Cell-gas Composition – An Important Factor in the Evaluation of Long-term Thermal Conductivity in Closed-cell Foamed Plastics

Dipl.-Ing. (FH) W. Albrecht

Forschungsinstitut für Wärmeschutz e.V. München (FIW)
Lochhamer Schlag 4, D-82166 Gräfelfing, Germany

Received: 27th July 2000; Accepted 31st August 2000

SUMMARY

In addition to the initial thermal conductivity value, the thermal conductivity of closed-cell foamed plastics over long periods of time depends to a large degree on the gas exchange processes between the blowing agent and the ambient air. It is very important to know and to show whether the cell gas remains in the foam for a short time or, to a large extent, for the whole lifetime of the foam material.

A lifetime of between c.20 to 50 years is assumed for thermal insulation materials in construction, and it will be shown that blowing agents remain to a large extent in the foam material over such periods.

The method most extensively applied for measuring cell-gas composition is to take a sample using a gas-tight syringe and then analyse by gas chromatography. In addition to the measuring method, possible sources of sampling errors and measuring uncertainty are indicated.

In order to show the relationship between thermal conductivity and cell-gas composition, thermal conductivity curves for PUR rigid foam materials blown with CFC 11 over a period of 30 years, and PUR foam materials blown with HCFC 141b or pentane over a period of 9 years are presented, with the corresponding measured values for cell-gas composition.

Cell-gas measurement continues to be applied as proof of the blowing agent used for consumers and official bodies, and also for compliance with regulations.

INTRODUCTION

In addition to the heat transfer of a thermal insulation material through the solid material structure and as a result of radiation, heat transfer of the gas phase (cell gas) makes a significant contribution in terms of total heat transfer. In the literature, figures of 40% to 70% of total heat transfer is attributed to heat transfer of the gas[1].

As a result of the blowing agent employed in the foaming process, the cell gas in the cells of closed-cell foamed plastics often exhibits a lower thermal conductivity than that of the ambient air (Figure 1). Through the

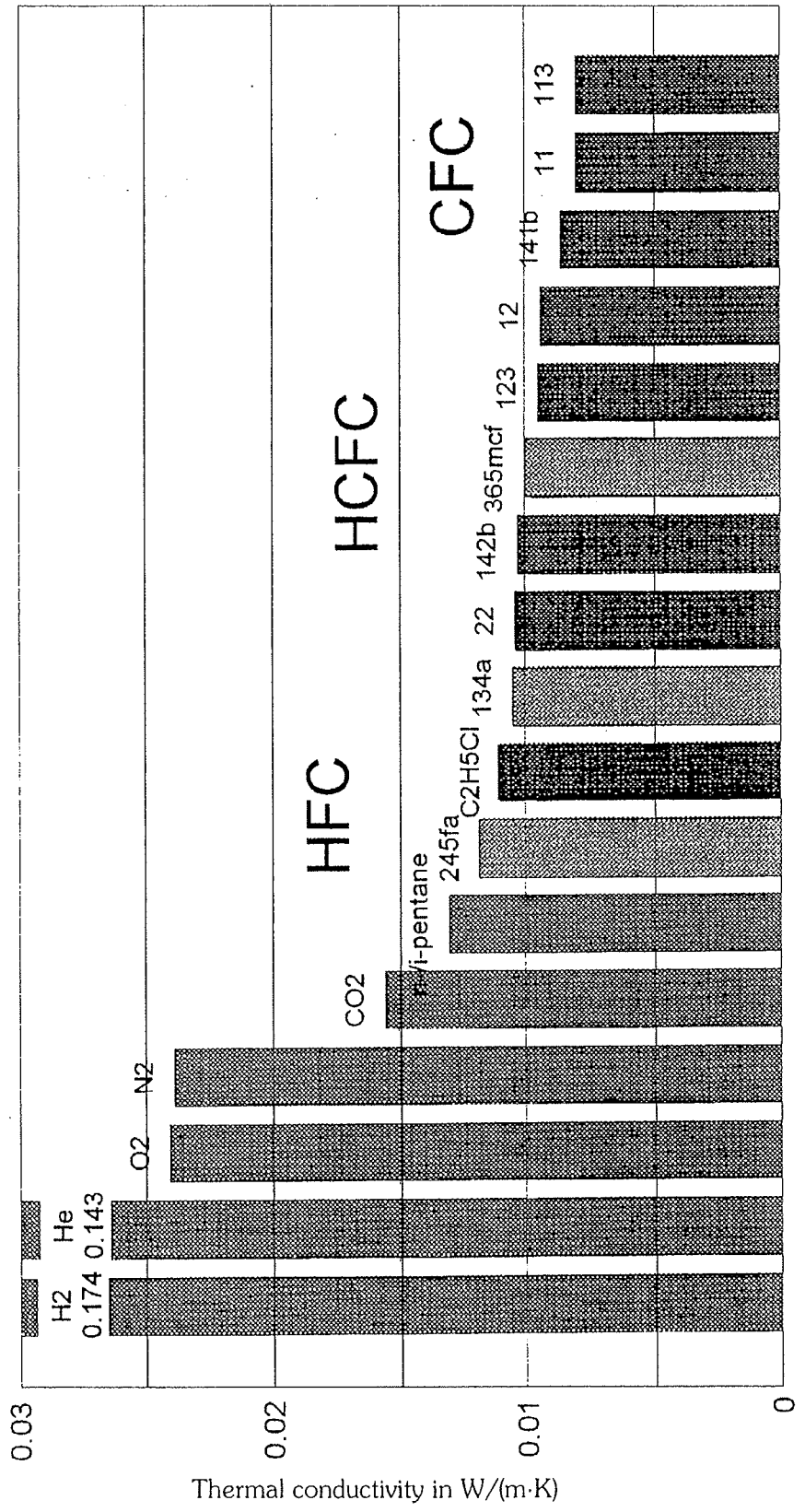


Figure 1 Thermal conductivity of certain blowing agents in gaseous form at 10°C

gas exchange processes with the ambient air, the cell gas composition alters constantly, and generally leads to an increase in the thermal conductivity of the thermal insulation material[2].

The thermal conductivity of the cell gas in a foam cell is therefore dependent to a large extent on the time and on the location of the cell in the insulation material, as the cells adjacent to the ambient air release the blowing agent into the surrounding air much more quickly than the foam cells in the middle of the insulation material.

The rate of gas exchange with the ambient air depends on the effective diffusion coefficients of the individual gas components in the foam material and from the initial concentration. The diffusion coefficients as well as the initial concentration of the individual cell gases can be established through the determination of the total pressure in the cells and the volumetric proportions of the individual cell gases using a gas chromatograph.

The determination of the total pressure in the foam cells is relatively complex, and only necessary for the calculation of the diffusion coefficients and the gas exchange processes.

The quantitative cell gas analysis[3] is a quick and cost-effective method for determining the blowing agent used and the quantity contained in the cell gas. This method also provides information on both the initial concentration of the cell gases and thus the thermal conductivity of the gas phase of the insulation material, as well as on the long-term development of the thermal conductivity of the gas phase. As a rule, the thermal conductivity of the solid material structure remains constant over the lifetime of the product, provided the foam material matrix does not absorb moisture or alters as a result of ageing processes.

Furthermore, measurement of cell gas composition allows conclusions to be made concerning the blowing agent used and whether significant quantities of the blowing agent will remain in the insulation material over the long term. In other words, whether it is a permanent blowing agent, as required in Annex C of the PUR draft standard prEN 13165[4].

For this reason, when new blowing agents were introduced for foam materials, stipulations were included in the German building supervisory approvals (Bauaufsichtliche Zulassungen) and later on the building regulation list (Bauregelliste A)[5] which required that measurements of cell gas composition be made for insulation materials in building made of Polyurethane (PUR), extruded Polystyrene (XPS) and phenolic foam (PF).

In Austria, measurement of cell content was included in the Austrian standard B 6010[6].

The measurement of cell-gas composition is also important from the environmental point of view and for consumer protection, in order to

show compliance with regulations, for example EC Council Regulation No. 3093/94, and as confirmation for the consumer that the designated blowing agent has been employed.

METHODS FOR MEASURING CELL-GAS COMPOSITION

Cell-gas composition is usually determined using a gas chromatograph with a packed column and a thermal conductivity detector. Thermal conductivity detectors can determine all blowing agents currently in use and gaseous compositions in the Vol.-%- range. The carrier gas used for the gas chromatograph is one which is not present in the cellular plastic to be examined (usually helium).

Samples are taken using a gas-tight syringe with a long hollow needle, from around the middle of the cellular plastic material to be examined[3]. It is expedient to determine the cell gas composition with the same specimen which was used to determine thermal conductivity in order to eliminate material variations. The specimens are not destroyed in the process, so that further measurements of thermal conductivity can be made.

Before samples are taken, the gas-tight syringe is rinsed three times with the carrier gas.

The needle of the syringe is then inserted approximately half-way through the thickness of the specimen. During insertion, cell-gas samples are taken from several foam cells by slowly drawing back the syringe piston. This process is repeated twice in order to rinse the syringe; the third cell gas sample is injected through the septum into the carrier-gas stream of the gas chromatograph.

The taking of cell-gas samples requires great care and some practice in order to ensure that the cell-gas samples are not contaminated with the ambient air.

It is easy to check whether the sampling technique employed effectively prevents the penetration of ambient air: the cell-gas composition in a foamed plastic specimen with gas-diffusion-tight facings manufactured shortly before testing is determined. Normally such foams contain practically no air.

With a good sample-taking technique measured values of < 1 Vol.-% air are obtained. The relative cell-gas composition of the sample is then determined using a gas chromatograph by retention period comparison and peak surface determination.

The sensitivity of the gas chromatograph detector must be set for each cell-gas component with appropriate gas-calibration mixtures (wherever possible within the concentration range of the subsequent measurements).

The cell-gas percentages obtained are multiplied by the sensitivity value of the detector and the cell-gas composition expressed in Vol.-%.

It is usual to examine three cell-gas samples from each test specimen. The result is expressed as an mean value in 1 per cent steps. If the results exhibit a high degree of dispersion, further cell-gas samples must be examined.

DETECTION LIMIT

In the process described the detection limit is at around 0.5 Vol.-%. The detection limit can be significantly reduced by using a flame-ionisation detector. In this case, however, the detector is able to measure only certain gas components, but not oxygen, nitrogen or CO_2. However, for thermal properties only quantities in the Vol.% range are relevant. For this reason the process as previously described is completely adequate for routine examinations.

VARIATION OF MEASURED RESULTS

As a result of gas exchange processes the cell-gas composition is to a large extent dependent on the thickness of the material. Therefore, cell-gas samples are as far as possible always taken from the middle layer of the thermal insulation material sample. In a more or less homogeneous insulation material, the dispersion of measured values amounts to approx. < 5 Vol.-%. For this reason, only the mean value is to be expressed in 1 per cent gradations.

If the test specimens are either thin (insulation thickness 5mm– 20mm) or not homogeneous, it may be advisable to state the measuring range.

LONG-TERM THERMAL CONDUCTIVITY MEASUREMENTS ON PUR RIGID FOAM

Measured values of thermal conductivity and cell-gas composition over several years have been obtained to date for Polyurethane (PUR) rigid foam with various blowing agents.

The test specimens have been stored in an air conditioned room at 23°C and about 50% relative humidity. The test specimens have a size of 500 mm x 500 mm in original thickness with original facings on the specimens.

The measurements of thermal conductivity were taken with a single-specimen symmetrical heat-flow meter apparatus with an overall apparatus size of 500 mm x 500 mm and a metering section of 300 mm x 300 mm

according to prEN 12667 and ISO 8301. This apparatus with a high repeatability and two heat flow meters offers the possibility to observe the differences of the two heat flow meters on warm and cold side and the stabilisation of the heat flow on both sides of the specimen.

Apparatuses with this size and placed in a well insulated cabin have the advantage that measurements can be taken in full thickness of the specimens up to 80 mm with facings and the same specimen can be measured always again.

This precautions give a high degree in accuracy which is supported by regularly apparatus checks and calibration procedures according to prEN 1946-3.

PUR rigid foam blown with CFC 11

Experience with PUR rigid foams blown with CFC 11 has been gathered over a longer period than for other foams; the corresponding changes in thermal conductivity have be followed for more than 30 years (Figure 2). In most countries the use of this blowing agent is no longer permitted. The curves are nevertheless very interesting, as they show that we are dealing with a really permanent blowing agent, a large part of which is still present even after 30 years. No measured values for cell-gas composition after manufacture are on hand for the 5 Polyurethane rigid foams shown in Figure 2.

The PUR products examined were obtained in the course of regular quality supervision measures and corresponded to the applicable standards DIN 18164 and DIN 18159 for PUR spray-foam.

In PUR rigid foam materials blown with CFC 11, the proportion of blowing agent in the cell gas shortly after manufacture amounted to approx. 40 to 70 Vol.-%, the remainder is CO_2, which diffuses out of the foam relatively rapidly if gas diffusion open facings are used. With initial values of 40 to 70 Vol.-% of the blowing agent in the cell gas, cell-gas values of between 15 and 25 Vol.-% are remarkably high after a period of 30 years, and these are also in equilibrium with the blowing agent contained in the foam material matrix.

The flat gradient of the curve leads us to expect that the thermal conductivity will remain in the range 0.024-0.029 W/(m·K) over a very long period.

For the assessment of the long-term thermal conductivity of PUR rigid foam materials with new blowing agents, these graphs also served as examples of the development of the curves for PUR rigid foams with a permanent blowing agent. The development of the thermal conductivity curves formed the basis for determining incremental values for ageing and

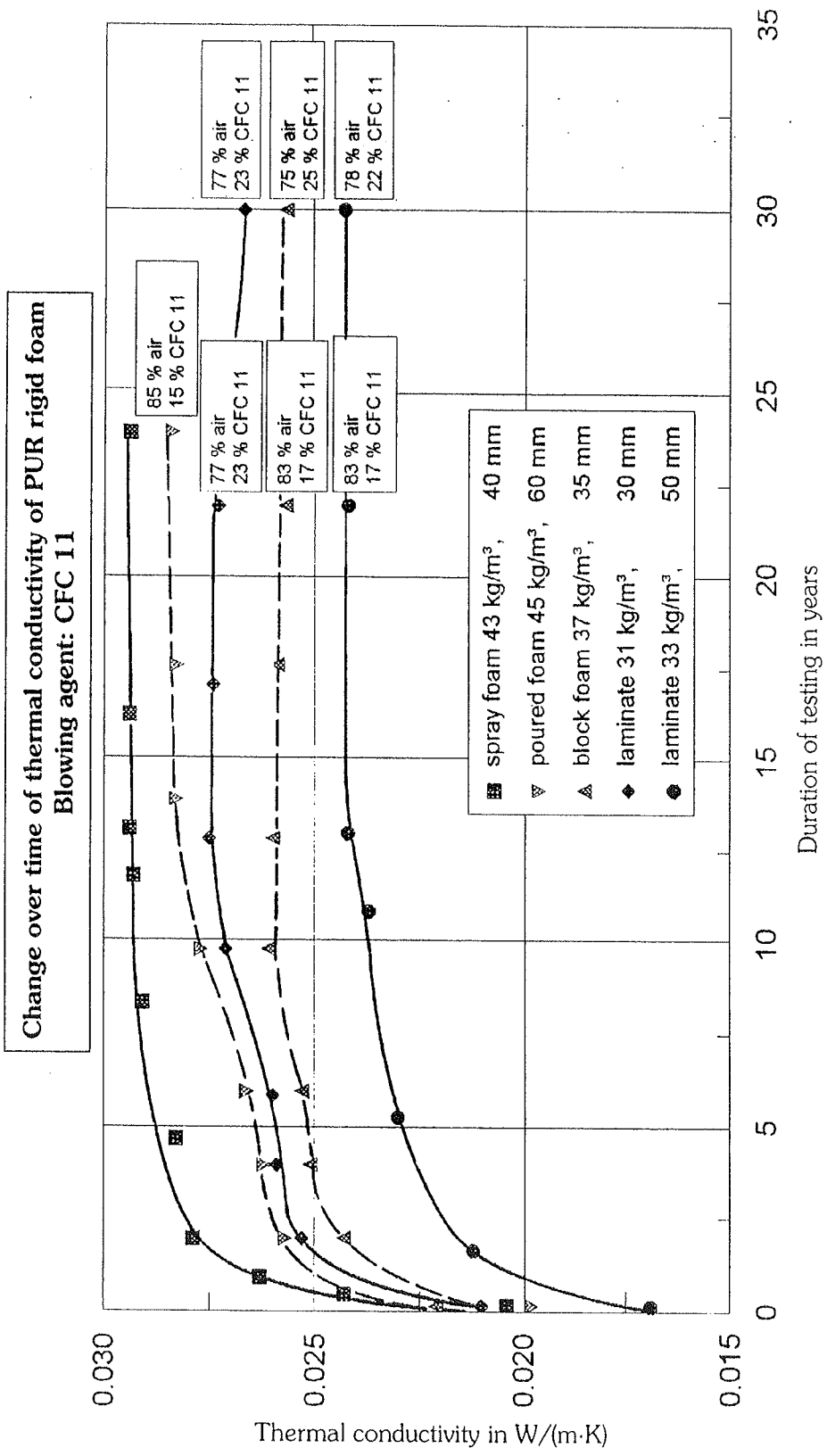


Figure 2 Change over time of thermal conductivity at 10°C mean temperature of PUR rigid foam boards blown with CFC 11 and manufactured in various processes and storage at room temperature. Measurements using a guarded hot plate apparatus in accordance with DIN 52612

establishing calculation values of thermal conductivity for the building sector[8].

PUR rigid foam blown with pentane

Figures 3 and 4 show the dependence of thermal conductivity on the age of the samples. The PUR rigid foam boards were of 40mm and 80mm thickness, blown with pentane and taken from 2 manufacturing plants.

After the initial measurements taken after 6 weeks' storage at 23°C, the specimens, measuring 500 mm x 500 mm, were stored under laboratory conditions at 23°C for either 8 or 9 years. The measurements of thermal conductivity were taken with a 300mm heat-flow meter apparatus in accordance with ISO 8301/DIN52616 at a mean temperature of 10°C. The thermal conductivity curves show that the greatest increase in thermal conductivity is complete after a period of 5 – 7 years, and that the increase in the curves for these thicknesses become less pronounced.

Shortly after the measurements of thermal conductivity were taken, 3 cell-gas samples from each of the specimens were taken and examined for the thermal conductivity outside the measured surface of 300mm x 300mm. The quantities of gas taken were so small – between 2 and 5 µl – that a detectable influence on the thermal conductivity within the measured surface is not expected.

For the two specified thicknesses examined, the gas exchange of CO_2 for the two air components is, to a large extent, complete after a period of 3 – 6 years. This results in a relatively stable blowing agent/air ratio of approx. 10 - 30 Vol.-% pentane to 70 - 90 Vol.-% air.

PUR rigid foam blown with HCFC 141b

Due to the low thermal conductivity of HCFC 141b as a gas (see Figure 1), the thermal conductivity curves of the 50mm and 80mm thick rigid foam boards blown with HCFC 141b are characterised by a more pronounced initial increase.

After storage at room temperature for between 3 and 4 years, the curves for the 50mm and 80mm thick PUR rigid foam boards become flatter.

Also in the case of boards blown with HCFC 141b, a largely stable blowing-agent/air ratio of 20 - 30 Vol.-% HCFC 141b to 70 - 80 Vol.-% air is arrived at after a period of between 2 and 4 years. In the case of thinner or thicker PUR rigid foam boards, the initial curves are correspondingly either steeper or flatter.

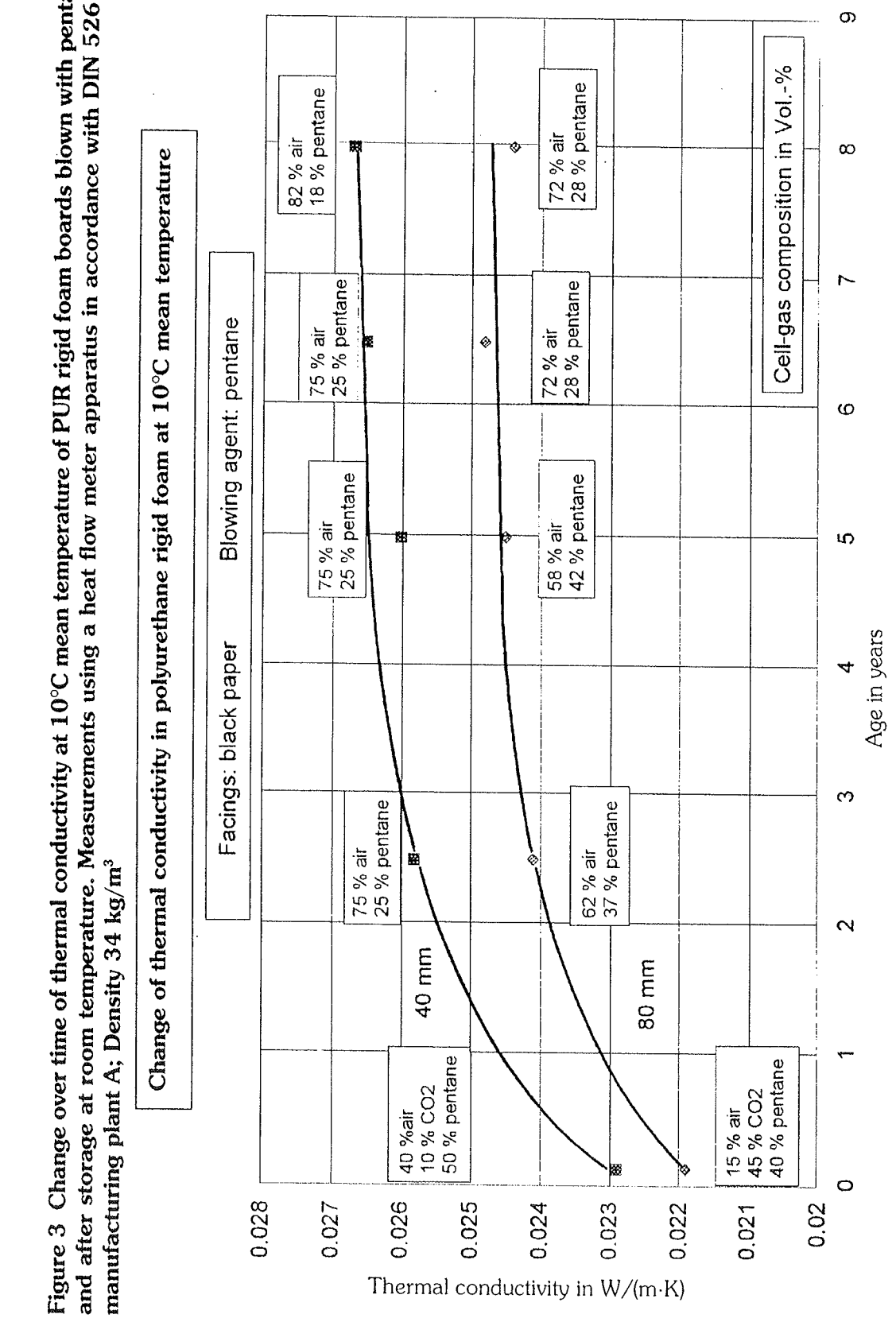
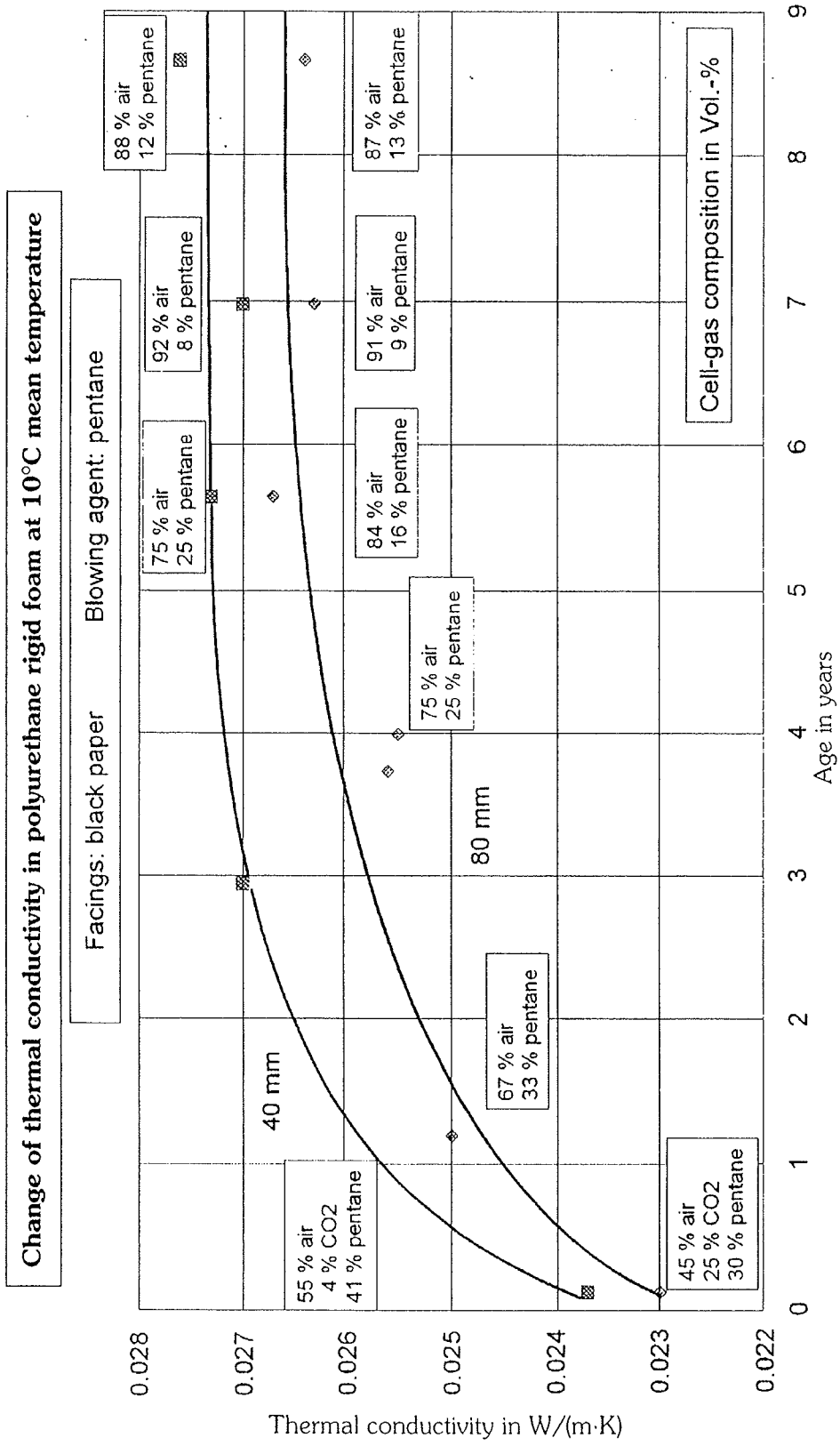


Figure 3 Change over time of thermal conductivity at 10°C mean temperature of PUR rigid foam boards blown with pentane and after storage at room temperature. Measurements using a heat flow meter apparatus in accordance with DIN 52616; manufacturing plant A; Density 34 kg/m³

Figure 4 Change over time of thermal conductivity at 10°C mean temperature of PUR rigid foam boards blown with pentane and after storage at room temperature. Measurements using a heat flow meter apparatus in accordance with DIN 52616; manufacturing plant B; Density 33-35 kg/m³



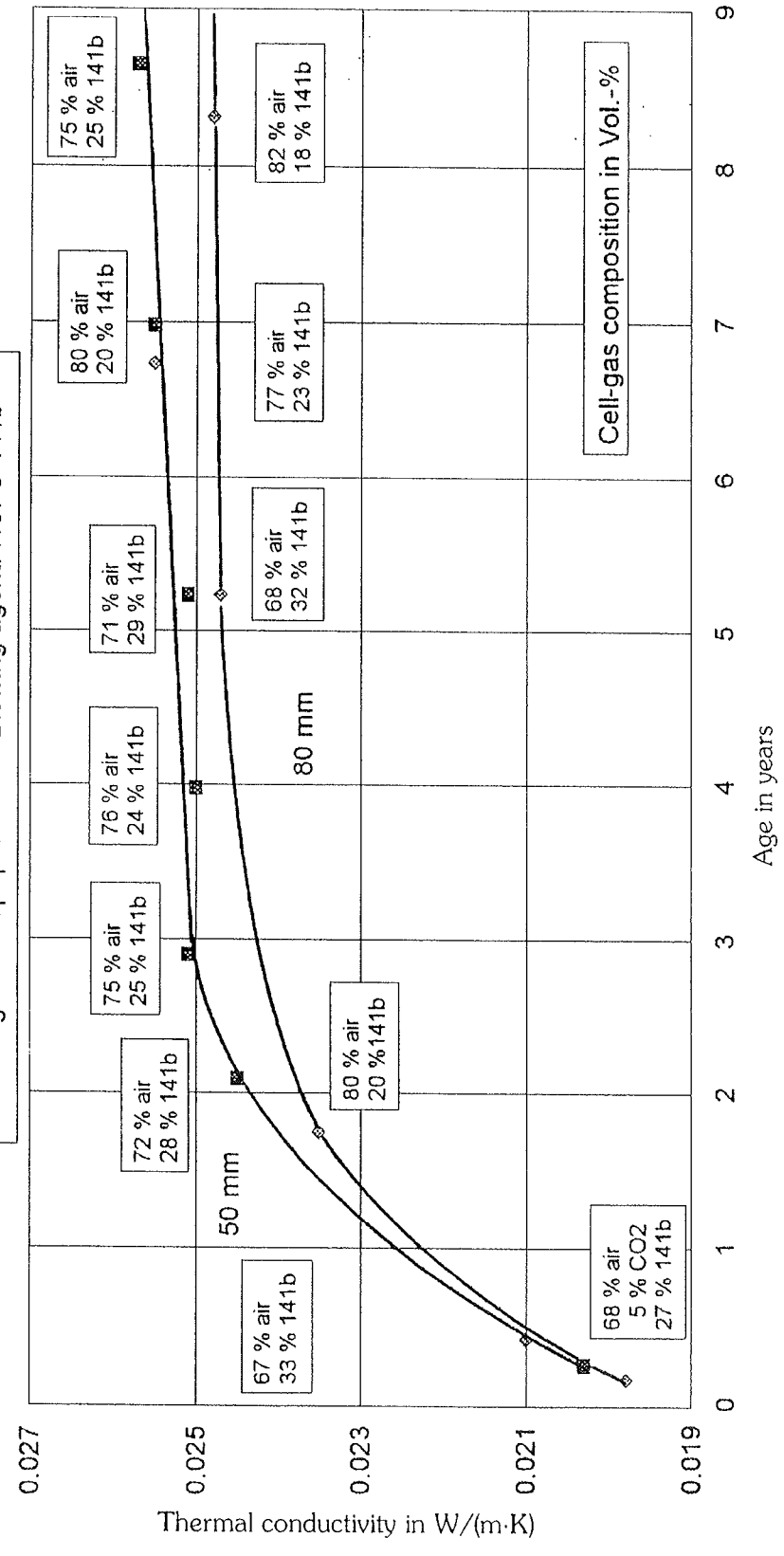


Figure 5 Change over time of thermal conductivity at 10°C mean temperature of PUR rigid foam boards blown with HCFC 141b and after storage at room temperature. Measurements using a heat flow meter apparatus in accordance with DIN 52616; manufacturing plant B; Density 30-34 kg/m³

It is also to be expected that in terms of the change in thermal conductivity, PUR rigid foam boards blown with pentane or HCFC 141b will behave in a similar manner to PUR rigid foam boards blown with CFC 11, and that over periods of more than 50 years their thermal conductivity will remain clearly below that of PUR rigid foams with air as cell gas (0.031 – 0.033 W/(m·K)).

CONCLUSIONS

The measured values for cell-gas composition show that all 3 blowing agents are permanent cell gases which accord with and explain the course of the previously determined thermal conductivity curves, and which can serve to support the estimates of future curve development.

The initial cell-gas composition of the PUR rigid foam (measured between 1 and 7 days after manufacture) is most important, as:

- proof of the blowing agent used, and whether this is a permanent or non-permanent blowing agent;
- percentage volume of the blowing agent in the cell gas;
- initial values for calculations and theoretical estimates of thermal conductivity curve development.

After longer periods, cell-gas composition is an important assessment factor

- as practical proof that the blowing agent remains in the cells over longer periods;
- for the interpretation of ageing curves of thermal conductivity;
- as explanation of thermal conductivity curve development in relation to mean temperature;
- for allocating PUR rigid foam to thermal insulation material specifications[4,5] and as component of third-party monitoring and certification.

The measurement of cell-gas composition continues to be the usual method of proof

- that statutory or voluntary regulations have been observed;
- for the consumer that the declared blowing agent has been used;
- for the disposal of unknown PUR rigid foam samples.

The cell-gas composition in a PUR rigid foam sample can vary very considerably depending on location. For most of the measurements

carried out, it is not the absolute value which is significant but only the relative size of the value measured.

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