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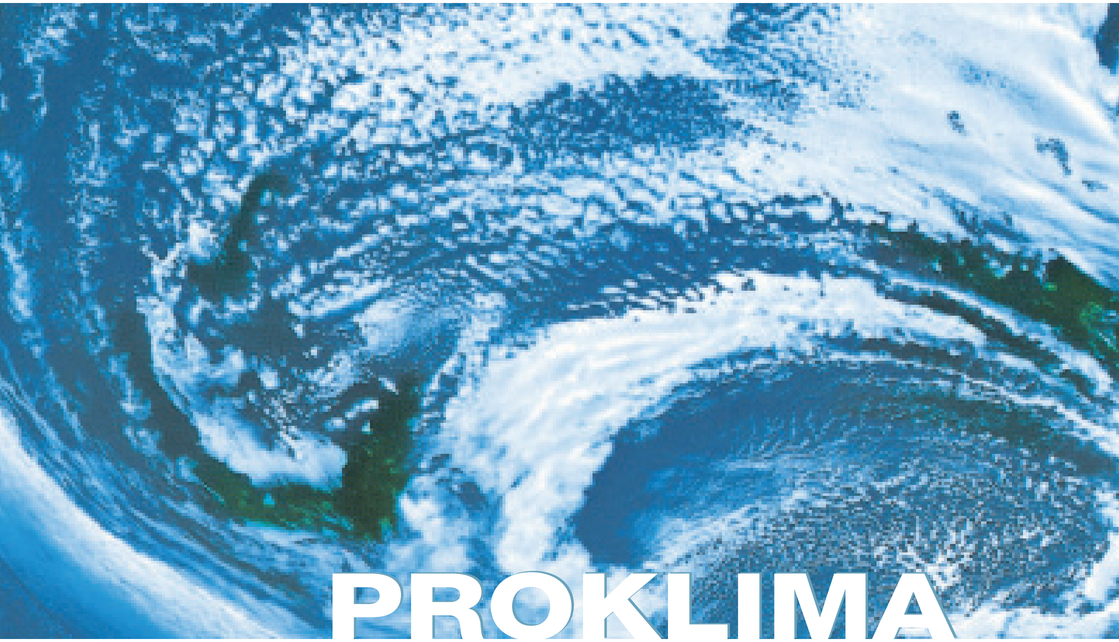

Natural Foam Blowing Agents

Sustainable Ozone- and Climate-Friendly Alternatives to HCFCs

giz Deutsche Gesellschaft für Internationale Zusammenarbeit (GIZ) GmbH

On behalf of

BMZ Federal Ministry for Economic Cooperation and Development

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PROKLIMA has been providing technical and financial support for developing countries since 1996 to implement the provisions of the Montreal Protocol on Substances that Deplete the Ozone Layer.

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Preface

Introduction

In the late 1970s and early 1980s, when it was discovered that chlorofluorocarbons (CFCs, used, amongst other things, as blowing agents in the manufacture of foams) would seriously destroy the ozone layer, the polyurethane foam industry underwent a radical shake-up. The thereupon 1987 concluded Montreal Protocol on Substances that Deplete the Ozone Layer regulated the phase-out of these CFCs and other ozone-depleting substances (ODS) in the following years and urged the foam industry to develop alternative technologies.

The state of the foam sector today has been significantly influenced by the provisions of the Montreal Protocol. At present, CFCs have been largely phased out as blowing agents. A main replacement option in the foam sector in developing countries were hydrochlorofluorocarbons (HCFCs), another fluorinated gas with significantly lower ozone depletion potential (ODP) than CFCs, but very high global warming potential (GWP). HCFCs are still used in integral skin foams and insulation foams, mainly in developing countries.

Global foam production is constantly growing as demand for insulation foams for buildings and appliances rises. Proper insulation of buildings is one of the most effective ways to reduce CO_2 emissions and is considered an important means to achieving more energy-efficient design for commercial and domestic buildings in the future. As decided by the 19th Meeting of the Parties to the Montreal Protocol in 2007, HCFCs will be subject to an accelerated phase-out in developing countries, with production and consumption frozen in 2013 to 2009/10 levels and subsequently phased out step by step by 2030. There are two major replacement options for HCFCs in foam manufacturing: hydrofluorocarbons (HFCs), a group of fluorinated greenhouse gases with zero ODP, but high GWP, controlled under the Kyoto Protocol, and a group of natural substances, known as natural blowing agents such as CO_2 and hydrocarbons.

The HCFC Adjustment Decision, taken by the 19th Meeting of the Parties to the Montreal Protocol in 2007, encourages Parties to promote the choice of alternatives to HCFCs that minimise environmental impacts, in particular impacts on climate, and

meet other health, safety and economic considerations. Natural substances clearly meet these requirements, since they have zero ODP and zero or negligible GWP.
For many foam applications, HFC-free technologies have already been successfully implemented and are now widely recognised as suitable, cost-efficient blowing agents in industrialised and many developing countries. Hydrocarbons are now the preferred blowing agent in the manufacturing of refrigeration appliances in many regions and are entering other applications. Pentane, a hydrocarbon, offers long-term environmental benefits (no ODP and very low GWP) at comparably low costs; it has good ageing characteristics and thermal insulation properties and is readily available in most regions. Safety risks associated with pentane, such as flammability, have been successfully controlled by implementing safety procedures and installing sound safety systems within companies.
Nevertheless, the upcoming HCFC phase-out poses a big challenge to manufacturers and end-users of HCFCs. Natural blowing agents are the only available ozone- and climate-friendly alternatives that provide long-term energy efficiency and cost benefits and should therefore gain preference over HFCs when designing HCFC phase-out plans in order to avoid a further costly transition to a different substance in the future. As a potent greenhouse gas, HFCs will most probably be subject to clear emission reduction targets under a new climate change regime and can no longer be considered as a long-term solution.

Purpose of the book

This volume is a collection of articles by experts from academia and governmental institutions, along with representatives from manufacturers, suppliers and end-users of HCFCs in the foam sector. It attempts to provide guidance to those involved in implementing the HCFC phase-out under the Montreal Protocol and all other kinds of climate protection projects in developing countries: policy stakeholders as well as manufacturers and end-users of HCFCs in the foam sector from both developed and developing countries.
Various issues relevant to the introduction of natural blowing agents will be covered: legislative and policy-related aspects, general properties, assets and drawbacks of natural blowing agents; different applications in the manufacturing of foams; innovative technology solutions, and case studies from Article-5 countries on how the technology conversion towards natural substances has successfully been implemented.
The first part of the book covers the policy-related aspects of technology transition towards ozone- and climate-friendly blowing agents. What impact do legislative changes have on the development and adaptation of alternative technologies?
The second part deals with the application of natural blowing agents in rigid and XPS foam, examines the conditions for conversion, and highlights special technologies.

The third part comprises case studies from selected developing countries. The contributions focus on typical challenges that occur when converting production plants to use natural substances and provide solutions illustrating how these hurdles may be overcome in practice.
We hope to provide useful information and stimulate project ideas for conversion to natural blowing agents.

I. Policy-Related Aspects of Technology Transition

Overview: Application of Blowing Agents in the Production of Foams

DR CORNELIA ELSNER, Federal Environment Agency, Germany

Introduction

This article focuses on the use of blowing agents in the production of various types of foam: rigid XPS foam, rigid PUR foams (including the following applications: insulation foam for appliances, flexible-faced laminates, sandwich panels and composites, rigid slabstock, in-situ PUR foam and pipe insulation) and flexible PUR foams. Natural blowing agents such as pentane or CO_2 can be used in all types of foam production and the technology has been successfully used by several large manufacturers for many years to produce high-quality products.

Basic terms and definitions

Thermal insulating materials for structural engineering can be subdivided into inorganic insulating materials (e.g. mineral wool and foam glass) and organic insulating materials (e.g. cellulose fibres, flax and hemp). Organic plastic foams are particularly relevant.

German standard DIN 7726 defines ‘foams’ as a mass made up of open or closed cells whose raw density is lower than the raw density of its matrix (DIN, 1982). The matrix of the foam may consist of organic polymers (plastic foams) or inorganic materials (foamed concrete, foam glass). The following article discusses plastic foams made of organic polymers, which can be classified into rigid foams, flexible foams and integral skin foams.

The technically predominant base polymers for the production of rigid foams are polystyrenes, polyurethanes and polyisocyanurates. In addition, polyolefins and formaldehyde resins also play a certain role in rigid foam production. Rigid foams are characterised by excellent insulating properties, moisture resistance and mechanical strength. Flexible foams show a relatively low resistance to deformation when exposed to pressure. The base polymer most commonly used to produce flexible foams is polyurethane.

German standard DIN 7726 defines integral skin foams as structural foams that are chemically homogeneous, but whose density continuously decreases from the outside to the inside. They are characterised by a soft or porous core and an vitually tough outer skin. Again, the most commonly used base polymer is polyurethane.
There are two ways to achieve a typical foam structure:

- By using a ‘chemical’ blowing agent that directly forms during the polymerisation process. An example of this is the foaming process for polyurethane, where water or carboxylic acids react during the polyaddition process with isocyanates forming CO_2 that has a blowing and foaming effect.
- By adding a ‘physical’ blowing agent which evaporates during the polymerisation process from the liquid solution or decomposes at a certain temperature to form gas (CO_2, N_2). Suitable physical blowing agents include volatile organic compounds (VOCs) such as pentane, but also CFCs, HCFCs or HFCs.

Using a physical blowing agent offers a number of advantages:

- No additional components enter the foam matrix.
- The evaporating blowing agent cools down the exothermal polyaddition reactions during polyurethane foaming.
- Certain blowing agents can be used as cellular gas to improve the thermal insulating effect of the foam.

Owing to the above-mentioned advantages of physical blowing agents, they are often the preferred option in many applications. The following discussion will therefore focus on the use of physical blowing agents.

Overview of blowing agent use

A number of different blowing agents are used worldwide. Forecasts up to 2015 in the IPCC/TEAP Special Report on Ozone and Climate (IPCC/TEAP, 2005) predict that the demand will continue to grow, due mainly to stricter insulation requirements for houses. Figure 1 shows the trend, ranked by blowing agent type (UNEP, 2007: 9):

Figure 1: Blowing agent use in rigid foams

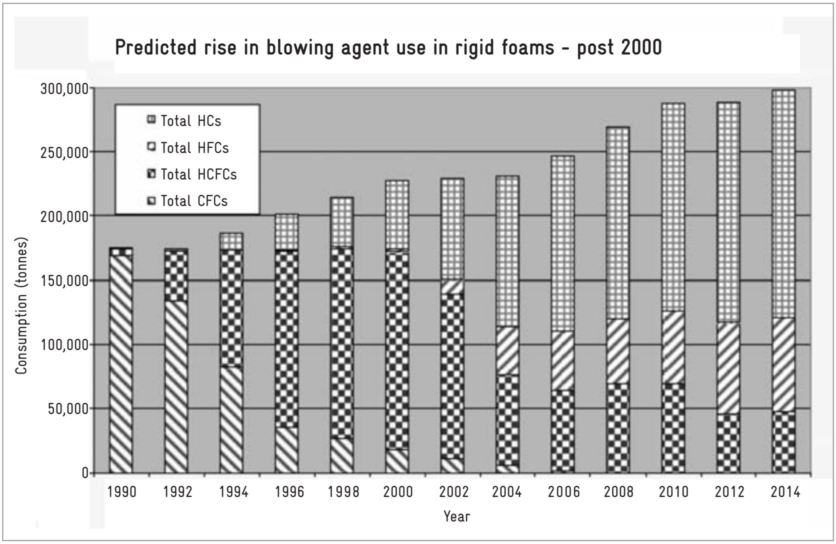
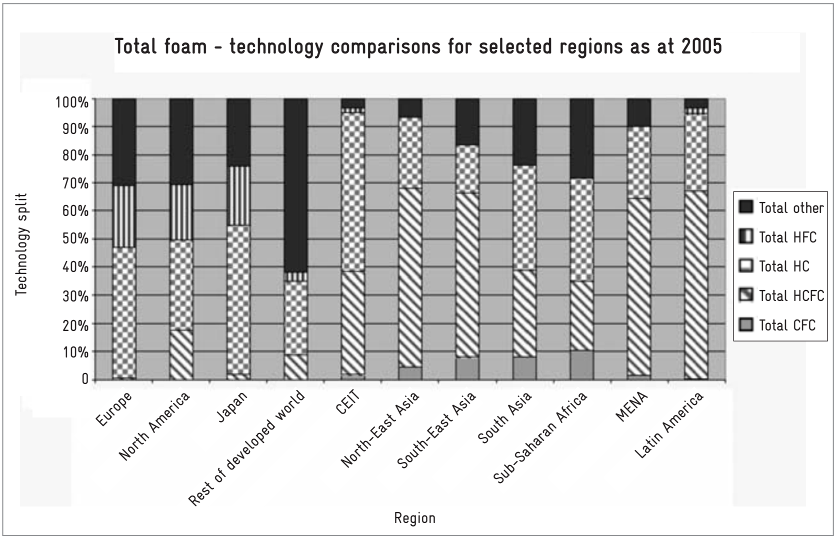


Figure 2 shows regional differences in the use of different blowing agents up to 2005 and thus makes it possible to draw a conclusion about CFC/HCFC phase-out and regional trends in the selection of alternatives (UNEP, 2007: 10).

Figure 2: Regional comparison of different blowing agents



The various types of foam are discussed in more detail below.

Rigid XPS foam

Extruded polystyrene (XPS), also known as extruded foam for short, is mainly used in structural engineering. Due to its closed-cell structure, rigid XPS foam does not absorb water even when brought into direct contact with it. It is resistant to rotting, highly pressure-resistant, but not UV-proof. The maximum temperature at which it can be applied is about 75°C (Anhörung, 2003).
Rigid XPS foam is produced in a continuous extrusion process: polystyrene pellets are fed into an extruder without a blowing agent, where they are melted. A blowing agent is then injected and the mixture is continuously forced through a wide-slot nozzle producing a homogeneous and closed-cell foam. The XPS panels produced vary in thickness from 20mm to 200mm.
Until about 1989/1990, CFC-12 was used in Germany for blowing rigid XPS foam (UBA, 1989). HCFC-142b or a blend of HCFC-142b and HCFC-22 were used thereafter on a transitional basis (Schwarz and Leisewitz, 1999). Once HCFCs were also prohibited, these CFC substitutes could no longer be used as blowing agents. In Germany, XPS foam is now produced predominantly without any fluorinated blowing agent.
In **structural engineering**, rigid XPS foam is often used as exterior insulation in areas that are exposed to extreme conditions, near or below subgrade, for instance beneath the base plate of a building or to insulate the exterior wall of the basement (known as perimeter insulation). Other application areas include reversed roofs and non-ventilated flat roofs that consist of one membrane only or flat roofs that are slightly inclined. As opposed to conventional warm roof constructions, the thermal insulation of a reversed roof is located above the weatherproof membrane, not below. A special type of application is thermal bridge insulation, which is becoming increasingly important. Today, the German structural engineering market mainly offers XPS products that are foamed with CO_2 or a combination of CO_2 and organic blowing agents (approximately 2 to 3% ethanol). As opposed to rigid PUR foams, the CO_2 used for XPS foaming is not the result of a chemical reaction, but needs to be added from the outside like other blowing agents. CO_2 is relatively difficult to handle in an extruder as a blowing agent. It requires a technology that differs from the former HCFC-based technology because it uses a different pressure in the manufacturing process. Thinner panels with a thickness of 60 or 70mm are produced in smaller machines that require little effort to convert. The conversion of machines designed to produce panels that are 80mm thick or more is technologically challenging. XPS manufacturers estimate that the con-

version costs of an existing machine amount to 30 to 50% of the cost of installing a new machine (Anhörung, 2003). It is possible to produce the whole range of products and achieve the same quality by using a combination of CO_2 with 2 to 3% organic blowing agent (ethanol). In addition to HFC-free XPS products, a number of manufacturers offer XPS insulation that is foamed with HFC-134a or a mix of CO_2 and HFC-152a (BASF, 2008; Dow, 2008; Gefinex, 2008; URSA, 2008). Currently, the use of insulating panels foamed with HFCs in structural engineering is an option in only a few cases, where panels of a given thickness are required to exhibit a particularly low thermal conductivity coefficient.
In addition to the conventional insulating materials used in the building and construction industry, rigid XPS foams are also used for **special applications**. These special products account for less than 10% of the European XPS insulation market, but offer a multitude of applications. Statistical data on these special products (types of application, quantities used) were not available (Anhörung, 2003). They can be divided into the following categories:

- sandwich panels (with surface coverings made of steel, aluminium or wood),
- underlay for parquet and laminate flooring,
- pipe insulation.

Sandwich elements are often produced with HFC-containing blowing agents. Possible HFCs for this application are HFC-152a and HFC-134a, either as individual substances or as blends that may include CO_2 or organic blowing agents (ethanol) (Schwarz and Leisewitz, 1999; BIPRO, 2008).
Impact noise insulation materials and parquet underlay made of XPS are generally produced without HFCs today. XPS foam is blown with butane in most cases (BIPRO, 2008).
Insulation for refrigerant pipes is produced almost exclusively with HFC-134a as the blowing agent. XPS pipe insulation can be used in a temperature range between -180°C to +75°C. Rigid XPS foams are not suitable for insulation of long-distance heating systems as temperatures in this sector are above 75°C (BIPRO, 2008).

Rigid PUR foam

Rigid PUR insulating materials are closed-cell, rigid plastic foams made of polyurethane. They have excellent thermal insulation performance. German standard DIN EN 13165 (DIN, 2005) defines quality requirements for factory-made rigid PUR foam panels. In the building and construction industry, rigid PUR foam panels are mostly used to insulate flat roofs, saddle roofs, ceilings, floors (also in combination with floor heating systems) and walls. Another area of application is insulation for low-energy houses.

Rigid PUR foams are available in a variety of different forms:

- appliance insulation foam (i.e. technical insulation for refrigeration appliances or hot water storage tanks),
- flexible-faced laminates (rigid PUR foam composites with flexible surface skins made of aluminium, foil, paper or glass fleece),
- sandwich panels (predominantly with surface skins made of steel),
- rigid slabstock (continuous production of rigid PUR foam, cut into panels, or discontinuous production of rigid PUR foam, used in blocks for various technical applications including the building and construction industry),
- spray foams (e.g. foam that is poured or sprayed in place for roof insulation),
- pipe insulation (e.g. for long-distance heating systems).

Rigid PUR foam can be foamed with process-related CO_2. It does not contribute to the thermal insulation performance of the foam, since it generally diffuses very quickly out of the newly formed foam cells. Therefore, in applications that require a high thermal insulation performance, a 'physical' blowing agent that stays in the foam cells is used in addition to the process-related chemical blowing agent CO_2. In the past, CFC-11 was generally used as a physical blowing agent. Today, HCFC-141b or a HCFC-22/-142b blend is used as a substitute in some cases outside the EU. HFC-based blowing agents for rigid PUR foam are mainly HFC-245fa and HFC-365mfc as a blend with HFC-227ea to inhibit flammability (UNEP, 1998; UNEP, 2003; Schwarz, 2005).
The situation in Germany is different. Since 1 January 1995, the use of fully halogenated CFCs has been prohibited under the CFC/Halon Prohibition Ordinance (FCKW-Halon-Verbots-Verordnung, 1991). Since then, the blowing agent most commonly used in Germany in rigid PUR foam production is the halogen-free hydrocarbon pentane. In domestic appliances, cyclopentane is exclusively used as a blowing agent. In the continuous production of insulating panels with flexible coatings, pentane is used in more than 90% of all cases. Like HCFCs, pentane remains in the foam cells and therefore contributes to the thermal insulation performance. The conversion from HCFCs to pentane requires explosion-proof equipment and other technological changes. Manufacturers of rigid PUR foam argue that the conversion to pentane entails high investment costs. Thanks to the low price of the blowing agent, the high investments would, however, soon pay off, provided the throughput is high enough (Anhörung, 2003).
Since 1998, the production of sandwich panels is also undergoing a conversion process. In the past, HCFCs were predominantly used to blow rigid PUR foam for this application. Since 2000, about half of the foam is blown with pentane, the other half mainly with CO_2 combined with HFC-134a (Anhörung, 2003). The HFC-134a remains in the foam to enable lower foam density and, therefore, a lower weight. The specific thermal insulation performance of the foam rises.

In Europe, there are different national planning and building regulations, standards and approvals. When the European single market was introduced, efforts to harmonise these standards and approvals were intensified. The overall objective was the introduction of a CE labelling system for building materials and products.

The most important property of thermal insulating material is its thermal conductivity (thermal resistance). Thermal insulating materials are durable products. They are expected to last 25 to 50 years. Therefore, the thermal conductivity value must be a realistic long-term value that takes ageing factors into account. German/European Standard DIN EN 13165 (DIN, 2005) on rigid PUR foams defines methods for determining the thermal conductivity of insulating material and takes product ageing into account. The above-mentioned standard required thermal conductivity to be indicated in intervals of 5 mW/(m•K) and classed in thermal conductivity groups (referred to as WLG from the German 'Wärmeleitfähigkeitsgruppen'). Typical for rigid PUR foam insulation are WLG 025 or WLG 030. WLG 025 includes calculated thermal conductivity values λ(R) from 0.021 to 0.025 W/(m•K). WLG 030 covers calculated thermal conductivity values λ(R) from 0.026 to 0.030 W/(m•K). DIN EN 13164 (DIN, 2001) and 13165 (DIN, 2005) require the thermal conductivity value (λ value) to be indicated in intervals of 1 mW/(m•K). It is questionable whether the new classification system will be successful on the market or not. In Germany, manufacturers have not yet begun to use the new system. Thermal insulating material made of rigid PUR foam with λ-values of 0.025 W/(m•K) or 0.030 W/(m•K) is still on the market. The manufacturers represented on the German market who are also members of the German association that monitors the quality of rigid polyurethane foam products (UEGPU) have decided to carry on using the current system. A 'faked' competition for thermal conductivity values that would only differ by 0.001 W/(m•K) does not make any sense, since differences as small as that cannot be guaranteed given the long lifespan and the long-term ageing behaviour of the products. According to information provided by the manufacturer, the λ-value of the new blowing agent/gas HFC-365mfc is 10.6 mW/(m•K), i.e. it lies between the λ-value of HCFC-141b and the λ-value of cyclopentane. The same applies to HFC-245fa. A rigid PUR foam manufactured with these blowing agents would therefore have a calculated thermal conductivity λ of 22 mW/(m•K). According to the currently used classification system, all the rigid foams mentioned above would fall into the thermal conductivity group WLG 025. This means that the thermal conductivity value of the rigid foam does not by itself represent a criterion for choosing a blowing agent. The choice of blowing agent has different technical – and often economic – consequences depending on the different applications that use rigid PUR foams. The various applications will therefore be considered separately.

A) Appliance insulation foam

Appliance insulation foam is used to insulate refrigeration appliances, hot water storage tanks and similar products. The production of rigid PUR foam for domestic refrigeration appliances has been fully converted to cyclopentane. In Germany, water heaters are produced exclusively with rigid PUR foam blown by carbon dioxide (BIPRO, 2008).

B) Flexible-faced laminates

Flexible-faced laminates are used to produce insulating panels for building construction. They are mainly used in the housing sector, for example to insulate floors, saddle roofs or under floor heating systems. Until 2004, HCFC-141b was mainly used. Today, PUR insulating panels for building construction are predominantly foamed with N-pentane. In special applications (that are associated with high fire protection requirements either during production or during use and with particularly high thermal conductivity requirements), HCFCs were still used until the end of 2003. Now, HFC-365mfc and HFC-245fa as a blend with HFC-227ea are used in these applications. These special applications account for less than 5% of the total market in Germany (BIPRO, 2008).

C) Sandwich panels, composites

Sandwich panels are predominantly used for roofs and walls in industrial engineering and in the construction of refrigerated warehouses and cold stores. Their production may be continuous or discontinuous.

In the **continuous production** of PUR insulating panels with a surface covering made of metal, pentane is predominantly used as a blowing agent. HFCs are used only for products destined for export to other European countries that have particular fire protection requirements (UK, France). However, the better thermal insulation performance argument is not convincing. Compared to pentane, the HFCs in question (HFC-134a, HFC-245fa or blends that may contain, in addition to HFC-365mfc, HFC-227ea to minimise the flammability of the blend) do not offer a better thermal insulating effect. Only the use of pure HFC-365mfc could slightly improve thermal insulation values, but the downside is the flammability problem.

The **discontinuous production** of PUR insulating panels with a metal surface covering is a batch-wise production which is often carried out at small production sites (Anhörung, 2003).

Investment barriers, not technical barriers, hinder the use of pentane. Pentane can be used as a blowing agent in discontinuous panel production without any technical difficulties. When pentane is used in a discontinuous process, the entire production process must be fitted with an exhaust ventilation system, which in most cases is only worth the effort in the case of large production sites (BIPRO, 2008).

D) Rigid slabstock

In most cases, rigid slabstock foam is produced in a continuous production process. The final product is not the foam block itself, but a more complex-shaped component like a pipe shell that is cut out of the block. Rigid slabstock is also used for the production of panels that are more than 180 - 200mm thick (Anhörung, 2003). Economically, the production of slabstock is far less important than the production of flexible-faced laminates. It is also associated with higher emissions, because when the foam blocks are cut, many foam cells are destroyed and the blowing agent contained in the cells is released. The use of pentane for the production of slabstock is generally state-of-the-art. For high fire protection requirements, a blend of blowing agents that contains HFC-227ea is commercially available as a substitute for HCFC-141b. For applications that involve particularly high fire protection requirements, a possible option is offered by alternative products like foam glass.

E) In-situ PUR foam

In-situ polyurethane foam is covered by DIN standard 18159-1 (DIN, 1991). At European level, DIN EN 14315-1 is available as a draft (DIN, 2002).

In-situ polyurethane foams are sprayed or poured directly on site and are therefore exposed to many influences. When in-situ foams are applied on flat roofs, external walls or storage tanks, the ambient temperature and humidity may vary greatly. This has a considerable influence on the quality of the foam. An important application of in-situ foams in structural engineering is insulation and rehabilitation of flat roofs on existing buildings (also called spray foam roofing). In this application, blowing agents or blends of blowing agents containing HFCs are still being used in many cases, although attention is paid to ensure that they contain a high proportion of non-flammable components (Anhörung, 2003). However, a lifecycle assessment prepared for in-situ PUR foams showed no significant advantage of HFC-containing blowing agents (UBA, 2002).

F) Pipe insulation

Pentane is used as a blowing agent in insulation for large pipes (long-distance heating systems). Better thermal insulation performance can generally be achieved by increasing the thickness of the insulating layer.

G) Integral skin PUR foam

According to German standard DIN 7726 (DIN, 1982), integral skin foams are foams whose density continuously decreases from the outside to the inside. Integral skin foams are characterised by a soft core and an virtually tough outer skin. The production of integral skin PUR foams is based on a moulding technique known as RIM (reaction injection moulding). The reactive blend is mixed under high pressure. The liquid phase is then poured into cold moulds. When the foaming reaction has finished, the moulds are completely filled. In principle, the chemical reaction takes place in the mould itself. During the foaming process, a temperature difference builds up between the inside of the mould and the outside of the mould. Due to the temperature difference, the evaporating blowing agent expands differently across the mould. This creates differences in the density of the foam and leads to the typical structure of integral skin foam described above. By changing the conditions under which the reaction occurs, it is possible to modify the rigidity of the foam and to produce a wide range of products (rigid integral skin foams, semi-rigid integral skin foams, flexible integral skin foams). Advanced or specialised RIM technologies are RRIM (reinforced reaction injection moulding) and SRIM (structural reaction injection moulding). RRIM involves mixing liquid components with solids (e.g. glass beads or artificial mineral fibres). SRIM means that mats (e.g. fibre glass mats) are placed into the mould before the resin is poured. Together with the resin they form a composite product. The reinforcement included in the material structure improves the mechanical properties of the plastic part.

Integral skin foams are used in many different applications:
- furniture manufacture (as seat and shaping cushions),
- the automotive industry (as seat and shaping cushions; in armrests, headrests and footrests; as protective foam cushions; in gear knobs, dashboards etc.),
- shoes and sports articles (soles, cushioning elements, protective foam cushions),
- as foam inserts for suitcases and tool boxes,
- in electrical devices (in particular rigid integral skin foams),
- as shaped parts in many other applications.

Since the prohibition of CFCs, blowing agents both with and without HFCs are used for (rigid and semi-rigid) integral skin foams. In addition to process-related CO_2, cyclopentane and N-pentane are commonly used non-HFC blowing agents. Among HFC-containing blowing agents, mainly HFC-365mfc (possibly in combination with HFC-227ea) is used today. This applies both to German and other European manufacturers of integral skin foams (BIPRO, 2008). Technically, it is possible to produce integral skin foams in every requested quality using pentane or CO_2. The necessary technology is available (Anhörung, 2003).

Flexible PUR foam

Compared to rigid foams, flexible foams offer less resistance to deformation when exposed to pressure. The most common base polymer for flexible foams is polyurethane. Flexible foams have a very wide spectrum of applications: it ranges from cushions and mattresses, foam cushions used in the fabrication of furniture or automotive industry to the production of toys, sports equipment, noise absorbers or packaging materials. Flexible foams are open-cell foams.

As early as 1990, techniques were developed and tested to produce flexible PUR foams without CFCs. One of these techniques was the VPF (variable pressure foaming) process. During the VPF process, the atmospheric pressure in a completely closed production unit is lowered until sufficient CO_2 has been formed by the reaction of isocyanate and water to produce flexible PUR foams with a cubic weight above 11 kg/m^3 (with a raw density ranging from 10 kg/m^3 to 70 kg/m^3). It is not necessary to add any physical blowing agents. The production, which takes place under defined atmospheric conditions, allows an optimised input of raw materials and leads to a better quality product. In Germany, HFCs are no longer used in the production of flexible PUR foams.

Caulking foam (one-component foam/OCF)

Both professional and DIY builders use PUR caulking foams in cans for many applications, predominantly for interior works on buildings. The most important applications are:

- caulking joints and gaps between door and window frames,
- filling different types of cavities, and
- sealing rolling shutter cases (Schwarz and Leisewitz, 1996).

Most of the caulking foams used are one-component foams. They are applied either with a simple aerosol can or with a drop-in caulking gun. Both can be used for the same purposes, but the caulking gun enables the user to work more precisely. One-component foam cannot expand on release from the can without a blowing agent. However, the blowing agent does not support the insulating effect of the foam. Most of it is emitted during application. Only a small amount remains in the foam for a maximum of one year (Schwarz and Leisewitz, 1999; Harnisch and Schwarz, 2003).

Two-component foams are a possible alternative. They do not require an additional blowing agent. They are foamed and spread by mixing the two components together which triggers a chemical reaction. Their use only makes sense when the entire contents of the can are used up at once. Otherwise the foam hardens in the can within just a few minutes. Generally, other materials and techniques can be used as a substitute for caulking foams.

After the complete phase-out of chlorinated blowing agents, mixtures of highly flammable hydrocarbons (propane, butane, dimethyl ether) and non-flammable or virtually non-flammable agents such as HFCs (HFC-134a or HFC-152a) were used in Germany. Since 4 July 2008, an extensive ban has been in effect in the EU, prohibiting caulking foams containing HFCs or HFC-containing preparations with a global warming potential of more than 150 from being placed on the market.

In Germany, caulking foam has to meet the requirements of Building Material Class B2 as defined in German standard DIN 4102-1, i.e. materials that are used in the building and construction industry must be 'normally flammable' (DIN, 1998). Foams that have to meet special fire protection requirements must satisfy the criteria of Building Material Class B1 ('not readily flammable') as defined in DIN 4202-1 (DIN, 1998). The majority of B2 foams (one- or two-component) can now be produced without HFCs. HFC-free alternatives now even exist for one-component foams in Building Material Class B1. However, substituting HFCs with alternative blowing agents necessitates greater use of flame retardants. Due to the explosion hazard, the application of highly flammable blowing agents in small rooms requires special safety precautions (Henkel, 2003). Safety instructions are therefore now issued with the products. No high-risk applications that would completely prohibit the use of HFC-free one-component foam have been identified.

Summary

HCFCs and HFCs as blowing agents can be replaced in many applications today. There are only a few applications in which they have not yet been substituted by non-halogenated systems.
In some applications, approved technical solutions exist, e.g. in the discontinuous production of PUR insulating panels with a metal surface. But small- and medium-sized manufacturers have found it difficult to meet the additional safety requirements associated with the use of pentane in the production process, primarily on economic grounds. Larger manufacturers have been using hydrocarbons as a blowing agent in the production of PUR insulating panels for many years.
In addition to converting to other blowing agents, it is also possible to replace HFC-containing foams in many cases by different tried-and-tested insulating materials.

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Conversion of HFC-Containing Propellants in canned PU Foam in Germany and the EU since 1990

Estimation of the reduction potential of emissions from one-component foam (OCF)

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Introduction

This article is based on a study conducted by Oeko-Recherche for the German Federal Environment Agency in January 2009 on the use of HFC propellants in OCF, which is PU foam for applications from cans, and the reduction potential of emissions from OCF. The first part of the article focuses on the applications of OCF and the role of the propelling agent in OCF manufacture. The second part explores in more detail the gradual conversion process of replacing the propellant gases in Germany and the EU, which has been driven by EU legislation since 1990.

Applications and types of canned polyurethane OCF

Polyurethane (PU) foam applied from aerosol cans (compressed gas containers) was introduced to the market in 1974. This new form of packaging allowed the non-industrial use of PU foam by craftsmen and do-it-yourselfers.

The main fields of application of canned PU foam are interior works on buildings (new constructions, old buildings and renovations). Today, it is used to only a small degree for mounting in the literal sense (e.g. for fixing door frames). It is mainly used for caulking and sealing joints and gaps between door and window frames, for filling various types of cavities, for sealing ducts in wall penetrations and bushings etc. The prevalence of OCF is facilitated by its easy applicability, its pressure stability when hardened, its insulation effect, and its adhesion to most surfaces. The technical advantages of OCF, the climate relevance of the propellant gases contained in OCF and technical alternatives are discussed in a report by the German Federal Environment Agency (Schwaab et al., 2004).

The importance of the propellant in canned OCF

In chemical terms, polyurethane foam is a plastic resulting from the polymerisation reaction of isocyanates with polyols. An oligomeric intermediate (prepolymer) is formed in the aerosol container (can) from the two components (and its additives). After being released from the can, it polymerises to form a macromolecular compound. The can contains pressurised gas, which propels the prepolymer mixture and acts as the initial blowing agent in the foam formation immediately after release. Outside the can, the free isocyanates of the prepolymer react with ambient water (humidity) and separate CO_2. This chemical blowing agent continues and completes the foam formation.

The combustibility of PU foam necessitates the addition of flame retardants. Consequently, in standard formulations, flame retardants are the third major component in the prepolymer mixture after isocyanates and polyols (Schwarz and Leisewitz, 2001). Most of them are additives, but some are reactive components of (halogenated) polyols. Their amount and type depend on the fire safety requirements of the cured foam. Further additives are used, such as cell stabilisers, agents to control viscosity, plasticizers, catalysts etc. The fourth main component in the formulation is the propellant gas.

The propellant (pure gas or gas mixture) has to meet three key requirements:

- Firstly, in the liquefied state it acts in the can as a solvent for the viscous prepolymer mixture, including all the additives.
- Secondly, in the gaseous state it generates pressure in the can to release the prepolymer mixture through the spray tube.
- Thirdly, it causes the expansion of the prepolymer immediately after the output and assists the inflation of the foam by CO_2.

It also acts as a cooling agent for the short-term stabilisation of the foam before the hardening reaction starts (Pauls, 1992).

The propellant makes a major contribution to the formation of the fine structure of the foam cells. However, it does not remain inside the pores of the cured foam for long enough to enhance the insulation effect. Unlike blowing agents in PU insulation boards with cover layers, the propellant degasses quite quickly as a function of its molecular size. In the case of HFC-152a (as well as propane and butane), instant and complete degassing is presumed; in the case of HFC-134a, about 5% of the propellant gas is assumed to remain in the foam for one year. Then, at the latest, the HFCs no longer have any insulation effect; thus, in practice, the insulation quality of the propellant gas does not play a significant role.

Until the 1990s, the three functions of the propellant – solvent, release agent and initial expansion agent – were best performed by CFCs (-11 and -12) and HCFCs (-22). This was still the case when limited quantities of hydrocarbons (propane and butane) were added. HFC-134a, which replaced the ozone-depleting substances, also has most of the properties of the previous propellants. Hence, manufacturers could easily supply foam of the same quality and adapt their formulations to the new propellant gas (with and without the addition of hydrocarbons). Likewise, application of the foam remained unchanged. Like CFCs and HCFCs, HFC-134a was incombustible and did not require special measures to prevent explosions. Both, the need to invest effort in adapting formulations and the need to put safety precautions in place, increased as the proportion of HFC-134a in the propellant gas mixture was reduced or even abandoned.

HFC-134a is not a flame retardant

At this point, it must be stressed that the inflammability of the propellant affects only the safety of application, not the reaction to fire of the cured foam. As mentioned above, the propellant gas remains in the foam cells only in small amounts and for a short time. Therefore, it does not act as a flame retardant in the hardened foam. HFC-134a is incombustible but cannot reduce the combustibility of the foam for a long time; on the other hand, propane/butane or HFC-152a do not increase its fire load.[1]

It is true that it was not easy for manufacturers (see below) to achieve 'normal' flammability (the German Building Material Class B2) without HFC-134a and to further guarantee the same quality foam. However, this was primarily due to the fact that the given prepolymer with its specific fire-retardant characteristics was completely adapted to the physicochemical properties of HFC-134a. The use of HFC-152a and pure hydrocarbons meant that the prepolymer had to be reformulated to include fire-proofing and other additives, such as stabilisers, cell openers, plasticizers etc. This was due to the fact that new propellant gas has different pressure, solubility, and expansion behaviour; it was not due to its flammability.

The conversion of the propellant was a long and costly process which was, however, successful in the end, as the next chapter will illustrate.

[1] The wording 'not for a long time' in the case of HFC-134a means that a minimal and short-term reduction in combustibility cannot be excluded. It is possible that a minimal fire suppressing effect will be found in the fire test on Building Material Class B2, which is carried out with fourteen-day-old foam. In this case, the adequacy of this test must be questioned because the product must show a lifetime of up to 50 years.

Conversion of propellant gas in Germany and in the EU since 1990

At the beginning of the 1990s, HFC-134a became commercially available in large quantities, so that ozone-depleting propellant gases in PU foam cans were gradually replaced: first in Scandinavia, then in Germany, and finally in the rest of the EU. European manufacturers abandoned the use of CFC-11 and -12 from 1.1.1992 as well as the use of HCFC-22 from 1.1.1996.

Early to mid-1990s: CFC phase-out and the 50g-rule

In Germany, the CFC/Halon Prohibition Ordinance ('FCKW-Halon-Verbots-Verordnung') banned the production (but not the use) of OCF containing HCFC-22 (and CFCs) from 1.1.1993. In the late 1980s, HCFC-22 had become a general OCF propellant gas all over Europe. In the five years up to 1992, the quantity used per can significantly decreased from 40% to 15 - 20% (Pauls, 1992). At the same time, more and more flammable hydrocarbons were added to the non-flammable gas because they were far cheaper.

At the beginning of the 1990s, even before the conversion from HCFC-22 to HFC-134a, the leading European manufacturers discussed in their organisation AKPU (European OCF Producer Committee) the maximum content of flammable gases in the propellant gas mixture (FCKW-Halon-Verbots-Verordnung, 1991). They were looking for ways to prevent explosions in confined spaces, realising that consumers were not used to handling flammable propellant gases. The manufacturers in AKPU voluntarily agreed on what was known as the 50g-rule. This rule implied that a standardised 750ml can should not contain more than 50g of hydrocarbons and ether. The concentration of hydrocarbons had to remain below the minimum threshold for explosions (propane: 31 g/m^3, butane: 33 g/m^3) when emptying a can completely in a space of 1.56 m^3 (Pauls, 1996).

Although this rule was applied to propane and N-butane only, it also implied that the quantity of gases with higher explosion thresholds could exceed 50g per 750ml can. Hence, the 50g-rule allowed 80g of dimethyl ether per can and even 158g of HFC-152a. This interpretation of the rule even made it possible for manufacturers to use pure HFC-152a as a propellant gas without HFC-134a. However, HFC-152a was not available on the market in sufficiently large quantities before 1996 (Klauck and Kluth, 1995).

Three kinds of HFC use in the EU before 2000

Developments with regard to propellant gases were not uniform across Europe in the 1990s. There were three different ways of dealing with these issues:

In Scandinavia, the 50g-rule was never applied. By the early 1990s, OCF cans with higher quantities of hydrocarbons had already been in use for a long time and without any accidents. The European manufacturers therefore decided not to set a limit for the content of hydrocarbons. In the other European countries, with the exception of Germany, the HCFC-22 phase-out was decided relatively late (1995) and the 50g-rule was not followed for a long time. As early as 1995/1996, manufacturers started using more hydrocarbons than HFCs on the basis of the positive experience with safety in Scandinavia. By 2000, only 20% of the cans sold still contained HFC-134a (Schwarz and Harnisch, 2003). In Germany, the regulations for explosion protection in OCF applications did not differ from those in the rest of Europe. However, cans without HFCs were not sold until 2000 (Van der Rhee and Geboes, 2002). This was due to specific fire protection requirements for hardened foam. The use of 'easily inflammable' materials (Building Material Class B3) in buildings is not permitted; they have to be at least 'normally inflammable' (Building Material Class B2).

For many years, it was not possible to comply with this requirement without HFCs. The reason for that was not that incombustible or hardly flammable propellants would make hardened foam more fire-resistant, but that HFCs – especially HFC-134a – were most suitable as a solvent, release agent and expansion agent for the more fire-resistant prepolymer (which contained larger quantities of different flame retardants) without changing its stability, volume and, above all, the cell structure of the cured foam.

There were two different groups amongst the OCF manufacturers:

One was the Swiss Rathor Group who had almost exclusively used HFC-152a for B2 foam already from 1995/1996 onwards. As mentioned above, due to its relatively high explosion threshold, this HFC made it possible to comply with the 50g-rule (Pauls and Niemeyer, 1999). The other manufacturers continued using HFC-134a to meet the Building Material Class B2 specifications.

Thus, for a long time, propellant gases for the German market continued to contain HFCs, primarily HFC-134a (Schwarz and Leisewitz, 1996 and 1999). It should be noted that the 50g-rule and the use of high proportions of non-flammable HFC-134a were maintained not for reasons of compliance with safety regulations, but because some manufacturers were not yet able to achieve the technical properties needed for B2 foam without using HFC-134a.

Reduction in HFC share by 2002/2003

Between 1995 and 2002, HFCs were not completely replaced by flammable gases in products for the German market, but the quantity of HFCs per 750ml can was steadily reduced in favour of flammable gases (Van der Rhee and Geboes, 2002). This was partly due to economic factors, since propane/butane costs were ten times lower than HFCs.

Furthermore, some progress in formulation made it possible to realise the production of Building Material Class B2 with relatively high proportions of hydrocarbons in the gas mixture. In 1995, the quantity of HFC per 750ml can was 100g on average; by 2000 only 65g were used, and by 2002 only 40g (Van der Rhee, 2003). The 50g-rule was no longer of importance in production. Therefore, in 2002, the manufacturers' organisation AKPU took this trend into account and replaced the 50g-rule by a 100g-rule. A gas mixture of 150g (per 750ml can) now had to contain at least 50g of HFC-134a. This rule, however, was not followed for long. Nowadays, this measure is seen as an attempt to stop the substitution of HFCs. The safety concerns on which the 50g-rule was based were no longer of importance.

New foam specifications from 2002

Subsequently, HFC substitution stagnated for a while. This was not so much a consequence of the recently introduced 100g-rule, but was related to new specifications for foams, such as fire protection foam, winter foam and high yield foam (mega or maxi foam). Unlike the common all-purpose foam, the new specifications required HFC-134a as propellant gas. At first, pure HFC-134a was used as an expanding agent; later it was added in combination with hydrocarbons.

New types of OCF that emerged from this situation:

- Fire protection foam is consistent with Building Material Class B1 specifications when hardened. Its high flame retardant content means the propellant gas must fulfil specific requirements.
- High-yield foam (mega or maxi foam) provides much higher quantities of foam (60 litres of high-yield foam and more compared to 45 litres of normal foam) while the size of the can remains the same and the same quantity of foam can be taken from a smaller can respectively. The customer uses fewer cans and can access small spaces more easily.
- Winter foam is no longer limited to the previously known minimum temperatures for storage and processing of about +5°C, but can be applied at -5 to -10°C. Thus, OCF can also be used in colder areas such as Northern and North-Eastern Europe. In Central Europe, winter foam is convenient in situations where the cans are stored outside etc. HFCs are particularly useful for creating high pressure in the can at low temperatures.

These three special types of foams account for up to 20% of the output of some manufacturers, depending on the climate in their main sales areas.

EU-Regulation on fluorinated gases and HFC phase-out from 2002

From 2002/2003 onwards, production trends reflected manufacturers' anticipation of the EU Regulation no. 842/2006, known as F-Gas Regulation. All suppliers on the German market reduced the HFC content per can (Van der Rhee, 2003). In 2002, the first all-purpose foams (B2) without HFC propellants were sold in Germany. Within several years, all producers for the German market were able to supply this type of general-purpose OCF. It took longer to replace HFCs in winter foam, mega foam (B2) and fire protection foam (B1).

Only today (at the end of 2008) can we say that all canned PU foam on sale in Germany complies with the defined requirements of the F-Gas Regulation. The regulation does not require that all foam products have to be free of HFCs, but specifies in Article 2 (5) only that ‘the total global warming potential of the preparation is less than 150’ (EU Regulation no. 842/2006). Consequently, the propellant may consist of pure HFC-152a (GWP 140) (IPCC, 2007). Furthermore, a propellant gas mixture (‘preparation’) may even contain up to 11.5 mass percent of HFC-134a (GWP 1,300) (IPCC, 2007) provided that the other gases do not have a significant greenhouse gas potential.

Given that propellant gases account for 18 mass percent on average in a 750ml can (propellant gas mixture 150g), an HFC content of up to 17g of HFC-134a is legally still allowed[2] and can be found in some products.

The situation in 2008: no more propellant mixtures with GWP over 150

Table 1 shows the situation on the German market at the end of 2008. Products with propellant gas mixtures of GWP<150 are available in all OCF specifications of at least Building Material Class B2 both in dispensers (A) and spray guns (G).

Table 1: OCF specifications for Building Material Classes B2/B1 with propellant gas GWP<150, on the German market, end of 2008

Manufacturer	All-purpose		Mega		Winter		Fire Protection (B1)	
Den Braven	A	G		G		G	A	G
Soudal	A	G	A	G		G	A	G
Rathor	A	G	A	G	A	G	A	G
Henkel	A	G	A	G		G		G
Illbruck	A	G		G		G		G
Selena	A	G						
TKK A	G	A	G	A		A	G	
KimTec	A	G		G*		G*		G

* KimTec does not offer one type of winter foam and one type of mega foam, but supplies a combined winter/mega foam.

[2] The possibility of continued use of HFC-134a in small amounts is the legal basis for manufacturers to fill OCF cans with propellant gas that has been recovered from used cans by PDR (‘Produkte durch Recycling’, a German recycling company).

In general, all-purpose foams are completely free of HFC-134a and HFC-152a and are offered by all of the eight manufacturers. Five of the seven suppliers of mega foam and fire protection foam in Germany state that they do not use HFCs in any of their products. One manufacturer uses HFC-152a in a small number of products in compliance with the F-Gas Regulation and another manufacturer adds HFC-134a in authorised quantities. The eighth manufacturer (Selena) does not sell these special types of foam in Germany. Krimelte, an Estonian company, uses HFC-152a in all its products, but does not supply the German market.

Conclusion

The study shows that it took a long time for European manufacturers to produce canned PU foam without halocarbon containing propellants, especially given the need to comply with German fire protection standards for buildings. In a period of ten years, manufacturers had to replace propellant gas three times: from CFCs to HCFCs, from HCFCs to HFCs, and finally from HFCs to hydrocarbons. International agreements on ozone-depleting substances, in conjunction with European legislation on climate-damaging F-gases, were the driving force in this long process towards natural propellant gases. The lesson learned by the European OCF manufacturers is that a timely focusing on natural fluids that are sustainable in the long-term would have saved a lot of time and money.

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Innovation and Legislation on Blowing Agents in PU Rigid Foams

Can pathways of product substitution be predicted or influenced?

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Introduction

In Japanese language chemistry is called kagaku – the science of change. The evolution chemistry with the aim of saving the world's ozone layer is just one more example for this change.
About one generation ago our fathers were enthusiastic about connecting people and businesses by transonic travel. This dream led to the emergence of atmospheric chemistry. We do not know what impact this academic research (published 1970 - 1974 and honoured with the Nobel Prize in 1995) had on transonic travel. We do, however, know that it had a huge impact on the refrigeration and insulation industry, spurred on by the ever increasing need to preserve food from degradation using the lowest possible energy input.

Based on a class of chemical substances called chlorofluorocarbons (CFCs), by 1985 this industry had reached a level of efficiency it has never attained since. CFCs are non-toxic, not flammable, not explosive, chemically inert, easy to produce and extremely efficient in thermal insulation. But, in 1985, atmospheric chemists detected what became known as the ozone hole in the earth's atmosphere. Atmospheric chemistry explained that, due to the stability of CFCs, these were abundant in the atmosphere and contributed strongly to the ozone destruction. The workhorse of the old insulation industry, CFC-11, is now the benchmark for ozone depletion potential (ODP). Legislation responded and in 1987, 24 parties agreed on an international treaty known as the Montreal Protocol. It has now been signed and implemented globally, limiting the use of all substances that have ODP. The treaty provides for different speeds of implementation for different countries and continuously evolving national legislation has led to further differentiation. Countries listed in Article-5 of the Montreal Protocol are subject to the least time pressure. Transition to non-ODP technologies in these countries is supported by the Multilateral Fund. The treaty led to high levels of investment in research and development and industrial production assets.

The science of change: knowledge drives legislation, which in turn drives innovation.

However, before enacting laws it is crucial to analyse what type of solutions a regulation might promote and what social, economic and ecological consequences can be expected. In the following, we will present four cases to indicate that industry structure and overall legislation and standardisation in the fields of health, safety, environment and quality are key determinants of the outcome of legislation and innovation.

Case 1: Transition along dominant pathways: domestic appliances

There is not enough food available to allow it to degrade: food needs to be kept cold during storage and transportation. All places where food is stored need to be very well insulated in order to minimise the energy consumption for cooling. Polyurethane has proven to be the most efficient solution for two reasons: it provides optimum efficiency both in insulation and in assembly. Reefer containers, cold stores, trucks, commercial and domestic appliances all have built-in polyurethane insulation using a variety of technologies and insulating blowing agents. The blowing agents that are retained in the cells of the foam are the key determinants of insulating efficiency and therefore the lifetime energy consumption of a refrigerator.

The transition from CFCs to alternative non-ODP blowing agents in Europe has been described in detail by a team at the 'Wissenschaftszentrum Berlin für Sozialforschung' (Social Science Research Center Berlin) (Albach, H., 1997; Albach, H. et al., 1997 and 1998). According to this research, all companies in the industry experienced first-mover disadvantages in cost or performance irrespective of the technology investigated: a 'technology trap'. The hypothesis of the authors was that in order to change towards environmentally more benign and more expensive technology, bundling of demand was a prerequisite. This happened in Germany in 1993 when an NGO collected orders for 70,000 appliances from environmentally conscious supporters and a catalogue retailer backed the product. The NGO acted as a broker to reduce the transaction costs and found consumers who were willing to pay higher prices for an environmentally more benign product.

There were other driving forces behind the astonishing speed with which the technology spread. One was that a German authority certified the safety of the new technology. Another was the fact that protection of intellectual property provided a basis for the industry to make enormous investments in developing application technology.[1] Eventually the technology based on flammable, zero-ODP and low-GWP refrigerants and

blowing agents gained the critical mass needed to lever the German market. Concentration of the industry in Germany meant that the German market was important enough to lever the entire European appliance industry. This critical mass was required to convince refineries to invest in the modifications needed to access the necessary cyclopentane. This was essential in finally closing the performance gap to the competitor: HCFCs. Many manufacturers in Article-5 countries now use pentane-based technologies without any problems when producing appliances for export into European and US markets.
The appliance industry in the USA followed a different route: no radical change occurred as in Europe, but a gradual change – first from CFCs to HCFCs and now to HFCs. Why? The NGO that had taken action in Germany also had an active branch in the USA. All the system suppliers that were actively developing pentane technology in Europe also had operations in the Americas. Many of the appliance manufacturers were active in both America and Europe and the supply side was also an oligopoly. Neither communications nor technology nor capital nor awareness nor products were lacking. So what reinforced the 'technology trap' in Canada and the USA? Among the many individual aspects, three main ones stand out and support the hypothesis of the team at the Social Science Research Center Berlin:

- There was no support in finding customers willing to pay more for zero-ODP/low-GWP appliances.
- There was a lack of environmental priorities: legislation to combat local air pollution would have required expensive air purification technology to eliminate the small quantities of the pentane blowing agent released from the extracted air during the foaming process.
- Pentane/water technology emerged at the beginning 1990s, but in its first years of development was not yet efficient enough to meet US energy efficiency regulations. There was no commercially viable niche with lower requirements in which the technology could develop until it eventually reached the required level of efficiency.

To sum up: for appliances or similar productions with an output of 100,000 units per year, cyclopentane/water-based technology should be considered the basic state-of-the-art wherever cyclopentane is efficiently available and where air-quality regulations permit its use. Insulation efficiency based on pentanes has not yet matched technologies based on HFC-245fa. However, cyclopentane technology easily matches HCFC technology in insulation efficiency with better ageing and mechanical properties. Ternary blends of cyclopentane/water with HFC or even advanced HFC/water technologies

[1] Patents still shape the technology landscape in the appliance industry. As an example, export of foam products from Article-5 countries to the USA, Canada, Japan and most European countries requires a formal royalty-bearing licence from Bayer MaterialScience if they contain HFC-245fa. In the case of foam containing HFC-365mfc, export to the USA and Canada is prohibited, export to Japan is free and export to most EU-countries requires a formal royalty-bearing licence from Bayer MaterialScience.

may be useful where further improvement in energy efficiency is required and cannot be achieved by increasing the insulation thickness.
All modern polyurethane foam technologies mitigate climate change through energy savings when used as insulation materials. Proper insulation of buildings is one of the most effective ways to reduce CO_2 emissions. A back-to-back comparison between different pentane and HFC technologies shows that four parameters determine the impact of insulation materials on the global climate:

- the source of electricity (coal-based electricity generation vs. hydropower),
- the average lifetime of appliances,
- the efficiency of the insulation throughout its entire lifetime,
- and the treatment of the insulation at the end of its useful life (Johnson, 2000), including the capture of gases (relevant for high GWP gases such as HCFCs and HFCs).

The optimum solutions will differ from country to country. BaySystems®[2] therefore develops PU insulating foam locally.

Case 2: Standardisation through direct political intervention: insulation for district heating pipes

District heating and district cooling are a very efficient use of power generation plant. Energy that cannot be used for electricity generation can still be used to create a comfortable temperature in homes. Since heat or cold need to be transported over long distances to reach enough customers, the pipelines need to be well insulated to minimise any change in temperature. Due to the effective assembly, mechanical strength over time and insulation efficiency at elevated temperatures above 140°C, polyurethane foam is the insulating material of choice in this application.
The district heating pipe industry is as highly concentrated as the appliance industry. Customers buying district heating pipes are very often directly controlled by local politics. In the existing political environment, it was easy to demand non-ODP products and justify any cost increase to the constituency. Here, local governments played the role of intermediary, bundling the demand for more expensive and environmentally more benign products. Through this oligopolistic supply and coordinated demand, district heating pipes produced and used in Europe are now insulated with PUR foam based on cyclopentane.

[2] BaySystems® is the umbrella brand for the global polyurethane systems business of Bayer MaterialScience. The worldwide network currently comprises 30 systems houses that are working closely with customers to develop solutions.

Case 3: Transition without a dominant pathway: boilers, water heaters and tanks

Boilers and hot water tanks are components in heating systems, solar energy converters, diverse types of industrial insulations and, last not least, most of our showers. The water is heated to a desired temperature and maintained at that level for use. An essential requirement is that the water should lose heat as slowly as possible, minimising the need for re-heating. Most boilers are therefore insulated with polyurethane foam. Technologies to apply this insulation are as diverse as the applications of boilers and tanks.

With regard to blowing agents, the boiler insulation industry had the same technological options as the appliance industry. But the boiler industry in the EU was hardly concentrated. Overall use and average use per site were much lower. Economies of scale did not support investment in technologies that use flammable products. The boiler and tank industry did not sell directly to end consumers in the way the appliance industry did, which meant that it was not easy for efficient brokers of information and labels to coordinate end consumers to make the shift to non-ODP technologies. The reaction to the challenges of Montreal was therefore different than it had been in the appliance and district heating industries.

The German and Nordic industries decided to redesign their products and increase the thickness of the insulation – accepting lower-performance PUR insulation materials. This led to increased materials consumption and initial cost increases of 100% for insulation. Only years of continuous development have brought this down to a 40% increase in specific materials consumption compared to 1990. So why did the industry accept such cost increases?

As in the example of the US appliance industry, differences in environmental legislation determined the outcome of the Montreal-initiated technology transition. Unlike in appliances, the cost of insulation materials plays a relatively small role in the overall cost balance of a boiler. A major part of the cost is the metal core. The industry has an interest in taking it back, removing the insulation and reusing the metal. The insulation material is waste. In Germany at least, ODP-containing waste is more expensive to dispose than ODP-free waste. The new ODP-free PUR insulation was coloured green to allow it to be easily separated from old CFC-containing material with natural colour.

There was less international competition and concentration than in the appliance industry. It therefore took much longer for the European boiler and hot water industries to adapt. HCFCs were used in many countries until the very last days that they were legally permitted. The diversity of technologies led to a broad range of energy performance. A European study under the SAVE programme identified significant energy-saving potentials (Lechner et al., 1998). But only less than a handful of plants

in Europe of sufficient size invested in low-GWP pentane technology. Already 10 years ago, 2% HFC-134a in the foam were used to have non-ODP insulation with reduced materials consumption; now the use of low levels of HFC-245fa and of HFC-365mfc insulating gas is often considered necessary to meet increasing energy standards.
By contrast, the US boiler industry is an oligopoly (significant economies of scale) with strong competition and less ambitious energy efficiency regulations compared to appliances. The industry therefore followed a least-cost pathway. The dominant players in the US boiler market changed first to HCFC and then to pentanes, because this meant that their materials costs would be lower than if they used HFC.

Case 4: Late transition: spray foam

Polyurethane spray foam is a very efficient way to insulate buildings and agricultural installations. It can generate employment for small family businesses, bring about energy savings and reduce CO_2 emissions. Investment in a new machine is very affordable and allows insulating 50,000 m² per year. There is a multitude of suppliers and a vast number of contractors buying spray foam systems: the lowest concentration in the polyurethane market. As expected for such a situation, spray foam markets initially followed the least-cost pathway from CFC to HCFC/water. Why did we not see a transition to non-ODP/low-GWP purely water-blown systems similar to the one that occurred in the boiler industry?
It is a question of quality management and monitoring. HCFC/water-systems were more sensitive to improper application and required contractors to take greater care. The introduction under cost pressure of solely water-blown closed-celled foams in Germany ten years ago increased the quality problems. In boiler production, any shrinkage of foam is immediately visible in the product and foam of inadequate quality cannot escape the notice of the end consumer. By contrast, in roof insulation the foam is well hidden. So eventually, despite joint industry efforts, insulation with polyurethane spray technology all but disappeared in Germany, also due to quality issues. By contrast, the Iberian, US and Japanese markets for spray foam insulation based on HCFC/water and subsequent HFC/water-technologies thrived. This was a result of strong quality management, both on the side of the supplier and the contractor. In large areas of Spain, this quality management was audited by state authorities. This was an efficient way to support insulation and energy efficiency in construction. It was also an efficient way of preventing low-quality water-based systems.
Markets with low concentration will always provide scope for interesting niche technologies. Water-based open-celled spray foams with very low GWP, low cost and also low insulation performance are available in the USA alongside the dominant technology of closed-celled HFC-blown spray foam. In Japan, advanced and expensive

polyisocyanurate (PIR) technologies are available to meet the demand of the construction industry for fire safety and optimum insulation efficiency. Both technologies are indicators of the two extremes in current technology evolution:
a) lower insulation efficiency and low materials cost based on water only,
b) very high efficiency and high materials cost based on HFC.

The role of this kind of product will depend on how prices for energy and blowing agents evolve. Legislation should fully cover all non-ODP blowing agent technologies and should be based on overall policies on energy and climate change; it should not focus solely on the chemical properties of the blowing agent. Otherwise, some options for energy saving and cutting greenhouse gases might be overlooked.
Pentane-based spray foam solutions that combine energy efficiency with very low GWP have been promoted by Exxon and an Italian system house. They are listed by US EPA as an acceptable substitute to HCFC-141b, provided working conditions are adequately taken into account (EPA USA, 1999). BaySystems filed a patent back in 2002 (Albach, R. et al., 2003). However, the safety of using in-situ-applications has not yet been sufficiently investigated and backed-up by a public authority in the way it was for industrial use of appliances, for example.

Lessons learned

The case studies demonstrate the importance of:

- The entire environmental regulation throughout the transition time, including legislation on energy efficiency, waste disposal and VOCs (volatile organic compounds), but not limited to these.
- Stability of environmental regulation in an economically interlinked region in order to allow for economies of scale of production – which in turn are required for investments in most efficient pentane-based technologies.
- Education and quality management in an industry, along the entire value chain, particularly during technological change.
- Continuous sharing of responsibility and intensive joint auditing of safety by industry and outside authorities in the installations supporting the ‘responsible care approach’.
- Protection of intellectual property with regard to technologies as a prerequisite for development.
- Availability of the blowing agent.

Most important are the economic parameters influencing product substitution towards pentane-based low-GWP/high-efficiency technologies. The following matrix gives an overview:

Table 1: Comparison of economic parameters for pentane-based technology

	Pentane-based solution much cheaper in materials cost than the alternative	**Pentane-based solution equal or more expensive in materials cost than the alternative**
Oligopoly on the supply side	Industry will switch to pentanes without outside intervention.	Coordination on the demand side can trigger change to pentane without prior legislation (broker, labelling).
No oligopoly, high diversity on the supply side	Industry may switch to pentane if investment is economically feasible and responsibility for health, safety, quality and environment is shared.	Path forward is slow, diverse and unpredictable.

Outlook: delivering solutions

The literature has covered many successful approaches to introduce adapted technology. Technology needs to take into account that education levels are different, access to credit lines and cash is different and that production parameters may not everywhere be kept as stable as they may be in European, Japanese or American environments. Governments may not support technologies that improve efficiency and quality by automation and reduce employment.

The delivery of fully blended, flammable polyol formulations (containing, for example, cyclopentane and/or methyl formate) may overcome some problems in transition situations. A proven tool has been to convert mid-scale production units to energy-efficient non-ODP/low-GWP technologies. This approach allows reduced investments on the user's side without the need to compromise on insulation efficiency or material consumption. A very good example is BaySystems Northern Europe in Denmark (formerly known under the name of Tectrade), which for a long time has been delivering formulations containing cyclopentane in bulk, special one-tonne containers and drums to different industries in Eastern and North-Eastern Europe. This example shows that investment in one blending facility can make it possible to reduce (not avoid) investment in many manufacturing plants.

Who can do it?

Anyone who works with producers of appliances or other insulation businesses needs to be part of the local industry culture and also part of a strong technology network. The case of the Nano car is such an example. There was no car in the world to serve the needs of people in India who could not afford more than $3,000 per car. So Tata developed one in India, for Indian customers. Tata did not rely on its Indian resources alone. It drew on the resources from a strong network of global technology from Italy, Germany, USA and more. The car is still made of steel and has four wheels and all the other components you expect in a car. It neither meets the expectations of American or German customers nor the laws of these countries. But there is reason to believe that it meets the expectations of Indian customers and Indian legislation. The same holds true for the polyurethane industry. There is no need to reinvent the wheel in polyurethanes. However, there is a need for local development of systems, technologies and logistics solutions that may not suit customers in America or Germany, but in Article-5 countries. Examples could include smaller pentane-proof packaging. This local development needs to be part of a global network that has access to all available technologies. BaySystems and a few others operate laboratories in many Article-5 countries like India, South Africa or Brazil as part of a global network, close to the special needs of customers in these countries and linked to laboratories that have already made the transition from (H)CFCs to new technologies before and in many different ways.

Summary

CFCs and HCFCs are no longer required for polyurethanes. The last 15 years mark a transition from an efficient 'one-size-fits-all' technology to a multitude of different technologies. Respect for customer and market diversities, coordination of consumer interests, efficiency in production and product, unbiased mastering of an increasing multitude of blowing agents and a clear focus on overall life-cycle minimisation, direct and indirect energy consumption and greenhouse gas emissions combine to form the basis for taking the next steps needed to save the ozone layer that protects the Earth and its climate, and leveraging the efficiency of polyurethane insulation for green building.

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Table 2: Performance of foam insulation for domestic appliances (Droege, 1997; Schilling, 2000; Albers et al., 2009)

	Standard HCFC-141b	Standard cyclopentane	Standard HFC-245fa	λ-Optimised HFC-245fa
Materials consumption (kg/m³ insulation)	34	35	32 – 35	43
Blowing agent content in the PUR system* (weight %)	6	7.5	10	9.5
GWP 'bank' per m³ (tonnes of CO_2 equivalent)	1.4	0.03	3.3	3.8
ODP 'bank' per m³ (R-11 kg)	0.24	none	none	none
Strength (MPa)	0.30	0.35	0.24 – 0.40	0.49
λ at 24°C mean temperature [W/m·K]		0.020	0.019 – 0.020	<0.019
λ at 2°C mean temperature [W/m·K]	0.017	0.019	0.017 – 0.018	<0.017
Heat leak (600-litre refrigerator)	269		263	

1 lb/ft³ = 16.02 kg/m³; 24°C = 75°F; 2°C = 35°F; 1 BTU.in/hr ft² °F = 0.1442 W/m·K (http://www.onlineconversion.com)
The data given are indicative and may vary according to manufacturing conditions.
* A polyurethane system is composed of a polyol formulation and a polymeric isocyanate (Desmodur). Mixing ratio for polyol formulation and Desmodur is approx. 1:1 by volume.

Figure 1 shows the evolution of thermal conductivity λ over time for laboratory specimens containing water and different blowing agents. Cyclopentane is usually found to be at least one mW/m•K better (i.e. lower) than N-pentane. Storage is at room temperature without facings (open diffusion) and time is given in days. As most products have lifetimes beyond one year, the graph shows that all alternatives easily compete with HCFC in the long run in terms of efficiency of insulation, irrespective of the values measured initially. The data given are indicative and may vary according to manufacturing conditions.

Figure 1: Evolution of thermal conductivity over time of different blowing agents

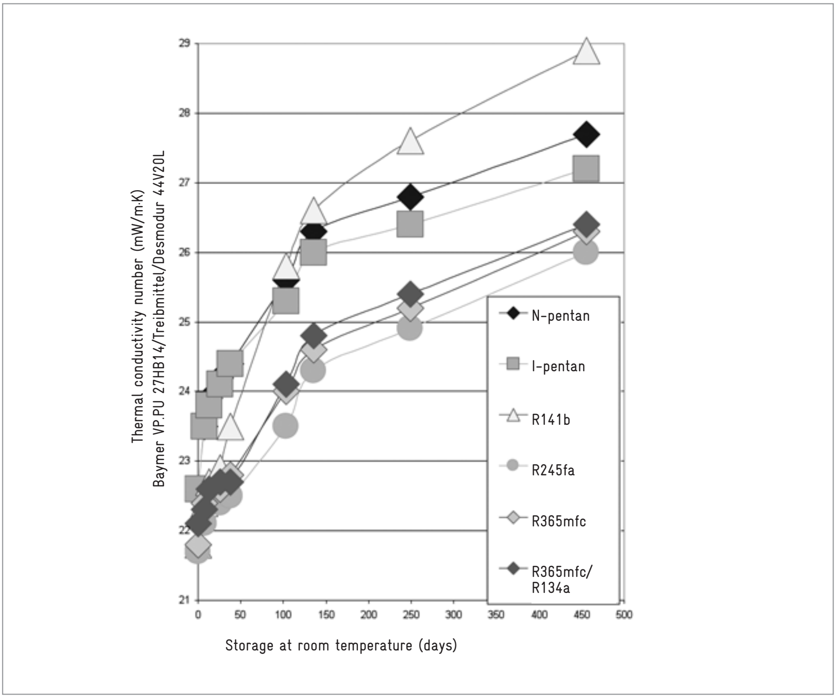


Table 3: Performance of foam insulation for domestic boilers and hot water storage

Boilers	HCFC/ water	Cyclo-pentane	HFC-245fa/ water	HFC-245fa/ water	HFC-245fa/ water	Water	Water (closed cells)	Water (closed cells)
Source	Fanney et al., 1998	Larsen, 2008	Fanney et al., 1998	Larsen, 2008	Rosner, 2008 and Zilio, 2008	Fanney et al., 1998	Larsen, 2008 and Zilio, 2008	Larsen, 2008 and Rosner, 2008
Materials consumption (kg/m³ insulation)	32	43	32.5	43	40 – 41	32.5	45 – 47	20
λ (10°C, fresh) [W/m·K]		0.020		0.0205	0.025		0.021	0.035 – 0.037
λ (ambient temperature) [W/m·K]	0.021 – 0.030		0.021		0.025	0.031 – 0.032	0.027	
λ (50°C, fresh) [W/m·K]		0.0245			0.030		0.026	0.042

In boiler production, considerable thermal leak occurs at the inlets and outlets. Improved insulation therefore does not always directly translate into reduced energy consumption. Figures have been rounded to the nearest 0.005 W/m•K. Water-based foam may age by 0.01 W/m•K if not covered by impermeable facings. Ageing for other types of foam is normally less pronounced. The data given are indicative and may vary according to manufacturing conditions.

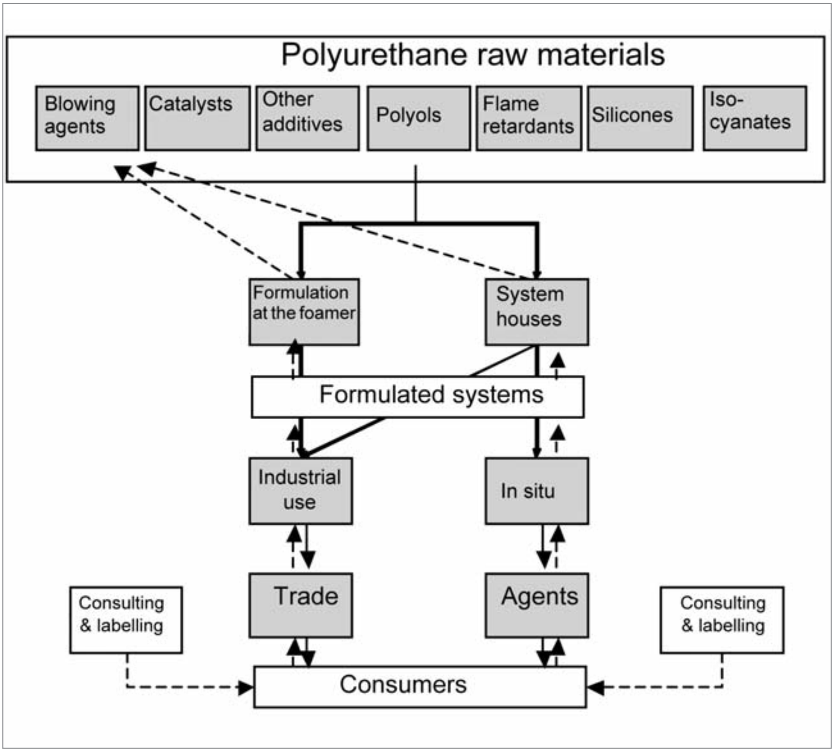
Table 4: Spray foam insulation of buildings in the Iberian market: transition to HFC technology with decreasing climate impact

Baymer Spray (Heinemann, 2008)	**HCFC/water**	**HFC/water**
Average consumption (kg foam system/m²); Layer thickness 3cm	Approx. 1.1	Approx. 1.2
Blowing agent content in the PUR system (weight %)	7 – 8	Approx. 6
GWP 'bank' per m^2 (tonnes of CO_2 equivalent)	Approx. 0.07	Approx. 0.05
ODP 'bank' per m^2 (R-11 kg)	Approx. 0.013	None
Thermal conductivity (aged, W/m·K)	<0.027	<0.028

The data given are indicative and may vary according to manufacturing conditions. A polyurethane system is composed of a polyol formulation and a polymeric isocyanate (Desmodur). Mixing ratio of polyol formulation and Desmodur is 1:1 by volume.

Figure 2: Containers for pentane-containing polyol formulations in BaySystems Northern Europe

Figure 3: PUR raw materials cycle



II. Conditions for Conversion and Special Technologies

Alternative Blowing Agents in Rigid Foam

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Introduction

As a result of the international Montreal Protocol agreement and individual country regulations controlling the production, consumption of and trade in CFCs and HCFCs, the Asian fluorocarbons market has undergone a number of major transitions and is now moving toward greater use of more environmentally friendly alternatives.
Rigid polyurethane foams are used primarily as thermal insulation in refrigerators and freezers, buildings, refrigerated transport containers and LNG (liquid natural gas) transportation ships. These foams also find use as pipe and tank insulation and as flotation material (e.g. buoys, deck supports, boats). Because of the desirable properties CFCs and HCFCs give to foam processing and quality, the polyurethane and polyisocyanurate foam insulation industry has used them as blowing agents for many years.
This article will briefly describe alternative blowing agents for polyurethane rigid foam, comparing them to HCFC-141b, the blowing agent currently in widespread use, looking at environmental impact, thermal resistance efficiency and foam properties.

Blowing agents' properties

Table 1: Blowing agents' properties (UNEP, 2007: 99)

Blowing Agent	CFC-11	HCFC-22	HCFC-141b	HCFC-142b	HFC-134a	HFC-152a	HFC-245fa	HFC-365mfc	N-pentane	I-pentane	C-pentane	CO_2
Formula	CCl_3F	$CHClF_2$	CH_3CCl_2F	CH_3CClF_2	CH_2FCF_3	CH_3CHF_2	$CF_3CH_2CHF_2$	$CF_3CH_2CF_2CH_3$	C_5H_{12}	C_5H_{12}	C_5H_{10}	CO_2
Molecular weight	137	86	117.0	100	102	66	134	148	72.1	72.1	70.1	44.0
Boiling point °C	24	-41	32.0	-10	-27	-25	15.3	40.2	36.0	28.0	49.3	-139
Flammability limit vol. %	-	-	7.3 – 16.0	6.7 – 14.9	-	3.9 – 16.9	-	3.8 – 13.3	1.4 – 8.0	1.4 – 7.6	1.4 – 7.6	-
ODP	1.0	0.055	0.11	0.065	0	0	0	0	0	0	0	0
GWP (100 years) ***	4000	1700	630	2000	1300	140	820	840	<25	<25	<25	1
Gas thermal conductivity at 10°C mW/m·K	7.4	9.9	8.8	8.4	12.4	14.3*	12.5**	10.6**	14.0	13.0	11.0	14.5

* measured at 25°C, ** measured at 24°C, *** UNEP, 2007 based on IPCC Report 1996

Table 1 summarises the properties of frequently used blowing agents in polyurethane rigid foam, including CFCs, HCFCs, HFCs, pentane isomers and CO_2.
A blowing agent for polyurethane foam must comply with a number of requirements. For example, it should be liquid with a boiling point lower than 50°C and be soluble in polyurethane raw materials polyol or isocyanate – yet insoluble in the polyurethane matrix. Preferably, the blowing agent should have low thermal conductivity, a low diffusion rate through the struts and membranes of the foam, be non-flammable, non-toxic and environmentally harmless. Its availability and production costs should also be considered.

CFCs

Fully halogenated chlorofluorocarbons contain only carbon, fluorine and chlorine. These are known ozone depleters and new production of these products for emissive uses has been phased out in all developed countries.

HCFC-141b

The industry used 1,1-dichloro-1-fluoroethane (HCFC-141b) as the blowing agent of choice during the transition from CFC blowing agents to HFC blowing agents since it has similar insulation properties to CFC-11. HCFC-141b is now being phased out as part of the Montreal Protocol on Substances that Deplete the Ozone Layer. Because the reaction of HCFCs with OH free radicals in the troposphere is faster than that of CFCs, their concentration in the stratosphere and thus their ozone depletion potential (ODP) is considerably lower, but not zero.

HFCs

Fluorocarbons contain only carbon, fluorine and hydrogen and do not contain chlorine or bromine (i.e. fully fluorinated and hydrofluorinated products). They are not stratospheric ozone depleters and their production is not prohibited under the Montreal Protocol. In contrast to CFCs, these newer replacement fluorocarbons typically have zero ODP, but they still have a quite high global warming potential (GWP) compared with hydrocarbons. The more fluorine atoms in the molecule, the more expensive the product and the higher its GWP, since its reaction rate with OH free radicals is lower and the number of infrared-absorbing C-F groups increases.

Pentane

Considering zero ODP and negligible GWP, halogen-free hydrocarbons such as pentane isomers were chosen as more environmentally friendly candidates due to their suitable boiling point range. The atmospheric lifetime of pentane is only a few days – dramatically shorter than that of HFCs, which is several years.

Blowing agents' usage

Figure 1: Global blowing agents' usage (BASF)

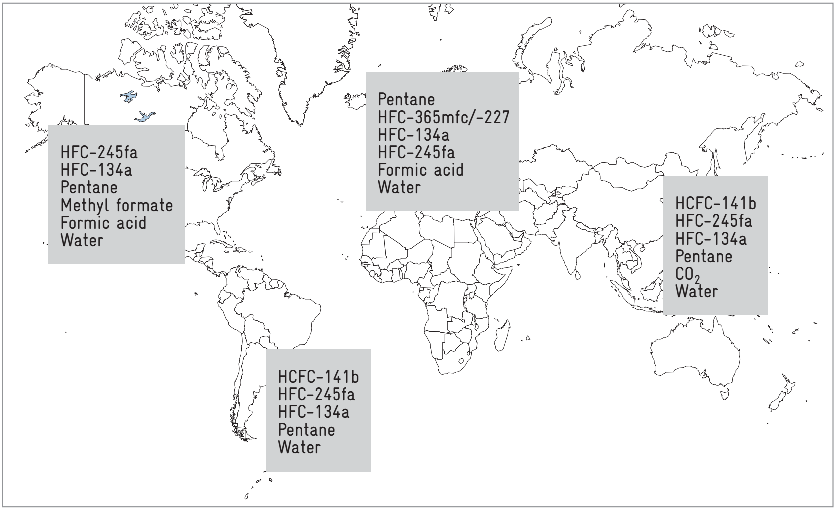


Figure 1 demonstrates the main blowing agents used globally. Generally, the involved PU foam blowing agents are similar including HFC-245fa, HFC-365mfc/-227, HFC-134a, pentane, methyl formate, formic acid, water and HCFC-141b etc., while differences exist in the leading and dominant product in each continent.

On the American continent, the leading fluorocarbon replacement product for PU is HFC-245fa. HFC-245fa has properties such as non-flammability, relatively low GWP and insulation efficiency that are similar to HCFC-141b, so that it can be used as a drop-in solution without necessitating much modification of the equipment currently in place.

In Western Europe, environmental issues remain among the most discussed topics and concerns among the public and within governments have not eased. In particular, the ozone issue and the issue of global warming are among the most crucial problems that need to be solved if the concept of sustainable development is to be safeguarded. It is understandable that more and more companies have decided to use alternative technologies and products, such as hydrocarbons, ammonia and carbon dioxide (i.e. products not containing any halogens).

In the Asia-Pacific region (with the exception of Japan, Australia and New Zealand, which are currently using only HFC and HC), HCFC-141b is still the predominant blowing agent for PU foams. Furthermore, a small number of manufacturers utilise HFC-365mfc and combinations, due to their cost and availability.

The accelerated HCFC-141b phase-out plan (freeze in 2013 and complete phase-out in 2030) is promoting the choice of alternative blowing agents based on the Asian situation.

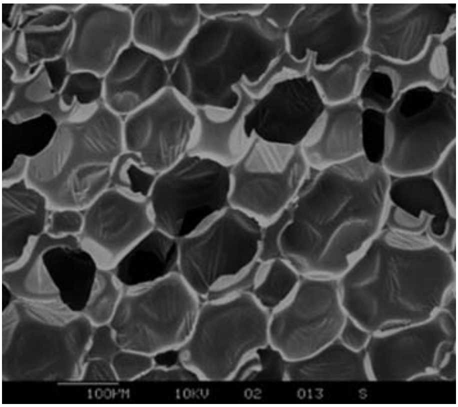
Thermal conductivity of PUR rigid foam (W/m·K)

The coefficient of linear thermal conductivity λF for PUR foam:

$$\lambda F = \lambda P + \lambda G + \lambda R + \lambda C$$

λP = heat conduction of the cell framework
λG = heat conduction of the cell gas
λR = heat transfer through radiation
λC = heat transfer through convection

Figure 2: Rigid polyurethane foam structure



Rigid polyurethane foams are generally used as insulating materials. A low thermal conductivity of the blowing gas is required since it gives the foam its insulating properties. The coefficient of thermal conductivity λF for PU foam consists of several factors, i.e. λP (heat conduction of the cell framework), λG (heat conduction of the cell gas), λR (heat transfer through radiation) and λC (heat transfer through convection). Although λG accounts for about 50 to 60% of the thermal conductivity of the foam, we should not regard the thermal conductivity of blowing agents as the only decisive factor. Many parameters influence λG, including the composition of the cell gas (usually consisting of the gaseous blowing agent, air and CO_2), the aging of the foam (gas diffusion rate through the polyurethane matrix and gas dissolving in the polyurethane matrix), and temperature influence.

By adjusting the polyurethane formulations to suit the new blowing agent and by optimising the cyclopentane or HFC-CO_2 ratio in the cell gas, a low foam thermal conductivity (0.019 W/m·K) target has now been attained and even improved.

Property comparison

Table 2: Property comparison

Blowing agent	Foam k-factor	Foam performance	Handling	Flammability	Environment
HCFC-141b	●	●	●	●	✖ (ODP) ▲ (GWP)
HFC-134a	▲	▲ Frothing process	▲	●	● (ODP) ▲ (GWP)
HFC-245fa	●	● Fastcream time	▲	●	● (ODP) ▲ (GWP)
Pentane	●	● Lower flame resistance foam	▲	●	● (ODP) ● (GWP)
Water (CO_2)	✖	▲ Lower flame resistance foam	●	✖	●

● Good ▲ Medium ✖ Worst

As indicated in Table 2, polyurethane foam using HCFC-141b as a blowing agent has superior properties, including high thermal resistance measured as a k-factor, foam mechanical performance, easy handling and good foam flame resistance. However, due to its environmental impact (relatively low ODP, but high GWP), it is seen as transitory and scheduled for phase-out.

HFC-245fa leads to foam with good k-factors, physical properties, and also flame resistance. Its relatively low boiling point (15.3°C, normally lower than room temperature) results in faster cream time and a higher processing requirement in production. However, its potential environmental impact (relatively high GWP) is still a cause for concern among the public.

Contrary to CFCs and HCFCs, pentanes used as polyurethane blowing agents have no environmental impact. However, pentanes are flammable and may become explosive if mixed with air when the concentration limit is attained. This means safety measures have to be put in place during processing. Accordingly, the flammability resistance of the foam obtained is slightly lower. The increased flammability of pentane foams can be overcome by adding additional flame retardant and by proper adjustment of the foam formulation.

Cyclopentane foam properties

Let us take cyclopentane as an example of an alternative blowing agent in rigid foam systems. In spite of its rather high boiling point, cyclopentane has a high gas yield in rigid foam: 6 - 10% cyclopentane is normally added into a resin system. The foam obtained has an initial thermal conductivity of 19.0 mW/m·K and aged thermal conductivity of 23.5 mW/m·K. Depending on the application, moulded densities of 30 ~ 34 kg/m^3 are chosen for refrigerators and moulded densities of 40 ~ 80 kg/m^3 for sandwich panels.

Cyclopentane foam properties:

- 6 - 10% cyclopentane in a resin system
  - Initial thermal conductivity, k-factor = 19.0 mW/m·K
  - Aged thermal conductivity, k-factor = 23.5 mW/m·K
  - Dimensional stability acceptable
- Moulded densities: 30 - 34 kg/m^3 (appliances)
- Moulded densities: 40 - 80 kg/m^3 (sandwiched panels)

Cyclopentane foam's potential economic impact

In terms of the potential economic impact of cyclopentane foam, the price of cyclopentane is quite attractive with about three quarters the cost of HCFC-141b, other pentane isomers cost even less. This price is far lower than that of HFC blowing agents.

However, the flammability of the pentane series necessitates relatively high capital investment, e.g. equipment and process modifications, such as explosion limit detectors, earthing, magnetic coupled, explosion-proof motors etc. Furthermore, the transportation and storage of polyol systems with pentanes must comply with individual country regulations.

Economic properties of cyclopentane:

- The cost of cyclopentane is about three quarters that of HCFC-141b; other isomers cost far less.
- Capital investment
  - Equipment & process modifications: e.g. explosion limit detectors, earthing, magnetically coupled, explosion-proof motors etc.
  - Storage systems for hydrocarbon
  - VOC (volatile organic components) regulations

Conclusion

This paper describes the advantages and disadvantages of commonly used blowing agents and provides a basic reference for changing blowing agent. In the decision process about switching to an environmental friendly blowing agent, manufacturers have to consider carefully the general properties of the foam, flame rating requirement, production process ability, and the investment in equipment safety needed and look at the cost impact. The system material will also need to be changed accordingly to suit the solubility and compatibility of the raw material used to produce the blowing agents.

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Comparison between Pentane and HFC-365mfc in PU Rigid Foam

Blowing agents for manufacturing roof insulation panels and refrigerated vehicles after phase-out of HCFC-141b

Findings from a study[1] by Ecofys and Oeko-Recherche on behalf of the German Federal Environment Agency (UBA)

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Introduction

HCFC-141b has been banned in the European Union (EU) since 2004. Although the vast majority of PU foam manufacturing companies in Germany switched directly from CFC-11 to hydrocarbons, in some applications in certain sectors HCFC-141b was used as the successor to CFC-11. Insulation for refrigerated vehicles is one of these sectors where the practice of using HCFC-141b persists. The main reason for choosing HCFC-141b over pentane was said to be the poorer insulation performance of hydrocarbons, which – for reasons of space – is difficult to compensate by increased thickness. It is a frequently cited example used to make the case for halogenated blowing agents. However, by 2003, German manufacturers had decided to convert their production to cyclopentane (C-pentane) – instead of the newly developed HFC-365mfc, a fluorinated gas with a GWP of 890 (2002). This article attempts to give an explanation for this decision and provides research findings comparing pentane with HFC-365mfc in two major applications: roof insulation panels made of polyurethane and insulation for refrigerated vehicles. The findings demonstrate the superiority of pentane (N-pentane und C-pentane) in several regards.

[1] Harnisch et al., 2004

The research setting

Two typical applications of PU rigid foam are roof insulation panels and insulation for refrigerated vehicles. In both cases, hydrocarbons as well as HFCs can be used as blowing agents. Compared with HFC-365mfc, hydrocarbons have 4 - 8% higher thermal conductivity λ (lambda), i.e. a lower specific insulating effect. In the first application, the reduced insulating effect can easily be compensated by increasing the foam thickness by a few millimetres. This is not the case with refrigerated vehicles, where there is little scope for compensating increased thermal conductivity by making the insulation thicker. In Germany, foam for this application is now normally blown with C-pentane (frequently in blends with N-pentane).

The insulation effect of PU rigid foam at a given thickness is higher with lower thermal conductivity λ of the blowing agent encapsulated in the foam cells.

Table 1 compares PU foam with HFC-365mfc (λ = 22) as a blowing agent with PU foam produced with C-pentane (λ = 23) and N-pentane (λ = 24) as blowing agents. There will be no further comparisons with HCFC-141b since this substance has been banned in the EU since 2003.

Table 1: Applied λ values for different blowing agents in PU rigid foam (mW/m·K)

Blowing agent	HCFC-141b	HFC-365mfc	C-pentane	C- / I-pentane	N-pentane
λ value	21	22	23	>23	24

Part 1: Aluminium foil faced PU insulation panels

Approx. 35% of the 65,000 tonnes of PU rigid foam used in Germany in domestic insulation (excluding PU foam for electrical appliances and polyurethane foam in cans) ends up in insulation panels. The most important application is insulation for pitched roofs, followed by insulation for walls, ceilings or floors etc.

PU rigid foam panels are increasingly being used to insulate pitched roofs in (new and existing) residential buildings. PU has only a 6% share of the German market for insulation materials – far behind mineral wool and expanded polystyrene (EPS). In contrast to this, PU rigid foam has a disproportionate share in high-performance insulation used on rafters (virtually eliminating thermal bridges). This is because the required insulation effect can be achieved with thin boards of a thickness below 14cm that can be nailed onto ordinary rafters without a problem (the predominant material used for insulation between rafters is mineral wool).

The most commonly used, standard PU roof panels are boards faced on both sides with aluminium foil, with a raw density of 32 kg/m³ (30 kg/m³ is the required minimum) and a thickness of 105mm.

German PU panel producers converted their manufacturing machinery back in 1995, switching directly from CFC-11 to the flammable hydrocarbon N-pentane, without making a detour via HCFC-141b. When using N-pentane, the insulation effect per square metre (u-value) is theoretically 14% lower than when HCFC-141b is used. In 2002, liquid HFC-365mfc came onto the EU market (in addition to the similar HFC-245fa) with a λ between HCFC-141b and pentane (see Table 1). The chemical industry offered this new blowing agent to manufacturers of PU insulation boards with very little success. Hydrocarbon-blown PU foam panels turned out to be superior to HFC-blown insulation boards both ecologically and financially.

Summarising the results on roof insulation panels

It has been shown that pentane-blown PU panels have a clearly better GHG balance than alternative panels blown with HFC. Even though with the same thickness of insulation foam, they have a slightly higher heating energy demand. The ecological disadvantage of HFC-blown panels is the high global warming emissions of HFCs (a) during manufacturing, (b) during use, and (c) on disposal of the boards. Even if 80% of the remaining blowing agent is recovered at end-of-life (a very optimistic assumption), the CO_2 equivalent HFC emissions per square metre of panel are still extremely high (~ 2.5 kg). At constant foam thickness, the pentane-blown panels cause slightly higher CO_2 emissions than HFC-blown panels because of the higher heating energy demand (increased heat loss through the panel). However, the additional CO_2 emissions from the heating are far lower than the CO_2 equivalent emissions arising from manufacturing, use, and end-of-life of the HFC-blown panels.

A sensitivity analysis, in which (1) the heating system, (2) the use phase of the insulation material, (3) the number of heating degree days and (4) the thickness of the insulation layer were varied, confirms this finding in favour of the pentane-blown panel for all parameters.

With a change of heating system type, the overall CO_2 emissions rise in the following order: gas condensing boiler, oil heating system and direct electric resistance heater. But, due to the losses of blowing agent, the HFC case always contributes the exactly identical amount more to the CO_2 equivalent emissions than the pentane-blown insulation (under otherwise equal conditions).

If the use phase of the insulation is varied from 50 years to 30 or 70 years, the additional contribution to the greenhouse effect from HFC-blown insulation foam drops with increasing length of use phase compared to pentane; losses of blowing agent are then spread over more years. In absolute terms, the total CO_2 equivalent emissions associated with HFC are always higher than for pentane.

A similar result can be stated for the variation in heating degree hours. The longer the heating phase per year, the smaller the difference in CO_2 equivalent emissions between

HFC-blown and pentane-blown insulation panels. However, the additional contribution from using HFC is not reduced significantly.
Modifying the foam thickness to compensate for the lower insulation performance of N-pentane and bring its u-value (the panel's heat transmission coefficient) up to that of foam blown with HFC-365mfc, requires an additional input of 9% PU foam. A pentane-blown panel of 11.45 cm thickness has the same insulation effect as an HFC-blown panel of 10.5 cm. 9% more material causes additional global warming emissions of 0.05 kg CO_2/year. This is, however, far less than the additional CO_2 emissions caused by the higher heating demand of the pentane insulation panel of original 10.5 cm thickness, which are saved now. From an ecological point of view, this seems to be the best option because in the reference case (gas boiler, 50 years usage, 66 khK/heating degree hours) the total global warming emissions from the 11.45 cm panel are 5 - 6% lower than in the case of the 10.5 cm thick pentane panel.
In terms of costs, there is no difference between the pentane-blown panel and the HFC panel. Despite the 9% increase in thickness, the total price of the insulation – taking into account the additional input of PU – is only slightly higher than the HFC-blown panel. This is because the higher price of the PU in the pentane-blown panel is offset by the higher price of the blowing agent in the HFC-blown panel. Mitigation costs here are €0/t CO_2 equivalent.
The disposal path has significant quantitative relevance for the total result. In the reference case, an 80% decomposition rate is assumed for the HFCs contained in the panels on disposal. This rate seems very optimistic in view of the present conditions and medium-term perspectives. However, even this favourable rate still leads to disadvantages of the HFC solution.
It must be noted that, even given 100% retention and complete decomposition (incineration, cracking) of the HFC blowing agent, the ecological bonus of the panel blown with N-pentane would be reduced, but it would still remain existent.

Part 2: Insulation for refrigerated vehicles using cyclopentane and HFC-365mfc

PU foam is used to insulate the walls of virtually all refrigerated vehicles used to transport perishable goods. High insulation performance and correspondingly low material thickness makes it possible to maximise the interior space and largely prevent ambient heat from entering.
Basically, in spite of higher heat transmission properties λ of a blowing agent, the total performance of an insulation system (expressed by the u-value in W/m^2K) may be maintained with greater thickness of foam. However, there are limits to how much the dimensions of exterior walls of refrigerated vehicles can be modified. Extension to the

outside must be ruled out because the maximum permitted vehicle width is already utilised. Extension towards the interior is limited because it has to be wide enough to allow transportation of standardised freight units (standard pallets).
In Germany, 3,000t of PU foam – approx. 4% of total inland consumption, excluding electrical appliances and OCF – are used per annum in insulation for refrigerated vehicles. This makes insulation for refrigerated vehicles a suitable reference case for examining the necessity of using halogenated blowing agents because the λ value of HFCs and HCFCs is considerably lower than that of pentane or cyclopentane. In the following, insulation properties for insulation using C-pentane-blown foam (u-value = 0.37) and HFC-365mfc-blown foam (u-value = 0.36) are compared.

Summarising the results on refrigerated vehicles

The ecological drawback of HFC-blown insulation foam is that it involves emissions of HFCs with high global warming potential during (a) manufacturing, (b) the use phase, and (c) disposal of the PU foam. On the other hand, the insulation performance of the cargo hold is approx. 2.5% higher than compared with C-pentane-blown foam. The thickness of the foam cannot be changed. Consequently, where C-pentane foam is used, the refrigeration unit (i.e. the compressor) consumes 2.5% more fuel (diesel) to maintain the same cargo hold temperature, resulting in 2.5% more CO_2 emissions from fuel combustion. In the reference case, the additional CO_2 emissions from the increased compressor running time are significantly lower than the CO_2 equivalent HFC emissions arising from the manufacturing, use phase, and end-of-life of the HFC-blown insulation foam.

In the application example of refrigerated vehicles it has been shown that:

- Even in cases where thickness is strictly limited, hydrocarbon alternatives have a better GHG balance than insulation made with HFC blowing agents if the present disposal conditions for the insulation foam from refrigerated vehicles (semi-mounted trailers) of virtually no recovery of blowing agent at the end-of-life cycle remain.
- The GHG balance of the examined refrigerated trailers basically comes down in favour of the pentane-blown option. However, this advantage is quite small in contrast to the previous comparison of insulation panels and can be reduced to an equal level by an increase in the annual operation time of the refrigeration unit. The far lower environmental benefit of the C-pentane system is based on technology: it is a result of the very high weight of CO_2 from combustion (here of fuel) in comparison to the CO_2 equivalent contribution of the blowing agent. The important role of fuel consumption is also represented in the cost balance. Not only in the reference case, but also in general, the operation costs for HFC systems are lower because the u-value and consequently the energy demand of the refrigeration system are lower.

- As long as the sensitivity analysis is based on currently realistic conditions, including total loss of blowing agent at the end-of-life, and reasonable operation times of the refrigeration system are assumed, the ecological advantage of a cargo hold insulated with cyclopentane-blown PU foam remains.
- If the refrigeration system operates for less than the typical 1,500 h/a, the GHG balance improves in favour of the C-pentane option – both in absolute and relative terms. If operation time is doubled to 3,000 h/a, the additional global warming HFC emissions (HFC option) drop in relative and absolute terms compared to the pentane option, but do not drop to the level of the latter (the same level would be achieved only if operation was almost continuous).
- If the refrigeration system is operated with diesel only, i.e. without the use of electrical power at standstill times, the CO_2 emissions from combustion increase. This gives the climate-relevant HFC blowing agent an even lower weighting in the total GHG balance. This means – under otherwise unchanged boundary conditions – that C-pentane's advantage narrows, without being lost completely.
- Even given a hypothetical improvement (decrease) in the u-value of the refrigerated vehicle insulated with HFC-blown foam of 2.5 - 5% compared to pentane, the pentane option would still result in less total CO_2 equivalent emissions. The two options would only be equal if the refrigeration system was operated for more than 5,000 hours over 18 years.
- The environmental benefit of insulation systems with pentane-blown foam in comparison to HFC-blown foam will only decrease and become negligible if the current disposal conditions for end-of-life refrigerated vehicles change.

If it is assumed that disposal of insulation foam improves fundamentally in Germany, then the GHG balance between HFC- and pentane-blown insulation foam would change considerably. If there were 70% decomposition of the insulation foam to be disposed (i.e. 30% loss of the remaining blowing agent when the refrigerated compartment is dismantled), CO_2 equivalent emissions would be equal assuming an annual operation time of the refrigeration unit of 2,700 hours, a value that may seem high but is not completely unrealistic.

Conclusion

It has been shown that:

- PU rigid foams blown with pentane have a better GHG balance than products where HFC-365mfc was used as the blowing agent because the higher energy consumption of pentane systems is more than offset by the high GWP of the HFC option.
- The special design of future disposal paths for PU rigid foams (incineration, deposition, material recycling) and consequently of emissions of the blowing agent is of central importance for the result of the analysis.

The question arises as to whether the results of the two cases analysed in this section can be transferred to other related applications. HFCs (-134a, -245fa and -365mfc) are potentially used in the following processes for the production of PU rigid foam:

- PU insulation panels – continuous production
- PU insulation panels – discontinuous production
- PU - block foam
- PU - spray foam
- PU - cast foam

Roof insulation panels are produced as continuous panels, whereas sandwich panels, e.g. for refrigerated vehicles, are produced in a discontinuous process. Since spray and cast foams are applied on site by the end user, e.g. on building sites, they inevitably need to comply with stricter safety requirements in terms of flammable blowing agents. Whereas this makes pentane questionable as a blowing agent for such applications, the results of this section are likely to be applicable to almost all industrial production processes for PU insulation panels and block foam. In discontinuous processes, there are virtually no technical objections prohibiting the application of pentane. Only in small enterprises with small throughput quantities of PU foam is it likely that the additional investments in fire and explosion protection needed to use pentane may render the operation uneconomical since the savings for the cheaper blowing agent per facility are small in comparison to the additional investments.
Over the long-term, ozone- and climate-friendly blowing agents such as pentane will be more sustainable and efficient than any of the fluorinated substances in both environmental and economical terms.

References

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Conditions for Conversion of XPS Foam Production to CO_2[1]

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Introduction

When discussing the conversion of XPS foam production, we actually mean the replacement of the (HCFC) blowing agent with a more environment-friendly alternative with zero ODP to fulfil the requirements of the Montreal Protocol. To assess such a replacement, the GWP characteristics of the blowing agent must be taken into account. Converting XPS foam production processes is not simple: several facets are involved, chemical as well as mechanical. We also have to consider that production lines run continuously, preferably 24 hours a day, and that unless conversion is of benefit to producers, they will not implement it.
In order to better visualise the production process, the following assumptions can be made: an extrusion line with a capacity of 500 kg/h, operating 24 hours a day for a total of 200 working days, produces 2,400 tonnes of XPS or approximately 70,000 m^3. This is only an estimate, as European and North American companies normally work with higher capacities and Article-5 countries (as defined in the Montreal Protocol) with lower output from a single machine. Nevertheless, it provides an insight into the logistical and cost aspects when discussing conversion.

Applications of XPS foam

XPS foam is mainly used in the construction industry as insulation material and as an alternative to traditional materials, such as mineral wool, EPS, polyurethane and others. The importance of proper insulation and its impact on the environment is well described in the following extract:

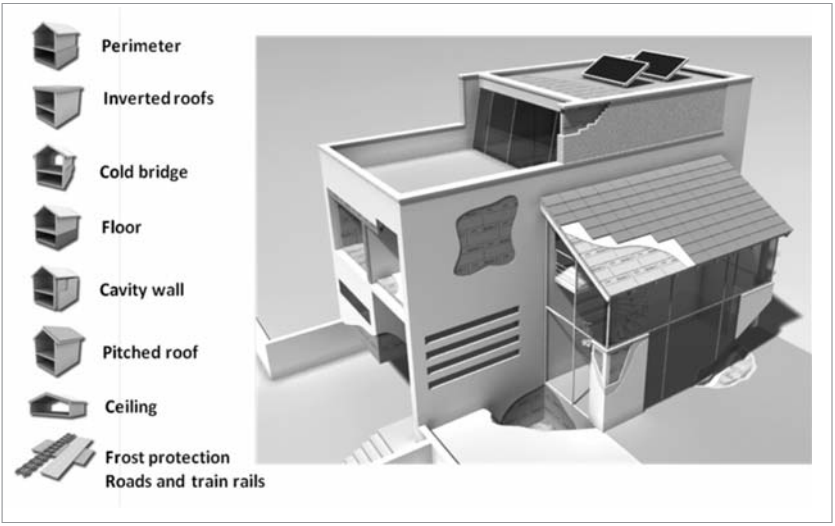
[1] Please note: the term CO_2 used in this article refers to 100% CO_2 as well as CO_2 + organic solvent

'In Europe, buildings account for 40% of total energy use with transport and industry accounting respectively for 32% and 28%. This makes buildings Europe's largest source of greenhouse gas emissions. Since it is possible to cut this energy use in half, through simple measures such as wall and roof insulation, buildings are arguably Europe's biggest energy wasters. Yet as insulation has been shown to be the most cost-effective measure to reduce CO_2 emissions, they have the potential to be turned from energy wasters into climate savers.' (Eurima, the European Insulation Manufacturers Association)

Article-5 countries in particular, with their growth rate in construction industry, provide an equivalent or higher potential for reducing greenhouse gas emissions.

Typical applications of XPS foam insulation are shown in Figure 1:

Figure 1: Examples of application of Styrodur[2]©



Raw materials used in the production of XPS foam

The main raw materials used to produce XPS foams are GPPS (general purpose polystyrene) and a blowing agent, plus small quantities of dye, flame retardants, nucleants and process aids. When discussing the conversion of XPS foam production, the main focus must be on the choice of blowing agent, since this component has the greatest impact on cost, the environment and machinery.

[2] Figure courtesy of BASF SE

The list of possible gases used is extensive. Table 1 gives a short overview of possible gases (CFC-12 has not been included as it will have been completely phased out by 2010).

Table 1: Gases used as blowing agents in XPS foam manufacturing

HCFCs	HCFC-22 HCFC-142b HCFC-22/-142b
HFCs	HFC-134a HFC-152a HFC-152a + acetone
HCs	Isobutane LPG (mixture of isobutane + propane)
CO_2	CO_2 + organic solvents e.g. ethanol, dimethyl ether 100% CO_2
Other	Vacuum technology HBA-1 (HFO-1,2,3,4ze), still experimental

In Europe, HCFCs were banned in 2002 (EU Regulation no. 2037/2000) and companies had to convert their production processes by switching to HFCs, HCs or CO_2. The European Union's Regulation no. 842/2006 restricts the use of certain HFCs as blowing agents and further limitations are expected within the next few years. It also stipulates that datasheets must specify the gas used in XPS boards. The quantity of gas remaining in the boards is not specified, but as most of the boards produced do not have facings, more than 90% of the gas will be emitted over time and replaced by air. Several authors have studied this phenomenon (Vo and Paquet, 2004) in which a differentiation is being made between blowing agents that have fugitive characteristics, i.e. within a short time are replaced by air (HCFC-22, HFC-152a and CO_2 for example), and blowing agents such as HCFC-142b or HFC-134a that are retained inside the XPS foam for longer periods. Boards foamed with fugitive blowing agents will have a thermal conductivity (λW/m•K) similar to air. Boards foamed with non-fugitive blowing agents will have better thermal conductivity. The choice of blowing agent and consequently the change in thermal conductivity may mean the thickness of the XPS board has to be increased to achieve the same R-value (thermal resistance m^2.K/W; definition and methods are described in EN 13164).

There are, however, several other factors that influence thermal conductivity, such as density, cell size, skin thickness and storage conditions. Additionally, the quality of the produced boards plays an important role. However, considering that small and medium-sized enterprises (SME) will most likely not have the same kind of laboratory equipment and quality control facilities as the major producers, especially for in-house measurement of thermal conductivity, this issue should not be considered the key factor in the decision to convert. Standard guaranteed thermal conductivity, based on air as cell gas and mechanical properties, in conjunction with long-term insulation properties, will provide a better tool for dimensioning buildings. GWP (considering ODP = 0 as standard) is considered to be more important for future conversion decisions, especially with regard to HCFC and HFC blowing agents. Furthermore, fugitive blowing agents such as HCFC-22 and HFC-152a, which do not give XPS board thermal insulation benefits, are usually expensive and not advisable. Hydrocarbons could be a solution for the future, but certification required by fire regulations can be an obstacle to using them as blowing agents.

Equipment change or retrofitting

What kind of changes to equipment have to be made when converting to a different gas? Since the physical properties of individual blowing agents are different and the blowing agent should be mixed in a liquid phase with the hot melt, the following issues have to be considered:

- Pressure rating of the extruder: for HCFC-22/-142b 90 bar, for CO_2 200 bar.
- How well the gas mixes with the hot melt can affect machine output. It may be necessary to set the screw's RPM at a slower rate and thus increase the mixing time. Design of the screw for optimum processes requires tailor-made screws.
- Design and expansion characteristics of the blowing agent to ambient pressure vary; the ΔP (pressure drop) therefore has to be adjusted.
- Cooling and heating characteristics.
- Safety systems for all HC and flammable mixtures.
- Market acceptance of thicker boards to achieve the required R-values.

In order to optimise the process, investments in new machinery will be required in most cases. This has to be offset against:

- Comparison of costs between raw materials and blowing agent used before and after the conversion.
- Physical properties of the XPS boards produced before and after conversion.

Considerations for conversion of XPS foam to HCFC-free alternatives

The first assumption is that manufacturers of XPS foam:

- encounter high demand for their products in their market,
- manufacture a product that complies with national regulations,
- offer their products at an appropriate price,
- are willing to convert their production process or are obliged to under national regulations.

Based on the above, it follows that the considerations listed below will play an important role in the selection of an alternative blowing agent to HCFCs:

- Considering the climate protection efforts that are being made worldwide, is a transition from HCFCs to HFCs worthwhile? Which alternative is most sustainable and economically beneficial, given the fact that HFCs are regulated by the Kyoto Protocol and scheduled to be reduced in the future?
- What will happen to the market position of a foam manufacturer if the conversion leads to higher direct costs for the product? It has to be taken into account that HFCs are more expensive than CO_2 or HCs and generally lead to lower thermal conductivity values.
- What is the availability of the blowing agent in the region?
- What are the reactions of competitors to conversion?
- How important is it to offer a product with a 'green' label and is this a marketing tool?
- Is the alternative technology a proven and established technology?
- Can the existing equipment be kept or will new equipment or a retrofit be necessary? Trials and errors with machinery not designed for the specific blowing agent can be costly.

At the moment, Proklima, GTZ's (Deutsche Gesellschaft für Technische Zusammenarbeit GmbH) programme to protect the ozone layer, is implementing a demonstration project in China. The project is funded by the International Climate Initiative launched by the German Federal Ministry for the Environment, Nature Conservation and Nuclear Safety. The project aims to convert the XPS foam production of a Chinese company from HCFC-22/HCFC-142b to CO_2 (+ organic solvent), an ozone- and climate-friendly blowing agent. The project's activities also include certification of the plants through TÜV and dissemination of the knowledge gained about cost-efficient and safe production of XPS insulation foams through the China Plastics Processing Industry Association.

The Chinese company Beijing Beipeng New Building Materials Co. Lt. has taken the decision to convert to CO_2 because they expect that it will yield significant cost benefits and also improve their position in the market. In contrast to many articles about conversion of blowing agents, we believe that the raw materials costs are a key factor in decisions to use natural blowing agents in continuous production processes. The conversion of plants will result in a total reduction of approximately 1.6 million tonnes/a of CO_2 equivalent direct emissions during production and use of foams.

Capital versus I(D)OC

Voluntary conversion will only occur if operating costs decrease (DOC) or the converted product has such beneficial characteristics that the market is prepared to accept higher costs and producers are willing to accept incremental operating costs (IOC). As most of the products are destined for applications in the construction industry, it is more likely that any conversion will be aiming to decrease product costs. Financial effects such as profit and loss balance sheets are secondary; the major consideration is reducing direct costs of the products, which can only be achieved by reducing the cost of:

a) raw materials and blowing agents,
b) energy,
c) manpower.

On a): Raw material costs can only be reduced by lowering the density of the product while retaining its mechanical and physical properties. Changing and optimising the blowing agent offers more opportunities for cost reduction.

On b): Given the same output and viscosities, there are few options for energy reduction. State-of-the-art plants with optimised heating, cooling and re-use of heat (released during cooling) will provide some benefits. However, this is also dependent on electricity costs, location of the factory and seasonal effects, since cooling water may be supplied from natural sources.

On c): Manpower costs are frequently an issue in developed countries, but in Article-5 countries they are often negligible compared with the high investment cost for equipment. A completely automated line from feeding through to cutting and packaging would run with 3 - 4 workers. In contrast, semi-automated lines need 2 to 3 times as many workers.

When considering converting the production process, the choice of the blowing agent offers the best potential for optimisation. The aim should be to reduce costs and select a blowing agent with the lowest GWP.

When looking at consumption levels for different blowing agents in Table 2, it can be seen that CO_2 has the lowest consumption, best GWP and, although it is not possible to quantify costs of blowing agents, since the variation between countries is too great and availability inconsistent, it can be said that CO_2 will be the lowest cost choice.

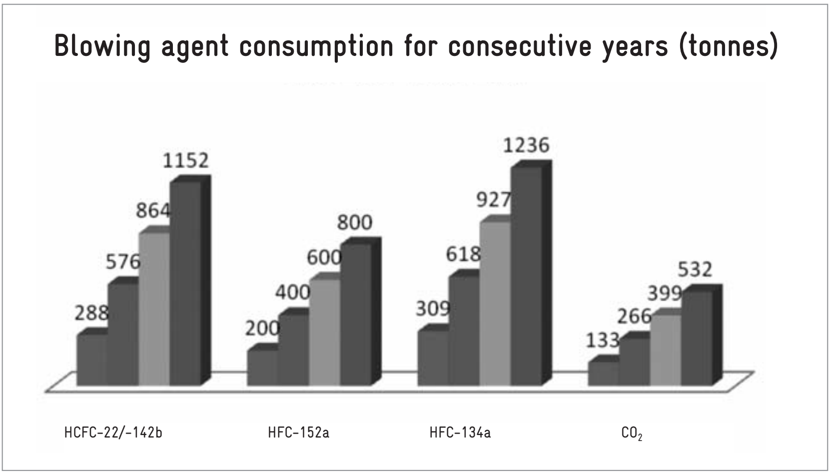
Table 2: Comparison of different blowing agents

GPPS (tonnes)	Blowing agent type	Blowing agent % on GPPS	Consumption of blowing agent (tonne/year)	Molecular weight	GWP 100yr
2400	HCFC-22/ -142b	12	288	95	≈ 2000
2400	HFC-152a	8	200	66	124
2400	HFC-134a	13	309	102	1430
2400	CO_2	6	133	44	1

GWP values IPCC report 2007
HCFC-22/-142b mixture ratio: 40%/60%

Note that a variety of combinations of blowing agent is being used and the percentage has been calculated on the basis of molecular weight.
For our example of the 500 kg/h plant and the percentage of blowing agent required, we can extrapolate the annual consumption from Table 2. The result is shown in Figure 2:

Figure 2: Blowing agent consumption for consecutive years



In a period of four years, the consumption of the blowing agent HCFC-22/-142b is about 600t higher than that of CO_2. This is just an example, but it is an important consideration when converting a production line. It is now up to producers to calculate their current blowing agent consumption and the benefit of changing to CO_2 or HFC-134a, for example. The calculation has to be carried out by the producer because there are several factors that influence consumption, primarily:

- machinery used, mixing capacity, design of the die,
- density achieved.

Statistical data for Article-5 countries are not yet available, which makes it impossible to carry out a comprehensive analysis at present.

On the other hand, we have to consider the investment costs for machinery. Conversion from HCFC to HFC will entail lower investment costs than conversion to CO_2. The reason is that an extruder using CO_2 must run at a higher operating pressure. If the extruder is not capable of handling these pressures, it will have to be replaced and the investment costs for the machinery offset against the gains from using more cost-effective blowing agents. HCs could also be considered, but flammability issues have not yet been resolved in all countries and some producers who have switched to HC have not been able to certify their products. HC would be similar to CO_2 in terms of costs and GWP but additional safety equipment would be required. In any case, the product costs of XPS boards will benefit directly from a more cost-effective blowing agent and will compensate for other economic drawbacks. Selecting CO_2 is the most environmentally friendly solution.

Conclusion

A company intending to convert has to critically review the costs of the blowing agent considering the impact on density, thermal conductivity and overall output since they directly influence the costs of the final product and therefore their ability to compete. They should calculate the costs of the blowing agent over a period of say four years and offset the benefits against capital costs for new machinery or retrofitting. Although there are many blowing agents to choose from, at present the most viable solution is CO_2 in terms of cost and consumption. This blowing agent has the best GWP, is available worldwide, and will not be subject to future regulations, as is currently the case with HCFCs and could apply to HFCs under a future climate change agreement.

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Ozone- and Climate-Friendly Blowing Agents in Foam Manufacture as an Alternative to HCFCs

JOACHIM MEYKE, KraussMaffei Berstorff, Germany

Introduction

The conversion of blowing agents for foams from 'ozone killers' to environmentally friendly ones has not yet taken place all over the world. A 100% conversion has been achieved only in Europe. The USA will follow suit in 2010; other countries, depending on their phase-out schedule, will follow by 2030 at the latest. But, in fact, it is not necessary to wait such a long time, since inexpensive and easy conversion solutions already exist. To give an example of such a solution, the following article will describe the conversion to environmentally friendly blowing agents used in the production of XPS foam insulating panels for the construction industry.

Conversion of XPS foam panel production

For more than 20 years, XPS insulating foam panels have been successfully used in the construction industry. Their main characteristics are pressure resistance and low hygroscopicity. Until 2000, these panels had been foamed with HCFCs. This was a physical foaming procedure, whereby a liquid blowing agent was directly injected into the resin flux through an extrusion plant. The foam panels were continuously produced, formed in line and automatically packed at the end of the line.

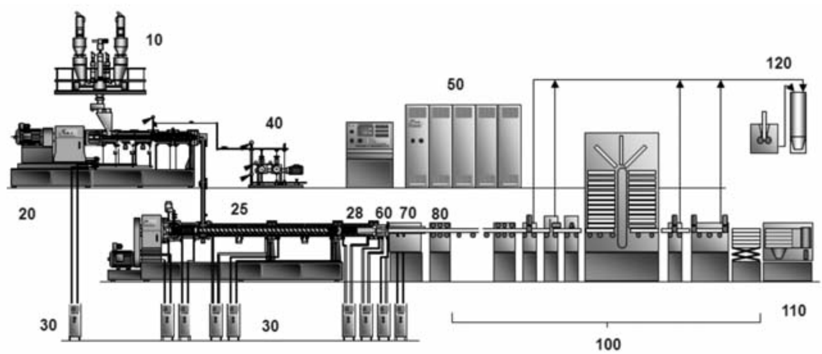
When choosing an alternative blowing agent to HCFC that maintains the required characteristics and quality of the foam, any possible economic and availability constraints have to be considered. After assessing the constraints and carrying out a number of tests during the conversion phase, CO_2 and ethanol seemed to be the overall best solution.

In Western Europe, most manufacturers of foam panels already converted their production to CO_2-based blowing agent systems six to eight years ago. CO_2 and ethanol are used as blowing agents for a foam thickness of up to 60mm. For thicker foams, a third blowing agent has to be used. This can be a hydrocarbon such as pentane or butane or an HFC.

CO_2-based blowing agents fulfil all the technical preconditions, are cheap and easily available. The qualities of CO_2-blown foams fulfil all requirements and test norms such as EN 13164. By making appropriate modifications and additions to their machinery, including safety-related changes if flammable blowing agents are used, the conversion to environmental friendly blowing agents has been successfully completed in the European foam industry.
The conversion costs depend on the age and size of the existing foam extrusion plant. Absolutely necessary purchases include additional blowing agent pumps with a tank plant, as well as a twin-screw extruder as the primary extruder to mix in the blowing agent. Installation of a gas warning system and an improved fire protection system is also recommended. Since the new blowing agent systems and the flame retardant can cause corrosion in the converting machine, the primary extruder should be made of corrosion-resistant steel. The total costs of converting technology in Europe to climate-friendly blowing agents at small plants with a 400 kg/h flow rate are about 40% of the investment costs for a new line; at large plants with a 1,500 kg/h flow rate about 60%. In any case, an exact analysis of existing machine technology is essential – including its economic efficiency. With some old plants, it can make more sense to invest in a totally new line.

Figure 1 shows the layout of a modern foam extrusion plant using environmentally friendly blowing agents.

Figure 1: Extrusion plant for XPS boards



10 Gravimetric feed system	60 Extrusion die
20 Twin-screw extruder ZE	70 Board calibrator
25 Single-screw extruder KE	80 Take-off unit
28 Static mixer/relaxing section	100 Cutting, stacking, milling
30 Temperature control units	110 Packaging
40 Blowing agents metering pump	120 Scrap-processing
50 Electrical Equipment	

A twin-screw extruder with a high screw speed provides good intrusion possibilities for the CO_2-based blowing agent, while maintaining good mass pressure and low energy influx. A large cooling extruder works during very low screw speed and optimised screw design with increased cooling capacity to balance the low cooling effect of CO_2. Because of the limited cooling effect when switching to CO_2, old plants must be run at a reduced flow rate.

As there has already been a move towards alternative blowing agents in XPS in Europe, KraussMaffei Berstorff has gained considerable experience. Both, blowing agent handling and the necessary plant engineering, have been very well tested and are now at a mature stage. Supported by early changes in legislation in Germany, industry was able to carry out the necessary conversion quite quickly. The investment costs were recovered quickly, since CO_2-based blowing agents are much cheaper than HCFCs. Industry's initial hesitancy to convert was soon overcome by the lower price of the CO_2-based blowing agent. As a rough guide, it can be assumed that one cubic metre of environment-friendly foam is about eight euros cheaper than HCFC-blown foam. That corresponds to 10% of the selling price of one cubic metre of foam.

KraussMaffei Berstorff is able to provide not only the equipment needed to convert to climate-friendly blowing agents, but also the necessary process support and help to start a plant. In its laboratory, there is a foam extrusion machine which offers the possibility to test clients' recipes, new blowing agents and processes.

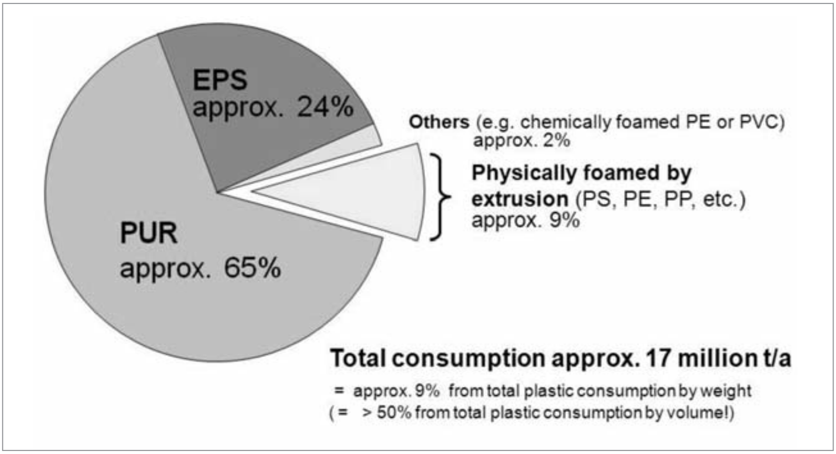
Focus on special injection technology

In Europe, climate-friendly blowing agents such as CO_2 and others have been in use for several years. Special injection technology and extrusion systems are needed to use these blowing agents. A tandem line consisting of a twin-screw extruder as a primary extruder in combination with a single-screw extruder as a secondary extruder for cooling is the best solution. With the twin-screw technology, up to three different blowing agents and polymers with different melt flow indices (MFI) and additives can be mixed in one stage. A large single-screw extruder is the best choice for cooling this 'blowing agent containing melt'. The following pages will elaborate on direct gassing by extrusion as a special technology for XPS, using environmentally friendly blowing agents.

What is direct gassing by extrusion?

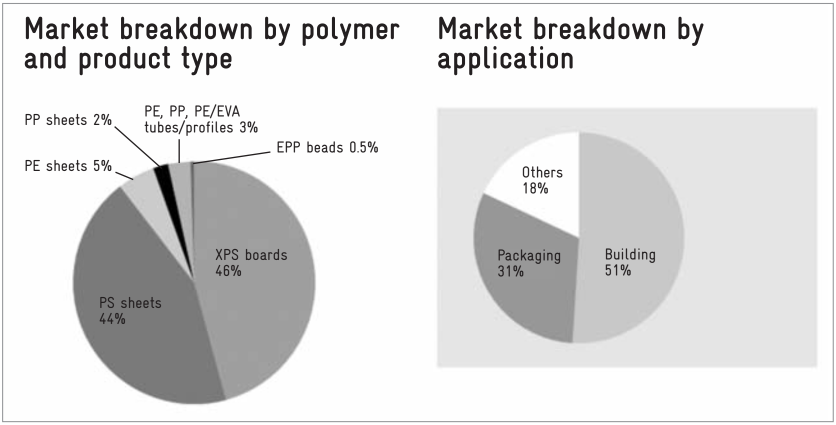
In 2006, total worldwide consumption of polymeric foams was approximately 17 million t/a. About 65% of this foam was PUR foam, 24% EPS, and 2% chemically foamed material such as PE and PVC. Roughly 9 - 10% was material that was physically foamed by extrusion, a method that is also called direct gassing by extrusion (see Figure 2).

Figure 2: Breakdown of polymeric foam consumption worldwide (source: KraussMaffei Berstorff)



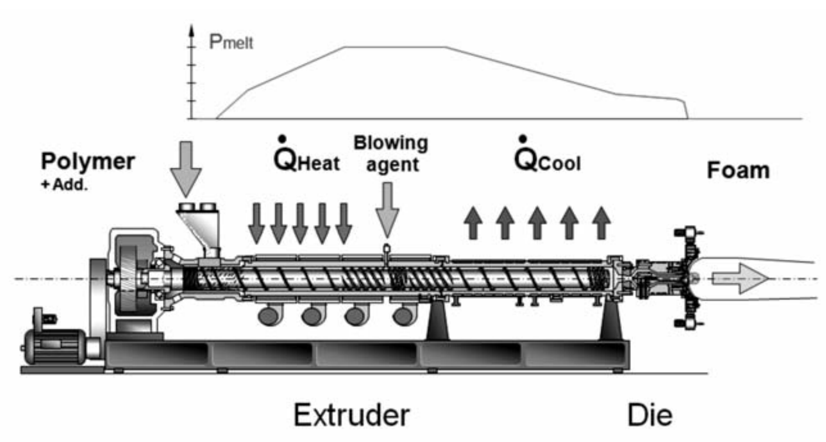
For this process, standard polymers such as PS, PE and PP are used most of the time, but PET, EVA, and others are also possible. The main market for these products is insulation material for the building industry, packaging products and products for the automotive industry and the leisure industry (see Figure 3).

Figure 3: Standard polymer market – a breakdown of usage (source: KraussMaffei Berstorff)



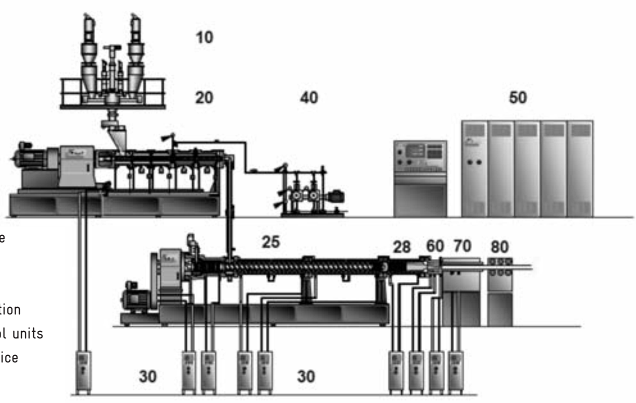
The principle of physical foaming by extrusion is shown in Figures 4 and 5. All additives and the polymer are fed into the extruder hopper and then melted into a homogeneous melt. At the length of 20 D, the liquid blowing agents are injected into the melt under high pressure (200 bar).

Figure 4: Principle of physical foaming with extruder, one-stage process



After mixing in the blowing agent, the melt has to be cooled down to the melting point of the main polymer. At the end of the extruder, there are different dies to form foam tubes, sheets or boards.

Figure 5: Principle of physical foaming with extruder, two-stage process



10 Gravimetric feeding device
20 Twin-screw extruder
25 Single-screw extruder
28 Static mixer/relaxing section
30 Liquid temperature control units
40 Blowing agent dosing device
50 Electrical Equipment
60 Wide extrusion die
70 Calibrator
80 Roller take-off

Environment-friendly blowing agents

In the following, we shall assess climate-friendly blowing agents in the light of several important requirements for blowing foam.

Environmental properties

The ranking of the environmental properties of the blowing agents is shown in Table 1. There are two main properties: ozone depletion potential and global warming potential. The ozone depletion potential of the 'bad types' CFC-11 and CFC-12 has been set to one and all other blowing agents will be compared to this. For global warming potential, the opposite is the case: CO_2 has been set to one and all other blowing agents are compared to CO_2.

Table 1: Environmental properties of different blowing agents

Blowing agent	Ozone depletion potential	Global warming potential, 100 year horizon
CFC-12	1	10,900
CFC-11	1	4,750
HCFC-142b	0.055	2,310
HCFC-22	0.055	1,810
HFC-134a	0	1,430
HFC-245fa	0	1,030
HFC-152a	0	124
		Data from IPCC
N-butane	0	11
N-pentane	0	11
I-pentane	0	11
Water	0	1
Carbon dioxide	0	1
Nitrogen	0	0
Ethanol	0	No data
		Data from AFEAS

Physical properties

The physical properties of different blowing agents are shown in Table 2. The best physical properties for a blowing agent are high molecular weight, a low boiling point, low vapour pressure and low vapour thermal conductivity.

Table 2: Physical properties of different blowing agents (Dechema, 1990)

Blowing agent	Molecular weight	Boiling point °C	Heat of vaporization kJ/kg	Thermal conductivity mW/m·K (°C)
CFC-12	120.9	-29.7	166	9.8
CFC-11	137.4	23.8	182	9.2
HCFC-142b	100.5	-9.8	221	12.9
HCFC-22	86.5	-40.6	235	10.5
HFC-134a	102.0	-26.5	217	13.7
HFC-245fa	134.0	15.3	-	14.0
HFC-152a	116.9	32.2	331	14.3
N-butane	58.1	-0.5	386	16.0
N-pentane	72.0	36.0	358	13.7
I-pentane	72.0	27.8	365	13.3
Water	18.0	100.0	2258	18.0
Carbon dioxide	44.0	-78.3	574	16.6
Nitrogen	28.0	-195.8	201	26.0
Ethanol	46.1	78.4	846	15.0

Most of these blowing agents have been tested in XPS foaming. Although their physical properties are not the best, CO_2 and ethanol have been chosen because some of the blowing agents with better properties have now been banned, are too expensive, or sometimes not available.

Flammability properties

For flammable blowing agents, it is recommended to install a gas warning system around the XPS foaming equipment. The following table will give an overview of the flammability of different blowing agents.

Table 3: Flammability of different blowing agents

Blowing agent	Vapour flame limits (vol. %)
CFC-12	None
CFC-11	None
HCFC-142b	6.7 – 14.9
HCFC-22	None
HFC-134a	None
HFC-245fa	None
HFC-152a	3.8 – 21.8
N-butane	1.8 – 9.0
N-pentane	1.3 – 8.0
I-pentane	1.4 – 7.6
Water	None
Carbon dioxide	None
Nitrogen	None
Ethanol	3.5 – 15.0

CFC/HCFC phase-out schedule

Under the Montreal Protocol on Substances that Deplete the Ozone Layer, the use of limited amounts of CFCs is still permitted (until 2010) and HCFCs (until 2030) in many parts of the world.

Product quality – foam density

Generally speaking, environmentally friendly blowing agents should achieve the same high foam quality and density as the CFCs and HCFCs that were used in the past. But CO_2 in particular is not easy to mix with polymers and the foam produced with it has a higher density and inferior physical properties. Mixtures of CO_2, ethanol and HCFCs or other substances (such as water, acetone etc.) were therefore used to obtain better foam properties.

There is a wide range of patents for blowing agent mixtures on the market and many companies are keeping their mixture secret. The blowing agent mixture is modified to achieve the particular features required of the final foam product. For that reason, it is not easy to pronounce judgement about the best solution.

Extrusion technology

Another important criterion for choosing a blowing agent and the technology needed to use it is price: CO_2/ethanol combinations are cheaper than HCFCs. Although the tank unit for CO_2 is more expensive and more complicated than that for HCFCs, the return on this investment can be achieved within one year, given a production volume of 150,000 m^3/year. The costs for the extrusion equipment are also higher than a standard line, but this is necessary to achieve good foam quality. In some cases, extra money has to be invested in corrosion protection for the screws and barrels.

Requirements for extrusion equipment for environment-friendly blowing agents

Intake of different polymers, additives and blowing agents

As we mentioned above, most foam producers use not just one environment-friendly blowing agent; they use two or three at the same time.

By using environment-friendly blowing agents such as CO_2 and ethanol, the amount by weight is lower than if CFCs and HCFCs are used. This increases the viscosity of the melt. To reduce the viscosity again – to ensure good cooling of the melt – it is advisable to mix two or three different MFI types of the polymer. For these two reasons, the best solution is a twin-screw extruder to ensure good mixing of the polymer types and a combination of two or three blowing agents.

Mixing capability

A co-rotating twin-screw extruder has excellent mixing capability. The possibility of a high screw speed and the fact that there are two screws guarantees very good mixing. A special screw design prevents a high shearing rate, but is also able to create enough melt pressure for the process. For a homogeneous distribution of the blowing agents in the melt, special mixing elements are required after the injection point. In the twin-screw extruder, various screw elements are mounted on a one-piece splined shaft. In that way, the screw configuration can be adapted to the process requirements. A wide range of screw elements with different geometries is available for conveying, mixing and shearing. Conveying elements with 0.75 L/D, 1 L/D, and 1.25 L/D have a different conveying capacity. Mixing blocks in different lengths are used for distributive mixing. Kneading blocks with 0.75 L/D and 1.25 L/D have a dispersive shear effect. Moreover, there are backwards conveying and kneading elements with increased pressure drop.

Cooling capacity

The second part of a single extruder or the secondary extruder of a tandem line has the task of cooling down the melt temperature. The requirements for good cooling behaviour are a low screw speed, a large cooling area and a low pressure drop over the length of the cooling extruder or cooling section. To achieve this, single-screw extruders with a diameter up to 400mm are used. The extruder barrels are cooled with water; the screw is designed as one large mixing element and runs at a very low screw speed, e.g. 2 - 3 RPM (rotations per minute) for a 400mm screw diameter.

The pressure difference between inlet pressure and outlet pressure of the cooling extruder is very important. It should be as low as possible. In practice, a delta p (difference of inlet to outlet pressure) of 10 - 20 bars can be achieved. The specific energy input of the cooling screw is only 0.03 to 0.07 kWh/kg (e.g. 75 kW for 1,500 kg/h).

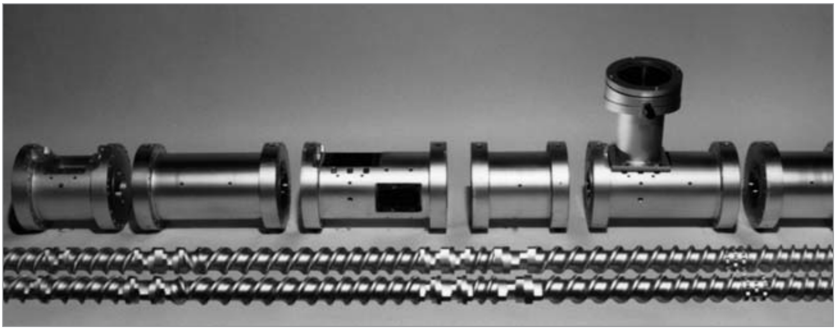
Solution: twin-screw/single-screw tandem system

Advantages of twin-screw/single-screw systems

The intake behaviour of a twin-screw extruder is far superior to that of a single-screw extruder. A twin-screw is able to take in a higher volume of recycled material and powder additives; some producers use a recipe that requires ten different components to be fed in. A twin-screw is more efficient for high throughputs up to 1,500 kg/h and much smaller than a single-screw extruder.

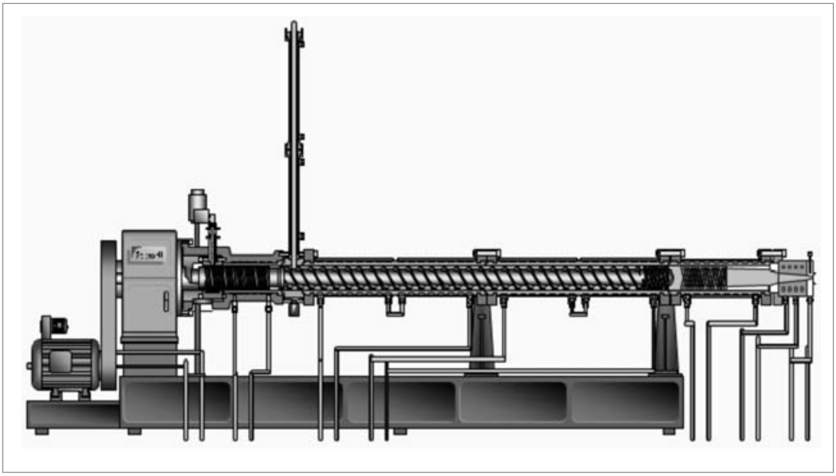
The modular design of the barrel and screw of a twin-screw extruder allows a wide range of possibilities for optimising the screw for special tasks such as split feeding, intake of powder and granulate, injection at different points etc. It is also possible to change the barrels, for example for higher cooling capacity (wet liner construction) or different lengths of 4 D or 6 D and additional injection rings. Finally, using a twin-screw improves the foam quality, creating better cell structure and cell distribution.

Figure 7: Modular design of twin-screw extruders



With its large barrel surface, one large cooling extruder has very high cooling capacity by comparison with other cooling systems. The cooling extruder works as a dynamic cooling mixer. This means the screw takes the melt from the cold inside surface of the barrel, allowing the warmer parts of the melt to contact the cold surface; the melt cools down and the insulation layer does not stick to the barrel. This high level of efficiency can only be achieved if the gap between the barrel and the screw is closed up (Figure 8).

Figure 8: Cooling extruder for foam lines



Active melt seal

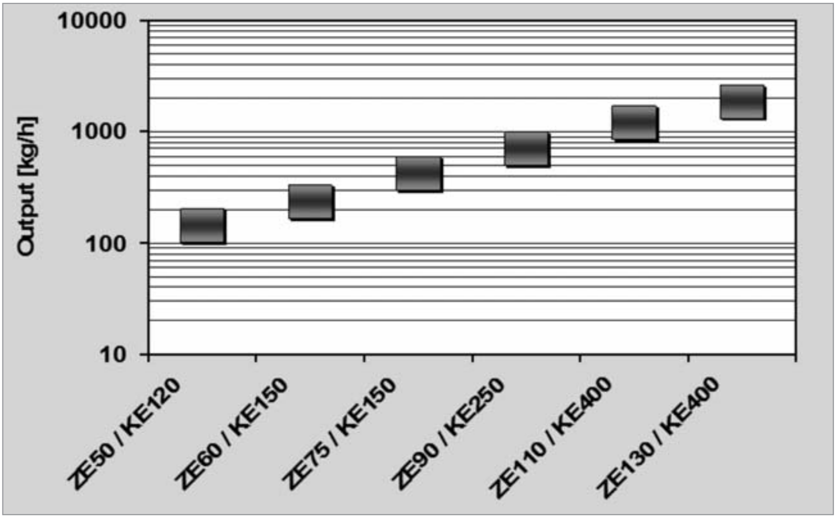
To prevent some of the blowing agents from escaping from the back of the cooling extruder, the active melt seal system was developed. The system works by feeding a small amount of polymer into the cooling extruder. Following intake of this polymer, the screw melts the material and the melt pressure that builds up is higher than the melt pressure in the pipe between the primary and the secondary extruder. This 'side feeding' of polymer, with a higher pressure than the main polymer flow, guarantees that no blowing agent can escape.

Figure 9: Active melt seal for cooling extruder

Different sizes of tandem line

For different outputs, different sizes of tandem line are used. Figure 10 shows extruder sizes from 200 kg/h up to 1,800 kg/h output. Using a tandem line with an output of less than 200 kg/h is not economical; for lower outputs a single extruder line is recommended.

Figure 10: Output and extruder sizes



Summary

In the last five years, many twin/single tandem systems have replaced the traditional single/single tandem systems to enable the use of environment-friendly blowing agents. The twin/single system is ideal for injecting different blowing agents and feeding different polymers and additives. For products made of amorphous polymers such as PS, and especially for XPS boards, CO_2 and ethanol and sometimes a third blowing agent (e.g. HCFCs) are used. For partly crystalline polymers (PE, PP) butane is used as a blowing agent in most cases where a low foam density (approximately 20 - 40 kg/m³) is required. High density foam (200 - 400 kg/m³) is produced by using only CO_2, N_2 or water (TPE-water foam).
Many companies are developing their own blowing agent mix, made up of the new environment-friendly blowing agents, to create a particular product quality.

Conclusion

A conversion to environmentally friendly blowing agents has already been successfully achieved in Europe. The necessary machine technology and process know-how are available and the foam products have been well accepted by the market. The expected disadvantages of CO_2 technology, such as loss in quality and higher prices, did not materialise. On the contrary, the conversion has proven worthwhile for producers and consumers alike and definitely for the environment!

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Retrofitting Foaming Plants to Use Pentane as a Blowing Agent

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Introduction

The knowledge that the use of blowing agents such as CFCs or HCFCs contributes to the destruction of the ozone layer and global warming, triggered changes in environmental legislation. The resulting bans on certain products and production methods prompted the development of new technologies. For the polyurethane industry this means that new blowing agents have to be used. Today, in the area of rigid or insulation foams, pentane is in widespread use as an environmentally compatible blowing agent.
The main applications of pentane as a blowing agent are in:

- the refrigerated appliance industry,
- foaming lagging around piping systems,
- the manufacture of metal compounds and insulating panels.

15 years ago, Hennecke GmbH was the first polyurethane machine and plant manufacturer to carry out plant retrofits in the refrigerated appliance industry. Since then, Hennecke GmbH has collected empirically proven figures from more than 500 completed pentane projects. The standards developed have been established worldwide and have delivered optimal performance in practice.
However, processors using pentane or pentane-containing polyurethane raw materials must take into account the potential hazard of explosive atmospheres being created. The explosion risk applies to the entire processing line, from the pentane storage area to the cured polyurethane foam. Hennecke has developed its Pentane Process Technology (PPT) to avoid these hazards.

Information required for a successful retrofit

To ensure a plant retrofit is effective, the plant-operating company should provide the following information:

A) Product information
- Dimensions of the end products
- Component weight
- Quantities/production volume
- Material consumption

B) Data on the foam system
- Amount of blowing agent in relation to polyol
- Polyol/isocyanate mixing ratio
- Raw polyol viscosity
- Isocyanate viscosity
- Blowing agent: C-pentane, N-pentane, I-pentane

C) Information on the place of installation
- Machine layout
- Floor plan
- Ambient conditions (temperature, height above sea level)
- Adjacent workplaces with potential ignition sources (e.g. welding or soldering)
- Raw material supply
- Form in which polyol, isocyanate and pentane are supplied (typically: drums, containers, tank vehicles)

D) Information on the existing plant or machine
- Machine type (wet-end), high-pressure or low-pressure
- Age, manufacturer, type
- Type of plant or machine control system
- Number of foaming places
- Description of the dry ends, plant components
- Description of foam filling (closed or open output)
- Type of mixhead guidance (manual guiding, robot, portal)
- Mould material (hazards due to static electricity)

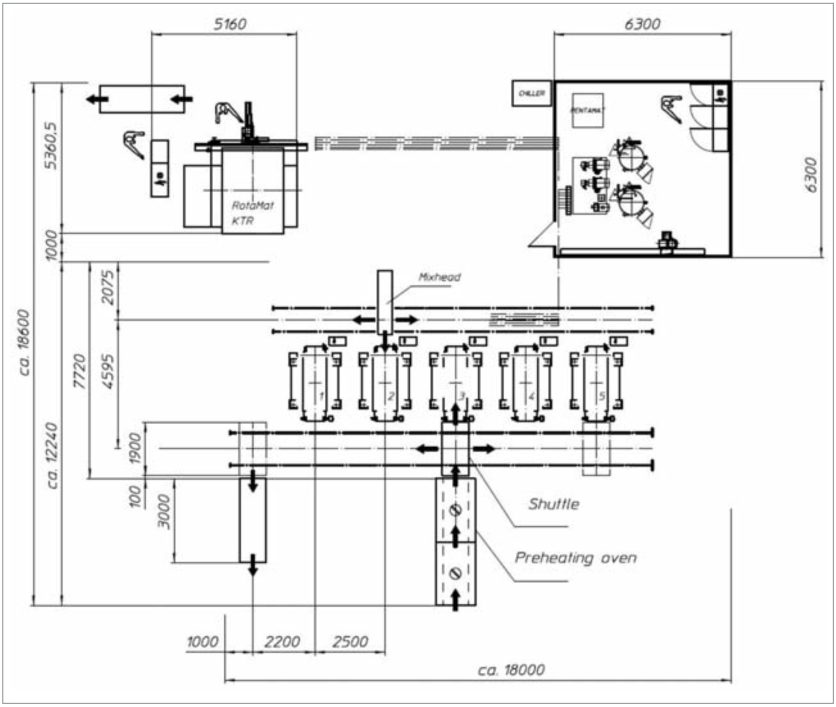
Pentane safety concept

The safe operation of a production system requires a consistent and comprehensive safety solution to be implemented right from the planning stage. Hennecke developed its Pentane Process Technology (PPT) to address this need. The PPT system is a graded and interlinked safety process comprising a combination of primary and secondary measures. All primary measures are aimed at one common, important goal: they prevent the formation of potentially explosive atmospheres at the outset. These measures cover the entire processing line, from the tank storage facility to the foaming station. This includes special fittings for the component lines, automatic switch-off devices, shut-off valves and nitrogen inerting equipment. Additional system and operational safety is provided by secondary measures such as:

- enclosures,
- special ventilation and exhaust systems,
- gas alarm systems with appropriate sensors,
- pentane extraction equipment,
- leakage monitoring and fault indicators,
- defined plant disables.

Case study 1

Figure 1: Retrofitting a plant for refrigerator manufacture



Characteristics of the plant:

Plant capacity:	240,000 refrigerator cabinets and doors p.a.
Working time:	4,800 hours p.a.
Cycle time:	72 seconds

Raw material consumption:

Polyol	910t p.a.
Isocyanate	1,000t p.a.
Pentane	135t p.a.

Retrofitting measures required:

A) Pentane storage
B) Polyol/pentane premixing station
C) PUR high-pressure foaming machines
D) Pentane-relevant dry-end retrofits
E) PPT safety control system (including all primary and secondary safety installations)

A) Pentane storage

Pentane is usually stored outside the factory building in underground or aboveground tanks. The design is similar to that of storage tanks at petrol stations.

Figure 2: Pentane tank

Designed as a buried tank, 20m³, double wall, filling gravimetrically by means of gas displacement line, including filling level indicator, overflow protection and integration into the pentane safety control system (PPT).

The following basic equipment must be provided:

a) Hoses
   Suitable hoses for liquid unloading and vapour return must be available and compatible with existing connections. Conductive hoses are required. Short liquid hose will minimise spillage after unloading has finished.
b) Level detection
   It is recommended that the tank level indicator should be readable at the unloading spot.
c) Overfill protection
   To be installed.
d) Manual emergency pushbuttons
   To be installed.
e) Emergency telephone
   To be positioned nearby.
f) Safety control system
   Unloading area to be included in the safety control system.

The different characteristics of underground or aboveground tanks are listed below:

Aboveground tank:

- Easy inspection
- Single-wall tank sufficient
- More protection required against fire, sun, weather
- Larger temperature variations – emission losses

Underground tank:

- Less protection required against fire, sun, weather
- Lower max. temperature
- Gravity sufficient for unloading truck
- Inspection difficult
- Double-wall tank with leak detection system needed

Instead of using tank storage facilities, the system can also be supplied from 1,000l containers or drums.
The selected design has to comply with national legislative requirements for the storage of substances that are easily flammable and detrimental to groundwater. Total explosion protection according to zone and alarm plans and integration into an approved safety concept must be ensured.

B) Polyol/pentane premixing station

At present, a commercial-scale supply of pre-mixed polyols is not available. In general, operators therefore have to prepare the mixture on site.

Primary safety measures for pre-mixing polyol:

- use of a double-shaft seal including safety sealing liquid system;
- pentane lines are equipped with two-ferrule tube fittings;
- polyol-pentane mix lines are equipped with two-edge cutting ring fittings;
- pipelines are equipped with two-edge fittings;
- safety sensors;
- use of pressure switch and safety valve technology.

As a secondary safety measure, integration into the extraction system and gas alarm system is necessary.

Figures 3 + 4: Pentamat premixing station, size 30

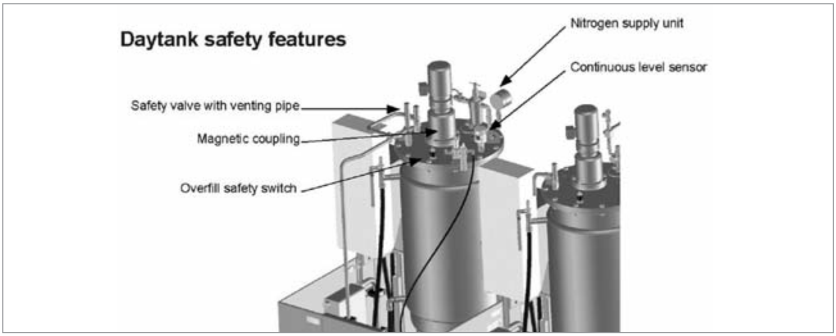
Design Pentamat 30, adjustable portion of pentane 4 – 25 vol.%, output base polyol: 26 l/min, metering output continuously controllable from 1.0 to 6.5 l/min.

C) PUR high-pressure foaming machine, two components

A high-pressure foaming machine is used for metering the mixture and blending polyol/pentane with isocyanate.

A basic requirement for the safe operation of the high-pressure metering machine is to prevent the formation of hazardous pentane/air-mixtures, i.e. the air-tightness of the system has to be ensured. For example, all dynamic seals are double and fitted with liquid safety sealing systems.

Figure 5: Daytank safety features



The different shot weight requirements for cabinets and doors are solved by putting in place a frequency converter for the high-pressure foaming machine's metering pumps.

The safety sealing system is a small container that is connected to the sealing gap. The container is filled with a sealing liquid and closed with a diaphragm. If a leak occurs, the level change in the tank is detected by a sensor and transmitted to the safety control system.

To avoid the formation of an explosive atmosphere, the following primary measures must be put in place for the polyol/pentane tank:

- the tank inside must be inerted with nitrogen;
- the stirrer shaft must be equipped with a double-shaft seal and safety sealing liquid system;
- double-sealing screw fittings;
- protection against overpressure;
- self-closing valves for filling and emptying;
- pentane-specific level metering and refill control;
- adjustable valve for nitrogen venting.

Figure 6: Daytanks for polyol/ pentane and isocyanate, size 500l including daytank 500l, structural size HK 1250 P, max. output approx. 2,500cm³ mix/s with 1 pc. mixhead type MX 26 for the cabinet plant and 1 pc. mixhead MX 18 for the door plant.

In addition, the work tank comes with automatic overfill protection and a permanently active level sensor that is integrated into the pentane safety control system.

Additional measures:
- Integration of the work tank into the extraction system
- Integration into the gas alarm system
- Integration into the PPT safety control system

Further primary safety measures are:
- Rigid pipe between machine and daytank
- Twin-type seal for drive shaft and hand wheel shaft/adjustment rod
- Closed venting system of the relevant analyse sections
- Closed filter
- Screw connections with double sealing function
- Mixheads with leakage monitoring
- Ring main closing valve with leakage monitoring
- Min./max. pressure monitoring
- Splash protection if required

Figure 7: High-pressure foaming machine, size HK 1250 with pentane extraction

D) Pentane-relevant dry-end retrofits

The dry part of a refrigerated appliance production line comprises supporting fixtures for the production of cabinets and stationary or mobile moulds for door production. Required safety measures:

- The area around the foam filling location requires a design that complies with the ATEX directive and implementation of the explosion and alarm zone plan.
- During the foam filling process, electrical loads such as the mould temperature control system must be disconnected.
- Integration of the plant into the equipotential bonding system.
- Integration into the gas warning system.
- Integration of the supporting fixtures or the door moulds into the extraction system. The extractors should be designed so that they capture the pentane gas right at the point of emission. The extraction system is controlled centrally by the PPT safety control system.

Fig. 8: Functional drawing, extraction system for supporting cabinet installation

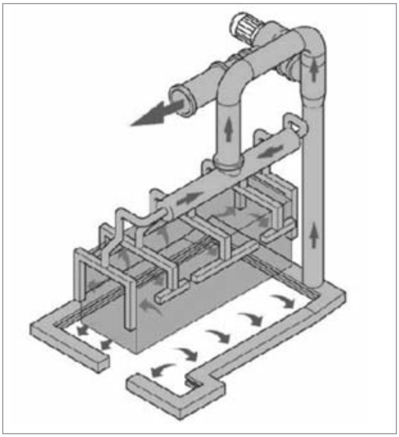


Fig. 9: Extraction system for supporting mould, cabinet – plant of type series KGS

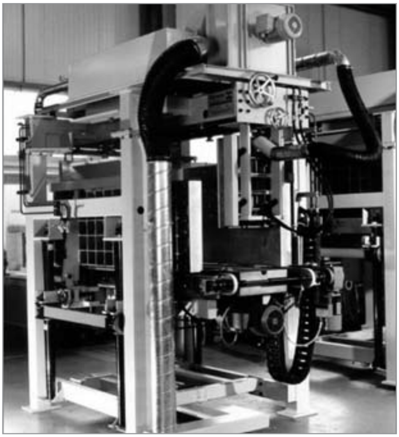
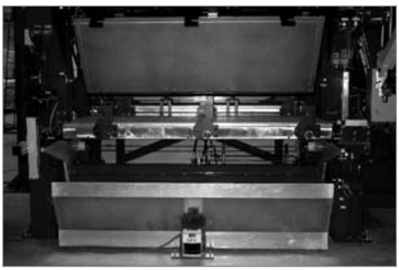


Fig. 10: RotaMat extraction system, reverse side

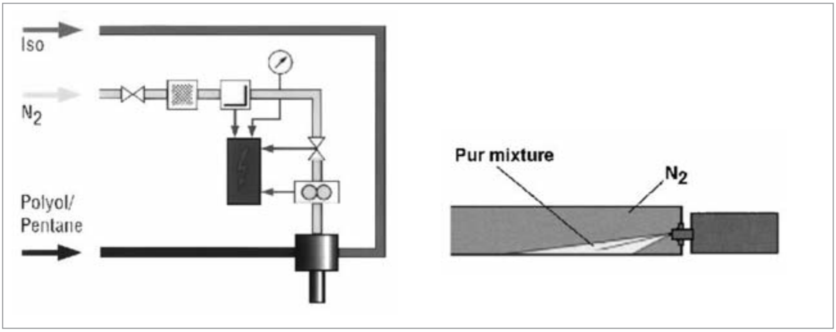
Fig. 11: RotaMat extraction system, operator's door plant



Inerting

Usually, foam is filled into the open mould for refrigerator doors. In contrast to closed-mould foaming, the mixture can be better distributed and charges can be smaller. Pentane gases emitted during the foam rise are diluted by the extraction system to maintain concentrations below explosive limits.
But when filling large, closed cavities such as refrigerator cabinets, an air exchange is not possible. The gas concentration may rise up to the explosion limit. Sparks that may ignite an explosion can be generated through the electrostatic charge of the refrigerator inliner or electric conductivity of the rising foam.
As a consequence, the cabinet is inerted with nitrogen. In the process, the oxygen concentration is reduced to a point at which an explosive gas mixture cannot be generated. The inerting process can be implemented either directly via the mixhead or by using a specific lance technique.

Figure 12: Functional drawing of the inerting process via MX mixhead



Specification nitrogen:

Consumption:	approx. 0.25 Nm^3/cabinet
Pressure:	13 - 15 bar
Consumption p.a.:	0.25 x 240,000 cabinets = 60,000 Nm^3 p.a.

E) PPT safety control system

The conversion to pentane and the additional need to handle explosive substances require an additional safety control system. This system allows the foaming machine to be started only if all fans are working properly and no pentane emissions or leakage have been detected. If a pentane emission or leakage is detected, plant controls must be disconnected from the power supply and fans switched to a higher speed.

The PPT control system includes:

- a wet part with a type HK 1250 P PUR high-pressure foaming machine and tanks, pentane sensors,
- the HK machine's sealing liquid monitoring system,
- a wet part extraction system, and
- an extraction system for the cabinet foaming line/door foaming line.

Fig. 13: Pentane sensor evaluation rack

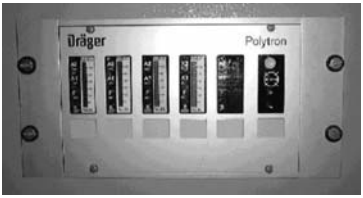
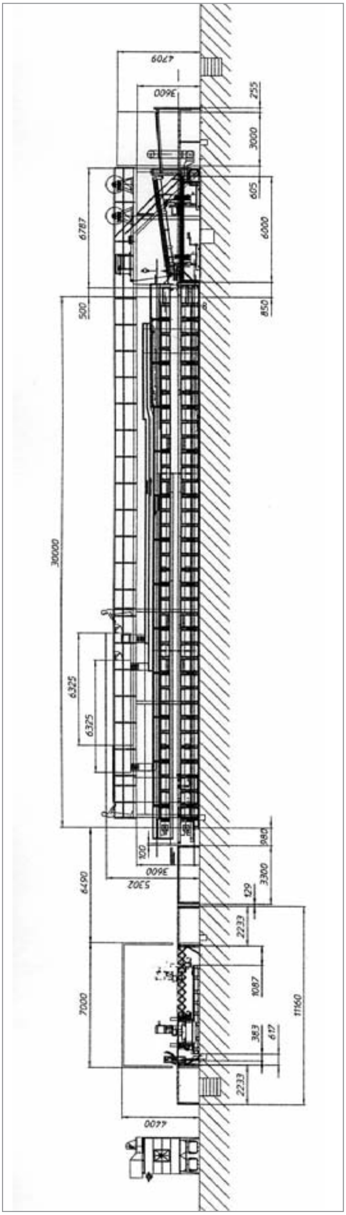


Fig. 14: Infrared pentane sensors

Figure 15: Retrofitting a plant for production of sandwich panels with metal facings



Characteristics of the plant:

Plant length:	Length of CONTIMAT pressure zone 30m
Production speed:	Depending on the element thickness, about 8 m/min on average
Production period:	230 days/year in a 1-shift system
Production volume:	About 1 million m²/year

Raw material consumption:

Polyol:	1,600 t/year
Isocyanate:	2,200 t/year
Pentane:	240 t/year

Retrofitting measures required:
A) Pentane storage
B) High-pressure metering unit
C) Plant retrofits such as extraction systems, pressure switches, safety thermostats
D) PPT safety control including central plant monitoring system

A) Pentane storage

In compliance with national regulations, pentane is stored either underground or aboveground (see above). Tank equipment should include a filling level monitor and overflow protection. The tank may be up to 30m³, double-walled, with a leakage monitoring device.

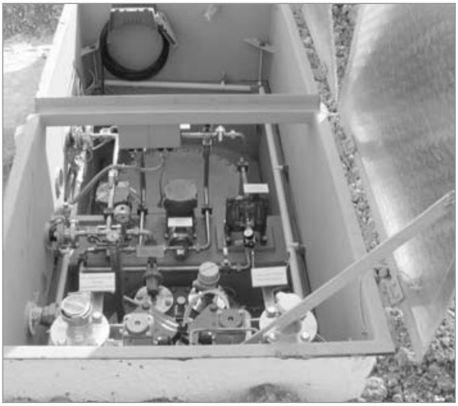


Figure 17: Dome shaft of pentane tank with feed pump set

Depending on the distance from the filling location, filling is either done gravimetrically or by means of a diaphragm pump and displacement line.

Figure 18: Filling location

B) High-pressure metering unit for pentane

For safety reasons, a metering unit to monitor pentane pressure is necessary. This can be in the form of a diaphragm pump.

Figure 19: Triple-diaphragm pump with extraction cabin

Designed as a leakage-free 3-head high-pressure diaphragm pump for outputs of up to 6.0 l/min. Pump heads with double diaphragm, with individual leakage monitoring, flow meter and electrical and/or mechanical components approved for use in explosion zone 1.

C) Plant retrofits such as extraction systems, pressure switches, safety thermostats

Extraction systems can be found in the following areas:

- Pentane metering
  The pentane metering station is installed in a booth, where it is ventilated constantly by changing the air about 30 times per hour.
  An incident occurs if about 20% of the LEL (lower explosive limit) is reached, the diaphragm rupture monitoring device of the pentane pump is actuated or the component pressure monitoring system is triggered.
  Encased in a sheet metal duct, the pentane high-pressure pipe is guided to the static mixer at the polyol pump table. This duct is connected to the booth's extraction system.
  To carry out maintenance work, a flexible hose with suction nozzle is installed in the cabin, thus enabling each point of the booth to be reached. The extraction system has to be switched on before the maintenance work is performed.

The exhaust air fan is admitted for extraction from explosion zone 1. The exhaust air is vented to an area where there are no ignition hazards.

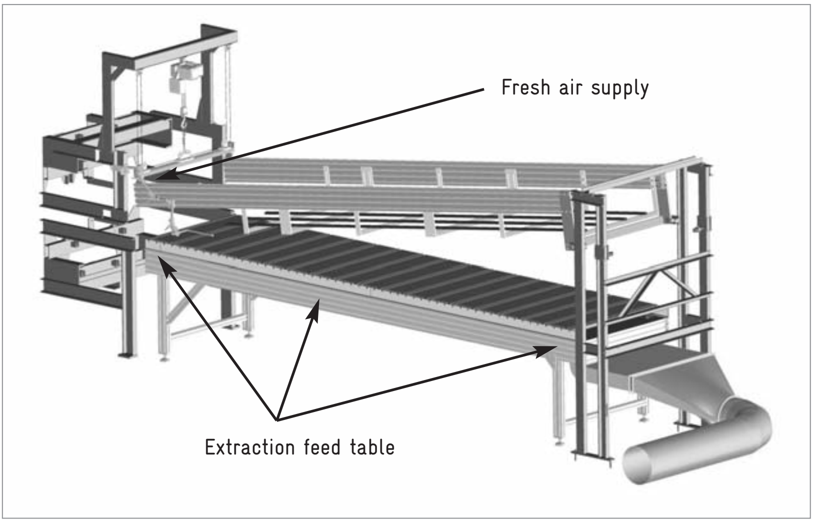
- Foaming zone

Figure 20: Foam injection area

The pentane emissions in the foaming area are collected directly at the point of origin. To this end, an extraction system is installed laterally beneath the feed table in order to remove the emissions. For any remaining emissions, additional extraction ducts are fitted to the floor in front of the conveyor inlet and beneath the feed table.

The exhaust air fan used is approved for use in explosion zone 2. The extraction system has its own power supply to ensure that it continues to operate even if the master switch is actuated in the event of an alarm.

Figure 21: Extraction system of foaming area



Differential pressure monitoring can be found at the extractors of the pentane metering unit and foaming area. The single-stage exhaust fans are a primary explosion protection measure for processing pentane. If a differential pressure switch is actuated, because a previously set operating vacuum and overpressure has not been reached, the plant is switched off immediately by the linked PPT control.

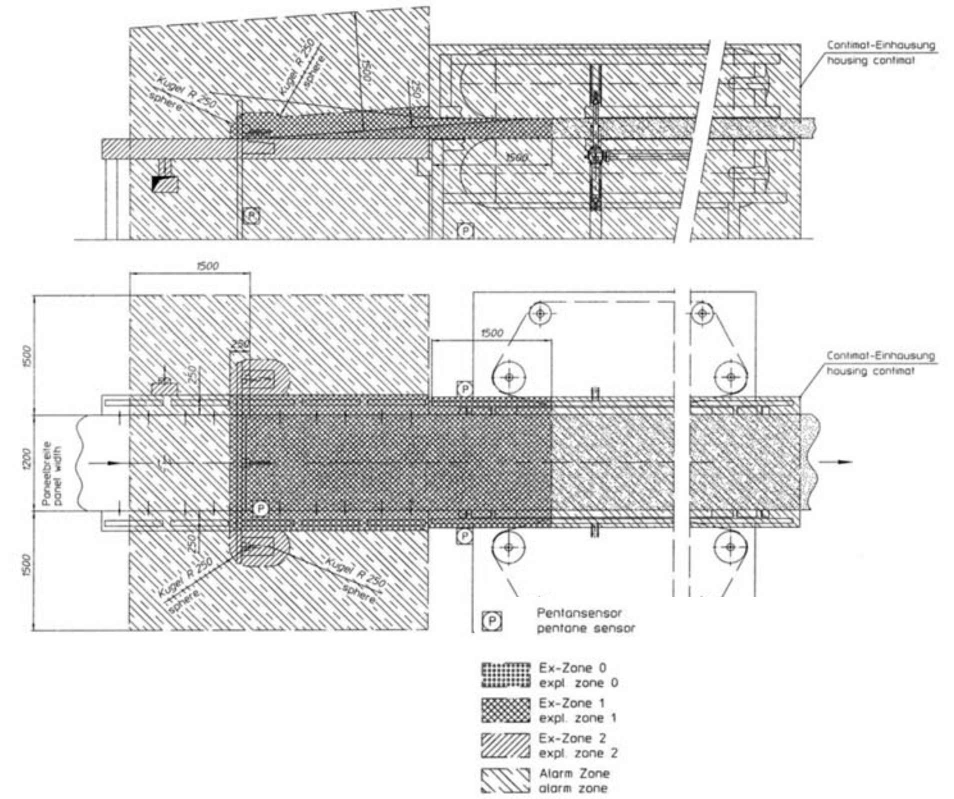
Figure 22: Differential pressure switch

Safety thermostats can be found in the CONTIMAT plant's forced-air heating system. A safety thermostat comprises a restart lockout, set to a temperature of 120°C max. (ignition temperature of pentane: 285°C). If the maximum temperature is exceeded, the plant is switched off immediately by the linked PPT control.

D) PPT safety control

The Hennecke PPT control concept was invented as a pentane monitoring system. An independent, decentralised control console displays all alarm indicators – relating to the primary and secondary measures – in order to make absolutely sure that no pentane or polyol-pentane mixture escapes into the environment or hazards arise from ignition sources. The electronic safety system monitors the entire plant and switches it off completely, if necessary.

Figure 23: Contimat's explosion/alarm zones



The most important alarm messages and responses to failures are:

- control of the extraction system at the foaming portal and safety cabin of the pentane metering unit;
- disconnection of the raw material supply and discharge;
- de-energising of inlet section, reaction casting machine, pentane metering unit, dispensing manipulator, CONTIMAT and cutting machine;
- general acoustic and visual fault alarm.

Gas alarm units are used to monitor a potential escape of pentane into the ambient air. These gas alarm devices monitor all critical plant areas, such as the metering, mixing and foaming sections, and provide for secondary safety. In the event of a failure, the ventilation system is switched to high-performance extraction and the entire plant is de-energised immediately.

Outlook

Not only is the use of pentane as a blowing agent an environmentally safe solution, it was also found that pentane-blown rigid PU foams have excellent insulation properties and allow optimum charge sizes. Pentane is available in most regions at relatively low cost. The label 'pentane-blown' is widely accepted by customers, so that manufacturers can use it as a marketing tool.

Another advantage of pentane is that there is no need to modify the actual foaming process in order to satisfy higher safety requirements. The necessary retrofit equipment is available and has been field-tested for many years. However, the key to achieving a successful retrofit is to define the necessary framework at an early stage in the project, nominate persons responsible for safety, and meet the requirements of the competent authorities.

Pentane technology is future-proof.

III. Case Studies

Cyclopentane as a Blowing Agent for PU Foam at two Brazilian Companies

KARL G. ALMEN, Consulting Engineer, Brazil

Introduction

The Montreal Protocol created the Multilateral Fund (MLF) to finance the elimination of ozone-depleting substances (ODS) in developing countries, including Brazil. Projects were developed for private companies using such substances with financing from this fund. The United Nations Industrial Development Organization (UNIDO) acted as an implementing agency for projects of this kind in Brazil for about ten years, from 1995 to 2005. UNIDO developed projects for more than 30 companies in the country, mostly producing commercial refrigeration, and also for some companies whose product was polyurethane foam for thermal insulation used mainly for refrigerated stores etc.

The PU formulation basically contains two reactive components: isocyanate and polyol. They must be metered and mixed thoroughly at the moment the mixture is injected into the mould. Different machines are used to do this. A blowing agent must also be included in the PU formulation; it is usually a liquid with a boiling point around 25°C. Due to the exothermic reaction of isocyanate/polyol, heat is liberated, which vaporises the blowing agent and causes it to expand until the PU foam fills the mould.

The standard blowing agent was CFC-11, but because of its high ODP had to be phased out with MLF financing. The obvious replacement was HCFC-141b. However, it has an ODP of 0.11, which is still relatively high, and like CFC-11, it also has high global warming potential (GWP). This was not originally taken into consideration by the MLF, but must be now and in the future.

One preferred blowing agent is cyclopentane which has an ODP of 0 and GWP of 3. It is highly flammable, which creates obvious handling and industrial processing risks. However, if safety rules and procedures are carefully implemented, cyclopentane performs as a very reliable and safe blowing agent. PU foam blown with non-flammable CFC-11 burns under certain conditions; PU foam blown with cyclopentane also burns, but not much more than CFC-11 blown foam. Cyclopentane's flammability is thus only of importance at the handling and processing stages.

UNIDO developed two projects for companies at Curitiba (Eletrofrio and Crios) in Brazil, in which CFC-11 was substituted by cyclopentane. Cyclopentane was chosen because of its zero ODP. The projects were concluded in 2001 and this article will look at what happened subsequently.

Eletrofrio Ltda.

The city of Curitiba is the capital of the state of Parana and is situated 400km southwest of Sao Paulo city. Curitiba has 1.8 million inhabitants and the Greater Curitiba area has more than 3 million. It is an important industrial centre with automotive industry (Volkswagen and Volvo trucks), domestic appliance manufacture (one of two Electrolux plants in Brazil) and is the site of Eletrofrio, the leading manufacturer of refrigeration for supermarkets in Brazil (and for Crios, the second project to be treated here).

Electrofrio was founded in Curitiba in 1946 and grew over the years into the largest supplier of refrigeration for supermarkets in Brazil. In 1996, it was identified by UNIDO as a possible recipient for a project funded by MLF.

The Eletrofrio plant is situated 15km south of downtown Curitiba, with a workforce of about 500 (400 of whom work in the production). The products are refrigerated displays for chilled and frozen foods and cold stores for larger supermarkets. They all include a central compressor plant. The company held a market share of 55% in the segment in 2007. The principal competitors in this segment are Carrier and Hussman, both funded by US capital, and Ameg, which is based on Italian capital.

Ownership and eligibility for MLF funding

A project was developed by UNIDO and later re-approved with some changes (using R-22 as a refrigerant instead of HFC-134a as originally intended). The project was approved by the MLF and the Brazilian Government and an agreement was concluded between UNIDO and the company. However, the company was then sold to US-based L.A. Darling Co, a member of the Marmon Group. Under MLF rules, a company with predominantly US interests is not eligible for funding, so discussions took place between UNIDO, the Brazilian Government and MLF on how to handle the new situation. The conclusion was that the Eletrofrio project had been approved according to Brazilian law and MLF rules when the company was still in Brazilian hands and a binding contract had been signed between UNIDO and the company. It was therefore concluded that the L.A. Darling Co, being the bona fide buyer of Eletrofrio, was the rightful owner of that company and all its assets, including the approved project, estimated at US$ 700,000 and that the implementation could therefore go forward.

When the Darling staff familiarised themselves with the project, they made a discovery that alarmed them: cyclopentane, a compound that is about as combustible as gasoline, would be stocked in great quantities on the premises and fed into an indoor industrial process.
The MLF would have been only too happy to rescind the contract and, besides, any modification of it would have rendered the contract null and void. But it was explained to Darling that, as a US company, they would not be eligible for any project financed by MLF with the exception of the existing project.
Reassuring evidence was also brought forward, demonstrating that the use of cyclopentane was not that dangerous. UNIDO demonstrated that at that time the product had already been used for a couple of years by some large manufacturers of domestic refrigeration, especially in Germany and, just to mention one example, by AEG at their Cassel plant. Ultimately, Darling conceded – albeit with misgivings – and the project went ahead.
In January 2002, L.A. Darling Co sold their interest in Eletrofrio to a group of private Brazilian investors and the awkward situation of having the Fund finance a US company thus resolved itself. This happened only two months after the cyclopentane foaming process became fully operational.

Safety situation

UNIDO took the safety situation very seriously: TÜV Süd in Germany, who had developed safety procedures for handling cyclopentane several years before, was entrusted with the safety aspects and approval of the installation and its certification for a fee of US$ 15,000. As required by TÜV, a back-up diesel generator was installed to supply power for the controls and evacuation fans of the foaming station in case of a power outage. A system for flushing the moulds with nitrogen before injection of the PU was also installed.
As stated by the company's CEO, Mr Luiz Renato Chueire, there had never been a case of explosion or fire at the plant since it was commissioned in 2001 – more than seven years ago. The cyclopentane was stored at Eletrofrio in a tank ($10m^3$ with thermal insulation and other safety items as specified by TÜV) 30 metres from the nearest building.
In rare cases (once or twice a year) the power supply might have been interrupted by problems at the power supply company, but to date the back-up power had always cut in and made it possible to safely shut down the foaming operation.
There are also safety rules in place that are rigidly enforced. The plant is subject to periodic preventive maintenance; it is shut down once a year during vacations and subject to a complete overhaul by a specialised maintenance technician.

Choice of refrigerant

At the time of the first project study (1996), the refrigerant used by Eletrofrio was basically CFC-12, which has an ODP of 1. The other alternatives considered in 1996 were HFC-134a and R-404a (for low temperature applications), both with zero ODP. The company had in the meantime set up one or two installations with R-134a, but had bad experiences with them: the extreme hygroscopic character of the lubricant oil and the difficulty of assuring absolute dryness in the extended pipe work caused major problems, so the project was re-examined and re-submitted in 1998 with HCFC-22 (ODP = 0.05) as the preferred substitute and with R-404a for low temperature applications. All three refrigerants have a relatively high global warming potential of over 1,000; in the case of 404a, it was as high as 3,800. This was not considered by MLF and was at the time ignored in Brazil. R-22 was favoured on the grounds that it was readily available in Brazil at a relatively low price. Compressors (open construction) for R-22 were also available in all parts of the country; compressors for the alternatives were not even available in Sao Paulo city. Thus, R-22 was the preferred choice.

Even today, the other substances remain problematic. To achieve zero ODP, the present alternatives would be R-404a or R-507. Both have a high GWP, which is a factor that has to be taken into consideration today. Thus, Eletrofrio themselves would not take the initiative of simply replacing R-22 with one of these alternatives, especially since their clients are not too concerned about ecological correctness. There are exceptions, however, and Eletrofrio is open to such cases. Thus, in Florianopolis (capital of the state of Santa Catarina, south of Parana), R-507 was used on request in a new supermarket installation. The owner was subsequently frustrated when it turned out that R-507 was not available locally and that no local refrigerant suppliers had any experience with this fluid. That situation will improve in the course of time.

Refrigerants with zero ODP and a low GWP include natural refrigerants, such as carbon dioxide, ammonia and hydrocarbons (e.g. propane). Reference installations do exist in Europe, but for all of them an indirect-type installation (with a brine circulation system or similar) would be necessary. In Brazil, on the other hand, direct expansion is still the standard. However, things are changing and Eletrofrio, who supply refrigeration for 200 to 300 supermarkets per year, installed indirect systems in 20 of them in 2007. This change of attitude among customers opens up perspectives for future use of the above-mentioned refrigerants.

Market situation

Eletrofrio had always been in the market segment of (larger) supermarkets with standardised modules for different types of displays, which are installed and connected to a separate machine room on site to fit in with the layout of the individual store. As part of the projects, Eletrofrio also supplied cold stores for their supermarket clients. The installation of the compressor room and the piping from the displays to the com-

pressors, charging, testing, commissioning etc. was carried out by Eletrofrio personnel or subcontractors.
The years from 1997 to 2004 were difficult for the industry, with low growth in the number of new supermarkets. The situation was aggravated by an increase in installed industrial capacity, with many new industries being established, especially subsidiaries of European or US companies. There was a fight for market share and fierce price competition which made life difficult for everybody.
From 2005, the rate of new supermarkets started to increase, which alleviated the situation in the industry. As the competition eased, it was no longer the case that market share had to be grabbed at any price. So the situation today is easier, although the total production capacity of the refrigeration industry is still greater than the actual market for new installations.
Eletrofrio has fared well in the years between 2001 and 2007, as the consumption data for raw materials for PU foam shows:

Table 1: Consumption of PU foam raw materials (in kg per year)

Year	Isocyanate	Polyol	Cyclopentane
2001	58,600	51,600	still R-141b
2007	245,950	185,700	22,000

Production

The impressive increase in PU foam production in those years depended in part on the fact that Eletrofrio gained market share in its segment. Furthermore, it depended on greater verticalisation of PU foam production. First, the production of PU insulated doors for cold stores (in supermarkets) was no longer farmed out (which hit Crios, as we shall see). Later, they preferred to buy the wall panels for the cold stores from a more efficient producer (with better prices than Crios). Since 2005, Eletrofrio has also been producing wall panels for the cold stores in their existing plant. These consist of a sandwich-structure with thin (0.8 mm) pre-painted aluminium outer panels and a core of 50 or 70mm PU foam, which can be linked together to form walls, roofs and floors for the cold chambers.
The project paper contains a sentence: *'The funds requested will in no way be used to expand the production level of the company.'* But there has been a considerable increase in the production level at Eletrofrio. It must, however, be taken into consideration that the capacity of the PU injectors supplied for the project (in kg/s) is determined by the quantity of PU needed per shot to fill the largest component being foamed. The reason for this is that the duration of the shot cannot be more than 10 or 20 seconds

because otherwise the foam would start to polymerise before the mould is completely filled, causing poor distribution of the foam. Thus, the time the injector is actually operating is an insignificant part of the production cycle. Most time goes into preparing the components for foaming and assembling them in the mould, sealing off any possible leaks with adhesive tape etc. and, after the foaming process, removing the moulds, letting them cool and then releasing and cleaning the foamed components. If the process can be organised efficiently with a plentiful supply of moulds being prepared and a way of bringing them to the PU injection station in rapid succession, production can be considerably increased using the existing equipment. These secondary means for increasing production were not supplied by MLF but by the company itself during the years to follow. The company also invested in a spare mixing head in case of emergency (if the foaming stops, the rest of the production would also grind to a halt).

During testing and initial production an unfortunate incident occurred: isocyanate was held for too long in the 70m feed line from the outside tank to the daytank on the injection platform, causing it to polymerise. The tubing had to be exchanged (at the company's expense). 'This would not happen today', said Mr Chueire, 'The isocyanate is now in constant circulation'.

Quality of the PU foam

As the foam is basically used for thermal insulation, the chief concern is its thermal conductivity. Everything else being equal, the new foam with cyclopentane should be slightly worse than the 'old' foam using CFC-11 because the conductivity of cyclopentane is slightly worse. In practice, this is not quite the case. We must compare the earlier situation at Eletrofrio when the foam was produced in a low-pressure machine using a mechanical (impeller) mixing head with the current situation in which the new foam is produced in a high-pressure mixing head that guarantees very homogenous foam with small cells. This in effect compensates for cyclopentane's slightly worse heat conductivity and the experience at Eletrofrio was that the heat transmission through PU insulated parts was practically unaltered 'before' and 'after'.

Furthermore, the majority of PU-insulated products are open displays where the main heat loading (more than 80%) comes not from heat conduction through the foam, but from infiltration of warm and humid outside air and from heat irradiation from the ambient air.

Another consideration related to the hot and humid climate in Brazil is condensation on the outside skin of the refrigerated display cases. In the past, the PU produced with a low-pressure machine was less uniform; there were streaks of 'bad' foam where the humidity of the air condensed, which caused complaints from the market. Now, the consistent quality of the foam means that condensation very rarely occurs and, if it does, it is uniform and can be attributed to extreme climatic conditions. This is normally accepted by the customers.

What would Eletrofrio's present situation be without an MLF project?

This is a hypothetical question, but Mr Chueire answered as follows:
Since CFC-12 has not been available on the market since 2004, the company would have had to switch to HCFC-22 as a refrigerant. If customers want a 100% 'green' installation, they must specify this, opt for a zero-ODP refrigerant and pay the additional cost.
Since CFC-11 has similarly been unavailable since around 2004, the company would have had to choose HCFC-141b as a blowing agent for PU, despite the fact that its ODP is as high as 0.11. Very probably, cyclopentane would not have been introduced due to the high investment costs involved. The company would probably still be using more modern versions of low-pressure injectors and not high-pressure machines, due to the high investment costs.

Crios Industrial Ltda.

When the project for Eletrofrio was being prepared, a supplier of theirs was identified with a fair consumption of CFC-11 for PU foaming. At the time, Eletrofrio purchased the insulating elements for cold stores (wall, roof and floor panels and insulated doors) from an independent supplier: Crios. Their consumption of CFC-11 at the time of the project was considerable: 46 t/year in 1996 and increasing. The decision was taken to set up a parallel project for Crios, utilising the synergetic effect.
Citing from the project document of 1998, two possible technologies for eliminating CFC at Crios were evaluated. They are shown in Table 2 below.

Table 2: Comparison of CFC replacement options

Blowing agent	ODP	GWP	Consequences
HCFC-141b	0.11	630	Almost drop-in replacement. Minor adjustments to production process and PU formulation.
Cyclopentane	0	3	Special technology needed. Additional equipment has to be installed to ensure safe operation. Different PU formulation.

The first alternative would have resulted in a fairly inexpensive project for the MLF, but phase-out would not have been complete. The second alternative was more interesting for Crios and for the ambitious project planner at UNIDO. But cyclopentane was a problem at the time – no projects with cyclopentane had been carried out in Brazil, partially because of prejudices against its flammability and ignorance about how to handle it. There was also the problem of supply – there was no market for cyclopentane in Brazil at that time.
The alternatives were put to Crios: either accept a project with HCFC-141b, but it will attract only a low level of funding because it involves little investment and has few associated problems; or we can carry out a cyclopentane project. This would attract the full quota of US$ per kg of CFC and an extra perk. We can ask 30% over the normal rate because we will be using a flammable substance (the MLF later revoked this rule on the instigation of the USA). You will acquire a great deal of equipment, all paid for by the MLF, and you will be one of the very few foam-processing companies in Brazil to be able to offer a 100% 'green' foam. But there will not be any money left for incremental operating costs and you will have to contribute by picking up some of the investment costs. Crios chose to pursue the cyclopentane project. A total of US$ 357,000 was requested from the MLF and the project began.

A specification of the incremental investment costs from the project document follows in Table 3.

Table 3: Overview project investment costs

Item	Description of activity	Quantity	Unit cost US$	Total US$
1	High-pressure foaming machine incl. metering pump, two mixing heads, control panel, two vessels (each 200 litres) with stirring equipment; with an output of up to 5kg a shot	1	140,000	140,000
2	Premixing station	1	60,000	60,000
3	Gas detection system (pentane sensors)	10	2,500	25,000
4	Exhaust and ventilating system (explosion-proof ventilators and motors, flow sensors)			
5	Tank for cyclopentane ($2m^3$) incl. transfer pump and safety equipment	1	10,000	10,000
6	Low-pressure system to circulate cyclopentane between the tank and foaming machine	1	10,000	10,000
7	Control and monitoring system	1	12,500	12,500
8	Modification of jigs and fixtures (design)	44	300	13,200
9	Nitrogen inertisation ring line	1	Crios contribution	
10	Emergency generator	1	Crios contribution	
11	Engineering, commissioning, start-up, training	1	20,000	20,000
12	Safety certification	1	15,000	15,000
Total funds requested				**305,700**

Difficult years for Crios

The project began in late 2000. From the beginning of 2001, CFC-11 (or any other halogenated hydrocarbons) were no longer used at Crios. At a final meeting at the company with representatives of UNIDO in 07/02/2001, Crios agreed with the project and reiterated their intent to produce 'green' PU foam exclusively in the future. However, there was the question of raw material costs:

Table 4: Raw material costs

CFC-11	2.30 US$/kg	Polyol/MDI for CFC-11	2.82 US$/kg
Cyclopentane	4.60 US$/kg	Polyol/MDI for cyclopentane	3.32 US$/kg

Cyclopentane was twice the price of CFC-11 but, on the other hand, only half as much is used in the formulation. But the new PU formulation was 18% more expensive and there was no compensation for that. Nitrogen flushing the moulds etc. also incurred additional costs so that in the end the new PU foam was more expensive. But it was hoped that the green foam would fetch a higher price than the traditional one and therefore at least compensate for the higher cost.

This hope did not materialise. The clients (Eletrofrio and others) did not show any inclination to pay more for the superior product. Then, on top of this, Eletrofrio decided to foam the cold store doors at their own plant – after all, they had fine new equipment. Furthermore, Eletrofrio found a better supplier for the wall panels in Danica of Joinville (130km away). They produced far greater volumes of insulated panels and could offer a better price. UNIDO subsequently also carried out a project with Danica, in which CFC-11 was replaced by cyclopentane.

So Crios struggled on, selling their green products in competition with various other smaller companies that still plodded on with CFC-11 as the foaming agent. When CFC-11 got scarcer and the price started to rise, these competitors migrated to HCFC-141b with modest investment costs. Price competition was fierce – those were the years when there was an expansion of the supply (of PU) without a corresponding increase in demand. Crios was at times near to closing down and most of its competitors did actually fold during these years.

No more cyclopentane in barrels

In the end, no storage tank for cyclopentane was supplied during the Crios project due to budget limitations. They therefore had to buy the liquid in barrels. A special pump was provided to pump it from the barrels to the machine's daytank. After a couple of years, in 2002, the supplier informed Crios that they would not supply the product in

barrels any longer, but only in bulk. They suggested Crios to install a tank similar to that owned by Eletrofrio ($10m^3$). This was out of the question for Crios: they did not have available funds and their consumption was not large enough to warrant a tank that size. They shopped around – without success – for other suppliers of cyclopentane who would supply in barrels. Today some do exist.
They were naturally resentful – first being encouraged to carry out a cyclopentane project and then being left out in the cold in terms of supply. After a difficult time, they found another solution, namely to use a new PU formulation (commercial name: Ecomate) that uses formic acid as the foaming agent (also with zero ODP) purchased from a Brazilian supplier in the state of Sao Paulo. The product was more expensive, but, on the other hand, was not inflammable, so the moulds did not need to be nitrogen flushed before injection.
Crios could have complained over the supply situation to UNIDO and UNIDO might have taken up the situation with PROZON, the Government agency that administrates MLF business in Brazil. This possibility did not occur to Crios – the problem was theirs, nobody would give them any real support (they felt) and they would have to find a solution for themselves.

Service problems

There is one renowned supplier of high-pressure PU injection machines that also has its own service organisation in Brazil. Due to budget restrictions, a competing manufacturer with a lower price was chosen for the Crios project. Later on this caused problems for them with regard to service, which was supposed to be the responsibility of the Brazilian agent of that manufacturer. 'This didn't work well', said Ms Kattie Paluch, managing partner of Crios. It seemed they were not really interested, spare parts often had to be imported and, when parts were available, the wrong ones were sometimes dispatched.
A critical situation occurred when one of the machine's high-pressure pumps broke down. The representative offered a spare pump for US$ 12,000 - FOB British port. It would have had to be imported with all costs – including freight, duty and taxes – paid by the buyer and with a delivery time of at least 40 days (!). And in the meantime, the production would be at a standstill. The solution Crios found was to buy a pump from a Brazilian dealer, in stock in Sao Paulo, at a price of US$ 34,000 plus 6,000 for taxes, freight and labour. Ms Paluch rapidly got a loan of US$ 40,000 (in local currency) through Crios' bank and within three days the new pump was in place and production running.
For preventive maintenance twice a year, the company uses a service technician from Porto Alegre (700km to the south), incidentally the same one as Eletrofrio. 'He is quite expensive, but worth it', said Ms Paluch in a conversation with the author.

New products with better margins

From 2005 onwards, things started to improve: demand for commercial refrigeration grew and Crios started to develop new more labour-intensive products for companies who had specialised in PU foam with zero ODP and were prepared to pay for it. Vacuum forming was developed and used for composite products (see examples below). The workforce is about the same size now as when the project was initiated 10 years ago: 30 people working in two shifts in the production plus six in administration and engineering. Far less PU, but significantly more labour goes into the present products. Three products/product lines account for 90% of the capacity:

A) Insulated doors for refrigerated counters
Gelopar is an important manufacturer of commercial refrigeration in Curitiba. The products are not site-installed, as is the case at Eletrofrio; they are self-contained refrigerated counters for bakeries etc. with a glass front and, at the rear, doors of about 600 x 500mm for access to the food. These doors are among Crios' main products. They make about 35,000 per year in different sizes with an average of 260g of PU foam or 9 t/year, exclusively for Gelopar. The doors have outer and inner liners of vacuum-formed high-impact polystyrene (HIPS) processed by Crios and a magnetic gasket, all foamed together into one rigid unit.

B) A line of insulation units for industrial valves for T&A (Tour&Andersson)
They have an outer shell of vacuum-formed HIPS and inner foam insulation – two halves, snapped together on the valve. They come in five sizes from TA 15 to TA 50. They use 2,100 pieces, equating to 120kg, of PU per year.

C) Insulated channels for supermarket installations
These channels house the tubing between food displays and the machine room in supermarket installations. The channels are of rectangular cross-section in ten sizes from 130 x 170mm to 250 x 520mm and have a unit length of 3m. They come with an outer cover of white or beige HIPS and are foamed out with 40 – 50mm of PU. Current production levels are 850 pieces and a total of 2.9 tonnes of PU foam per year. The channels are installed on site, on top of cold rooms etc. or under the ceiling. The tubing is installed in the channels which are then covered and foamed out with one-component PU foam.

Figure 1: Current Crios products

Door for Gelopar counter

Insulation for T&A valve

Conclusions

In a certain sense, the Crios project was bad business for MLF because it did not lead to a very large reduction in the quantity of ozone-depleting substances in Brazil. On the other hand, the Eletrofrio project was in the same way good business, because today they process almost four times as much PU foam as when the project was planned and with zero ODP and almost zero GWP.
Crios, of course, benefited from the project. Without the MLF equipment they would probably have had to close the business during the difficult years between 2000 and 2005. Today, they have access to a high-pressure injection machine that produces excellent quality foam. Some of their present products (the Gelopar doors) could not have been produced on the machine they had before and the current machine makes it possible for them to quote on components that not everyone in the business can produce.
Since the new PU formulation is not inflammable, the safety equipment (diesel generator, pentane sensors, nitrogen flushing etc.) is not in use, but is on stand-by should the situation change.

Implementation of Natural Blowing Agents in Companies with low ODP Consumption[1]

Case studies from MLF projects under the CFC phase-out scheme supported by the United Nations Development Programme (UNDP)

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Introduction

This article presents three MLF-funded projects, implemented by UNDP, that address the application of ozone- and climate-friendly blowing agents as alternative substances to CFCs. It focuses on the specific problems of each project and how the conversion from CFCs to natural blowing agents took place.

Egypt: Application of LPG in XPS manufacturing

In Egypt, UNDP prepared a project to phase out the use of CFC-12 in extruded polystyrene (XPS) foam as early as July 1992. Although this project – for a company named Al Sharif – received approval, its implementation faced budget, legal and economic problems from the beginning and therefore took until November 2001 to complete. By then, a close connection had been forged with the engineer/plant manager who stuck with the project all the time. Two other XPS companies fared no better and their projects had to be cancelled. However, in 2001, another XPS producer made itself known. Its production facility was part of a larger unit making other kinds of plastic disposables, which meant it had been overlooked by UNDP's identification programmes until the local government advertised its intention to phase out the use of CFCs in the foam sector.

[1] Information about the projects was kindly provided by UNDP and the respective National Ozone Offices

The standard replacements for CFC-12 in XPS are butane, isobutane or LPG (liquid propane gas). Because LPG is the lowest cost option, most recipients try to use it. This is not a problem, provided the LPG always comes from the same gas field, which could be assured in this case.

UNDP had already prepared a final phase-out plan and therefore, although it was possible to substitute recipients, funding was fixed, so that only US$ 250,000 were available for the project compared to US$ 495,000 for Al Sharif ten years earlier! The company offered US$ 50,000 counterpart funding but nevertheless the implementation plan had to be cost-effective.

Rather than contracting internationally, and in view of the fact that Egypt has a sizeable oil and oil components industry, UNDP asked the Al Sharif engineer mentioned above to source local contractors. Apart from the metering pumps, this turned out to be possible and the engineer was contracted to implement the local part of the project. The budget was adjusted as follows:

Table 1: Adjusted budget for phase-out

Budget line	**Budget in US$**	**Revision in US$**	**Explanation**
Butane tank – complete, installed	50,000	40,000	Local manufacture
Extruder retrofitting – pumps/electrical Static eliminators	80,000 10,000	50,000 5,000	Changed vendor/ local manufacture
Civil works	50,000	45,000	Local contractor
Aeration/exhaust	40,000	30,000	Local contractor
Gas alarm system	25,000	25,000	
Other safety measures	5,000	5,000	
Technical assistance	15,000	25,000	To pay for self-design
Contingencies	27,500	25,000	
Total budget	**302,500**	**250,000**	
Approved grant	250,000		

The project implementation took somewhat longer than usual because of the many local contractors involved, but performed well in achieving the expected savings. Only the metering pumps required an international supplier and installation supervision. A side-effect for the recipient was that, with the help of the local engineer/expert and vastly improved gas dosing, the quality of the foam improved considerably. The foam had now a softer touch (which consumers prefer) and was less brittle. Its density was also reduced, which improved the market position of the company involved (Hamed Moussa). The project was completed by a safety audit that concluded: 'The plant is deemed fit for safe operation with LPG as a blowing agent.'

Argentina: Conversion of the use of CFC to liquefied carbon dioxide (LCD) in flexible foam manufacturing

When Argentina started – in 1993 – to address in earnest the possibility of using CFCs in its foam industry, it decided to apply zero ODP alternatives whenever possible and to avoid the replacement of chemicals with health risks from exposure attached. This was a challenge, since the use of chemicals that would qualify was at that time still in development and the MLF accepted only mature technologies.

Table 2: Earmarked technologies

Technology	(Sub)sector	Implementing agency
Cyclopentane	Domestic refrigeration	IBRD
N-pentane	Insulated panels	UNDP
Butane	Extruded polyethylene/ polystyrene	UNIDO
Liquid carbon dioxide (LCD)	Flexible foam (slabstock)	UNDP

The initial situation was that there were seven foam/mattress plants, all operating relatively new, with continuous equipment supply of about 90% of the market in Argentina. These plants were owned by four enterprises. After originally opting for different technologies, the enterprises decided to revise their decisions and to make a joint choice on technology. They opted for the application of liquid carbon dioxide (LCD), a natural blowing agent. This decision was taken after several seminars and study tours, in the full knowledge and acceptance that the participating companies would undergo a lengthy and difficult learning process. The installations were delivered in 1998 and are (still) operating to satisfaction. The programme was completed by mid-2002. Some of the companies have forged ahead and even replaced methylene chloride, which was historically used as a co-blowing agent. After China, the programme is the largest for the MLF in LCD technology, which is regarded as a rather difficult technology for Article-5 countries, and is a shining example of how cooperation and thorough preparation can bear fruits.

Argentina: Implementation of pentane in panel manufacturing

There are six relatively large panel manufacturers in Argentina. Four of them chose to use N-pentane as a substitute for CFC-11. The other two companies, which are foreign owned, wanted to implement their own replacement programme without MLF assistance. The substitution programme included replacing or retrofitting foaming, blending and storage equipment along with elaborate safety measures such as electrical grounding, and the installation of ventilation and gas detection equipment. In one case, the company's insurers insisted on a sprinkler system that was paid for by the enterprise as co-financing. All the companies provided significant funds for plant redesign, local works and trials. Because this all happened during a recession that lasted almost four years, it constituted a hardship for the enterprises. It did cause delay, but the companies never wavered from their determination to finalise the projects. The last conversion was successfully completed in April 2002.

Both UNDP conversion programmes, which were supported by assistance and guidance from the Argentinian Government's Ozone Office (OPROZ), show that even under adverse economical conditions it is possible to carry out an environmentally sound ODS replacement programme. The companies have been able to remain competitive on quality and cost.

Conclusion

The MLF-funded projects assisted the industry to introduce natural blowing agents with zero-ODP and low-GWP in a manner that provided foams of a similar quality and enabled manufacturers to continue to supply a quality product.

The projects described show that the conversion to natural blowing agents, as implemented under the CFC phase-out activities in Egypt and Argentina, can entail legal and economic problems, but when coordinated by national governments and with financial support, may facilitate a successful switch to an environmental friendly production process and a qualitative enhancement of the product.

Experiences with Pentane Technology in Foam Industry: Questions and Answers from an Iranian Perspective

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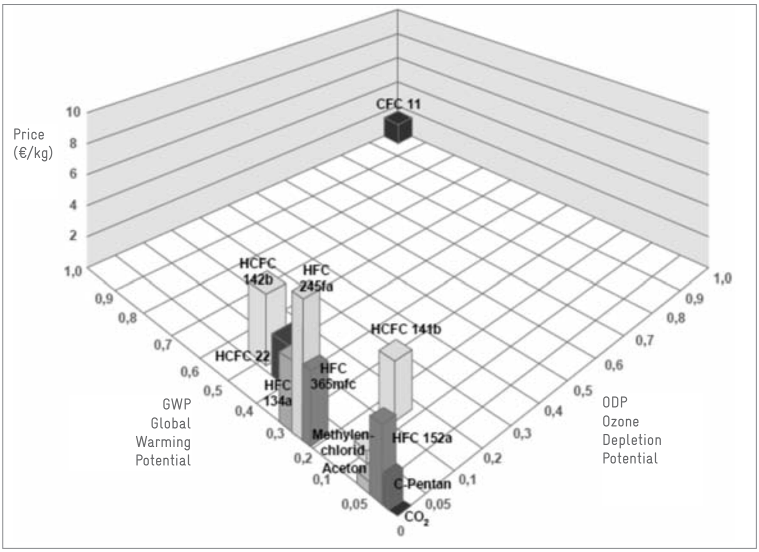
Introduction

Polyurethane (PUR) products are used in a large number of applications in Iran because they offer several advantages, including weight-saving sandwich construction, excellent thermal insulation and a wide range of physical properties. PUR foams have a very large market with an annual consumption of nearly 80,000 tonnes of raw materials.

The usage of HCFC-141b, one of the main blowing agents in the PUR foam industry, will be frozen at 2009/2010 levels in 2013 and subsequently phased out and replaced with alternative substances to comply with the decisions taken by the 19th Meeting of the Parties to the Montreal Protocol. As Figure 1 shows, hydrocarbons (HCs) such as pentane are considered to be preferable alternative substances, having zero ozone depletion potential (ODP) and very low global warming potential (GWP). In addition, HCs have a lower raw material price than HCFCs.

Figure 1: Comparison of GWP and ODP of different blowing agents (Kompe and Bohländer, 2008)



The exact formulation used by each producer of these blowing agents varies, depending on the expected thermal conductivity, functional characteristics, physical properties etc. However, they are mostly a blend of the following components (in order of their share in the mix):

C-pentane, mostly used in European production
N-pentane
Isopentane

Table 1: Properties of pentane (Hong et al., 2001)

	Molecular weight	**Boiling point (°C)**
C-pentane	70.14	50
N-pentane	72.15	35

As technical members of the Iranian project on CFC and ozone-depleting substances phase-out, we have visited many PUR foam producers who use different blowing agents in their production lines. In this study, we have tried to review some of the frequently asked questions about the application of pentane as a blowing agent in PUR production with special reference to rigid foam production. Based on these questions, we have tried to illustrate the current situation and usage of pentane as a blowing agent in the Iranian market and its perspective as a potential substitute for other ODS products.

Frequently asked questions about pentane usage

How would the quality of our products be affected if we switch to hydrocarbon (pentane) technology?

Many foam producers are concerned about the quality of their foam products if they are offered the opportunity of switching to pentane as their blowing agent. The trapped blowing agent is responsible for nearly 65% of the heat transfer through the foam structure and its effectiveness is recognised by its thermal conductivity in the gas-phase relative to the thermal conductivity of the air. Many of the polyurethane producers consider pentane to be a weak blowing agent that has no proper insulation properties and also has some severe aging problems. Apart from all the present rumours about pentane, we have tried to clarify for potential and current pentane consumers the precise differences between pentane technology and previous blowing agents. In fact, as Figure 2 shows, all the potential low-ODP gases including the pentane gases for blowing agents have dramatically lower thermal conductivities (typically 27 $mWm^{-1}K^{-1}$

at 300K) than air (Dohrn et al., 2007). Yet, it can be seen in Figure 3 that none of the substitute gases has a thermal conductivity comparable to chlorofluorocarbon (CFC-11) (Perkins et al., 2001) which, because of its negative impact on the ozone layer, must be phased out under the Montreal Protocol on Substances that Deplete the Ozone Layer.

Figure 2: Temperature dependence of thermal conductivity at 0.1MPa of N-pentane (Dohrn et al., 2007)

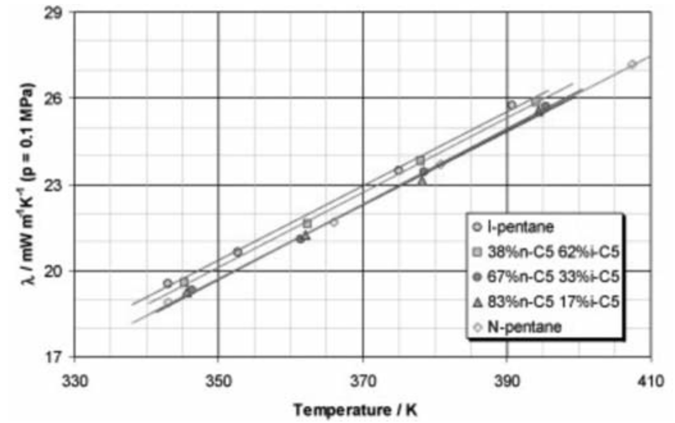
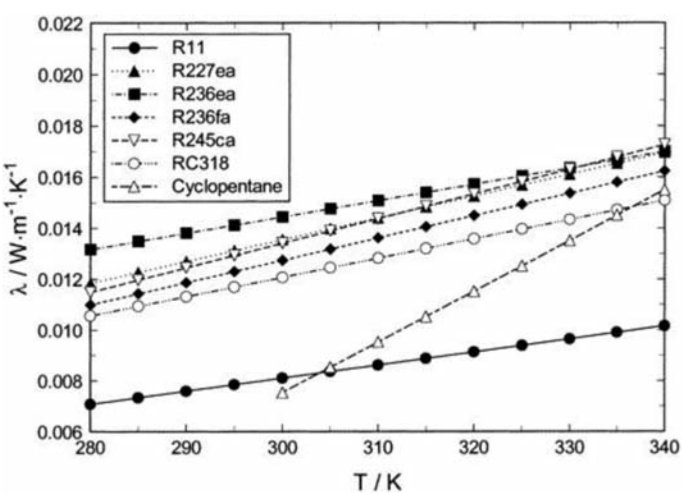


Figure 3: Thermal conductivity of fluorinated propane derivatives, fluorinated cyclic alkane and 75% cyclopentane + 25% pentane compared with that of CFC-11 (Dohrn et al., 2007)



Although not as efficient as CFC-11 as a blowing agent, pentane has a conductivity which is much lower than that of air. Therefore, the products blown with pentane will be able to meet most of the market demands. When carefully designed, these kinds of foam can have a finer cell structure that will reduce the free surface available for air diffusion inside the closed cells and produce better insulation capabilities. Moreover, as already mentioned, they do not have the property of ODS to break down over time in the presence of strong UV radiation and thus release bromine or chlorine, which are then likely to react with ozone molecules. Thus, the use of pentane technology should not noticeably affect product quality.
The other remaining issue will be the foams' aging problem. During the aging process, the counter diffusion of the blowing agent and air decreases a foam's insulation properties. It has been shown that this phenomenon is a complex function of blowing agent diffusivity and solubility. Based on several analyses, it can be concluded that, apart from pure cyclopentane (most of the blowing agents in use are mixtures of different types of pentane), all the other ozone-friendly blowing agents would be good candidates as substitutes for CFC-11 (Hong et al., 2001).

Would there be a safety risk in using pentane?

Although pentane mixed with air can be explosive (between 1.7 and 7 vol.% pentane in the air), explosion proofing can be achieved with careful precautions and procedures. In Iran, we have some factories where fire has broken out during the use of pentane gas, caused by improper handling of the technology and lack of safety procedures. One Iranian company had a fire accident due to an electrical short circuit about five years ago. Most of the PUR machines (nearly five machines) were burned in that accident and the damage percentage was almost 70% on average for each machine. The pentane tank and ventilation system were completely destroyed by the fire and, unfortunately, the company did not have a stringent and precise contract with an insurance company. After that accident, the company decided to transfer the remains of the production machine to their new site and installed a new production line for flexible foam production. Later, they successfully repaired and reconstructed four of the five received machines and added another high-pressure machine to replace the lost one. However, they shifted to HCFCs as their new blowing agents to eliminate any fire risk. During our visits, we tried to explain the real cause of the fire accident, the advantages of pentane technology and the upcoming phase-out of HCFC gases. In fact, the main procedure and safety control devices that have to be implemented in factory design are a temperature-controlled pentane storage room that should have separate foundations independent of the main production line, a pre-mixing unit for polyol and pentane and a working and foaming area that should have certain pentane level sensors and alert devices and a suitable ventilation system.

There are always two explosion proofing methods: primary and secondary.

The first method includes:
- monitored air changing,
- gas warning system,
- neutralisation of daytanks and moulds with inert nitrogen, and
- equipotential bonding (earth-up).

The second method includes:
- avoidance of ignition sources, and
- use of explosion proofed parts.

Unfortunately, the company did not consider the main safety measures when producing PUR foam. By explaining the advantages of pentane technology and the inevitable future shift to alternative blowing agents, we were able to persuade them to test the pentane technology on a limited scale at their current production line and check its potential for total replacement of existing blowing agents at some point in the future. Also, as they are going to enlarge their production line, they will consider pentane technology for their future production technology.

Why do raw material producers not insert the pentane gas inside the polyol?

Many foam producers, such as Mammut Co., Arasanat Asia Co. and others who use pentane as a blowing agent, are asking if it might be possible for the raw material producers to pre-blend blowing agents with polyol. Pre-blending of hydrocarbon into polyurethane is possible and it is considered to be useful as it may abolish the pre-mixing procedure for end-users. The rationale behind not mixing the polyol with pentane is the following: there is no chemical affinity between the non-polar low molecular weight HC components and the polar polyol with relatively high molecular weight molecules, as most of the current polyol are prepolymer products (the general rule of like dissolves like) (Tang et al., 2002). Therefore, even if the raw material producers tried to force pentane gas into the polyol by exerting enough shear forces (mixing), it would not be thermodynamically favourable. Over time (transportation), there would be a phase separation. Thus, while pre-blending may facilitate the foam production procedure, blending exerts so many limitations on insulating the barrels and IBCs, which would result in additional costs for transportation. There would also be a high risk that phase-separated raw materials would be used, affecting the product quality. Until the producers find a way to stabilise the pentane in the polyol (maybe by using some functional groups in the polyol structure or a surfactant), mixing must be performed in the PUR production line.

Conclusions

This study has tried to discuss some of the key problems encountered by Iranian foam producers and to give a realistic picture of the conditions for application of pentane technology in the future.

CFC-11 and HCFC-141b have been widely used in insulation foams because of their ease in transportation and application and because of properties that persist in the foam for a long period of time. However, the complete ban on CFC-11 and the upcoming phase-out of its replacement HCFC-141b require a change in the usage of blowing agents in Iran. Although some large companies have already replaced their systems with a pentane-compatible production line, most of the small and average foam producers are unaware of future changes in the situation and blowing agents market and, in particular, of the restrictions of the application of HCFC-141b in the near future. In this current situation, it seems necessary to provide these types of company with precise and reliable information about the advantages and disadvantages of this new technology and prepare them for the future.

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Annex

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Dr Winfried Schwarz has worked on the ozone layer and climate protection since 1990, conducting reports on the use and substitution of ozone-depleting substances and fluorinated gases – mainly on behalf of the German Environment Agency and the EU Commission (DG ENV). He is familiar with the political process involved in the Regulation/Directive on Certain Fluorinated Gases (through participation in the ECCP process, for example). He has contributed to several specialist publications (e.g. IPCC 2006).

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Bert Veenendaal has been working as a consultant on project preparation and implementation for UNDP since 1992. He is section chair of the UNEP Foams Technical Options Committee (FTOC) and has collaborated on IPCC/FTOC reports on HCFCs, end-of-life issues and ozone and climate. He has prepared special reports for the MLF on available CFC replacement technologies for foams, on special technologies and project design, using methylene chloride or liquid carbon dioxide, for example and on variable pressure technology, exothermic management technology, and cost-effective approaches to ODS phase-out projects. He has also designed and conducted safety inspections for projects that use highly flammable substances.

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Glossary

Article-5 Countries (Montreal Protocol)

Article-5 of the Montreal Protocol on Substances that Deplete the Ozone Layer includes a definition of countries that have been granted a ten-year grace period in the Protocol's phase-out schedule and are eligible for assistance under the Multilateral Fund. These countries have been defined as developing countries with an annual per capita consumption of ODS of less than 0.3 kg.

Blowing Agent (Foam)

A substance (gas, liquid, chemical) that is able to produce cells in the plastic structure of a foam. This process can vary according to the property of the substance: a liquid may develop cells when changing into gas, a gas may expand when pressure is released, a chemical may react under certain conditions to form a gas.

Building Material Class

The German standard, DIN 4102 [16] defines three different Building Material Classes: B3 (easily flammable), B2 (normally flammable) and B1 (hardly flammable). Construction materials for long-term use in buildings must be 'normally inflammable'. This is a minimum requirement of the German Building Regulations, which explicitly prohibit the use of easily inflammable construction materials.

CE Labelling System

CE is a European product safety label, with which producers certify that their products comply with European regulations. The CE label is not a quality label.

CFCs (Chlorofluorocarbons)

CFCs are halocarbons containing carbon, chlorine and fluorine. They were widely used as refrigerants, aerosol propellants and foam blowing agents but, because of their huge ozone depletion potential (ODP), they are scheduled to be phased out under the Montreal Protocol.

Climate Change

Climate change refers to a change in the state of the climate that can be identified (e.g. by using statistical tests) by changes in the mean and/or the variability of its properties, and that persists for an extended period, typically decades or longer. Climate change may be due to natural internal processes or external forcings, or to persistent anthropogenic changes in the composition of the atmosphere or in land use. (IPCC 4th Assessment Report 2007)

European Climate Change Programme (ECCP)

This is a programme that was launched in June 2000 by the European Commission. Its goal is to identify and develop the key elements of an EU strategy to implement the Kyoto Protocol.

F-Gas Regulation

This is a European regulation (No. 842/2006) that was published in June 2006. The objective of the Regulation is to contain, prevent and thereby reduce emissions of the fluorinated greenhouse gases (such as HFCs) covered by the Kyoto Protocol. It therefore has implications for manufacturers dealing with such gases (including applications and equipment containing or using such gases).

Global Warming Potential (GWP)

Global warming potential (GWP) is a measure of how much a given mass of greenhouse gas is estimated to contribute to global warming. It is a relative scale that compares the contribution to global warming of the gas in question to that of the same mass of carbon dioxide (whose GWP is by definition 1) over a defined time horizon. For instance, methane is a significant contributor to the greenhouse effect and has a GWP of 21 (100-year time horizon). This means methane is approximately 21 times more heat-absorptive than carbon dioxide per unit of weight.

Greenhouse Effect

Greenhouse gases effectively absorb infrared radiation emitted by the Earth's surface, by the atmosphere itself due to the same gases, and by clouds. Atmospheric radiation is emitted to all sides, including downwards to the Earth's surface. Thus greenhouse gases trap heat within the surface-troposphere system. This is called the greenhouse effect. (…) An increase in the concentration of greenhouse gases leads to an increased infrared opacity of the atmosphere, and therefore to an effective radiation into space from a higher altitude at a lower temperature. This causes a radiative forcing, an imbalance that can only be compensated for by an increase of the temperature of the surface-troposphere system. This is called the enhanced greenhouse effect. (IPCC 4th Assessment Report 2007)

Greenhouse Gas (GHG)

Greenhouse gases are those gaseous constituents of the atmosphere, both natural and anthropogenic, that absorb and emit radiation at specific wavelengths within the spectrum of thermal infrared radiation emitted by the Earth's surface, the atmosphere itself, and clouds. This property causes the greenhouse effect. Water vapour (H_2O), carbon dioxide (CO_2), nitrous oxide (N_2O), methane (CH_4) and ozone (O_3) are the primary greenhouse gases in the earth's atmosphere. Moreover, there are a number of entirely human-made greenhouse gases in the atmosphere, such as the halocarbons and other chlorine- and bromine-containing substances, dealt with under the Montreal Protocol. Beside CO_2, N_2O and CH_4, the Kyoto Protocol deals with the greenhouse gases sulphur hexafluoride (SF_6), hydrofluorocarbons (HFCs) and perfluorocarbons (PFCs). (IPCC 4th Assessment Report 2007)

HCFCs (Hydrochlorofluorocarbons)

HCFCs are halocarbons containing hydrogen, chlorine, fluorine and carbon atoms. Like CFCs, they contribute to ozone depletion and have therefore (since the end of 2007) been included in the substances to be phased out under the Montreal Protocol.

HFCs (Hydrofluorocarbons)

HFCs are halocarbons that contain carbon, hydrogen and fluorine. Since these halocarbons do not include chlorine, bromine or iodine atoms, they do not affect the ozone layer. However, like other halocarbons, they are potent greenhouse gases (see above).

IPCC

The Intergovernmental Panel on Climate Change (IPCC) was established in 1988 by the World Meteorological Organization (WMO) and the United Nations Environment Programme (UNEP). The role of the IPCC is to assess on a comprehensive, objective, open and transparent basis the scientific, technical and socio-economic information relevant to understanding the scientific basis of risk of human-induced climate change, its potential impacts and options for adaptation and mitigation.

Kyoto Protocol

The Kyoto Protocol to the United Nations Framework Convention on Climate Change (UNFCCC) is an international agreement that was adopted at the Third Session of the Conference of the Parties to the UNFCCC in 1997 in Kyoto, Japan. It contains legally binding commitments to reduce greenhouse gas emissions (to about 5% below 1990 levels in the so called first commitment period 2008 to 2012) for developed countries (as defined in the Annex to the Protocol). Mechanisms to achieve the targets set in the Protocol include (besides national measures) emissions trading, Clean Development Mechanisms and Joint Implementation. The Kyoto Protocol entered into force on 16 February 2005.

Montreal Protocol

The international treaty 'Montreal Protocol on Substances that Deplete the Ozone Layer' was agreed in 1987 after scientists discovered that certain man-made substances, such as CFCs, were contributing to the depletion of the Earth's ozone layer. The ozone layer protects life below from harmful UV radiation. So far it has been ratified by 194 countries (March 2009). The Protocol aims at protecting the ozone layer and therefore regulates the successive phase-out of substances that could harm the ozone layer through the restriction of production, import und use of such substances according to a specific timetable. The phase-out of ODS will enable the ozone layer to repair itself.

Multilateral Fund (MLF)

The Multilateral Fund was established in 1990 as a financial mechanism for the implementation of the Montreal Protocol. By financing technology transfer and cooperation, the Fund assists developing (so called Article-5) countries to meet their commitments under the Montreal Protocol, that means to enable these countries to phase out and replace ODS within an agreed time frame. Industrialised countries agreed to contribute to the Fund in order to help Article-5 countries achieve the Protocol's goals. Financial and technical assistance (closure of ODS production plants and industrial conversion, technical assistance, information dissemination, training and capacity building) is provided in the form of grants or concessional loans and is delivered primarily through four implementing agencies (UNEP, UNDP, UNIDO, World Bank).

National Phase-Out Plan (NPP)

This is the part of the Country Programme under the Montreal Protocol that describes a government's strategy statement, defining the phase-out time schedule for each controlled substance and the government actions to be taken for achieving phase-out. It contains a prioritised list of projects to be undertaken and takes into account the specific industrial, political and legislative situation in the country. (IPCC/TEAP Special Report: Safeguarding the Ozone Layer and the Global Climate System 2005)

Ozone Layer

A layer in the stratosphere (within about 15 to 50km from the ground) where the concentration of ozone molecules is greatest. Ozone molecules are very important, as they shield life on earth from the harmful effects (such as skin cancer) of the sun's UV radiation. Ozone molecules can be changed during a chemical reaction with chlorine atoms (separated from CFCs or HCFCs through UV radiation) into oxygen, which leads to a decrease of ozone in the atmosphere. The strongest depletion of the ozone layer has occurred over the Antarctic region, producing what is known as the ozone hole.

Ozone-Depleting Substances (ODS)

These are substances that damage the ozone layer in the upper atmosphere. They are widely used in refrigerators, air-conditioners, foam extrusion, fire extinguishers, dry cleaning, industrial cleaning, as solvents for cleaning, electronic equipment and as agricultural fumigants. They are defined in Annex A of the Montreal Protocol. Ozone-depleting substances include:

- chlorofluorocarbons (CFCs),
- halon,
- carbon tetrachloride, methyl chloroform,
- hydrobromofluorocarbons (HBFCs),
- hydrochlorofluorocarbons (HCFCs),
- refrigerant blends containing HCFCs,
- methyl bromide,
- bromochloromethane (BCM).

Ozone Depletion Potential (ODP)

This is a relative value that indicates the potential of a substance to destroy ozone gas (and thereby damage the Earth's ozone layer) as compared with the impact of a similar mass of chlorofluorocarbon-11 (CFC-11), which is assigned a reference value of 1. Thus, for example, a substance with an ODP of 2 is twice as harmful as CFC-11.

Phase-Out

In this context, phase-out means a successive limitation and production ban on substances that deplete the ozone layer according to a defined schedule for different groups of countries as regulated under the Montreal Protocol.

Sustainable Development

This means an economic, ecological or social development that takes into consideration the needs of current and future generations. Development should not be at the expense of future generations. In the field of the environment that includes for example conserving the world's natural resources and ecosystems and preventing climate change.

Acronyms and Abbreviations

AEG	'Allgemeine Elektricität Gesellschaft'(German company)
AKPU	Association of European OCF/PU producers
ATEX	'Atmosphère explosible' (French for explosive atmosphere, European legislation regulating explosion protection)
BASF	'Badische Anilin- & Soda-Fabrik' (German company)
BCM	Bromochloromethane
BiPRO	'Beratungsgesellschaft für integrierte Problemlösungen' (German consulting group)
B.P.	Boiling Point
BSH	'Bosch und Siemens Hausgeräte GmbH' (German company)
CE	'Conformité Européenne' (European labelling system)
CEO	Chief Executive Officer
CFC	Chlorofluorocarbon
CH_4	Methane
CO_2	Carbon Dioxid
D	Diameter
DIN	'Deutsche Industrienorm' (German Industry Standard)
DIY	Do-it-yourself
DOC	Decreasing Operating Costs
EC	European Community
ECCP	European Climate Change Programme
EG	'Europäische Gemeinschaft' (German for European Community)
EN	European Norm
EPA	Environmental Protection Agency
EPP	Expanded Polypropylene
EPS	Expanded Polystyrene
EU	European Union
EURIMA	European Insulation Manufacturers Association
EVA	Ethylene Vinyl Acetate
FCKW	'Fluorchlorkohlenwasserstoff' (German for CFC)
FOB	Free on Board (international commercial term)
FTOC	Foams Technical Options Committee
GHG	Greenhouse Gas
GPPS	General Purpose Polystyrene
GTZ	'Gesellschaft für Technische Zusammenarbeit GmbH' (German technical cooperation agency)
GWP	Global Warming Potential
HBFC	Hydrobromofluorocarbons
HC	Hydrocarbon
HCFC	Hydrochlorofluorocarbon
HFC	Hydrofluorocarbon
HIPS	High Impact Polystyrene
H_2O	Water
HP	High Pressure
IBRD	International Bank for Reconstruction and Development
IBC	Intermediate Bulk Carrier
IMAF	Institutional Monitoring Assistance Facility
IOC	Incremental Operating Costs
IPCC	Intergovernmental Panel on Climate Change
IR	Infrared
LCD	Liquid Carbon Dioxide
LEL	Lower Explosion Limit
LNG	Liquid Natural Gas
LPG	Liquid Propane Gas
MFI	Melt Flow Index
MLF	Multilateral Fund
N_2	Nitrogen
N_2O	Nitrous Oxide
NGO	Non-Governmental Organisation
NOU	National Ozone Unit
NPP	National Phase-Out Plan
O_3	Ozone

OCF	One-Component Foam
ODP	Ozone Depletion Potential
ODS	Ozone-Depleting Substances
OFP	Overfill Protection
OH	Hydroxyl
OPROZ	Oficina Programa Ozono (Argentinian Ozone Office)
PDR	'Produkte durch Recycling' (German recycling company)
PE	Polyethylene
PET	Polyethylene Terephthalate
PFC	Perfluorcarbon
PIR	Polyisocyanurate
PP	Polypropylene
PPT	Pentane Process Technology
PROZON	Brazilian Interministerial Executive Committee for the Protection of the Ozone Layer
PS	Polystyrene
PU	Polyurethane
PUR	Polyurethane
PVC	Polyvinyl Chloride
RIM	Reaction Injection Moulding
RPM	Rotations per Minute
RRIM	Reinforced Reaction Injection Moulding
SAVE	Specific Actions for Vigorous Energy Efficiency
SF_6	Sulphur Hexafluoride
SME	Small and medium-sized Enterprises
SRIM	Structural Reaction Injection Moulding
SROC	Special Report on Ozone and Climate
TA/T&A	Tour and Andersson
TEAP	Technology and Economic Assessment Panel
TPE	Thermoplastic Elastomer
TÜV	'Technischer Überwachungs-Verein' (German testing and certification organisation)
UBA	'Umweltbundesamt' (German Federal Environment Agency)
UEGPU	'Überwachungsgemeinschaft Polyurethan-Hartschaum' (German certification body)
UK	United Kingdom
UNDP	United Nations Development Programme
UNEP	United Nations Environmental Programme
UNFCCC	United Nations Framework Convention on Climate Change
UNIDO	United Nations Industrial Development Organization
USA	United States of America
UV	Ultra Violet
VOC	Volatile Organic Compound
VPF	Variable Pressure Foaming
WLG	'Wärmeleitfähigkeitsgruppen' (German for thermal conductivity groups)
WMO	World Meteorological Organization
WZB	'Wissenschaftszentrum Berlin für Sozialforschung' (Social Science Research Center)
XPS	Extruded Polystyrene

Index

GIZ Proklima has compiled this publication to provide information on natural foam blowing agents as ozone- and climate-friendly alternatives to HCFCs. Similar to the 'Natural Refrigerants' handbook published in July 2008, this volume contains various articles from academia, governmental institutes and manufacturers of foam equipment and related suppliers, who have introduced natural substances and who are able to provide useful insights and lessons learned from their conversion processes. The first section of the book covers policy-related aspects of technology transition towards natural foam blowing agents and examines the impact legislative changes have on development and adoption of alternative technologies. The second part deals with the use of natural blowing agents in rigid and XPS foam, the conditions for conversion and special technologies. Part 3 comprises case studies from developing countries. The contributions focus on typical challenges that occur when converting production plants to natural foam blowing agents and provide solutions illustrating how these hurdles may be overcome in practice.

The publication attempts to provide guidance to those involved in implementing the HCFC phase-out in a sustainable and climate-friendly manner. Developing countries shall be encouraged to consider sustainable solutions based on natural blowing agents as HCFC replacements, instead of choosing high-GWP HFCs.

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