PASCAL™ Technology: A Novel Breakthrough Polyurethane Foaming Technology for Domestic Appliance Insulation

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ABSTRACT

Dow announces the first industrial implementation of the PASCAL™ foam technology, a novel polyurethane breakthrough foaming technology for the manufacture of domestic refrigerators and freezers. Dow PASCAL™ foam technology offers an advanced combination of excellent rigid polyurethane insulation and efficient appliance case filling that addresses the productivity needs of manufacturers and the energy efficiency demands of consumers. The technology improves the energy efficiency of cold appliances whilst offering large space for design improvement and also addressing government standards with a long term sustainable solution. With hydrocarbon based PASCAL™ foam systems the energy efficiency of conventional foam systems using HFC 245fa blowing agent can be easily met.

The PASCAL™ foaming technology is based on the use of a controlled reduced in-mold pressure in the fixture where the cold appliance is injected with the polyurethane foam system, using equipment specifically developed by Cannon S.p.A. Applying this concept significantly improves the flow-ability of the polyurethane foaming mass which has led to the development of a new generation of foam systems specifically tailored for use in the PASCAL™ foam technology. We believe that these new PASCAL™ foam systems offered by Dow provide a cost effective solution for the need to improve the energy efficiency of refrigerators and freezers whilst allowing the appliance manufacturer to increase the output-rate.

INTRODUCTION

Globally, the household sector is one of the largest users of electrical energy. Even though there have been continued technical improvements in the efficiency of electrical appliances, these improvements have been offset by the increase in the use, numbers and size of large appliances launched in the market. Specifically, the cold appliances global industry is required to produce refrigerators and freezers matching very stringent energy legislations that continuously evolve requiring end-use energy efficiency of high standard.

Currently several different types of blowing agents (BAs) are being employed globally in the manufacturing of polyurethane (PU) foam for the insulation of domestic appliances, such as hydrochlorofluorocarbons (HCFCs), hydrofluorocarbons (HFCs) and hydrocarbons (HCs).

Tight restrictions were imposed on HCFCs like for instance HCFC 141b due to their ozone depletion potential (ODP). The Montreal Protocol calls for a complete phase-out of HCFCs by 2030, but so far, no restrictions on the use of HFCs, which exhibit zero ODP but have high global warming potential (GWP) values, have been put in place yet. Those employed for cold appliances, such as HFC 134a and HFC 245fa have a GWP of 1030 and 1250 respectively (GWP of CO₂=1) [1].

Though being less expensive and having negligible GWP values (only up to 11), hydrocarbons have traditionally lower performance in terms of insulation and require greater material usage leading to higher foam densities. Being flammable, HCs also require investments allowing safe production process management through the installation of extensive ventilation, equipment grounding and explosion proof hardware.

Despite their flammability, HCs have gained wide acceptance as viable alternative blowing agents in the manufacture of rigid polyurethane foams worldwide and are today globally the most used BAs. Among the HCs, cyclo-pentane is the best alternative to HCFC’s and HFC’s due to its insulation behavior. Extensive studies to improve the insulation properties of the hydrocarbon blown foam systems without compromising on the foam process and costs have culminated in new solutions provided by Dow offering appliance manufacturers the option to take advantage of both improved energy efficiency and high productivity, saving costs and selecting the product best satisfying any specific demand in each region of the globe [2,
The newly developed low k polyurethane systems provide the lowest thermal conductivity and the best refrigerator energy efficiency using hydrocarbons as a blowing agent in a conventional single shot injection foaming process.

These solutions have reduced the gap versus HFC 245fa blown foams even if such a gap cannot be closed without material and technology innovation applied to cyclo-pentane blown foam. HFC-245fa has been the predominant choice in U.S. appliance applications where a high standard of thermal insulation is needed to meet strict energy-efficiency requirements on the commercialized products. While HFC 245fa remains so far the leading technology for low k, the very high material cost versus the performance achieved as well as its unfavorable environmental characteristics in terms of GWP have reduced the attractiveness of PU foam systems containing HFCs for the global domestic appliance industry.

In this scenario, an innovative HCs technology offering the same insulation behaviors as HFC 245fa at economically attractive cost would offer a valid and sustainable long term solution to the global appliance industry and for consumers, mitigating the environmental impact of manufacturing high efficiency cold appliances.

A close cooperation between Dow and Cannon has recently led to the development of the PASCAL™ foaming technology which offers an innovative advanced foaming process enabling excellent polyurethane insulation properties and high efficient appliance productivity. The Dow PASCAL™ foam systems combined with the new Cannon vacuum assisted injection (VAI) process technology offers the most innovative and high performing solution required by the global appliance industry to satisfy increasing requirements on energy efficiency of cold appliances. Novel Dow polyurethane chemistry leading to polyurethane foams having low thermal conductivity, combined with the Cannon vacuum-assisted polyurethane foaming technology, specifically developed for processing these new foam formulations, allows for the achievement of these challenging targets using a low GWP and zero ODP blowing agent such as cyclo-pentane to produce high performing insulating foams.

TECHNOLOGY CONCEPT

Controlled vacuum assisted injection was industrially implemented for the first time in 1998 for sandwich insulation panels foaming technology as a result of a joint development program among MISA (an Italian sandwich panel manufacturer), Manni (a polymerization press-manufacturer), Cannon (producer of the foaming machine and mixhead) and Dow Italia (the supplier of the polyurethane chemical components) [4]. The technology concept relied on the control of the in-mold pressure applied to the panel cavity maintained at constant level during the PU foam injection and expansion. The desired negative pressure allowed higher productivity, improved density distribution, enhanced panel surface quality, and a reduction in PU raw materials and labor cost. Many blowing agents including HCs with a wider range of boiling point could be used with this new technology concept. The resulting panels exhibited both a very even foam density distribution across the whole panel length and excellent adhesion behavior between the foam and the metal facings, with significant improvements compared to the standard process employed at atmospheric pressure.

The successful industrial implementation of the vacuum-assisted injection for discontinuous panel production (DCP) stimulated the cooperation between Dow and Cannon to extend this technology concept to other discontinuous process applications like the production of refrigerators and freezers. However, in the case of cold appliance insulation, the geometry to be filled is significantly more complex than for panels. Each refrigerator model has its own design with variable wall thicknesses and a complicated internal cavity to be filled by the foam. The cavity can contain steps, cables, pipes, ducts and various inserts (like the evaporator or the frost-free air conducts). Last but not least, compared to the discontinuous panels the industrial refrigerator production process requires much faster demolding times and significantly lower foam k-factors to satisfy the need for the best insulation behavior possible with the necessity to improve the output-rate of the whole process. As a consequence, while it was sufficiently easy to apply and maintain the desired vacuum level of the sandwich panel geometry, the application of vacuum assisted injection to the refrigerator’s cavity was significantly more challenging and required an in-depth re-engineering of the process to guarantee its successful implementation.

In parallel, the PU formulation technology has been completely modified, targeting high performance foams for domestic appliance insulation exhibiting the best possible k-factor leading to appliances with the best in class energy efficiency performance. A fundamental development study has been carried out in the Dow R&D laboratories to design new PU foam systems able maximize the advantages and savings offered by the PASCAL™ foam technology.
This technology applies the concept of foaming into a cavity at controlled reduced in-mold pressure. The refrigerator’s cavity is injected with the PASCAL™ polyurethane foam system using the VAI-equipment specifically developed by Cannon S.p.A. The reduced in-mold pressure results in significantly improved flow-ability of the polyurethane foaming mass. The concept is shown in Figure 1 where the minimum fill density of a given PU system, designed for the PASCAL™ foaming process, flowing into the Brett mold is recorded versus the internal mold pressure.

As expected, the minimum fill density is reduced with lower applied in-mold pressures. Basically, the PU system flows much more easily into the cavity to be filled due to the lower back-pressure. As a consequence, the PU formulation can be designed in a different way, capitalizing on the improved flow characteristics to improve the overall performance of the polyurethane foam.

Lower in-mold pressure also offers the advantage of reducing the refrigerator post-expansion at the time of demold, improving the productivity of the whole process. As can be seen in Figure 2, when a lower in-mold pressure is applied to the cavity to be filled, the maximum residual foam pressure at the time of demold is lower than in the conventional foaming process at atmospheric pressure. Optimized PASCAL™ PU systems offering the best curing performance will take additional advantage of this physical effect maximizing the reduction of demolding time.
Improved flow-performance gives more options for improving foam k-factor hence the energy efficiency of the appliance without penalties on the process-ability of the PU-system. Typically, in conventional foaming processes, low k-factor foam systems do not always exhibit the best demold performance and often higher densities are applied to obtain good density distribution and foam robustness. In this case, applying a lower in-mold pressure offers the possibility to develop low k-factor PU systems optimizing the formulation recipe in terms of:

- Cell gas composition, balanced in favor of the physical blowing agent versus CO₂.
- Reactivity, since faster reaction-times yields foams with smaller average cell size.
- Base polyol composition: Polyols with higher viscosity, higher aromaticity and higher functionality can be used without detrimental effect on flow, applied density and demold.

**IMPROVING THE THERMAL CONDUCTIVITY OF A FOAM SYSTEM**

The thermal conductivity (k-factor) of a foam system can be described by the following general equation [5]:

$$k = k_s + k_g + k_r + k_c$$  

Where:
- $k_s$ = conductivity of the solid;
- $k_g$ = conductivity of the gas; $k_r$ = heat transferred by radiation and $k_c$ = heat transferred by convection.

Because of the very fine cell structure of the polyurethane foam, the heat transfer term by convection can normally be neglected [6]. The solid contribution is closely related to the density of the foam and cannot be significantly impacted when the overall density is kept relatively constant [7].

As such, efforts have concentrated on influencing the thermal conductivity of the polyurethane foams by working on the conductivity of the cell-gas, which makes up for 50 to 60% of the overall thermal conductivity of a foam, and by influencing the radiation heat transfer component, which contributes around 20% to the final thermal conductivity of rigid polyurethane foam in the for domestic appliance relevant applied density range [7, 8].

The effect of the cell-gas composition has been modeled using the Wassiljewa equation which sums the weighted individual thermal conductivities of the pure components [9]:

$$k_g = \sum w_i k_i$$  

Where: $k_g$ = conductivity of the gas, $w_i$ = weighting factor of component I and $k_i$ = thermal conductivity of component i.

From equation-2 and Table-1 it is clear that altering the ratio CO₂/cyclo-pentane in the foam the thermal conductivity can be influenced. The PASCAL™ foam technology allows for foam systems with relatively low water content which improves the thermal conductivity of the foam and shifts it more towards the performance of HFC-245fa blown foams.

<table>
<thead>
<tr>
<th>Property / Blowing agent</th>
<th>HFC245fa</th>
<th>Cyclo-pentane</th>
<th>Carbon dioxide</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular weight (g/mol)</td>
<td>134</td>
<td>70</td>
<td>44</td>
</tr>
<tr>
<td>Boiling point (°C)</td>
<td>15</td>
<td>49</td>
<td>-78</td>
</tr>
<tr>
<td>Vapour pressure at 20°C (bar)</td>
<td>1.24</td>
<td>0.34</td>
<td>56.55</td>
</tr>
<tr>
<td>Gas k-factor at 25°C (mW/m.K)</td>
<td>12.2</td>
<td>12.6</td>
<td>16.3</td>
</tr>
<tr>
<td>Ozone Depletion Potential (CFC11=1)</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Global Warming Potential 100-yr</td>
<td>1250</td>
<td>11</td>
<td>1</td>
</tr>
<tr>
<td>Atmospheric life-time (year)</td>
<td>7 - 10</td>
<td>0.05</td>
<td>120-200</td>
</tr>
</tbody>
</table>
The radiation heat-transfer contribution is directly related to the average cell-size, which shows a linear relation based on the following simplified equation as derived by L. D. Booth [8]:

$$k_r = 16 C_d \ (W/ \text{m}^2 \cdot \text{K})$$

Where: $C_d = \text{average cell diameter}$

The PASCAL™ foam technology also allows for foam-systems with very fast reaction times. Due to early vitrification of the cells, excessive bubble-growth and coalescence is prevented, leading to lower overall cell-size. Moreover, introducing specific high viscosity base polyols helps nucleation leading to a further reduction in cell size and as a result in improved thermal conductivity performance [9, 10].

**EXPERIMENTAL**

**Dow Laboratory Set-Up**

Foam physical property evaluations using reduced in-mold pressure have been carried out in both the “Brett mold” and the “Jumbo” mold, specifically modified allowing the set-up of the internal mold pressure control. Both molds have been sealed to maintain the desired internal pressure at a constant level and a pressure transducer was used to record the internal pressure evolution during foaming. The vacuum Brett mould was equipped with a transparent heated glass on the top side covering the whole length allowing to visually monitoring the foam flow and its rise evolution into the mold. A scheme of the laboratory set up is shown in figure 3 for the Brett mold.

The foaming procedure when using the vacuum Brett mold can be described as follows:

- The mold is pre-heated to 45 °C and positioned at a 45 degree angle.
- The mold is evacuated by activating the vacuum pump connected to a large vacuum tank, equipped with a pressure indicator.
- Once the internal cavity pressure has reached its desired constant level, the mold is injected with the right amount of PU foam.
- The vacuum level is maintained at constant level throughout the mold filling time so that foam flow is homogeneous and its rise is relatively smooth.
- When the foam has completely filled the mold, the valve on top of the Brett mold can be closed, the PU foam Brett panel will cure until the end of polymerization when it can be demolded.

![Figure 3. Dow laboratory set-up for PASCAL™ foam evaluations.](image)

**Evaluations in Dow Laboratories: Foaming Procedure and Foam Properties Testing**

All samples described in this study were prepared in the polyurethanes research and development laboratories of Dow Europe GmbH in Switzerland and of Dow Italia S.r.l. Foam samples and moldings were prepared using high pressure injection machines and dispensing equipment from Afros-Cannon (Cannon S 20 and A-40). All machines were equipped with an L-shaped self-cleaning mix-head.

The formulated polyol and blowing agents were premixed and maintained at 20+/-2°C. The polyol and isocyanate were processed on the high pressure machines at temperatures of 20+/-2°C using a mix-pressure of 150+/- 20 bar.

All systems were evaluated and compared in terms of reactivity, flow, density distribution, compressive strength, thermal conductivity and demolding properties. The isocyanate index was kept constant for all experiments reported in this paper unless noted otherwise.
-Reactivity and free rise density. A free rise bun was prepared to measure the system reactivity and free rise density (FRD): cream time, gel time and tack free time were recorded during foam rise, the FRD was measured 24 hours after foaming, determined from a 10x 10x 10 cm block, cut from the center of the foam-sample. These measurements were always carried out under ambient conditions.

- In-mold pressure. This was regulated by means of a 1500 l/min. medium sized vacuum-pump, which was connected to the Brett and Jumbo-mold via a pressure buffer-tank of 500 liters, used to maintain the pressure in the cavity during the foaming experiments.

-Foam physical properties. The foam physical properties were evaluated using the Brett mold, with the standard dimensions of 200x 20x 5 cm. For the experiments in Dow Italy the dimensions were slightly different: 194x 35x 6 cm. These molds were filled keeping the mold at a 45 degree angle, applying a mold-temperature of 45°C. After determination of the minimum fill density (MFD), which is dependent on the in-mold pressure, panels at various over-pack levels were produced. The molded density (MD) was determined from the mass of the Brett panel divided by its volume (20 liters). The system flow is measured by the Flow Index (FI), as the ratio of MFD divided by the FRD. The ratio of MD with MFD gives the overpacking of the Brett-panel.

The filling time (FT) is defined as the time between the start of the injection and the time at which the foam reaches the topside of the Brett. The overall foam density of each sample was determined by mass (skin density) and the average density distribution (ADD) is calculated from these samples.

The ADD is calculated according to the following formula:

\[
ADD = \frac{1}{n} \sum_{i=1}^{n} \left| d_i - \bar{d} \right|
\]

Where: \( n \) = number of samples; \( d_i \) = average density; \( d_i \) = density of the \( i^{th} \) sample.

The core density (CD) is measured by weighing foam samples after removing of the skin of the foam (a layer of 1 cm foam is removed from the top and bottom side of the sample) and dividing the weight by the volume of the sample. The core density is reported in kg/m³.

The thermal conductivity (k-factor) is measured on the bottom side and the top-side of the Brett panel. These measurements were carried out at an average plate temperature of 10°C using a LaserComp Fox 200.

Compressive strength (CS) and ADD samples were obtained from evenly spaced dimensioned samples cut along the length of the Brett panel. For the determination of the ADD 15 blocks dimensioned 20x10x5 cm were used. For the CS 5 blocks dimensioned 10x 10x 5 cm were used and the average value is subsequently reported. For the CS measured from core samples, the dimensions of the specimens were 10x 10x 3 cm. All CS samples reported are measured at 10% deflection.

The closed cell content was measured with a pycnometer using the samples taken for the determination of the thermal conductivity. The number is not corrected for the cell-destruction on the surface of the sample.

-Demolding properties. The demolding behavior was determined with the so called Jumbo mold (70x 35x 10 cm) pre heated to 45°C. Jumbo panels were mostly produced with an overpack ratio of 115% over the MFD and were demolded at different curing times. Subsequently the post-expansion of the foam was measured 24 hours after demold, and is reported in mm. as the maximum thickness of the foam-sample from the mold minus the original thickness which is 100 mm. This is a metric to predict productivity of a foam-system during the actual production of refrigerator-freezer cabinets (cycle-time).

Evaluations in Cannon Laboratories: Cabinet Foam Properties Testing

Several industrial validations have been carried out in the Cannon SpA laboratory where an industrial fixture for vacuum assisted injection (VAI) having the same functionality, heating and movements of a typical commercial cabinet fixture has been installed. In this case, the fixture has been completely sealed to provide an airtight cavity. The vacuum is applied through the upper plate and is controlled with a vacuum-pump and a 500 liter pressure buffer-tank. The injection point is located at the bottom side of the refrigerator in the compressor area, with the refrigerator positioned in the breakers up configuration. The foaming machine is a Cannon A-200 high pressure two components PU metering machine, equipped with a self- cleaning L-shaped FPL-24 mix-head proving an output of 1.5– 2.0 kg/sec.
A large variety of physical property testing was carried out on the final cabinets, such as average density distribution, compressive strength, thermal conductivity, closed cell content, cell size and the tensile bond strength, which is a metric to determine the adhesion properties of the foam to both cabinet liners. Samples are normally taken from various positions of the cabinets. Typically samples from 12 different positions were used for the ADD and CS measurements, and samples from 7 different positions were used for the determination of the thermal conductivity. On the appliances a reverse heat leakage test was also carried out, which was determined at a certified, independent test-institute.

This reverse heat leakage test (RHL) is performed to determine the influence of the foam quality on the energy efficiency of the appliance. In this test the appliance is put into a temperature controlled environment. The inside temperature of the cabinet is then brought to a fixed value, higher than the outside temperature. During this test, the inside temperature is maintained with an electrical heating coil. After reaching steady-state conditions the heating coil power input is determined and averaged over a 24 hour period. The actual RHL is the amount of energy going into the heating element normalized for the temperature difference maintained between inside and outside of the appliance, as per the following equation:

\[ Q = \alpha \cdot dT \]  

(5)

Where: \( Q = \) heating coil power input (W); \( dT = \) the temperature difference (K) and \( \alpha = \) heat-loss coefficient (W/K), determined from the experiments, often referred to as the k*A value.

The test has been carried out with an outside temperature of 5°C and an inside temperature of 25°C when the refrigerator part was tested, and an outside temperature of 5°C and an inside temperature of 45°C in case the freezer section was tested.

| Table 2. Laboratory evaluations using VORATEC® SD 308 Polyol. |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Formulation     | Ref             | Ref             | Low water       | Low water       | Units           |
| VORATEC® SD 308 Polyol (excl. Water) | 97.7            | 97.7            | 98.1            | 98.1            | pbw             |
| Additional blow/gel catalyst | 0               | 0               | 0.9             | 0.9             | pbw             |
| Water           | 2.3             | 2.3             | 1.0             | 1.0             | pbw             |
| Cyclo-pentane   | 14.5            | 14.5            | 16.0            | 16.0            | pbw             |
| VORATEC® SD 100 Isocyanate | 144             | 144             | 130             | 130             | pbw             |
| Free Rise       |                 |                 |                 |                 |                 |
| Gel-time        | 40              | 40              | 46              | 46              | s               |
| Free Rise Density| 22.2            | 22.2            | 26.4            | 26.4            | kg/m³           |
| Brett           |                 |                 |                 |                 |                 |
| In-mold pressure| 1.0             | 0.8             | 1.0             | 0.8             | bar             |
| Minimum Fill Density | 30.6            | 22.5            | 40.1            | 30.4            | kg/m³           |
| Molded Density  | 35.3            | 32.6            | 44.1            | 35.7            | kg/m³           |
| Overpack        | 115.4           | 144.9           | 110.0           | 117.4           | %               |
| Compressive Strength, avg. of 5 | 133             | 120             | 182             | 122             | kPa             |
| k-factor (10°C), Bottom | 19.9            | 19.9            | 19.5            | 19.4            | mW/mK           |
| Jumbo           |                 |                 |                 |                 |                 |
| Post Expansion, 7 minutes | 3.0             | 3.1             | 6.4             | 1.4             | mm              |
| Post Expansion, 6 minutes | 3.9             | 3.8             | 6.7             | 1.8             | mm              |
| Post Expansion, 5 minutes | 5.5             | 5.2             |                 |                 | mm              |

RESULTS AND DISCUSSION

Formulation Development

As discussed previously, applying a reduced in-mold pressure shows benefits in terms of the polyurethane foam system flow properties, due to the lower ambient back pressure. This is highlighted in detail in Table-2, where a standard k-system, developed for the conventional foaming process, is used in ambient as well as in a reduced pressure environment. The gain in flow measured as the minimum fill density in a Brett mold is obvious. In a further experiment the same system is modified for the use in a reduced pressure environment. The water content was reduced to lower the blowing capacity of the foam and to improve the k-factor by altering the cell-gas composition. As water also contributes to the overall foam reactivity, the catalyst level was increased to maintain the reaction speed. It is clear that the reduced water level compromises the flow at ambient conditions, increasing the minimum fill density from 30.6 to 40.1 kg/m³. The minimum
fill density is recovered by reducing the in-mold pressure from ambient to 0.8 bar. Compared to the reference foam system the system modification resulted in a k-factor improvement due to the changed cell-gas composition as well as an improvement in demold performance due to a lower foam pressure peak as discussed earlier. All this was achieved maintaining the flow, assisted by the lower in-mold pressure, resulting in similar applied densities for both foam systems.

A second way of improving the foam properties, and in particular the k-factor performance, is by increasing the speed of reaction. This can be done simply by adding catalysts to an existing foam system until the desired reaction times are obtained, and/or by modifying the base polyol composition of the system as well to obtain the maximum benefit in performance. The results are depicted in Table 3. For reference both a standard k-system and a conventional low k system have been used to position the new technology. The majority of the domestic appliance market using hydrocarbons as blowing agents has moved to this type of systems, which are typically showing an improvement in k-factor in the range of 3-6% [2, 3]. The low k system has been used as a basis to further speed up the reactivity to a gel-time of about 20 seconds by adding catalyst, whilst reducing the water level to accommodate the use in a reduced pressure environment. This experimental system-A with increased catalyst level resulted in a k-factor improvement of about 2-3% compared to the reference low k system. However, demold performance was not affected. The real step up in improvement could only be made when the back-bone of the polyol system was drastically changed. With a specific tailored system developed for the process, named experimental system-B, which is consisting of different type of base polyol reactor grades, enabling a reduction in catalyst level compared to experimental system A, a more significant performance improvement was obtained. The k-factor performance was improved of 6-7 percent compared to the conventional low k system and of 9-10 percent compared to the standard k foam system. At the same time, demold performance, measured as post-expansion after demolding jumbo mould foams was significantly improved. Similar post expansions were obtained with 2 minutes less curing time compared to the experimental system A with increased catalyst level. The flow ability of the high reactive, experimental foam systems was obviously compromised at ambient conditions. The minimum fill density at ambient pressure was 35.9 and 36.6 kg/m³ for the experimental foam systems A and B respectively. Applying a reduced in-mold pressure brought the minimum fill density back to the values of the reference foam system to around 30 kg/m³. It is important to note here that the closed cell values are by no means compromised by applying a reduced in-mold pressure.

The results clearly indicate that the maximum benefit could be taken from this processing technology by totally changing the formulation concept and tailoring the recipes for the novel process-environment. This extensive technology development took the direction of defining new, specific base polyol reactor grades, which were included in the new systems for the Dow PASCAL™ foams technology, allowing maximization of foam performance improvements. The development finally led to the definition of the DSV 1103.01 Polyol, which is currently used in the PASCAL™ foam process. The recipe of the foam system and its performance in a laboratory environment is outlined in Table 4 and Figure 4, against a standard k and low k foam system currently marketed in Europe and Asia/Pacific. As can be seen from the results, a clear improvement in
Table 4. Laboratory results of the PASCAL™ foam system compared to reference foam systems.

<table>
<thead>
<tr>
<th>Formulation</th>
<th>k-factor</th>
<th>low-k</th>
<th>PASCAL™</th>
<th>Foam</th>
</tr>
</thead>
<tbody>
<tr>
<td>DSD 300.02 Polyol</td>
<td>100</td>
<td>0</td>
<td>0</td>
<td>0.16</td>
</tr>
<tr>
<td>DSD 426.01 Polyol</td>
<td>0</td>
<td>100</td>
<td>0</td>
<td>0.04</td>
</tr>
<tr>
<td>DVS 1103.01 Polyol</td>
<td>0</td>
<td>0</td>
<td>106</td>
<td>0.08</td>
</tr>
<tr>
<td>Formulation Std-k</td>
<td>144</td>
<td>78</td>
<td>150</td>
<td>0.05</td>
</tr>
<tr>
<td>Formulation Low-k</td>
<td>145</td>
<td>148</td>
<td>118</td>
<td>0.05</td>
</tr>
<tr>
<td>Flex Box</td>
<td>45</td>
<td>24</td>
<td>19</td>
<td></td>
</tr>
<tr>
<td>Flex Box Density</td>
<td>23.1</td>
<td>23.9</td>
<td>23.5</td>
<td>0.49</td>
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**Result**

<table>
<thead>
<tr>
<th>Property</th>
<th>DSD 300.02</th>
<th>DSD 426.01</th>
<th>DSV 1103.01</th>
<th>Foam</th>
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<tr>
<td>Post-expansion (mm)</td>
<td>10.6</td>
<td>17.0</td>
<td>11.8</td>
<td>15</td>
</tr>
<tr>
<td>Demold time (min.)</td>
<td>18.6</td>
<td>20.1</td>
<td>19.1</td>
<td>18.2</td>
</tr>
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</table>
| Demold-performance of 36 kg/m3 density foams

**Figure 4.** Demold performance of the PASCAL™ foam system using the Jumbo-mold.

k-factor can be obtained using the Dow PASCAL™ foam technology, such as 9-10% compared to the standard k foam system DSD 300.02 Polyol and 7-8% against the low k foam system. The k-factor improvement can be explained partially by the different cell gas composition of the PASCAL™ foam system, but the largest improvement comes from the average cell size reduction. This is highlighted in Figure-5, where a scanning electron microscopy (SEM) image of the PASCAL™ foam made with the DSV 1103.01 Polyol is compared with the foam made with the low k system DSD 426.01 Polyol. Average cell size was reduced from 230 to approximately 140 microns. This can be achieved whilst maintaining other critical properties like applied density and mechanical strength. In addition the closed cell values of the PASCAL™ foams are at least as good as for the reference foams. Figure-4 shows the post-expansion/demold performance of the DSV 1103.01 PASCAL™ foam system. An improvement in demold-time of around 50% compared to the DSD 300.02 Polyol and about 25% compared to the DSD 426.01 Polyol is achievable. In the actual application, this of course heavily depends on model-design like dimensions, geometry and wall thickness of the appliance. The use of the reduced in-mold pressure is key in order to obtain the flow ability of the system, and is helping the demold performance due to the lower internal pressure peak.
Figure 5. SEM images of foams made in the Dow laboratories using a low k foam-system and a PASCAL™ foam-system applying a magnification-level of 200.

<table>
<thead>
<tr>
<th>Cabinet-type</th>
<th>Combi, bottom freezer</th>
<th>Side by Side</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyol type</td>
<td>DSD 300.02</td>
<td>PASCAL™</td>
</tr>
<tr>
<td>Gel-time (s)</td>
<td>43</td>
<td>16</td>
</tr>
<tr>
<td>Molded density (kg/m³)</td>
<td>36</td>
<td>36</td>
</tr>
<tr>
<td>Core density (kg/m³), average</td>
<td>31.0</td>
<td>32.5</td>
</tr>
<tr>
<td>k-factor (10⁻⁹ C), average</td>
<td>20.2</td>
<td>18.5</td>
</tr>
<tr>
<td>RHL-refrigerator (W/K)</td>
<td>0.91</td>
<td>0.86</td>
</tr>
<tr>
<td>RHL-freezer (W/K)</td>
<td>0.47</td>
<td>0.44</td>
</tr>
<tr>
<td>Average RHL-improvement (%)</td>
<td>6.0</td>
<td>3.9</td>
</tr>
</tbody>
</table>

Industrial Validation at Cannon

Several industrial validation trials with real time cabinets have been carried out at Cannon with different OEM’s. During each validation a reference system was run as well to be able to benchmark the performance of the PASCAL™ foam systems under the same test conditions. A variety of cabinets, such as different type of 2 door combi-models, side by side models and even single door coolers, have been tested using the pilot facilities at Cannon. The pressure level which was used while processing the PASCAL™ foam system was optimized for each different type of appliance.

Overall, the test-results from the cabinet trials were mostly confirming the findings from the laboratory. The cabinets could be processed with at least the same applied density as the reference foam system. In some cases, even a density reduction could be achieved. The flow of the PASCAL™ foam system was very good which resulted in a density distribution of the material very similar to that of the reference foam systems. In addition, no defects were observed due to the flow around obstacles like cables and ducts in the cavities. Overall, the void performance or number of defects in the foam was equal or better when applying the PASCAL™ foam system. Other properties like mechanical strength, adhesion and closed cell content did not show any deterioration compared to the commercial reference systems.

The thermal conductivity results and energy performance, measured as RHL, are highlighted in Table-5 for two specific different cabinet types. On average, in one case the k-factor was improved by close to 9% compared to a standard k foam system (DSD 300.02 Polyol) and close to 6.5% compared to a low k system (DSD 426.01 Polyol) in another case. This
translated into an improvement in RHL of 6.0% and 3.9% respectively. It is known from the past that, depending on the type of appliance, a low k system can bring an improvement of about 2.5-3.5% in RHL-performance [2, 3]. This results in a reverse heat leakage performance improvement between 6 and 7% when using a PASCAL™ foam system compared to a standard k foam system, as depicted in Figure-6.

**INDUSTRIAL IMPLEMENTATION OF PASCAL™ FOAM TECHNOLOGY**

Qingdao Haier Co. Ltd (Haier), as one of the world’s leading manufacturer of household refrigerators and major appliances, is aware of the challenges in designing new, sophisticated refrigerators and freezers because of the difficulty to apply polyurethane into the complex shaped cavities. For example it is known that the energy efficiency of cold appliances can be improved when using a low k polyurethane foam system. However, such formulations typically lead to higher overall production costs. Due to reduced flow properties the applied density is increased, and in some cases longer curing times are needed during the production of cold appliances.

To address these issues Haier was looking into new technology concepts and as such they were the first appliance manufacturer accepting to validate the PASCAL™ technology in the Cannon pilot line with one of their own refrigerator models, to confirm the advantages of the PASCAL™ foam technology.

Upon a positive industrial validation confirming the successful performance of the technology in a commercial cabinet foaming process, Haier decided to implement this novel technology in a new commercial production plant.

Dow unveiled PASCAL™ foam technology in conjunction with Haier at the World Appliance Expo in Shanghai in March 2011.

**CONCLUSIONS**

Dow PASCAL™ foam technology is a novel PU breakthrough foaming technology for the manufacture of domestic refrigerators and freezers which has been industrially validated and implemented at one of the world’s leading household manufacturers of refrigerators and freezers, namely Qingdao Haier Co. Ltd.

This technology has been developed as part of a close partnership with Cannon. It is based on the use of a controlled, reduced in-mold pressure in the fixture where the cold appliance is injected with the newly developed Dow PASCAL™ PU system which offers the following performance benefits:
In terms of the refrigerator’s energy efficiency: The lowest k-factor values for cyclo-pentane blown foams in the market have been confirmed. k factor values as low as 18.5 mW/m.K on average (measured at 10°C average plate temperature) were obtained from refrigerators, the foam has been shown to exhibit a very fine cellular structure. This resulted in a very significant reduction in the energy efficiency derived from the reverse heat leakage measurements.

The refrigerator’s plant productivity: The fastest refrigerator’s demolding times, with improvement levels of 25 to 50% compared to the best conventional foam-systems, were obtained by the combination of a fast curing system coupled with the PASCAL™ process application.

The best foam flow irrespective of the cabinet geometry, resulting in a homogeneous density distribution with very few foam defects.

The overall process cost: The process allows for very good foam flow properties, even with appliances with complex geometries, resulting in optimized raw material consumption.

The new series of Dow PASCAL™ PU systems designed and tailored specifically for the PASCAL™ foam process include modified polyurethane chemistry, based on novel base polyl reactor grades. This has led to high-performing rigid polyurethane foams offering an unique advanced combination of excellent insulation performance with a long term sustainable solution addressing government standards whilst allowing the appliance manufacturer to increase the output-rate due to the significantly improved demolding times addressing simultaneously the major challenges of the appliance industry today.

ACKNOWLEDGEMENTS

The authors would like to thank Greg Wagner and Lorenzo Lusvardi for assisting in the machine-trials at Dow, Jorge Jimenez and Giuseppe Lista for their role in the development of new base polyl grades, Ricky Ye and Jinglu Chen for the SEM images and their contributions to implement the technology at Haier, Bruno Barbet, Gu Wei and Michael Jin for their commercial support and Cannon for their support in carrying out the cabinet validation trials in their labs.

REFERENCES

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Vanni Parenti joined the commercial refrigeration group of DOW Italy in Correggio in 1989. His work concentrated on the development of CFC free rigid polyurethane foam for large appliance and water heaters applications. Vanni holds a degree in Physical Chemistry from the University of Modena (1986). In 1994 he joined the appliance TS&D group at the Polyurethane International Development Center located at Meyrin (Geneva) Switzerland. Relocated to the Polyurethane System R&D in Correggio, he is currently DOW Global Technology Leader for Domestic Appliance Refrigeration.

Hans Kramer

Hans Kramer joined Dow Benelux B.V. in Terneuzen in 1989, after receiving his degree in chemical engineering from the Technical University of Eindhoven in 1988. Before his relocation in 2005 to Switzerland Hans was part of the Technical Service & Development department working on rigid PU foam for construction applications. His current role is Research Scientist in the Application Technology Development Group in Horgen (CH), covering Domestic Appliance Foams in Europe, and as such he is one of the project leaders for the PASCAL™ foam technology development.