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Aging of Polyurethane Insulation Foamed with Second- and Third-Generation Blowing Agents*

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Results are presented on two studies of the effect of aging on the apparent thermal conductivity of polyurethane foam insulation for refrigerators. Both studies are cooperative projects between the Oak Ridge National Laboratory and the Appliance Research Consortium. The first study has been ongoing for four years and involves evaluation of second generation blowing agents: HCFC-141b and HCFC-142/22 blend with CFC-11 for comparison. The second study has recently started and involves third generation blowing agents: HFC-134a, HFC-245fa, and cyclopentane with HCFC-141b for comparison. Both studies consist of periodic thermal measurements on panels made with solid steel and/or plastic skins and a core of foam to simulate refrigerator walls, and measurements on thin slices with cut faces to characterize the core foam. Laboratory data are presented on four years of aging of panels containing second-generation blowing agents. Preliminary data are presented for the third-generation blowing agents. The data on panels are compared with predictions of computer models of foam aging.

INTRODUCTION

Polyurethane foam insulation derives its good thermal performance from the low thermal conductivity gases with which it is blown. However, there is a tendency for the thermal conductivity to increase over time, or age, as air diffuses into the cells of the foam and as the blowing agent diffuses out. In July of 1991, a Cooperative Research and Development Agreement (CRADA) was signed between the Appliance Industry-Government CFC Replacement Consortium (also known as the Appliance Research Consortium, or ARC) and the Oak Ridge National Laboratory. One phase of that CRADA involved the aging characteristics of polyurethane foam insulation produced with second-generation blowing agents. While that CRADA was concluded in 1996, studies of the aging characteristics of second-generation blowing agents have continued. With support from the U. S. Department of Energy, the U. S. Environmental Protection Agency, and the Appliance Research Consortium, a similar, but more detailed, study has been started on the aging characteristics of polyurethane foam insulation blown with third-generation blowing agents. Results to date on both of these studies are presented in this paper.

SPECIMENS

Two types of specimens have been studied. Specimens of one type were fabricated as panels that simulate the construction of a door or wall of a refrigerator. The panels were about two inches thick and had lateral dimensions of 24 by 24 inches. The faces of the panels were bounded by solid sheets. For the 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. For the 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 face in a real refrigerator 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 for the second-generation study were foamed with CFC-11 (to provide a base case), HCFC-141b, and a blend of HCFC-142b and HCFC-22. The panels were fabricated by three foam suppliers, with each supplier using a different blowing agent. The panels were fabricated around the end of 1993 and since foams blown with second-generation blowing agents had not been optimized at that time, results with these blowing agents are not necessarily representative of current capabilities.

The panels for the third-generation study were foamed with HCFC-141b (to provide the base case), HFC-134a, HFC-245fa, and cyclopentane. At the present time, the latter three blowing agents are the only commercially available 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. Again, foams made with third-generation blowing agents may not yet be optimized.

Aging of complete panels depends upon permeation of gases through the solid boundary materials and diffusion of the gases through the foam. 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.

EXPERIMENTAL PROCEDURES

Thermal resistance measurements were made using two 24-inch square and two 12-inch square heat-flow-meter-apparatuses (HFMAs), which conform to ASTM C 518.[1] 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 test panel, a correction was made for the thermal resistances of the steel and/or 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. Second-generation specimens were stored at 90°F, while third-generation specimens were stored at 90°F, 40°F, and -10°F in order to span most of the range of conditions to which the foam would be exposed in a refrigerator application. Thermal tests on second-generation specimens were performed at a 75°F mean temperature, while tests on third-generation specimens were routinely performed at both 75°F and 45°F with a few measurements at other temperatures.

RESULTS AND DISCUSSION

Second-Generation Core Foam

Thermal conductivity measurements were made on the core foam specimens over a period of 180 days, with the aging period starting immediately after the specimens were sliced to their test thicknesses. As shown in Figure 1, the thermal conductivity increases rapidly at first as air diffuses into the cells and then more gradually as the blowing agent diffuses out. The curves in Figure 1 were obtained from linear regressions of the logarithm of the thermal conductivity versus the square root of the aging time divided by the slice thickness, with separate regressions for the two stages of aging.[2] At short times, the conductivity of foam blown with HCFC-141b is about 5 to 6 percent higher than that of foam blown with CFC-11, and the values for HCFC-142b/22 are about 15 to 16 percent higher than those for CFC-11. The long-time conductivity for HCFC-141b is about 3 to 4 percent higher than that for CFC-11, and the values for HCFC-142b/22 are about 7 percent higher.

Second-Generation Panels

Thermal measurements have been made on the full-thickness panels over a period of 4 years. As was the case with the thin-slice specimens, the initial thermal conductivities of the foam blown with second-generation blowing agents were higher than that for CFC-11. For the full-thickness panels, the conductivities were higher by about 16 and 11 percent for HCFC-141b and HCFC-142b/22, respectively. Again, it should be noted that these specimens were produced in late 1993/early 1994, and at that time the formulations for the HCFC blowing agents had not been optimized.

The foam thermal conductivities derived from the tests on panels are plotted versus aging time in Figure 2. The solid lines were obtained from linear regressions of the thermal conductivity versus the square root of the aging time. This is the form that the regression used for the core foam takes at small amounts of aging. The dotted lines are the 95% confidence intervals derived from the regressions. (See Reference 3 for a discussion of confidence intervals, which apply to the mean curve, versus prediction intervals, which apply to individual data points.) The dashed line is the thermal conductivity calculated from the curve in Figure 1 for the CFC-11 core foam, with the time being scaled to correspond to the thickness of the foam in the full thickness panels. Comparison of the panel data with the core foam curve clearly shows the great reduction in aging rate due to the solid boundary sheets. After four years of aging, the thermal conductivities of the foam in the panels have increased by about 8%, 13%, and 4% for CFC-11, HCFC-141b, and HCFC-142/22 respectively.

Since it is very desirable to make some prediction of the long-term performance of the panels based on data obtained over a limited time period, the regressions were extended out to an aging time of 10 years. Admittedly, extrapolation far beyond the range of measured data is dangerous, especially when the coefficients of determination (r^2) of the regressions are not large (they were 0.36, 0.63, and 0.46 for CFC-11, HCFC-141b, and HCFC-142b/22, respectively). Hopefully the true long-term performance will fall within the confidence intervals. The validity of these extrapolations will be determined as we continue to make measurements on these panels. In addition, aging in operating refrigerators is expected to be less since the exposure temperatures would generally be lower than 90°F.

A one-dimensional mathematical model, similar to those described in the literature [e.g.,4,5] but with the addition of the resistances to gas permeation through the solid surface sheets, was used to predict the change with time of the thermal conductivity of the foam in the panels. Given initial partial pressures of gases within the cells of the foam and the partial pressures of the gases surrounding the foam, the model calculates the time variation of the partial pressures within the cells. These partial pressures are used to calculate the thermal conductivities of the gas mixtures within the cells through the Lindsay-Bromley formulation of the Wassiljewa equation.[6] The various parameters needed for the model were taken from the literature and are given in Table 1. We have assumed that the only gas initially within the cells is the blowing agent at an initial partial pressure of 0.7 atmospheres.[4] We have not yet included any effects of condensation of the blowing agent nor have we included other starting gases such as carbon dioxide.

Figure 3 compares the model predictions with measured data for the panels blown with CFC-11 and HCFC-141b. For these calculations, the aging model was forced to match the regression curve at the start of aging. Figure 3 shows that the model is in reasonably good agreement with the regression curves and with the data points. Further refinements in the model will be made as we accumulate more long term aging data and material parameters that are more specific to the test panels.

Third-Generation Core Foam

Thermal conductivity measurements on core foam made with third-generation blowing agents were started in the fall of 1997 and were still in progress at the time of this writing. This section presents the available results, which were measured on specimens with each blowing agent from one foam supplier.

Table 2 shows a comparison of the thermal conductivity at 75°F on freshly-cut specimens. The thermal conductivity of the thinner slices was consistently three to four percent higher than that of the thicker slices. This is probably largely due to the larger amount of damaged surface layers with the thinner slices where air immediately displaces the blowing agent in cut cells. Table 2 also shows 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 [12].

Figure 4 shows the variation of thermal conductivity with temperature for 1.5 in.-thick specimens before any appreciable aging has occured. The conductivity varies linearly with temperature for HFC-134a, which is gaseous over the temperatures studied. Condensation of the other blowing agents would occur within this temperature range, causing the curves to tend to flatten at lower temperatures. The results in Figure 4 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 cellular structure with HCFC-141b but the presence of many larger bubbles with the alternate blowing agents.

Figure 5 shows the variation of thermal conductivity with time for HCFC-141b specimens tested at 75°F and aged at three different temperatures. The thicker slices have changed very little over the time span of the tests, while the thinner slices show significant increases. The temperature at which the specimens were aged has a large influence on the aging rate: The thermal conductivity increases less than one-half as fast when aging occurs at 40°F than at 90°F, and about one-tenth as fast at -10°F.

Figures 6, 7 and 8 compare the aging rates for thinner slices with the four blowing agents for two aging temperatures and two test temperatures. The rates of aging with the different blowing agents do not appear to be greatly different, but there is some tendency for the specimens blown with HFC-245fa and HFC-134a to age at a faster rate. This is seen most clearly in Figure 8 for the 45°F test temperature, where the curves for HCFC-141b and HFC-245fa cross each other.

Third-Generation Panels

Tests on panels made with third-generation blowing agents were underway at the time of writing, but insufficient data were available for a meaningful presentation. These data will be given in future publications.

SUMMARY AND CONCLUSIONS

Thermal conductivity measurements have been made over a 4-year period on polyurethane foam insulation contained in test panels that simulate walls and doors of refrigerators. The test panels were blown with three blowing agents (CFC-11, HCFC-141b, and a HCFC-142b/22 blend) and were aged at 90°F. Thermal conductivity measurements were also made on specimens of the core foam taken from the panels. The data show that encapsulation of the foam insulation between solid steel and plastic boundaries greatly reduces the rate of aging of the foam. After four years of aging, the thermal conductivity of the foam in the panels had increased by 8%, 13%, and 4% for CFC-11, HCFC-141b, and HCFC-142b/22, respectively. Thermal conductivities predicted by a mathematical aging model are in reasonable agreement with the data and with the regression curves. Further refinements in the models and in extrapolatons of the data will be made as more long-term aging data are accumulated.

A study of the aging characteristics of polyurethane foam insulation blown with third-generation blowing agents has been started. This study includes both panels and core foams blown with HCFC-141b, HFC-134a, HFC-245fa, and cyclopentane. Preliminary results on core foam show that the lowest thermal conductivity for unaged foam occurs with HCFC-141b, followed by HFC-245fa (3% higher), cyclopentane (13% higher), and HFC-134a (21% higher). The aging rate was found to be very sensitive to aging temperature. Aging at 40°F is about one-half as fast as at 90°F, and about one-tenth as fast at -10°F. The rates of aging with different blowing agents were not greatly different, but there was some tendency for faster aging with HFC-134a and HFC-245fa. Tests on panels are underway, but not enough data are available for a meaningful presentation. The tests on both panels and core foam are continuing and further results will be presented in future publications.

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Table 1. Parameters used in Model of Aging of Foam Insulation in Test Panels

Gas	Thermal Conductivity at 75°F, Btu•in./h•ft²•°F	Effective Diffusion Coefficient at 90°F, cm^2/s	Permeance of ABS Plastic, cc(STP)•mil/ 100 in.²•atm•day
N_2	0.178 [7]	0.043×10^{-6} [9]	21 [11]
O_2	0.179 [7]	0.28×10^{-6} [9]	125 [11]
CFC-11	0.058 [8]	0.0027×10^{-6}[10]	2.46
HCFC-141b	0.068 [8]	0.0050×10^{-6}[10]	1.34

Notes: Numbers in brackets are the references. Permeances of ABS plastic to the blowing agents were estimated by assuming the ratio of the permeance of the blowing agent to that of nitrogen to be the same as the ratio of the diffusion coefficients. The permeance of 24 gauge steel was taken to be zero.

Table 2. Thermal Conductivity of Freshly-Cut 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.

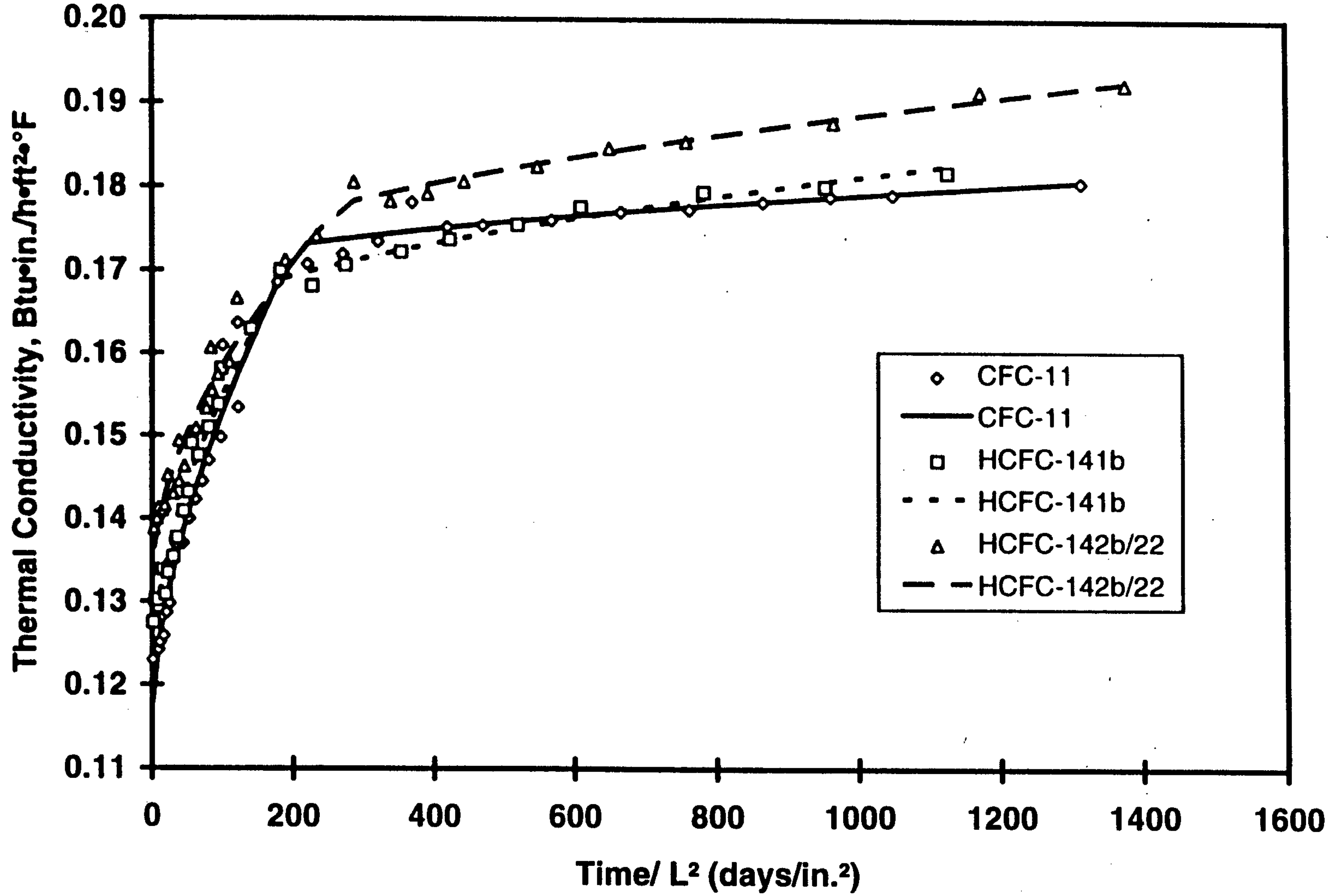

Figure 1. Aging of second-generation core foam. Thermal tests were performed at 75°F. Specimens were aged at 90°F. L is the slice thickness.

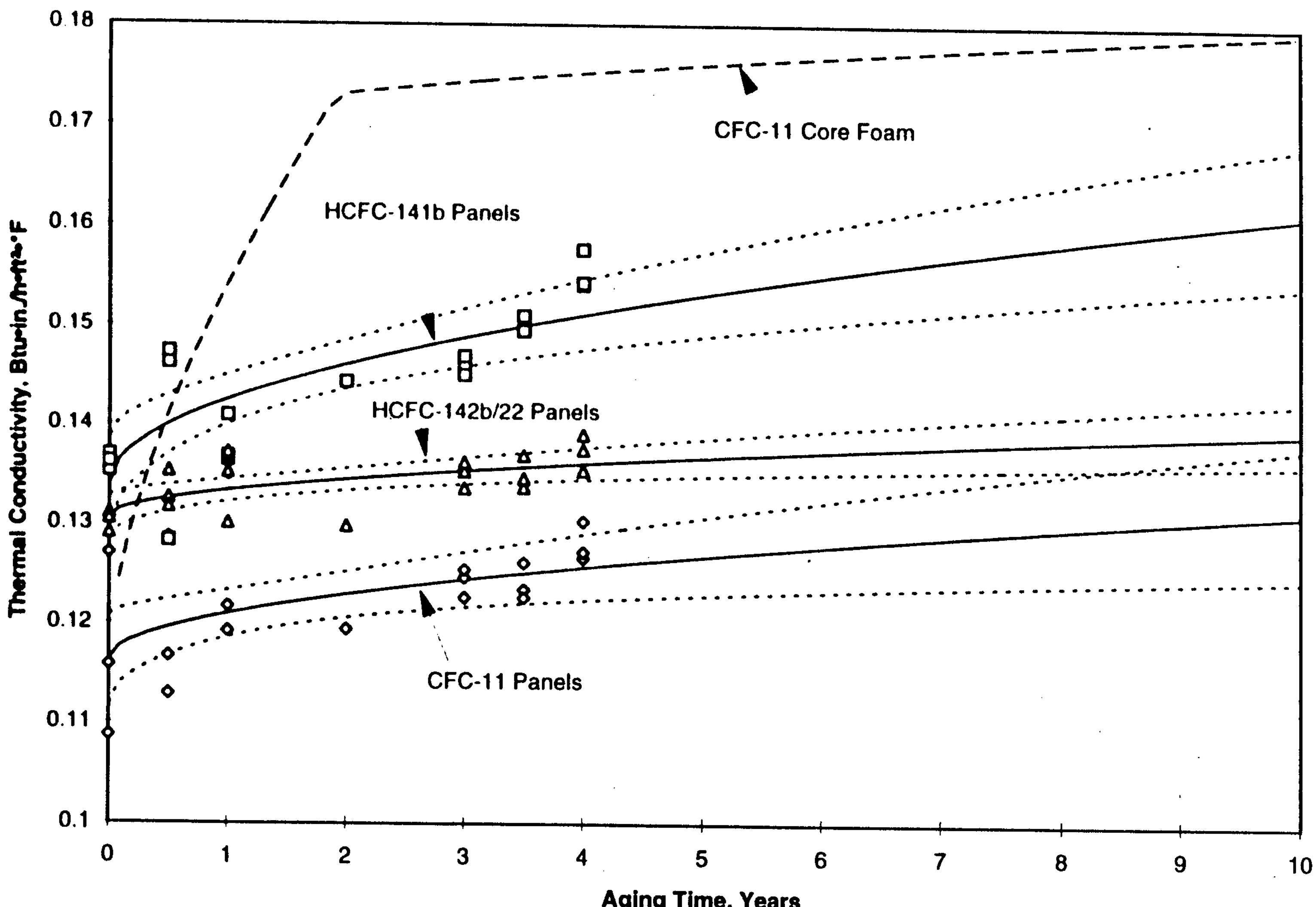

Figure 2. Aging of foam in panels blown with second-generation blowing agents. Thermal tests performed at 75°F; aging at 90°F. Solid lines are regressions; dotted lines are 95% confidence intervals.

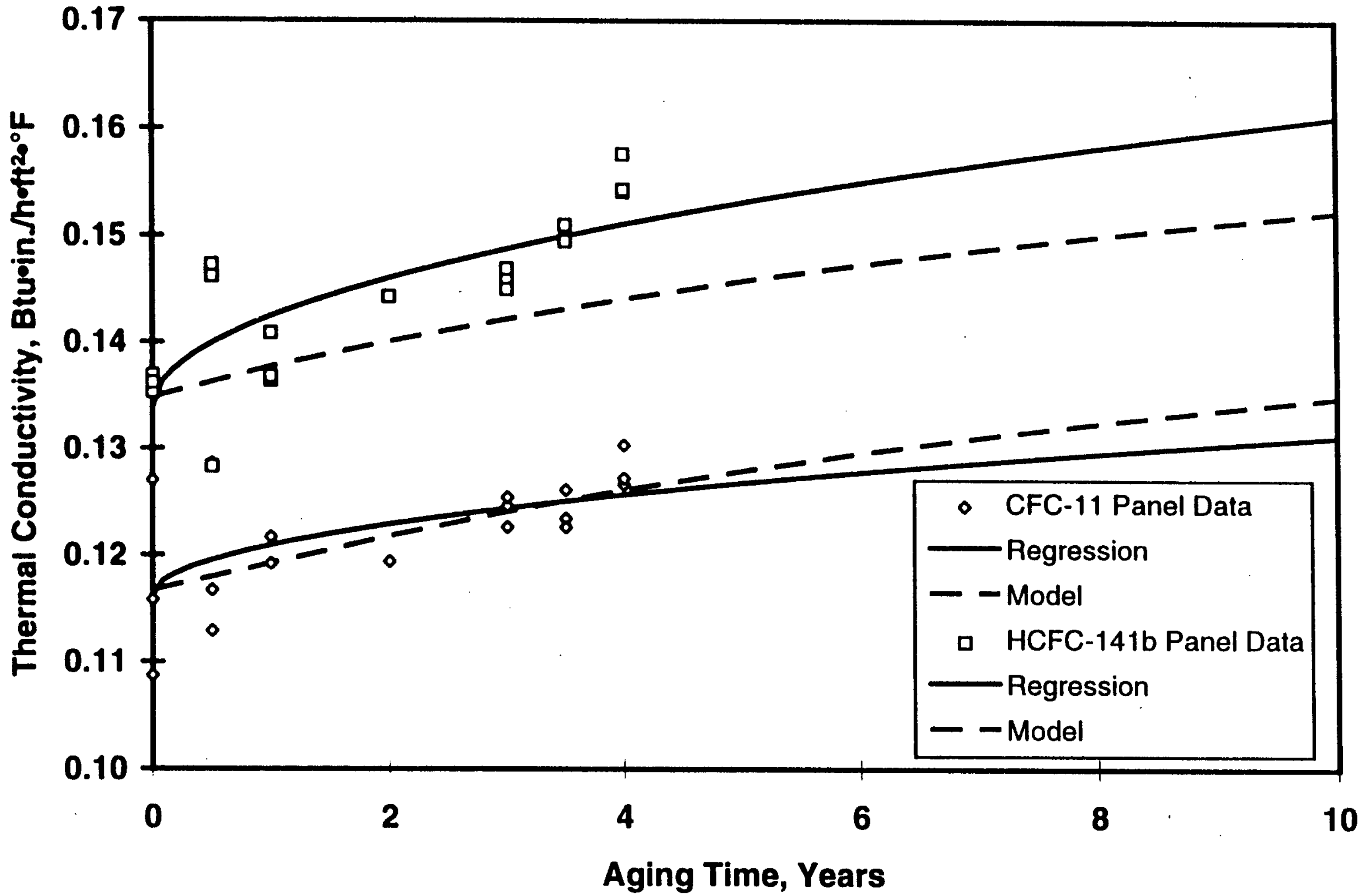

Figure 3. Comparison of Predicted and Measured Thermal Conductivities of Foams from Test Panels

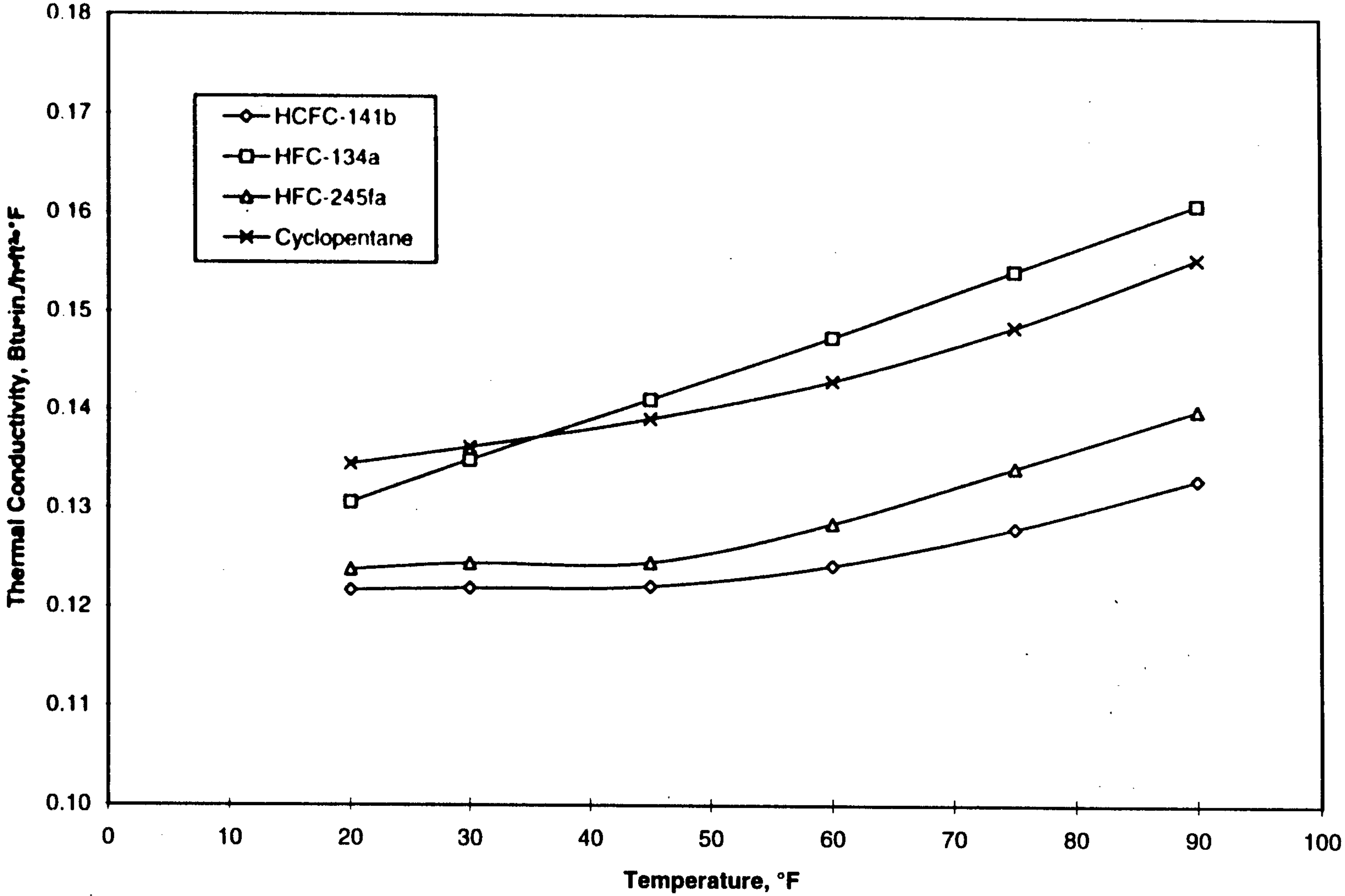

Figure 4. Thermal conductivity of thick core foam specimens with third-generation blowing agents, measured before any appreciable aging has occured.

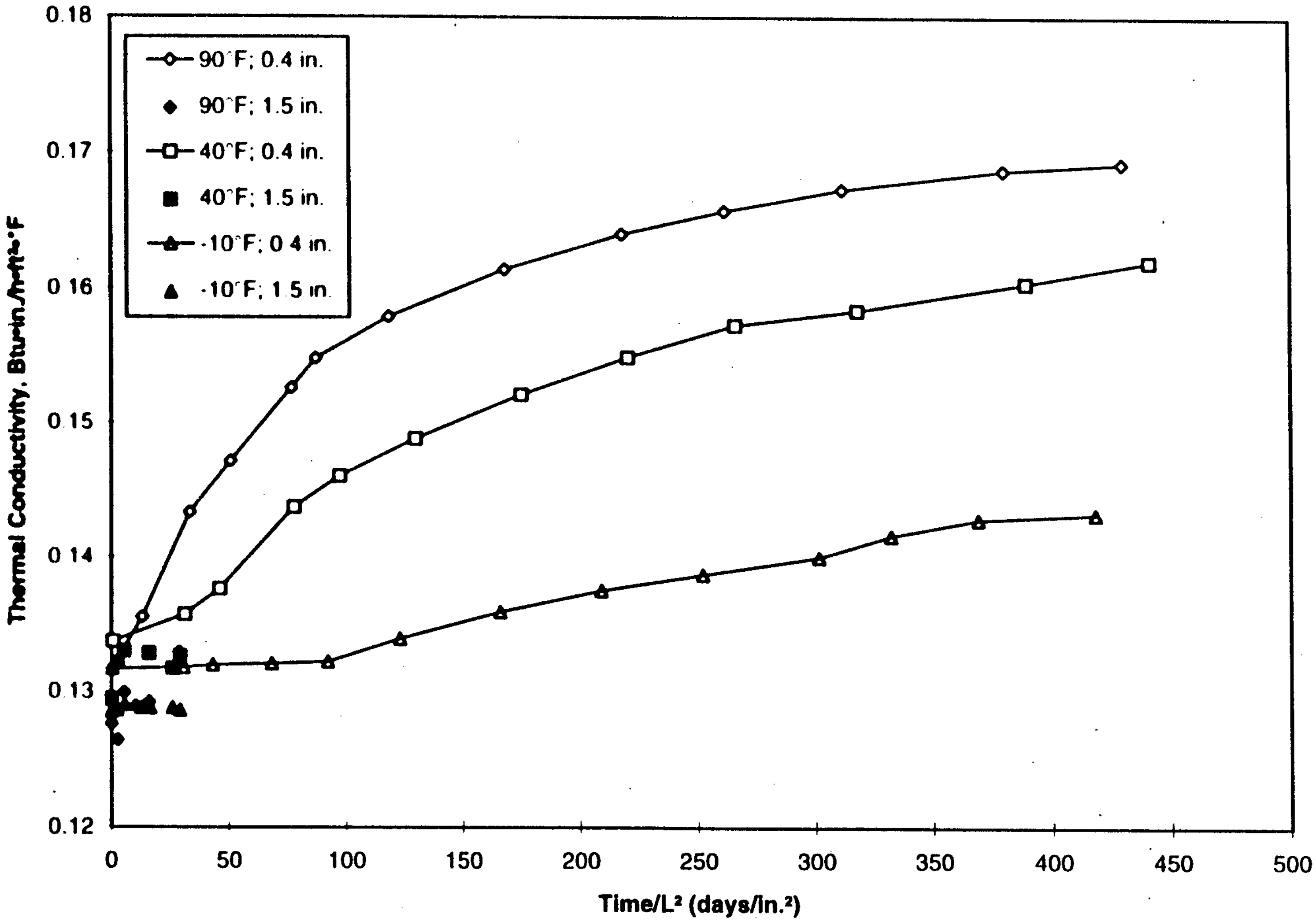

Figure 5. Aging of core foam specimens blown with HCFC-141b. Thermal tests were performed at 75°F. The legend shows the aging temperature and the slice thickness (L).

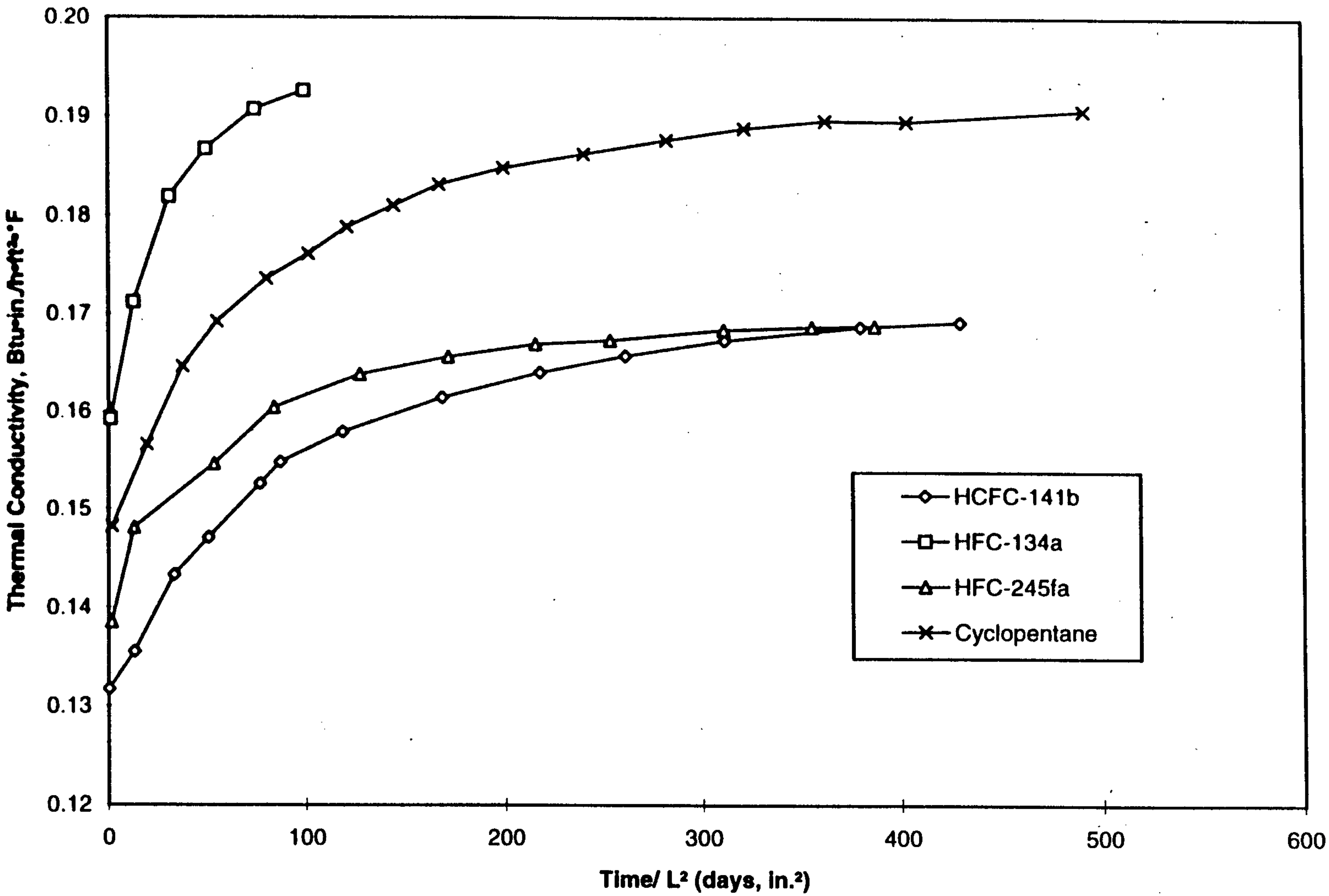

Figure 6. Aging of core foam specimens with third-generation blowing agents. Thermal tests performed at 75°F. Specimens were aged at 90°F. L is the slice thickness.

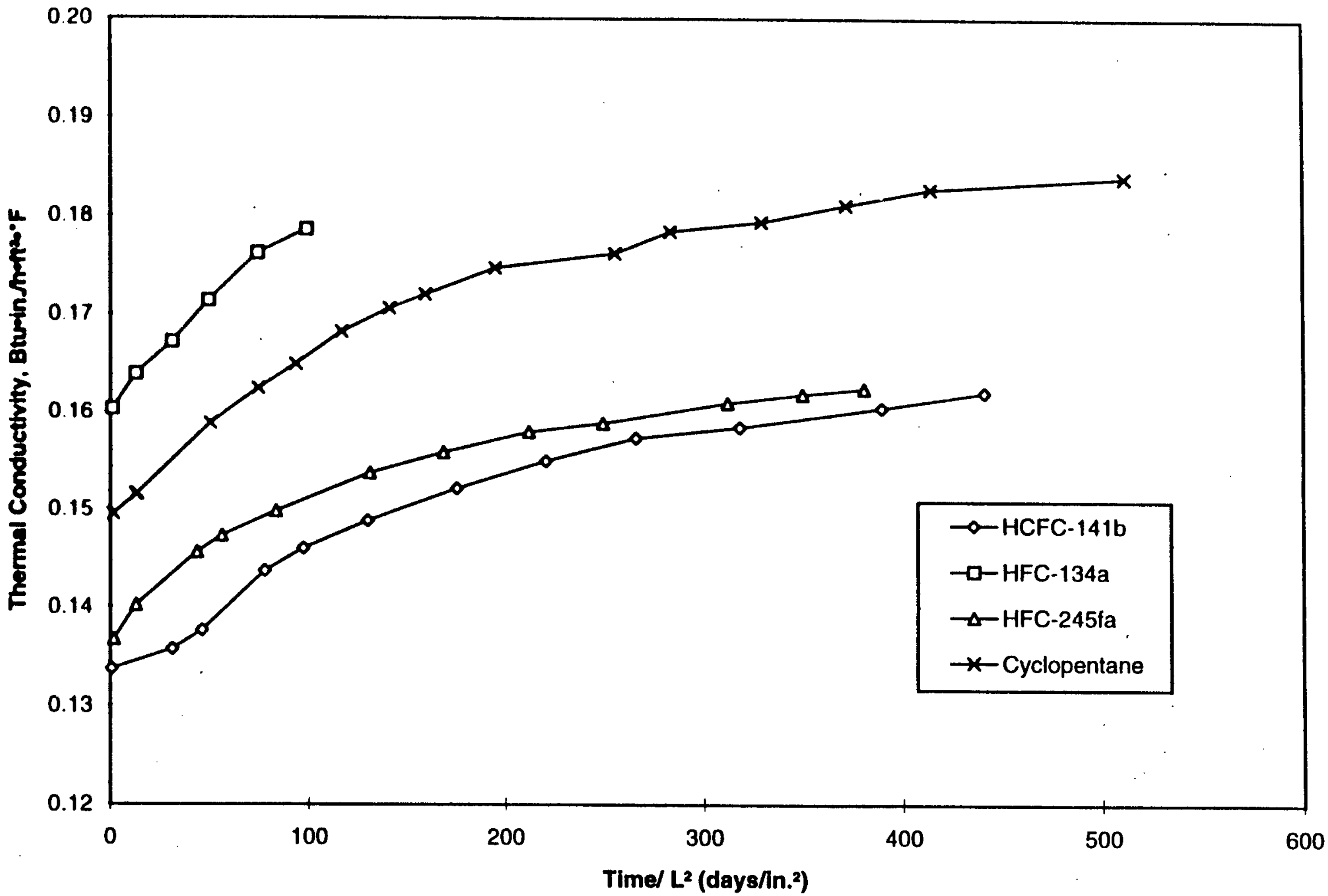

Figure 7. Aging of core foam specimens with third-generation blowing agents. Thermal tests performed at 75°F. Specimens were aged at 40°F. L is the slice thickness.

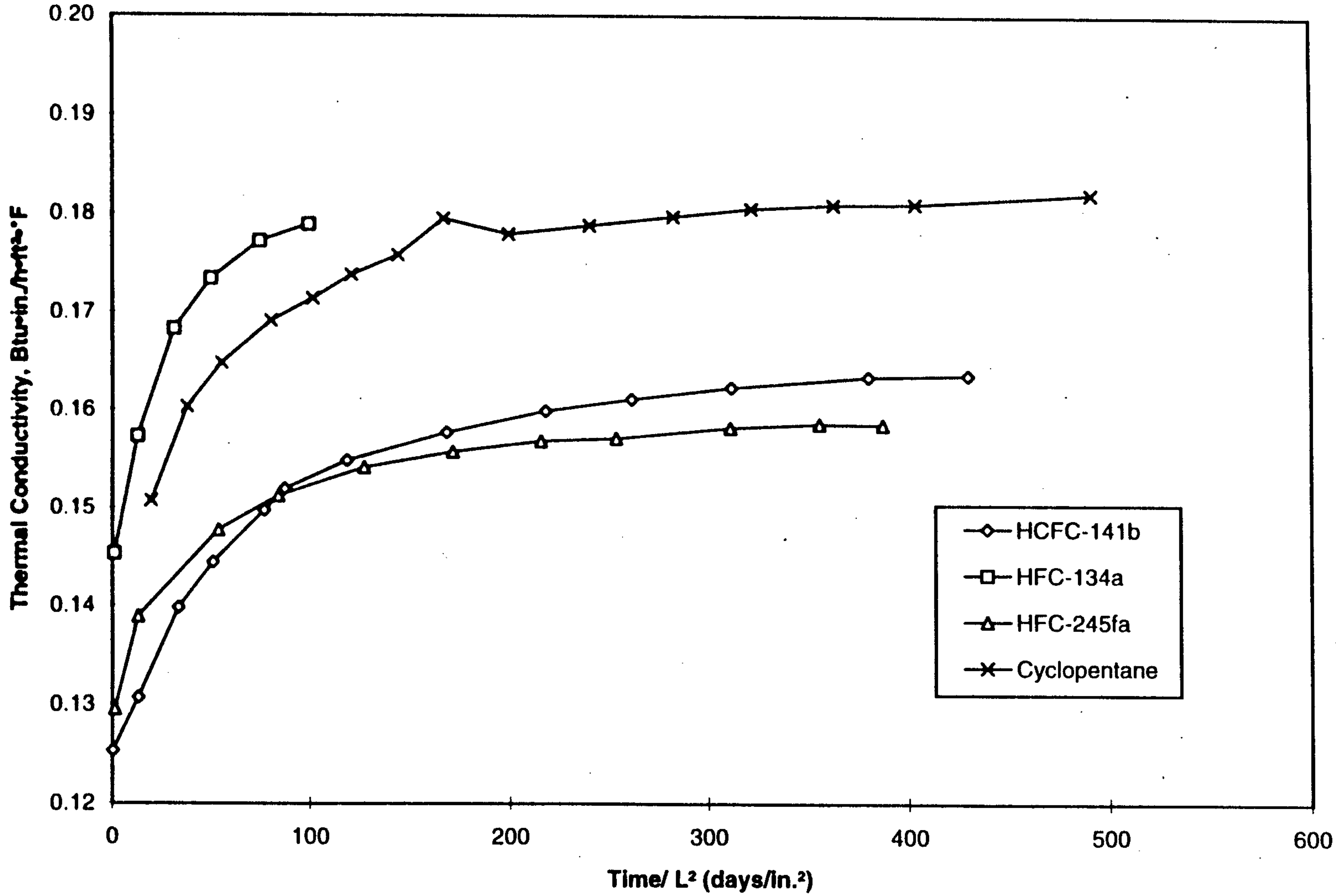

Figure 8. Aging of core foam specimens with third-generation blowing agents. Thermal tests performed at 45°F. Specimens were aged at 90°F. L is the slice thickness.

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