ALCIMED

Dangerous chemicals in different insulation products
(insulation foam, insulation products made of animal or vegetable fibers and "thin reflective insulation" products):

Present state

ALCIMED - 57 bd de Montmorency - 75016 Paris - France - Tel: [redacted] - Fax: [redacted]

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Glossary of terms

ACERMI	Association pour la Certification des Matériaux Isolants (Association for the Certification of Insulating Material)
ACGIH	American Conference of Governmental Industrial Hygienists
ATSDR	Agency for Toxic Substances and Disease Registry
BAM	Bundesanstalt für Materialforschung und –prüfung (Federal Institute for Materials Research and Testing)
CFC	Chlorofluorocarbon
CIMA	Cellulose Insulation Manufacturers Association
CSTEE	Comité Scientifique sur la Toxicité, l'Ecotoxicité et l'Environnement (Scientific Committee on Toxicity, Ecotoxicity and Environment)
DBDPE	Decabromodiphenyl ether
DHHS	Department of Health and Human Services
DIBT	Deutches Institut für BauTechnik (German Building and Construction Institute)
ECB	European Chemical Bureau
EPA	Environmental Protection Agency
EPS	Expanded Polystyrene
ESIS	European chemical Substances Information System
FSC	Forest Stewardship Council
GWP	Global Warning Potential
HBCD	Hexabromocyclododecane
HCFC	Hydrochlorofluorocarbon
HDI	Hexamethylene Diisocyanate
HFC	Hydrofluorocarbon
HSDB	Hazardous Substances Data Bank
IARC	International Agency for Research on Cancer
IBO	Institut für Baubiologie und Ökologie (Institute for Building Biology and Ecology)

IPCS	International Program on Chemical Safety
MDI	Methylene Diphenyl Diisocyanate
MPA NRW	Materialprüfungsamt Nordrhein-Westfalen (Material test office)
MSDS	Material Safety Data Sheet
NIOSH	National Institute for Occupational Safety and Health
ODP	Ozone Depleting Potential
OEL	Occupational Permissible Level
OSHA	Occupational Safety and Health Administration
ÖTI	Österreichisches Textil-Forschungsinstitut (Austrian Research Institute on Textile)
PBDE	Polybrominated Diphenyl Ether
PEL	Permissible Exposure Limit
PUR	Rigid Polyurethane
RDP	Resorcinol-bis-diphenylphosphate
R.E.D.	Reregistration Eligibility Decision
REL	Recommended Exposure Limit
STEL	Short Term Exposure Limit
TCPP	Tris(chloropropyl)phosphate
TDI	Toluene Diisocyanate
TLV	Threshold Limit Value
TWA	Time Weighted Average
XPS	Extruded Polystyrene

ALCIMED

Final presentation
November 17th, 2005

Dangerous chemicals in insulation foams: present state of the associated risks

ALCIMED - 57 bd de Montmorency - 75016 Paris - France - Phone: [redacted] - Fax [redacted]

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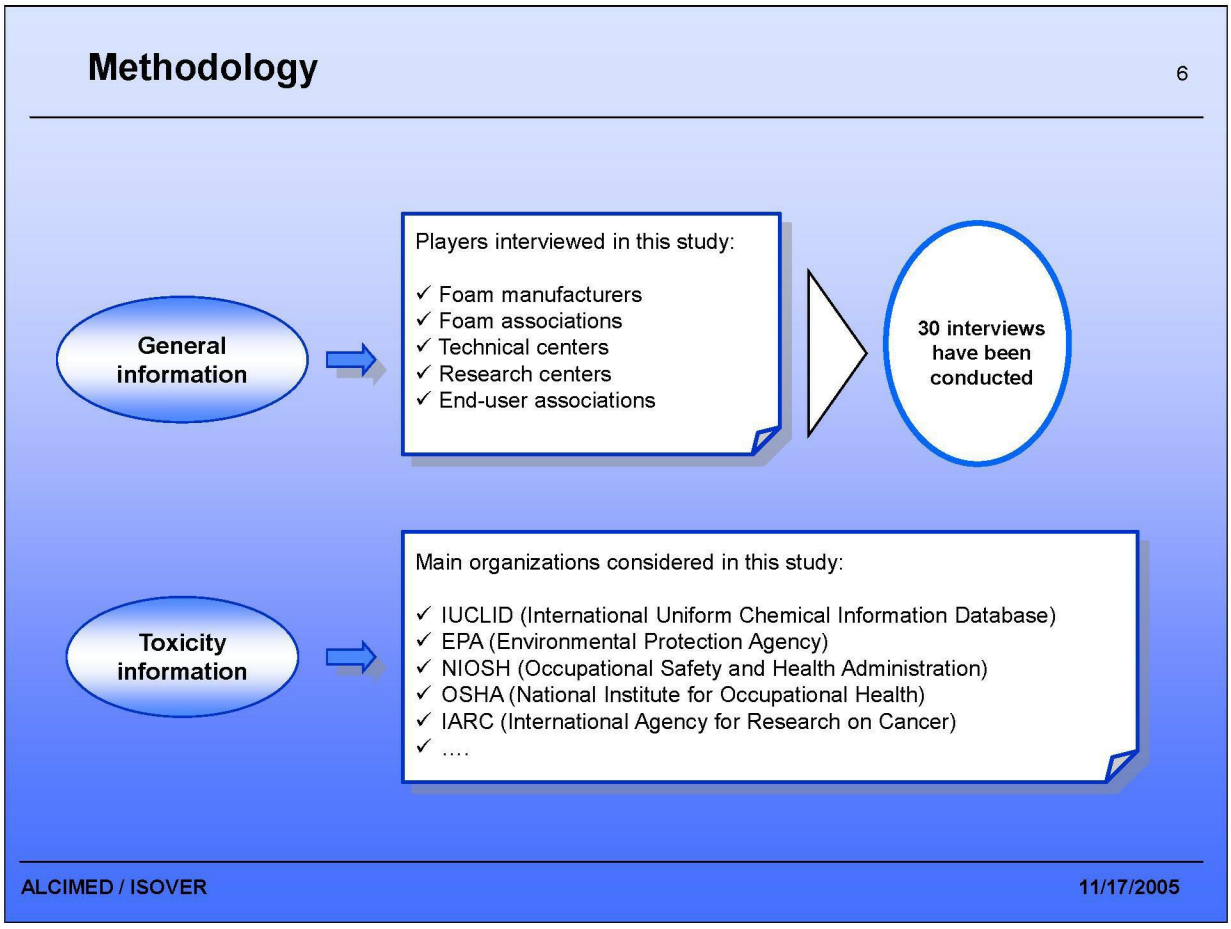
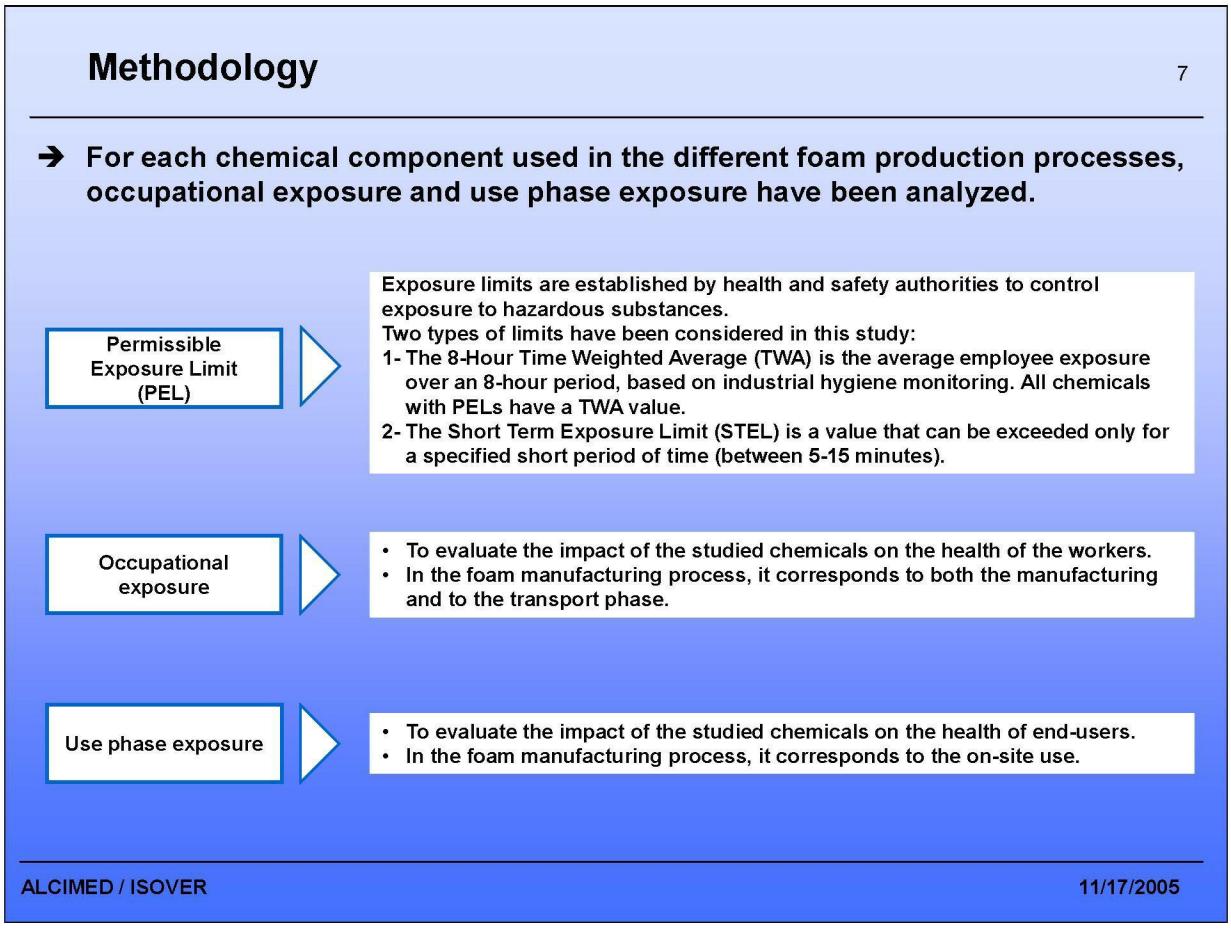
Background

- ✓ In October 2001, ten European standards (EN 13162 through EN 13171) dealing with insulation materials and products were introduced in Europe.
- ✓ Among other properties like thermal conductivity and fire performance, the mandate requested to standardize a so called “initial type test (ITT)” for the release of dangerous substances to be performed by an independent testing laboratory.
- ✓ However, due to the lack of experience and due to a non-existing European harmonized common method for testing and classification, this property could not be included in the standards.
- ✓ Some laboratories (FIW Munich, BAM Berlin) are working to develop a harmonized European testing standard for the emission of dangerous substances from insulation foams.



A Chemical Data Sheet contains data on:
General information
Physico-chemical data
Environmental Fate and Pathways
Ecotoxicity
Toxicity

Site web IUCLID:
Flexible data maintenenace of chemical substances according to EU and OECD regulationsA database of existing chemicals is being compiled by the European Chemicals Bureau (ECB). The database includes all data sets submitted by industry following council regulations (EEC) 793/93 on the "evaluation and control of risks of existing substances." The regulation mandates that industry submit all readily available data on High Production Volume Chemicals (HPVCs). Existing chemicals are those substances that entered the European market before September 18, 1981 and that are listed in the EINECS inventory (European Inventory of Existing Commercial chemical Sunstances). EINECS contains 100,106 substances.



Mould: moule (molde)

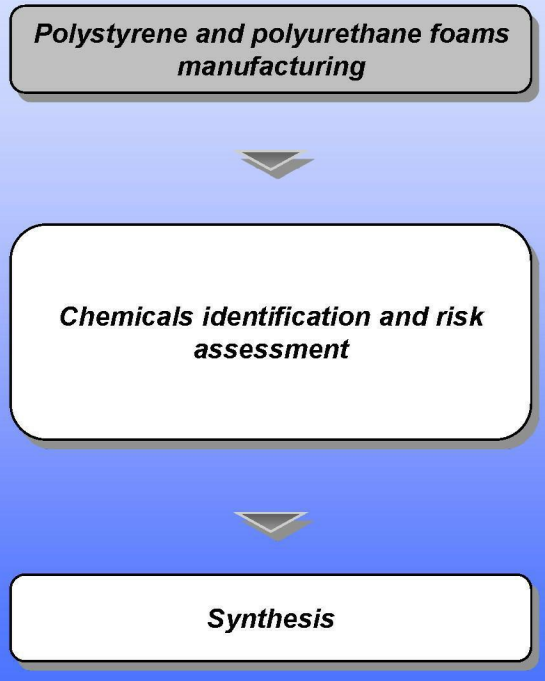
Outline of the presentation

Polystyrene and polyurethane foams manufacturing

Chemicals identification and risk assessment

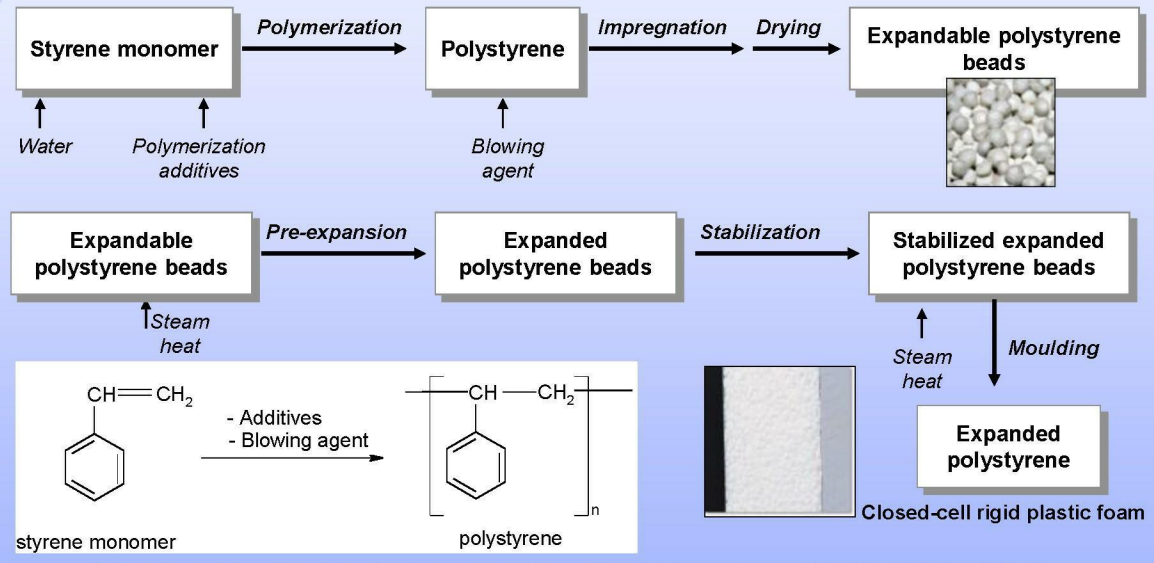
Synthesis

Polystyrene and polyurethane foams manufacturing



EPS manufacturing

➔ **Expanded polystyrene is obtained from expandable polystyrene in three stages: pre-expansion, stabilization and moulding.**

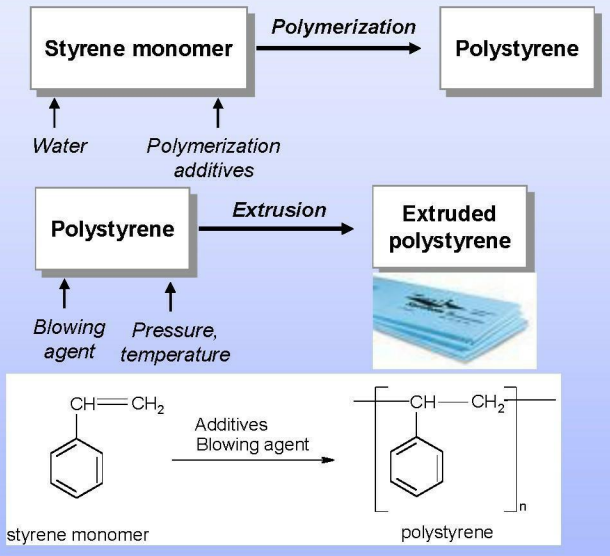


(Data extracted from "Analysis of both the properties and the development potential of foams in the field of insulation"- ALCIMED/ISOVER - September 21th 2005)

Mould: moule (molde)

XPS manufacturing

➔ **To produce XPS, polystyrene is extruded at elevated temperature and under pressure through a slit orifice to the atmosphere.**



(Data extracted from "Analysis of both the properties and the development potential of foams in the field of insulation"- ALCIMED/ISOVER - September 21th, 2005)

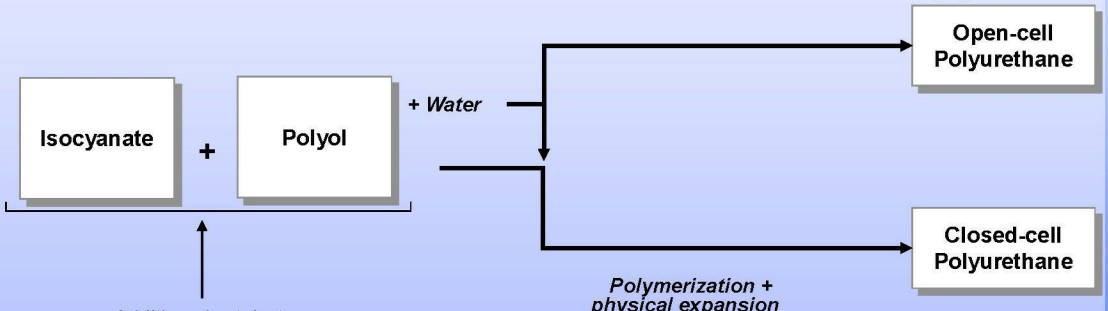
Shape: donner forme

PUR manufacturing

➔ **Polyurethane is typically produced as a result of a chemical reaction between an isocyanate and a polyol.**

Polymerization + Chemical expansion

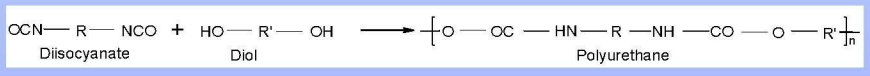
The reaction of the isocyanate with water produces CO_2, which acts as an in situ produced propellant. In this case the foam formation does not need the addition of a blowing agent.



Additives / catalysts
(stabilizers, tin catalysts, crosslinkers, …)

Polymerization + physical expansion

The foam formation is due to the evaporation of the added blowing agent initiated by the exothermal reaction polyol + water + isocyanate = physical blowing agent reaction.



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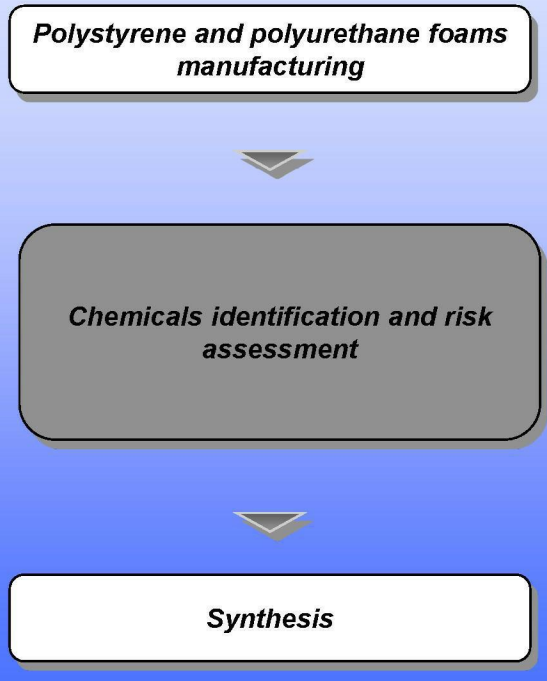
Chemicals identification and risk assessment



Chemicals identification and risk assessment
overview

➔ **The different foam compounds can be classified in three main categories: monomers, blowing agents and additives.**

	PUR	XPS	EPS
Monomer: *The starting material or single unit from which the foam is built*	Isocyanate and polyol	Styrene	
Blowing agent: *Gaseous or liquid substance which vapor expands the foam, creating gas-filled cells*	HFC, CO_2, hydrocarbons *The blowing agent can be produced during the chemical reaction (CO_2)*		Pentane
Additive: *Substance added to the polymer intended to add a new property to the foam or to modify or to increase the foam properties*	- Flame retardants, heat stabilizers, colorants - Lubricants, antioxidants, catalysts ...		

Chemicals identification and risk assessment
PUR monomers

	PUR	XPS	EPS
Monomer: *The starting material or single unit from which the foam is built*	Isocyanate and polyol	Styrene	
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Additive: *Substance added to the polymer intended to add a new property to the foam or to modify or to increase the foam properties*	- Flame retardants, heat stabilizers, colorants - Lubricants, antioxidants, catalysts ...		

PUR monomers
overview

➔ **The choice of the polyol to manufacture a polyurethane foam depends on the properties that producers want to give to the foams, while the choice of the isocyanate depends on its toxicity.**

Isocyanate

- ✓ A chemical compound containing the isocyanate group (-N=C=O).
- ✓ Toluene diisocyanate (TDI), methylene diphenyl diisocyanate (MDI) and hexamethylene diisocyanate (HDI) are (or were) the most common isocyanates used to produce PUR foams.

- ✓ Isocyanate constitutes the reactive element to produce PUR foams.
- ✓ Isocyanate choice depends mainly on both its toxicity and its volatility.

- ✓ Isocyanates are obtained from reactions using benzene as raw material.
- ✓ Isocyanates are harmful substances.

Potentially dangerous chemical susbtances
Its dangerousity in the PUR foam should be analyzed

Polyol

- ✓ A chemical compound containing multiple hydroxyl groups (-OH).
- ✓ Polyols used to produce PUR are polyethers polyols and polyesters polyols.
- ✓ A big variety of polyols can be used in PUR manufacturing. These polyols are different depending on their functionality, viscosity, reactivity …

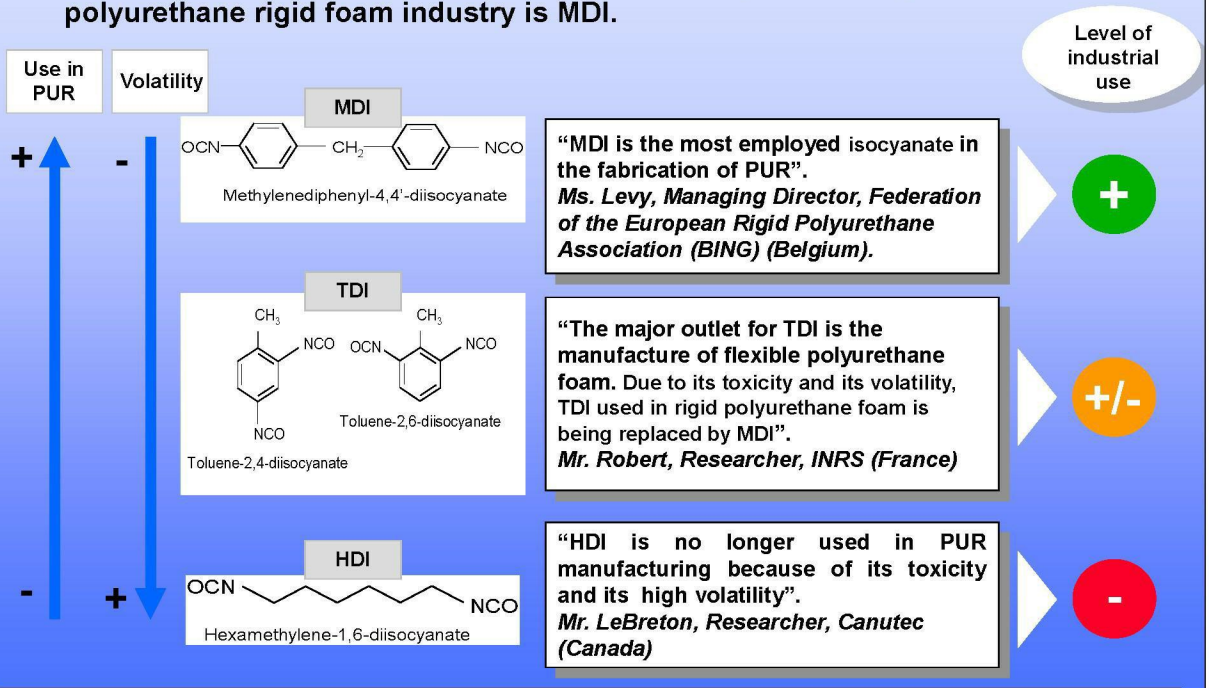
- ✓ Polyols give properties to PUR foam.
- ✓ Polyol choice depends on the property that we want to give to the foam (mechanical, thermal ...)

- ✓ While some polyols may be slightly irritating to the eyes and skin, most are not harmful.

Considered as non harmful chemical substances
Polyol will not be in depth analyzed in this study

Isocyanates
most common isocyanates

➔ **Due to its less volatility, the most common isocyanate compound used in the polyurethane rigid foam industry is MDI.**



Isocyanates

toxicity summary – main identified hazards

➔ **Among all the isocyanates, which are irritant, MDI is harmful and TDI and HDI are toxic by inhalation.**

		CAS number	Main identified hazards	Comments
MDI and TDI precursor	Benzene	71 – 43 – 2	- Carc. Cat 1* - Flammable - Muta. Cat 2* - Irritant - Toxic	Benzene is a known carcinogen on human. Directive EC 1996/62 identifies benzene as an air pollutant, without fixing any limit.
Precursors to produce PUR foam	MDI	101 – 68 – 8	- Harmful by inhalation - Irritant (**)	Among the most common used isocyanates, MDI is the less harmful.
	TDI	26471 – 62 – 5	- Carc. Cat 3* - Irritant - Toxic by inhalation	Although studies have demonstrated that TDI is a carcinogen on animals, there is limited evidence of a carcinogenic effect on human.
	HDI	822 – 06 – 0	- Irritant - Toxic by inhalation	Due to its high volatility and its toxicity, HDI presents a high hazard.

** Definitions are given in appendix*

*** Based on Swedish and German proposals for classification of MDI for carcinogenicity, the European classification and labeling is looking forward to discuss the carcinogenic as well as the mutagenic properties of MDI*

Isocyanates

toxicity summary – main identified hazards

➔ **Only MDI and TDI will be deeply analyzed since benzene is not present in isocyanate and HDI is no more used.**

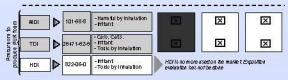
		CAS number	Main identified hazards	Permissible Exposure Limit (PEL)	Occupational exposure	Use phase exposure
MDI and TDI precursor	Benzene	71-43-2	- Carc. Cat 1* - Flammable - Muta. Cat 2*- Irritant - Toxic	*- No literature has been found concerning the presence of benzene in isocyanates.* *- However, very low concentration of free benzene should be present in isocyanates (< 0.1 %), so in the final foam.* *- Benzene will not be considered as a dangerous substance.*		
Precursors to produce PUR foam	MDI	101-68-8	- Harmful by inhalation - Irritant (**)	☒	☒	☒
	TDI	26471-62-5	- Carc. Cat 3* - Irritant - Toxic by inhalation	☒	☒	☒
	HDI	822-06-0	- Irritant - Toxic by inhalation	*HDI is no more used on the market. Exposition evaluation has not been studied.*		

** Definitions are given in appendix*

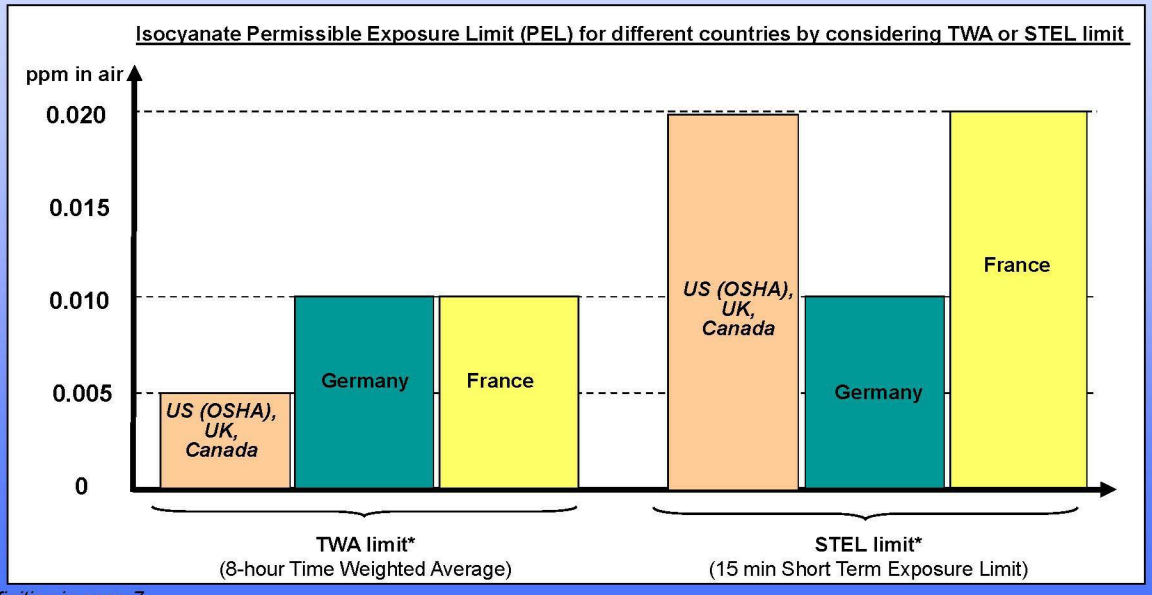
*** Based on Swedish and German proposals for classification of MDI for carcinogenicity, the European classification and labeling is looking forward to discuss the carcinogenic as well as the mutagenic properties of MDI*

Isocyanates

TDI and MDI Permissible Exposure Limit



➔ **Generally, the current Permissible Exposure Limit for TDI and MDI is below 0.01 ppm when expressed as TWA* and below 0.02 ppm when expressed as STEL*.**



*Definition in page 7

Isocyanates
TDI occupational exposure

➔ **Problems in lung function have been detected in workers who manufacture foams for panel or spray PUR.**

Identified studies	Main results
US EPA, 1986 Hartung, 1994 US EPA 1999	Chronic inhalation exposure on humans to TDI has resulted in significant decreases in lung function of workers; it causes an asthma-like reaction and it has effects on the liver, blood and kidneys.
US EPA, 1986 Hartung, 1994	Chronic low-level exposure to TDI results in sensitization to the chemicals.
US EPA, 1986	Some individuals have suffered poor memory or concentration even after exposure has stopped.
Diem *et al*., 1999	A decline in lung function is observed on workers involved in TDI production.
Jones *et al*., 1992	A 5-year study was conducted in workers involved in polyurethane foam production. Personal 8-hour TWA low-exposure levels were 0.00042 ppm and high-exposure levels 0.00126 ppm. Prevalence of chronic bronchitis was significantly associated with exposure.
IARC 1986, 1999	TDI exposure levels reported during the spray application of < 0.14 ppb to > 0.14 ppm have been found in the workplace.

Isocyanates
MDI occupational exposure

➔ **Some cases of asthma and sensitivity to MDI have been detected in workers who manufacture foams for panel or spray PUR.**

Identified studies	Main results
Zammit-Tabona *et al*., 1983 **Vandenplas *et al*., 1993** **Baur *et al*., 1984**	These studies describe sensitivity to MDI and ascribe hypersensitivity pneumonitis and occupational asthma, but exposure levels are unknown.
Bernstein *et al*., 1993	Only three cases of occupational asthma were identified in a 3-year study conducted with 243 foam workers.
EPA, 1998	The evidence from cancer incidence and mortality studies of workers exposed to MDI are insufficient to determine if exposure to MDI is causally associated with cancer.
Crespo and Galan, 1999	Levels of exposure to MDI during the process of insulating buildings with sprayed polyurethane foam in indoor applications were up to 0,008 ppm. **"When workers install the foam, windows are not installed yet in the house, so there is no problem in ventilation".** ***Jesús Crespo, Health and Security at Work Center (Spain).***
Robert and Ducos (INRS) ***(not published yet)***	They are studying the biologic supervision of workers exposed to MDI. **"Because of its low volatility, the main MDI danger for both panel and spray workers, is the skin or oral way due to possible isocyanates projections when producing the foam". Alain Robert, Researcher, INRS (France).**

Isocyanates
TDI use phase exposure

➔ **Even if residual amounts of unreacted TDI are often found in TDI-based polyurethane foams, its concentration in air after three days post-production is very low and it is not problematic to end-users.**

Identified studies	Main results
Hugo *et al.*, 2000 (The Dow Chemical Company)	It is not likely that TDI would be released from three-day post-production polyurethane foams in amounts to produce air concentration concern.
Marand *et al.*, 2003	Isomers and dimers of TDI were observed in polyurethane foam extraction solutions.
"Little information is communicated related to user exposure because there are only a few of independent laboratories". *Mr. Skarping, Researcher. Work Environment Chemistry, Stockholm University (Sweden).*	

- **Free TDI could be present in the polyurethane foam**
- **The monomers concentrations emitted from polyurethane foams are very low and decrease very rapidly with time**
- **TDI use phase exposure don't seem to be a big issue as no problems have been identified concerning user exposure**

Isocyanates
MDI use phase exposure

➔ **As MDI has a low volatility, there is no problem of MDI emissions in normal conditions of use.**

Product consideration

In normal temperature conditions, there is no MDI emissions.

"MDI has a low volatility. There is MDI emission only at high temperatures (200-300 °C)".
Mr. Mix, Researcher. Federal Institute for Material Research and Testing (BAM) (Germany).

In the case where MDI could be emitted from foams, concentrations should be very low due to its low volatility compared to TDI.

There is no degradation of the foam with time

"In urea-formaldehyde foams, there is a slow degradation of the material, which lead to formaldehyde emissions. MDI-based polyurethane foams are very stable products, they don't degrade".
Jesús Crespo, Health and Security at Work Center. (Spain).

Standard test consideration

There is no specific ISO or ASTM standard test to measure free MDI in the foam.

Research consideration

No research study on MDI emissions in using phase has been identified.

Due to its low volatility compared to TDI, the MDI exposure in the use phase does not appear as a big issue

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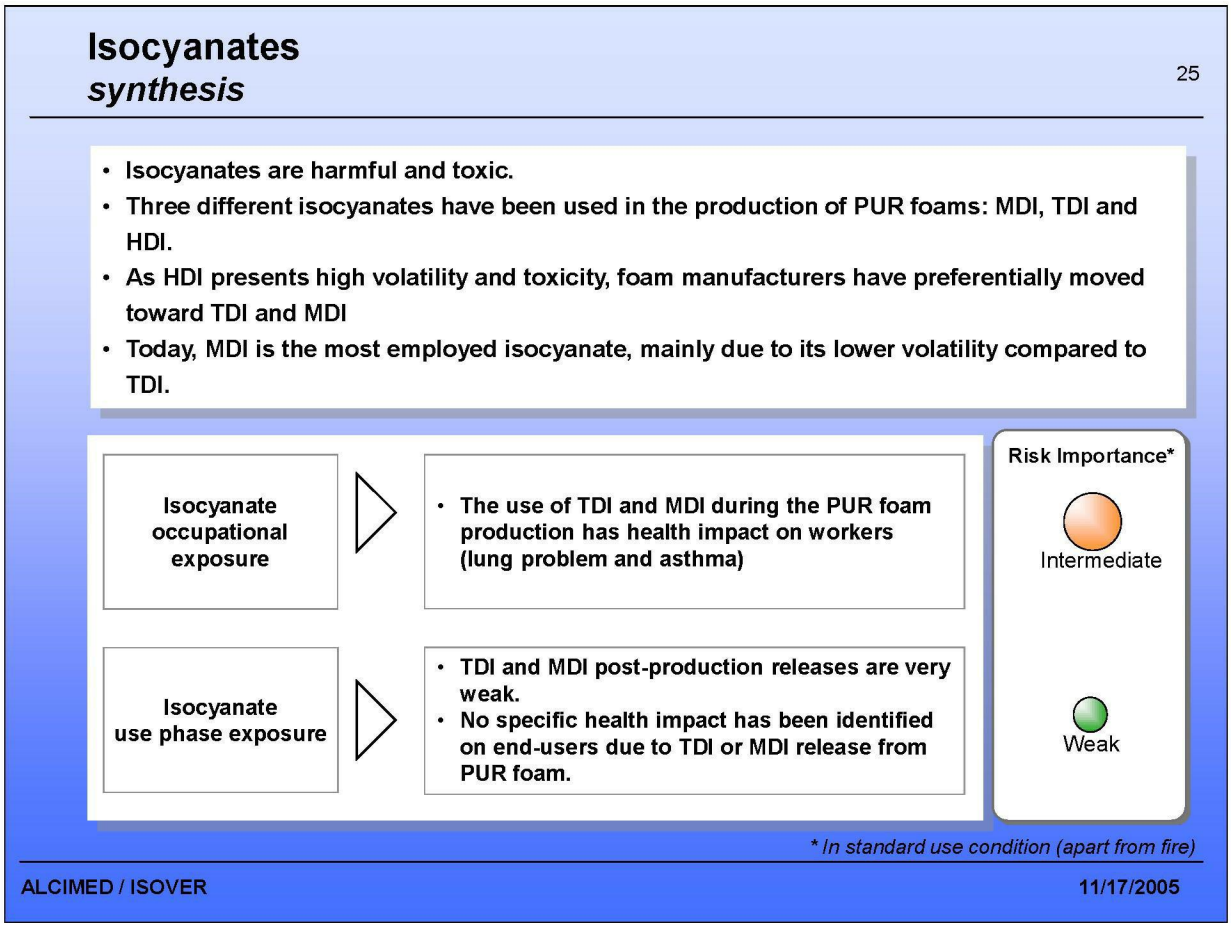

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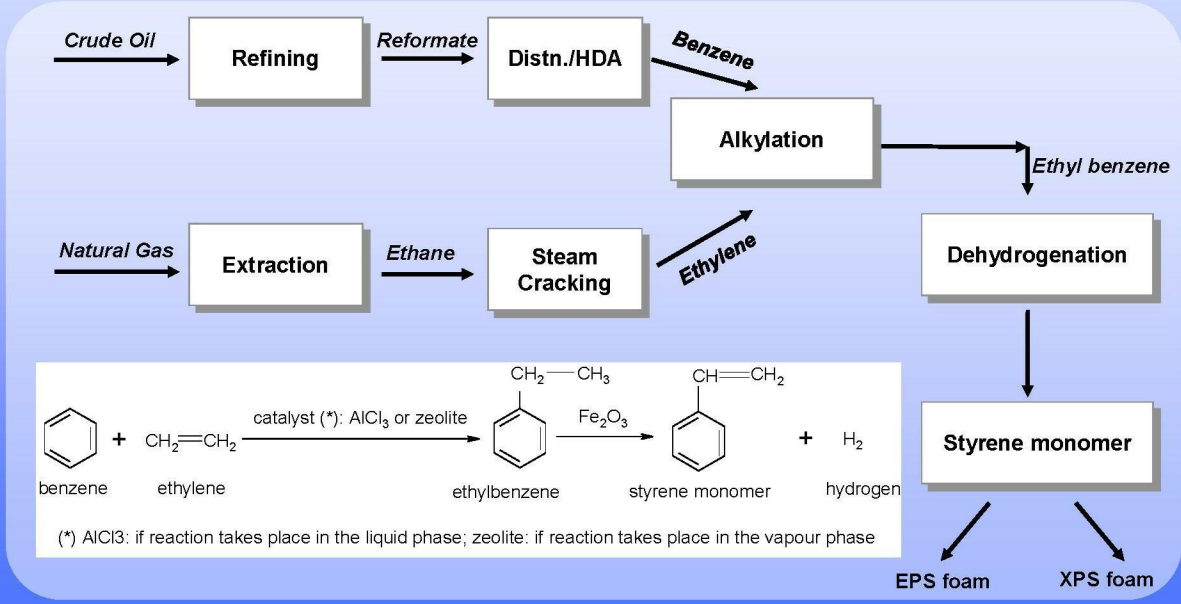
Chemicals identification and risk assessment
XPS/EPS monomer

	PUR	XPS	EPS
Monomer: *The starting material or single unit from which the foam is built*	Isocyanate and polyol	Styrene	
Blowing agent: *Gaseous or liquid substance which vapor expands the foam, creating gas-filled cells*	HFC, CO_2, hydrocarbons *The blowing agent can be produced during the chemical reaction (CO_2)*		Pentane
Additive: *Substance added to the polymer intended to add a new property to the foam or to modify or to increase the foam properties*	- Flame retardants, heat stabilizers, colorants - Lubricants, antioxidants, catalysts ...		

XPS/EPS monomer
overview

➔ **Styrene monomer used as raw material in polystyrene foam manufacturing is produced from benzene and ethylene.**



Styrene

toxicity summary – main identified hazards (1/2)

➔ **Styrene, the main component of both EPS and XPS foams, is harmful and irritating to eyes and skin but not toxic by inhalation,...**

		CAS number	Main identified hazards	Comments
Styrene precursors	Benzene	71 – 43 – 2	- Carc. Cat 1* - Flammable - Muta. Cat 2* - Irrit. to eyes - Toxic and skin	While benzene is a known carcinogen on human, ethylene and ethyl benzene don't present an important hazard. Directive EC 1996/62 identifies benzene as an air pollutant, without fixing any limit.
	Ethylene	74 – 85 – 1	- Flammable	
	Ethyl benzene	100 – 41 – 4	- Flammable - Harmful by inhalation	
Precursor of XPS / EPS foams	Styrene monomer	100 – 42 – 5	- Flammable - Harmful by inhalation - Irritant - Carc. Cat 2B	Styrene is classified as a possible human carcinogen by the EPA and the IARC.

** Definitions are given in appendix p.66-67*

Styrene
toxicity summary – main identified hazards

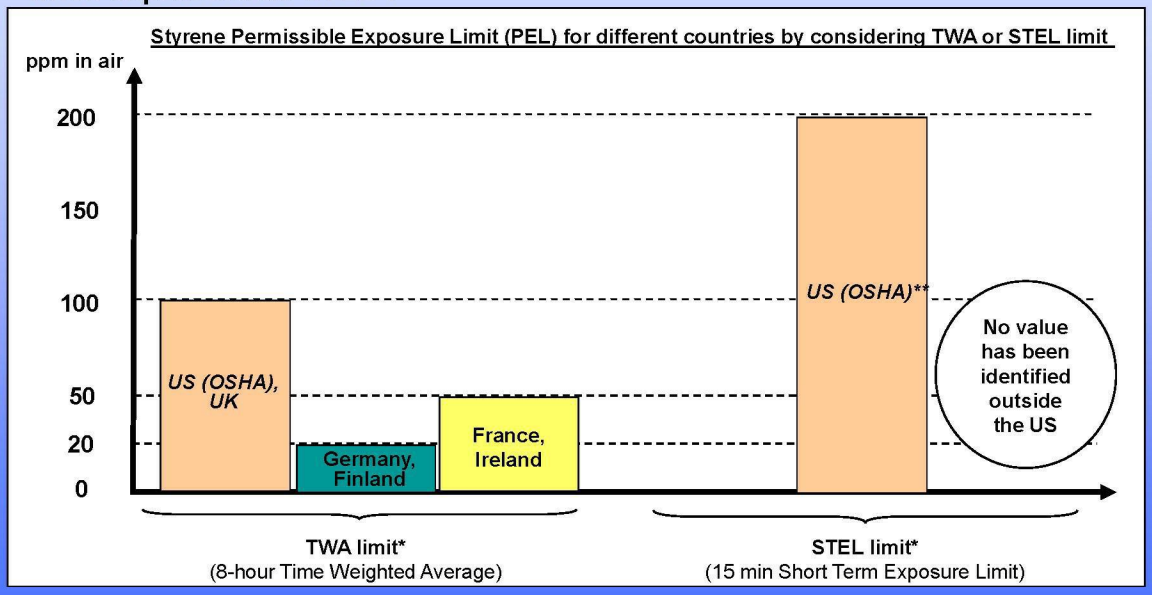
➔ **… and will be in depth analyzed to evaluate its health impact in the insulating foam applications.**

		CAS number	Main identified hazards	Permissible Exposure Limit	Occupational exposition	Use phase exposition
Styrene precursors	Benzene	71-43-2	- Carc. Cat 1* - Flammable - Muta. Cat 2* - Irrit. to eyes - Toxic and skin	*-No literature has been found concerning the presence of these 3 chemical substances in styrene* *-However, very few amounts of benzene, ethylene and ethyl benzene should be present in styrene and then in the final foam.* *- These substances will not be considered as dangerous substances in EPS or XPS foam.*		
	Ethylene	74-85-1	- Flammable			
	Ethyl benzene	100-41-4	- Flammable - Harmful by inhalation			
precursor of XPS / EPS foams	Styrene monomer	100-42-5	- Flammable - Harmful by inhalation - Irritant - Carc. Cat 2B	☒	☒	☒

** Definitions are given in appendix p.66-67*

Styrene
Permissible Exposure Limit

➔ **The current Permissible Exposure Limit for styrene expressed as TWA* is between 50 to 100 ppm depending on the country and 200 ppm in the USA when expressed as STEL*.**



*Definition in page 5

Styrene
occupational exposure

➔ **Styrene exposition concerns mainly workers involved in the styrene monomer production since the level of the released styrene in the foam production is relatively low.**

Styrene monomer production

Polystyrene foam manufacturing

Identified studies	Main Results
IARC, 2002	Studies to investigate the possible carcinogenicity of styrene to exposed workers have been conducted in the production of styrene monomer. The increase in risk of tumors observed in some of the studies are generally small and statistically insignificant.
EPA, 2005	The main sources of air emissions are typically molding and extruding processes, during which chemicals are processed under high heat and pressure.
European Union Risk Assessment Report, 2002	About 1 kg styrene/tons polystyrene is released in air during EPS production.

- **Risks associated with styrene are mainly observed during the styrene monomer production.**
- **However, the impact of styrene on human health is not clearly understood.**
- **No health impact study concerning the release of styrene during foam production has been identified.**

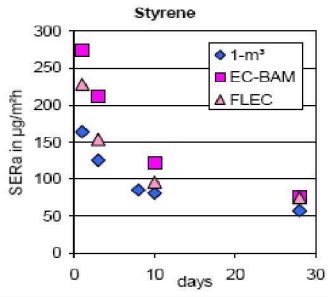
Styrene
use phase exposure

➔ **There can be a release in air of residual styrene monomer from XPS and EPS foams but this release is not hazardous for users, and it decreases with time.**

Styrene can be released from XPS and EPS foam at low level

BASF, LaFarge, SNPA*	No styrene emissions from the foam (EPS, XPS), polymerization is complete.
BPB Placo	Few amounts of styrene monomer (some ppm) can be found as free styrene in the EPS foam.
European Union Risk Assessment Report, 2002	They suggest a emission factor of styrene monomer from EPS foam of about 0,03% (0,3 g of styrene/kg EPS).
The Expanded polystyrene Association of south Africa, Feb 2002	German research in 1987 showed that styrene emissions from EPS are very low, even less than 1% of the Maximum Admissible Concentration (MAC) value in Germany at the time (100 mg/m³). Even when the detection limit of 0.05 mg styrene m³ was lowered to 0.01 mg/m³, no styrene was measurable.

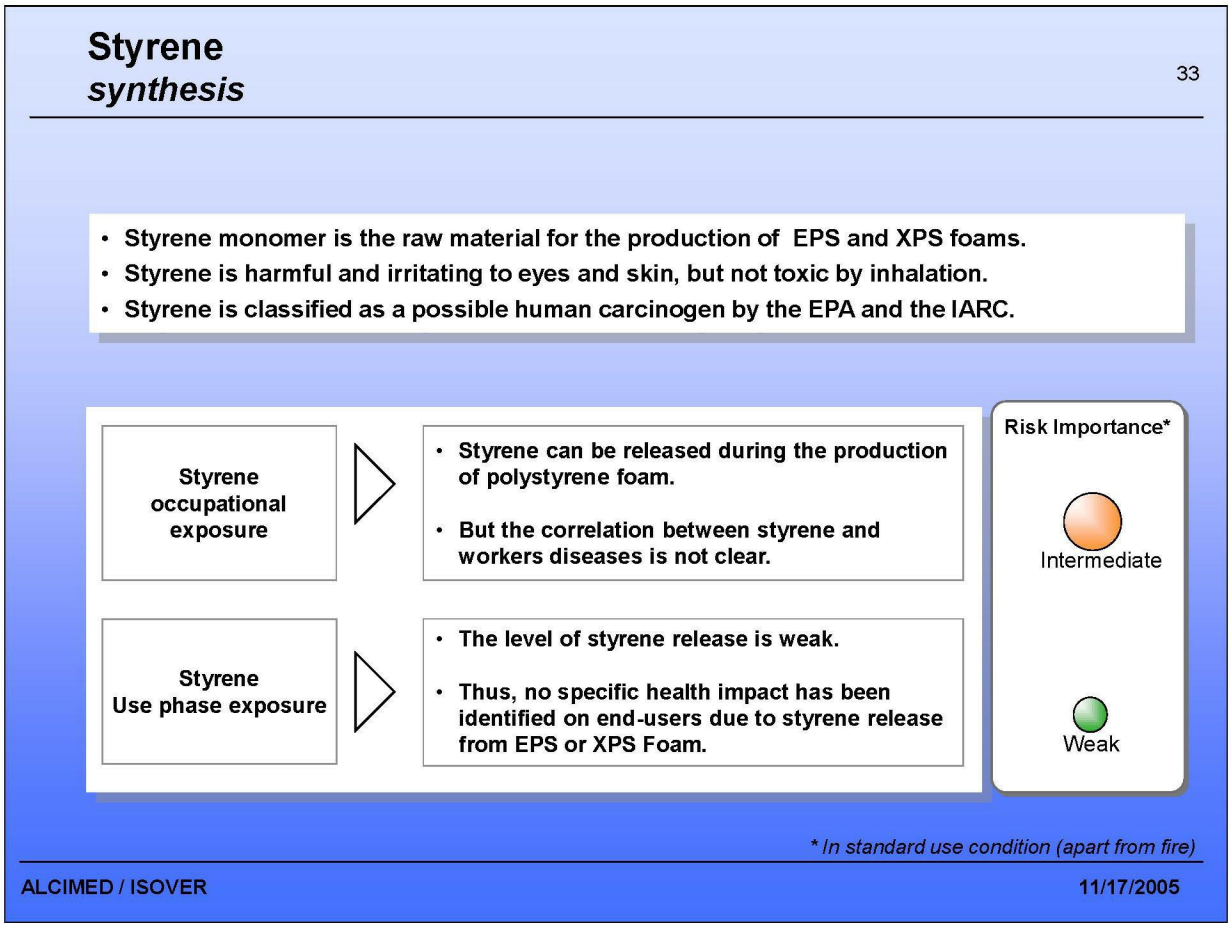
The level of styrene released from EPS/XPS foam decreases with time



Slope of emission curves from styrene emitted from a EPS foam in 2 emission cells (EC-BAM, FLEC) and a chamber (1 m³).

"These styrene monomer emissions are not hazardous to human".

Mr. Horn, Researcher, Federal Institute for Materials Research and Testing (BAM) (Germany).



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Chemicals identification and risk assessment
PUR/XPS blowing agent

	PUR	XPS	EPS
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Blowing agent: *Gaseous or liquid substance which vapor expands the foam, creating gas-filled cells*	HFC, CO_2, hydrocarbons *The blowing agent can be produced during the chemical reaction (CO_2)*		Pentane
Additive: *Substance added to the polymer intended to add a new property to the foam or to modify or to increase the foam properties*	- Flame retardants, heat stabilizers, colorants - Lubricants, antioxidants, catalysts ...		

PUR/XPS blowing agent
overview – past situation

➔ **Due to environmental concerns, PUR/XPS manufacturers have stopped using CFCs, and HCFCs from their foams.**

CFCs

- ✓ CFCs (chlorofluorocarbon compounds) are a group of chemical compounds, consisting of alkanes, with one or more halogens linked.
- ✓ In Montreal Protocol, CFCs were determined to be harmful to the earth's ozone layer.
- ✓ CFCs are today banned and no foam manufacturers use it anymore.
- ✓ Foam manufacturers switch to HCFCs.

HCFCs

- ✓ HCFCs (hydrochlorofluorocarbons compounds) are a group of chemical compounds, made of alkanes, with an hydrogen and one or more halogens linked.
- ✓ HCFCs are declared by Montreal Protocol harmful for the ozone layer but less than CFCs because hydrogen makes them less stable.
- ✓ As CFCs, HCFCs are today banned and no foam manufacturers use it.
- ✓ Foam manufacturers moved to HFC, hydrocarbures, CO_2, other blowing agents and no external blowing agent (this one only for PUR foam).

Insulation foams that were installed in buildings some years ago still contain these environmental hazardous blowing agents, but nowadays, no manufacturers use CFCs nor HCFCs,

PUR/XPS blowing agent
overview – present situation

➔ **Today, foam manufacturers use zero Ozone Depleting Potential substances as blowing agents such as HFCs, hydrocarbons, CO_2 or their mixtures.**

Foam manufacturers have introduced new type of blowing agents

HFCs

- ✓ HFCs (hydrofluorocarbon compounds) are a group of chemical compounds, made of alkanes, with one ore more fluorines linked.
- ✓ HFCs have a greenhouse effect.
- ✓ Concerning the Kyoto Protocol, and in order to reduce the greenhouse gas emissions, **HFCs could be more and more regulated in the future** *(see details in appendix p.67)*

Hydrocarbons

- ✓ Hydrocarbons used as blowing agent are short-chain.
- ✓ Pentane is the most used hydrocarbon blowing agent.
- ✓ Hydrocarbons have a greenhouse effect, but much lower than HFCs
- ✓ **Foams with hydrocarbons as blowing agent have a worse thermal insulation than those insulated with HFCs**

CO_2

- ✓ In the case of XPS foam , CO_2 is an external blowing agent.
- ✓ In the case of the PUR foam, CO_2 is an internal blowing agent: it is produced from the reaction between polyol and isocyanate in water.

Others

- ✓ Other examples of zero Ozone Depleting Potential blowing agent are: azodicarbonamide and methylal.
- ✓ An increasing trend in blowing agent technology is the use of blends of two or more blowing agents to obtain optimized properties.

HFCs / hydrocarbons

toxicity summary – main identified hazards

➔ **These compounds are not hazardous to human health, but they contribute to the greenhouse effect and are hazardous to the environment.**

	Main identified hazards	Comments	Occupational Exposure	Use Phase Exposure
HFCs	- Important Global Warning Potential*	HFCs are going to be banned in all foams starting from January 2009	☒	☒
Hydrocarbons	- Low-to-moderate Global Warning Potential* - Flammable	May accumulate in explosive concentrations.	☒	☒
CO_2	- Low Global Warning Potential*	Not a big environmental problem	*Not in depth analyzed*	

* Global Warning Potential: contribution to the greenhouse effect

HFCs / hydrocarbons
occupational exposure

➔ **While HFCs do not present a risk for workers, some hydrocarbons can be accumulated in explosive mixtures during the foam manufacturing.**

- **HFCs are not harmful for workers but they are harmful for the environment.**
  - "HFC does not present any risk for workers, but due to its greenhouse effect, it seems that its use could be forbidden soon, perhaps in 2012*".
    M. Destin, Commercial Department, The Dow Chemical Company (France).
  - "HFC is zero Ozone Depleting Potential compound but it has an important Global Warning Potential and it contributes to the greenhouse effect".
    M. Gendron, Researcher, Industrial Material Institute (Canada).

- **Due to its explosive risk when accumulated, hydrocarbons can be harmful for workers while they do not present an important harmful for the environment.**
  - Much attention must be taken when working with hydrocarbons; special tool is needed to evacuate the gazes from the working place and care must be taken when stocking hydrocarbons blowing agents.
  - Hydrocarbons, as well as CO_2, contribute to the greenhouse effect, but less than HFC. So, hydrocarbons are not considered as important harmful substances for environment.
    EPA rapport.

* See details in appendix p.68

HFCs / hydrocarbons
use phase exposure

➔ **During the use phase, blowing agents are rejected from foams which have a strong environmental impact.**

Blowing agents diffuse from foams…

- Blown cellular plastics are known to age in the first years of their life through a process of gas exchange diffusion between gas in the cells and the ambient air

… but this has only an environmental impact

- HFCs and hydrocarbons are not considered as harmful chemical substances
- Two environmental impacts are associated with these substances: Ozone Depleting Potential and Global Warning Potential

Ozone Depleting Potential

- It only concerns foams blowned with CFC or HCFCs that were installed some years ago.
- For example, releases of CFC-11 alone are expected to continue at a rate of 40,000 to 70,000 tonnes annually until 2010

Source: Development of a Global Emission Function for Blowing Agents used in closed cell Foams – AFEAS (2000)

Global Warning Potential

-The current foams with GWP compounds are mainly HFCs.

- CFCs and HCFCs are GWP compounds, but they are no longer used in foams

- Hydrocarbons and CO_2 are GWP compounds, but less than HFCs

Chemical substances identification and risk assessment
EPS blowing agent

	PUR	XPS	EPS
Monomer: *The starting material or single unit from which the foam is built*	Isocyanate and polyol	Styrene	
Blowing agent: *Gaseous or liquid substance which vapor expands the foam, creating gas-filled cells*	HFC, CO_2, hydrocarbons *The blowing agent can be produced during the chemical reaction (CO_2)*		Pentane
Additive: *Substance added to the polymer intended to add a new property to the foam or to modify or to increase the foam properties*	- Flame retardants, heat stabilizers, colorants - Lubricants, antioxidants, catalysts ...		

EPS blowing agent
overview

➔ **No changes have been done in the blowing agent of EPS foams and pentane is still the most commonly blowing agent used in EPS.**

Pentane
(*n*-pentane and *iso*-pentane)

- ✓ **Pentane is the blowing agent used in all foams manufacturers leaders.**
- ✓ **Pentane does not represent a hazardous for human nor for the environment.**
- ✓ **EPS foams present a good environmental image: environmental declarations have been done by manufacturers and Styrofoam has received the Greenguard label.**

"EPS foam is a very good insulating product in terms of environmental concern. It is used in the High Environmental Quality Operations ".
Mr. Denimal, product manager. BPB Placo (France).

"Environmental declaration is a voluntary approach of construction material manufacturers. The environmental declaration of EPS has been done by the main EPS foam manufacturers".
Ms. Amoy, General Secretary. Syndicat National des Plastiques Alveolaires (SNPA) (France).

- ✓ **Manufacturers do not envisage to change the blowing agent of EPS foam.**

Pentane
toxicity summary – main identified hazards

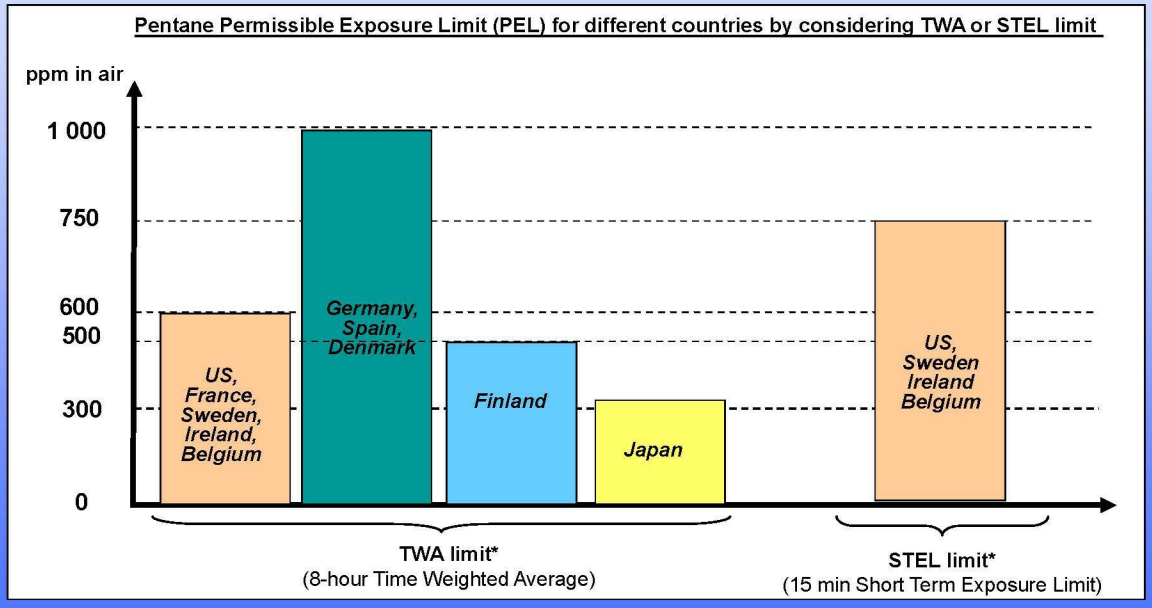
➔ **Pentane is not hazardous to human nor to the environment and even if it is explosive, it is not considered as a big problem in the EPS foam.**

	CAS number	Main identified hazards	Comments	Occupational exposure	Use Phase exposure
Pentane	109-66-0	- Extremely flammable - Toxic to aquatic organisms - Harmful if swallowed - May cause skin dryness - No human and animal data are available on the carcinogenicity of pentane	May accumulate into explosive concentrations	☒	☒

"Pentane is the main and the only problem concerning EPS foam. But pentane is not an hazardous compound, so the problem with EPS foam is very limited" *Ms. Amoy, General Secretary. Syndicat National des Plastiques Alveolaires (SNPA) (France).*	Since pentane forms explosive mixtures, precautions must be taken. *EPA rapport.*

Pentane
Permissible Exposure Limit

➔ **The Permissible Exposure Limit associated with pentane is below 1000 ppm, Japan being the most stringent country with 300 ppm.**



*Definition in page 5

Pentane
occupational exposure

➔ **As pentane is a flammable substance, special care must be done during manufacturing and stock of expandable polystyrene beads.**

Pentane emissions during manufacturing	More than 1g of pentane is emitted during manufacturing of 20g expanded polystyrene foam. This corresponds to 87.5% of pentane content. *Source: Environmental declaration, Alveolar Plastic National Association (SNPA) (France)*
Pentane emissions during stock of beads	After storage containers are opened, a time lag of 10 minutes is suggested to allow fumes or pentane vapors to dissipate out of the containers. *Source: Compilation of Air Pollutant Emission Factors. Environmental Protection Agency (EPA)*
Pentane emissions during transport of beads	0.024g of pentane is emitted during transport of 20g of expanded polystyrene foam. This corresponds to 2.04% of pentane content. *Source: Environmental declaration, Alveolar Plastic National Association (SNPA), France.*

Pentane
use phase exposure

➔ **Blowing agent dissipation from the foam is declared by EPS foam manufacturers in the environmental declaration but while concentration is not high, some of them say blowing agent does not dissipates from the foam.**

Pentane emissions during the use phase

At the use phase, it remains 0.08g of pentane in 20g of the EPS foam, which dissipates during the use phase. This corresponds to 6.80% of the initial pentane content.
Source: Environmental declaration, Alveolar Plastic National Association (SNPA), France

Industrial perception

"Pentane diffuses when the foam has just being processed, but in the use phase there is no diffusion".
Mr. Denimal, Comercial. BPB Placo (France)

"Once that foam has been manufactured, there is no problem with pentane diffusion".
Comercial Department. BASF (France)

Research or Consumer Association perception

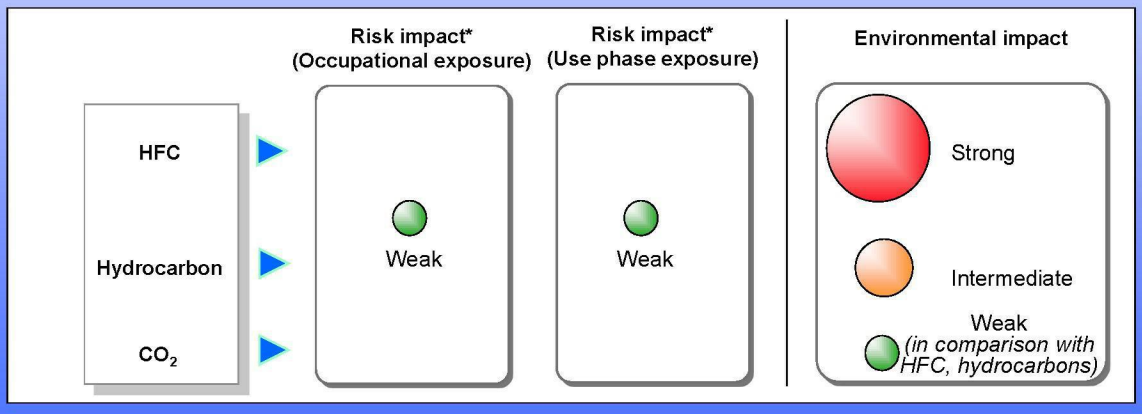
"EPS foam diffuses low concentrations of pentane during its life".
Ms. Gil, Project Manager, Eco-Conso (Belgium)

"As low concentration of pentane is emitted from the foam, it is not hazardous for human".
Mr. Horn, Researcher, Federal Institute for Material Research and Testing (Germany).

- The level of pentane emission is very low
- No study has been identified concerning the health impact of pentane on end-users

Blowing agent
synthesis

- **The current used blowing agents are not considered as strong hazard chemical substances for the human health.**
- **Today, no impact on the human health can be associated with the usual blowing agent used in the insulating foam panels.**
- **The main concern is environmental protection because of their contribution to the green house effect.**



** In standard use condition (apart from fire)*

Chemical substances identification and risk assessment
additives

	PUR	XPS	EPS
Monomer: *The starting material or single unit from which the foam is built*	Isocyanate and polyol	Styrene	
Blowing agent: *Gaseous or liquid substance which vapor expands the foam, creating gas-filled cells*	HFC, CO_2, hydrocarbons *The blowing agent can be produced during the chemical reaction (CO_2)*		Pentane
Additive: *Substance added to the polymer intended to add a new property to the foam or to modify or to increase the foam properties*	- Flame retardants, heat stabilizers, colorants - Lubricants, antioxidants, catalysts ...		

PUR / XPS / EPS additives
overview

➔ **Additives are generally added in very low concentrations, less than 1%, excepting for flame retardants which can be added in concentrations varying from 0.1 to 10%.**

Flame retardants

- ✓ Reduce the tendency of the plastic to burn.
- ✓ Brominated, organic-phosphorous-based and inorganic compounds.

Concentrations: 0.1 to 10%

Heat stabilizers

- ✓ Assist in maintaining the chemical and physical properties of the foam.
- ✓ Lead, barium, cadmium, tin, zinc …

Concentrations: <1%

Colorants

- ✓ Impart color.
- ✓ Titanium dioxide, iron oxides, anthraquinones, carbon black …

Concentrations: <1%

Lubricants

- ✓ Assist in easing the flow of the foam in the molding and extruding processes.
- ✓ Stearic acid, waxes, fatty acid esters, fatty acid amines …

Concentrations: <1%

Antioxidants

- ✓ Inhibit the oxidation of plastic materials.
- ✓ Phenols, amines, organic phosphites and phosphates, esters …

Concentrations: <1%

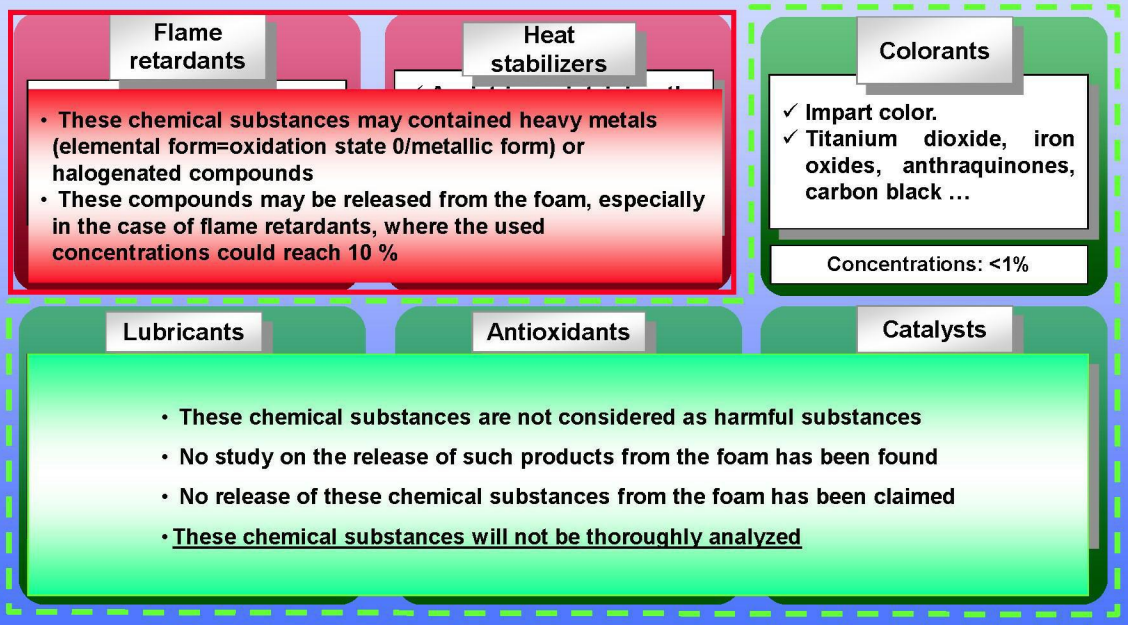
Catalysts

- ✓ Promote reactions.
- ✓ $AlCl_3$, zeolite, tin catalysts …

Concentrations: <1%

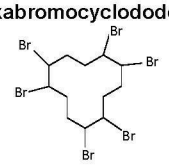
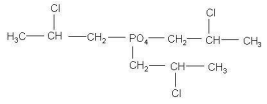
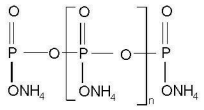
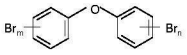
PUR / XPS / EPS additives
potential dangerous chemicals

➔ **Flame retardants and heat stabilizers could be harmful chemicals since some of them contain halogen compounds and heavy metals.**



Flame retardants
overview – main identified hazards

➔ **There are three main current types of flame retardants: brominated, organic phosphorous and inorganic flame retardants, used in the different foams.**

Brominated flame retardants	Organic phosphorous-based flame retardants	Inorganic flame retardants
HBCD (Hexabromocyclododecane)  Used in: XPS, EPS	TCPP (tris(chloropropyl)phosphate)  Used in: PUR, PIR	Ammonium polyphosphate  Used in: PUR
PBDE (Polybrominated diphenyl ether)  Most used in: EPS and PUR (penta-, octa-, deca- BDE)	RDP (resorcinol-bis-diphenylphosphate) Used in: PUR	Red phosphorous P_n Used in: PUR

Flame retardants
toxicity summary

➔ **While inorganic flame retardants are generally not toxic, halogenated flame retardants are bioaccumulative, environment persistent and toxic.**

	CAS number	Main identified hazards	Comments
HBCD	25637-99-4	- Bioaccumulation - Changes in behavior, learning and memory (studies with mices)	To date (June 2004), it has not been found to bioaccumulate in human (to be evaluated).
TCPP	13674-84-5	- Accumulation in aquatic systems and in liver and kidneys (animal studies).	Significant additional research is needed on carcinogenic effects.
Ammonium polyphosphate	68333-79-9	- Not toxic	No significant environmental or health concerns identified. Generally considered as safe.
PBDE	Several CAS numbers*	- Bioaccumulation - Changes in behavior, learning and memory (studies with mices)	There is no evidence of toxicity of deca- PBDE PBDE has been found in breast milk
RDP	57583-54-7	- Not toxic	There is no evidence of bioaccumulation. Few studies on carcinogenic effects; additional research needed.
P_n	7723-14-0	- Not toxic	Bioaccumulation does not occur. Few health and environmental concerns. Generally considered as safe.

**: tetra-: 40088-47-9; penta-: 32534-81-9; hexa: 36483-60-0; hepta: 68928-80-3; octa-: 32536-52-0; nona: 63936-56-1; deca-: 1163-19-5*
The most commercialy used are penta- octa- and deca-

Flame retardants
regulations

➔ **Due to their toxicity, the use of PBDE has been forbidden in electronic equipments and the use of penta- and octa-PBDE is banned in the European Community and in Canada.**

The use of PBDE has been banned in electronic equipment.

→ The ROSH Directive 2002/95/EC of 27 January restricted the use of certain hazardous substances in electronic equipment put on the market. Some of these substances are polybrominated biphenyls (PBB) and polybrominated diphenyl ethers (PBDE)

The use of penta- and octa- PBDE has been banned in the European Union and in Canada

→
- Penta- and octa-bromodiphenylethers have been banned from August 2004 in the European Union and from beginning 2006 in California.
- The USA State Senate has approved a new legislation that would restrict the use of brominated diphenyl ether (BDE)-based flame retardants.

In the near future, PBDE (penta, octa, deca BDE) will no longer be used in foam applications

Flame retardants
occupational exposure

➔ **Even if exposure occurs at low levels, a risk is observed for workers because flame retardants such as HBCD, TCPP and PBDE are bioaccumulative substances.**

Identified studies	Main Results
IPCS, 1994	Studies performed to determine whether PBDE is present in the fumes emitted during thermal processes, such as extrusion and molding under normal processing conditions at temperature in the range of 200 °C to 250 °C. PBDEs air levels during processing were < 2 ng/m^3 with the exception of two samples at the extruder head (128 ng/m^3).

- **Workers can be exposed to flame retardants during foam production.**
- **Even if levels of exposure are not high, halogenated flame retardants present a risk because they are bioaccumulative.**
- **But today, no occupational exposure limits have been identified**

Flame retardants
use phase exposure

➔ **As flame retardant emissions have been detected in PUR, PIR, XPS and EPS foams and as these substances are bioaccumulative, complementary studies should be carried on in the future.**

Identified studies	Main Results
Kemmlein *et al.*, 2003	Flame retardants emissions have been tested on a number of consumer goods and building materials, including EPS, XPS, PUR and PIR insulation foams. The results are not sufficient for a comprehensive representation of the emission behavior and interpretive assessment of flame retardants. There are further gaps, for example, concerning the explanation of **high flame retardants concentrations in house dust**.

"Very low concentrations (ng/m^3) of flame retardants are emitted from the foams and this is very difficult to measure".
M. Horn, Researcher, Federal Institute for Materials Research and Testing (BAM) (Germany)

- Flame retardants emissions from foam insulating panels can be possible but at a low level of concentration
- No health impact has been identified on end users
- However, flame retardants are bioaccumulative substances

- As the presence of flame retardants is the house is an important topic, further impact studies will be done in the future.
- **A continuous bibliographic review on organic flame retardants should be done**

Heat stabilizers

toxicity summary – main identified hazards

➔ **Even if these compounds are highly toxic, low hazard is identified in industrial manufacturing because their release during manufacturing is well controlled.**

	CAS number	Main identified hazards	Comments
Lead	7439-92-1	- Probable human carcinogen - Irritating - May cause reproductive disorders and tetratogenic effects	Sufficient animal evidence for carcinogenity but inadequate human carcinogenity data.
Barium	7440-39-3	- Irritating to the nose, respiratory tract, mouth, eyes and skin.	Barium poisoning is unknown in industry, although the potential exists when the soluble forms are used
Cadmium	7440-43-9	- May cause cancer - Flammable in air - Very toxic by inhalation - Risk of irreversible effects	Release of cadmium to the environment from the manufacture of cadmium products are well controlled.
Tin	7440-31-5	- Highly flammable - Irritating - May cause dermatitis	Low hazard for usual industrial handling. Moderate toxicity because of poor absorption and rapid tissue turnover
Zinc	7440-66-6	- Very toxic to aquatic organisms - Irritating - May cause chronic bronchitis	The toxicological properties of this substance have not been fully investigated

Heat stabilizers
occupational and use phase exposure

➔ **Heat stabilizers health impact is rather limited since no release of this products from the foams has been identified.**

Global approach

- Cadmium Permissible Exposure Limit: 0,005 mg/m^3 (OSHA limit – US)
- Lead Permissible Exposure Limit: 0.05 mg/m^3 (OSHA limit – US)
- Use of cadmium and lead are strongly regulated on an occupational exposure point of view

Insulation foam approach

- Cadmium and lead are used in low concentrations (< 1%) in insulating foams.
- No emission of these compounds from foams has been identified during manufacturing and using.

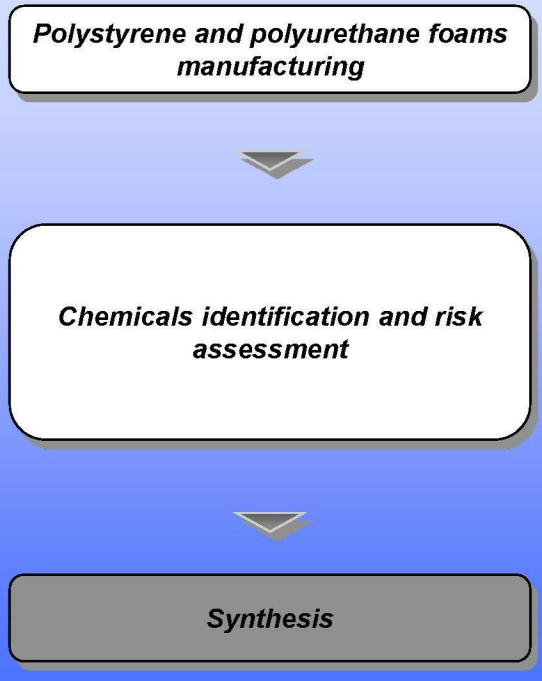
Health impact associated with heat stabilizers, particularly with cadmium and lead, appear to be very limited

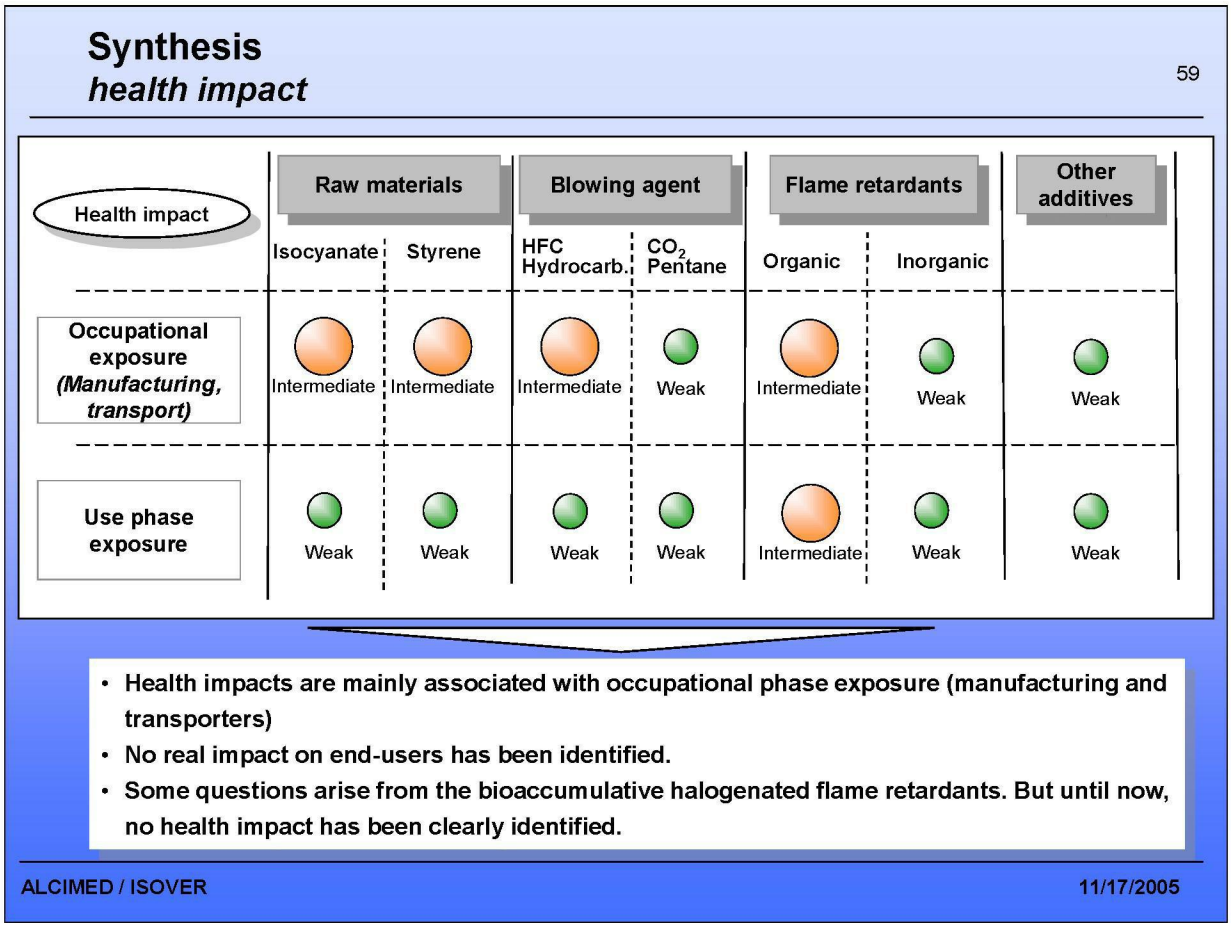
Additives
synthesis

- Except flame retardants, which can be used at concentrations between 1 to 10 %, additives are generally used at low concentrations, below 1%.
- Among the used additives, only flame retardants and heat stabilizers could have a potential health impact because some of then content heavy metals and halogenated compounds.
- Concerning flame retardants, only bioaccumulative halogenated substances that could represent a potential danger. At this time no real health impact during the use phase of foams has been identified.
- In the case of heat stabilizers, toxic products such as cadmium or lead are used. But their use is strongly regulated. Moreover, no health problem has been identified on end-users.

** In standard use condition (apart from fire)*

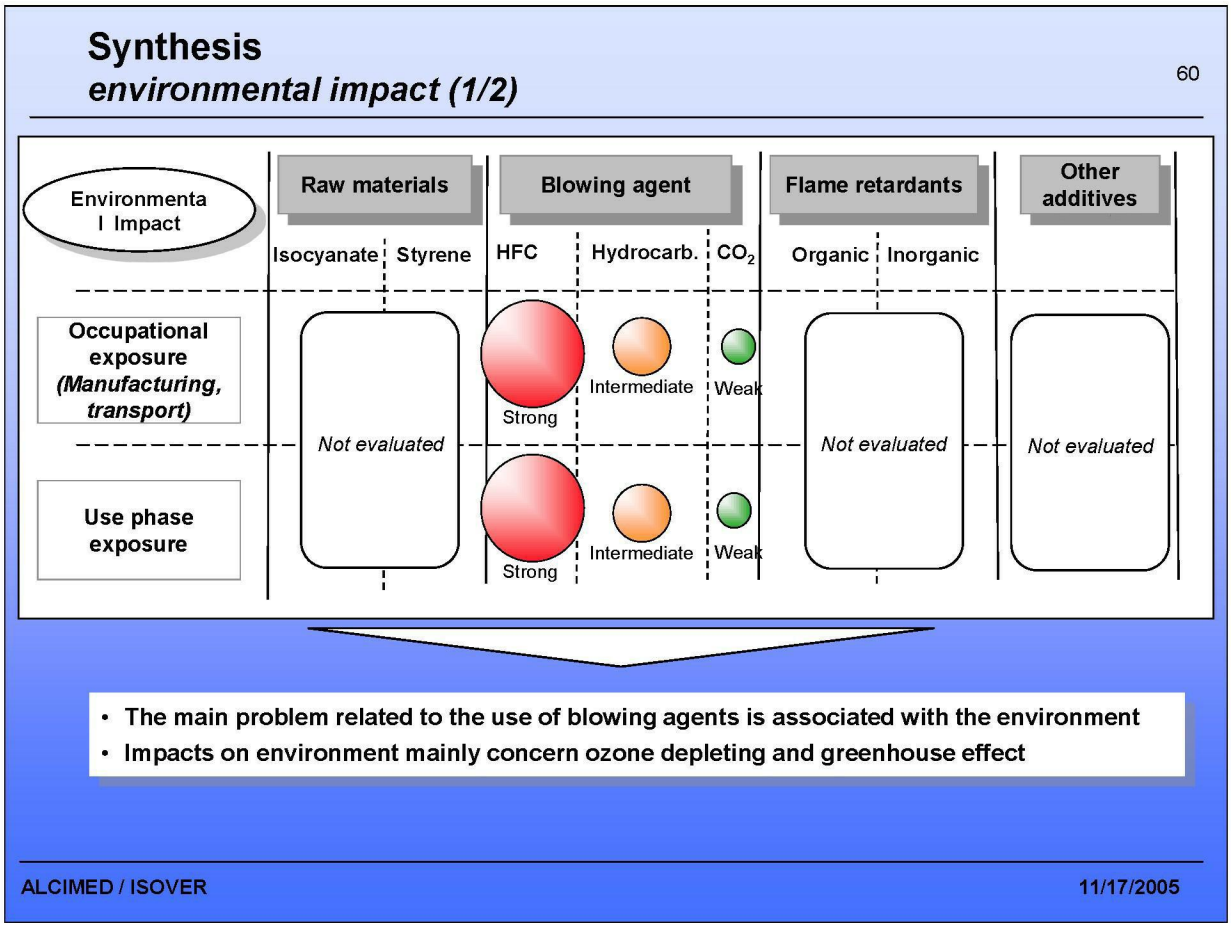
Synthesis





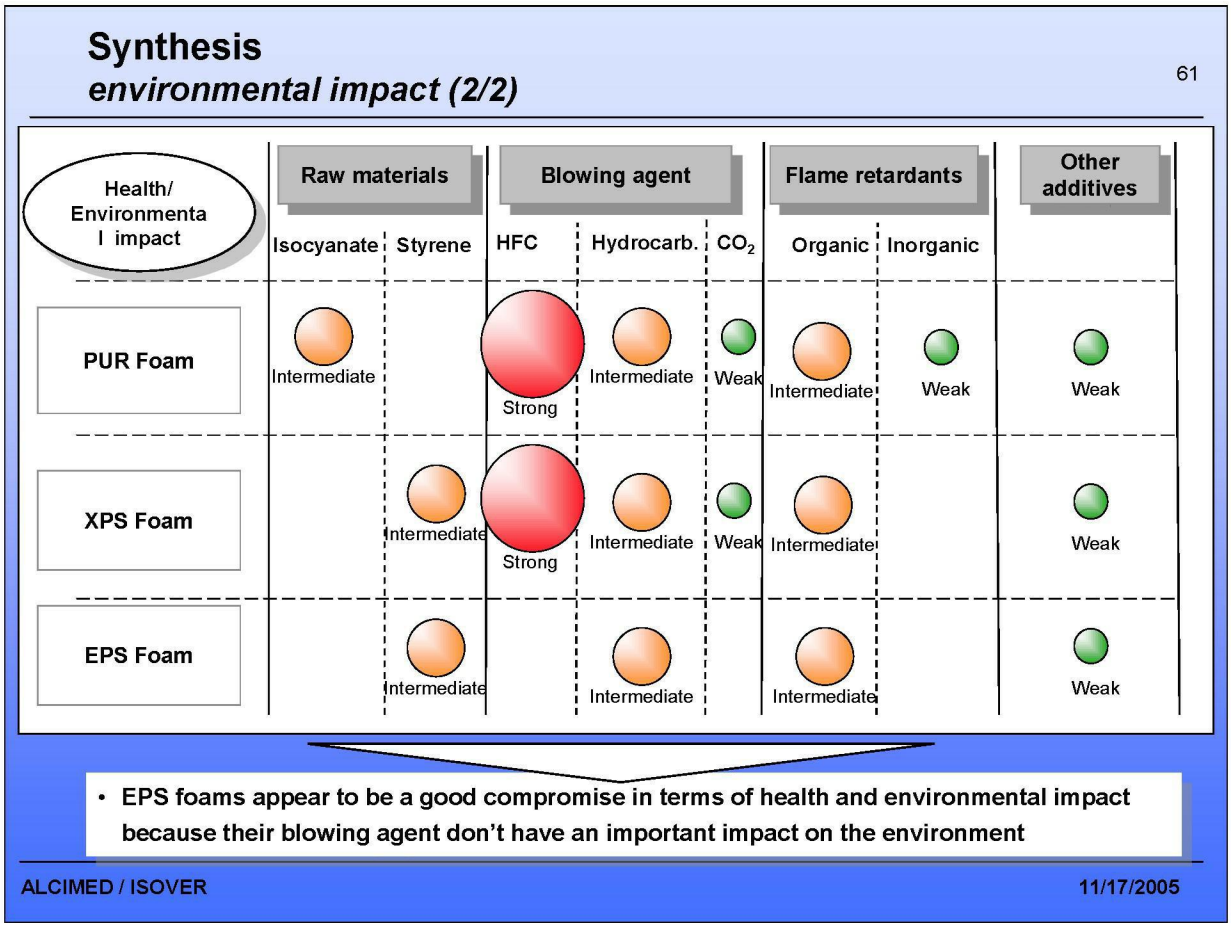
Implement: mise en œuvre

Lead: plomb



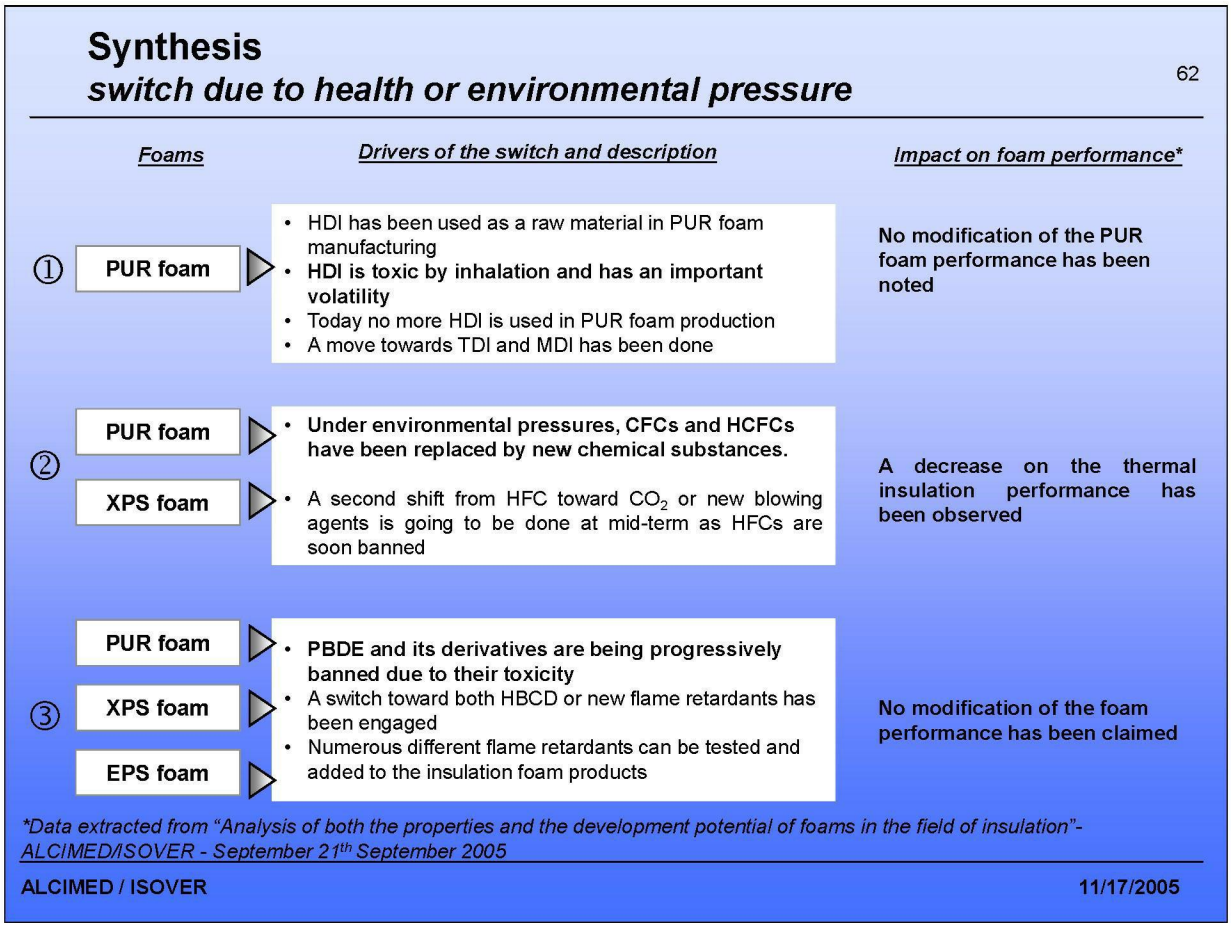
Implement: mise en œuvre

Lead: plomb



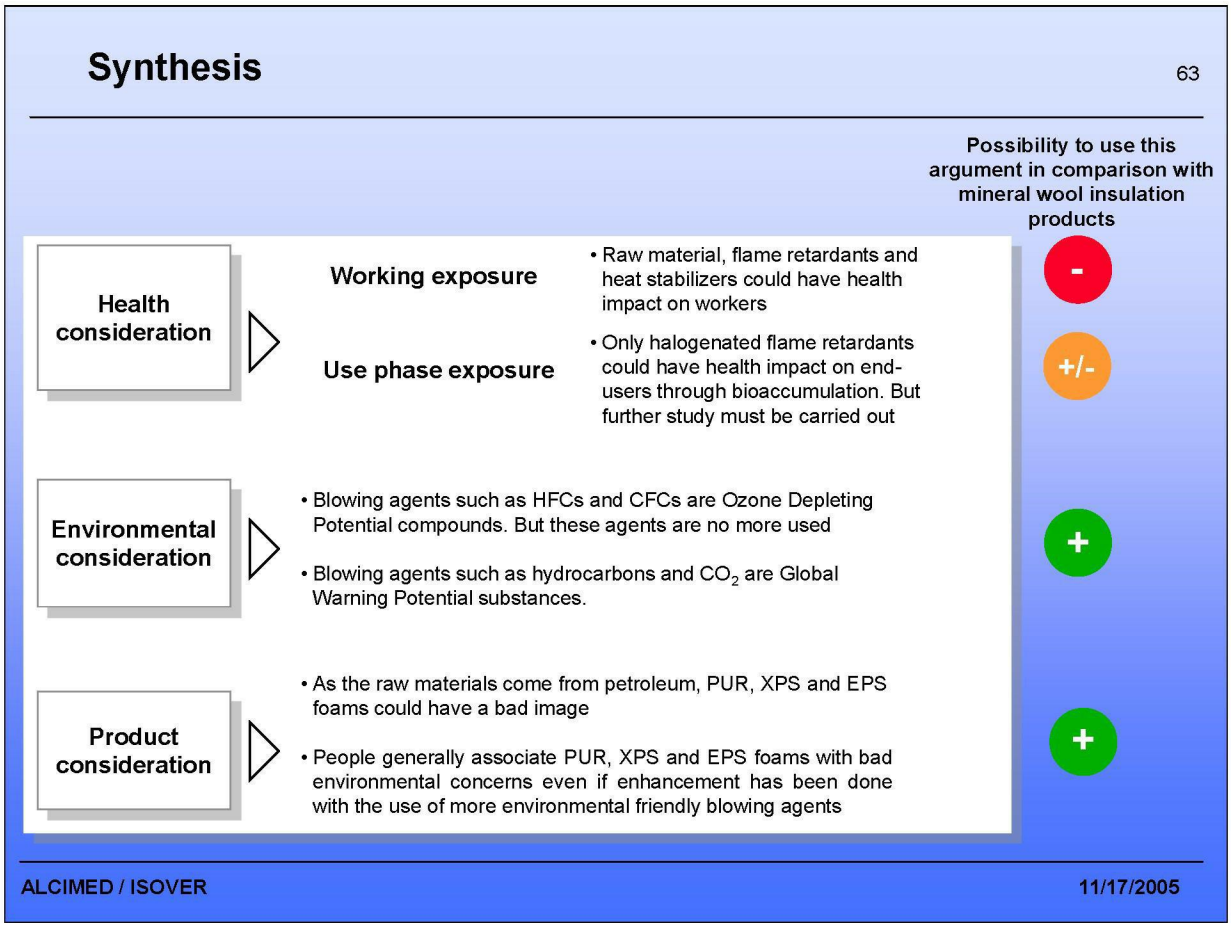
Implement: mise en œuvre

Lead: plomb



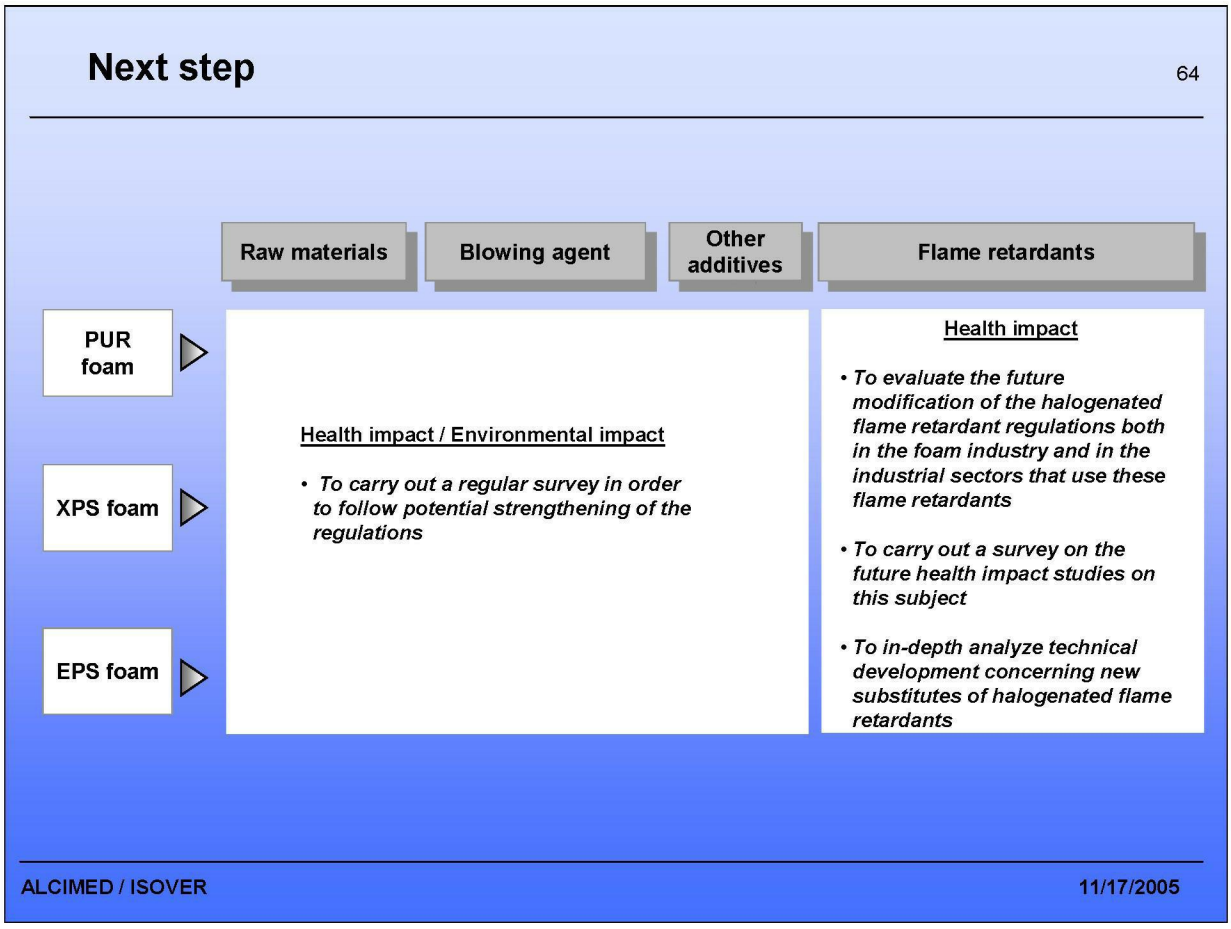
Implement: mise en œuvre

Lead: plomb



Implement: mise en œuvre

Lead: plomb



Implement: mise en œuvre

Lead: plomb

Appendix

Carcinogen Categories

The evidence relevant to carcinogenicity from studies in humans is classified into one of the following categories (IARC):

Group	Description
1	Know human carcinogen
2A	Probable human carcinogen
2B	Possible human carcinogen
3	Not classifiable as to its carcinogenicity to humans

Substances or preparations which, if they are inhaled or ingested or if they penetrate the skin, may induce cancer or increase its incidence

Mutagen Categories

The evidence relevant to mutagenicity from studies in humans is classified into one of the following categories (IARC):

Group	Description
1	May cause heritable genetic damage
2	
3	Possible risk of irreversible effects

Substances and preparations which, if they are inhaled or ingested or if they penetrate the skin, may induce heritable genetic defects or increase their incidence

HFC regulation
key points

August 2003:

The Commission put forward a proposal to regulate emissions of fluorinated gases part of EU to reduce global warming under the Kyoto protocol. Objective: to reduce by almost one quarter the projected fluorinated gas emission by 2010

June 2005: *The proposal is split between:*

- ***A directive*** *(to be transposed in national legislation) to phase out HFC-134 in vehicle air conditioning as of 2011 for new models, as of 2017 for all new cars.*
- ***A regulation*** *(applicable immediately) for all other applications. It mainly aims to improve containment of F-gases by setting a minimum standards for inspection and recovery. Monitoring and reporting on emissions are strengthened including training and certification of personnel in charge of inspections. Labeling of products is introduced so that consumers can make informed choices. A ban will apply for uses where containment is deemed inappropriate (magnesium die-casting, vehicle tyres, windows, footwear, non-refillable containers, certain foams, self-chilling drinking cans, certain aerosols, new fire protection systems, fire extinguishers)*

Octobre 2005, the 11th:

European Parliament environment committee voted in favour of an amendment to Annex II of the proposal for a Regulation on fluorinated gases which would prohibit the use of HFCs in all foams as from January 2009.

October 2005, the 26th:

The EU parliament Second Reading has adopted a legislative Resolution making few amendments to the Common Position. On the Regulation on Certain Fluorinated Greenhouse Gases, the parliament has accepted the EU Council Common Position confirming its containment policy, and rejecting the earlier Environment committee amendments to impose bans of most F-gases.

A provision was added to allow member states to maintain or adopt stricter F-gas controls if these are in line with their national greenhouse gas reduction targets under the Kyoto Protocol (Sweden, Denmark and Austria have more stringent national rules)

Next steps: A coming Environment Council should adopt a political agreement on the issues. It is also possible that Council and Parliament would have to negotiate the final version, either informally or through the formal Conciliation Procedure.

Dow / BASF
first elements on their CO_2 strategy

- German manufacturers already replaced CFC-12 as blowing agent and cell gas by HCFCs in 1990, namely either by 142b or by a mixture of 142b and 22.
- In 1996, the two most important producers in Germany, BASF and Dow Chemical, entered into a voluntary agreement to dispense with HCFCs from 2000 onwards. It is thus not expected that the producers switch from the 142b/22 mixture, which will be banned from 2000 onwards, to pure 142b, which will continue to be permitted for a further four years.
- Instead, all four German producers are working on systems using zero-ODP substances, which will be used entirely from 2000 onwards, most German producers are orienting themselves to HFC systems. The blowing agents coming into question here are 152a and 134a, either alone or mixed with each other
- German producers are in agreement that high-quality XPS panels can be produced with 152a and 134a. Nonetheless, BASF views HFCs only as a transitional solution and is currently planning to convert its production in Germany from 2000 onwards entirely to CO_2 or CO_2 plus ethanol. However, if market acceptance is lacking, BASF states that it would see itself forced to use HFCs (Boy 1999).

Source: Emissions and potential reductions of hydrofluorocarbons, perfluorocarbons, Sulfur hexafluoride in Germany Dr Schwartz & Dr Leisewitz – Büro für Umweltforschung und –Beratung Franckfurt am Main – Germany, Oct 1999

CO_2 technology in XPS foam production
first elements

- As in PU rigid foam, CO_2 is a candidate blowing agent. However, in XPS it is not formed by a chemical reaction but must be provided externally.
- With CO_2 alone, only a small part of the product range can at present be produced without loss of insulation performance. Among the panel thicknesses ranging up to 200 mm, only those with thicknesses of less than 60-70 mm have a quality comparable to those foamed with HCFCs.
- However, when applied in combination with 2-3% organic blowing agent, namely ethanol, the entire product mix can be produced without loss of quality – as stated by the developer of this process, BASF (Boy 1999). However, production facilities need to be structurally modified for the flammable blowing agent, which entails high capital investment.
- As CO_2 has lower solubility than fluorinated gases, XPS production demands higher pressure values, leading difficulties in the stabilization of the foam.