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New formulations of low smoke, low acidity, no dripping, flame retardant PVC

About IPOOL

IPOOL is R&D – Technology company, Spin-Off company of Italian National Council of Research institute (CNR), established on July 2011 in Pisa (ITALY). IPOOL, working in international projects from Europe to Middle East, from Russia to Asia, from Northern to Southern America, is specialist in:

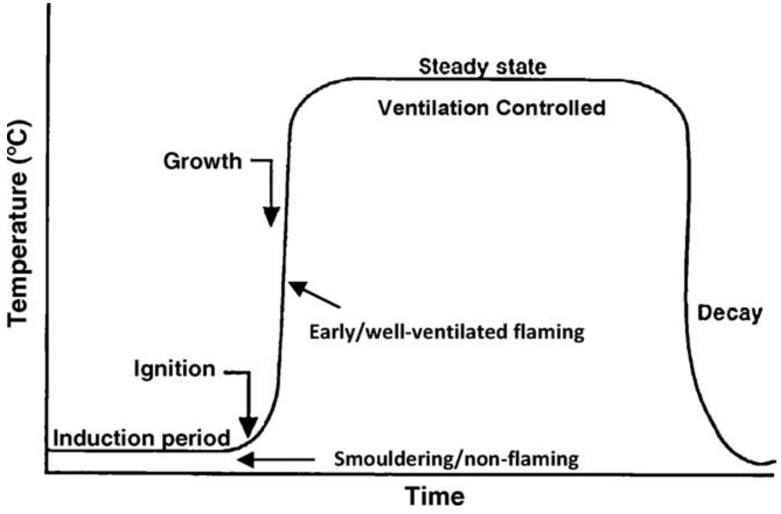
- **Raw materials for PVC and HFFR compounds for cables**
- **Equipment for compounding of cable materials (twin screw extruders, co-kneaders, internal mixers, ...)**
- **Optimization of extrusion of insulation and sheathing compounds**
- **Flame retardant fillers for PVC and halogen free compounds**
- **Laboratory testing equipment for R&D and QC**
- **Selection and training of technical people for R&D activities (experimental thesis)**
- **Design of marketing strategy for new products and new additives**

Safety in case of fire

- To retard the spread of fire development and the spread of fire and smoke in the work so as to enable occupants near and/or remote from the room of fire to have sufficient time to escape.

- To enable the fire brigade/rescue teams to control the fire before it is too large.

Available Safe Escape Time (ASET) must be greater than ***Required Safe Escape Time*** (RSET) by a margin of safety.

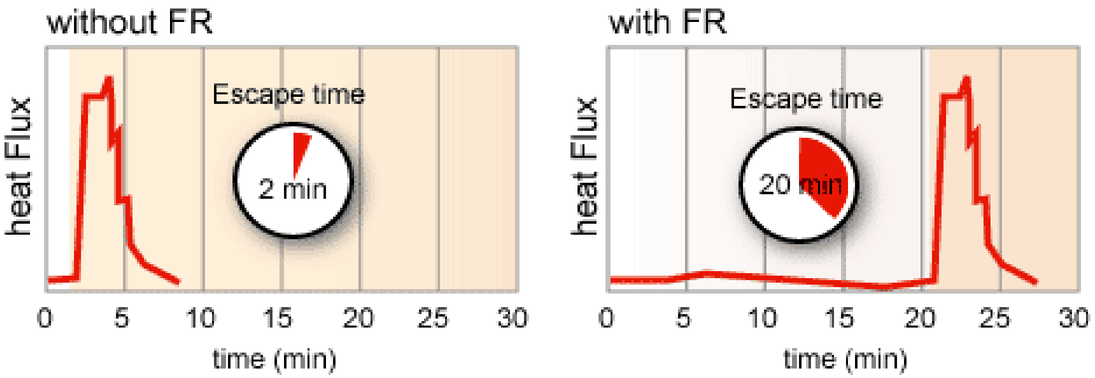


During fires, the acute survival risks are reduced vision caused by **smoke** which greatly increases the time to exit, confusion, panic, loss of orientation, pain and breathing problems caused by irritating products and loss of consciousness caused by asphyxiating gases and burns derived from exposure to radiant and convective heat, which could lead to collapse.

Main compounded materials for cables

Polymers	Insulation	Bedding	Sheathing
XLPE	●		○
EPR/EPDM	●	●	
PVC	●	●	●
Thermoplastic HFFR	●	●	●
XL-HFFR	●		●
CPE	○		●
NBR/PVC			●
TPU			●

- Increasing demand of flame-retardant materials
- Increased role of FR bedding compound (competitive cost, high FR)
- Global competition between halogenated and halogen-free materials



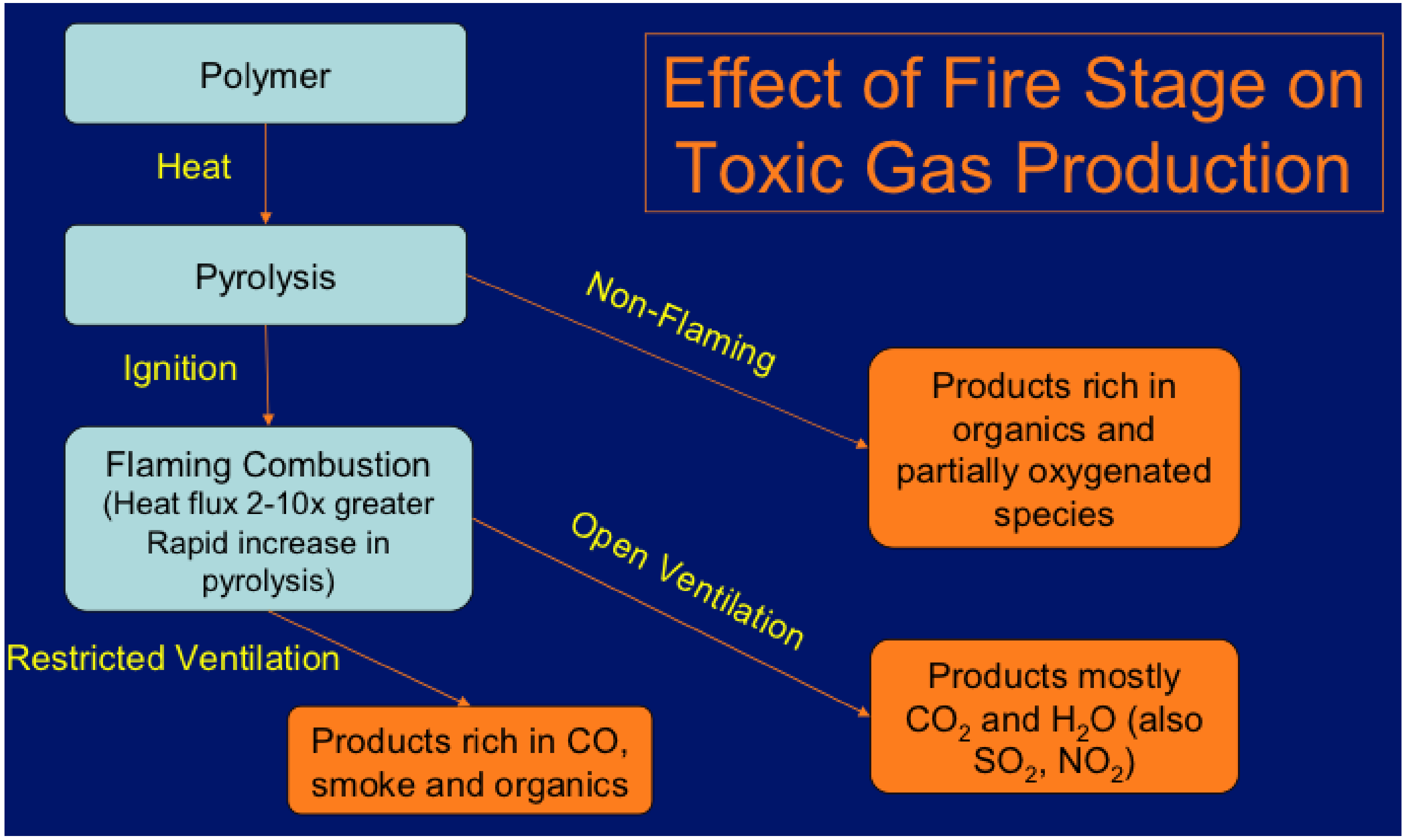
Comparative behaviour of main base polymers in fire

Code	Description	Self-ignition T (°C)	Heat of combustion MJ/kg	LOI (%)	Flame spread	Tendency to drip	Smoke release
EVA/EVM	Poly(ethylene-vinyl acetate)	320	38-42	<20	High	Medium	Medium
EPR/EPDM	Ethylene-Propylene rubber	350	44	<20	High	Medium	Medium
PE/POE/PP	Polyethylene, Polypropylene and related plastomers	350	44	<20	High	High	Medium
SBS/SEBS	Styrene thermoplastic rubber	300	44	<20	High	High	High
CPE	Chlorinated polyethylene	400	30-35	22-24	Low	No	High
PVC	Polyvinyl chloride	450	<20	42	Low	No	High
p-PVC	Plasticised Polyvinyl chloride	250-300	25-30	23	Low	No	High

- Flexible polymers with low crystallinity (and low T_g) could be modified with high loading of flame retardants and smoke suppressants additives and minerals.
- The high content of (highly burnable) plasticiser penalizes behaviour of PVC and SBS/SEBS in fire.
- To guarantee cables pass fire tests, different FR additives, FR minerals and FR synergists are used for the different base polymers.

Main parameters influencing toxic product yields in fires

- the elemental composition of the material that is burning (% content of C, H, O, N, P, Cl, Br, F, S, inert fillers and flame retardants fillers)
- the organic composition considering the presence of aliphatic or aromatic compounds together with the compound behaviour during combustion (char forming or decomposition).



Toxic product yields depending on FR additives

The use of Flame Retardant materials is considered an advantage in order to reduce flammability and fire hazards derived to flame and heat.

Systems with reduced organic emissions relative to the polymer matrix, are:

- Not decomposing fillers (talc, glass fibres, silicates, silica…)
- Alumina trihydrate and Magnesium Hydroxide
- Nano-clay and other anti-dripping systems
- Char forming or layer forming systems locking up fuel carbon (like nitrogen-phosphorus systems)

There are also few flame retardant **systems significantly increase the smoke emissions**:

- Chlorinated paraffins
- Brominated organic flame retardants
- Antimony trioxide

Results from full-scale fire tests

1. The average available escape time was **>15 time greater for the FR products** in the room burn tests.

2. The amount of material consumed in tests of the FR produce was <half the loss in the NFR tests.

3. FR products gave **1/4 the heat release of NFR products**.

4. The total quantities of **toxic gas released by the FR products was 1/3 of that for the NFR products.**

⇒ The FR additives did decrease the overall fire hazard compared to the neat materials

⇒ Fire retardants (any kind of) improves life safety in case of fire

SMOKE TOXICITY: Real safety issue for polymers in case of fire?

"***Although roughly 2/3 of fire victims die as a direct effect of smoke toxicity, it is extremely rare that their deaths are caused by the inhalation of smoke from a specific very toxic material**. In fact, probably well over 90% of fire deaths are the result of fires becoming too big and thus resulting in too much toxic smoke, whatever are the burning materials generating the smokes.*

***At flashover, <u>every polymer</u> will give off ca. 20% of its weight as CO**: that is toxic enough to be lethal. Toxic potency is a minor contributor to fire hazard and it is most critically dominated by CO concentration. Fire hazard and life safety are best served by ensuring that fires remain small, meaning that they need to exhibit heat release rates as small as possible.*"

M.M. Hirschler, Fire safety, smoke toxicity and acidity, Proc. Flame Retardants 2004

⇒ The fire toxicity may drive tenability in situation where there is severe reduced mobility of occupants (like, for example, in aircraft or in ships)

COMBUSTION CONDITIONS IN MODELLED FIRE SCENARIOS

ISO 19700 steady state tube furnace (Purser furnace)

Bench-scale apparatus for fire toxicity analysis under controlled conditions.

The ISO/19700 tube furnace permits the measurement of heat of combustion and toxic product yields as a function of equivalence ratio.

Φ = fuel to air ratio/ stoichiometric fuel to air ratio

Φ = 1 *"Stoichiometric" combustion*

Φ < 1 *Well-ventilated fires (fuel lean flames)*

Φ > 1 *Under-ventilated fires (fuel-rich flames)*

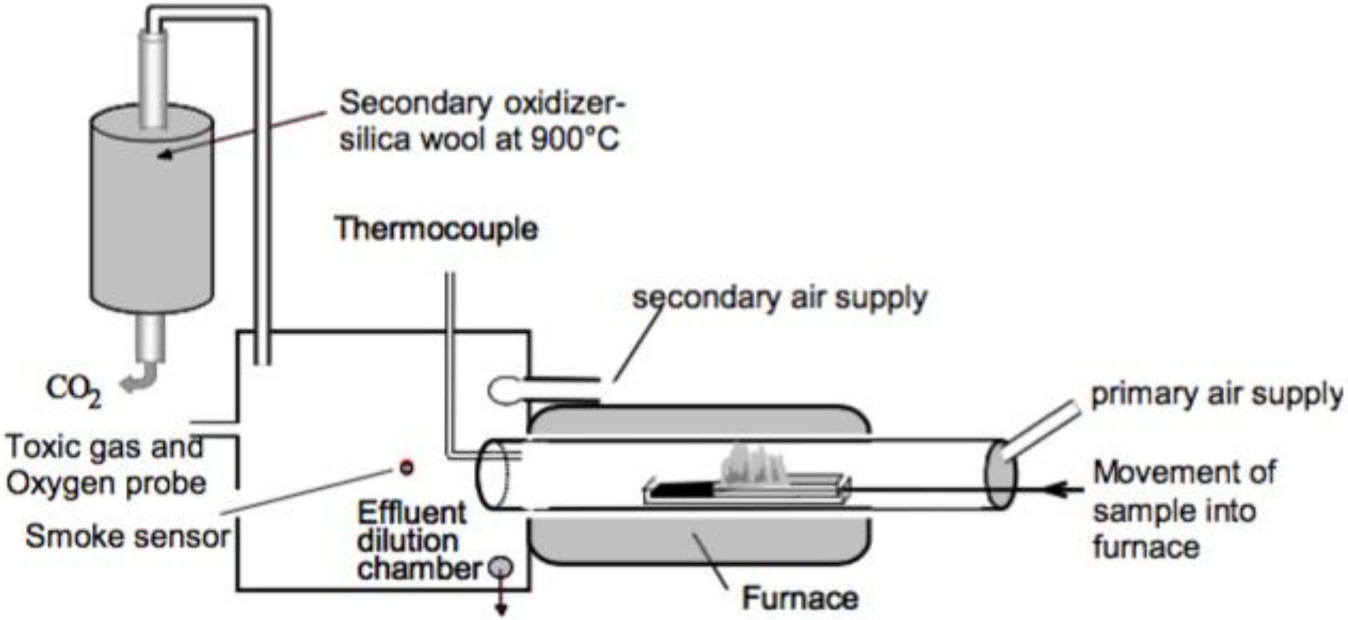


Fig. 2. The steady state tube furnace apparatus (Purser furnace).

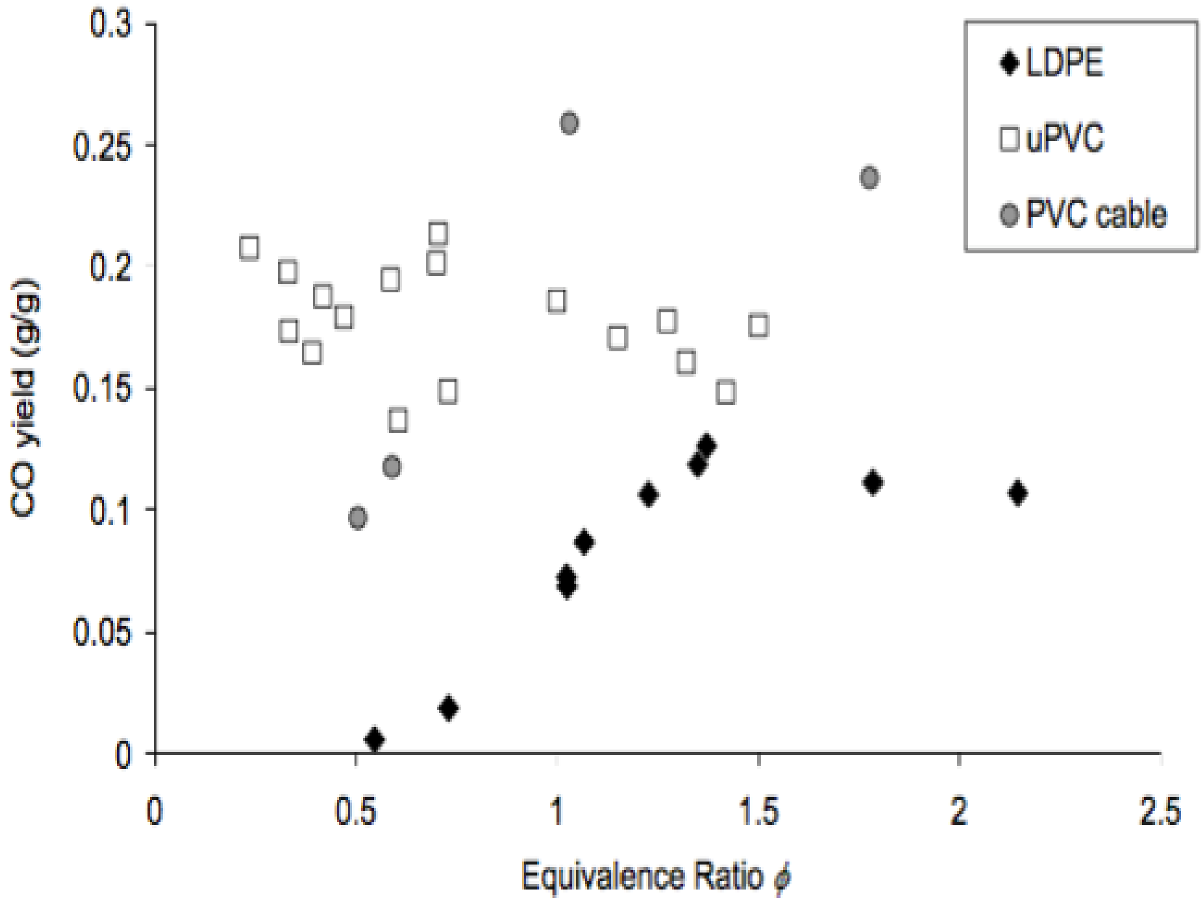
CO yield from PVC

⇒ The yields of CO produced per kg mass loss change considerably with equivalence ratio and it depends also upon the carbon content of the fuel.

⇒ For PVC, the yields of CO and HCl are high over all combustion conditions.

⇒ Yield of CO in under-ventilated conditions for the plasticised PVC (~20% Cl content) is higher than that of uPVC (~60% Cl). **Role of plasticisers**.

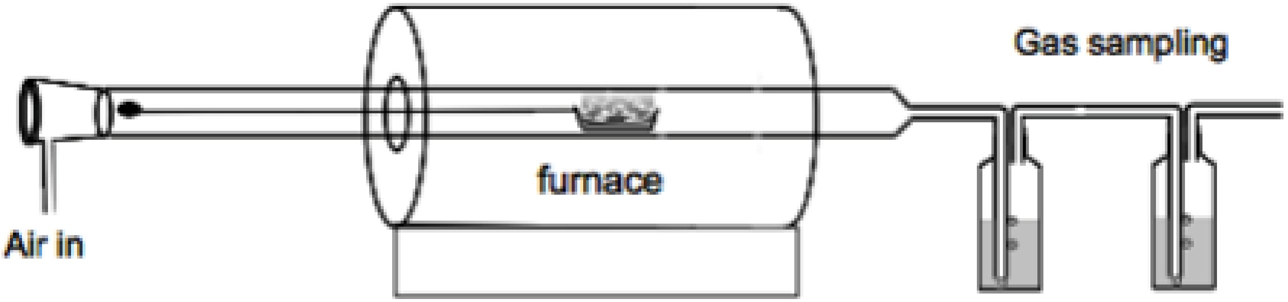
⇒ At Φ >1.5 (under-ventilated), CO produced by PVC and LDPE is the same, due to under-ventilated conditions (like during *flash over*)



The Acid Gas Test

The **Construction Products Regulation (CPR) for cables** establishes the incorporation of the standard **EN 60754-2 where introduction of sample is done directly into tube at 935-960°C** for the determination of the acidity of the gases evolved from combustion of materials from cables.

⇒ *Conditions applied from **EN 60754-1 (from 23°C to 800°C at 20°/min**, not incorporated into CPR) are very close to ISO 19700 (Purser furnace), in other words are closer to real fire conditions happening in real scale fire event.*



As demonstrated by Dr. G. Sarti (CABLES 2020) at Berlin Conference (2019), results of the above apparatus are strictly dependent on burning conditions, especially the temperature ramp and final temperature.

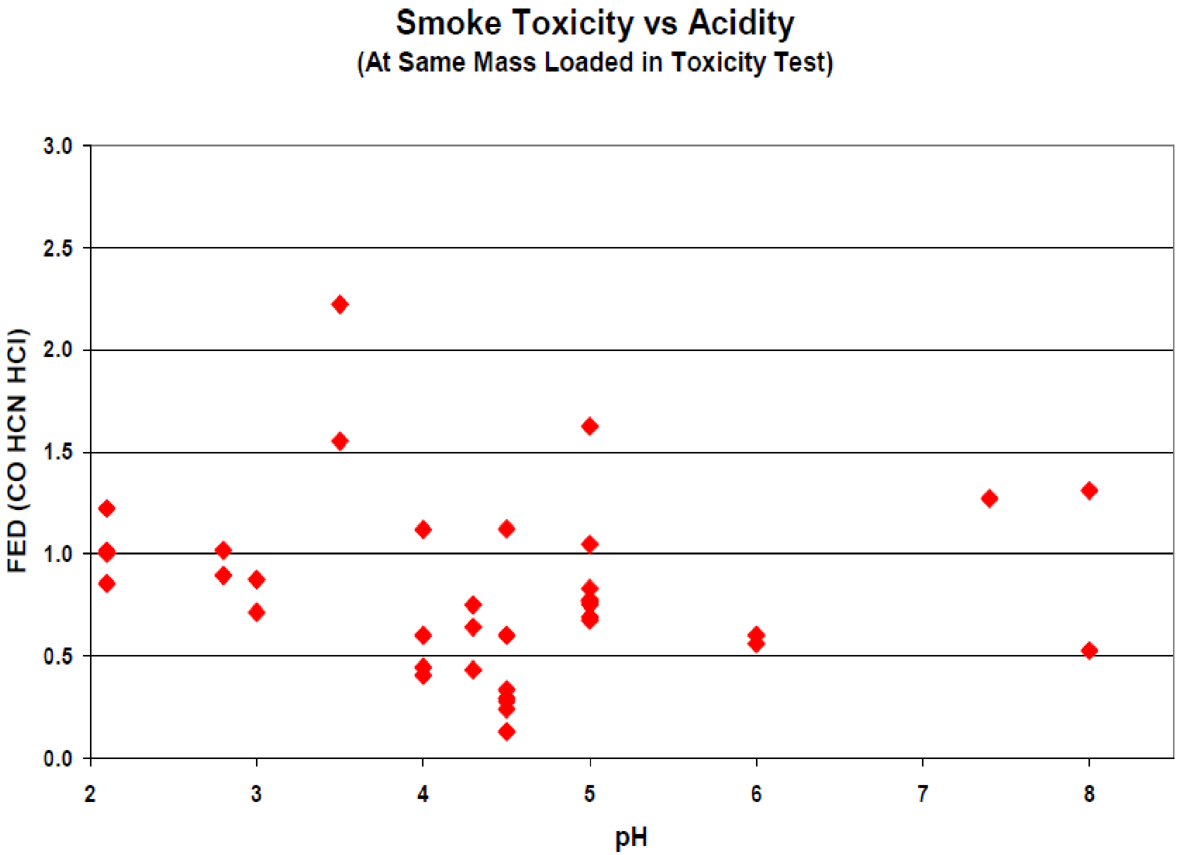
⇒ This test SHOULD BE ONLY used for commercial identification of cables, by taking into account the two main types of cables used in buildings, PVC based and low smoke zero halogen (LSZH), and NOT TO RATE the safety in case of fire.

ACIDITY = TOXICITY?

⇒ For a series of materials (halogen-free polyolefins, wood, styrenics, PVC, wool, cotton, nylon, ...) **there is no correlation between smoke toxicity and acidity.**

⇒ The only real conclusion is the acidity classification can be used for discriminating between the two common cable types (LSZH and PVC), **without any toxicologic relationship**.

⇒ NIST (USA) showed that the contribution of HCl to toxicity in PVC smoke is **negligible in full scale studies**.



Magnesium hydroxide flame retardant

Flame retardancy is achieved through five different mechanisms:

- Forming of a protective char layer;
- Reducing the amount of inflammable material available for combustion
- Generating a highly reflective magnesium oxide coating to deflect heat away from the polymer
- Releasing of water (31%) at temperatures of 340°C and higher
- Absorbing heat from the combustion zone to reduce the risk of continued burning

MDH is a white crystalline powder manufactured by **chemical** processes (*synthetic crystallised MDH* or *synthetic precipitate MDH*) or by **grinding** processes of naturally occurring brucite (*natural milled MDH*).

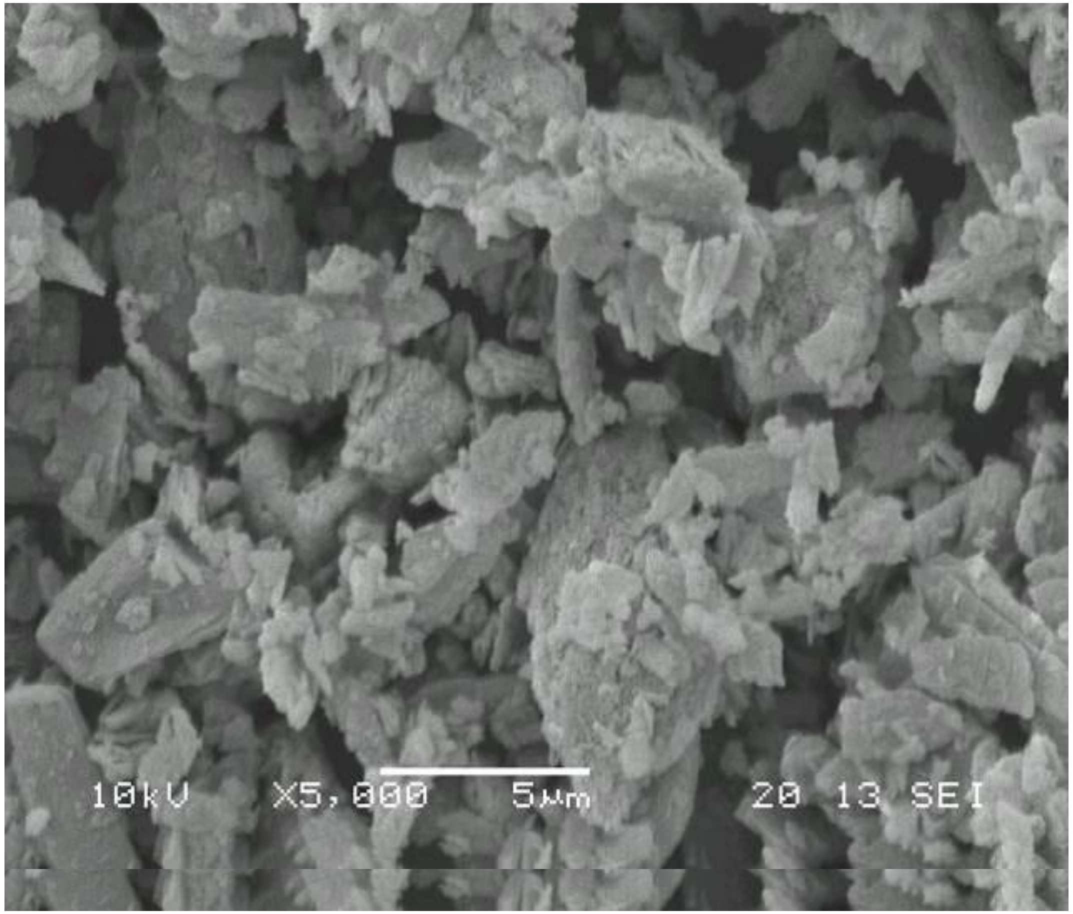
⇒ **Efficiency of natural and chemical MDH equivalent (*when purity is guaranteed*)**

⇒ **Thanks to higher thermal stability and higher performance/cost ratio, natural MDH is the most preferred FR and smoke suppressant filler in PVC**

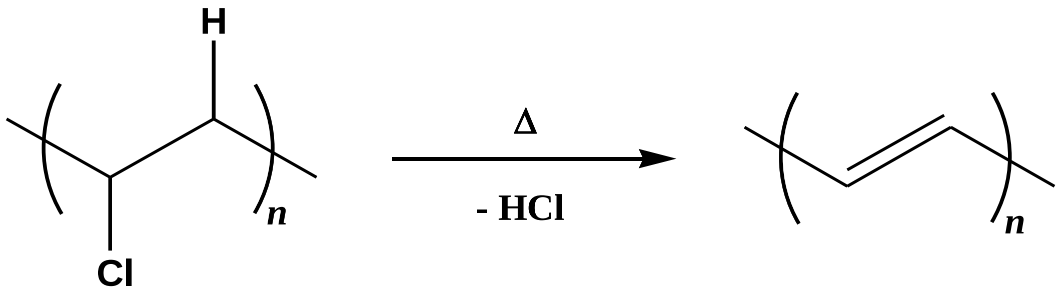
Milled natural MDH (Brucite)

- Available from Russia (≈90% purity) and China (≈75% purity).
- Typical composition of Russian natural MDH is 90-92% MDH, 6-8% of carbonates, <2% other minerals like serpentine. Iron Fe_2O_3 <0.13%
- Available in different granulometries, **from 3 to 800 μm**.
- Surface coated grades with stearic acid and silanes are available for easier dispersion.
- Widely used in cable compounds and also in PVC, bitumen and TPO roofing membranes.

⇒ Used in PVC as flame retardant, acid scavenger and smoke suppressant.



Hydrogen chloride Evolution



The evolved HCl can be partially trapped if in the compound are present fillers, in accordance with the reactions:

$$Al(OH)_3 + 3\ HCl \nrightarrow AlCl_3 + 3\ H_2O$$

$$MgCO_3 + 2\ HCl \rightarrow MgCl_2 + CO_2 + H_2O$$

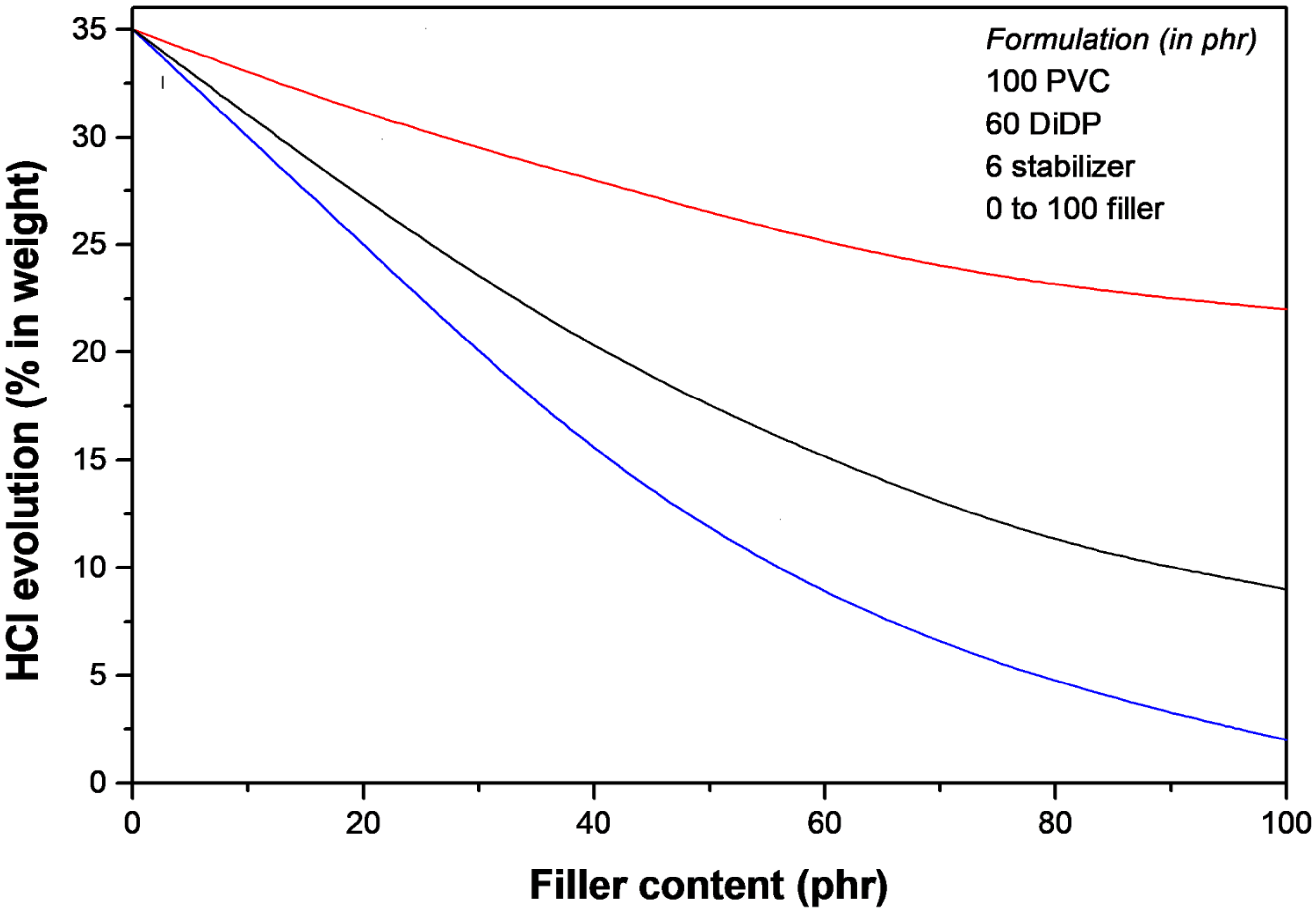
$$Mg(OH)_2 + 2\ HCl \rightarrow MgCl_2 + 2\ H_2O$$

$$CaCO_3 + 2\ HCl \rightarrow CaCl_2 + CO_2 + H_2O$$

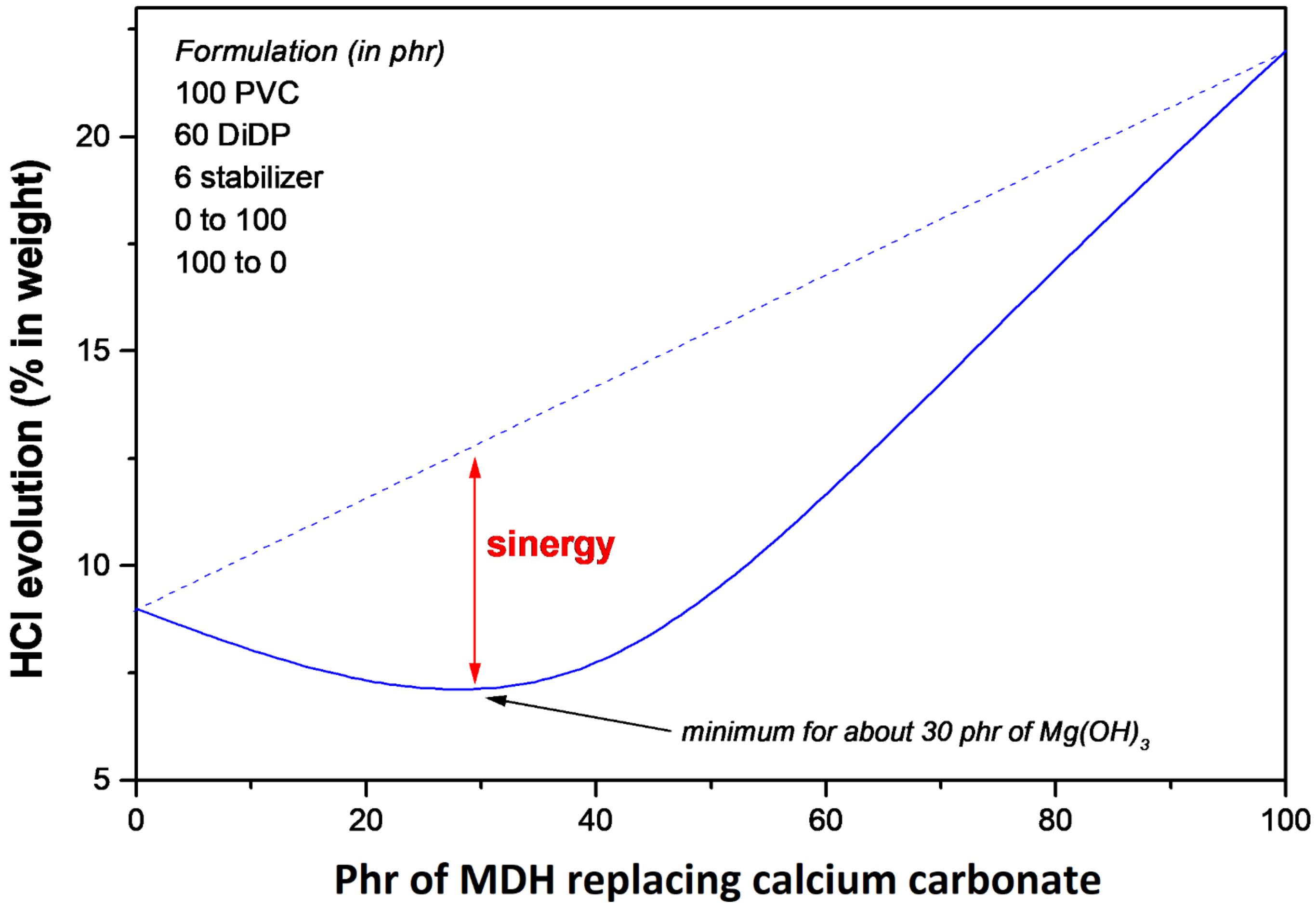
⇒ **Reaction of HCl depends on type, content and *surface area* of the fillers**

Trapping of HCl versus filler loading

Red line = natural MDH
Black line = milled $CaCO_3$
Blu line = precipitate $CaCO_3$



Synergism between natural MDH and $CaCO_3$



Reduction of Smoke density of FR PVC compounds

- **Zinc Borate** is the common smoke suppressant in PVC, used in combination with ATO.
- **Chloroparaffin** is used as secondary plasticiser. It is FR and *cost competitive*, but it has negative impact on smoke emission, and limited in USA and Europe by norms.
- **Aryl phosphate plasticizer**s are efficient FR. Effect on smoke release if function of ratio between aryl and alkyl groups. Grades used in *plenum* cables show excellent performances
- **ATH and MDH** reduce smoke density by releasing water during combustion of polymeric materials. In case of PVC, **MDH** shows the *highest performance/cost ratio as FR, smoke suppressant, acid scavenger*.
- **Molybdenum and Tin compounds** (like MoO_3 or AOM and $ZnSn(OH)_6$ or $ZnSnO_3$) are very efficient FR and smoke suppressant, used in *special* applications like *plenum cables* in USA.
- Few **synergistic additives** have been designed to optimize performances/cost in partial/total replacing of ATO to provide FR and simultaneously low smokes (mix of oxides, Adins clay nano additives, …)

Competition between halogen free and PVC compounds in cables

(Standard building wire application)

Name	FR PVC	FR LS PVC	HFFR cmpd	CPR grade HFFR cmpd
LOI	28-36	32-38	32-36	38-42
Specific gravity	1.52	1.55	1.45-1.50	>1.54
Extrusion speed	High	High	Medium	Low
Electrical properties	Medium	Medium	High	High
Recyclability	Yes	Yes	Yes	Yes
Smoke emission	High	Medium	Low	Low
Smoke acidity	High	Medium	Low	Low
Typical CPR target	$B2_{ca}\ s_3\ d_0\ a_3$	$B2_{ca}\ s_2\ d_0\ a_3$	$D_{ca}\ s_1\ d_2\ a_1$	$C_{ca}\ s_1\ d_1\ a_1$
Relative price	1	+10%	+20%	+50%

PLENUM CABLES: NFPA 262 fire test

Extremely tough because must guarantee the perfect safety of **cables installed inside ventilation conduits**: so, in case of fire event, cables must not propagate fire inside to ventilated pipes, as well as there must not be any gas release to avoid spread of gas all around the plenum spaces. **Till nowadays no technical neither commercial success for halogen free compounds in this application**.

Plenum Cables are the application where halogen free compounds are not yet able to work as PVC in terms of **low propagation of fire and low emission of smokes** in order to guarantee the maximum safety in case of fire.

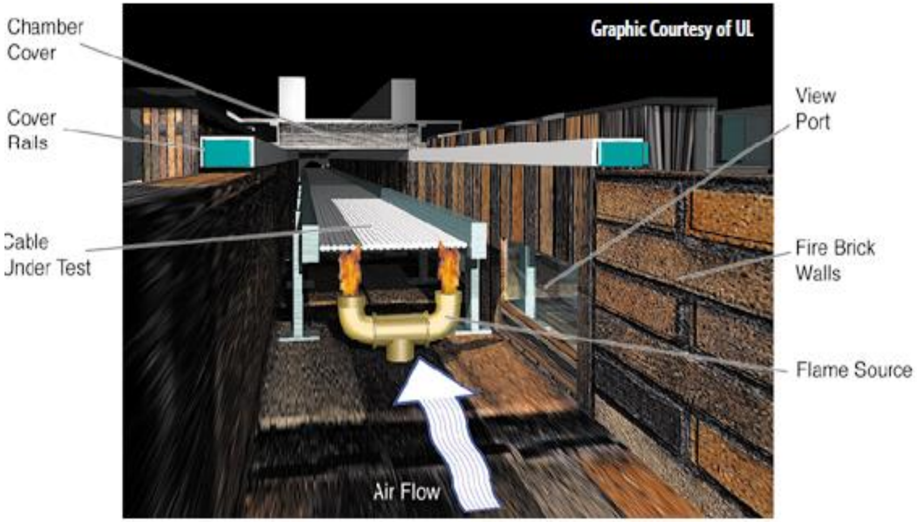
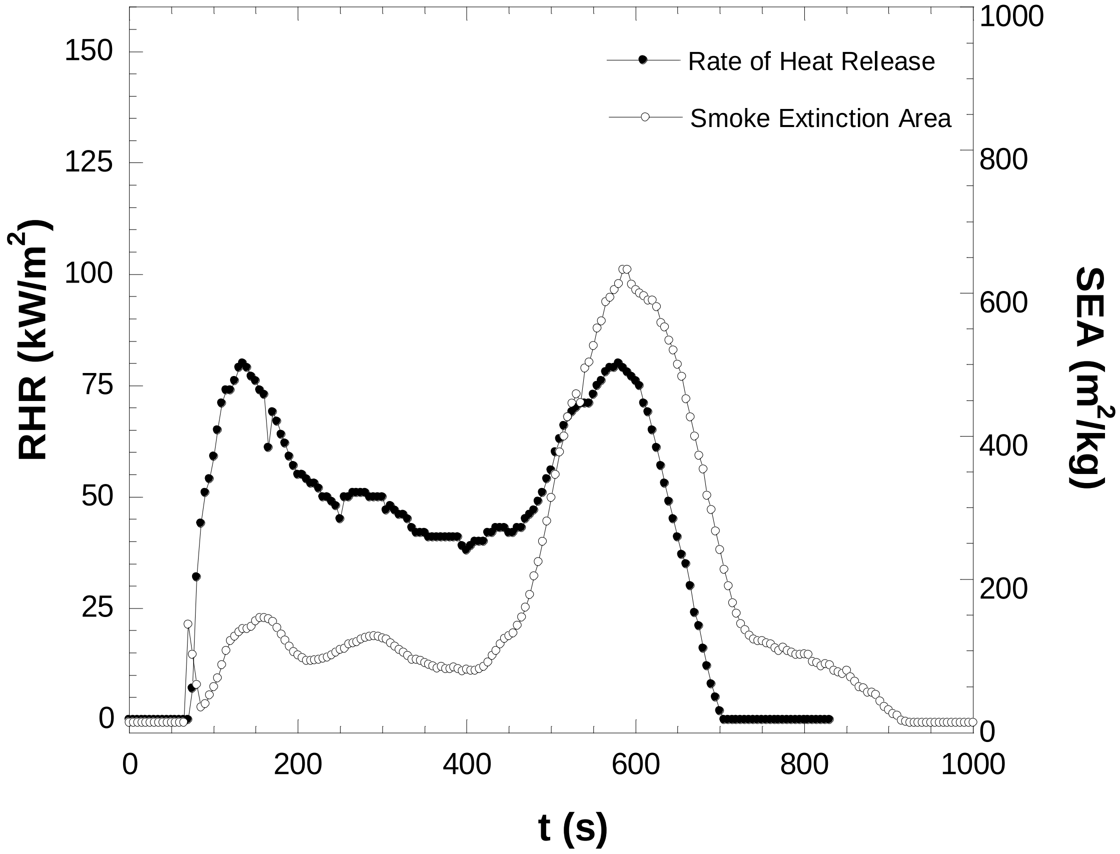


Figure 7: NFPA 262 (UL 910 Steiner Tunnel) test setup

CPR grade HFFR compound at cone calorimeter test

Results at irradiation energy=50 kW/m²:

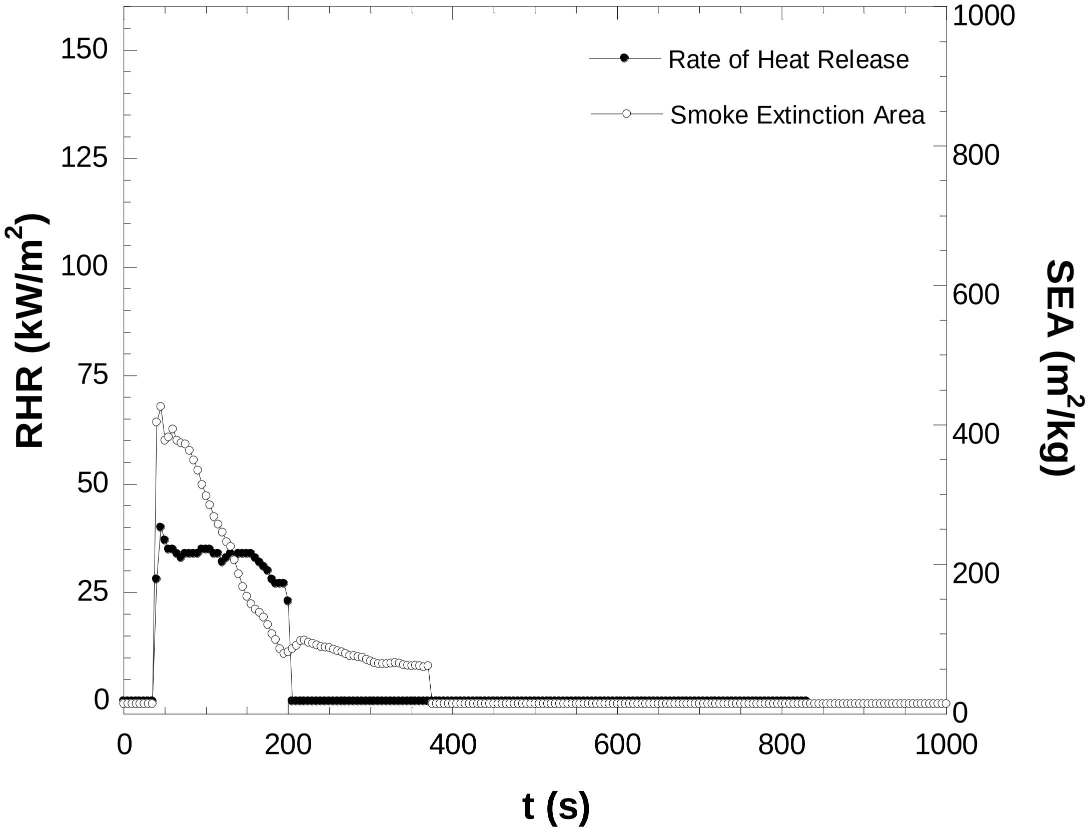
Weight of the sample:	57 g
Time of ignition (TTI):	75 s
Peak of RHR:	80 kW/m²
Time of PRHR from TTI:	60 s
Average of RHR:	53 kW/m²
Average of RHR (3 min):	60 kW/m²
Av.smoke extinction area:	111 m²/kg
Av.smoke extinction area (3 min):	100m²/kg
Residual weight:	43.7%
Specific heat released:	5.78 kJ/g



PVC plenum grade at cone calorimeter test

Results at irradiation energy=50 kW/m²:

Weight of the sample: 59 g
Time of ignition (TTI): 40 s
Peak of RHR: 40 kW/m²
Time of PRHR from TTI: 5 s
Average of RHR: 40 kW/m²
Average of RHR (3 min): 33 kW/m²
Av.smoke extinction area: 155 m²/kg
Av.smoke extinction area (3 min): 231m²/kg
Residual weight: 56.2%
Specific heat released: 0.92 kJ/g



⇒ PVC plenum grade with almost no flame at all even after long time of heat irradiation and almost no smoke emission.

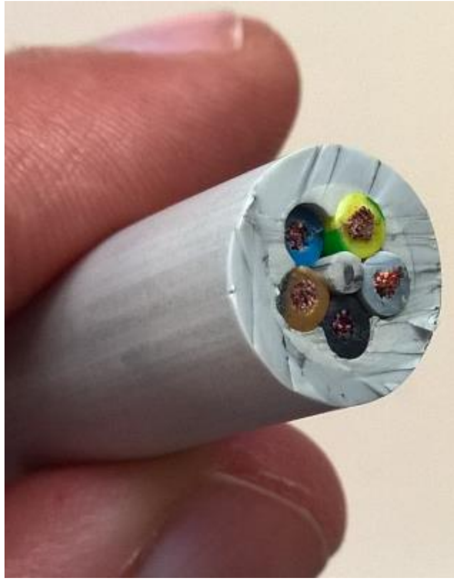
Conclusions

- In real fire events, CO concentrations regularly exceed toxicity limit (LC_{50}), while those of HCl and HCN (coming from burning of materials containing chlorine and nitrogen) and that of acrolein (coming from burning of HFFR compounds) rarely exceed their LC_{50}. In other words, there is so much more CO than anything else in fire atmospheres that **CO is the big toxic killer in smoke**.

- **The smoke toxicity of virtually all materials is almost identical, within the margin of error**. Modern plastics generally produce the same types and levels of carcinogenic volatile organic carbons (VOCs) than do wood products in fires. The smoke toxicity of all polymeric compounds has been studied extensively and found to be quantitatively similar amongst them.

- **Acidity is totally inadequate as a representation of smoke toxicity**. Although smoke corrosivity (or acidity) may have some relevance to property damage it has no relation to life safety or even to smoke toxicity. The use of acidity as the basis on which to assess toxicity of fire effluents may provide an illusion of life safety which is, in fact, incorrect, since the most common toxicant (CO, carbon monoxide) is not acidic and not taken into account.

- PVC irradiates only a minimum amount of heat; this means a minimum contribution to heat diffusion. **PVC is self-extinguishing** and has intrinsically a high potential to resist to ignition sources: it does not contribute, or only minimally contributes, to the generation and spread of a fire (it usually does **NOT drip** during burning due to high charring tendency).



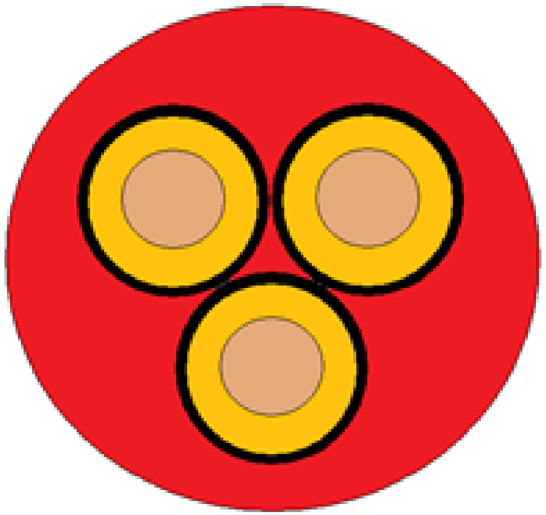
- **Natural MDH** is cost competitive, widely available, smoke and acidity suppressant flame retardant filler, used in PVC and in halogen free compounds.

- PVC can obtain the highest fire reaction results: if properly formulated, it allows to produce cables complying with **Euroclass $B2_{ca}$ d_0** the safest class in European standard (CPR), and complying with NFPA 262 specification for ***plenum cables* in USA**.

- As consequence of above conclusions, a **HFFR cable classified as $B2_{ca}$ d_0 s_1 a_1** and a **PVC cable classified as $B2_{ca}$ d_0 s_1 a_3** would guarantee **the same safety** in case of fire. But, at today, no PVC cables classified as “s_1” have been certified and proposed to market (not yet).

Thank you for the kind attention!

Questions are welcome



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Presentation available upon request