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Aging of Polyurethane Foam Insulation in Simulated Refrigerator Panels - Initial Results
with Third-Generation Blowing Agents*

Kenneth E. Wilkes, W. Alex Gabbard, and Fred J. Weaver

Oak Ridge National Laboratory

P. O. Box 2008

Building 4508, MS 6092

Oak Ridge, Tennessee 37831-6092

(423) 574-5931

FAX (423) 576-3894

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**AGING OF POLYURETHANE FOAM INSULATION IN SIMULATED
REFRIGERATOR PANELS - INITIAL RESULTS
WITH THIRD-GENERATION BLOWING AGENTS**

Kenneth E. Wilkes, W. Alex Gabbard, and Fred J. Weaver

Oak Ridge National Laboratory

Oak Ridge, TN 37831-6092

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 about 250 days of aging for the core-foam specimens and for the first six months of aging for the full-thickness panels.

INTRODUCTION

Polyurethane foam insulation used in refrigerators and freezers in the United States is blown primarily with HCFC-141b. Since domestic production of HCFC-141b is scheduled to cease by the end of 2002, the refrigerator/freezer industry is faced with finding a suitable replacement blowing agent. 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 study was 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] While long-term tests are still being conducted on those panels, the focus has shifted to 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. The purpose of this paper is to present results that are available to date.

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, with each supplier providing specimens with each of the four blowing agents. This will provide information on supplier-to-supplier variations in foam formulations that were not obtained in the second-generation study. It should be noted that the foams made with the alternative blowing agents may not yet be optimized for thermal performance.

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. The core-foam specimens were cut from full-thickness foam sheets that were encased in aluminum foil. The intent of the foil was to hinder aging before the specimens could be prepared and testing started.

EXPERIMENTAL PROCEDURES

Thermal resistance measurements were made using one 24-inch square and two 12-inch square heat-flow-meter-apparatuses (HFMA's) that conform to ASTM C 518.[3] 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°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, with a few measurements at other temperatures.

RESULTS AND DISCUSSION

Core-Foam Specimens

Thermal conductivity measurements on the core foam were started in the fall of 1997 and were still in progress at the time of this writing. Since the thermal conductivity of these specimens changes fairly rapidly after slicing, the measurements were made very frequently at first and hence only a limited number of specimens could be studied at any given time. As the aging slows down, the

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

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

Thermal conductivity units are Btu·in./h·ft²·°F. Each value represents an average over three specimens.

measurements can be made less frequently and additional specimens can be added to the testing sequence. Results on specimens from one supplier (denoted here as Supplier A) with all four blowing agents are now available over a time period of about 250 days, and are reported here. Tests are underway on specimens from another supplier and these results will be reported in the future.

Table 1 shows a comparison of the thermal conductivity at 75°F for freshly-sliced specimens at two different thicknesses. 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. The thickness of the destroyed surface layer (TDSL) for the HCFC-141b specimens has been measured to be 0.0036 in., which accounts for 1.8% of the specimen thickness (counting both sides of a 0.4 in.-thick slice).[4] Table 1 also shows that the lowest thermal conductivity is found with HCFC-141b, followed by HFC-245fa (3% higher), cyclopentane (13% higher), and HFC-134a (21% higher). This relative ranking is the same as has been observed by Haworth.[5]

Figure 1 shows the variation of thermal conductivity with temperature for 1.5 in.-thick specimens before appreciable aging has occurred. The conductivity varies linearly with temperature for HFC-134a, which is gaseous over the temperature range studied (boiling point is -15.1°F). Condensation of the other blowing agents would occur within this temperature range (boiling points are 89.6, 59.5, and 120.6°F for HCFC-141b, HFC-245fa, and cyclopentane, respectively), causing the curves to tend to flatten at lower temperatures. The results in Figure 1 are in reasonably good agreement with Haworth's observations. However, he shows HFC-245fa having a lower thermal conductivity than HCFC-141b below about 60°F. The differences between the two studies may be due to differences in foam formulations and resultant differences in foam structure. For example, 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.

Figure 2 shows the variation of thermal conductivity over a period of about 250 days for two thicknesses of HCFC-141b specimens tested at 75°F and aged at three different temperatures. The initial rapid increase in conductivity is attributed to diffusion of air into the cells of the foam, while the later more gradual increase is attributed to diffusion of the blowing agent out of the cells. Aging temperature has a large effect on the aging process. The time required for a given change in conductivity at 40°F is about twice as long as at 90°F, and the time required at -10°F is about 10 times as long as at 90°F. The thickness of the slices also has a large effect on the aging rate, with the thinner specimens aging much more rapidly than the thicker slices. When the thermal conductivity is plotted versus the aging time divided by the square of the slice thickness as in Figure

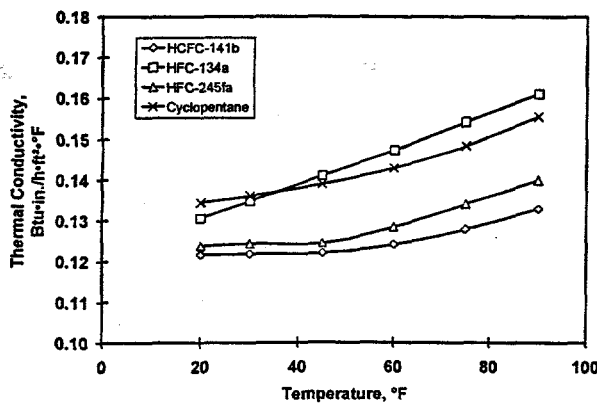


Figure 1. Thermal conductivity of thick core-foam specimens blown with third-generation blowing agents by Supplier A, measured before appreciable aging has occurred.

3, the curves for the two different slice thicknesses tend to fall on top of each other (except for a small vertical shift as in Table 1). The effects of temperature and the scaling with time divided by the square of the thickness are as would be expected for aging controlled by a thermally activated diffusion process.

Figure 4 compares the aging rates for the thinner (0.4 in.-thick) slices with the four blowing agents for three aging temperatures and for the two test temperatures. Aging temperature has a large effect with all four blowing agents. Except for crossover of the curves for HCFC-141b and HFC-245fa, the relative ranking of the blowing agents is preserved through the aging process. For a given blowing agent and aging temperature, the thermal conductivity measured at 45°F (on the same specimen) is always lower than that measured at 75°F. Except for crossing of the curves for HCFC-141b and HFC-245fa at an earlier time and some small differences in relative spacings, the aging curves for the 45°F test condition are very similar to those at 75°F.

The conditions for a refrigerator insulation thickness of 2 in. at the end of the nominal lifetime of a refrigerator (20 years) correspond to a scaled time of 1825 days/in.². Thus the thermal conductivities measured on the thin core-foam slices after aging for about 290 days would give an upper bound on the thermal conductivity to be expected in a refrigerator wall after 20 years. While data have not yet been measured on the thin slices over this full time period, Figure 4 shows that only small additional increases in thermal conductivity would be expected. Similarly, core-foam data may be used to estimate upper bounds for changes in the full-thickness panels over time.

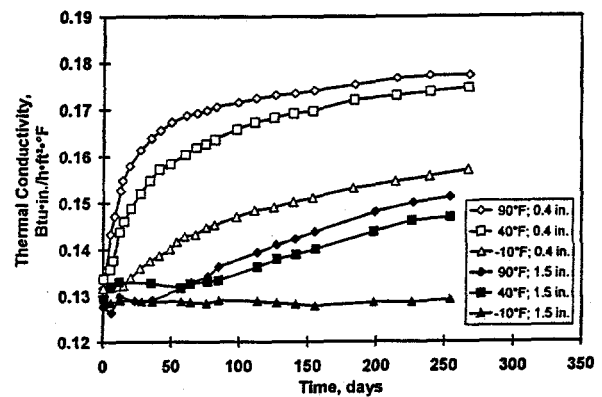


Figure 2. Aging of core foam blown with HCFC-141b by Supplier A. Tests were performed at 75°F. The legend shows the aging temperature and the slice thickness.

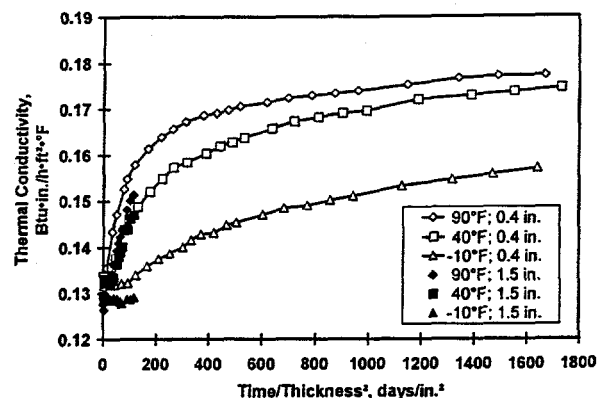


Figure 3. Aging of core foam blown with HCFC-141b by Supplier A. Tests were performed at 75°F. The legend shows the aging temperature and the slice thickness.

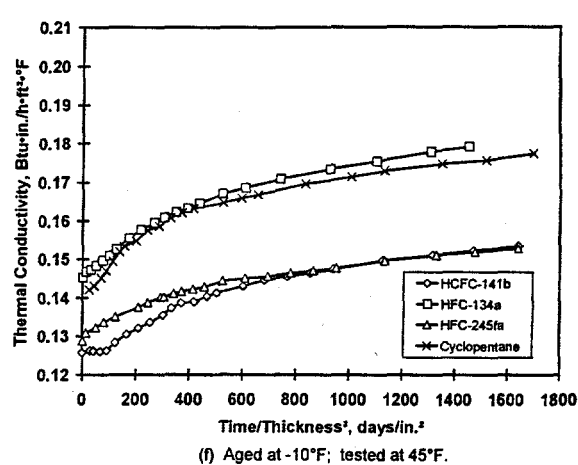
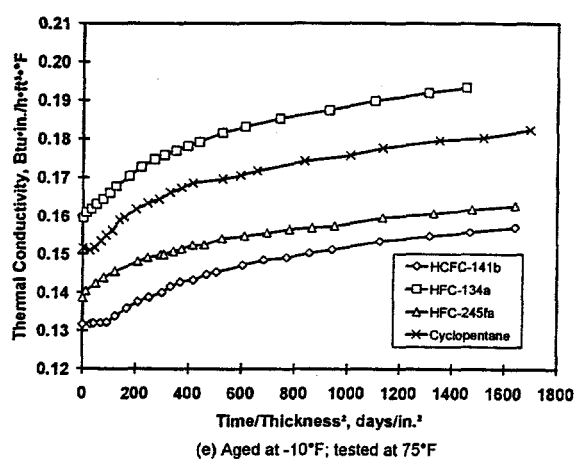
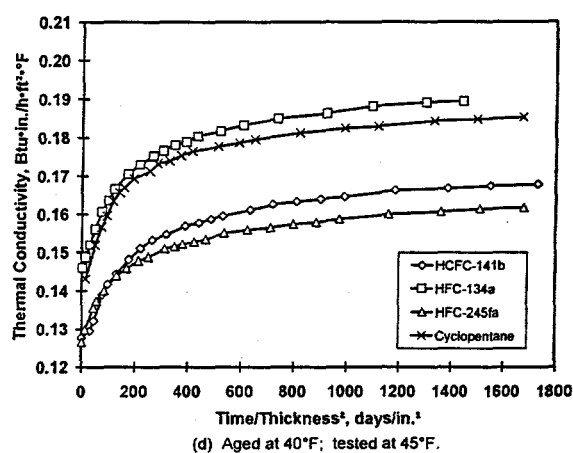
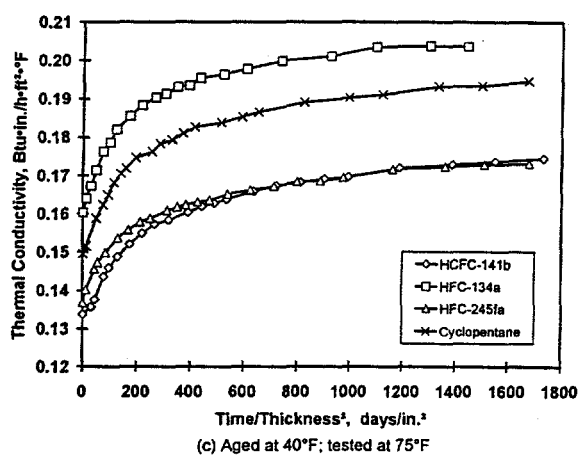
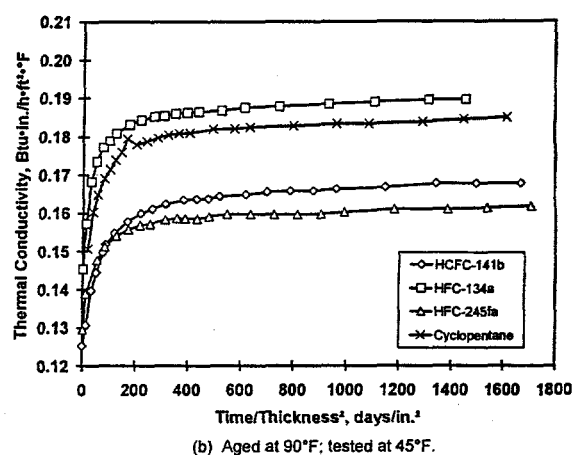
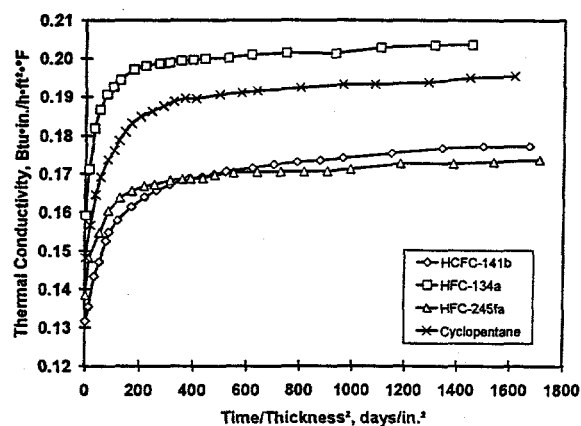


Figure 4. Aging of thin (0.4 in.-thick) core-foam specimens blown with third-generation blowing agents by Supplier A. Captions show aging and testing temperatures.

Full-Thickness Panels

Thermal measurements on the full-thickness panels were started late in the fall of 1997. Initial measurements on the set of 96 panels were completed early in 1998, and measurements after aging for six months in the controlled temperature aging cabinets were underway at the time of this writing.

Data on the panels are reported in a normalized fashion because we have found that the directly measured values are biased due to the construction of the panels. Through tests on standard reference materials, we have found that heat flows caused by the aluminum foil tape around the edges of the test panels result in thermal conductivities measured in the center of the panel that are too low by a few percent. Rather than reporting the directly measured thermal conductivity values, we report normalized results. The normalization was done by averaging the 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.

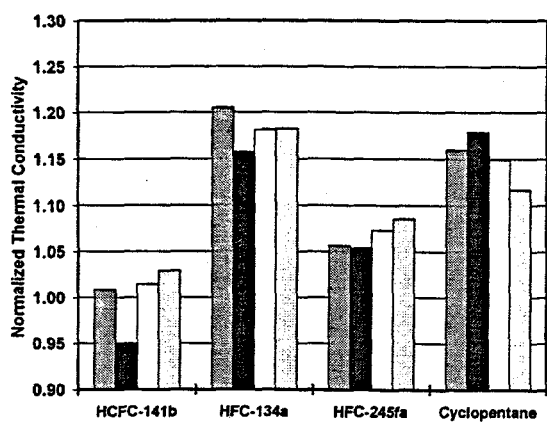
Initial results normalized in this manner are given in Table 2. The table identifies the blowing agent, plastic liner material, aging temperature to which to panel has been assigned, and the foam supplier (denoted as Suppliers A, B, C, and D). The results in the table give an indication of the variation in thermal conductivity within specimens from a particular supplier and among the four different suppliers. For example, the panels blown with HCFC-141b have 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 data on the six panels for each supplier and each blowing agent gives the comparisons shown in Figure 5. 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-134a, HFC-245fa, and cyclopentane were 16%, 4%, and 16% higher than for HCFC-141b.

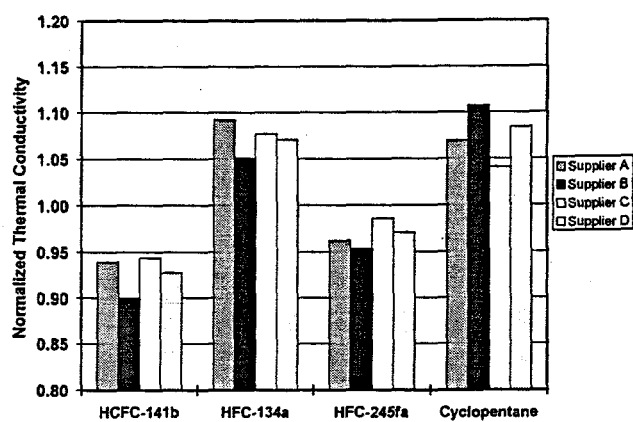
Tests after six months of aging in the controlled temperature cabinets have been completed for the 24 panels from Supplier A. Percentage changes in the 45°F and 75°F thermal conductivities of each of these panels are given in Figure 6 for aging at 90°F, 40°F, and -10°F. Using the time scaling shown in Figure 3, the data on 1.5 in.-thick core foam were used to calculate the percentage change expected for 2 in.-thick core foam at six months of aging, and these calculated values are shown in Figure 6 for comparison with the data on the test panels. These results show that both of the plastic materials reduce the rates at which air enters the foam and/or at which the blowing gas leaves. The results also show that ABS plastic is more effective than HIPS in reducing the rates of gas movement. This is in agreement with literature data on the permeance of these two plastics which show the permeance of HIPS to be about three to four times larger than for ABS.[6] Figure 6 again

Table 2. Results of Initial Thermal Conductivity Tests on Full-Thickness Panels. Values are normalized to the average of the results for HCFC-141b at 75°F test temperature.

Blowing Agent	Plastic Liner	Aging Temp., °F	45°F				75°F			
			Supplier A	Supplier B	Supplier C	Supplier D	Supplier A	Supplier B	Supplier C	Supplier D
HCFC-141b	ABS	90	0.94	0.90	0.95	0.93	1.01	0.95	1.03	1.04
HCFC-141b	ABS	40	0.94	0.91	0.95	0.92	1.01	0.95	1.01	1.03
HCFC-141b	ABS	-10	0.94	0.89	0.95	0.93	1.01	0.95	1.02	1.04
HCFC-141b	HIPS	90	0.94	0.90	0.94	0.93	1.01	0.95	1.01	1.02
HCFC-141b	HIPS	40	0.94	0.90	0.94	0.93	1.00	0.95	1.01	1.03
HCFC-141b	HIPS	-10	0.94	0.90	0.94	0.93	1.01	0.95	1.01	1.02
HFC-134a	ABS	90	1.09	1.07	1.07	1.06	1.21	1.17	1.17	1.17
HFC-134a	ABS	40	1.09	1.04	1.08	1.07	1.20	1.14	1.17	1.18
HFC-134a	ABS	-10	1.09	1.05	1.08	1.07	1.21	1.16	1.18	1.18
HFC-134a	HIPS	90	1.10	1.04	1.08	1.08	1.20	1.15	1.19	1.18
HFC-134a	HIPS	40	1.10	1.04	1.08	1.08	1.21	1.14	1.18	1.19
HFC-134a	HIPS	-10	1.09	1.07	1.08	1.08	1.21	1.17	1.19	1.19
HFC-245fa	ABS	90	0.97	0.95	0.99	0.97	1.06	1.04	1.07	1.09
HFC-245fa	ABS	40	0.96	0.96	0.99	0.97	1.05	1.07	1.07	1.09
HFC-245fa	ABS	-10	0.96	0.94	0.99	0.96	1.06	1.04	1.07	1.09
HFC-245fa	HIPS	90	0.96	0.94	0.98	0.97	1.05	1.05	1.08	1.08
HFC-245fa	HIPS	40	0.97	0.95	0.99	0.97	1.06	1.05	1.08	1.08
HFC-245fa	HIPS	-10	0.96	0.98	0.98	0.97	1.05	1.08	1.07	1.09
Cyclopentane	ABS	90	1.07	1.10	1.04	1.08	1.16	1.18	1.14	1.11
Cyclopentane	ABS	40	1.06	1.10	1.04	1.07	1.16	1.18	1.14	1.12
Cyclopentane	ABS	-10	1.06	1.11	1.05	1.07	1.16	1.18	1.14	1.12
Cyclopentane	HIPS	90	1.09	1.12	1.02	1.10	1.17	1.19	1.16	1.11
Cyclopentane	HIPS	40	1.06	1.11	1.05	1.09	1.15	1.18	1.15	1.12
Cyclopentane	HIPS	-10	1.07	1.11	1.05	1.09	1.16	1.17	1.15	1.12



(a) Tested at 75°F.



(b) Tested at 45°F.

Figure 5. Average normalized thermal conductivity for full-thickness panels before controlled aging. Data are normalized with respect to average for HCFC-141b tests at 75°F.

shows the marked effect of aging temperature on the aging rate, with the aging rate decreasing significantly as the aging temperature is reduced. It should be noted that any of the changes that are of the order of $\pm 2\%$ are considered to be within the experimental uncertainty. This would include all of the data for the test panels with ABS sheets, and some of the data for panels with HIPS sheets. However, changes with HIPS sheets at 90°F and 40°F are considered to be significant (outside the experimental uncertainty). Data at longer times, as planned, are needed to be more definitive about aging rates of the full-thickness panels.

The data presented for the test panels should not be interpreted directly as a quantitative indication 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 be an impermeable steel sheet. Since gases would only permeate through one surface, the changes in thermal conductivity would be less than those presented here. It is expected that models that are being developed will allow the presence of a steel sheet to be taken into account.

SUMMARY AND CONCLUSIONS

Thermal conductivity measurements have been made over a 250 day period for cut slices of polyurethane foam insulation blown with HCFC-141b, HFC-134a, HFC-245fa, and cyclopentane by one foam supplier. Initial results with these core-foam specimens showed that the lowest thermal conductivity at 75°F mean temperature was found with HCFC-141b, followed by HFC-245fa (3% higher), cyclopentane (13% higher), and HFC-134a (21% higher). 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. Aging curves for two different slice thicknesses could be scaled by the square of the slice thickness, allowing projections of upper bounds on the thermal conductivity of foam in refrigerator walls and doors over the lifetime of a refrigerator.

Thermal conductivity measurements have been made on a set of full-thickness test panels containing polyurethane foam blown with the four blowing agents and confined between solid sheets made of ABS and HIPS plastics. The panels were made by four foam suppliers. 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. At a 45°F mean temperature, similar differences were 16%, 4%, and 16%.

Tests on the panels from one foam supplier have been completed after six months of aging at controlled temperatures. The conductivity of foam enclosed with ABS plastic sheets showed little or no change over this time period. The panels with HIPS sheets showed increases of 4 to 11% with aging at 90°F, and less than 5% changes for aging at 40°F and -10°F. For both 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, with ABS providing a greater resistance to aging than HIPS.