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Note Technique / Technical Memo

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OBJET / SUBJECT : N° Projet – Annual Review of Fumes & Toxicity on Insulation Materials

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RÉSUMÉ / ABSTRACT :

This report summarizes the analysis on fumes & toxicity of insulation materials (PIR, PUR, PF, EPS, GW, SW). The first part is related to the selection of a standard to study and compare the emission of toxic effluents of a wide range of insulations products.

The second part focuses on the testing of the insulation materials with a Navy military standard formulation (AFAP- 3). The analysis revealed that foam formulation influence the toxic products yields, obtaining toxicity index (TI) as follows: PUR = PIR = PF > EPS > GW = SW. For PF foams the main toxic effluents are SO2> HCN > HCl and for PIR and PUR foams HCN > CO > NOx > HCl.

To further understand the rigid foams (PIR, PUR and PF) behavior under a fire it will be necessary to understand the influence of formulation and additives. Collaboration with fire expert has been started in the middle of 2015 (UClan) to:

- Study foam combustion mechanism
- Deep analysis on smoke opacity and material toxicity under different fire conditions
- Screen different potential additives to reduce toxicity index

1. Preliminary studies

The fire statistics show that the main causes of death in fires arises from the inhalation of toxic effluents. Some of these gases are irritants as hydrogen chloride (HCl) and hydrogen bromide (HBr), asphyxiants as carbon monoxide (CO) and hydrogen cyanide (HCN).[1,2]

In the past Saint Gobain launched some external studies (ALCIMED – 2005 & ENVIRON Corp – 2011) to evaluate and identify the toxicity of PIR/PUR (polyisocyanurate/polyurethane) as insulation materials compared to other insulation products in the market. The chemical nature of PIR/PUR foams promotes to look closer to different products as (HCN & CO). Among the gases analyzed, the major gases contributing to its toxicity are hydrogen cyanide (HCN), carbon monoxide (CO), clorhydric acid (HCl) and bromhydric acid (HBr)[3]. The conclusion of both studies was that there is limited data regarding risk from thermal decomposition products of PUR/PIR and that there is not dedicated referential on building's regarding toxicity.

To continue these studies we have focused in:

(1) Identify a toxicity standard (in transportation field) that could ne use to assess the building materials. The selected laboratory was the Laboratory national de métrologie et d'essais (LNE)
(2) Study the toxicity behavior of different commercial insulation materials and suppliers
(3) Deep study on in-house PIR insulations products by the analysis of laboratory samples (different chemistries)

2. Scope on fumes & toxicity standards in different fields

The LNE compiled a report summarizing the toxicity standards on transportation field in France and Europe, these standards are described in **Table 1** by combustion products and toxicity limits in different domains.

The selected standard was the Allied Fire Assessment (AFAP-3) by the OTAN in 2010[i] which have a number to delimited the toxicity index (TI < 10) giving us the possibility to compare the different materials. The selection of this standard was done in two main points:

- The number of combustion gases analyzed at different temperatures
- The possibility to compare the products among them thanks to the use of the Index of Toxicity (IT)

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[1] Fire statistics, London, U.K. Departament for Communities and Local Government. **2010**
[2] Molyneux, S.; Stec, A.; Hull, R. Polym Degrad Stab. **2013**, 1-11
[3] Wilhelm,F.; Giersig, M. *Rev. Environ Contam Toxicol.* **2001**, 170, 1-11

Table 1. Summary on regulations to measure fire toxicity effluents

Domain	Legislation	Gas	Method	Observations
ERP	Standard from 4 November 1975	HCl, HCN	Tube furnace NF X70-100 at 700°C under N2, analysis by different analytical methods	
French rail standard	NF F 16_101: 1998 NF16-102:1992	HCl, HCN,**CO,CO2,HBr,SO2, HF**	Tube furnace NF X70-100 at 600°C or 800°C under air. analysis by different analytical methods	
European rail standard	NF EN 45545-2:2013	HCl, HCN, CO,CO2,HBr,SO2, HF,**NOx**	Depends on situation: - Smoke room (ISO 5659-2) + IRTF analysis (ISO 19702) several modes of thermic exposition - Tube furnace (NF X 70-100) with different specific methods	Nox=NO+NO2
Boating regulation	MSC:307(88) (code FTP:2010)	HCl,HCN,CO,HBr,SO2,HF, NOx	Smoke room (ISO 5659-2)) + IRTF analysis (ISO 19702)	Missing CO2
Navy	IT 4390:1992 (national navy, surface navy)	HCl,HCN,CO,HBr,SO2,HF, NOx,**C2H3CHO, HCOOH,HCHO**	Tube furnace NF X70-100 at 800°C under air. Analysis by different analytical methods	NOx = NO2
Navy	AFAP-3:2010 (OTAN)	HCl,HCN,CO,HBr,SO2,HF, Nox,C2H3CHO,HCHO, **C6H5OH**	Tube furnace (NF X 70-100) at 350°C and 800°C under air	Formic acid missing
Navy	RT10.4 (submarines and national navy)	HCl,HCN,CO,HBr,SO2,HF, NOx,C2H3CHO, HCOOH,HCHO,C6H5OH, **NH3**	Tube furnace (NF X 70-100) at 350°C and 800°C under ai	NOx = NO2

3. Methods

The selected commercial insulation products and laboratory samples are summarized in **Table 2 & 3** respectively.

Table 2. Insulation commercial products

Supplier	Product	Product Reference	Density (Kg/m3)	Lambda (mW/m.K)	Application	Additional comments
Placo	EPS	Cellomur ultra	16.5	31	Outdoor	Grey EPS
		DMM1	15	37.5	Outdoor	White EPS
Isover	GW	GR32 Kraft	2.8	32	Outdoor	
	SW	Sillatherm	17	35	Outdoor	
Kingspan	PF	K5	35	20	Outdoor	
		K7	35	20	Outdoor	
		K8	35	20	Outdoor	
	PIR	TW50	30	22	Outdoor	
		TP10	30	22	Outdoor	
Celotex	PIR	GA4000	22	30	Indoor	Index n = 250
		FR5000	21	32	Indoor	Index n = 400

Table 3. Laboratory PIR products from Celotex

Supplier	Product	Product Reference	Amount of fire retardant (TCPP)	Additional comments
Celotex	PIR	n= 2,5	-	Foams synthesized at laboratory scale
		n= 2,5	3%	
		n= 2,5	10%	
		n= 4	-	
		n= 4	3%	
		n= 4	10%	

* n= index

Navy regulation (AFAP-3)

The Allied publication: The test method is directed at the analysis of a specified set of gaseous species which are commonly present in combustion products of materials used in military applications and which may cause lethality at the time of the fire.

The toxicity index is defined in the AFAP-3 as the capacity of a substance to cause harmful effects in living organisms including, irritation, narcosis, or death. In this standard, the contribution of individual toxicants to the overall toxicity should be equal to or less than 10. A research internally done to understand why 10 have not been fruitful, at present we take this value as a reference without knowing about the possibility to directly be applied as it is for the building applications.

The method of analysis for the AFAP-3 utilizes a steady tube furnace (NF x 70-100) in 1gr of product. The test is done using an air flow of 2l/min of air at 350°C and 800°C depending on the gas analyzed. In **Table 4** are summarized the critical factor in concentration (limit value to be inhaled during 30min) of the different gases and their temperature analysis.

Table 4. The Cf values for the different gases

Compound	Formule	Critical factor (*Cf*)* (ppm)	Temperature of test
Carbon dioxide	CO_2	100000	800°C
Carbon monoxide	CO	4000	800°C
Nitrogen Oxide/dioxide	$NO + NO_2$	100	800°C
Sulfur dioxide	SO_2	400	800°C

Fluorhydric acid	HF	50	800°C
Bromhydric acid	HBr	150	800°C
Clorhydric acid	HCl	500	800°C
Hydrogen cyanide	HCN	90	800°C
Phenol	C_6H_6OH	250	800°C
Formaldehyde	HCHO	500	350°C
Acrolein	C_2H_3CHO	5	350°C

*Cf values are taken from the following reports:

- Defence Science & Technology Laboratories – Knowledge Services, Kentigern House, 65 Brown Street, Glasgow, G2 8EX, UK.

- Report for DERA Holton Heath on toxicity of inhaled gases. IL1003/1/TM/BIO/U/999/95. 1995. (DRIC Ref. CDL 57733)

- Toxicity of inhaled gases. DERA/CBD/CR96/046/1.0. 1997. (DRIC Ref. CDL 56521)

- ***Calculation of TI***

To determine the concentration of each gas, we use the following equation to calculate C_θ (ppm)

$$C\theta = \frac{Ci \text{ x } 100 \text{ x } V}{m} \qquad \textbf{(Eq. 1)}$$

C_θ = gas concentration produced under the conditions of the test, scaled up for 100g of material into a volume of $1m^3$ (ppm)

Ci = is the gas concentration in the volume V of combustion gas (ppm)

V = volume of the sample of combustion products (m^3)

The toxicity index is calculated then by the following equation:

$$\text{TI} = \sum \frac{C\theta i}{Cfi} \qquad \textbf{(Eq. 2)}$$

$C_{\theta i}$ = gas concentration produced under the conditions of the test, scaled up for 100g of material into a volume of $1m^3$ (ppm)

Cfi = the concentration of a gas considered fatal to man for 30 minute exposure (ppm)

To be in the limit of the toxicity index (TI) should be equal or lower than 10 (TI ≤ 10)

4. Results

The analysis of commercial products by AFAP-3 (**Figure 1**) confirmed the low emissions of toxic effluents of GW, SW and EPS[4], its toxicity index is < 10.

The PUR, PIR and PF products revealed a toxicity index higher than 10, this fact is supported by a greater number of publications[5]. The PIR and PUR foams at 300°C show a complete degradation of polyols and MDI components producing toxic volatile products.

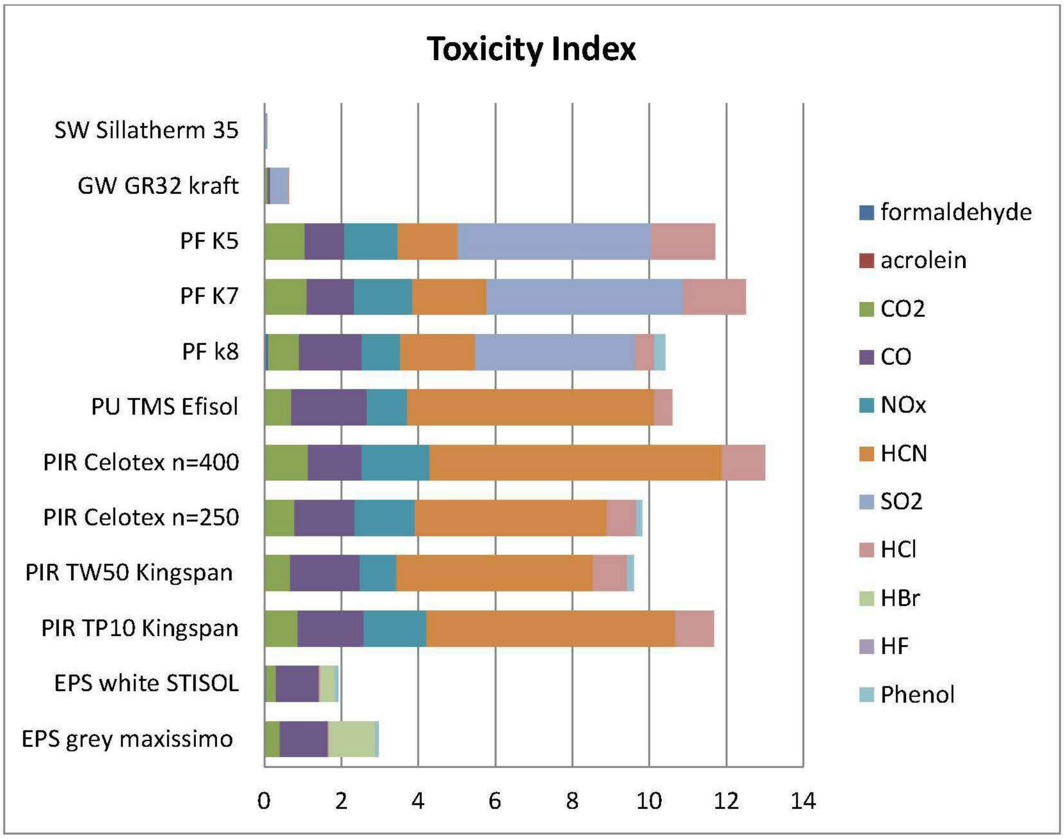

Figure 1. AFAP-3 studies on commercial insulation foams

[4] Stec, A. A.; Hull, T. R. *Energy Build.* **2011**, *43*, 498-506.
[5] Woolley, W. D.; Field, F. *Fire Res Note* 1971, 880, 1.

The PF foams showed as a main combustion product the SO2 followed by HCN, HCl, NOx and CO. The emissions of these effluents are originated from the nature of the phenolic foam as exception of HCl that is a toxic effluent from the fire retardant degradation. For PIR and PUR foams the main toxic product yield is HCN followed by CO, NOx and HCl. The main toxic products are HCN and CO that act together to reduce the body of oxygen, the toxicity index increase when the index (n = NCO/OH) increase, in this case means increase of NCO (isocyanate)

The PIR and PUR products from Celotex have been studied deeper by the synthesis of laboratory foams with different index and amounts of fire retardants, to understand the influence of index content (NCO/OH) and fire retardant on its toxicity (**Figure 2**). It is important to note that the laboratory samples cannot be compared right away with the commercial products from Celotex due to process and raw materials differences, but tendencies can be extracted.

The results on **Figure 2**, showed that the addition of higher amounts of isocyanate (Higher index) showed an increase on HCN emissions and at therefore an increase on the toxicity index. As it was described above the HCl is originated from the fire retardant degradation, this fact is confirmed by the increase of HCl emission when higher amounts of fire retardants are added to the foam formulation.

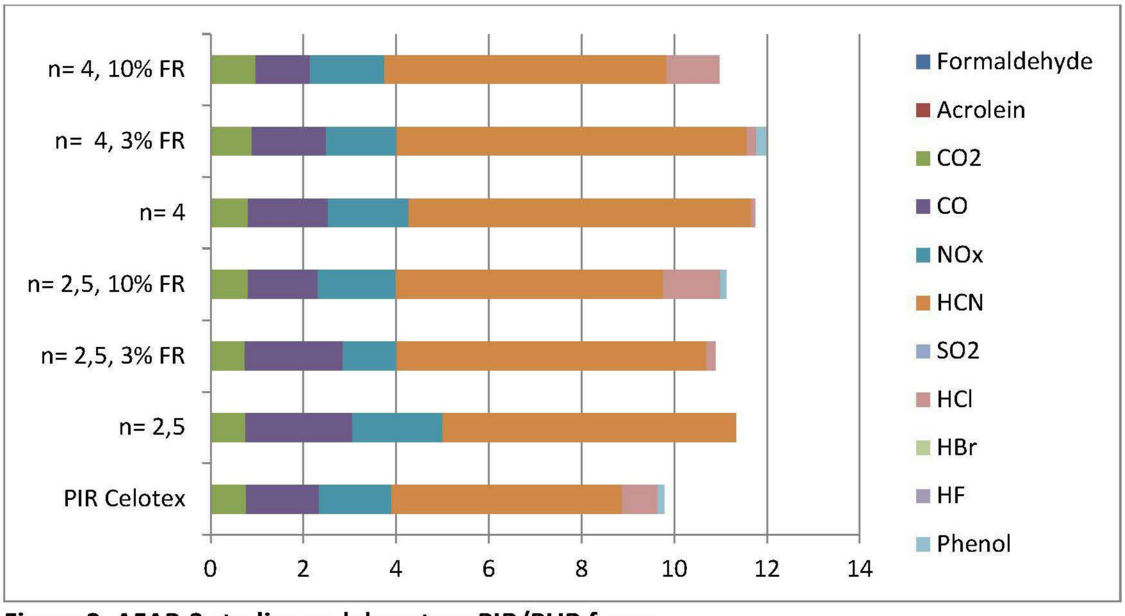

Figure 2. AFAP-3 studies on laboratory PIR/PUR foams

The toxicity from laboratory foams is higher than for commercial products, this can be related to a difference in formulation during process. In this point it can be consider the possibility to reduce the emissions of HCN.

In order to quantify the percentages of HCN that have to be decreased to reach a value significantly lower than 10 for the toxicity index, 3 commercial samples of each index have been analyzed in the APAF-3 standard, for foams with an index of 250 & 400 the % HCN should be reduced in 14% and 6% respectively (**Table 5**)

Table 5. Commercial PIR Celotex foams analysis to TI and HCN

Product	Average TI	TI (% to decrease)	HCN (% to decrease)
PIR Celotex n = 400	**12,7 ± 0,6**	**29 %**	**14 %**
PIR Celotex n = 250	**10,3 ± 0,5**	**12 %**	**6 %**

5. Conclusion and Next steps

The selection of standard to analyze the toxicity of a wide range of products has been done with a Navy military method AFAP-3. The AFAP-3 method has a TI limit of < 10 which allows to compare the different insulation materials among them. The results revealed that foam formulation influences the toxic products yields, obtaining a high toxicity index (TI) for PUR = PIR = PF > EPS > GW = SW.

To further understand the PIR formulations, Celotex had synthesized laboratory PIR products. Taking together, the data from commercial and laboratory products confirms that higher amounts of isocyanate and fire retardant increase the toxicity index.

Based on this results it is necessary to

- Quantify the emission of toxic effluents and smoke opacity under different conditions
- Further understand the PIR behavior during a fire and to be able to decrease the TI or HCN emissions on PIR foam. However

To reach these goals collaboration with fire expert (UCLan Fire toxicity Laboratory experts in UK) have been started lately in 2015.

Next steps:

It has been selected PIR, PUR and PF materials to be study in a wide range of conditions by fire experts (University of Lancashire UCLan), laboratory leaded by Prof. Hull. The material evaluation will be done in two parts:

(1) Study the fumes & toxicity, smoke opacity of the products by the steady tube furnace (SSTF) in well-ventilated, small under-ventilated and large under-ventilated flaming. This technique will let to identify the majors toxicants present in the materials.
(2) Study the materials combustion mechanism to understand the factors driving the formation of HCN during a fire and decrease its emissions by the addition of additives

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ANNEXES / APPENDED :

Figure 1. Benchmark statistics on insulation products in AFAP-3 test