

White Book:
An Extensive Review of Polyurethane Insulation



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Objective:

The objective of this White Book is to raise awareness about the characteristics of polyurethane foam for building insulation and about the way it is produced. It aims at answering the major questions that may be raised about polyurethane and polyisocyanurate, materials that are largely unknown within PPC, and far from the core product of Isover i.e. glass wool.

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Executive Summary:

Polyurethane is among other things a polymer organic closed-cell foam with a low thermal conductivity which can be used as an insulating material in buildings.

Production

It is manufactured by mixing together a polyol (plus additives), an isocyanate and a blowing agent, the latter being a low thermal conductivity gas responsible for the formation of closed cells within the foam.

Ageing:

With time, gas diffusion will occur between the gases contained in the cells and the atmosphere, leading to an increase in the thermal conductivity of the material. Without facing, the diffusion, and as a consequence the increase in thermal conductivity, will be a lot faster leading to a significant degradation in the insulating properties of the board. However, the gas diffusion can be significantly reduced by adding aluminium facings to the PU board, making the performances of the material almost constant with time.

Environment, Health and Safety:

Regarding EHS issues, MDI, which is the most widely used isocyanate to manufacture polyurethane rigid foam due to its lower toxicity, must be handled with care as it is irritating for the lungs and can cause asthma in case of exposition over long periods of time. This risk can be mitigated with adequate procedures in the production facilities including ventilation system.

Pentane, used as blowing agent in most of the cases, is highly flammable and explosive and thus requires proper handling as any other flammable substance (propane, butane,...).

There are no other EHS issues specific to the production of polyurethane and the product is risk-free for the end-user in normal conditions of use.

Basic knowledge about polyurethane

Polyurethane is a very common polymer used in many applications ranging from shoes, paint, mattresses to car dashboards, domestic appliances and building insulation.

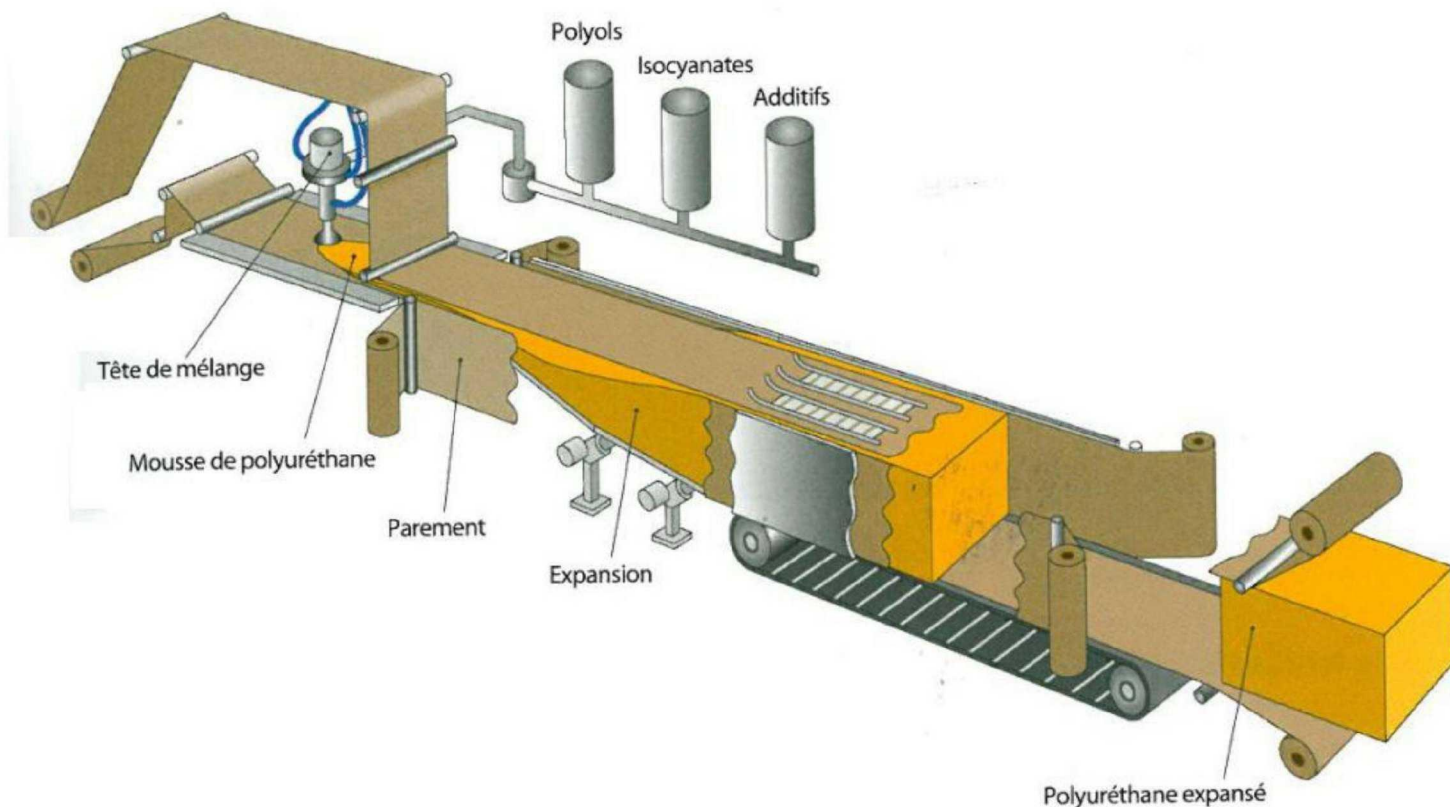


Figure 1: Examples of polyurethane products

It is obtained by mixing a polyol with an isocyanate and other additives. The polyol and the isocyanate used are crucial in the final properties of the synthesized polyurethane.

For the insulation of buildings, polyurethane is used as a foam that can either be manufactured in plants and sold as rigid boards or made on the jobsite by mixing together the polyol (polyol polyester and polyol polyether) and the isocyanate (usually MDI (methylene diphenyl diisocyanate)) and spraying this blend on the surface to insulate. In the US and in Japan, the latter technique is very common, whereas in Europe (apart from Spain for roofs and walls and Belgium for floors), PU is mainly sold as rigid, ready-to-use foam boards easier to apply by non-specialized companies.

The manufacturing process of polyurethane rigid boards is fairly simple and requires limited capital expenditure (10 to 20 M€ for a greenfield plant). However, fine tuning the chemical compositions requires extensive know-how and experience.



**Figure 2: Manufacturing process of polyurethane mattresses (similar to boards manufacturing process)
(the extent of the expansion is modified according to the desired thickness)^[1]**

Rigid polyurethane foams (PUR/PIR) are produced through a chemical reaction between two base components in liquid form and a low-boiling point blowing agent such as pentane or CO₂. The base materials react directly on mixing and build a polymer matrix: polyurethane. The heat released during this reaction causes the blowing agent to expand which forms the closed-cells.

The expanded foam volume and thus the density of the foam are controlled through the quantity of blowing agent added. The foam material formulations can be modified by using various additives in order to produce the required properties.

^[1] Source : Le Grand Livre de l'Isolation, Ed. Eyrolles, 2009

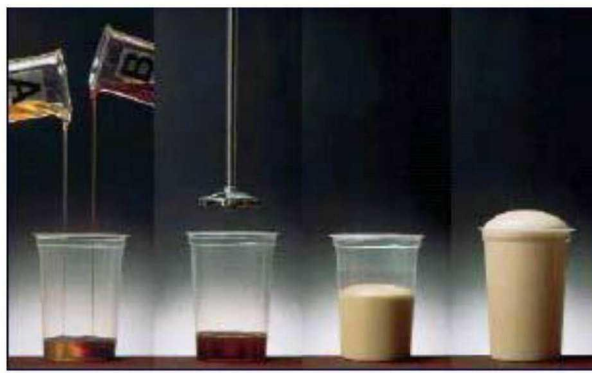


Figure 3: Polyurethane polymerization^[2]

PU foam is a closed-cell foam whose cells contain the blowing agent, CO₂ released during the chemical reaction and air. As these gases, trapped in the cells, have low thermal conductivities, PU foam is therefore an insulating material.

The gases contained in the cells tend to diffuse out whereas atmospheric air tends to diffuse in, at different speeds according to their diffusion coefficients i.e. their ability to go through the polymer matrix. With time, gas diffusion modifies the gas composition of the cells and therefore the thermal conductivity of the material. As the blowing agent is replaced by the air (which has a higher thermal conductivity), the thermal performances of the PU foam tend to worsen. However, products with a diffusion-tight facing will retain a better thermal conductivity.

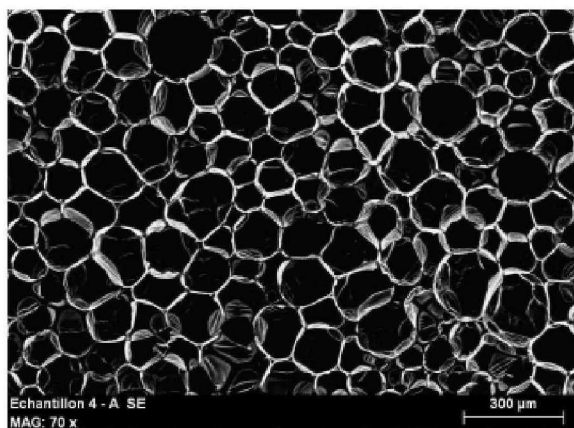


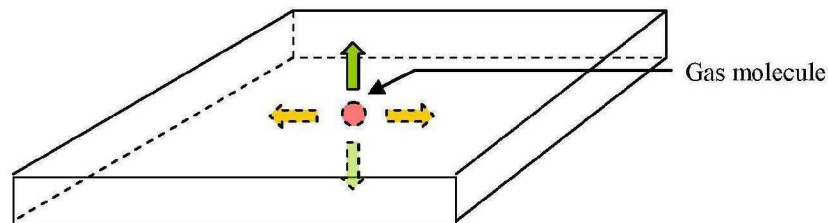
Figure 4: MEB photograph of a PU foam sample^[3]

^[2] Source : PU Europe, PU manufacturers Trade Association

^[3] Source : Centre Scientifique et Technique du Bâtiment (CSTB)

Gas diffusion speed is a function of the diffusion coefficient of the gas, of time and of the material thickness. The thicker the board, the longer the distance the gas molecules will have to go before reaching the atmosphere.

Therefore, gas diffusion can be significantly reduced by adding diffusion-tight facings such as aluminium foils at the board surface as this will increase the diffusion path.



➡ Preferred diffusion path without diffusion-tight facing

➡ Preferred diffusion path with a diffusion tight-facing on the upper and lower side

Questions & Answers

Raw materials

What are the blowing agents used?

CFCs (chlorofluorocarbons) and HCFCs (hydrochlorofluorocarbons) are now banned and are no longer used. Pentane is the most common blowing agent but small players still use HFCs (hydrofluorocarbons) as they cannot afford the investments needed to deal with explosion risks related to the use of pentane.

Is there a correlation between oil prices and MDI prices? Are the raw material prices volatile?

Many chemical reactions are needed to obtain MDI from the initial oil-derived raw material called naphtha. Therefore, there is no clear link between oil prices and MDI prices as many other factors can influence the MDI price during its synthesis. In the last decade, apart from the increase followed by the drop in prices due to the crisis, MDI prices have been growing very slowly.

For pentane isomers, there is no risk of shortage and prices do not vary significantly from one isomer to another.

How is the raw material market?

Polyester is very easy to manufacture and suppliers easily interchangeable, making polyester a non-strategic raw material which Huntsman Polyurethane (HPU) do not produce.

Five companies control the MDI market: three major players (BASF, Bayer and Huntsman) and two medium-size players (Dow and a Chinese manufacturer). This raw material is much more strategic and needs to be controlled.

PIR versus PUR

What is the difference between polyurethane (PUR) and polyisocyanurate (PIR)?

Polyurethane is made by blending a mix of polyether polyols and various additives (catalysts, fire retardants,...) with MDI, an isocyanate. The ratio between polyol and isocyanate is between 100 and 160, meaning that there is 60% more MDI than polyol.

Polyisocyanurate (PIR) is made similarly but instead of polyether polyols, a blend of polyether and polyester polyols is used and the isocyanate index is between 180 and 500. The isocyanate in excess trimerizes and forms isocyanurate.

Due to isocyanurate rings, PIR fire resistance is increased (it decomposes at 100°C above PU). The current formulations make it no longer friable.

The production lines are much faster with PIR (around 50m/min versus 15m/min for PUR for thickness up to 100mm). PIR also has a lower initial thermal conductivity as less water is required for its production.

All in all, PIR is cheaper to produce than fire-retarded PUR, as fire retardants are expensive, and can be cheaper than standard PUR depending on polyester prices and density reduction (PIR density is lower than PUR density).

PIR has been known to be more brittle than PUR. Has this been improved?

PIR was brittle when the first boards were produced. This is no longer the case as the formulations are now optimised, notably thanks to the use of different polyesters. PIR is now said to be less brittle than PUR. PUR is still largely used in France as it is used in flooring applications, where brittleness is not a problem. In the USA, there is almost only PIR now.

It has been noticed that aged foams have higher compression modules because of the air diffusion within the cells (total pressure is no longer inferior to the atmospheric pressure).

What will be the evolution of PIR and PUR?

PIR is bound to replace PUR in the years to come as it is cheaper to produce and its performances are better than PUR ones. The change is taking some time as it is not easy to switch from PUR to PIR production and master it. An increasing proportion of laminators switch from PUR to PIR. However, some old production lines cannot be converted.

PIR/PUR performances

What are the contributions of gas, solid and radiative heat transfers?

Solid conduction accounts for 3.5 mW/(m.K), radiative transfer for 4 mW/(m.K) and gas for around 14.5 mW/(m.K). Which leads to an initial thermal conductivity of for example 22 mW/(m.K) at 10°C.

When diffusion is not prevented by diffusion tight facings, air will gradually reach atmospheric pressure in the cells while the majority of pentane will still be maintained due to its slower diffusion. After air saturation (known as the lambda plateau), the above foam will have a lambda of typically 27-28 mW/(m.K).

How are these contributions affected by structural characteristics?

There is a correlation between gas molecular weight and its thermal conductivity. The higher the gas molecular weight, the lower the thermal conductivity.

An increase in cell diameter leads to an increase in thermal radiative conductivity. An increase in density will have the opposite effect.

At low densities (28-35kg/m³), the increase in λ_{sol} due to the increase in density is compensated by the decrease in λ_{rad} but at higher densities, λ_{sol} increases faster than λ_{rad} , leading to an overall increase in thermal conductivity. At 28kg/m³, $\lambda_{rad} = 4$ mW/(m.K), $\lambda_{sol} = 3$ mW/(m.K) but at 90kg/m³, $\lambda_{rad} = 2,5$ mW/(m.K) and $\lambda_{sol} = 9$ mW/(m.K).

What is the typical boardstock density?

32kg/m³ and pentane accounts for 8% in the recent boards. When pentane started to be used as a blowing agent, there was a lot less pentane trapped in the cells, around 2% in weight in a board.

What is the typical thickness of a board?

It is possible to manufacture boards up to 240mm but the usual thickness is 150mm which means a thermal resistance superior to 5m².K/W

What are the partial pressures of the gases in the cells after manufacturing?

$P_{pentane} = 0.5$ bar, $P_{air} = 0.05$ bar, $P_{CO_2} = 0.15$ bar. The cell total pressure is less than atmospheric pressure after manufacturing.

Is there still room for thermal conductivity reduction?

In the lab, with optimal density and cell size, samples were produced with $\lambda=17$ mW/(m.K) but this cannot be transferred to industrial production.

There are ongoing R&D projects to reach $\lambda = 20\text{mW}/(\text{m.K})$, aged lambda (18.5mW fresh). This goal will be reached within a couple of years by optimising density and cells size in the production process.

Are the boards dimensionally stable after production and during use?

With CO₂ blown foam, due to the fast outward diffusion of CO₂, the boards would tend to collapse and higher foam densities would be needed to prevent it. With pentane-blown foams, this phenomenon does not occur as the depression is too small.

There is a tendency for the boards to swell but this remains inferior to the 5% limit. This is adequate for most applications but the formulation will have to be adapted to decrease the swelling if the ETICS market is to be addressed.

Boards are flat if the same facing is used on both sides.

What is PU behaviour regarding moisture and water uptake?

If the cells are closed, which they should be in a standard board, water uptake is extremely low.

Regarding moisture, PU with facing is better than existing EPS but XPS tends to be the optimal solution in applications with high humidity rates (underground, basement).

PU is authorized in flood-prone areas in the UK.

PIR/PUR ageing

How are measured the diffusion coefficients? What are the orders of magnitude?

A sample is taken from the foam core, aged and crushed. The gas concentrations are measured with a helium gas chromatograph.

Orders of magnitude:

Gas	Pentane	N ₂	O ₂	CO ₂	H ₂ O
D _{eff} (m ² /s)	10 ⁻¹³	10 ⁻¹² - 10 ⁻¹¹	10 ⁻¹¹	10 ⁻¹⁰	10 ⁻⁶ – 10 ⁻⁷
Time for 99% equilibrium*	>200 years	~ 40 months	~ 15 months	~ 1 month	< 1 day

**For a 5cm x 5 cm x 5cm foam cube without facings*

Equilibrium completion is proportional to $D_{\text{eff}} \cdot t / L^2$ with L the thickness of the sample and t the ageing time. The thicker the sample, the slower the equilibrium is reached.

What is the lambda increase after ten years? What is the influence of a facing on ageing?

For thin diffusion open boards i.e. without facing, the thermal conductivity increases from 22mW/(m.K) after manufacturing to almost 28mW/(m.K) after 10 years at ambient temperature.

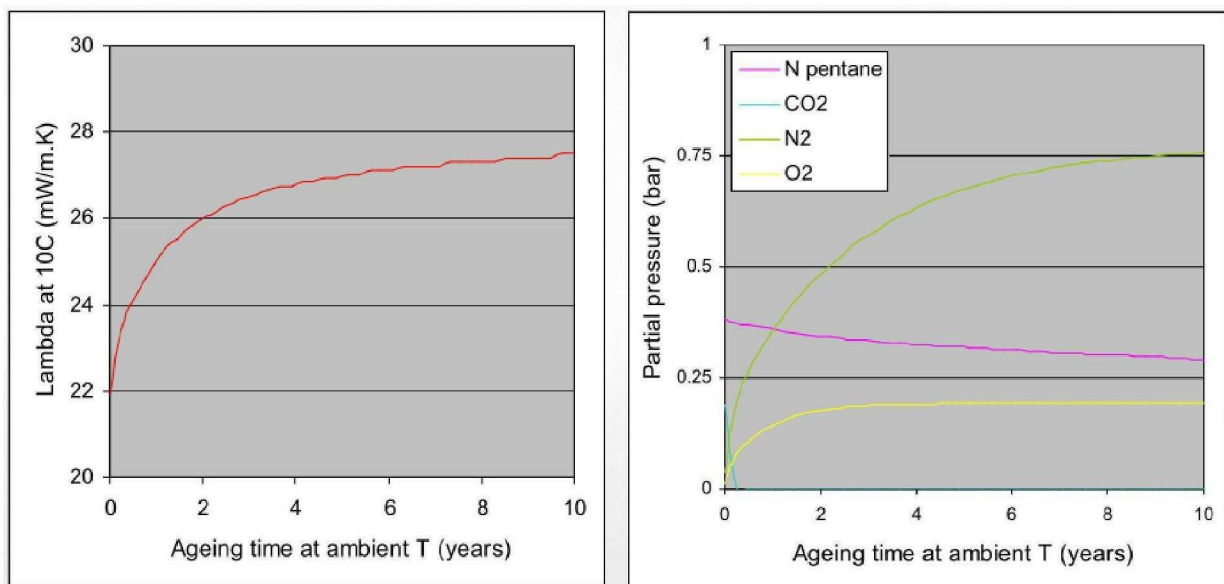


Figure 5: Ageing of a diffusion-open board, thickness: 5 cm (Source: PU Europe)

The lambda increase of about 5 - 5.5 mW/m.K is due to air ingress. The speed of lambda increase slows down when the foam gets closer to air saturation and finally reaches a plateau corresponding to air saturation. At this point, loss of pentane is still very small.

As stated before, the board thickness has a great influence on ageing: a 5cm board reaches 27mW after 10 years whereas a 20cm board reaches 24-25mW (initial value: 22mW).

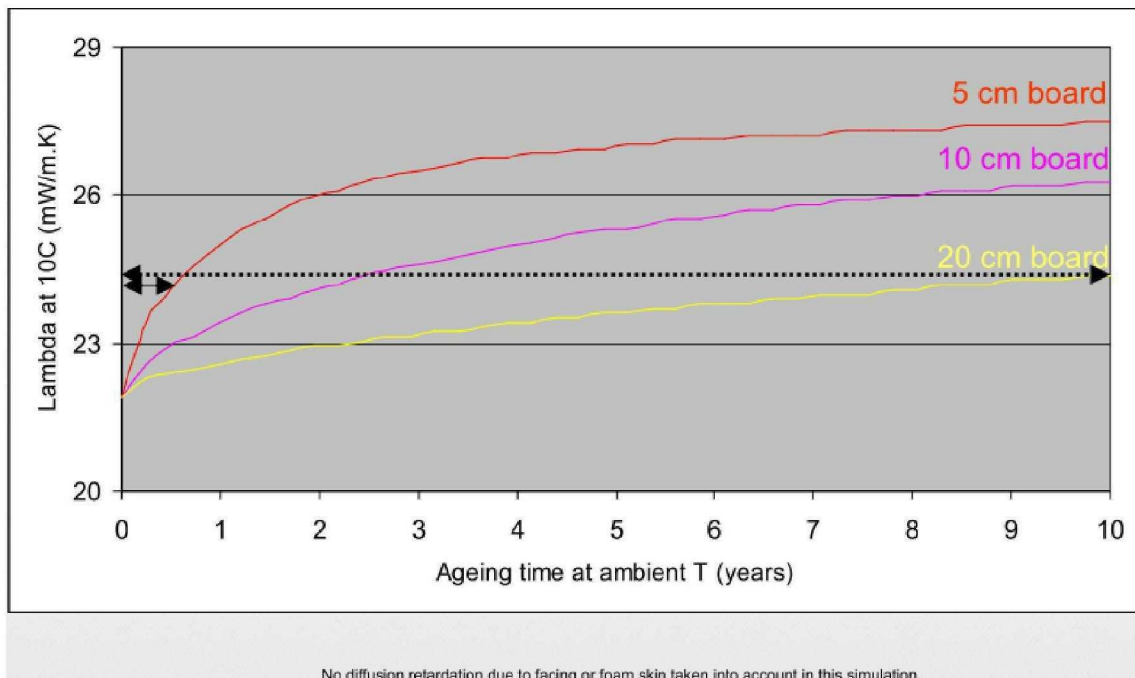


Figure 6: Influence of thickness on gas diffusion (Source: PU Europe)

With a diffusion-tight facing, diffusion mostly occurs at the board edges which slows down the diffusion process a lot, leading to an increase of only 0.4mW after 10 years. Unlike for VIPs, if the facing is not completely diffusion-tight, this will not lead to a significant increase in lambda.

PU boards are more and more manufactured with diffusion-tight facings, typically a 50µm aluminium facing that passed an O₂ diffusion normalised test. The facing tightness is specified on the product datasheet.

N.B.: these values come from numerical simulations and not from actual aged samples.

What is the influence of the temperature on ageing?

For nitrogen, a board ages 8 to 12 times faster at 70°C than at 20°C, and 20 to 30 times more at 100°C.

Some experts claim that an increase in temperature affects differently the coefficient diffusion of the different gases. This would mean that accelerated ageing by increasing the temperature is not representative of the actual ageing that would occur at ambient temperature. We lack objective data to settle this point.

Have HPU ever measured the thermal conductivity of PU samples aged at ambient temperature for several years?

This has not been done recently and would not be relevant as the chemical compositions have been modified significantly and the blowing agent changed. Several years ago, foam cores were sliced (2cm) and aged at ambient temperature for a year and the end result was good.

PU Europe, the European trade association for PU, have recently opened a 30 year-old PU-insulated flat roof and sent some samples to the FIW (German equivalent of CSTB) for lambda measurement. The first results show that $\lambda = 26\text{mW}/(\text{m.K})$ for these PU samples showing that simulations might overestimate the ageing. The definitive results are to be published in the months to come.

EHS issues

What are the products used by HPU that are listed on the REACH registers?

All of the products used by HPU will be REACH registered. HPU is the lead registrant for MDI

Are there any raw materials presenting high EHS risks during the manufacturing phase or the end-use phase?

Polyols are not classified as hazardous substances.

MDI is harmful for the respiratory system as it is an irritating chemical. It can induce asthma and other respiratory chronic diseases when inhaled over long periods of time. MDI is classified as carcinogenic in the European Union (*category 2, May cause cancer*) but not by the International Agency for Research on Cancer (IARC) (*category 3: Not classifiable as its carcinogenicity to humans*); it is not a Substance of Very High Concern (SVHC). Adequate procedures including ventilation systems in the manufacturing facility are sufficient to mitigate the risks during production. There is no risk for the end-user during normal condition of use as there is no free MDI in the final foam. HPU produce MDI and know how to deal with such a chemical substance (cf. product stewardship ISOPA programme).

Pentane is not a harmful substance per se when inhaled or when in contact with the skin. The main risk comes from its high flammability and risk of explosion. As with any other

flammable substance, some precautions must be taken when using such a chemical but nothing unusual.

HPU have an ISO accreditation to measure the VOCs (Volatile Organic Compounds) in their manufacturing facilities.

Are the manufacturing sites under special regulations due to the chemicals used?

The plants are classified Seveso II because of the pentane and ICPE (*Installations Classées pour la Protection de l'Environnement*) in France

What are the fire retardants used by HPU? What about their toxicity? Will some of them be banned in the future?

HPU use two fire retardants: TCPP (trichloropropylphosphate) and TEP (triethylphosphate). Both of these chemicals are toxic only if swallowed and do not present EHS risks. However, in Germany, the general opinion tends to be against chlorine-containing products and TEP is increasingly used but there is no legal requirement to use TEP rather than TCPP.

TEP is anyway better than TCPP and the former will replace the latter, depending also on availability and price dynamics.

What about VOC emissions?

VOC emissions are extremely low.

Pentane is detectable but has no health impact. All the MDI molecules are trapped within the polymer matrix and even if there were some free molecules, MDI is a large molecule, unlikely to diffuse out (boiling point: 314°C).

The VOC emissions are inferior to the AgBB thresholds making PU suitable even for use in interior spaces.

What about production waste? Is it possible to recycle polyurethane rigid boards?

Production waste are generated in low quantities and can only be recycled externally, notably through external uses (concrete, bricks,...).

Depending on the quality of waste, polyurethane can be buried in a landfill, incinerated to produce energy or recycled through chemical (pilot plant in the UK to produce methanol from PU) or mechanical treatment (ground to powder for oil spillage cleaner, concrete) according to the end use.

At the time being, it is not economically viable to recycle PU in closed loop: in France and in the UK, 90% of the old PU is buried in landfills; in Germany, Denmark and the Netherlands, it is mainly incinerated.

For old PU containing CFCs, incineration in cement kilns or municipal waste incinerator is possible as CFC will be also burnt.

Are there any issues with PUR/PIR in case of fire?

PUR is a flammable material and produces large amounts of toxic, vision obscuring smoke. During PUR combustion, carbon monoxide (CO), isocyanates and hydrogen cyanide (HCN) are emitted and can lead to asphyxia. Thick smoke can prevent people from escaping.

PU and EPS smoke toxicity are comparable (PU smoke per se is more toxic than EPS smoke but EPS produce a lot of lung-obstructing particles). When taking into account the quantities of burning material when insulation is involved in a fire, the toxicity thresholds are exceeded regardless of the foam. One should also consider the fact that furniture and upholstery contain important quantities of flexible polyurethane foam (mattresses, sofas, chairs,...) that are more likely to be involved in a fire than insulation materials. Toxicity limits will be exceeded just if these items burn in a room.

It is to be noticed that PIR has a better fire behaviour than PUR as it hinders the flame spread and it produces smaller amounts of vision obscuring smoke.

Is there a higher risk of fire when using PUR/PIR rigid foam?

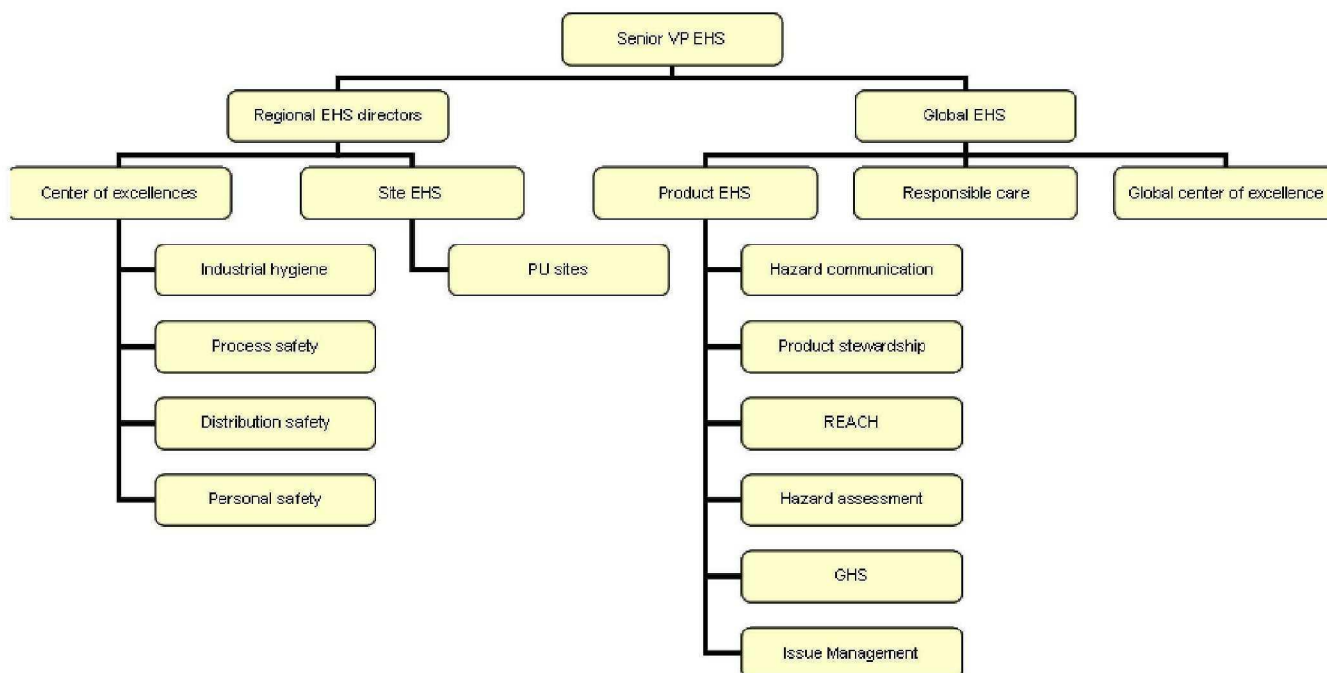
According to the 2007 UK Fire Statistics, among the 53 000 accidental residential fires that occurred in the UK, 0.7% of the fires were due to insulation and killed nobody whereas 5% of these fires were due to flexible foam and killed 63 people (20% of the victims).

Contrary to flexible foams, rigid foams are not likely to be in direct contact with flame or heat sources. The only risk is in large, developed fires.

Can tougher fire regulation prevent PU from gaining market shares?

Current regulation forbids the use of PUR/PIR in high-rise buildings and there are some restrictions in France and Germany for flat roofs as well as for the applications where A1/A2 classification is required. Factory Mutual, the American insurance company, accepts systems containing PIR in flat roofs in the USA.

For any other applications, PUR/PIR is widely accepted: low height building, private home, exterior walls, internal wall, dry-lining,...



What about the Life Cycle Analysis of PU? Is it assessed similarly to glasswool and EPS/XPS?

HPU method and approach are similar to ours and they also value environmental performance declarations of the building products and the insulation materials in particular.

For PU, 90% of the impact is due to the raw material as it is derived from oil and the facing impact is negligible. Thus, LCAs vary only slightly from one manufacturer to another.

Due to the different ratio of isocyanates, PIR and PUR have different LCAs, with PIR having a better environmental profile.

In comparison to EPS and XPS, since the raw materials of these three insulation materials are oil-derived chemicals, the differences between the LCAs are not significant.

For phenolic foams, no LCA has been published so far.

Phenolic foams

Have HPU ever tried to manufacture phenolic foams? Can this material be a challenger to PU?

HPU have never produced phenolics.

Five years ago, due to their very good fire properties and low lambda, this product could have been a challenger to PU.

However, it is very difficult to produce phenolic foams: many have tried and few have succeeded. The production rate is a lot lower than PIR and PUR at 5-10 m/min. The use of a strong acid (sulphuric acid or p-TSA) as a catalyst is also a problem and due to the chemical reaction, one third of the raw material goes out as water and the foam needs to be dried, thus increasing the production costs.

Phenolic foams are very hygroscopic and moisture degrades the thermal conductivity (up to 15mW). This does not appear in the ageing tests as phenolics are aged at 110°C and moisture is thus removed, improving greatly the foam thermal properties.

Phenolics will remain more expensive to produce than PIR for equivalent performances. The lower lambda of phenolics is often due to the use of HFCs.

List of abbreviations:

AgBB: Health-related Evaluation of Building Products (*Ausschuss zur gesundheitlichen Bewertung von Bauprodukten*)

CFC: chlorofluorocarbon

HCFC: hydrochlorofluorocarbon

HFC: hydrofluorocarbon

HPU: Huntsman Polyurethane

IARC: International Agency for Research on Cancer

ISO: International Standardization Organization

MDI: methylene diphenyl diisocyanate

PIR: polyisocyanurate rigid foam

p-TSA: paratoluenesulfonic acid

PU: generic denomination of polyurethane and polyisocyanurate foams

PUR: polyurethane rigid foam

TCPP: trichloropropylphosphate

TEP: triethylphosphate

VOC: Volatile Organic Compound