Demonstration project to validate the use of Hydro-Fluoro-Olefins (HFO) for discontinuous panels in Article 5 Parties through the development of cost-effective formulations

UNDP REPORT
Submitted on behalf of the Government of Colombia

APRIL 2018

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DEMONSTRATION PROJECT TO VALIDATE THE USE OF HYDRO-FLUORO-OLEFINS (HFO) FOR DISCONTINUOUS PANELS IN ARTICLE 5 PARTIES THROUGH THE DEVELOPMENT OF COST- EFFECTIVE FORMULATIONS

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Executive Summary

This project was developed as response to the Decision 76/29 of the Multilateral Fund Executive Committee and is part of a limited group of projects with the objective to assess new technology options that use non-ODP and low GWP blowing agents.

In the context of Decision XIX/6 there is a concern on the availability in Article 5 parties of validated cost effective and environmental sound technologies to phase-out HCFC-141b. This is particularly critical for the applications of polyurethane (PU) rigid foam, discontinuous panels, small appliances, spray foam, etc., where most of the end users are small enterprises with a poor control of the operation and safety discipline. Several work orders are done in-doors with limited ventilation. Safety is the main barrier for the introduction of flammable technologies (hydrocarbons, methylal and methyl formate) in this market segment.

The proven non-flammable technical options to replace HCFC-141b as blowing agent for PU rigid foam are mainly limited to high GWP HFCs as HFC-245fa and the blend of HFC-365mfc/HFC-227ea, which have GWP values of 1030 and 964 respectively. Recent publications show promissory results with the new unsaturated HFC/HCFC blowing agents, commonly known as Hydro-Fluoro-Olefins (HFO), that exhibit GWP values lower than 10.

The project was designed to evaluate two HFO molecules as co-blowing agent in association with CO_2 derived from the water-isocyanate reaction: HFO-1336mzz(Z) and HFO-1233zd(E). The foam processing and physical properties obtained with these substances along with their respective formulating costs were compared to those of HCFC-141b based systems.

Espumlátex, the largest Colombian 100% owned PU system house, served as local technical host to coordinate the demonstration, foam application and testing activities. The experimental protocol included a statistical full factorial design with 2 factors for polyurethane foam (PUR). The factors (independent variables) were the type of HFO and the HFOs/CO_2 ratio in the foam cell. To determine the physical properties of the foam, the samples were prepared and analysed following ASTM standards in Espumlátex laboratories. In addition, three samples (one with each blowing agent) were sent for the E-84 fire performance testing at QAI laboratories in the United States.

The following conclusions can be pointed out:

1. The foam HFO based technology is not flammable. It does not deplete the ozone layer (0 ODP) and has a low GWP (< 2). Compared to HCFC-141b it does not present any incremental EH&S issue.
2. In the framework of this project supported by the Multilateral Fund, HFO based formulations with blowing agent reductions of 61 to 64 by weight were developed. This is equivalent to an HFO reduction in the gas cells of 60%.
3. Compared to HCFC-141b, the HFO reduced formulations showed:

- Better foam flow reflected by a lower flow index (ratio between the free rise density and the minimum fill density).
- An initial foam K factor higher by 7% in laboratory (Brett injections). This value was reproduced at industrial plant.
- Similar values of foam K factor when measured one month after injected.
- Similar laboratory and production plant values of compression strength, dimensional stability and adhesion to metal.

4. There was not observed -from a statistical point of view- a difference between the performance of foam based on the two types of HFO: 1233zd(E) and 1336mzz(Z).
5. The handling and processability at the production plant of the HFO reduced formulation was similar to HCFC-141b.
   - In hot weathers the PU systems based on HFO-1233zd(E) could require a storage conditioned at low/ medium temperatures.
6. Nowadays the HFO reduced systems have higher costs than HCFC-141b by 16.4 and 33.2%, but these figures could be lower in the future.
7. Thanks to the technology formulation it was possible to significantly reduce the cost of the HFO based formulations.

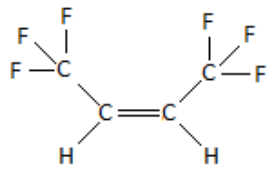
1. INTRODUCTION

In the context of Decision XIX/6 there is a concern on the availability in Article 5 parties of validated cost effective and environmental sound technologies to phase-out HCFC-141b in the different foam applications.

This project was developed as response to the Decision 76/29 of the Multilateral Fund Executive Committee and is part of a limited group of projects with the objective to assess new non-ODP and low GWP technology options to replace HCFC-141b as blowing agent. The present project was designed to evaluate the use of HFOs for discontinuous panels in Article 5 Parties through the development of cost-effective formulations.

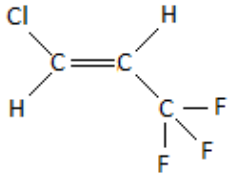
For developing countries, the proven technical options to replace HCFC-141b as blowing agent for PU rigid foam are mainly limited to high GWP HFCs as HFC-245fa or HFC-365mfc/HFC-227ea blend, which have GWP values of 1030 and 964 respectively (100yr ITH, IPCC 4th Assessment Report 2008). Recent publications show promissory results with the new unsaturated HFC/HCFC blowing agents, commonly known as HFOs, that exhibit GWP values lower than 10 (Bodgan, 2011; Costa, 2011). The barrier for the well-known hydrocarbon technology in this rigid foam application is safety during foaming because of flammability. This issue is particularly critical for this sector where most of the enterprises are small in size with a poor control of the operation and safety discipline. Several work orders are done in-doors with limited ventilation.

The project was designed to evaluate two HFO molecules as co-blowing agent in association with CO_2 derived from the water-isocyanate reaction: HFO-1336mzz(Z) and HFO-1233zd(E). Figures 1 and 2 show the chemical formulas of the blowing agents evaluated in this project and Table 1 summarizes their physical properties.



cis-1,1,1,4,4,4-hexafluoro-2-butene

Figure 1. HFO-1336mzz(Z)



(E) 1-chloro-3,3,3-trifluoropropene

Figure 2. HFO-1233zd(E)

Table 1. Physical properties of HCFC-141b and HFOs

Characteristics	HCFC-141b	HFO-1336mzz(Z)	HFO-1233zd(E)
Suppliers		Chemours	Honeywell/Arkema
Bowling point (°C)	32	33	19
Thermal conductivity of gas (Mw/m.K) to 25°C	9.5	10.7	10.0
ODP	0.11	0	0
GWP	782	2	1

2. PROJECT OBJECTIVES AND IMPLEMENTATION

In accordance to Decision 76/29 of the Executive Committee adopted in its 76th meeting held in Montreal in May 2016, the project objective is:

> *Validate the use of HFOs for discontinuous panels in Article 5 parties through the development of cost-effective formulations*

Espumlátex, the largest Colombian 100% owned PU system house, served as local technical host to coordinate the demonstration, foam application and testing activities.

The start-up of the project took place the week of November 30, 2016 after the administrative arrangements between the Government of Colombia, the UNDP local office and Espumlátex were agreed. The implementation was done in a team effort among the company Ingeniería de Refrigeración Industrial Rojas Hermanos S.A., Espumlátex, the Ministry of Environment and Sustainable Development of Colombia, through the National Ozone Unit (UTO), and UNDP. The activities that were carried out are shown in Table 2.

Table 2. Activities developed during the project

Activity	Date
Bibliographic review.	November 30, 2016 - January 2017
Raw materials acquisition.	November 30, 2016 - January, 2017
Definition of evaluation plan and experimental protocol.	November 30, 2016 - December, 2016
Development of HFO based formulations: laboratory tests at Espumlátex (hand-mix and Brett mould injections). Preparation of foam samples to test physical properties.	November 30, 2016 - March, 2018
Evaluation of foam physical properties (Espumlátex, QAI laboratories).	November 30, 2016 - April, 2018
Selection of the best cost/performance formulations for an industrial trial: Injection of discontinuous panels at Rojas Hermanos plant.	January, 2018
Presentation of the final results and conclusions in an international seminar.	February, 2018
Preparation of Final Report.	January – April, 2018

3. EXPERIMENTAL

3.1. Experimental Design

When a specific process or experiment is repeated under what are, as nearly as possible, the same conditions, the observed results are never identical (Box & Hunter & Hunter, 2005). This statement is particularly true in the field of PU foam. This fluctuation that occurs from one repetition to another is called *experimental error* and refers to variations that are unavoidable such as human errors of measurement, analysis and sampling. The no consideration of experimental error can lead to false conclusions about the *real* effect of a specific independent variable. In the line of these thoughts and having in mind that usually is most efficient to estimate the effects of several variables

simultaneously, it was decided to apply for this project the technique of statistical design of experiments, commonly known as DOE.

One simple 2 x 5 full factorial design was planned. *Genuine* replicates were made in all points of the design to have the best estimate of the error variance across the experimental region.

3.1.1. Factors and levels

The factors (independent variables) and levels considered for the experimental design are described in Table 3.

Table 3. Experimental Design	
Factors (independent variables)	**Levels**
Type of HFO	HFO-1336mzz(Z)
	HFO-1233zd(E)
Mole fraction of HFO into the gas cells (reduction percent of HFO compared to HCFC-141b formulation)	0.83 (0 %)
	0.66 (20 %)
	0.50 (40 %)
	0.33 (60 %)
	0.17 (80 %)

A commercial formulation blown with HCFC-141b, having a 0.83 mole fraction into the gas cells, was used as comparison standard. Three genuine replicates of this standard were done.

Figure 3 illustrates the HFO reduction into the gas cells. The mole fraction value of HCFC-141b into the gas cells of the standard formulation, that is 0.83, was taken as the starting point: it represents the 0% reduction of blowing agent. The 20% reduced gas will have a HFO mole fraction equals to 0.83 x 0.80 = 0.66, as it is shown in the figure. The 40% reduced gas will have a HFO mole fraction of 0.50, etc., etc.

The isocyanate/polyol index (equals to 1.20), the gel time (measured at machine) and the free rise density were kept constant throughout all the experiments.

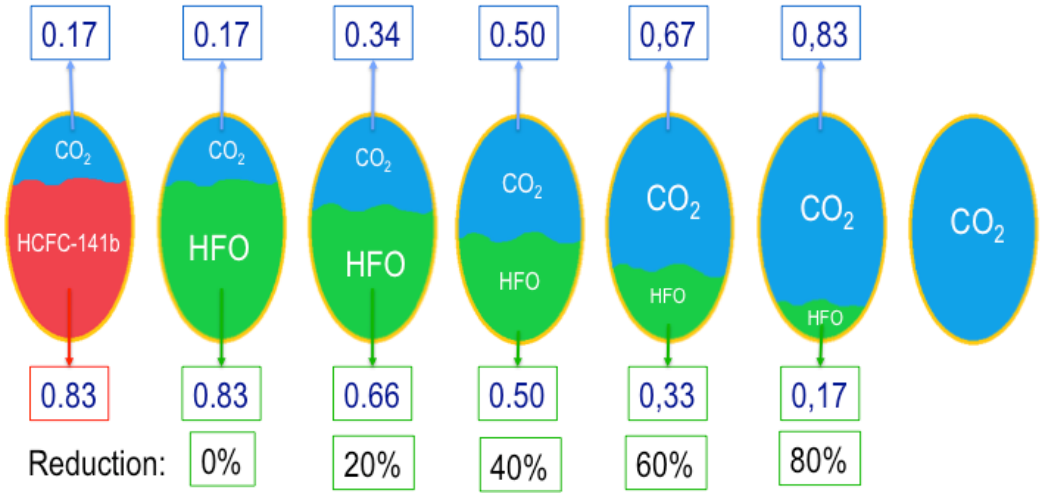


Figure 3. Mole fraction of HCFC-141b/CO_2 and HFO/CO_2 into the gas cells

3.1.2. Responses and test methods

Table 4 lists the responses (dependent variables) along with the test methods that were used for their determination.

Table 4. Responses and Test Methods			
Property		**Test**	**Testing Laboratory**
Reactivity at machine		Visual	In-situ during application
Density		ASTM D-1622	Espumlátex
K-Factor		ASTM C-518	Espumlátex
Compressive strength		ASTM D-1621	Espumlátex
Adhesion strength		ASTM D-1623	Espumlátex
Dimensional stability		ASTM D-2126	Espumlátex
Aging (*)	K-Factor	ASTM C-518	Espumlátex
	Compressive strength	ASTM D-1621	Espumlátex
Fire Performance		ASTM E-84	QAI Laboratories

(*) For K-Factor: 2 weeks, 4 weeks, 2 months, 6 months, 1 year, 2 years
For Compressive strength: 1 month, 2 months

3.2. Laboratory Testing Procedures

3.2.1 Stability of polyol blend

It is known that some amine-based catalysts currently used in the industry may interact with HFO, particularly the unsaturated HCFCs, causing a deterioration of the system reactivity (longer gel times). The stability of the fully formulated polyol was evaluated by monitoring the hand-mix reactivity (cream, gel and tack free time) over time.

3.2.2 Preparation of foam samples

After blending the fully formulated polyol, composed of base polyols, catalysts, surfactant, additives, water and blowing agent, its mixture with isocyanate was injected using a high pressure machine Cannon AP at the conditions shown in Table 5.

Table 5. Conditions at Laboratory Foam Injection	
Injection pressure, bar	150
Isocyanate Temperature, ºC	21 +/- 0.5
Polyol Temperature, ºC	20 +/- 0.5
Output, g/s	200
Mould surface temperature, °C	45

A Brett mould (5 cm x 20 cm x 200 cm), made of aluminium and equipped with water heating, was used for the preparation of foam. With the mould in horizontal position the iso/polyol mixture was

injected through a hole located 15 cm from the bottom; immediately after the mould was changed to the vertical position and remained so until reaching the de-mould time (6 or 8 minutes).

Once the machine reactivity (cream, gel, tack free time and free rise density) was verified the minimum fill density (MFD), corresponding to the minimum amount of foam material needed to fill the mould, was determined. Based on the MFD value, for each experimental point, six additional Brett panels were shot at six levels of over-packing: 6, 8, 10, 12, 14 and 16%. The pieces at 6, 10 and 14% were de-moulded at 6 minutes and the foam expansion was measured; the remaining were de-moulded at 8 minutes. This data on foam expansion is used to compare the de-mould characteristics among different PU systems.

Figure 4 illustrates the determination of minimum fill density (MFD) and Figure 5 the corresponding measurement of foam expansion at Brett mould.

Figure 4. Determination of Minimum Fill Density (MFD)

Figure 5. Measurement of foam expansion at Brett mould

After 24 hours of the injection, each Brett panel was cut to prepare the foam samples required to measure the physical properties listed in Table 4: one for K factor; fifteen for compressive strength at 24 hours, one and two months; six for dimensional stability at -30 and 70 °C. For the determination

of the minimum freeze stable density, 10 cm thick bricks of the Brett panels at the six different over-packings were left overnight at -30°C.

4. RESULTS AT LABORATORY LEVEL

4.1. Polyol Aging

The reduced HFO formulations up to the 60% level were prepared with conventional amine catalysts: pentamethyl-diethylene triamine, N,N.dimethyl cyclohexylamine, 1,3,5-tris (3-(dimethyylamino) propyl) and N,N dimethylethanolamine., The variation of the gel time over time is shown in Figures 6, 7, 8 and 9 (testing at longer time intervals, 4 and 6 months, is planned). A slight catalyst deactivation with HFO based systems was observed. However the longer gel times did not have a particular effect on foam processability and properties when the 40 and 60% reduced systems were run at industrial level (section 6). For the formulation of 80% reduced systems special catalysts - recommended by one of the HFO suppliers- were used (section 7.3) and a better blend stability was observed (testing at longer times is also planned). This point deserves further investigation and monitoring during implementation of investment projects.

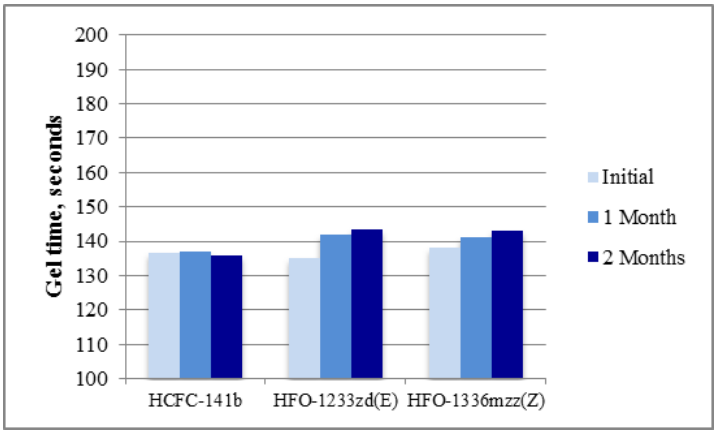


Figure 6. Gel time over time. 0% reduced systems

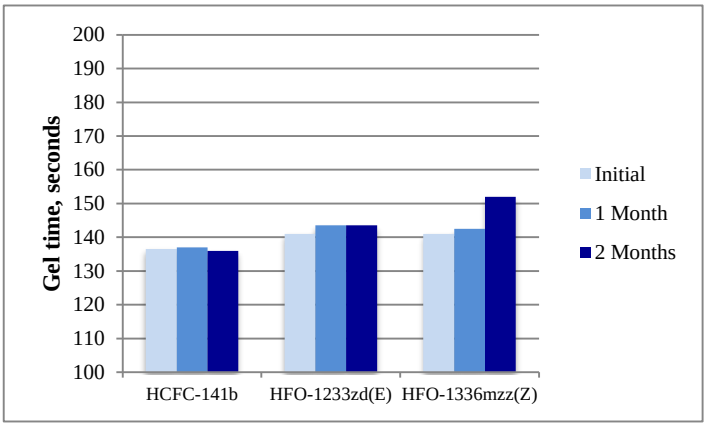


Figure 7. Gel time over time. 20% reduced systems

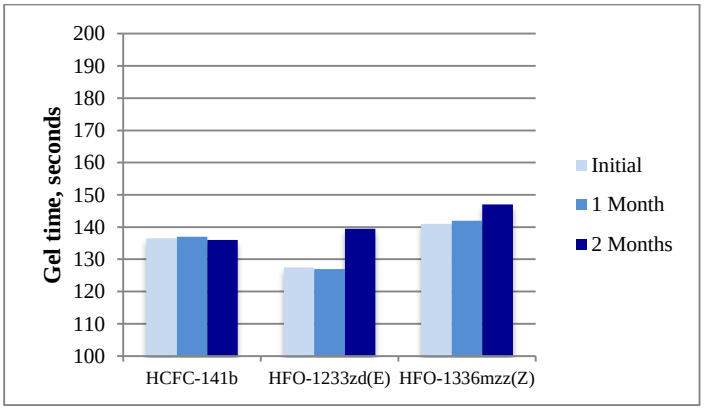


Figure 8. Gel time over time. 40% reduced systems

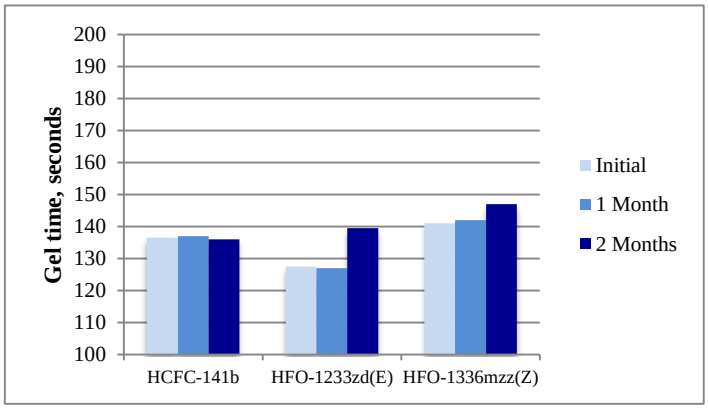


Figure 9. Reactivity polyols over time, reduced by 60% molar

4.2. Brett expansion

Figures 10, 11, 12 and 13 show the results for Brett expansion at the two demould times (6 and 8 minutes) and the different percentages of reduction.

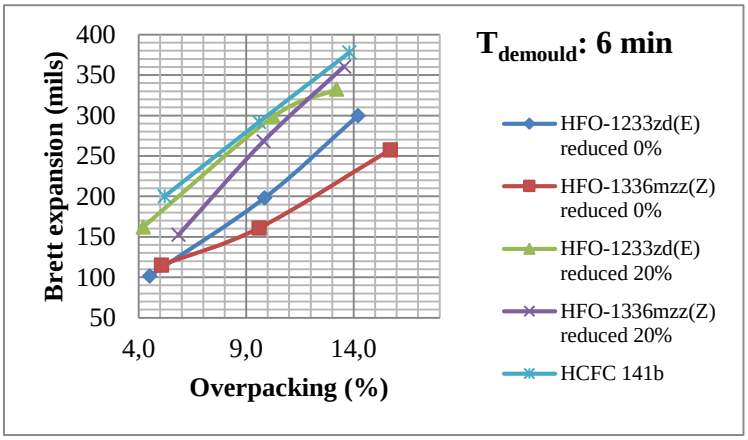


Figure 10. Brett expansion ($T_{demould}$: 6 min), 0% and 20% reduced

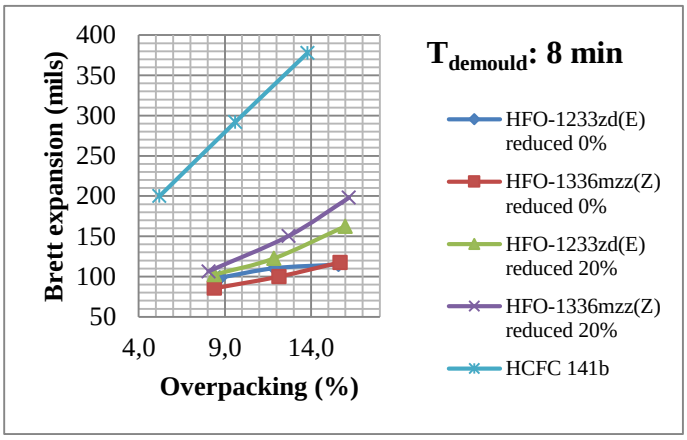


Figure 11. Brett expansion ($T_{demould}$: 8 min), 0% and 20% reduced

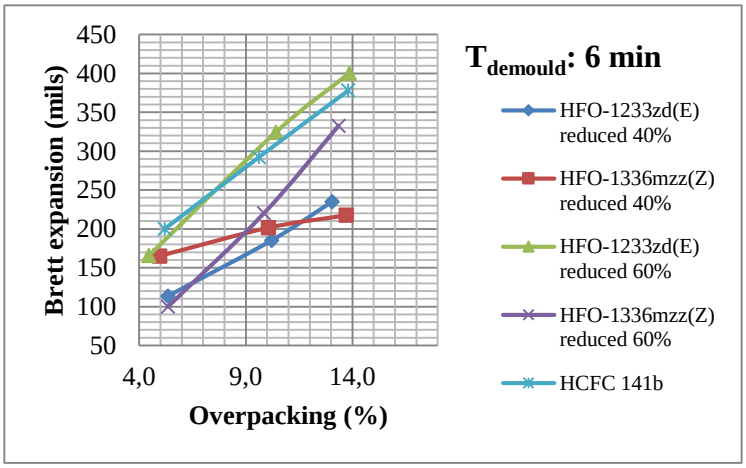


Figure 12. Brett expansion ($T_{demould}$: 6 min), 40% and 60% reduced

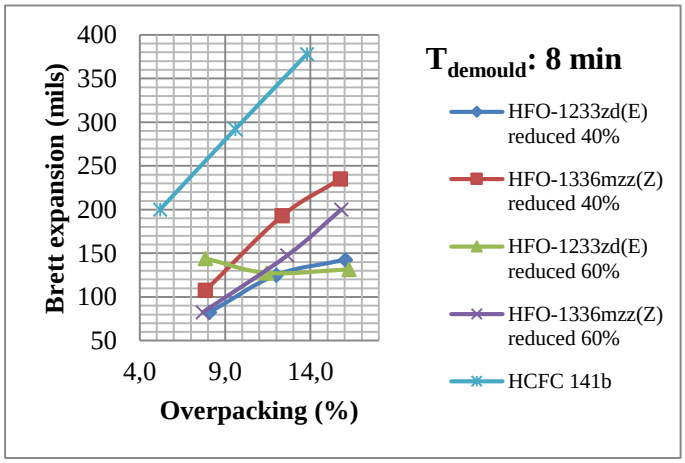


Figure 13. Brett expansion ($T_{demould}$: 8 min), 40% and 60% reduced

4.3. Physical Properties

Table 6 summarizes the initial results for both mechanical and thermal properties of the injected panels.

Table 6. Initial results of mechanical and thermal properties of panels.
Reported data are an average of 2 genuine replicates

Blowing agent	**HCFC- 141b**	**HFO-1233zd(E)**				**HFO-1336mzz(Z)**			
Mole fraction in the gas cells	0.83	0.82	0.66	0.51	0.32	0.83	0.66	0.50	0. 33
Weight percent of Blowing Agent in formulation (%)	12.89	13.41	9.81	7.37	4.86	16.57	11.98	9.62	6.50
Reduction percent by weight (%)			26.85	45.04	63.76		27.70	41.94	60.77
Machine reactivity									
Cream/ Gel/ Tack Free times (s)	10/111/155	8/129/187	8/142/204	8/138/216	8/125/244	8/140/207	9/141/193	8/139/216	8/140/244
Free rise density (kg/m^3)	20.1	19.7	20.6	21.0	21.4	19.5	19.7	21.2	21.1
MFD (kg/m^3)	29.3	27.7	28.1	27.8	27.5	26.2	27.2	27.5	27.0
Foam moulded density (kg/m^3)	34.6	32.4	33.0	31.4	32.1	30.6	32.0	32.1	31.6
K factor (mW/m.K)									
Initial	21.51	22.31	23.05	23.43	23.65	22.70	22.50	23.00	23.60
2 weeks	22.94	23.06	23.53	23.63	23.85	23.40	23.10	23.50	23.90
1 month	23.76	23.98	24.35	23.47	24.82	24.20	24.10	24.10	24.20
Compressive strength (kPa) at 16% over-packing									
Compressive strength initial	107.6	102.7	108.5	85.9	86.9	95.1	113.2	102.8	105.2
Core density (kg/m^3) initial	25.4	25.1	26.2	26.0	27.9	24.6	25.9	26.4	25.8
Compressive strength initial adjusted at 32 kg/m^3	172.3	169.0	162.2	130.9	114.0	164.5	173.1	150.6	162.1
Compressive strength 2 months	105.8	98.1	106.6	74.5	85.4	88.6	111.2	106.0	111.8
Core density 2 months (kg/m^3)	25.4	24.7	25.7	25.9	27.2	24.5	25.7	26.4	25.8
Compressive strength 2 months adjusted at 32 kg/m^3	170.8	167.7	166.3	114.8	124.0	155.1	174.0	155.3	171.9
Dimensional stability 70°C (%ΔV)									
1 day	1.02	-0.19	-1.52	-2.41	-3.16	-0.64	-0.63	-2.94	-1.36
1 weeks	1.90	0.63	-0.35	-1.32	-2.12	1.79	1.18	-1.47	-0.78
2 weeks	2.47	1.05	0.38	-0.25	-1.01	2.79	1.70	0.69	0.22
Dimensional stability -30°C (%ΔV)									
1 day	0.38	0.32	-0.13	0.13	0.24	-1.23	-0.65	-0.58	-0.74
1 weeks	0.10	0.05	-0.19	-0.05	-0.07	-0.26	-0.03	-0.23	-0.10
2 weeks	0.11	-0.09	-0.23	-0.12	-0.50	-0.29	0.04	-0.34	-0.47
Adhesion strength to metal (kPa)	166.03	169.35	198.15	236.1	216.5	155.95	215.5	151.95	148.7

* All data points correspond to the average of two genuine duplicates with the only exception of those of "HCFC-141b" column that are the average of three genuine replicates.

5. ANALYSIS OF RESULTS (LABORATORY LEVEL)

To assess the statistical significance of the effect of the different factors on the foam properties, an analysis of variance (ANOVA) was developed for each property. In this section the ANOVA of few selected foam properties, critical for the thermal insulation performance, such as initial and aged K factor (lambda value), aged compressive strength, dimensional stability an adhesion to metal will be shown.

5.1. Initial K factor

The results of the initial K factor are summarized in Table 7 and Figure 14.

Table 7. K factor, 24 Hours, mW/m*K

Reduction Percentage	HFO-1233zd(E)		HFO-1336mzz(Z)		AVERAGE
0%	22.51	22.11	23.10	22.30	22.51
20%	22.85	23.25	22.60	22.40	22.78
40%	23.05	23.80	22.70	23.40	23.24
60%	23.60	23.69	23.40	23.80	23.62
AVERAGE	23.11		22.96		
HCFC-141b standard: 21.51					

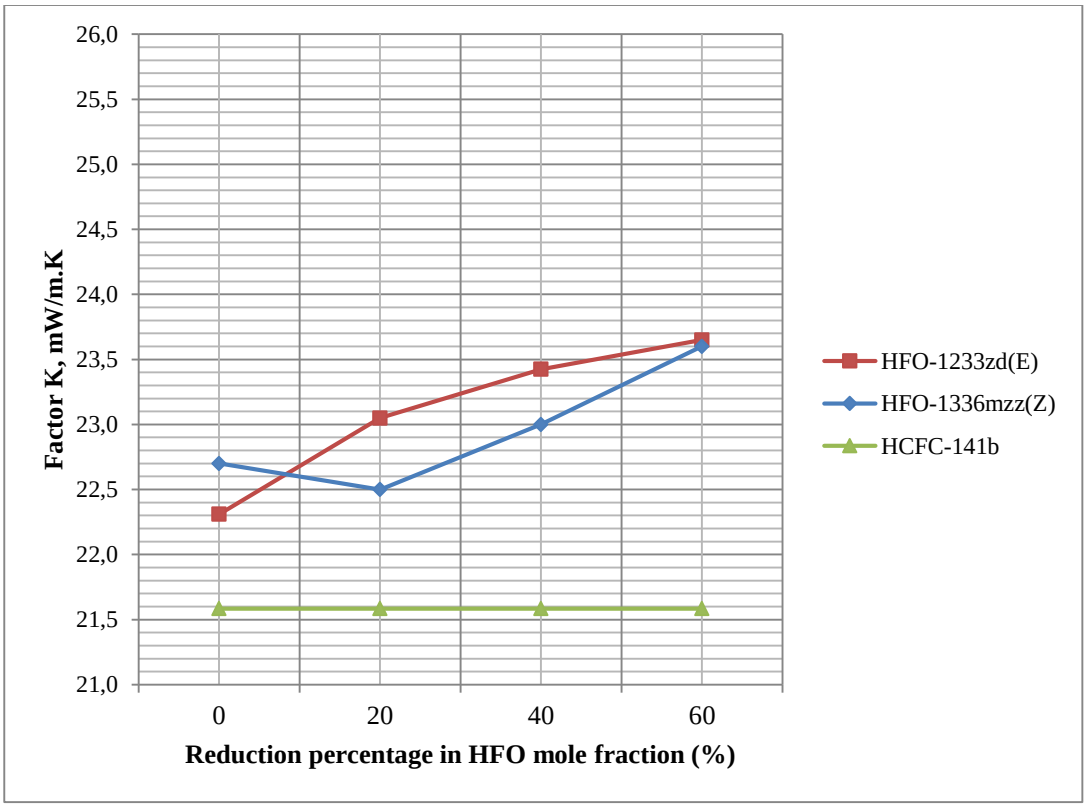


Figure 14. K factor (initial) vs. Reduction percentage in HFO mole fraction

Table 8 shows the ANOVA results of K factor for 24 hours. It is concluded that the molar HFO/CO_2 ratio has a statistically significant effect on the initial foam K factor. No significant difference between the two types of HFO, HFO-1233zd(E) and HFO-1336mzz(Z), was observed.

Table 8. ANOVA of K factor, 24 hours

Factor	Degrees of Freedom	Sum of Squares	Mean Square	F	P(1)	
Type of blowing agent (A)	1	0.084	0.084	0.606	0.459	
Mole fraction (B)	3	2.939	0.980	7.058	0.012	Significant
A*B	3	0.513	0.171	1.232	0.360	
Pure Error	8	1.110	0.139			

(1) Probability of Type I error (rejecting the null hypothesis when it is in fact true). If $P < 0.05$ it is considered that the effect of the factor is significant.

Tables 9 and 10 that statistically compare HCFC-141b with the HFO reduced systems (40 and 60%) led to the conclusion that there is a significant difference in initial K factor between the HCFC-141b and the two types of HFO.

Table 9. ANOVA of K factor, 24 Hours: HCFC-141b vs. HFO-1336mzz(Z) (40% reduced) vs. HFO-1336mzz(Z) (60% reduced)

Factor	Degrees of Freedom	Sum of Squares	Mean Square	F	P	
Type of blowing agent	2	4.340	2.170	11.010	0.042	Significant
Pure Error	3	0.591	0.197			

Table 10. ANOVA of K factor, 24 hours, HCFC-141b vs. HFO-1233zd(E) (40%) vs. HFO-1233zd(E) (60%)

Factor	Degrees of Freedom	Sum of Squares	Mean Square	F	P	
Type of blowing agent	2	5.120	2.560	13.910	0.030	Significant
Pure Error	3	0.552	0.184			

5.2. K factor measured 4 weeks after injection

Table 11 and Figure 15 show a summary of the results of the foam K factor measured 4 weeks after injection.

Table 11. K factor, 4 weeks, mW/m*K

Reduction Percentage	HFO-1233zd(E)		HFO-1336mzz(Z)		AVERAGE
0%	24.23	23.72	25.00	23.50	24.11
20%	24.29	24.40	23.80	24.40	24.22
40%	24.49	22.45	23.80	24.30	23.76

Table 11. K factor, 4 weeks, mW/m*K					
Reduction Percentage	**HFO-1233zd(E)**		**HFO-1336mzz(Z)**		**AVERAGE**
60%	24.57	25.07	24.10	24.30	24.51
AVERAGE	24.15		24.15		
HCFC-141b standard: 23.76					

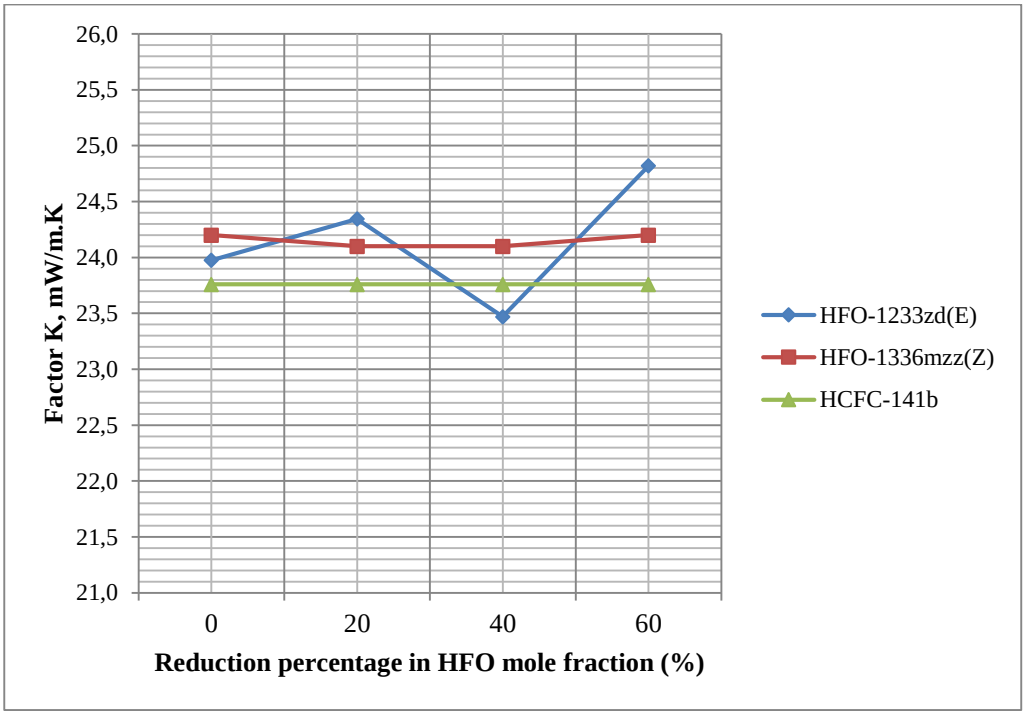


Figure 15. K factor (4 weeks) vs. Reduction percentage in HFO mole fraction

Using the ANOVA results of the foam K factor measured 4 weeks after injection, shown in Table 12, it is concluded that, oppositely to what happened with the initial K factor, the HFO/CO_2 ratio did not show a statistically significant effect on the foam K factor when measured 4 weeks after injection. In the same manner no significant difference between the two types of HFO, HFO-1233zd(E) and HFO-1336mzz(Z), was observed.

Table 12. ANOVA of K factor, 4 Weeks						
Factor	**Degrees of Freedom**	**Sum of Squares**	**Mean Square**	**F**	**P**	
Type of blowing agent (A)	1	0.000	0.000	0.000	0.994	
HFO/CO_2 ratio (B)	3	1.150	0.385	0.811	0.523	
A*B	3	0.856	0.286	0.602	0.632	
Pure Error	8	3.790	0.474			

Similarly to section 5.1, Tables 13 and 14 compare the HCFC-141b with the HFO reduced systems (40 and 60%). In this case, when the foam K factor was measured 4 weeks after injection and as it

could be expected from the Figure 15, a statistically significant difference between the HCFC-141b and the HFO based formulations was not observed.

Table 13. ANOVA of K factor, 4 weeks, HCFC-141b vs. HFO-1336mzz(Z) (40%) vs. HFO-1336mzz(Z) (60%)						
Factor	**Degrees of Freedom**	**Sum of Squares**	**Mean Square**	**F**	**P**	
Type de blowing agent	2	0.200	0.100	0.151	0.866	
Pure Error	3	1.990	0.663			

Table 14. ANOVA of K factor, 4 weeks, HCFC-141b vs. HFO-1233zd(E) (40%) vs. HFO-1233zd(E) (60%)						
Factor	**Degrees of Freedom**	**Sum of Squares**	**Mean Square**	**F**	**P**	
Type of blowing agent	2	2.020	1.010	0.748	0.545	
Pure Error	3	4.050	1.350			

5.3. Compressive Strength measured 2 months after injection

Table 15 and Figure 16 show a summary of the results of the foam compressive strength measured 2 months after injection.

Table 15. Compressive Strength (kPa), 2 Months, adjusted at 32 kg/m^3					
Reduction Percentage	**HFO-1233zd(E)**		**HFO-1336mzz(Z)**		**AVERAGE**
0%	177.80	157.60	147.10	163.60	161.53
20%	146.90	185.80	171.10	177.10	170.23
40%	111.20	118.60	166.10	144.60	135.13
60%	129.60	118.30	166.90	177.00	147.95
AVERAGE	143.23		164.19		
HCFC-141b standard: 170.85					

Compared to HCFC-141b low compressive strength values were obtained with two HFO-1233zd(E) systems, those reduced at 40 and 60%. From a theoretical point of view and the reported data, this could not be explained by the difference in blowing agent but by other formulation parameters[1]. Further results at the industrial level contradicted these experimental points.

[1] Compressive strength is directly affected by the structure of the polyurethane polymer and this is related to the blend of polyols used in the formulation. When high water levels are introduced in the formulation, to counterbalance the undesirable effects of poliurea "softer" type of polyols (low functionality, high molecular weight) are used. For each tested formulation (blowing agent, % of blowing agent reduction) it was necessary to develop a specific polyol blend.

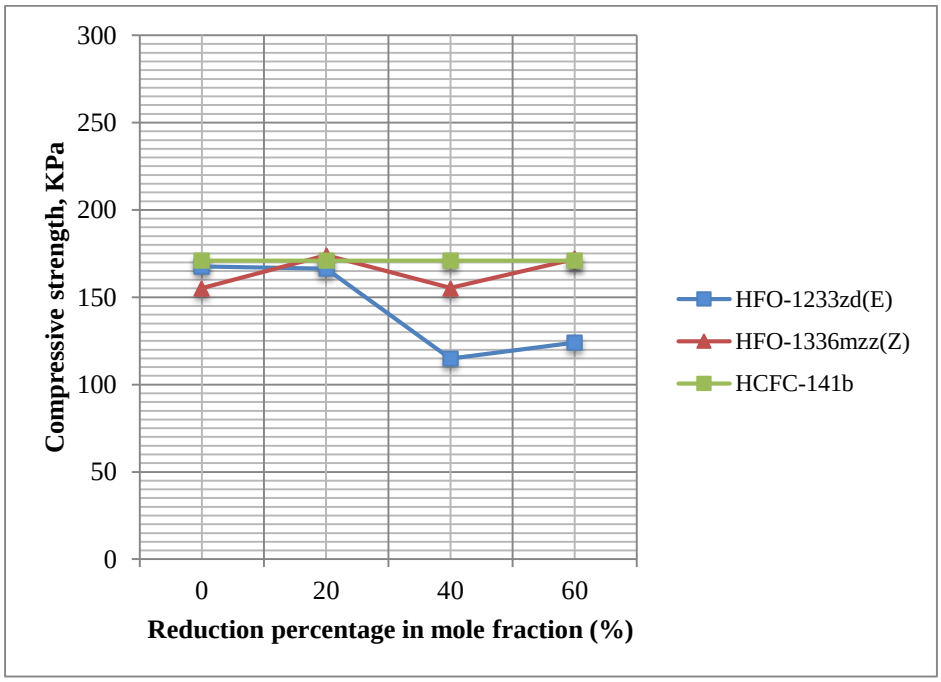


Figure 16. Compressive strength (2 months) vs. Reduction percentage in HFO mole fraction

As expected from the mentioned low compressive strength values, the ANOVA, shown in Table 16, concludes that both factors, the type of HFO and the HFO/CO_2 molar fraction ratio and its interaction, have a statistically significant effect over this physical property.

Table 16. ANOVA of Compressive Strength Adjusted to 32 kg/m^3, 2 months						
Factor	**Degrees of Freedom**	**Sum of Squares**	**Mean Square**	**F**	**P**	
Type of blowing agent (A)	1	1757.710	1757.710	9.450	0.015	Significant
HFO/CO_2 ratio (B)	3	2849.600	949.870	5.110	0.029	Significant
A*B	3	2395.080	798.360	4.290	0.044	Significant
Pure Error	8	1488.110	186.010			

In accordance to Table 17, that compares HCFC-141b with the HFO-1336mzz(Z) reduced systems (40 and 60%), a significant difference in compressive strength measured after two months is not observed.

Table 17. ANOVA of Compressive Strength, 2 Months, HCFC 141b vs. HFO-1336mzz(Z) (40%) vs. HFO-1336mzz(Z) (60%)						
Factor	**Degrees of Freedom**	**Sum of Squares**	**Mean Square**	**F**	**P**	
Type of blowing agent	2	344,680	172,340	0,888	0,498	
Pure Error	3	582,260	194,090			

As expected from the above discussion, Table 18 led to conclude that there is a significant difference in compressive strength at 24 hours between the HCFC-141b and the HFO-1233zd(E).

Table 18. ANOVA of Compressive Strength, 2 months, HCFC 141b vs. HFO-1233zd(E) (40%) vs. HFO-1233zd(E) (60%)						
Factor	**Degrees of Freedom**	**Sum of Squares**	**Mean Square**	**F**	**P**	
Type of blowing agent	2	3.607,940	1.803,970	13,830	0,031	Significant
Pure Error	3	391,350	130,450			

5.4. Aging of Compressive Strength, 2 months versus 24 hours

Table 19 shows the variation percentage of compressive strength, 2 months versus 24 hours. According to the ANOVA, presented in Table 20, there is no evidence of aging difference between the two types of HFO.

Table 19. Variation percentage in compressive strength (%) 24 hours vs. 2 months, adjusted at 32 kg/m^3					
Reduction Percentage	**HFO-1233zd(E)**		**HFO-1336mzz(Z)**		**AVERAGE**
0%	3.13	-4.83	-8.41	-2.97	-3.27
20%	-6.61	11.12	-0.35	1.43	1.40
40%	-26.65	7.62	-3.26	11.57	-2.60
60%	11.05	6.29	-3.47	16.91	7.70
AVERAGE	0.14		1.43		

Table 20. ANOVA of variation percentage in compressive strength, 24 hours and 2 months						
Factor	**Degrees of Freedom**	**Sum of Squares**	**Mean Square**	**F**	**P**	
Type de blowing agent (A)	1	1.6700	6.6700	0.048	0.833	
Mole fraction (B)	3	306.290	102.100	0.728	0.563	
A*B	3	210.370	70.120	0.500	0.693	
Pure Error	8	1121.420	140.180			

5.5. Dimensional Stability at 70°C and -30°C

The dimensional stability results at 70 ºC and -30°C are shown in Tables 21 and 22 and illustrated in Figures 17 and 18. The negative values represent foam contraction and the positive ones foam expansion. The ANOVA results are shown in the annex 1, Tables A-1 to A-6. In average, at 70 ºC,

the HFO based systems provides lower values than HCFC-141b. There was no evidence of any significant difference among the systems based on the three analysed blowing agents.

Table 21. Dimensional Stability at 70 ºC , 2 Weeks, Vol. %

Reduction Percentage	HFO-1233zd(E)		HFO-1336mzz(Z)		AVERAGE
0%	0.73	1.36	2.79	2.79	1.92
20%	0.26	0.50	2.24	1.16	1.04
40%	0.21	-0.70	0.69	-1.83	-0.41
60%	-1.01	-1.11	0.22	-0.27	-0.54
AVERAGE	-0.31		0.37		
HCFC-141b standard: 1.62					

Table 22. Dimensional Stability at -30 ºC, 2 Weeks, Vol. %

Reduction Percentage	HFO-1233zd(E)		HFO-1336mzz(Z)		AVERAGE
0%	-0.13	-0.05	-0.29	-0.19	-0.17
20%	-0.13	-0.32	0.04	-0.24	-0.16
40%	-0.18	-0.05	-0.15	-0.38	-0.19
60%	-0.47	-0.52	-0.24	-0.69	-0.48
AVERAGE	-0.28		-0.28		
HCFC-141b standard: 0.07					

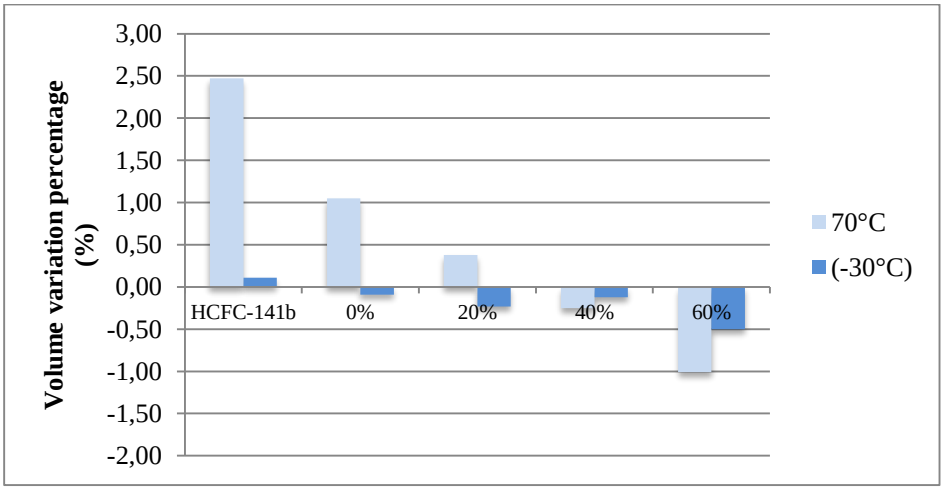


Figure 17. Percentage variation by volume. HFO-1233zd(E)

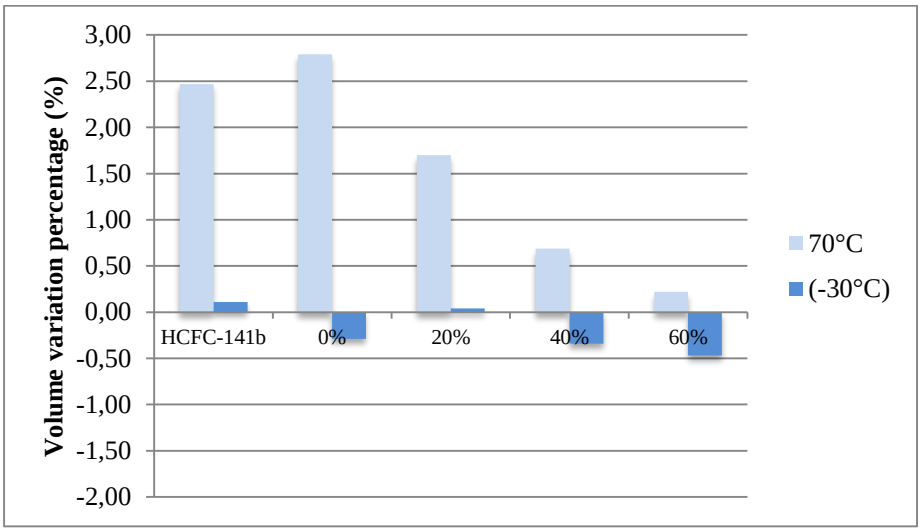


Figure 18. Percentage variation by volume. HFO-1336mzz(Z)

5.6. Adhesion to Metal

The results of the foam adhesion strength to metal (galvanised steel) measured one week after injection are shown in Table 23 and Figure 19. It was observed a better behaviour of the HFO based systems than the standard blown with HCFC-141b.

Table 23. Adhesion Strength to Metal (galvanised steel), kPa

Reduction Percentage	HFO-1233zd(E)		HFO-1336mzz(Z)		AVERAGE
0%	159.10	179.60	148.00	163.90	162.65
20%	171.70	224.60	224.60	206.40	206.82
40%	246.50	225.70	148.40	155.50	194.02
60%	216.50	216.50	151.20	146.20	182.60
AVERAGE	216.92		172.05		
HCFC-141b standard: 166.03					

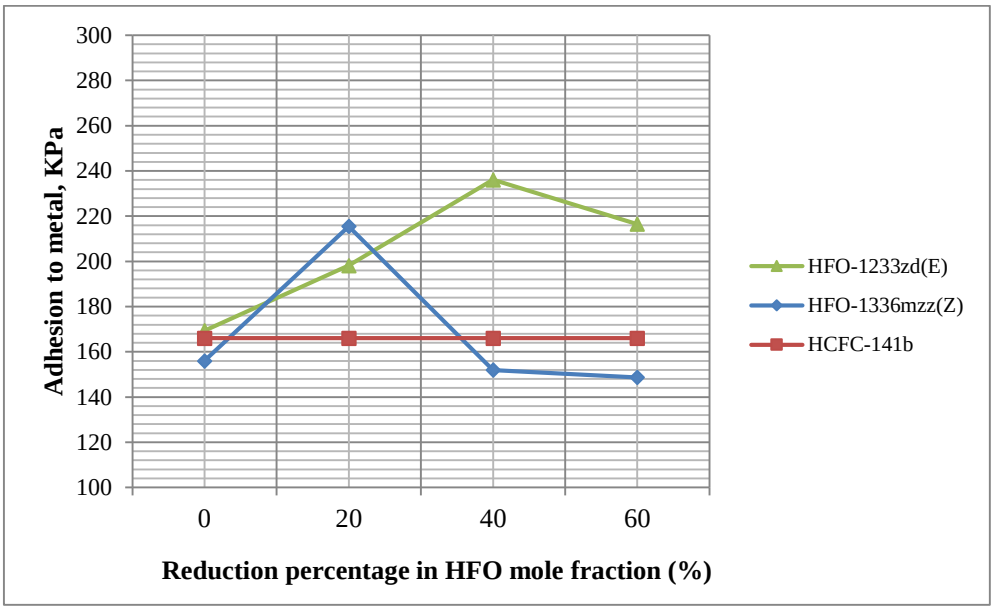


Figure 19. Adhesion to metal vs. Reduction percentage in HFO mole fraction

6. FIELD TESTS

Rojas Hermanos, a Colombian manufacturer of PU foam discontinuous panels for thermal insulation located in Bogota, equipped as shown in Figure 20, with a high pressure injection machine and two Manni type presses, was chosen to conduct the field tests. In two different working days 40 and 60% reduced formulations of HFO-1233zd(E) and HFO-1336mzz(Z) were run. The commercial HCFC-141b system, used as standard for the described laboratory trials, was run both days for comparison.

Figure 20. Field trials conducted at Rojas Hermanos

3m x 1m x 0.05m panels were injected at a single point located 1.3 m from the bottom. Pre-heated stainless steel faces were used. Once the minimum fill density was determined the panels were

injected aiming at the same moulded density currently used in the industrial production (40 kg/m^3). Surface temperature was taken at three different points as illustrated in Figure 21.

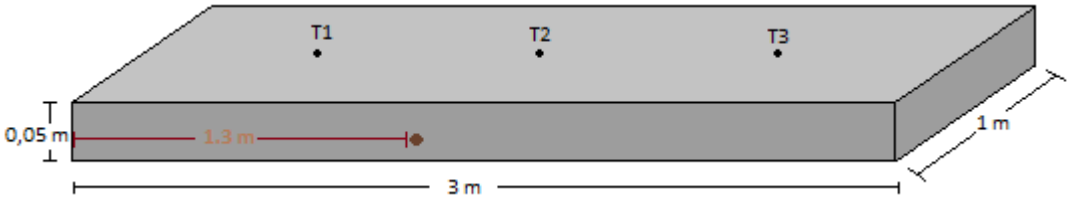


Figure 21. Injection Panel Scheme

An additional panel with 8 m x 1 m x 0.05 m dimensions was injected for each formulation to run the flammability test. Figure 22 illustrates this additional panel.

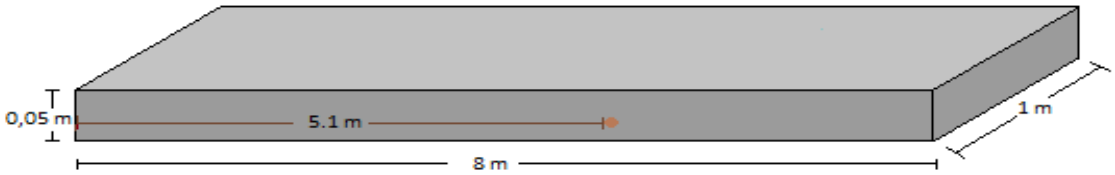


Figure 22. Injection Panel Scheme for Flammability Test

The injection conditions are described in Table 24.

Table 24. Injection Conditions at Rojas Hermanos	
Machine	Cannon A-Compact 200FC
Operative pressure, bar	130 +/- 10
Isocyanate Temperature, ºC	20 +/- 2
Polyol Temperature, ºC	19 +/- 2
Output, g/s	1300
Substrate Temperature, °C	39 +/- 1

After adjusting the injection conditions, the determination of the Minimum Fill Density (MFD) was done, as shown in Figure 23.

Figure 23. Determination of Minimum Fill Density (MFD) at Rojas Hermanos

The results of the foam properties measured 24 hours after injection are summarized in Table 25. No differences were observed between the 40 and 60% reduced systems. The HFO based formulations provided a superior foam flowability (lower flow index), similar compressive strengths and K factor values 3.8 and 7.2% higher than HCFC-141b.

Table 25. Initial results of mechanical and thermal properties of panels

Blowing agent	HCFC 141b (1)	HFO 1233zd(E)		HCFC 141b (2)	HFO 1336mzz(Z)	
Mole fraction in the gas cells	0.83	0.50	0.33	0.83	0.50	0.33
Machine reactivity						
Cream/gel/tack free time (s)	17/119/149	8/121/184	8/112/167	13/115/151	7/133/228	7/106/177
Free rise density (kg/m^3)	18.7	19.8	21.7	18.9	19.3	22.4
Minimum Fill Density (kg/m^3)	26.9	24.8	26.2	26.4	24.3	26.0
Flow Index	1.44	1.25	1.21	1.39	1.26	1.16
Moulded density (target) (kg/m^3)	40.0	40.0	40.0	40.0	40.0	40.0
De-mould time (minutes)	22					
K factor (mW/m.K)	20.62	22.17	21.90	20.59	21.97	22.26
Compressive strength (kPa)	168.2	169.3	156.7	160.8	172.9	171.9
Dimensional stability, 70°C (% ΔV), 24 hours	0.91	-0.68	-1.15	1.11	-0.18	-1.02
Dimensional stability, -30°C (% ΔV), 24 hours	-0.06	-0.26	0.22	0.25	-0.19	0.13

(1) (2): replicates run at two different days

7. COSTS OF HFO BASED POLYURETHANE SYSTEMS

7.1. Incremental Capital Cost

Compared to HCFC-141b no additional capital was required for the preparation and testing -at laboratory and industrial levels- of the HFO formulations. As it is shown in Table 1 the HFO 1233zd(E) and 1336mzz(Z) have boiling points of 19 and 33 ºC and the trials were run in Bogota at an ambient temperature ranging from 10 to 20 ºC. At hotter climates there may be a need with the HFO 1233zd(E) to cool the formulated polyol storage and the formulated polyol day-tank to 20- 25ºC storage to avoid the excessive build-up of pressure. It should be also noted that all the moulds used during the tests were equipped with heating systems and associated temperature controls (39 and 45ºC). This is a critical condition to ensure a good performance with reduced HFO PU formulations.

7.2. Incremental operating cost

The disaggregated formulation costs of the HFO reduced systems compared to the HCFC-141b based formulation are shown in Tables 26 and 27. The different blends of polyols (sugar/glycerine, glycerine and amine initiated) used to formulate the PU systems had a similar cost that ranges between US$2.14 and US$2.16 per kg. The only exception was the 60% reduced HFO-1233zd(E) based formulation which required the introduction of a special relatively expensive polyol. A similar statement applies for the additives packages (catalysts, silicon surfactant, flame retardants) whose costs per kg varied between US$ 1.47 and US$ 1.61.

The reduction of the HFO mole fraction in the gas cells made possible a significant decrease of the cost of HFO based systems. In the case of HFO-1336mzz(Z), compared to the cost of the unreduced

HFO system, a 60% reduction represented a 31.45% less expensive formulation. In the case of HFO-1233zd(E), by going from a mole fraction of 0.82 (0% reduction) to 0.32 (60% reduction), the system cost was cut off by 19%. This is illustrated in Figure 24.

Table 26. Cost of PU systems based on HFO-1233zd(E)

	HCFC-141b	**HFO-1233zd(E)**			
		0% reduced	**20% reduced**	**40% reduced**	**60% reduced**
Mole fraction in the gas cells	0.83	0.82	0.66	0.51	0.32
Reduction percent of HFO by weight (%)		0	26.85	45.04	63.76

FORMULATION	**PPHP**	**US$/ kg**	**PPHP**	**US$/ kg**	**PPHP**	**US$/ kg**	**PPHP**	**US$/ kg**	**PPHP**	**US$/ kg**
Polyol blend	100.00	2.16	100.00	2.15	100.00	2.15	100.00	2.14	100.00	2.42
Additives (catalysts, surfactant, additives)	27.39	1.47	27.48	1.53	27.43	1.52	27.63	1.55	27.58	1.61
Water	1.54		1.34		2.39		3.22		4.28	
Blowing agent	47.25	2.97	45.76	12.00	33.82	12.00	22.88	12.00	14.92	12.00
FORMULATED POLYOL	176.18	2.25	174.58	4.61	163.64	4.05	153.73	3.46	146.78	3.17
PMDI	190.28	3.18	166.67	3.18	180.98	3.18	156.68	3.18	160.01	3.18
TOTAL SYSTEM COST	**2.73**		**3.91**		**3.59**		**3.32**		**3.18**	

Table 27. Cost of PU systems based on HFO-1336mzz(Z)

	HCFC-141b	**HFO-1336mzz(Z)**			
		0% reduced	**20% reduced**	**40% reduced**	**60% reduced**
Mole fraction in the gas cells	0.83	0.83	0.66	0.50	0.33
Reduction percent of HFO by weight (%)		0	17.70	41.94	60.77

FORMULATION	**PPHP**	**US$/ kg**	**PPHP**	**US$/ kg**	**PPHP**	**US$/ kg**	**PPHP**	**US$/ kg**	**PPHP**	**US$/ kg**
Polyol blend	100.00	2.16	100.00	2.14	100.00	2.16	100.00	2.16	100.00	2.14
Additives (catalysts, surfactant, additives)	27.39	1.47	27.63	1.53	27.45	1.51	27.18	1.48	27.33	1.50
Water	1.54		1.29		2.34		3.48		4.78	
Blowing agent	47.25	2.97	56.71	20.00	42.28	20.00	32.33	20.00	21.89	20.00
FORMULATED POLYOL	176.18	2.25	185.62	7.49	172.07	6.41	162.99	5.54	153.99	4.50
PMDI	190.28	3.18	156.51	3.18	180.75	3.18	173.22	3.18	182.90	3.18
TOTAL SYSTEM COST	**2.73**		**5.52**		**4.75**		**4.32**		**3.78**	

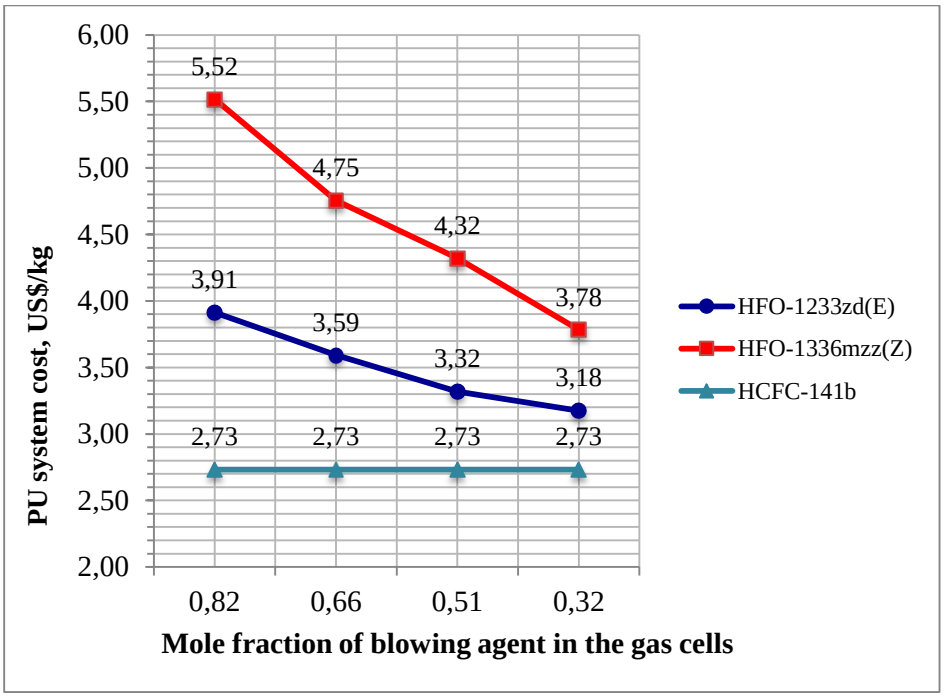


Figure 24. Cost of PU systems vs. Mole fraction of blowing agent

7.3. Final words about further trials with better cost/performance balance

At the end of the project and after an extensive formulation work, stable HFO based systems reduced by 80% were developed using N, methyl dicyclohexylamine and two tertiary amine catalysts of proprietary composition (Dabco 2039 and 2040). The results of the foam testing were promising and are shown in Table 28.

Table 28. Physical properties of 80% reduced HFO formulations

Blowing agent	HCFC 141b	HFO 1233zd(E)	HFO 1336mzz(Z)
Mole fraction in the gas cells	0.83	0.17	0.17
Machine reactivity			
Cream/ gel/ tack free times (s)	10/111/155	8/69/99	9/78/110
Free rise density (kg/m^3)	20.1	21.2	21.2
Minimum Fill Density (kg/m^3)	29.3	31.5	31.8
Flow Index	1.46	1.49	1.50
K-Factor initial (mW/m.K)	21.51	22.48	22.48
Compressive strength 24 hours (kPa) adjusted at 32 kg/m^3	107.6	147.1	161.9
Dimensional stability, 70°C (% ΔV), 24 hours	1.02	-3.47	-2.74
Dimensional stability, -30°C (% ΔV), 24 hours	0.38	-0.48	-1.23

8. SAFETY AND INDUSTRIAL HYGIENE

The Material Safety Data Sheets (MSDS) of the HFOs referenced for the project evaluation are provided by separate in Annex 2. The HFO-1233zd(E) and 1336mzz(Z) are non-flammable substances and no special precautions are needed from the safety point of view. There are no additional issues concerning industrial hygiene compared to HCFC-141b. The 8-hour Time Weighted Average (TWA), reported by the suppliers, are 800 ppm for 1233zd(E) and 500 ppm for 1336mzz(Z).

The specialised literature concludes that these specific HFO do not generate any significant amount of trifluoroacetic acid (TFA) in the atmospheric degradation process[2].

9. CONCLUSIONS

From the above results and analysis the following conclusions can be pointed out:

1. In the framework of this project supported by the Multilateral Fund, HFO based formulations with blowing agent reductions of 61 to 64 by weight were developed. This is equivalent to an HFO reduction in the gas cells of 60%.
2. Compared to HCFC-141b, the HFO reduced formulations showed:
   - Better foam flow reflected by a lower flow index (ratio between the free rise density and the minimum fill density).
   - An initial foam K factor higher by 7% in laboratory (Brett injections). This value was reproduced at industrial plant.
   - Similar values of foam K factor when measured one month after injected.
   - Similar laboratory and production plant values of compressive strength, dimensional stability and adhesion to metal.
3. There was not observed -from a statistical point of view- a difference between the performance of foam based on the two types of HFO: 1233zd(E) y 1336mzz(Z).
4. Considering that the foam HFO based technology is not flammable, it does not deplete the ozone layer (0 ODP) and has a low GWP (< 2), it was confirmed that compared to HCFC-141b, the foam HFO based technology does not present any additional environmental and safety and industrial hygiene issue.
5. The handling and processability at the production plant of the HFO reduced formulation was similar to HCFC-141b.
   - In hot weathers the PU systems based on HFO-1233zd(E) could require a storage conditioned at low/ medium temperatures.
6. Regarding to the Incremental Capital Cost of the foam HFO based technology, it is important to point out that at hotter climates there may be a need with the HFO 1233zd(E) to cool the formulated polyol storage and the formulated polyol day-tank to 20-25ºC storage to avoid the excessive build-up of pressure. Additionally, it is relevant to consider that for discontinuous panels and other rigid foam applications, the moulds should be equipped with heating systems and associated temperature controls to ensure a good performance with reduced HFO PU formulations. Costs related to these items must be considered.

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[2] For 1336mzz(Z) see: Baasandorj, M., et al. (2011), *J. Phys. Chem.* A 115(38): 10539-10549. Chiaperro, M. S., et al. (2006), *J. Phys. Chem.* A 110(43): 11944-11953. Cadle, R. D., (1980). *Rev. Geophys. Space Phys.* 18: 746-752.
For 1233zd(E) see: Wallington T.J., et al. (2015), *Chemosphere* 129: 135–141. Sulbaek Andersen M.P., et al (2012), *Phys. Chem. Chem. Phys.*14: 1735-1748.

7. Thanks to the technology formulation it was possible to significantly reduce the cost of the HFO based formulations. Nowadays the HFO reduced systems have higher costs than HCFC-141b by 16.4 and 33.2%, but these figures could be lower in the future.
8. Notwithstanding the positive results of this project, further trials are required to take into consideration the diverse boundary conditions (climate, injection equipment, etc.) typical of the SMEs universe and the higher cost of the special catalysts of proprietary composition that may be necessary.

REFERENCES

Ata S., Loh G., Jovicic J., *Recent Development of Formacel® 1100 – a Zero ODP and Low GWP Foam Expansion Agent*, American Chemistry Council 2015, DuPont Company, p. 2-9.
Bodgan M., Gittere C., Ross M., *Honeywell's Next Generation (LGWP) of Blowing Agents for Global Spray Foam Applications*, Polyurethanes 2011 Technical Conference, Nashville, Tennessee.

Box G. E. P., Hunter W. G., Hunter J. S., *Statistics for Experimenters*, New York, John Wiley & Sons, 1978, p. 1-14.

Bowman J., Szymanski J., Mejía S., *Cold Chain Industry: Energy Efficiency Solutions Solstice® LBA / Cyclopentane Blend Performance*, Honeywell International, 2011, p. 4-8.

Bowman J., Williams D., *Solstice™ Liquid Blowing Agent: Functional Performance and Development Status*, Honeywell International, 2011, p. 4-18.

Costa J., Chen B., Abbas L., Seshadri S., *Forane® 1233zd – Continued Improvement in Resin Shelf Stability with this Low GWP Liquid, Non-flammable Blowing Agent*, American Chemistry Council 2014, Arkema, p. 2-10.

Costa J., Abbas L., Chen B., Seshadri S., *An Investigation of a New Low GWP Blowing Agent for Spray Polyurethane Foam*, Polyurethanes 2011 Technical Conference, Nashville, Tennessee.

Foams Technical Options Committee, 2008 Progress Report, Mat 2008 TEAP Progress Report, Nairobi, 2008, p. 77-83.

Gum Wilson, Riese Wolf, Ulrich Henri (Editors), *Reaction Polymers*, Munich, Carl Hanser Verlag, 1992, p. 567 and 568.

Loh G., Creazzo J. A., Robin M. L., *Continued Development of FEA-1100: a Zero ODP and Low GWP Foam Expansion Agent with Desired Properties*, Polyurethanes 2011 Technical Conference, Nashville, Tennessee.

Loh G., Creazzo J., Robin M., *Further Development of FEA-1100: a Low GWP Foam Expansion Agent*, DuPont Company, Wilmington, p. 5-13.

Loh G., Grover V., *Formacel® 1100– a HFO with Unique Characteristics for Polyurethane Foam Applications*, American Chemistry Council 2014, DuPont Company, p. 1-16.

Mehta P., Borgohain A., Chidambaram S., Selwynt W., *Technical Comparisons of Foams Using Various Blowing Agent Blends Containing HCFC-141b, HFC-245fa, Solstice® Liquid Blowing*

Agent, and Hydrocarbons in Domestic Appliances, American Chemistry Council 2014, Honeywell International, p. 3-9.

Randall David, Lee Steve (Editors), *The Polyurethanes Book*, Huntsman International LLC, John Wiley & Sons, Ltd, p. 278.

Rose M., Parenti V., Riccio R., Altoe P., *Assessment of Formacel® 1100 (FEA-1100) Blowing Agent in Rigid Polyurethane Insulating Foams for Domestic Appliance*, DuPont Company, p. 3-7.

Sesoko Y., Tokumoto K., *The Impact of Amine Catalyst in Hydrohaloolefin Blown Rigid Polyurethane Foam Systems*, American Chemistry Council 2016, Tosoh Corporation, p. 2-8.

ANNEX 1. ANALYSIS OF VARIANCE OF THE FOAM PROPERTIES

In Section 6 of the report, the ANOVA corresponding to the foam K-Factor and its aging and compressive strength were presented. In this annex the results of the ANOVA analysis of the rest of the foam properties are shown.

A.1 Dimensional Stability at 70°C

Table A-1. ANOVA of Dimensional Stability at 70 ºC, two weeks

Factor	Degrees of Freedom	Sum of Squares	Mean Square	F	P	
Type de blowing agent (A)	1	3.560	3.560	6.300	0.036	Significant
Mole fraction (B)	3	16.850	5.620	9.930	0.005	Significant
A*B	3	2.400	0.801	1.420	0.308	
Pure Error	8	4.520	0.566			

Table A-2. ANOVA of Dimensional Stability at 70 ºC, two weeks, HCFC 141b vs HFO-1336mzz(Z) (40%) vs. HFO-1336mzz(Z) (60%)

Factor	Degrees of Freedom	Sum of Squares	Mean Square	F	P	
Type HFO	2	2,030	1,020	1,460	0,362	
Pure Error	3	2,100	0,699			

Table A-3. ANOVA of Dimensional Stability at 70 ºC, two weeks, HCFC 141b vs HFO-1233zd(E) (40%) vs. HFO-1233zd(E) (60%)

Factor	Degrees of Freedom	Sum of Squares	Mean Square	F	P	
Type HFO	2	1,360	0,679	1,300	0,393	
Pure Error	3	1,570	0,523			

A.2 Dimensional Stability at -30°C

Table A-4. ANOVA of Dimensional Stability at -30 ºC, two weeks

Factor	Degrees of Freedom	Sum of Squares	Mean Square	F	P	
Type de blowing agent (A)	1	0.005	0.005	0.207	0.661	
Mole fraction (B)	3	0.286	0.095	3.753	0.060	
A*B	3	0.056	0.019	0.740	0.557	
Pure Error	8	0.203	0.025			

Table A-5. ANOVA of Dimensional Stability at -30 ºC, two weeks, HCFC 141b vs HFO-1336mzz(Z) (40%) vs. HFO-1336mzz(Z) (60%)

Factor	Degrees of Freedom	Sum of Squares	Mean Square	F	P	
Type HFO	2	0,160	0,080	1,820	0,304	
Pure Error	3	0,132	0,044			

Table A-6. ANOVA of Dimensional Stability at -30 ºC, two weeks, HCFC 141b vs HFO-1233zd(E) (40%) vs. HFO-1233zd(E) (60%)						
Factor	**Degrees of Freedom**	**Sum of Squares**	**Mean Square**	**F**	**P**	
Type HFO	2	0,221	0,111	24,130	0,014	Significant
Pure Error	3	.0137	0,005			

A.3 **Foam adhesion to metal (galvanised steel)**

Table A-7. ANOVA of Adhesion strength to metal						
Factor	**Degrees of Freedom**	**Sum of Squares**	**Mean Square**	**F**	**P**	
Type de blowing agent (A)	1	5476.000	5476.000	20.325	0.002	Significant
Mole fraction (B)	3	4215.045	1405.015	5.215	0.028	Significant
A*B	3	6682.645	2227.548	8.268	0.008	Significant
Pure Error	8	2155.380	269.423			

Table A-8. ANOVA of adhesion to metal, HCFC 141b vs HFO-1336mzz(Z) (40%) vs. HFO-1336mzz(Z) (60%)						
Factor	**Degrees of Freedom**	**Sum of Squares**	**Mean Square**	**F**	**P**	
Type HFO	2	339,220	169,610	13,410	0,032	Significant
Pure Error	3	37,940	12,650			

Table A-9. ANOVA of adhesion to metal, HCFC 141b vs HFO-1233zd(E) (40%) vs. HFO-1233zd(E) (60%)						
Factor	**Degrees of Freedom**	**Sum of Squares**	**Mean Square**	**F**	**P**	
Type HFO	2	5.228,260	2.614,130	36,210	0,008	Significant
Pure Error	3	216,560	72,190			

ANNEX 2. MATERIAL SAFETY DATA SHEETS (MSDS) OF THE REFERENCED HFOs