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AGING OF POLYURETHANE FOAM INSULATION IN SIMULATED REFRIGERATOR WALLS

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ABSTRACT

Laboratory data are presented on the thermal conductivity¹ of polyurethane foam insulation in composite test panels that simulate refrigerator walls. The test panels consisted of a steel skin, an ABS plastic liner, and a polyurethane foam core. Foam cores were produced with three different blowing agents (CFC-11, HCFC-141b, and a HCFC-142/22 blend). Periodic thermal measurements have been made on these panels over a three and one-half year period in an effort to detect aging processes. Data obtained on foam encased in the panels were compared with measurements on thin foam slices that were removed from similar panels. The data show that the encapsulation of the foam in the solid boundary materials greatly reduces the aging rate. The plan is presented for a follow-on project that is being conducted on the aging of foams blown with HCFC-141b, HFC-134a, HFC-245fa, and cyclopentane.

INTRODUCTION

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.

SPECIMENS

Specimens for the aging studies were fabricated as panels that simulate the construction of a door or wall of a refrigerator. The panels were about two inches thick and were bounded by a sheet of 24 gauge (0.024 inch thick) steel on one side and by a 0.12 inch thick sheet of acrylonitrile-butadiene-styrene (ABS) plastic on the other side. The steel sheet represents the outside of a refrigerator cabinet, while the plastic sheet represents the inside lining. The space between the two sheets was filled with polyurethane foam. The lateral dimensions of the panels were 24 by 24 inches, and the edges of the panel were sealed with aluminum foil tape to simulate the

¹ Since heat transfer through foam insulation is a combination of conduction and radiation, the term "apparent thermal conductivity" is sometimes preferred. In this paper, the term "thermal conductivity" is used for simplicity.

configuration in a refrigerator where there are no cut, exposed foam edges.

The panels were fabricated by three foam suppliers, each of which used a different foam blowing agent. The three types of blowing agents used were CFC-11, HCFC-141b, and a HCFC-142b/22 blend. The CFC-11 panels were intended to represent a base case with which the second-generation blowing agents could be compared. These panels were fabricated around the end of 1993, and at that time foams produced with second-generation blowing agents had not been optimized. Hence the results obtained on specimens blown with the second-generation blowing agents are not necessarily representative of current capabilities.

In addition to the panel specimens, core foam specimens were prepared by removing the foam from panels, cutting out 12 inch squares, and then slicing them. Typical slice thicknesses were about 0.35 and 1.5 inches. A stack of four of the 0.35 inch-thick slices made up one test specimen.

EXPERIMENTAL PROCEDURES

Thermal resistance measurements were made using two heat-flow-meter-apparatuses (HFMA's), which conform to ASTM C 518.[1] Tests on the core foam specimens were made in a HFMA that accepts specimens up to 12 inches square, while tests on the panels were made using a HFMA that accepts specimens up to 24 inches square. For the tests on the panels, intervening layers of foam rubber were placed between the panel and the hot and cold plates of the apparatus to eliminate any undesirable air gaps between the specimen and the plates and also to protect the plates from the rigid test panel. Thermocouples were taped directly to the faces of the test panels so that the temperature difference across the test panel was 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 plastic sheets to obtain the thermal conductivity of the foam insulation. Tests on the core foam specimens gave the thermal conductivity directly.

All HFMA tests were performed with the hot and cold plates maintained at 95°F and 55°F, respectively, giving a mean temperature of 75°F. During the time periods between thermal tests, the specimens were stored in closed atmospheric pressure aging chambers that were maintained at a constant temperature of 90°F.

RESULTS AND DISCUSSION

Thermal conductivity measurements were made on the core foam specimens over a period of 180 days. The specimens were sliced soon after the foam was blown, and the aging period started immediately after the specimens were sliced to their test thicknesses. Results are shown in Figure 1, where the thermal conductivity is plotted versus the square root of the aging time divided by the slice thickness ($\sqrt{t/L}$). The data are seen to be divided into two nearly linear regions. The first region is associated with the diffusion of air into the cells of the foam, while the second region is associated with the diffusion of the blowing agent out of the cells. The lines on Figure 1 were obtained from linear regressions of the logarithm of the thermal conductivity [$\ln(100k)$] versus the square root of the aging time divided by the slice thickness ($\sqrt{t/L}$). This type of relationship

has traditionally been used in the past, but as can be seen in Figure 1, the curves are nearly linear when the thermal conductivity is plotted versus the same time-thickness parameter. 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. At long times, the differences among the blowing agents are diminished. 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.

Thermal measurements have been made on the full-thickness panels over a period of 3-1/2 years. Foam thermal conductivities obtained from these measurements are given in Table 1. 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 from the tests on composite panels are plotted versus aging time in Figures 2 through 4. The data on the core foam given in Figure 1 showed that, for each of the two phases of aging, the thermal conductivity is approximately a linear function of the square root of the aging time. Following this lead, the thermal conductivity data from the full thickness panels were fitted by the method of least squares to an equation linear in the square root of aging time. The solid lines in Figures 2 through 4 are the regression curves, and the dotted lines are the 95% confidence intervals derived from the regressions.² The dashed lines are the thermal conductivities calculated from the curves in Figure 1 for the core foam, with the time being scaled to correspond to the thickness of the foam in the full thickness panels.

As was expected, aging curves obtained only from measurements on core foam specimens cannot be used to predict the rate of aging of the foam in the panels. After 3-1/2 years, the thermal conductivity of the CFC-11 panel foam increased about 6 percent, while the core foam showed a 53 percent increase. Similar differences exist for the other two blowing agents. Clearly, encapsulation of the foam between the solid steel and plastic sheets and sealing of the edges with aluminum foil tape greatly decreases the rate at which gases can diffuse into or out of the cells of the foam. Core foam data, however, are valuable in that they provide information on the characteristics of the foam itself, while the aging behavior of panels depends upon the characteristics of both the foam and the bounding surface layers.

The regressions in Figures 2 through 4 are extended out to an aging time of 10 years. Admittedly, extrapolation far beyond the range of measured data is dangerous. This is especially true when

² Two types of intervals are used with regression analyses: confidence intervals and prediction intervals. Confidence intervals apply to the mean curve from the regression. Prediction intervals apply to an individual data point, and are wider than confidence intervals. Confidence intervals were chosen for use here, since our main interest is in the mean curve. For a discussion of these types of intervals, see a statistics textbook, such as Reference 2.

the coefficients of determination (r^2) of the regressions are not large (they were 0.24, 0.52, and 0.35 for CFC-11, HCFC-141b, and HCFC-142b/22, respectively). However, it is very desirable to make some prediction of the long-term performance of the foam based on data obtained over a limited time period. 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. Based on the 95 percent confidence intervals, the thermal conductivity of the foam blown with CFC-11 is expected to increase by 3 to 18 percent after aging for 10 years at 90°F. Conductivity increases for HCFC-141b and HCFC-142b/22 are expected to be 10 to 23 percent and 3 to 8 percent, respectively. There is an additional element of uncertainty in attempting to apply these changes to the insulation in operating refrigerators since the exposure temperatures would generally be lower than 90°F.

A mathematical model of foam aging was used to predict the change with time of the thermal conductivity of the foam in the composite panels. The one-dimensional model is similar to those described in the literature for diffusion of air and blowing agent through the foam.[e.g.,3,4] We have added the resistances to gas movement due to the finite permeances of the solid sheets on the surfaces of 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.[5] The various parameters needed for the model were taken from the literature and are given in Table 2. For the predictions given here, we have assumed that the only gas initially within the cells is the blowing agent and that its initial partial pressure is 0.7 atmospheres.[3] In addition, we have not yet included any effects of condensation of the blowing agent, such as may occur with high-boiling-point blowing agents.

Figure 5 compares the predictions of the aging model with measured data and regressions of the data for the panels blown with CFC-11 and HCFC-141b. For these calculations, the aging model was forced to match the initial point of the regression curve at the beginning of aging. Figure 5 shows that the model is in good agreement with the regression curves. For both blowing agents, the shape of the model curves are very similar to the regression curves, and predict very similar increases in thermal conductivity. In both cases, the model curve is within a few percent of the regression curve. It should be emphasized that the only parameter in the model that we have adjusted to match the data is the initial thermal conductivity; all other parameters were taken from the literature. Better agreement might be obtained if the parameters that apply to the specific materials used in the panels were available. The good agreement between the model and the regression curves shows that the regression curves are physically realistic and gives some added credence to the extrapolations of the data to long time periods.

PLAN FOR THIRD-GENERATION BLOWING AGENT STUDY

The study of third-generation blowing agents will examine the effect of several factors on the aging characteristics of polyurethane foam. The first of these factors is, of course, the blowing agent itself. HCFC-141b will be used as a base case. Other blowing agents that will be studied are HFC-134a, HFC-245fa, and cyclopentane. At the present time, these three blowing agents are

the only commercially available replacements for HCFC-141b. The second factor is the aging temperature. Three aging temperatures have been chosen: 90°F, 40°F, and -10°F. These temperatures span most of the range of temperatures to which the foam would be exposed in a refrigerator application and will help to reduce the uncertainty in applying data obtained on test panels to the insulation in operating refrigerators. The effect of temperature on aging characteristics is expected to be complex. It is expected that the rate of diffusion of gases through the foam and permeation of gases through the liners will vary with aging temperature. Also, the blowing gases have boiling points that range from -15°F (for HFC-134a) to 121°F (for cyclopentane), and thus the liquid-vapor equilibrium will have an effect on aging characteristics.

Another factor that will be studied is the effect of different plastic materials that are used for refrigerator linings. In addition to the ABS plastic that has been used for the earlier studies, test panels will be fabricated using high-impact polystyrene (HIPS). Since gases permeate through HIPS faster than through ABS, aging of the foam insulation should occur faster with HIPS linings.[10] The plastic sheets will be 0.040 inches thick; this is considered to be a more typical thickness for use in refrigerators than the 0.12 inch thick plastic sheets that were used in the earlier study. For this study, both sides of the panels will have plastic sheets. This will allow gases to permeate through both sides of the panel and will provide an acceleration of the aging over that which would occur with steel on one side. It is expected that the effect of a steel boundary can be accounted for by the use of mathematical models.

In addition to the above factors, the test panels will be made by four foam suppliers, thus providing some information on variability of aging characteristics with foam formulations.

It is planned to perform thermal measurements on the panels at about six month intervals over a long period of time to track their aging characteristics. In addition to tests on full thickness panels, thin-slice core foam specimens will be prepared and measurements will be made on them over at least a 180 day period. Measurements on both the panels and core foam specimens will be performed at mean temperatures of 45°F and 75°F. Auxiliary measurements are planned for initial cell gas compositions, gas permeances of the plastic liner materials, and coefficients of diffusion of gases through the foams. Finally, the data obtained in this study will be compared with the predictions of mathematical aging models. These comparisons will be useful in validating the models and/or in providing information for further improvements of the models.

SUMMARY AND CONCLUSIONS

Thermal conductivity measurements have been made over a 3-1/2 year period on polyurethane foam insulation contained in composite 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 liner boundaries greatly slows down the aging of the foam. For example, after 3-1/2 years of aging, the thermal conductivity of the CFC-11 blown foam in the test panels had increased by about 6 percent, while the thermal conductivity of unencapsulated core foam would have increased about 53 percent. Regression techniques have

been used to extrapolate the thermal conductivity out to 10 years. Confidence intervals from these regressions suggest that at the end of 10 years of aging at 90°F, the thermal conductivity of the foam in the panels will increase by 3 to 18, 10 to 23, and 3 to 8 percent for CFC-11, HCFC-141b, and HCFC-142b/22 blowing agents, respectively. A mathematical model was constructed for the diffusion of air and blowing agents through the foam and for the permeation of these gases through the solid boundaries. Thermal conductivities predicted by the model are within a few percent of the extrapolated regression curves, lending some credence to the extrapolations.

A study of the aging characteristics of polyurethane foam insulation blown with new alternative blowing agents has started. This study includes foams blown with HCFC-141b, HFC-134a, HFC-245fa, and cyclopentane. This study will examine the influence of aging temperatures from -10°F to 90°F. Solid boundaries on test panels will be 0.040 inch thick ABS or HIPS plastics. One goal of this study will be to validate and/or improve mathematical models for aging of foam insulation contained within panels that simulate the construction of refrigerator walls and doors.

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Table 1. Thermal Conductivity of Foam Insulation from Composite Test Panels

Blowing Agent	Aging Time, months					
	0	6	12	24	36	42
CFC-11	0.1158	0.1286	0.1192	-	0.1246	0.1234
"	0.1270	0.1129	0.1192	-	0.1226	0.1226
"	0.1087	0.1167	0.1217	0.1194	0.1254	0.1261
HCFC-141b	0.1369	0.1462	0.1409	-	0.1460	0.1510
"	0.1353	0.1473	0.1364	-	0.1469	0.1510
"	0.1362	0.1283	0.1368	0.1443	0.1450	0.1495
HCFC-142b/22	0.1311	0.1353	0.1372	-	0.1353	0.1369
"	0.1291	0.1326	0.1352	0.1298	0.1362	0.1337
"	0.1305	0.1317	0.1301	-	0.1336	0.1346

Note: Thermal conductivity values have units of Btu·in./h·ft²·°F.

Table 2. Parameters used in Model of Aging of Foam Insulation in Composite Test Panels

Gas	Thermal Conductivity at 75°F, Btu·in./h·ft ² ·°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 [6]	0.043×10^{-6} [8]	21 [10]
O ₂	0.179 [6]	0.28×10^{-6} [8]	125 [10]
CFC-11	0.058 [7]	0.0027×10^{-6} [9]	2.46
HCFC-141b	0.068 [7]	0.0050×10^{-6} [9]	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.

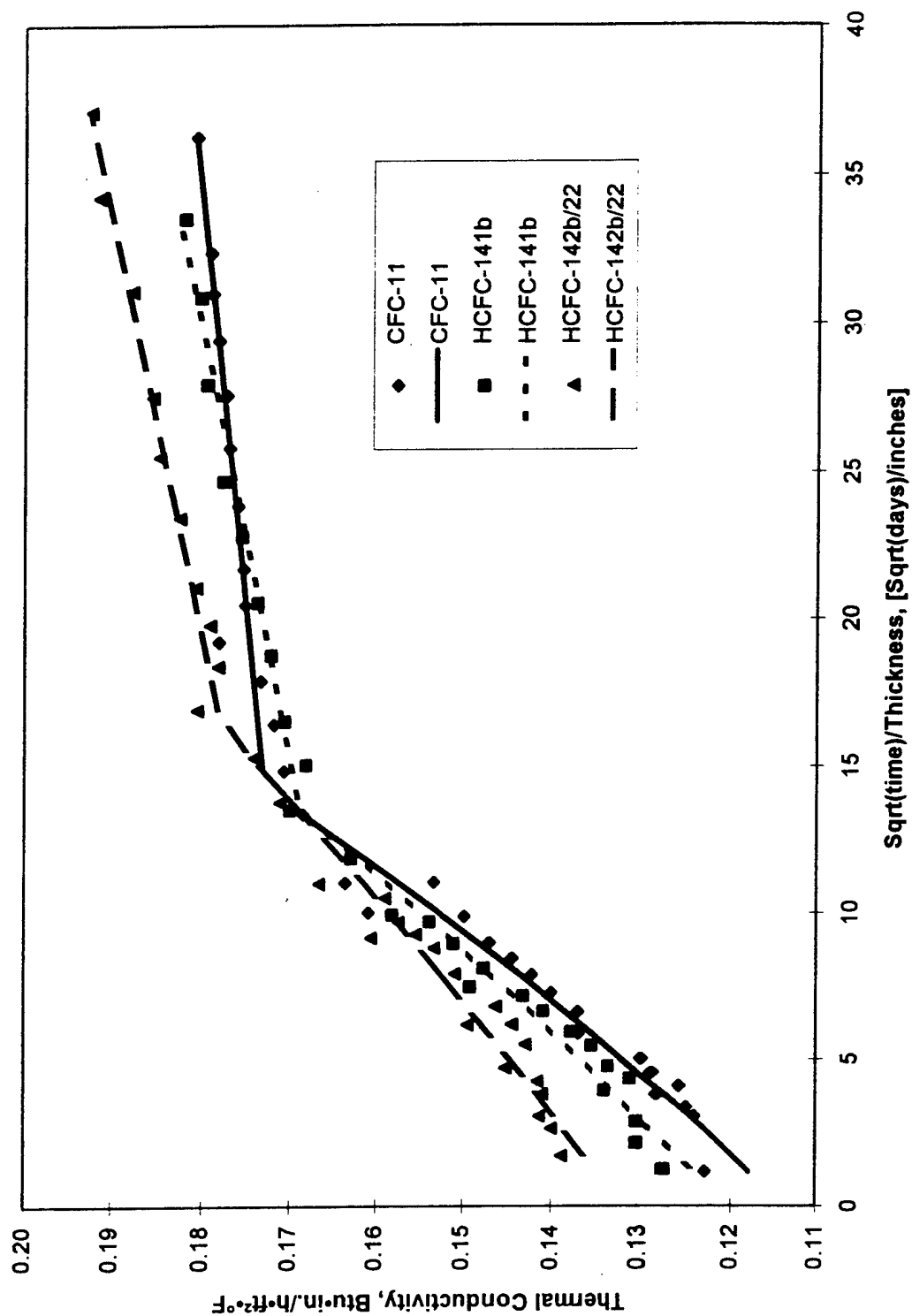


Figure 1. Thermal Conductivity of Core Foam Specimens

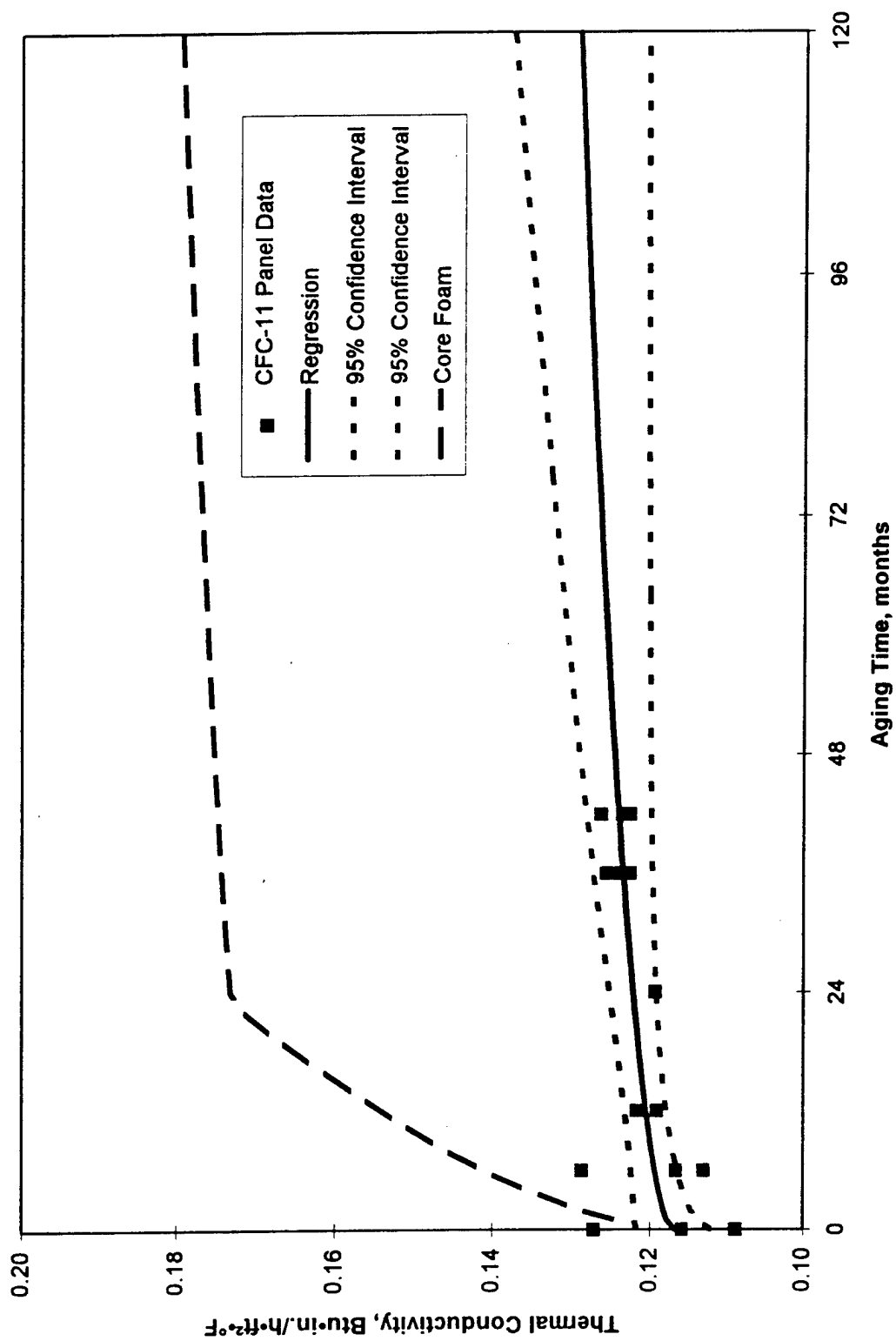


Figure 2. Thermal Conductivity of Foam Blown with CFC-11

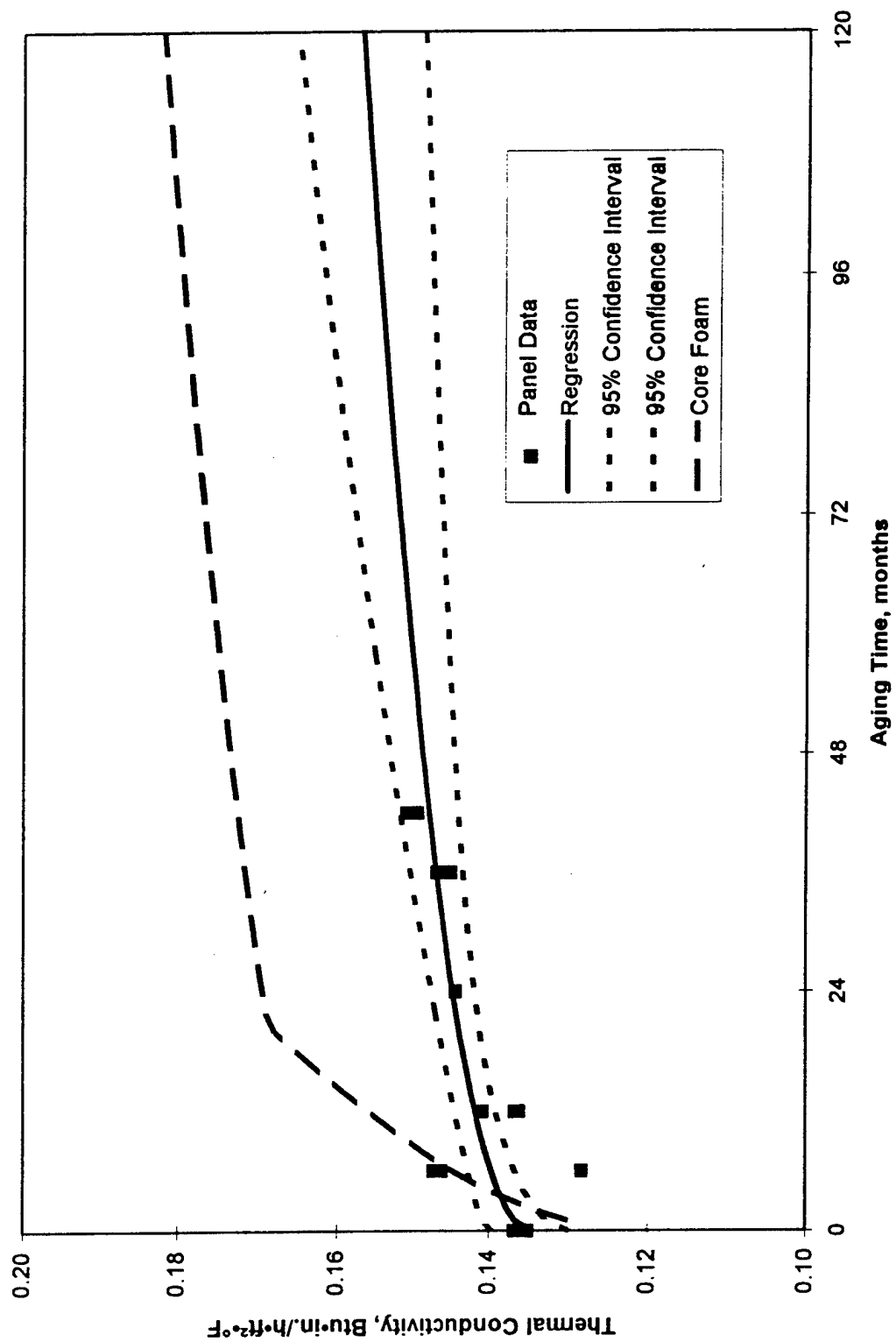


Figure 3. Thermal Conductivity of Foam Blown with HCFC-141b

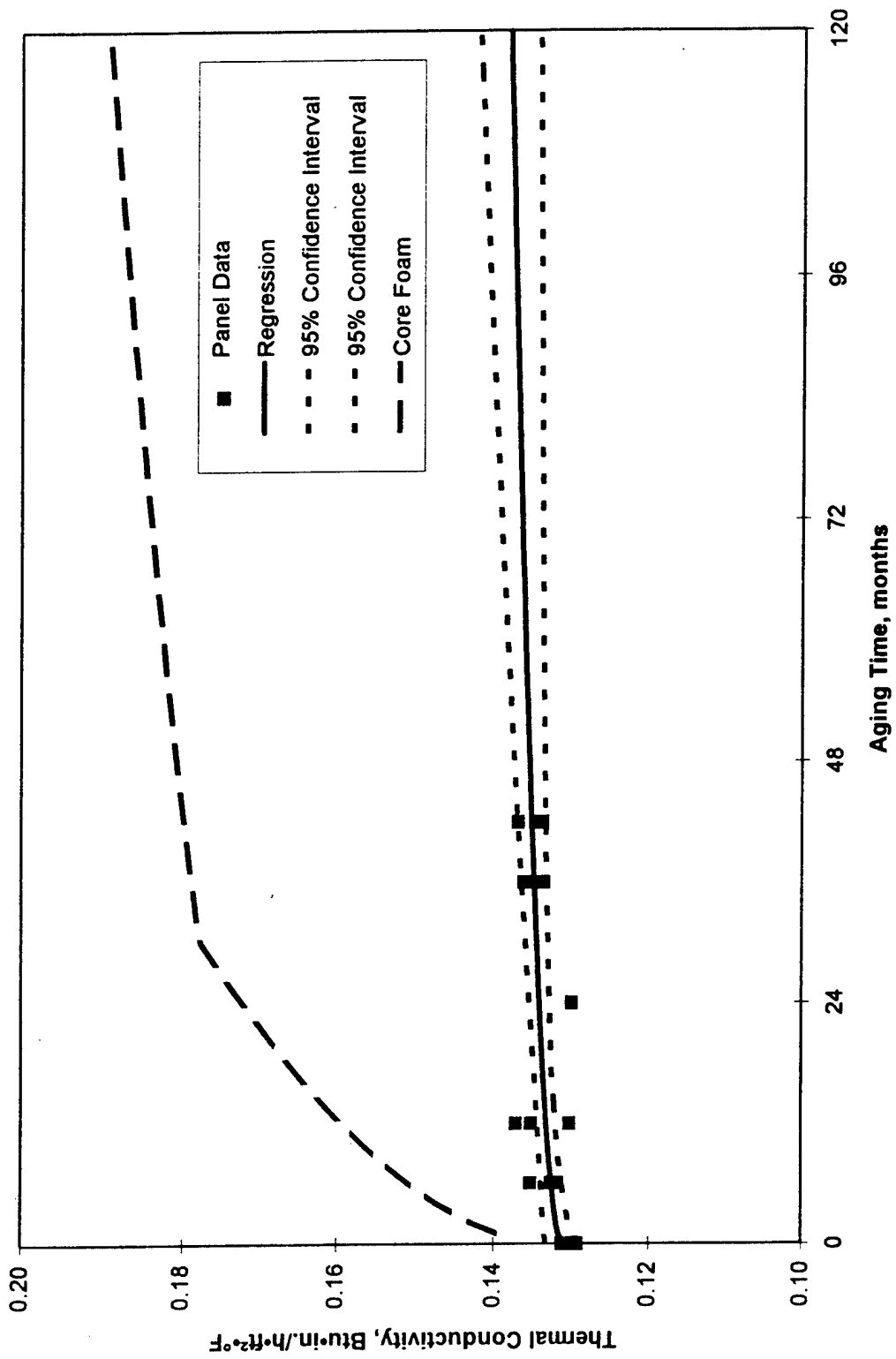


Figure 4. Thermal Conductivity of Foam Blown with HCFC-142b/22

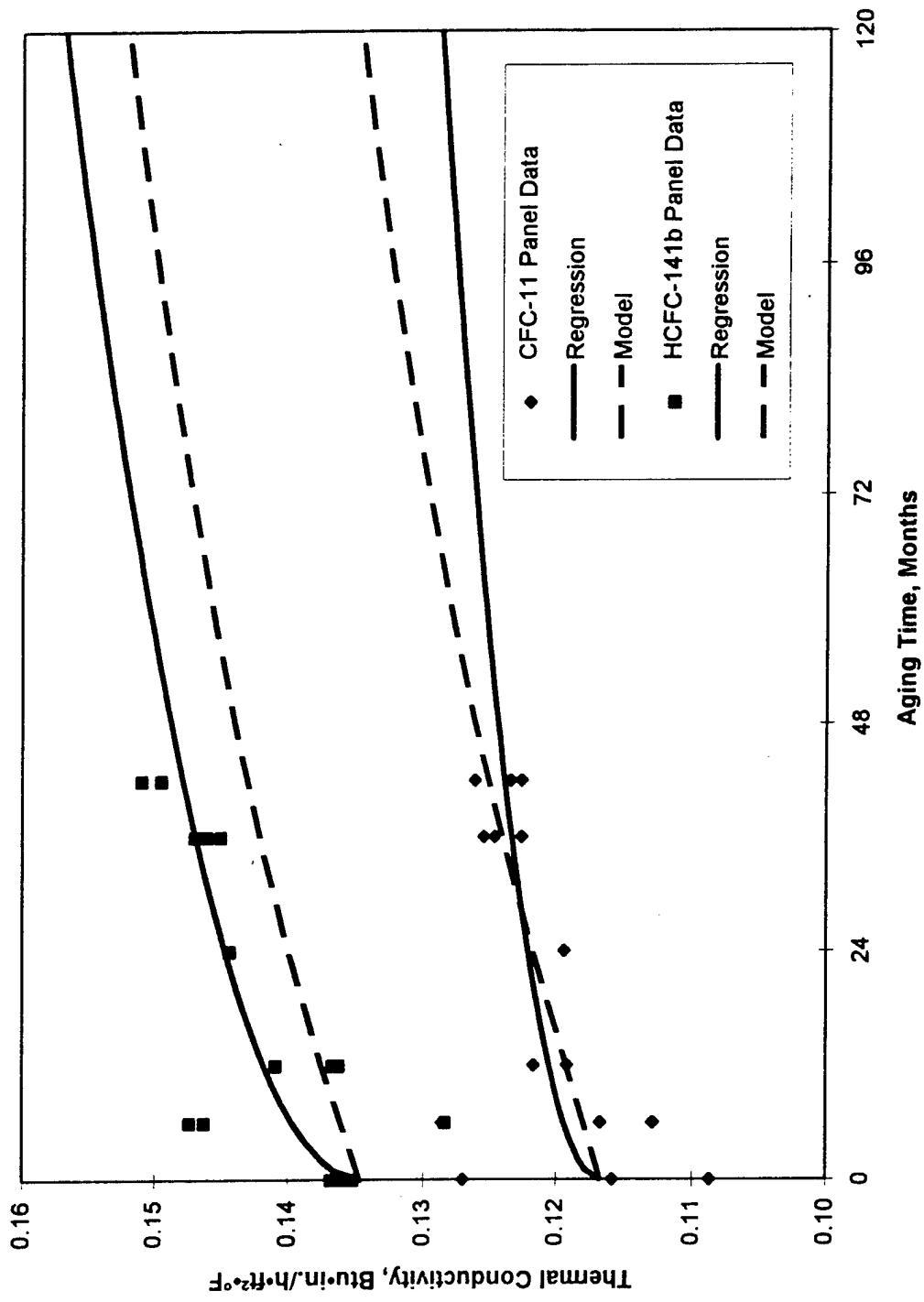


Figure 5. Comparison of Predicted and Measured Thermal Conductivities of Foams from Composite Test Panels

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