glycerine 539 MW	520	27,000	30
190 Sucrose/Glycerine 460 MW	490	5500	30
SPA-357 Sucrose/Diethanol Amine/PO 880 MW	335-365	2500	30
Mannich based polyether polyols			
R-425X 422 MW	425	4500	30
R-470X 394 MW	470	8200	30
Sorbitol based polyether polyols			
S-490 Sorbitol/PO 700 MW	490	9000	30
Aromatic Polyester polyols			
5100 Functionality 2.2	295	6000	20
2541 Functionality 2.0	240	3200	30
3510 Functionality 2.0	240	6000	30
PS-2352 Functionality 2.0	240	3000	20
R-925 Functionality 2.4	295-315	11,000	30
Polymeric MDI	% NCO		
150 - 200 cps polymeric MDI	31.2	190	30
700 cps polymeric MDI	30.8	700	30

- * Per manufactures' literature
- ** Centipoise at 25°C per manufacturer's literature
- *** Maximum level tested

Reference:

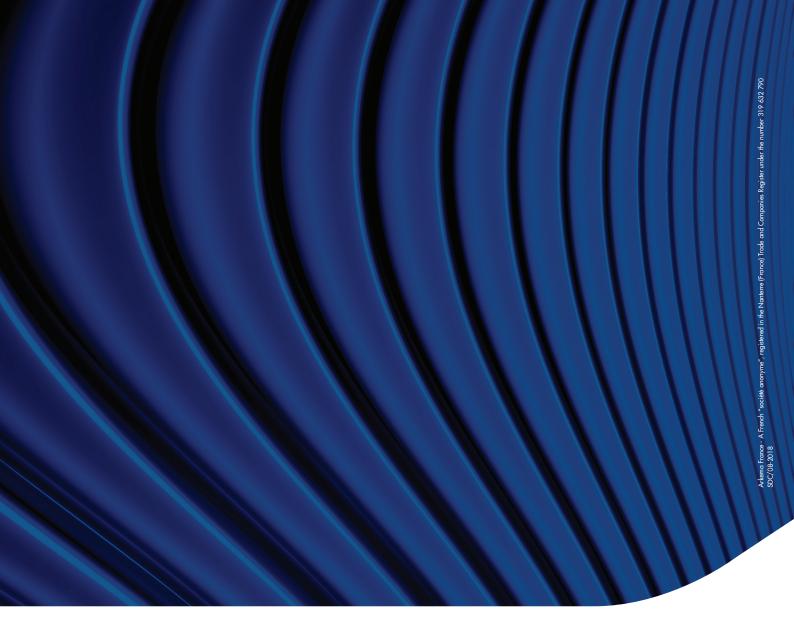
- 1 Arkema Internal Studies
- 2 Reference: Phys. Chem. Chem. Phys., 2012,14,1735–1748, Atmospheric chemistry of HCF3CHQCHCI: products and mechanisms of the gas-phase reactions with chlorine atoms and hydroxyl radicals; M. P. Sulbaek Andersen, O. J. Nielsen, M. D. Hurley and T. J.Wallington
- 3 Atmospheric Lifetime Determination for the Hydrochlorofluoroolefin" Research work by
- National Institute of Science and Technology (NIST), Gaithersburg, Maryland under CRADA CN-5094 in 2008
- 4 Arkema Internal Studies, determined by ASTM D 3278-96
- 5 Arkema Internal Studies, determined by ASTM E681
- 6 Arkema internal Studies, determined by ASTM D1133 KB

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