Polyurethanes

Blowing agent options for insulation foam after HCFC phase out
In 1987, the Montreal Protocol was signed to protect the ozone layer by phasing out the production of a number of substances responsible for ozone depletion such as CFCs (chlorofluorocarbons) and HCFCs (hydrochlorofluorocarbons). CFCs have been phased out since 1996 in industrialised countries, and recently in developing countries.

Because of their lower ODP (Ozone Depletion Potential), HCFCs have been an established intermediate alternative to CFCs. In regions such as the European Union or the United States of America, the use of HCFC141b in foam applications has been banned for almost a decade. In most developing (article 5) countries and in some industrialised (non article 5) countries, such as the Russian Federation, HCFC141b has been the preferred blowing agent in the last decade. However, in 2007 at the 19th meeting of the Montreal protocol, nations signed up to accelerate the phase-out of HCFCs (see Figure 1). For developing countries, as of 1st January 2013, the consumption of HCFC141b will be capped and 2 years later, as of 1st January 2015, it will be gradually reduced until 2030.
Blowing agent evolution

The transition process from HCFC141b to alternative blowing agents has been taking place in most industrialised countries in the beginning of the previous decade. As can be seen in Figure 2, various blowing agent choices are available, depending on technical, regulatory and economical drivers. In Europe, an estimated 85 to 90% of all insulation foams are currently blown with pentane technology, which has an excellent track record for both foam performance and safe handling.

Examining alternatives for HCFC141b, it is important to consider the global warming potential (GWP) of replacement blowing agents. Since the Kyoto Protocol identified HFCs as industrial gases requiring emissions control because of their high GWP, several producers have started the development of HFOs (hydrofluoroolefins). HFOs have a very low GWP but availability at an industrial scale is expected to take a few years.
Alternatives to HCFC141b

The table shows the properties of alternative blowing agents relative to HCFC141b. There is no “drop-in” replacement for HCFC141b that combines ease of use and processing alongside low operating costs. Huntsman has acquired a broad technical expertise with all blowing agent alternatives, both by the application development teams located in Ternate (Italy) and by regional teams implementing dedicated solutions at customers.

<table>
<thead>
<tr>
<th>Properties of other blowing agents relative to HCFC141b</th>
<th>Pentane</th>
<th>HFC245fa HFC365mfc/227ea</th>
<th>Water</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blowing agent price</td>
<td>Lower</td>
<td>Much higher</td>
<td>None</td>
</tr>
<tr>
<td>Foam thermal conductivity</td>
<td>5-10% higher</td>
<td>5-10% higher</td>
<td>±20% higher</td>
</tr>
<tr>
<td>Foam density</td>
<td>5% lower density feasible</td>
<td>Similar</td>
<td>5-10% higher</td>
</tr>
<tr>
<td>Machine adjustments</td>
<td>Explosion proof equipment needed</td>
<td>Almost none</td>
<td>Almost none</td>
</tr>
<tr>
<td>GWP</td>
<td>Low Long term solution</td>
<td>High</td>
<td>Low Long term solution</td>
</tr>
<tr>
<td>Foam processing</td>
<td>Limited solubility in polyols</td>
<td>Comparable</td>
<td>Worse surface and adhesion</td>
</tr>
</tbody>
</table>

**PENTANE** is a cheap blowing agent, which produces low density foams with low thermal conductivity and good properties. However, the investment to handle a flammable blowing agent is not always justifiable, especially for small foam producers. In most cases, pentane is added to the polyol blend at the customer’s premises to avoid the transportation of a flammable polyol blend. In continuous operations (lamination), pentane is added in line, just before the mixing head. In discontinuous operations, pentane is pre-blended to the polyol blend with suitable equipment.

**WATER** is obviously a cheap blowing agent but has limitations for both foam processing and final foam properties. Foam density is substantially higher and good adhesion and foam surface quality are more difficult to achieve. Waterblown foams also have a higher thermal conductivity. Waterblown foams, which are not protected by diffusion tight facings, are subject to a gradual increase of thermal conductivity over time, much more than is the case for foams produced using a physical blowing agent.

**HFC365mfc/227ea** and **HFC245fa** can be implemented easily as replacements of HCFC141b without major changes in foam processing. In view of the high cost of HFCs, formulations have been finetuned towards an optimum cost / performance ratio. HFCs are typically added by the polyol blend supplier and transported to the customer as a non-flammable polyol blend. The pressure build-up of HFC containing polyol blends is normally limited, but appropriate packaging of the polyol blend needs to be chosen as a function of HFC content, HFC compatibility with the polyol blend and storage conditions.

**METHYLFORMATE** and **DIMETHOXYMETHANE** are potential blowing agents for rigid foam, but current industrial experience is limited in the European market. These blowing agents can be interesting options in certain cases, particularly in combination with one of the aforementioned options.
Blowing agent choice per application

In contrast to HCFC141b, where one blowing agent was chosen for all rigid foam applications, different blowing agent choices will be available after the HCFC phase out. Pentane is generally preferred when the foam consumption is high (e.g. in board or panel lamination). In figure 3, the blowing agent choice in industrialised countries is schematically given.

The three corners of the triangle represent a situation where a market segment has been entirely converted to pentane, HFC or to a fully water blown solution. Positions within the triangle indicate the relative amount of producers within a segment, that have chosen any of the three blowing agent options.

Physical properties of blowing agents

The physical properties of blowing agents are given in the table. It is interesting to note the differences between the three pentane isomers. There are significant differences in boiling point, gas thermal conductivity and polyol solubility, which leads to very different foam properties and processing characteristics. Cyclo/iso pentane mixtures tend to produce the lowest thermal conductivity foams and are preferred in applications such as refrigerators. Cyclopentane is, in certain cases, preferred when local storage regulations are less stringent than for other pentanes.
Huntsman Polyurethanes warrants only that its products meet the specifications agreed with the buyer. Typical properties, where stated, are to be considered as representative of current production and should not be treated as specifications.

While all the information and recommendations in this publication are to the best of our knowledge, information and belief accurate at the date of publication, NO GUARANTY, WARRANTY OR REPRESENTATION IS MADE, INTENDED OR IMPLIED AS TO THE CORRECTNESS OR SUFFICIENCY OF ANY INFORMATION OR RECOMMENDATION OR AS TO THE MERCHANTABILITY, SUITABILITY OR FITNESS OF ANY PRODUCTS FOR ANY PARTICULAR USE OR PURPOSE.

IN ALL CASES, IT IS THE RESPONSIBILITY OF THE USER TO DETERMINE THE APPLICABILITY OF SUCH INFORMATION AND RECOMMENDATIONS AND THE SUITABILITY OF ANY PRODUCT FOR ITS OWN PARTICULAR PURPOSE. NOTHING IN THIS PUBLICATION IS TO BE CONSTRUED AS RECOMMENDING THE INFRINGEMENT OF ANY PATENT OR OTHER INTELLECTUAL PROPERTY RIGHT AND NO LIABILITY ARISING FROM ANY SUCH INFRINGEMENT IS ASSUMED. NOTHING IN THIS PUBLICATION IS TO BE VIEWED AS A LICENCE UNDER INTELLECTUAL PROPERTY RIGHT.

Products may be toxic and require special precautions in handling. The user should obtain Safety Data Sheets from Huntsman Polyurethanes containing detailed information on toxicity, together with proper shipping, handling and storage procedures, and should comply with all applicable safety and environmental standards.

Hazards, toxicity and behaviour of the products may differ when used with other materials and are dependent on the manufacturing circumstances or other processes. Such hazards, toxicity and behaviour should be determined by the user and made known to handlers, processors and end users.

Huntsman Polyurethanes is an international business unit of Huntsman International LLC. Huntsman Polyurethanes trades through Huntsman affiliated companies in different countries such as Huntsman International LLC in the USA and Huntsman Holland BV in Western Europe.

Except where explicitly agreed otherwise, the sale of products referred to in this publication is subject to the general terms and conditions of sale of Huntsman International LLC or its affiliated companies.

Copyright © 2011 Huntsman Corporation or an affiliate thereof. All right reserved.

Editor: Kristof Dedecker