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Improvements of Flame Retardancy and Safety of PVC Compounds in case of fire

GLOBAL PVC COMPOUNDING & PRODUCTION CYCLE FORUM
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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 is specialist in:

- **Raw materials for PVC and HFFR compounds for cables**
- **Equipment for compounding of cable materials (twin screw extruders, Buss-type co-kneaders, Bambury 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**
- **Training and selection of technical people for R&D activities**
- **International standard for fire test, including new European CPR (Construction Products Regulation)**
- **Marketing strategy and market approach for new products and new additives**

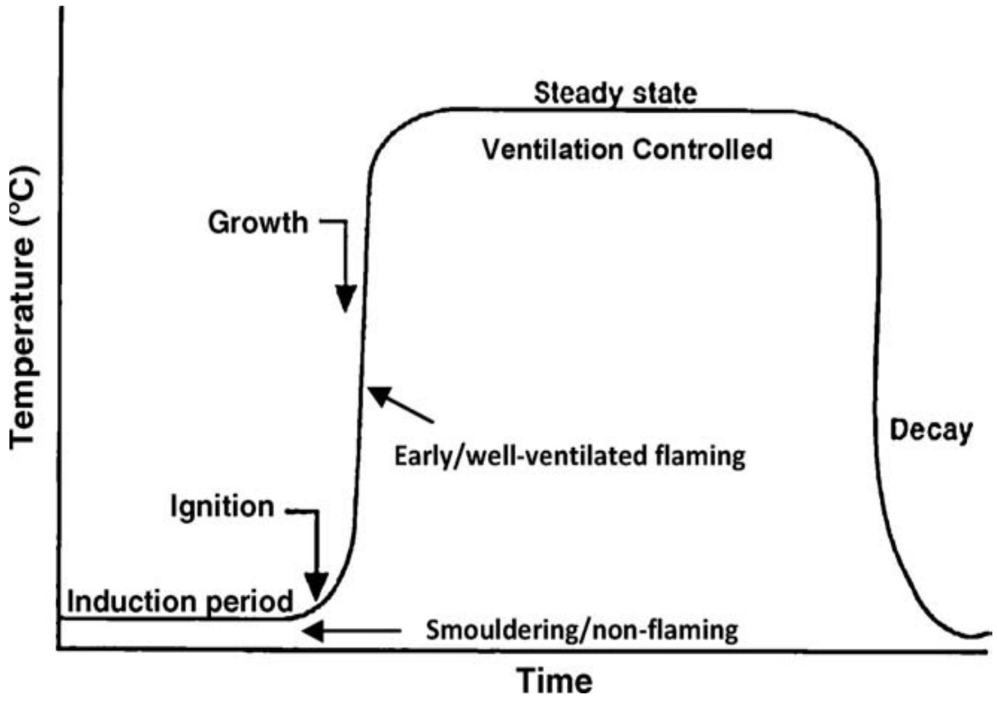
Introduction to Fire Safety

Europe "Safety in case of fire" Statement of Principle:

• 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.

In fire safety engineering terms, it is necessary to ensure that ***available safe escape time*** (ASET) is greater than ***required safe escape time*** (RSET) by an acceptable margin of safety.



Results from full-scale fire tests /1

∅=actual 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)

During fires the acute survival hazards are the **impaired vision caused by smoke**, pain and breathing problems caused by irritant products, confusion and loss of consciousness caused by asphyxiant gases and burns derived by radiant and convected heat exposure, which could take to collapse.

Results from full-scale fire tests /2

The most interesting results were those from those full-scale fire tests, which also helped to identify the importance of heat release rate as the most important physical variable in these tests which is a predictor of the fire hazard. It has been then demonstrated for FR products that significantly enhanced fire performance can be obtained, in that:

1. The average available escape time was >15-fold 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, on the average, 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.
5. The production of smoke was not significantly different between FR and NFR products.

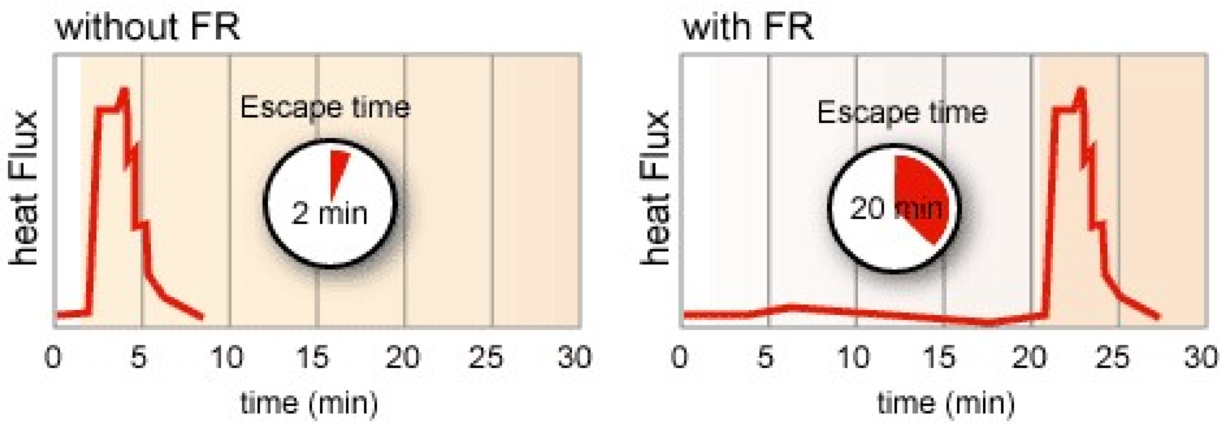
⇒ The FR additives did decrease the overall fire hazard compared to the neat materials
⇒ Proper selection of fire retardants improves fire and life safety

Introduction to Flame Retardants

The most important application area for flame retardants is the construction sector. An increasing amount of flammable materials are used in thermal insulation, impermeabilization and improvement of energy efficiency of residential buildings. **Pipes and cables, aluminum composite panels (ACP)**, and PVC, TPO, bitumen **roofing membranes** are required to reduce flammability, smoke emission and smoke acidity and toxicity.

In a global context, Aluminum Trihydroxide (ATH) is the most commonly used type of flame retardant, with about half of total market volume. **Natural magnesium (Di)hydroxide (MDH)** is the faster growing mineral flame retardant in polymeric applications, thanks to total/partial replacement of synthetic ATH and to synergistic flame-retardant action with Antimony Trioxide (ATO).

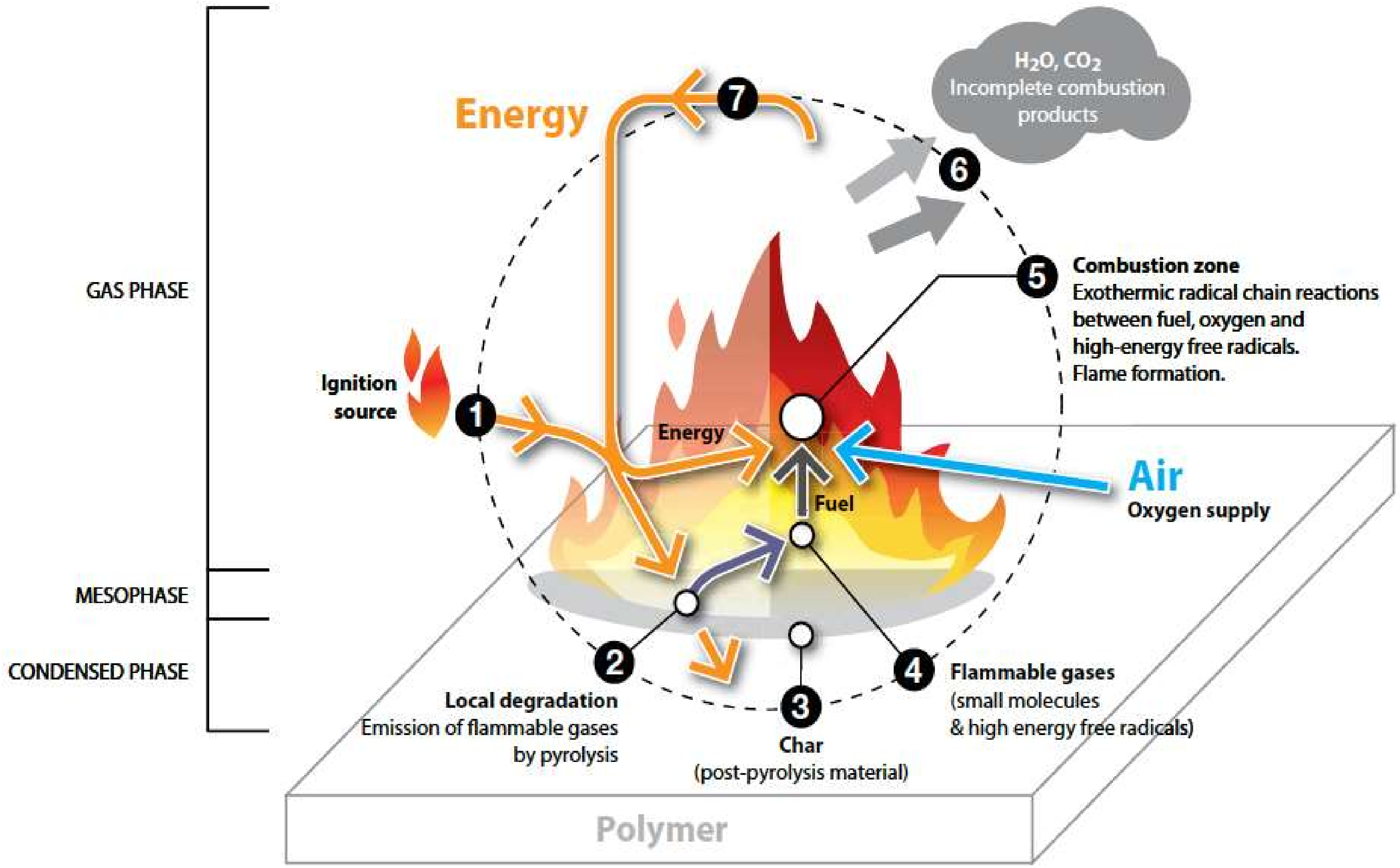
The current growing sensitivity of consumers and institutions favours technological solutions with high environmental sustainability. PVC and competitor materials must be safe and easy to recycle in a **circular economy perspective**.



Schematic description of combustion of polymers

- Smoke can limit visibility during a fire, avoiding the escape for victims.

- Smoke can contain different asphyxiant gases causing incapacitation, soot, acid gases able to irritate eyes and nasal passage and to cause respiratory pain and inhibition of breathing.



General comparison amongst common polymers during burning

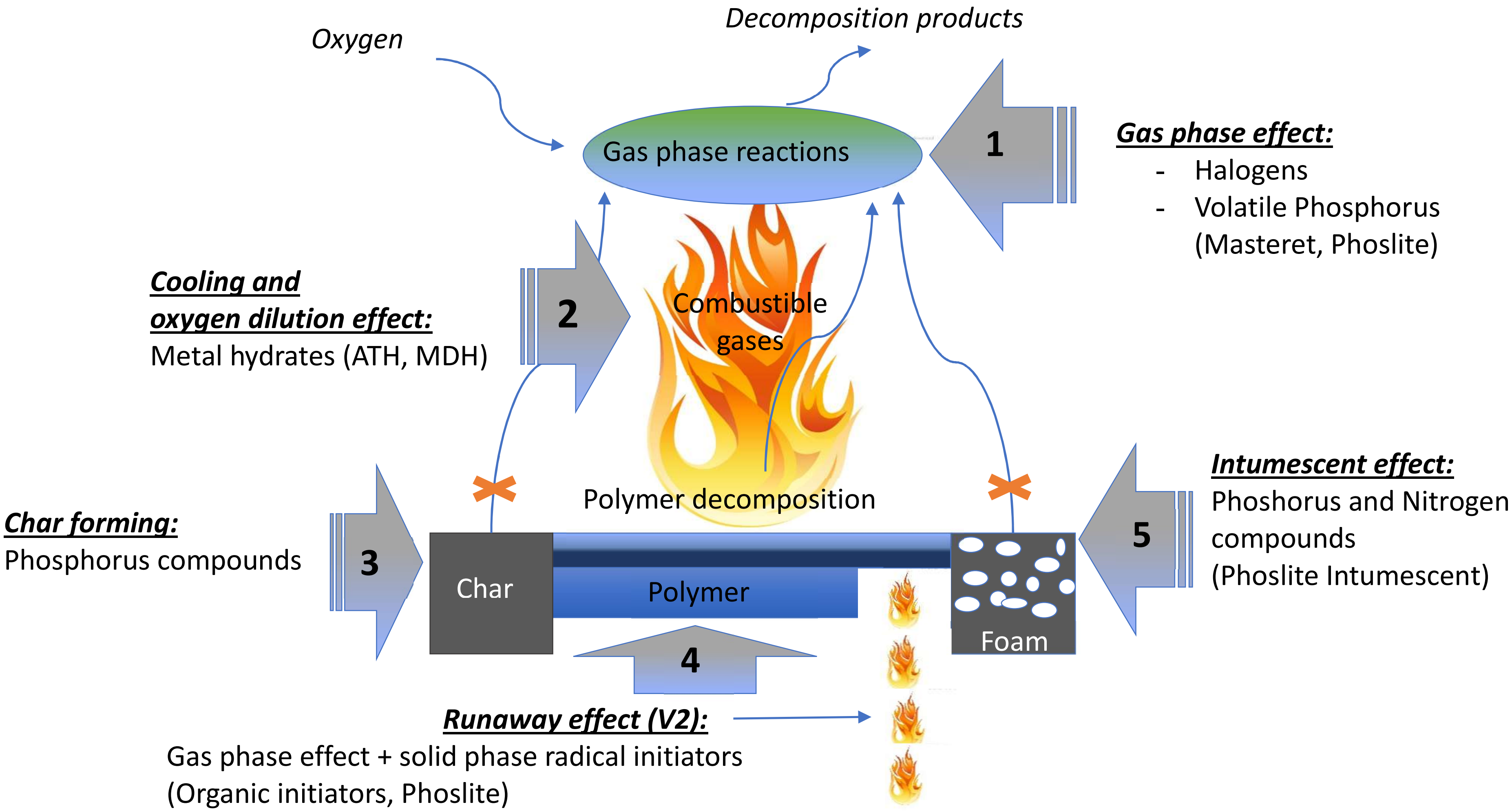
Code	Desctiption	Self-ignition T (°C)	Heat of combustion MJ/kg	LOI (%)	Flame spread	Tendency to drip	Smoke release
PE	Polyethylene	350	45	18	High	High	Medium
PP	Polypropylene	350	45	18	High	High	Medium
PS	Polystyrene	490	42	18	High	High	High
PVC	Polyvinyl chloride	450	<20	42	Low	No	High
EVA	Poly(ethylenevinylacetate)	320	42	19	High	Medium	Medium
PA	Polyamide 6 (and 6,6)	>450	26	24	Medium	Medium	High
PET	Poly(ethylene terephthalate)	390	23	18	High	High	Medium

⇒ Type and toxicity of smokes depend on combustion conditions.

⇒ Flexible polymers with low crystallinity and low T_g could be modified with high loading of flame retardants and smoke suppressants.

⇒ Due to content of (highly burnable) plasticiser, original good flame retardancy of PVC is reduced, but the improved flexibility allows to introduce high loading of fillers (uPVC vs pPVC).

Flame Retardant mechanisms of action: ***the 5 effects***



Flame retardant features:

- ✓ Self-extinguish behaviour
  - ✓ Delay of Ignition
    - ✓ Smoke suppression
      - ✓ Fire spread prevention

⇒ The goal of FR additives is to improve as many as possible FR properties

The ideal fire-retardant system acts in the solid phase and minimises the release of organic fuel vapours, acid gases and dense smokes.

⇒ Mineral fillers are ideal FR and smoke/acidity suppressants

Demands of material properties in case of fire:

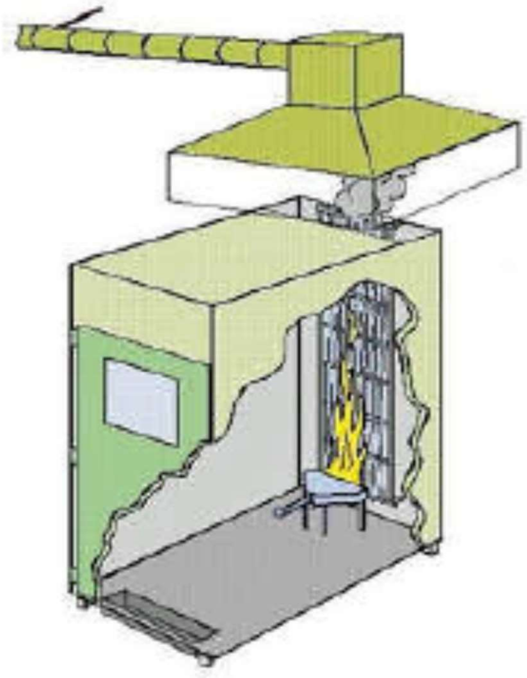
1. Low flammability, Low flame spread and No dripping.
2. Low smoke emission and low smoke's toxicity.
3. Low acidity and low corrosivity of gases of combustion.

⇒ PVC can be this material, if properly formulated

Thanks to large use of mineral fillers and FR synergists, **Flame-Retardant Low-Smoke PVC in Italy, Middle East, Russia and India is compounded and applied for over 20 years in cable industry**.

With *very competitive cost*, this family of plasticised PVC compounds is fast growing in many markets as reaction to new "***green***" feeling of market, institutions and end-users, by defending and promoting **business and reputation of PVC**.

CPR (EN 50399)



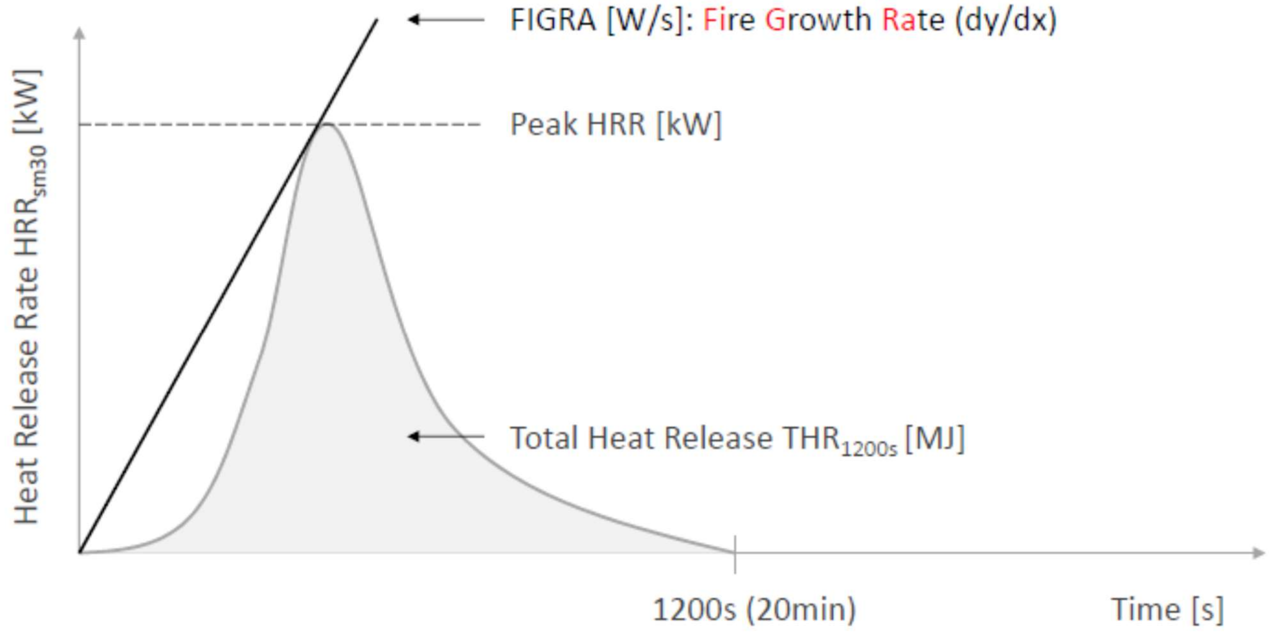


Figure 1: schematic representation of a fire chamber according to EN 50399

CPR: Classification

Classification	Class	Test method	Evaluation criteria	Additional evaluation criteria
Non-inflammable	Aca	EN ISO 1716 (bomb calorimeter)	PCS ≤ 2.0MJ/kg	
Low risk of fire	B1ca	EN 50399 (30kW ignition source)	FS ≤ 1.75m and THR_{1200s} ≤ 10MJ and PHRR ≤ 20kW and FIGRA ≤ 120W/s	**s1** (**s1a** or **s1b**), **s2** or **s3** **d0**, **d1** or **d3** **a1**, **a2**, **a3** or no declaration
		EN 60332-1-2	H ≤ 425mm	
	B2ca	EN 50399 (20.5kW ignition source)	FS ≤ 1.50 m and THR_{1200s} ≤ 15 MJ and PHRR ≤ 30kW and FIGRA ≤ 120W/s	
		EN 60332-1-2	H ≤ 425mm	
	Cca	EN 50399 (20.5kW ignition source)	FS ≤ 2.0 m and THR_{1200s} ≤ 30 MJ and PHRR ≤ 60kW and FIGRA ≤ 300W/s	
		EN 60332-1-2	H ≤ 425mm	
	Dca	EN 50399 (20.5kW ignition source)	THR_{1200s} ≤ 70MJ and PHRR ≤ 400kW and FIGRA ≤ 1300W/s	
		EN 60332-1-2	H ≤ 425mm	
Standard cable	Eca	EN 60332-1-2	H ≤ 425mm	
No classification	Fca			

CPR: Classification - additional evaluation criteria

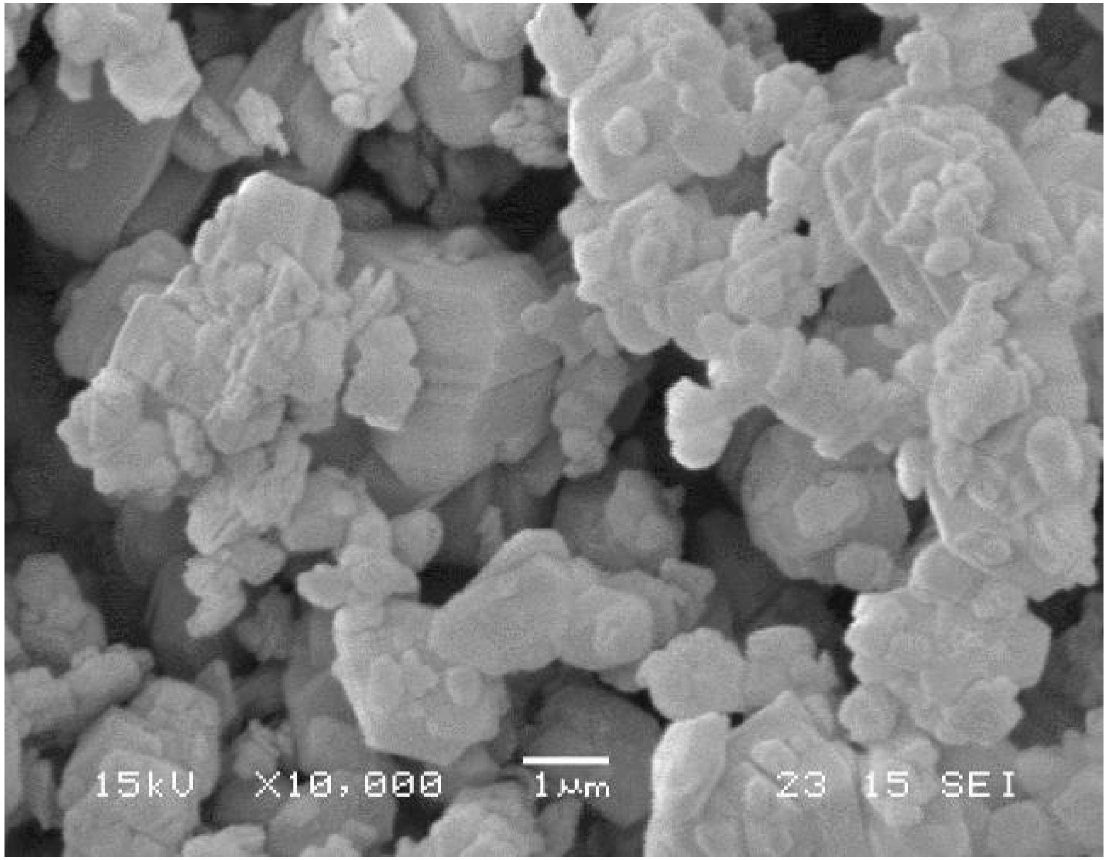
Criterion	Class	Evaluation criteria
Flue gas density	s1	TSP ≤ $50m^2$ and PSR ≤ $0.25m^2/s$
	s1a	s1 and translucency ≥ 80%
	s1b	s1 and translucency ≥ 60% < 80%
	s2	TSP 1200 ≤ 400 and PSR ≤ $1.5m^2/s$
	s3	not s1 or s2
Droplets	d0	no burning droplets within 20 minutes
	d1	no burning droplets longer than 10s within 20 minutes
	d2	not d0 or d1
Acidity of the flue gases	a1	Conductivity < 2.5µS/mm and pH > 4.3
	a2	Conductivity < 10µS/mm and pH > 4.3
	a3	not a1 or a2
	No description	No classification

General effects on combustion of fillers and of flame-retardant fillers.

General effects of Fillers on polymer ignition and combustion:	Main *additional* effects of Flame-Retardant fillers:
a) dilution, reducing the amount of fuel available for combustion; **b)** change of the heat capacity and thermal conductivity of material; **c)** thermal effects such as reflectivity and emissivity; **d)** formation of solid residue; **e)** slowing down the rate of diffusion of oxygen and pyrolysis products; **f)** influence on polymer melt rheology (reduction of dripping).	**a)** heat adsorption due to endothermic decompositions; **b)** release of gases, providing a significant dilution and cooling of pyrolysis products, together with insulation of substrate from radiative energy transfer; **c)** solid state effects depending the chemistry, surface or shape of the additive (strong charring effect).

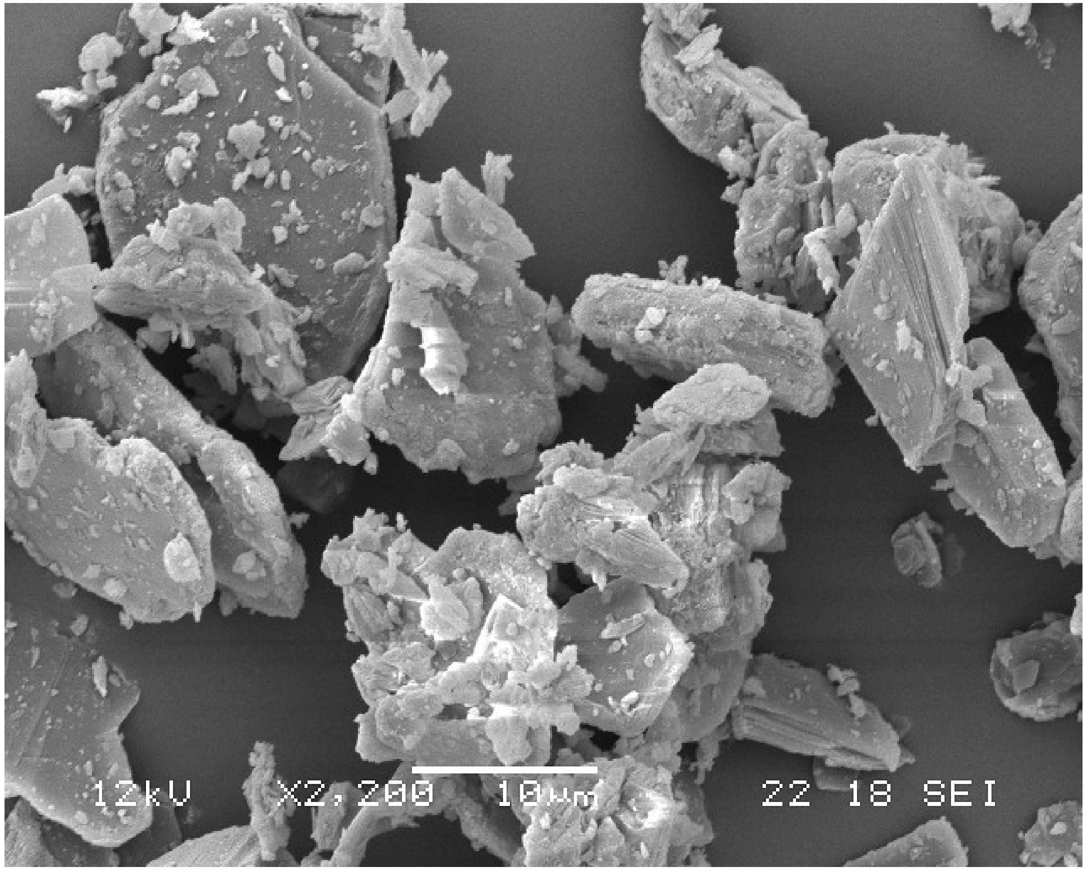
Fine precipitated Aluminum Hydroxide (ATH)

- It's the main FR filler in cable industry for HFFR **cables** compounds for insulation and sheathing.
- **Used also in PVC and TPO roofing membranes.**
- Most used grade in cables is d_{50}=2μm with surface area 4 m^2/g,
- Uncoated grades are typically used, even if some coated grade is available.
- Used at more than 60% dosage mainly in EVA and POE/ULDPE, where compounding and extrusion are below 180°C.
- Used also in PVC as smoke suppressor at around 30 phr together with Sb_2O_3.
- Chemical product with highly fluctuating price, correlated to price of the Aluminum metal.



Milled Aluminum Hydroxide (ATH)

- Largely available from Bayer Process in coarse powder (60-100 microns) as intermediate product of metallic aluminum production.
- Main use is for thermoset resins (especially polyesters), rubber compounds for bedding (cables), bitumen roofing membranes, aluminum composite panels, **PVC flooring and roofing….**
- Most used grade is d_{50}=10-20μm with surface area 4-6 m^2/g.
- Fine milled grades at d_{50}=1-3 μm result highly hygroscopic and with high surface area with possible problems of viscosity and porosity.



Families of Magnesium hydroxide (MDH) - $Mg(OH)_2$

Flame retardancy is achieved through five different mechanisms:

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

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

⇒ FR efficiency of natural MDH and of chemical MDH are equivalent (*when purity is guaranteed)*

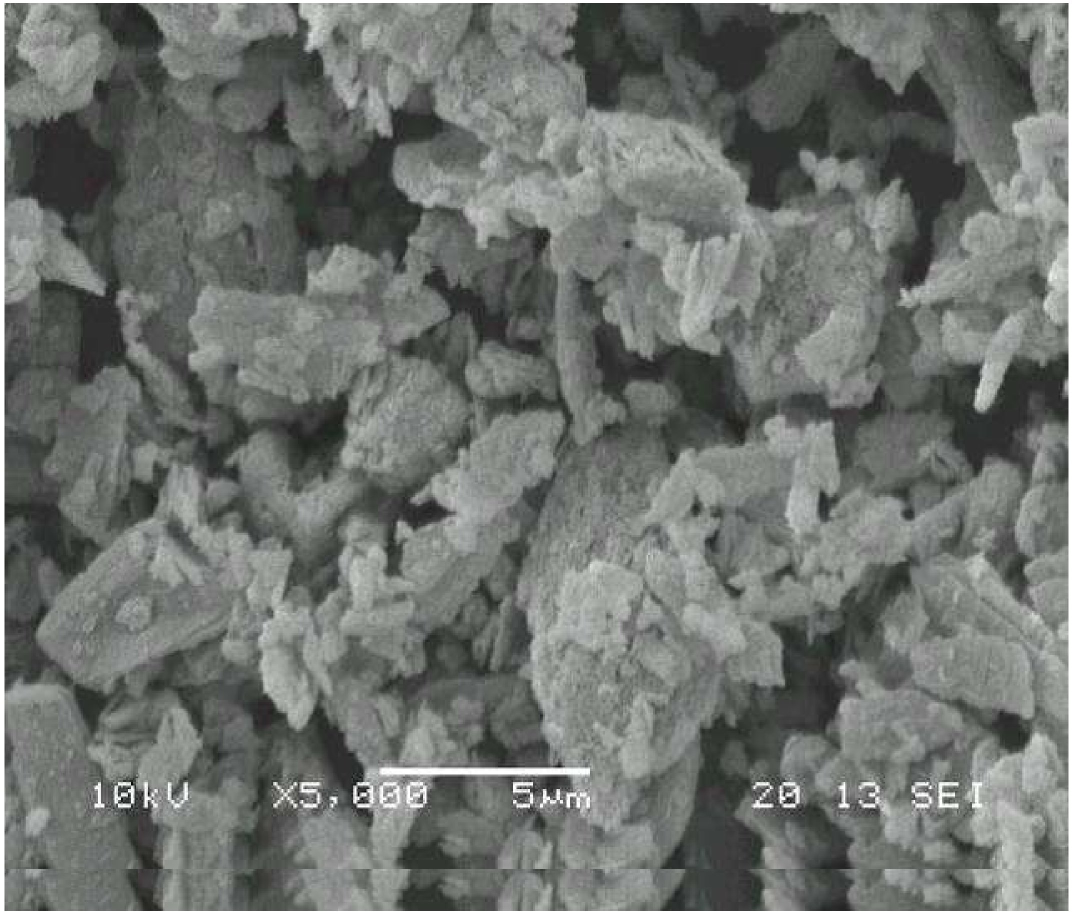
Like ATH, **MDH is non-toxic and environmentally friendly**, but thanks to its **high decomposition temperature**, MDH is mostly used when high processing temperatures and high speed of extrusion/production are required, where ATH risks to decompose.

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

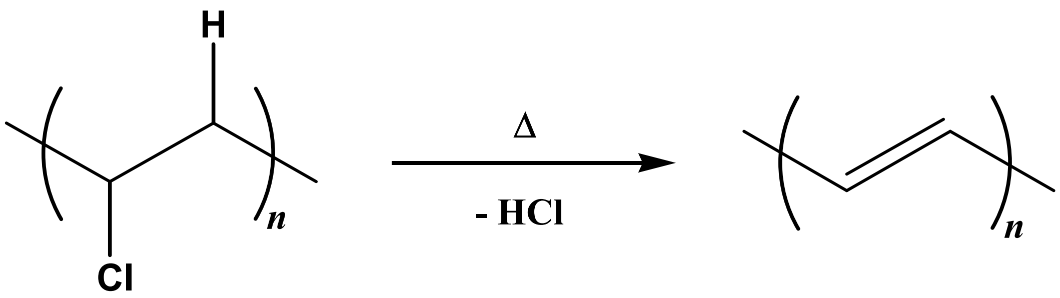
Milled natural MDH (Brucite)

- 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. **Almost no Iron Fe_2O_3**
- Available in different granulometries, **from 3 to 200 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:

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

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

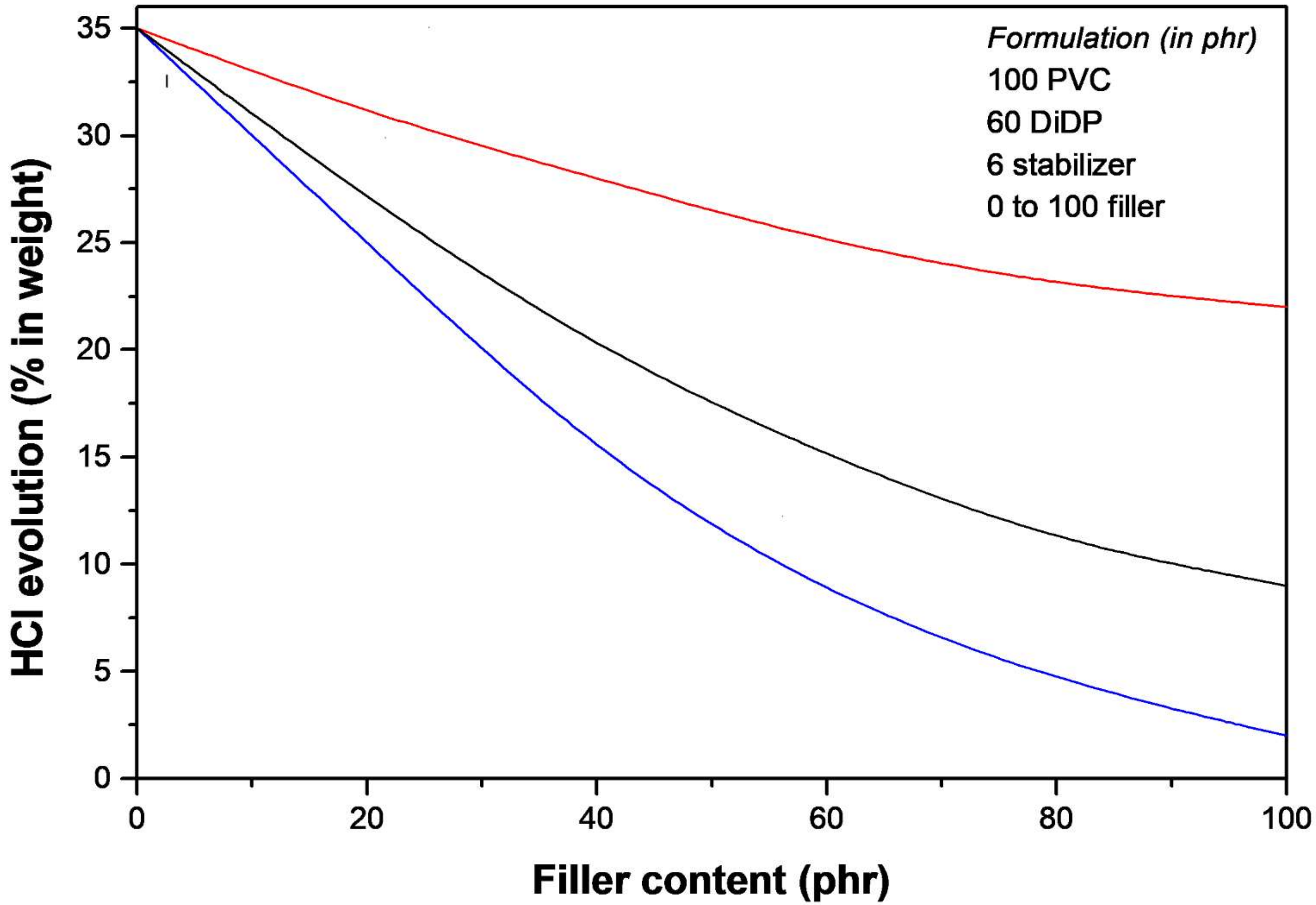
$$Mg(OH)_2 + 2\ HCl \rightarrow MgCl_2 + 2\ H_2O$$

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

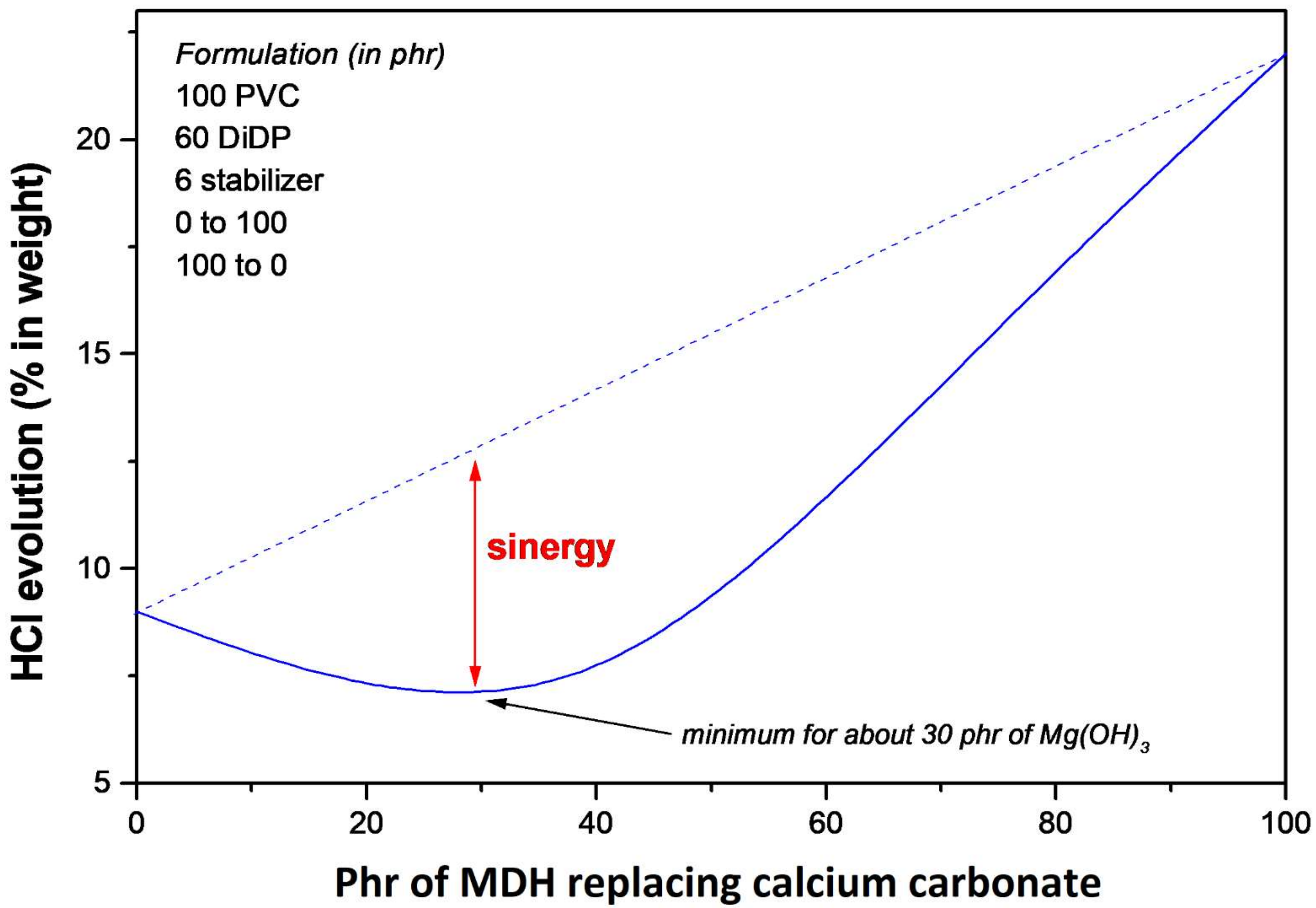
⇒ Reaction of HCl depends on type, content and *<u>surface area</u>* of the fillers

Trapping of HCl versus filler loading

Red line = $Mg(OH)_2$
Black line = milled $CaCO_3$
Blu line = precipitate $CaCO_3$



Synergism between $Mg(OH)_2$ and $CaCO_3$



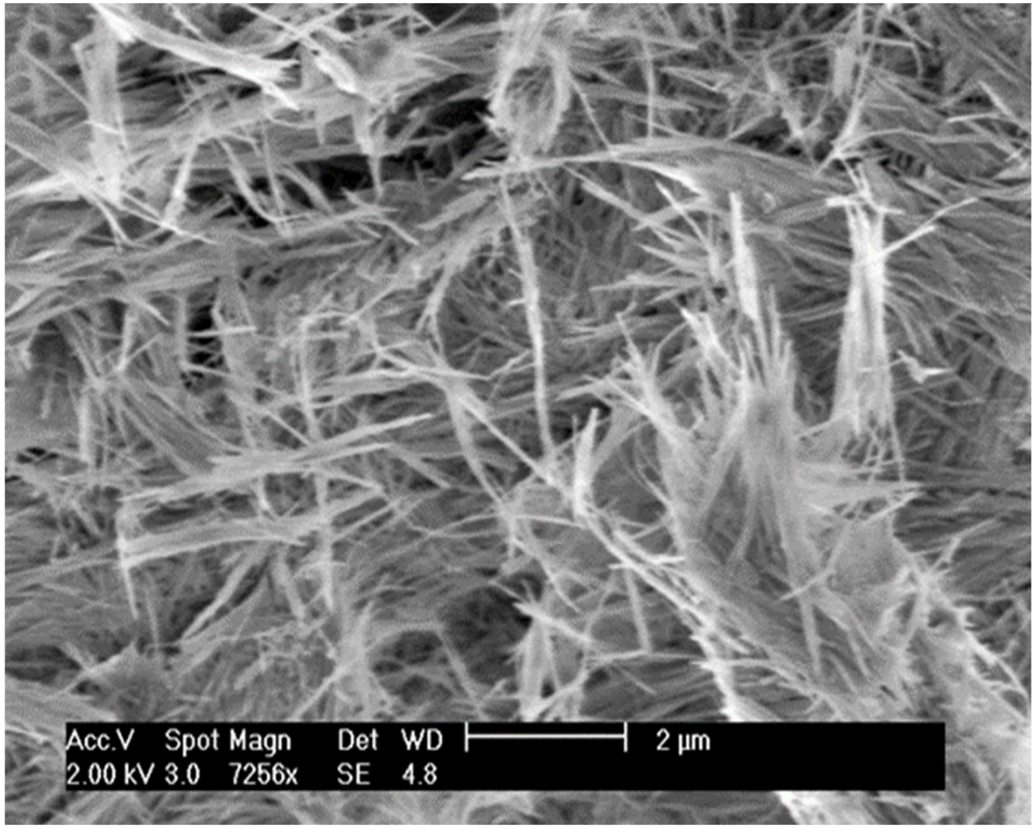
Reduction of Smoke density of FR PVC compounds

The easiest way to reduce smokes of PVC compounds is to reduce ATO. **But what about FR**?

- **Zinc Borate** is the common smoke suppressant in PVC, used in combination ATO:ZB = 2:1 or even 1:1.
- **Chloroparaffin** is used as secondary plasticiser. It is FR and *cost competitive*, but it has negative impact on smoke emission, creates some compatibility issue (migration out) and in some country like USA and Northern Europe it's NOT welcome.
- **Aryl phosphate plasticizer**s are efficient FR but frequently they increase smoke emission, except some *special* alkyl aryl phosphate.
- **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, by Huber, by Indian Oxide, by Tolsa, …

Sepiolite: Mineral FR synergist

- Natural Magnesium Silicate with a needle-like structure (1-2 microns, high specific surface)
- Open bundle of treated fibres to achieve homogeneous dispersion of single fibres.
- Surface coated grades to reduce hydrophobicity, avoid water absorption, improve dispersion and reduce viscosity.
- FR synergist to enhance char structure, by improving gas barrier to reduce smoke emission and melt dripping. **Typical dosage 2.5-5%wt**.
- Used in plasticised PVC as synergist for Sb_2O_3, *antidripping* and *smoke suppressant* additive



Sepiolite in highly plasticised PVC compound (80 Shore A)

	Ref.	Improved
PVC resin k70	100	100
DINP	55	55
Chloroparaffin 52%	20	20
$CaCO_3$	80	80
ATO	5	5
Ca/Zn Stabilizer	5	5
Adins clay SIL-1	-	10
TOTAL	263	273
FR PROPERTIES	**Ref.**	**Improved**
UL-94 classification (1,6mm)	**V2**	**V0**
Total burning time (s)	35	23
Longer burning time (s)	6	4
Dripping 1st application of flame	NO	NO
Dripping 2nd application of flame	YES	NO
Other properties	**Ref.**	**Improved**
Thermal stability CR (mins)	108	94
Colour	Off-white	Light grey

- PVC has very little almost no tendency to drip during burning.
- But when high flexibility is required, due to higher dosage of plasticisers, PVC can drip when ignited.
- Data of left table show benefit of mineral antidripping agent to improve FR rate from V2 to V0 of flexible PVC.
- Smoke reduction is under testing (expected -20% smoke release, based on previous data from Tolsa).

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	28-32	34-38	32-36	38-42
Specific gravity	1.52	1.55	1.48-1.52	>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	1.0	1.1	1.3	1.7

PLENUM CABLES *(special application, **maximum** fire safety)*

Plenum cables are electrical cables that are laid in the plenum spaces of buildings. In the United States, all materials intended for use on wire and cables to be placed in plenum spaces are designed to meet rigorous fire safety test standards in accordance with NFPA 262.

This fire test is 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.

*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**.*

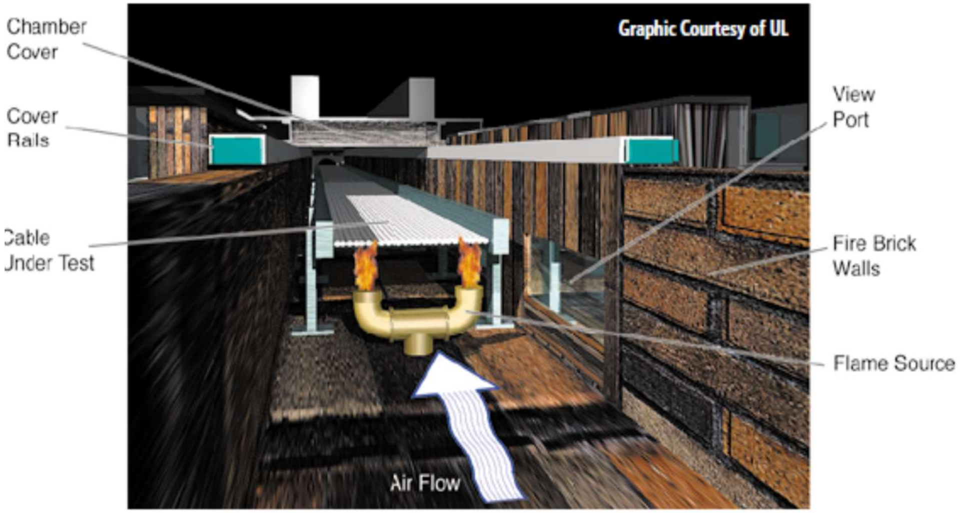


Figure 7: NFPA 262 (UL 910 Steiner Tunnel) test setup

Conclusions

✓ 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).

✓ PVC irradiates only a minimum amount of heat; this means a minimum contribution to heat diffusion.

✓ Hydrogen Chloride (HCl) contained in the smoke is irritating and corrosive for electric/electronic device but it could be minimized thanks to dosage of proper acid scavenger mineral fillers.

✓ PVC can obtain the highest fire reaction results compared with any thermoplastic commodity material: 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.

Thank you for the kind attention!

Questions are welcome