# Aging of Polyurethane Foam Insulation in Simulated Refrigerator Panels — One-Year Results with Third-Generation Blowing Agents\*

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For presentation at the

The Earth Technologies Forum

Washington, DC

September 27-29,1999

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<sup>\*</sup>Research sponsored by the the Appliance Research Consortium, the U.S. Environmental Protection Agency, and the Office of Building Technology, State, and Community Programs, U.S. Department of Energy under Contract No. DE-AC05-96OR22464 with Lockheed Martin Energy Research Corp.

### AGING OF POLYURETHANE FOAM INSULATION IN SIMULATED REFRIGERATOR PANELS — ONE-YEAR RESULTS WITH THIRD-GENERATION BLOWING AGENTS

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#### ABSTRACT

Laboratory data are presented on the effect of constant-temperature aging on the apparent thermal conductivity of polyurethane foam insulation for refrigerators and freezers. The foam specimens were blown with HCFC-141b and with three of its potential replacements — HFC-134a, HFC-245fa, and cyclopentane. Specimens were aged at constant temperatures of 90°F, 40°F, and -10°F. Thermal conductivity measurements were made on two types of specimens: full-thickness simulated refrigerator panels containing foam enclosed between solid plastic sheets, and thin slices of core foam cut from similar panels. Results are presented for the first year of a multi-year study for the full-thickness panels and for about 1-1/2 years of aging for the core-foam specimens.

#### **INTRODUCTION**

Polyurethane foam insulation currently used in refrigerators and freezers in the United States is blown primarily with HCFC-141b. Because of its potential for depleting the ozone layer, the Montreal Protocol mandates that domestic production of HCFC-141b cease by the end of 2002, requiring that a replacement blowing agent be used after that time. Since 1993, the Oak Ridge National Laboratory has been cooperating with the Appliance Research Consortium on studies of the aging characteristics of polyurethane insulation foamed with various blowing agents. The early studies were aimed at the replacement for CFC-11, and results of aging studies on simulated refrigerator panels blown with CFC-11, HCFC-141b, and a blend of HCFC-142b and HCFC-22 have been reported previously.[1,2] A long-term study is currently underway on aging of foam blown with HCFC-141b and several potential replacements — HFC-134a, HFC-245fa, and cyclopentane. Tests with these third-generation blowing agents started in the fall of 1997 and are planned to continue for the next few years. Results on full-thickness specimens after six-months of aging at controlled temperatures were presented at this conference in 1998.[3] This paper presents results after one year of aging.

#### **SPECIMENS**

Two types of specimens are being studied. Specimens of one type were fabricated as panels that simulate the construction of a door or wall of a refrigerator. The panels are about two inches thick and have lateral dimensions of 24 by 24 inches. The faces of the panels are bounded by solid sheets. For the previous study of second-generation blowing agents, the solid sheets consisted of 24 gauge (0.024 in. thick) steel on one side and 0.12 in. thick acrylonitrile-butadiene-styrene (ABS) plastic on the other side.[1,2] For the present study of third-generation blowing agents, 0.040 in. thick plastic sheets were used on both faces, with separate sets of panels being made with ABS and high-impact-polystyrene (HIPS) plastic. The thinner plastic was considered to be more representative of current refrigerator production, and plastic was used on both sides to accelerate the aging experiments by allowing gases to permeate through both sides of the

panels. It was felt that the effect of a steel sheet on one side could be simulated using models that are being developed. The edges of the panels were sealed with aluminum foil tape to simulate the configuration in a refrigerator where there are no cut, exposed foam edges.

The panels were foamed with HCFC-141b (to provide the base case), HFC-245fa, HFC-134a, and cyclopentane. At the present time, the latter two blowing agents are the only commercially available non-ozone-depleting replacements for HCFC-141b. The panels were fabricated by four foam suppliers (denoted here as suppliers A, B, C, and D), with each supplier providing panels with each of the four blowing agents.

To provide a characterization of the foam itself, specimens were also made that consisted of core foam cut into 12 in. squares and sliced into thicknesses of about 0.4 and 1.5 inches. A stack of four of the 0.4-in.-thick slices made up one test specimen.

It should be noted that the foams made with the alternative blowing agents may not yet be optimized for thermal performance. Visual observations of the sliced specimens showed a very uniform fine cellular structure with HCFC-141b but the presence of many larger bubbles interspersed within the fine cellular structure for the other blowing agents.

## **EXPERIMENTAL PROCEDURES**

Thermal resistance measurements were made using one 24-inch square and two 12-inch square heat-flowmeter-apparatuses (HFMAs) that conform to ASTM C 518.[4] Intervening layers of foam rubber were placed between the panel specimens and the hot and cold plates of the apparatus to eliminate any undesirable air gaps between the specimens and the plates and also to protect the plates from the rigid test panels. Thermocouples were taped directly to the faces of the panels so that the temperature differences across the test panels were measured directly. Since the measurements gave the overall thermal resistance of the center of the test panel, a correction was made for the thermal resistance of the plastic sheets to obtain the thermal conductivity of the foam insulation. Tests on the core foam specimens gave the thermal conductivity directly.

The specimens were stored in closed, constant temperature, atmospheric pressure aging chambers between HFMA tests. Aging temperatures of 90°F, 40°F, and  $-10^{\circ}$ F were used in order to span most of the range of conditions to which the foam would be exposed in a refrigerator application. Thermal tests were performed at 45°F and 75°F mean temperatures, using a temperature difference of 40°F.

### **RESULTS AND DISCUSSION**

### **Core-Foam Specimens**

Thermal conductivity measurements on the core foam started in the fall of 1997 and were still in progress at the time of this writing. Because of the frequency of testing that is required, only a limited number of specimens could be accommodated. A complete set of data on core foam from Supplier A has been collected over a period of 1-1/2 years, and these data are presented here.

Slice Thickness, in.	HCFC-141b	HFC-134a	HFC-245fa	Cyclopentane		
0.4	0.132	0.160	0.138	0.150		
1.5	0.128	0.155	0.132	0.145		

Table 1. Thermal Conductivity of Freshly-Sliced Core-Foam Specimens at 75°F

Thermal conductivity units are Btu•in./h•ft<sup>2</sup>•°F. Each value represents an average over three specimens. Specimens are from Supplier A.

The thermal conductivity of freshly sliced foam at 75°F is shown in Table 1 for the two slice thicknesses. This shows that the lowest thermal conductivity was found with HCFC-141b, followed by HFC-245fa (4% higher), cyclopentane (13% higher), and HFC-134a (21% higher). This relative ranking is the same as has been observed by Haworth.[5] Table 1 also shows that the thermal conductivity of thinner slices was consistently 3 to 4% higher than that of the thicker slices. This is at least partly due to the larger amount of damaged surface layers with the thinner slices where air immediately displaces the blowing agent in the cut cells. While the data for the thicker slices are more representative of that in the full-thickness panels, the thinner specimens age much more rapidly and are useful for comparing potential differences in long-term performance with the different blowing agents.

Figure 1 compares the aging characteristics of the thinner (0.4 in.-thick) slices with the four blowing agents for three aging temperatures and for the two test temperatures. The data were taken over a period of about 1-1/2 years. Since numerous previous studies have shown that the aging of unfaced foam scales with the square of the thickness (see [3] and ASTM C 1303 [6]), the data are plotted as thermal conductivity versus the aging time divided by the square of the slice thickness. With this scaling, data obtained over a time period of 1-1/2 years on slices 0.4 in. thick are good predictors of the variation of the thermal conductivity of unfaced 2 in.-thick specimens over a period of 37.5 years, well beyond the nominal refrigerator lifetime of 20 years.

The curves in Figure 1 show several trends. For all conditions, the curves show an initial rapid increase in thermal conductivity which is attributed to diffusion of air components into the cells of the foam, followed by a more gradual increase which is attributed to diffusion of the blowing agent out of the cells. Except for crossover of some of the curves for HCFC-141b and HFC-245fa, the relative ranking of blowing agents given in Table 1 is preserved throughout the aging process. The time required for a given change in thermal conductivity with aging at 40°F is roughly twice as long as for aging at 90°F, while the time required at -10°F is about 10 times as long as at 90°F. The curves for tests at 45°F and 75°F mean temperatures show the same general variations, but the values measured at 45°F are always lower than those measured at 75°F.

Data read from the curves in Figure 1 and companion data for the thicker (1.5 in.-thick) slices are compared with data obtained on full-thickness panels in the next section. In general, the data obtained on core-foam specimens may be used to estimate upper bounds for aging of the foam in the full-thickness panels.



Figure 1. Aging of thin (0.4 in.-thick) core-foam specimens blown with third-generation blowing agents by Supplier A. Captions show aging and testing temperatures.

#### **Full-Thickness Panels**

Thermal measurements on 96 full-thickness panels have been performed before and after aging under controlled temperatures for one year. Data on the panels are reported as normalized values because the directly measured values are biased due to the construction of the panels. From tests on standard reference materials, we have found that heat flows due to the aluminum foil tape around the panel edges result in measured center-of-panel thermal conductivities that are too low by a few percent. The data were normalized by averaging the pre-aging thermal conductivities measured at 75°F on the 24 panels that were blown with HCFC-141b, and then dividing the individual measured thermal conductivity values by this average. This normalization procedure was considered to be justified since the bias caused by the aluminum foil tape should be nearly the same from one panel to another.

Normalized results before and after aging for one year are given in Table 2. The results in the tables give an indication of the variation in thermal conductivity among specimens from a particular supplier and among the four different suppliers. For example, the panels blown with HCFC-141b have pre-aging normalized conductivities at 75°F that range from 0.95 to 1.04, but for a given supplier the variation is 2% or less. Similar levels of variation are seen for the other blowing agents.

Averaging the pre-aging data on the six panels for each supplier and each blowing agent gives the comparisons shown in Figure 2. On average, the 75°F thermal conductivity of foam blown with HFC-134a was about 18% higher than for HCFC-141b, while the conductivities for HFC-245fa and cyclopentane were about 7% and 15% higher. For Supplier A only, the average conductivities for HFC-134a, HFC-245fa, and cyclopentane were 20%, 5%, and 15% higher, respectively, than for HCFC-141b. These relative differences are in good agreement with the values given in Table 1 for the core foam, also from Supplier A. At the 45°F test temperature, the average conductivities for HFC-245fa, and cyclopentane were 16%, 4%, and 16% higher than for HCFC-141b.

Most of the panels were measured after six months of aging as well as after one year. Data at six months for the panels from Supplier A were presented at this conference in 1998.[3] Figure 3 shows the variation with time for panels from Supplier A as they were aged at 90°F and 40°F and tested at 75°F. Data for -10°F aging are not shown because the changes were essentially negligible. Separate graphs are given for the panels with ABS and HIPS sheets, since the panels with HIPS aged faster, as had been noted previously.[3] Also, as was noted previously, aging at 40°F is slower than at 90°F. Figure 3 shows that the relative ranking of the four blowing agents is maintained during aging over the one year period, but there is some tendency for crossover of the 90°F HIPS curves for HCFC-141b and HFC-245fa and also for the curves for HFC-134a and cyclopentane. While there appears to be some curvature for the 90°F HIPS curves for HFC-134a and cyclopentane, deviations from linearity for all the curves are less than  $\pm 1.5\%$ , and data over longer time periods are needed to determine the shape of the curves more accurately.

Figure 4 shows percentage increases in thermal conductivity after one year of aging. The values were obtained by averaging the percentage increases for the four suppliers (except for HFC-245fa with HIPS at  $-10^{\circ}$ F, where the anomalously high values for Supplier B were not included in the average). Also shown for comparison are the percentage increases for 2 in.-thick core foam. The values at one year and 20 years of aging were obtained by scaling the results for 1.5 in.-thick and 0.4 in.-thick core-foam specimens, respectively. The results show that the plastic sheets significantly reduce the rate of aging, with ABS being

Table 2. Results of thermal conductivity tests on full-thickness panels before and after one year of aging at controlled temperatures. Values are normalized to the average of the pre-aging results for HCFC-141b at 75°F test temperature.

Blowing	Plastic	Aging	Aging Time,		7	5°F			4	5°F	
Agent	Liner	Temp., °F	Years	Supplier A	Supplier B	Supplier C	Supplier D	Supplier A	Supplier B	Supplier C	Supplier D
HCFC-141b	ABS	90	0	1.01	0.95	1.03	1.04	0.94	0.90	0.93	0.95
HCFC-141b	ABS	40	0	1.01	0.95	1.01	1.03	0.94	0.91	0.92	0.95
HCFC-141b	ABS	-10	0	1.01	0.95	1.02	1.04	0.94	0.89	0.93	0.95
HCFC-141b	HIPS	90	0	1.01	0.95	1.01	1.02	0.94	0.90	0.93	0.94
HCFC-141b	HIPS	40	0	1 00	0.95	1 01	1.03	0.94	0.90	0.93	0.94
HCEC-141b	HIPS	-10	0	1.00	0.00	1.01	1.00	0.01	0.00	0.00	0.01
		10	0	1.01	0.00	1.01	1.02	0.04	0.00	0.00	0.04
	ABC	00	0	1.01	1 17	1 17	1 10	1.00	1.07	1.06	1.09
11FC-134a	ADS	90	0	1.21	1.17	1.17	1.10	1.09	1.07	1.00	1.08
HFC-134a	ADO	40	0	1.20	1.14	1.17	1.19	1.09	1.04	1.07	1.08
HFC-134a	ABS	-10	0	1.21	1.16	1.18	1.18	1.09	1.05	1.07	1.08
HFC-134a	HIPS	90	0	1.20	1.15	1.19	1.17	1.09	1.04	1.08	1.07
HFC-134a	HIPS	40	0	1.21	1.14	1.18	1.18	1.09	1.04	1.08	1.08
HFC-134a	HIPS	-10	0	1.21	1.17	1.19	1.19	1.09	1.07	1.07	1.08
HFC-245fa	ABS	90	0	1.06	1.04	1.07	1.09	0.97	0.95	0.97	0.99
HFC-245fa	ABS	40	0	1.05	1.07	1.07	1.09	0.96	0.96	0.97	0.99
HFC-245fa	ABS	-10	0	1.06	1.04	1.07	1.09	0.96	0.94	0.96	0.99
HFC-245fa	HIPS	90	0	1.05	1.05	1.08	1.08	0.96	0.94	0.97	0.98
HFC-245fa	HIPS	40	0	1.06	1.05	1.08	1.08	0.97	0.95	0.97	0.99
HFC-245fa	HIPS	-10	0	1.05	1.08	1.07	1.09	0.96	0.98	0.97	0.98
Cvclopentane	ABS	90	0	1.16	1.18	1.14	1,11	1.07	1.10	1.07	1.04
	ABS	40	0	1 16	1 18	1 14	1 12	1.06	1 10	1.07	1 04
	ABS	-10	0	1.10	1.10	1.14	1.12	1.00	1.10	1.07	1.04
Cyclopentane		-10	0	1.10	1.10	1.14	1.12	1.00	1.10	1.07	1.03
Cyclopentane		30	0	1.17	1.10	1.10	1.11	1.09	1.12	1.10	1.02
Cyclopentane		40	0	1.15	1.10	1.15	1.12	1.00	1.11	1.09	1.05
Cyclopentane	пігз	-10	0	1.10	1.17	1.15	1.12	1.07	1.11	1.09	1.05
	4.5.0			4.00	1.00	4.00	4.00	0.07	0.00	0.00	0.00
HCFC-141b	ABS	90	1	1.06	1.00	1.09	1.09	0.97	0.92	0.98	0.99
HCFC-141b	ABS	40	1	1.04	1.00	1.07	1.08	0.93	0.90	0.95	0.96
HCFC-141b	ABS	-10	1	1.02	0.96	1.06	1.05	0.93	0.88	0.93	0.94
HCFC-141b	HIPS	90	1	1.13	1.06	1.18	1.19	1.04	0.99	1.07	1.10
HCFC-141b	HIPS	40	1	1.06	1.01	1.13	1.11	0.97	0.92	1.02	1.02
HCFC-141b	HIPS	-10	1	1.03	0.95	1.07	1.05	0.94	0.88	0.96	0.95
HFC-134a	ABS	90	1	1.26	1.23	1.25	1.30	1.13	1.11	1.12	1.13
HFC-134a	ABS	40	1	1.23	1.19	1.24	1.23	1.10	1.05	1.10	1.10
HFC-134a	ABS	-10	1	1.22	1.18	1.22	1.22	1.09	1.06	1.09	1.10
HFC-134a	HIPS	90	1	1.33	1.23	1.33	1.30	1.21	1.10	1.20	1.19
HFC-134a	HIPS	40	1	1.27	1.20	1.27	1.24	1.13	1.07	1.13	1.11
HFC-134a	HIPS	-10	1	1.23	1.21	1.24	1.22	1.10	1.08	1.10	1.09
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HFC-245fa	ABS	90	1	1.10	1.07	1.12	1.13	0.98	0.96	1.00	1.02
HFC-245fa	ABS	40	1	1.08	1 11	1 11	1 13	0.96	0.97	0.97	1.00
HFC-245fa	ABS	_10	1	1.00	1.06	1 10	1 12	0.00	0.07	0.07	1.00
HEC 245fa		-10	1	1.00	1.00	1.10	1.12	1.04	1.01	1.07	1.00
LEC 2451a		90		CI.I	1.13	1.10	1.10	1.04	1.01	1.07	1.07
HEC 24518		40		1.11	1.09	1.14	CI.I	0.99	0.96	1.01	1.03
nru-2451a	пгэ	-10	1	1.08	1.31	1.11	1.11	0.97	1.20	0.99	1.00
Qualant 1	4.0.0			1.00	1.00	1.00	4.40		1.10		
	ABS	90	1	1.22	1.22	1.22	1.18	1.13	1.16	1.17	1.11
Cyclopentane	ABS	40	1	1.19	1.21	1.21	1.16	1.07	1.12	1.11	1.05
Cyclopentane	ABS	-10	1	1.17	1.20	1.20	1.14	1.05	1.10	1.10	1.04
Cyclopentane	HIPS	90	1	1.33	1.30	1.32	1.28	1.25	1.25	1.27	1.22
Cyclopentane	HIPS	40	1	1.24	1.24	1.26	1.23	1.13	1.16	1.19	1.14
Cyclopentane	HIPS	-10	1	1.19	1.19	1.21	1.16	1.07	1.11	1.14	1.07



Figure 2. Average normalized thermal conductivity for full-thickness panels before aging. Data are normalized with respect to average for HCFC-141b tests at 75°F before aging.



Figure 3. Aging of foam in full-thickness panels blown with third-generation blowing agents by Supplier A. Tested at 75°F.







more effective than HIPS. The difference between ABS and HIPS may be explained by the relative gas permeances of the two plastics.  $CO_2$ ,  $O_2$ , and  $N_2$  permeances were measured on specimens of the plastic sheets and were found to be four to six times larger for HIPS than for ABS.[7] Figure 4 also shows that decreasing temperature produces large decreases in the rate of aging, with the changes at 40°F being about one-half as large as at 90°F and with the changes at -10°F being very small. This is in agreement with the effect of temperature observed on core foam, and also in agreement with the effect of temperature on the permeance of the plastic sheets for which the permeance at 40°F was found to be 0.4 to 0.7 of the 90°F value.

The data presented for the test panels should not be interpreted directly as quantitative indications of the changes that would be expected in the walls and doors of refrigerators. This is because only one surface in a refrigerator will have a plastic sheet, while the other surface will have an impermeable steel sheet. Physical arguments suggest that the time to produce a given change in thermal conductivity would be two to four times longer when one plastic sheet is replaced with a steel sheet. The factor of two would apply if the permeance of the plastic sheets were the dominating resistance to gas transport, while the factor of four would apply if diffusion through the foam were the dominating resistance. Aging models being developed will allow a more definitive estimate of the effect of a steel surface.

## SUMMARY AND CONCLUSIONS

Thermal conductivity measurements have been made over a 1-1/2 year period on cut slices of polyurethane foam insulation blown with HCFC-141b, HFC-134a, HFC-245fa, and cyclopentane. Initial results at 75°F mean temperature before aging showed that the thermal conductivities of foam blown with HFC-134a, HFC-245fa, and cyclopentane were 21%, 4%, and 13%, respectively, higher than with HCFC-141b. The aging rate was very sensitive to aging temperature, with aging at 40°F being about one-half as fast as at 90°F, and with aging at -10°F being about one-tenth as fast. Except for crossover of the curves for HCFC-141b and HFC-245fa, the relative ranking of the blowing agents was preserved through the aging process.

Thermal conductivity measurements have been made on a set of full-thickness test panels containing polyurethane foam confined between solid sheets made of ABS and HIPS plastics. The panels simulated the walls and doors of a refrigerator or freezer except that the steel sheet normally on one side was replaced with a plastic sheet. Initial measurements at 75°F mean temperature before controlled aging showed that the conductivity of foam blown with HFC-134a, HFC-245fa, and cyclopentane averaged 18%, 7%, and 15%, respectively, higher than that with HCFC-141b.

Tests on the panels after one year of aging at controlled temperatures have been completed. For both ABS and HIPS plastics, the conductivity increases were less than those predicted for unenclosed full-thickness core-foam, showing that the plastic liners reduce the rate of aging. The panels with HIPS sheets showed increases of 8 to 15% with aging at 90°F, 2 to 8% at 40°F, and less than 5% at -10°F. The panels with ABS sheets showed smaller increases of 2 to 7% at 90°F, and less than 5% at 40°F and -10°F. These differences in aging rates correlate with measurements of gas permeances of the plastic sheets.

### ACKNOWLEDGMENTS

The authors would like to acknowledge the contributions of a number of organizations. Funding for this project was provided by the Appliance Research Consortium, the U. S. Environmental Protection Agency, and the U.S. Department of Energy, Office of Building Technology, State, and Community Programs under contract number DE-AC05-96ORR22464 with the Oak Ridge National Laboratory, managed by Lockheed Martin Energy Research Corp. Test panels were fabricated by BASF Corp., Bayer Corp., Dow Chemical Corp., and ICI Chemicals, Inc. Aging chambers were contributed by Sub-Zero Corp. Dr. David W. Yarbrough is thanked for many helpful discussions.

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