Dr. Camillo Cardelli

Flame Retardancy with Low Smoke and Low Acidity: current status, future trends and competition between last generation of PVC and polyolefin compounds.

April 5th 2019

Abstract

In the recent years, PVC has been under scrutiny due to environmental health and safety concerns of the pristine polymer and of its combustion products. Thanks to the development of new materials and the discovery of new synergisms, last generation of PVC compounds can now compete with polyolefin compounds in terms of fire safety with a reduced smoke opacity and acidity.

This talk will review the current PVC grades including the most commonly used fillers, specific stabilizers and organic coatings designed to address aging (e.g., discolouration/pinking) and processing (e.g., gelification/viscosity). Synthetic and natural mineral fillers offer green and competitive solutions to reduce smoke and improve flame retardancy without affecting the final cost.

Antimony-free (and borate-free) flame retardant solutions are also more and more available at very interesting performances/cost ratio, and provide new technical solutions for the increasing demand of environmentally friendly technologies.
The last generation of PVC and polyolefin grades, already widely applied in Europe, Middle East and India, will be discussed.

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Table of contents

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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 from Europe to Middle East, from Russia to Asia, 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**

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PVC Forum Italia

PVC Forum Italia is the Italian association composed by the leader companies producing, and processing PVC, and the producers of additives and equipment/machinery for PVC.

PVC Forum Italia is an associate member of vinyl plus

Main activities:

- ✓ Information and technical-scientific training for associates, public opinion in general, institutions and the press, with particular attention to issues related to sustainability and product stewardship
- ✓ Organization of conferences and debates on PVC
- ✓ Coordination and dissemination of information provided by national and European associations
- ✓ Development of contacts with institutions, institutions and associations
- ✓ Realization and dissemination of studies and documentation on features, different applications, the regulatory framework, environmental compatibility and current and future PVC scenarios.

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Introduction

Flame retardants prevent or delay the combustion of materials and are indispensable in the protection of plastic products, electric devices, construction materials or textiles. An increasing demand for plastics in the construction sector, automotive industry and the segment electrics and electronics results in a continuing growth of the market for flame retardants.

In 2013, more than 2 million tons of flame retardants were consumed worldwide. Asia-Pacific is the largest sales market for flame retardants, (China single-handedly accounts for almost 24% of global demand), followed by the American market and by Western Europe. Driven by China and India, Asia-Pacific will gain market shares in the future. The Middle East and South America will be large growth markets as well.

The most important application area for flame retardants is the construction sector. An increasing amount of flammable materials are used in thermal insulation and improvement of energy efficiency of residential buildings. Pipes and **cables** made of plastics are used both in the construction of new buildings and the refurbishment of old ones, and are increasingly replacing conventional products such as pipes made of metal in emerging countries as well - fire protection has to be improved accordingly.

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The transportation industry (vehicles and aerospace) has also been notably increasing demand for high-performance, flame retardant plastics in the past years. In the future, the sector electrics and electronics will be the largest growth market. Manufacturers in the subsegment smartphones and tablet computers in particular will not only raise demand for flame retardant materials, but also put a rising value on the environmental impact of the flame retardants consumed.

The market for halogenated flame retardants (brominated and chlorinated flame retardants) is rapidly losing market shares to environmentally friendly products.

In a global context, ATH (aluminum hydroxide) is the most commonly used type of flame retardant. In both Western Europe and North America, **ATH compounds account for about half of total market volume**.

Synthetic and natural magnesium hydroxide are the faster growing mineral flame retardants in construction sector due to replacement of ATH: aluminum composite panels, roofing membranes and energy cables (halogen free and PVC) are more and more using magnesium minerals to reduce flammability, smoke emission and smoke acidity.

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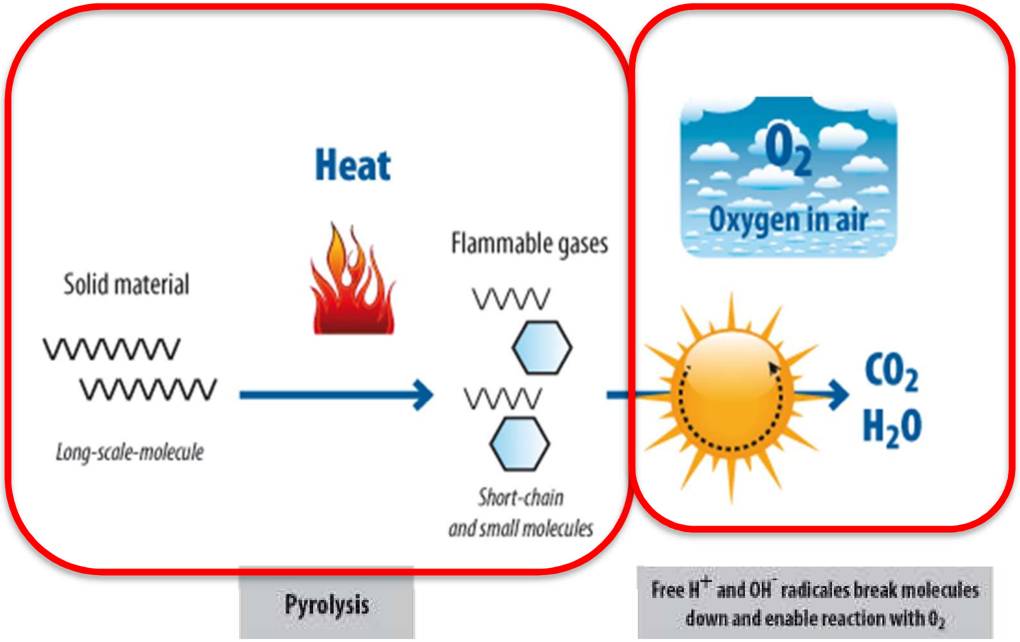
Basics Regarding Flame Retardants

During a fire, the following phases can be discerned:

1. Pyrolysis
2. Combustion
3. Burning
4. Spreading of flames/flash over



During pyrolysis, small and volatiles fractions of polymers evaporate as gases. These gases react with the oxygen in the air and form visible flames. The presence and interaction of heat, combustible materials, and oxygen in a fire can cause spreading: Combustible materials are thermally broken down into flammable gases by heat, the air becomes heated up and thus becomes more reactive.

Flammable gases mix with air and result in a fire. The fire, in turn, generates heat, keeping the cycle of combustion going.

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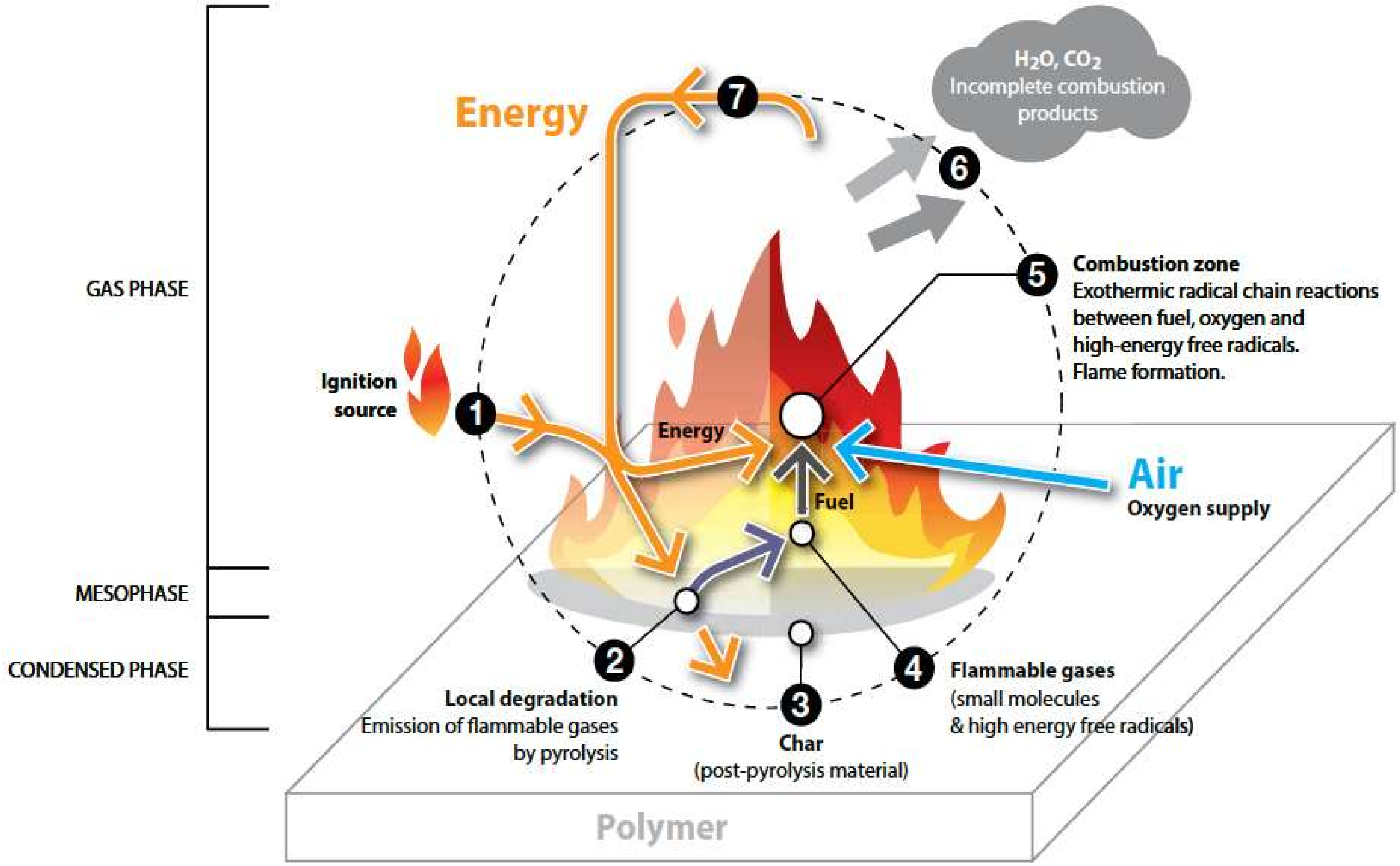
Schematic description of combustion of polymers

- 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.



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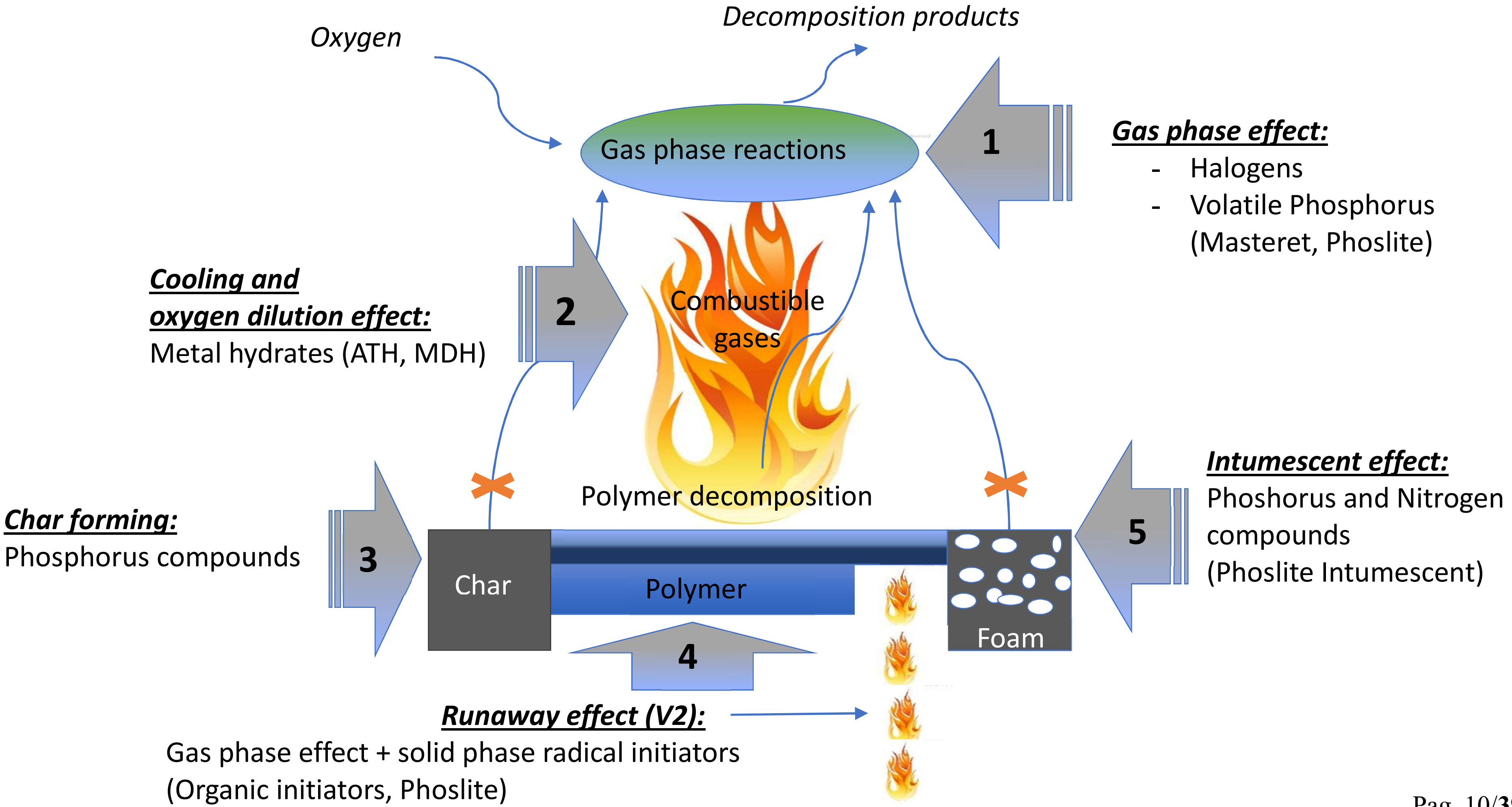
Flame Retardant mechanisms of action: *the 5 effects*



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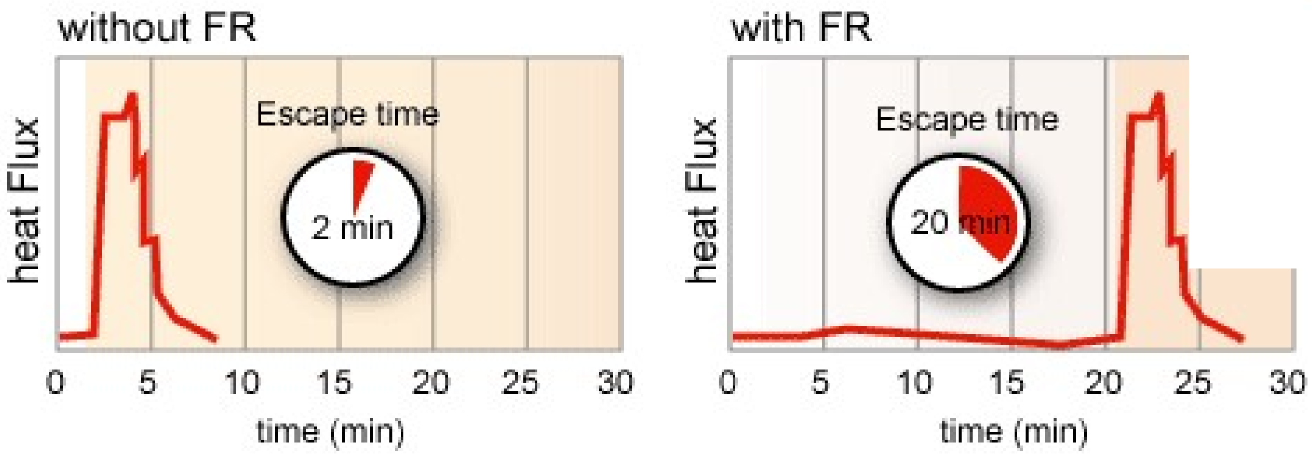
A polymeric material is named flame retardant not only if it cannot ignite and burn, but also if it is characterized by **ONE flame retardant property**:

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

⇒ The goal for flame retardant materials should be to improve more fire properties as possible!



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The main classification of FR additives is between **Halogenated Flame retardants** and **Halogen free flame retardants**. There are issues with halogenated flame retardants:

- ☠ Halogen-containing compounds also tend to release heavy, black smoke, which can prevent people from finding their way out of a burning building.
- ☠ In case of fire, halogenated compounds release toxic fumes, which can be fatal either directly or by debilitating people, who are thus prevented from escaping from the fire.
- ☠ Both halogenated organic compounds and the most common synergists (ATO and chloroparaffin) are suspect from the point of view of impact on the environment and from a Health and Safety perspective
- ☠ Corrosive gases damage the concrete reinforcement as well as electronic devices like PCs, alarms, servers, elevators

So, destiny of PVC is to disappear?

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Demands of material properties in case of fire:

1. Low flammability and Low flame spread.
2. Low smoke emission and smoke's toxicity.
3. Low acidity and low corrosivity of gas of combustion.

⇒ **PVC can be this material, if properly formulated**

FRLS PVC in Middle East, Russia and India is already reality in the last 10 years

Low smoke emission, low smoke acidity plasticized PVC is growing in those markets as reaction of PVC industry vs new "*green*" feeling.

⇒ **Mineral fillers are the economically and technically most suitable solution for fire safe and environmentally green PVC**

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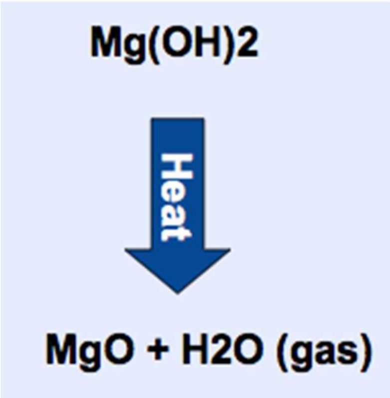
Flame retardant mineral fillers

General effects of **fillers** on polymer ignition and combustion:	**Main** **additional** **effects of Flame Retardant fillers:**
✓ dilution of fuel ✓ heat capacity modification ✓ thermal effects ✓ solid residue formation ✓ less diffusion of O_2 and fuel ✓ rheological effects	✓ **ENDOTHERMAL DECOMPOSITION:** - heat adsorption - release of gases - $T_{surface}$ and T_{gas} decrese - insulation from radiative energy ✓ solid state effects (char)



Mostly cooling and charring agents

Name	ATH	MDH	Huntite/Hydromagnesite 60/40
Chemical formula	$Al(OH)_3$	$Mg(OH)_2$	$Mg_3Ca(CO_3)_4$ $Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$
Start of decomposition (°C)	180-200	300-320	220-240
Enthalpy of decomposition (J g^{-1})	1300	1450	1000

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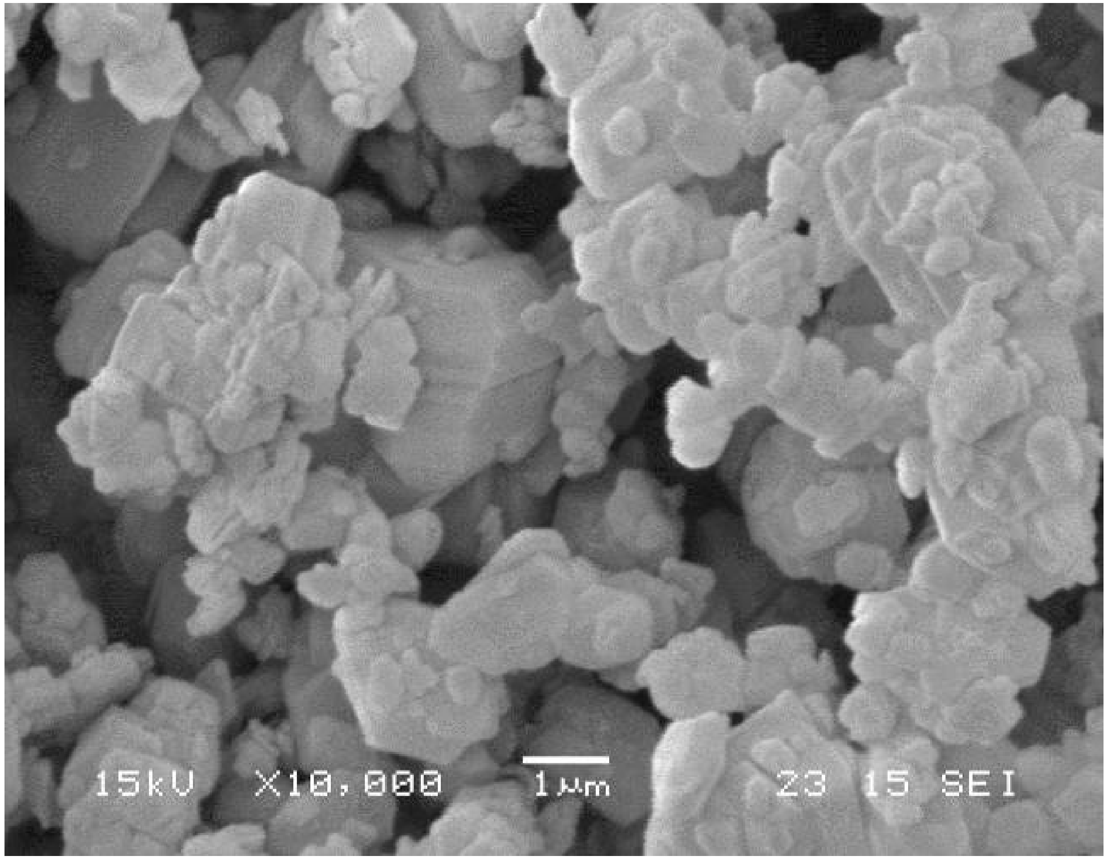
Fine precipitated Aluminum Hydroxide (ATH)

- 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 at around 30 phr as Sb_2O_3 replacement and smoke suppressor.
- Fluctuating price, correlated to price of the Aluminum metal.



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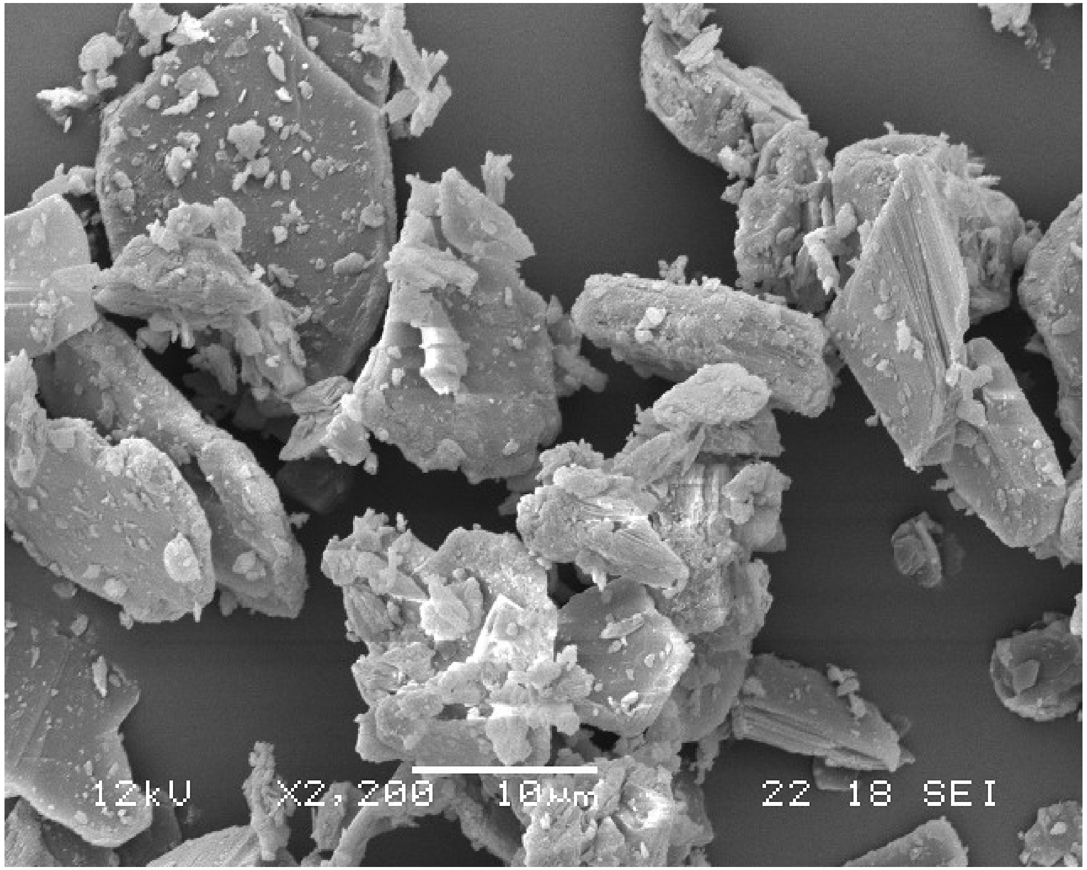
Milled Aluminum Hydroxide (ATH)

- 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}=15-20μm with surface area 4-6 m^2/g.
- Fine milled grades at d_{50}=1-3 μm result highly hygroscopic and with very high surface area with relevant problems of viscosity into final HFFR compounds.



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Magnesium hydroxide (MDH)

MDH is a white crystalline powder manufactured either from different minerals by a chemical process (**synthetic MDH**), by precipitation from seawater/brine (**seawater MDH**) or by grinding processes of naturally occurring brucite (**natural milled MDH**).

Because of its **high decomposition temperature (>300°C)**, it is mostly used when high processing temperatures are required and/or higher application temperatures of the flame retarded end product are needed.

MDH is non-toxic and regarded as environmentally friendly. 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.

Compared to ATH, MDH offers several advantages, including **higher decomposition temperature, reduced smoke levels and reduced acidity of the smokes**. Most of these performances come from **high surface and high basic reactivity MgO** generated by fire from $Mg(OH)_2$.

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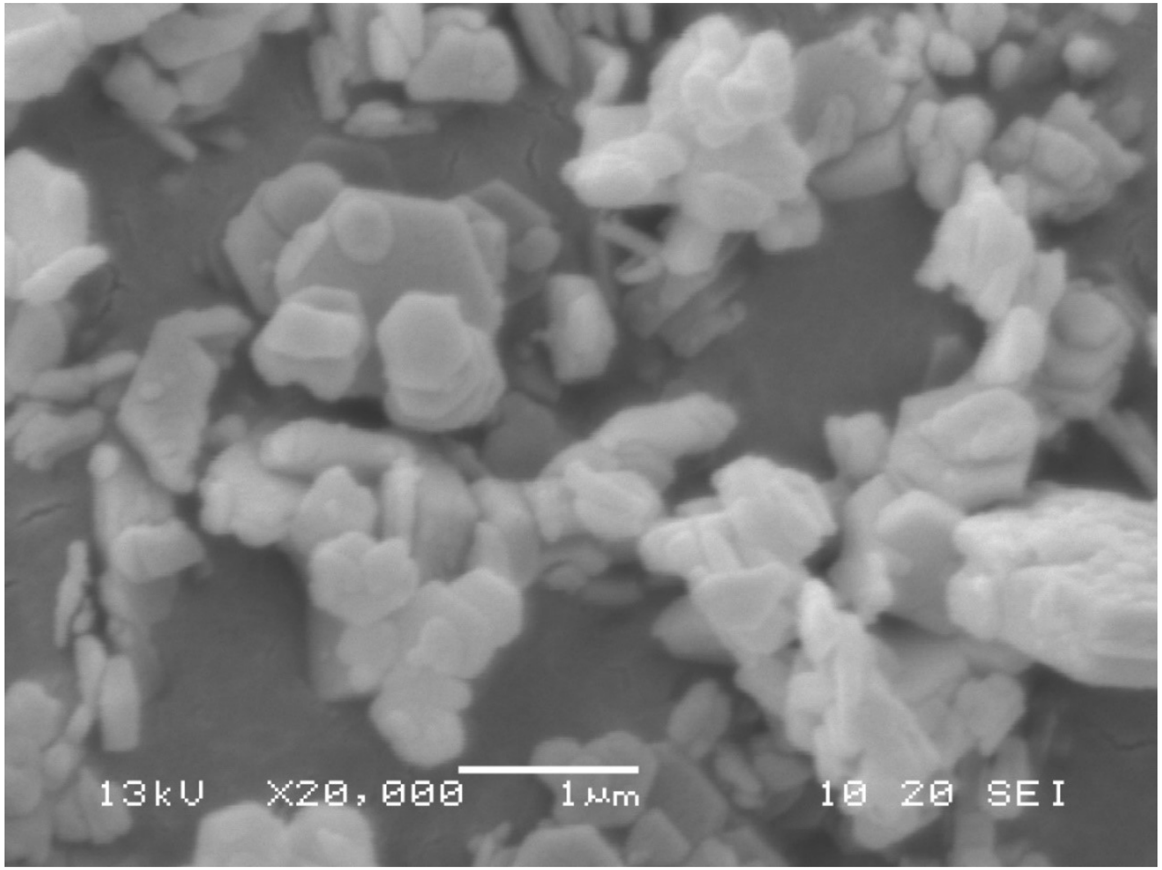
Synthetic Magnesium hydroxide (MDH)

- The most expensive mineral flame-retardant filler worldwide used.
- Smaller market than ATH (mainly for price reasons). Japan and Korea the most enthusiastic users.
- Grades available with different granulometry: d_{50}=0.7-3.5 μm with surface area 3-12 m^2/g.
- Used in very high demand applications (XL-HFFR, PP T3 automotive)
- Used in all polyolefins where compounding and extrusion can reach 250°C.
- Used also in brominated FR recipes (automotive) as smoke and acid suppressor.
- **Not used in PVC due to high price.**



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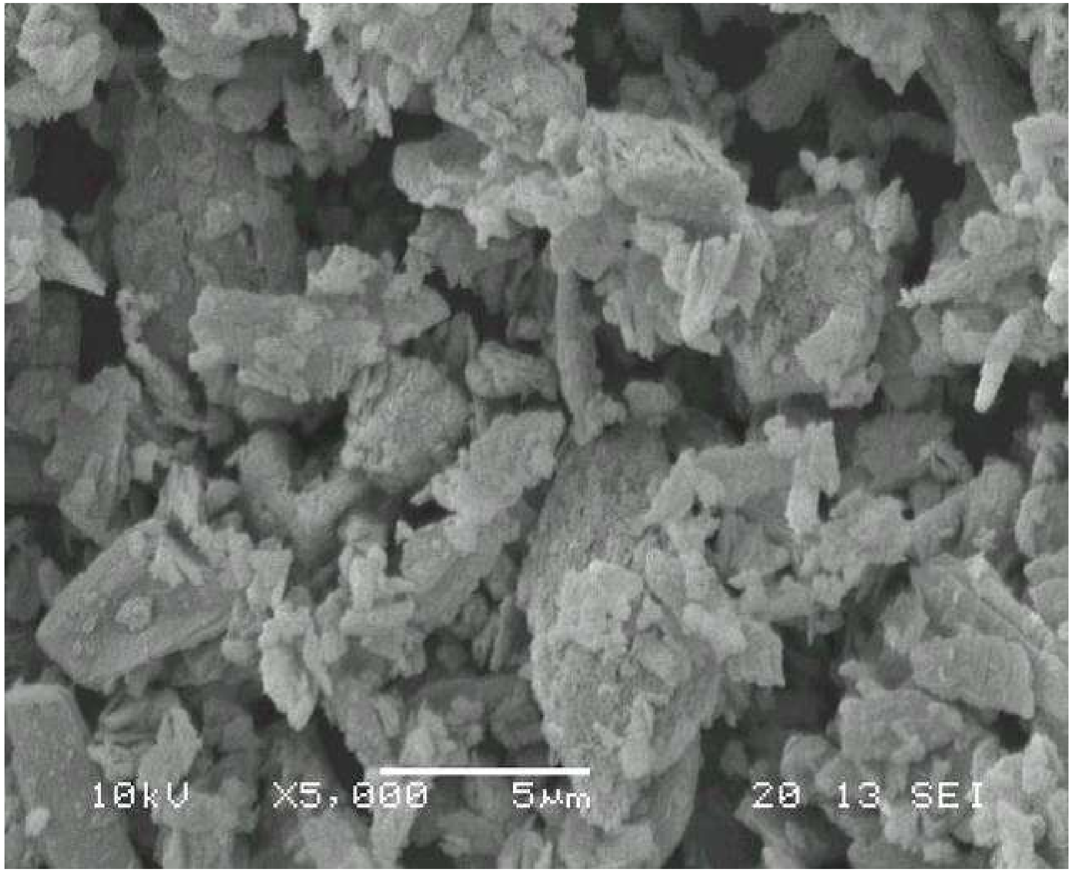
Milled natural MDH (Brucite)

- It's the 2nd main FR filler, beating synthetic MDH, available from Russia and China.
- Typical composition is 90-94% MDH, 6-8% Magnesite/Calcite, <2% other minerals like serpentine.
- Available different granulometry from 1.5-15 µm, with surface area 4-13 m^2/g.
- Surface coated grades with stearic acid and silanes are available to make dispersion less difficult.
- **Used in PVC as Sb_2O_3 replacement, acid scavenger and smoke suppressor**
- In HFFR cable compounds for sheathing is used in EVA in combination with ATH.
- Coarser grades of milled natural MDH are used in ACP panel production.
- In southern Europe, widely used also in bitumen and TPO roofing membranes.



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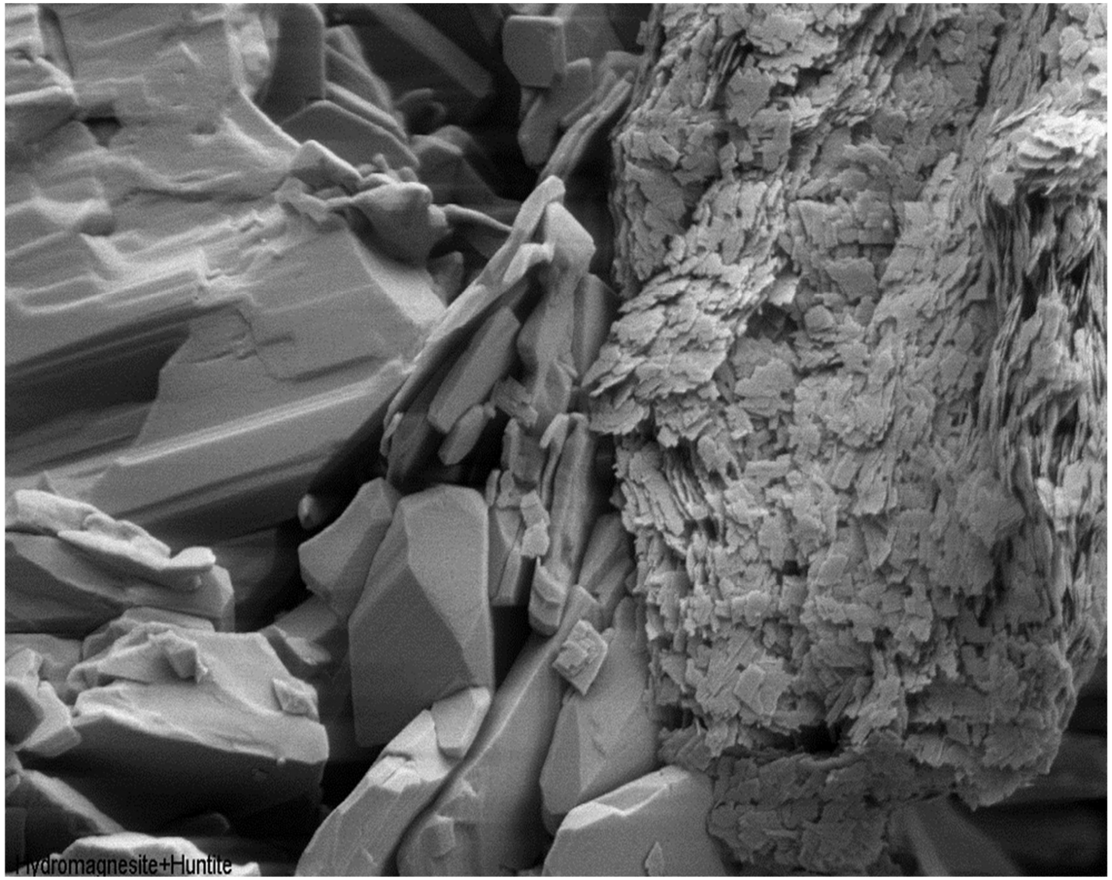
Natural milled Huntite/Hydromagnesite

- Natural blend of 60-70% Magnesium Carbonate (Huntite) and 40-30% Magnesium Hydroxy Carbonate (Hydromagnesite).
- Granulometry from 1.5-3 μm, with surface area >15 m^2/g.
- In **PVC is good as ATO replacement, smoke suppressor and acid scavenger**, also due to "platy" particle shape.
- Thermal stability till 220-230°C.
- Used also in EVA based compounds in combination with fine precipitate ATH.
- Due to high surface area (and lamellar form), Huntite/Hydromagnesite is appreciated mainly as smoke suppressant in PVC and as reinforcing agent in rubber compounds.



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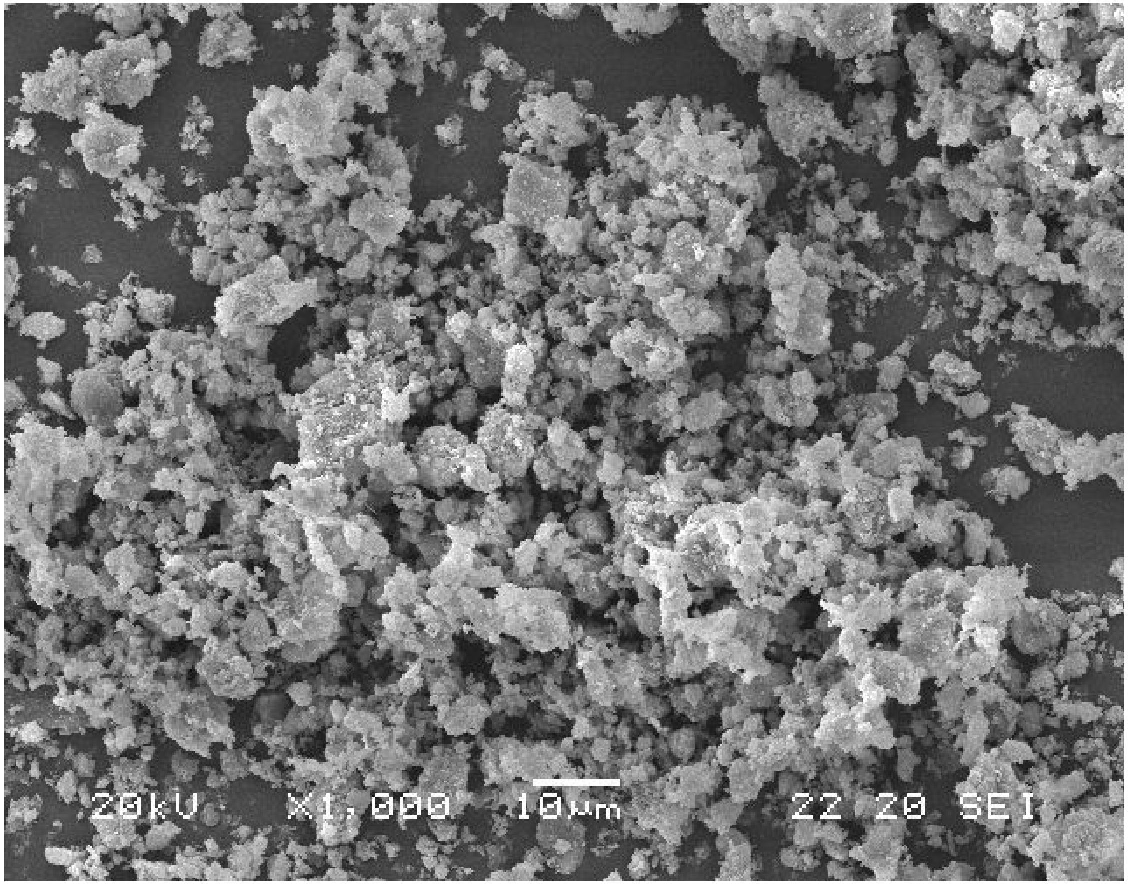
Milled natural Magnesium Carbonate (Magnesite)

- **Flame retardant filler for PVC, less efficient than MDH**.
- NOT hygroscopic and with good electrical properties (no hygroscopic).
- Granulometry 2.3-3 μm, with surface area >15 m^2/g.
- Decomposition temperature is >500°C.
- Milled Particles have smooth spherical shape which makes easier the dispersion into the polymer.
- As calcium carbonate, magnesium carbonate is not hydrophilic and much less polar than MDH. This gives compounds with lower viscosity, but it's much less efficient as smoke suppressor and acid scavenger due to lower reactivity and very high decomposition temperature.



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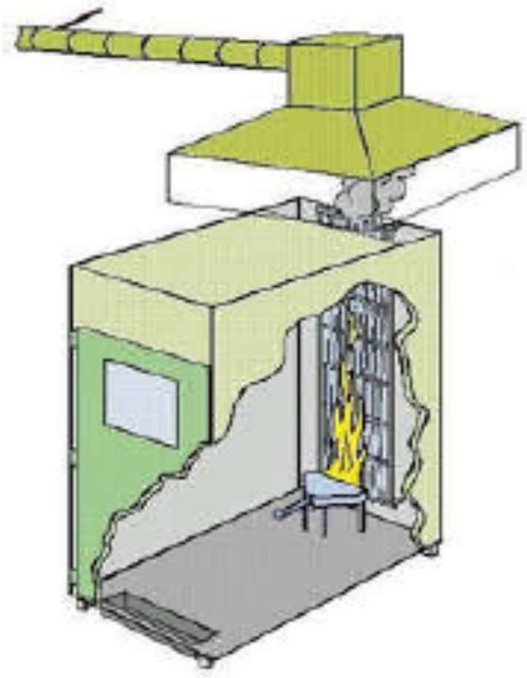
CPR (EN 50399)



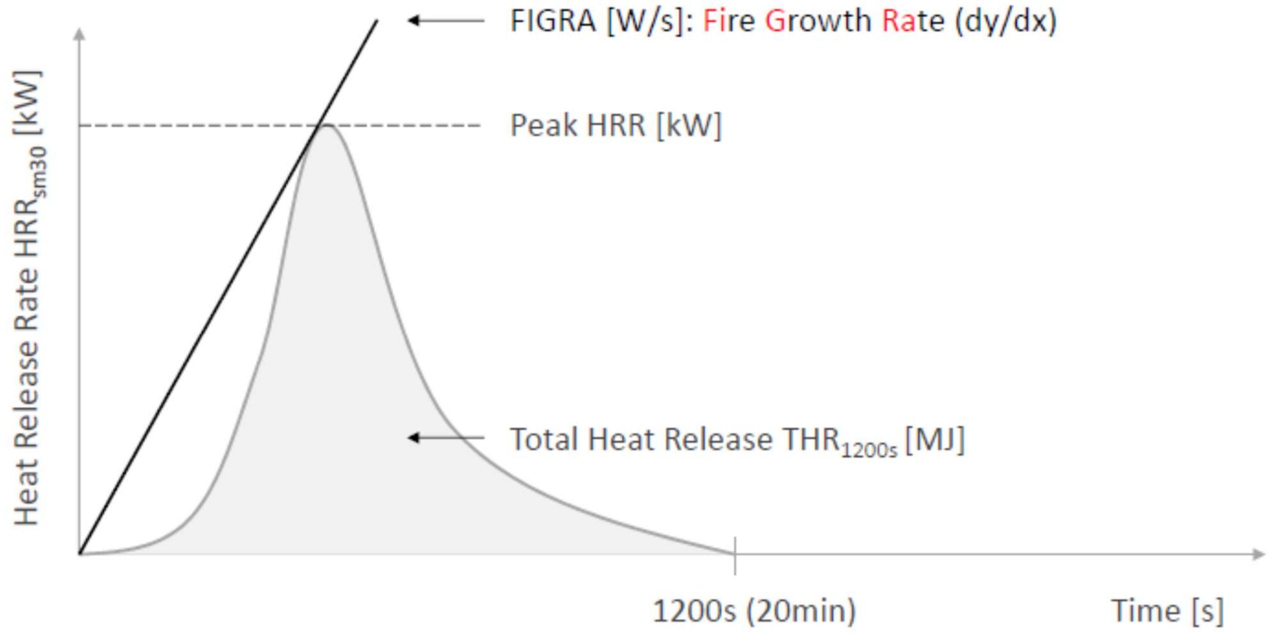


Figure 1: schematic representation of a fire chamber according to EN 50399

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**			

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CPR: Classification - additional evaluation criteria

Criterion	Class	Evaluation criteria
Flue gas density	s1	TSP $\leq 50m^2$ and PSR $\leq 0.25m^2/s$
	s1a	s1 and translucency ≥ 80%
	s1b	s1 and translucency ≥ 60% < 80%
	s2	TSP 1200 ≤ 400 and PSR $\leq 1.5m^2/s$
	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

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Application to PVC cables

New Cables	Class	Smoke	Droplets	Acidity
FG16OR16	$B2_{ca}$	S1	d0	a2

CPR Cables	Class	Smoke	Droplets	Acidity
FG16OR16	C_{ca}	S2	d0	a3

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Smoke acidity measurements

EN 60754-2

- Tubular Oven at fixed temperature ranging b/w 935°C up to 960°C
- Determination of pH and conductivity
- Requirements 1 for class a2: pH > 4,3, Conductivity [mS/mm] < 10
- Requirements 2 for class a1: pH > 4,3, Conductivity [mS/mm] < 2,5
- The requirement 1 defines what is an Halogen Free

EN 60754-1

- Tubular Oven at temperature ranging b/w 790°C up to 810°C
- Temperature ramp @ 20°/min
- Determination of mg of halogens in 1 g of compound

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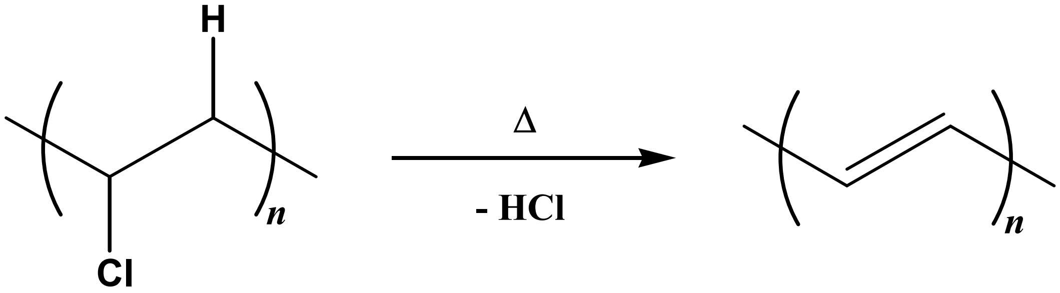
Hydrogen chloride Evolution



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**

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Trapping of HCl by different fillers

Formulation	**ATH**	**MDH**	**CaCO3**
PVC S K70	100	100	100
$Al(OH)_3$	80	-	-
$Mg(OH)_2$	-	80	-
$CaCO_3$	-	-	90
DINP	50	50	50
Ca/Zn stab	5	5	5
Properties			
LOI (%O_2)	**28**	**28**	**23**
pH	2,22	2,27	2,59
Conductivity	212 µS/mm	188 µS/mm	107 µS/mm

⇒ **$CaCO_3$ traps more HCl, but the consequence is reduction of LOI due to less chlorine into gas phase**

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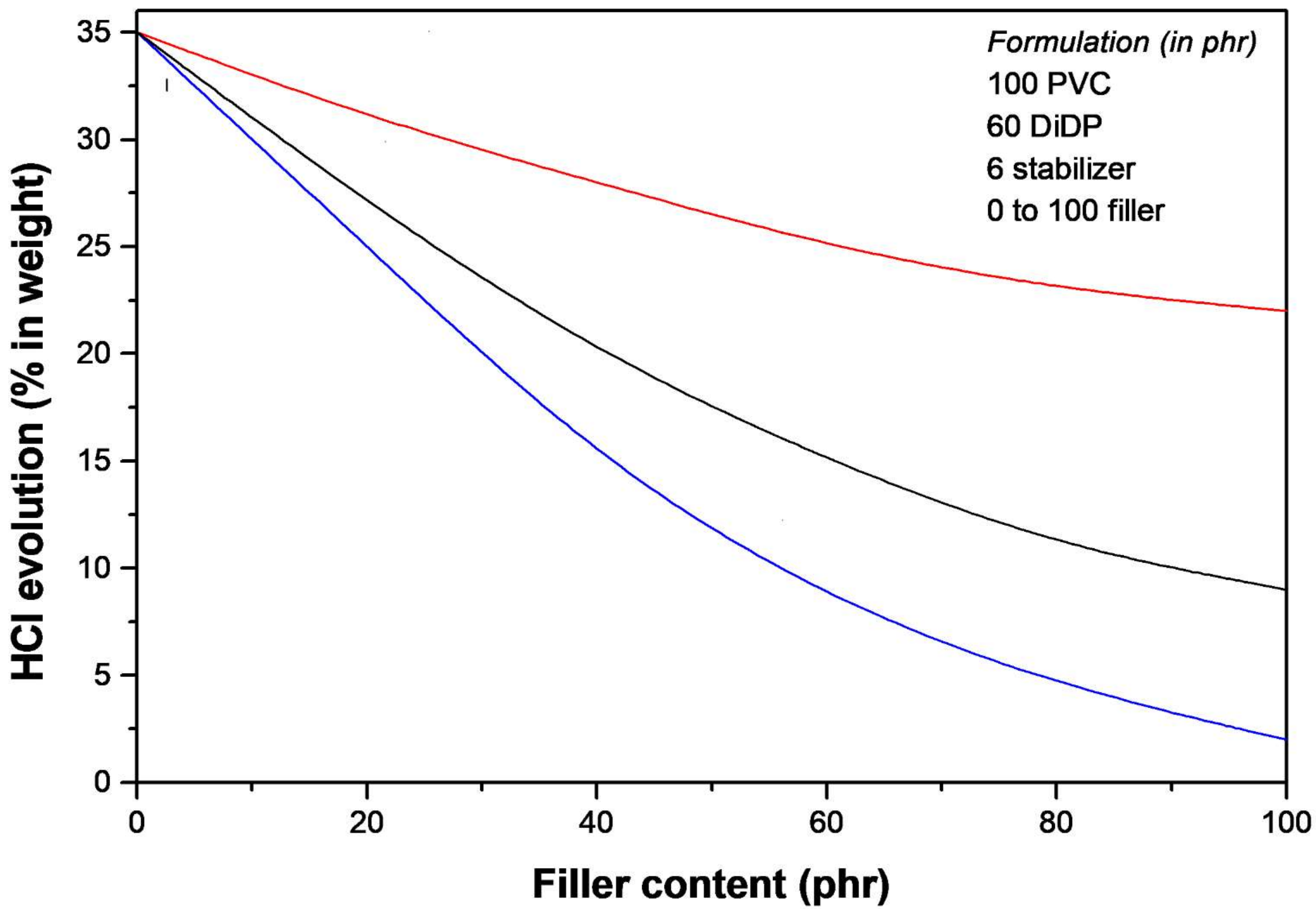
Trapping of HCl versus filler loading

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



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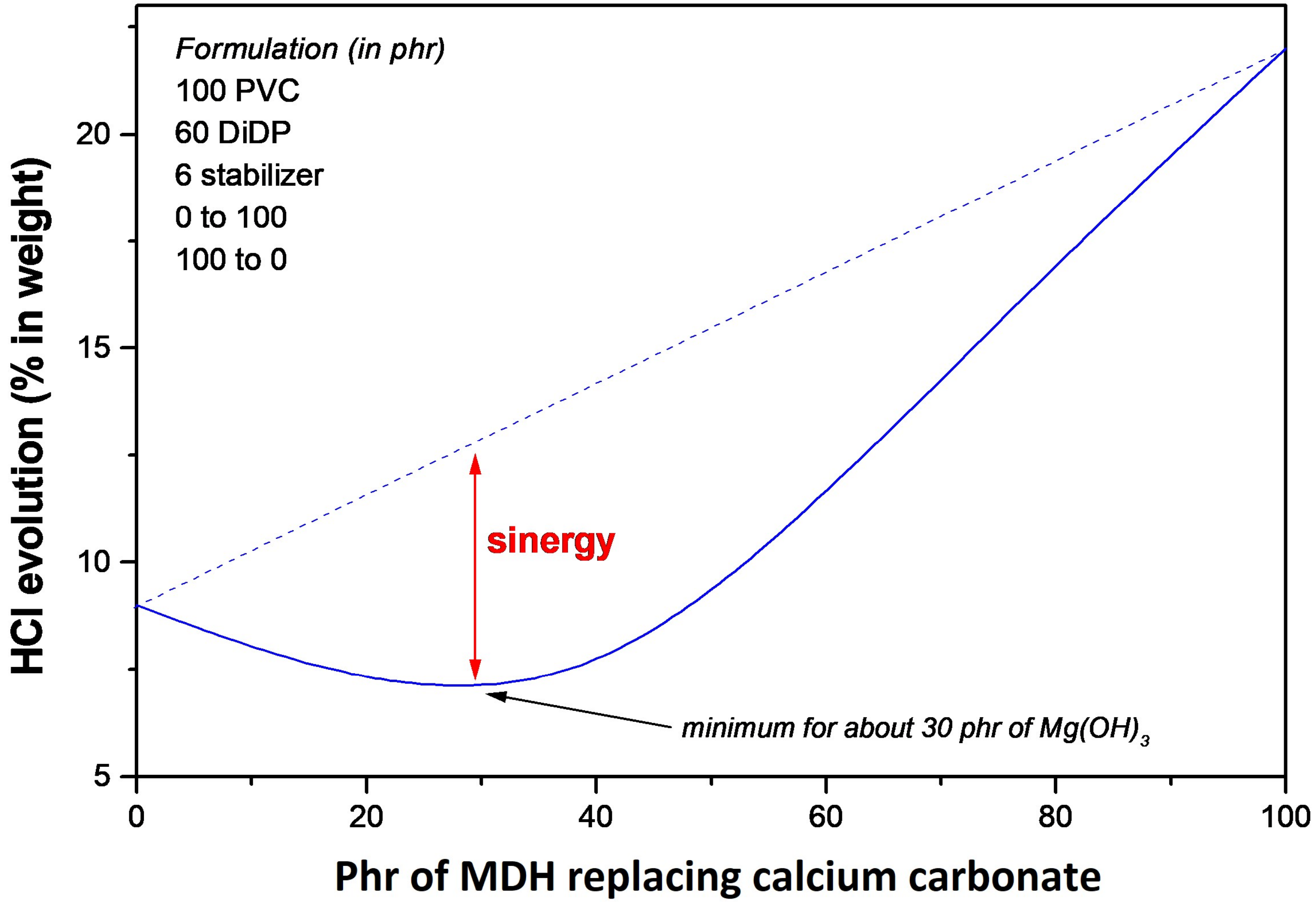
Synergism between $Mg(OH)_2$ and $CaCO_3$



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HCl emission vs temperature of combustion

	EN 60754 part 2 (T=till 960°C)			EN 60754 part 1 (T=till 800°C)		
Formulation #	pH	Conductivity [µS/mm]	H^+ [mol/L]	pH	Conductivity [µS/mm]	H^+ [mol/L]
54	3,54	10,4	$2{,}88 \times 10^{-4}$	4,00	3,80	$1{,}00 \times 10^{-4}$
90	3,75	7,10	$1{,}78 \times 10^{-4}$	4,24	3,00	$5{,}75 \times 10^{-5}$
91	2,46	140,0	$3{,}47 \times 10^{-3}$	2,65	90,4	$2{,}24 \times 10^{-3}$
94	3,52	13,5	$3{,}02 \times 10^{-4}$	4,07	3,90	$8{,}51 \times 10^{-5}$

⇒ Part of the Chlorine “trapped” by the fillers is released as $MgCl_2$ decompose

⇒ High presence of Calcium produces more stable $CaCl_2$

⇒ EN 60754-1 gives higher values of pH e lower values of conductivity in comparison to EN 60754-2.

Which one is the more realistic??

EN 60754-1 (before CPR) vs EN 60754-2 (CPR)

From 23°C to 800 +/-10 °C @ 20°/min	Fixed b/w 935°C and 960°C
At 800 °C few inorganic chlorides are thermally stable	A high temperature gives less of stable substances
With temperature ramps acid scavengers have time to efficiently trap the evolving HCl.	Thermal decomposition makes free HCl again.
The ramp of temperature is more similar to a real fire scenario	Immediate immersion into high temperature furnace at 935-960°C reduce efficiency of acid scavengers

⇒ ***Which is the real temperature evolution in most of fire events?***

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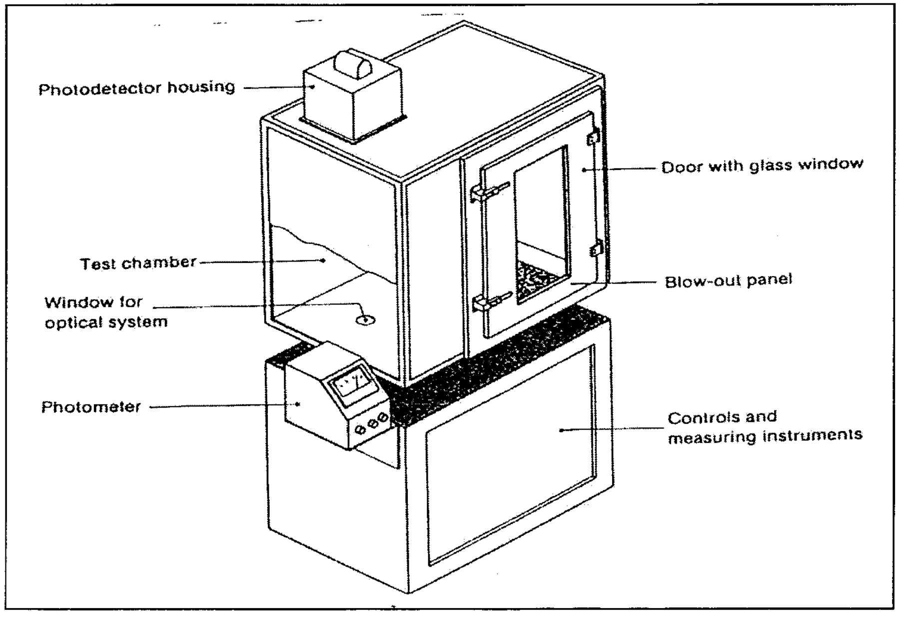
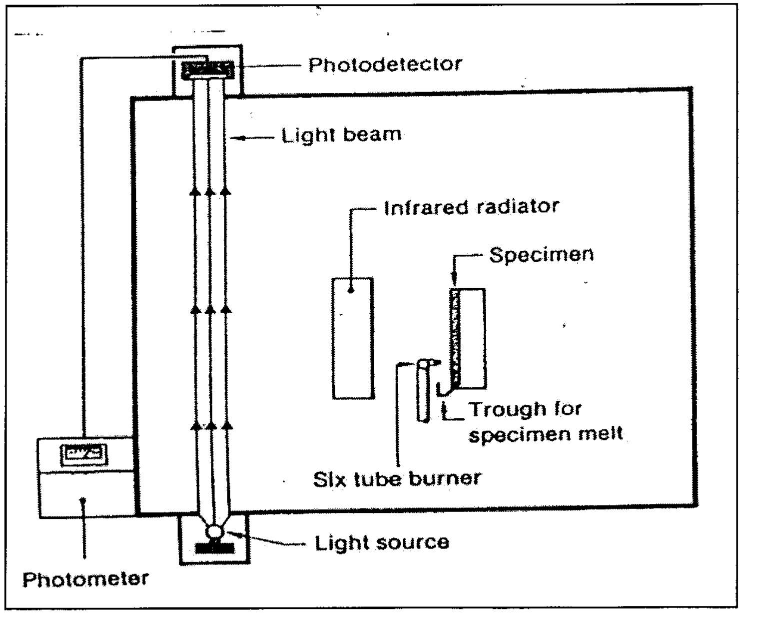
Measurement of Smoke density (ASTM E 662)

This test assesses the attenuation of the light beam caused by smoke collecting in the test chamber. The smoke is generated by pyrolysis (*smoldering conditions*) or combustion (*flaming conditions*).





- **NO FLAMING MODE**: the heat source is a vertical furnace with a radiation flux of 2.5 W/cm^2
- **FLAMING MODE**: there is also a flame applied 6.4 mm away and above the bottom of the sample

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- Sb_2O_3 has the maximum effect on the smoke density.
- Without the Sb_2O_3 the chloroparaffin doesn't increase the smoke density (thanks also to alkyl phenyl phosphate).
- MDH and $CaCO_3$ have a synergistic effect on smoke reduction.

Formulation	**A1**	**A2**	**A3**	**A4**	**A5**	**A6**
PVC K70 resin	100	100	100	100	100	100
DINP	45	45	45	45	20	20
Alkyl phenyl phosphate	-	-	-	-	15	20
Chloroparaffin 52%	-	-	-	-	15	20
$CaCO_3$	80	-	40	40	-	-
Stearic coated MDH	-	80	40	40	80	120
Ca/Zn stabilizer	5	5	5	5	5	5
Sb_2O_3 (ATO)	-	-	-	3	-	-
Properties	**A1**	**A2**	**A3**	**A4**	**A5**	**A6**
Hardness (Shore A)	89	90	89	90	91	89
Thermal stability @200°C (mins)	90	60	71	71	75	70
Specific weight (g/cm^3)	1.55	1.50	1.52	1.53	1.52	1.57
LOI (%)	23	27	26	31	30	31
Smoke density in the smoldering mode	311	226	261	-	149	109
Smoke density in the flaming mode	**445**	**164**	**150**	**450**	**119**	**102**

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Reduction of Smoke density

- The best way to reduce smokes of PVC compounds is to remove/reduce ATO.
- Plasticizers usually increase smoke emission, except some special alkyl phenyl phosphate
- ATH and MDH reduce smoke density by releasing water during combustion of polymeric materials. In case of PVC, magnesium hydroxide shows higher efficiency as smoke suppressant (see next page).
- Zinc Borate is a smoke suppressant in PVC containing ATO.
- Molybdenum compounds and tin Compounds are the most efficient smoke suppressant, but at extremely high cost.
- Many synergistic additives have been designed to optimize performances/cost in replacing ATO to provide high LOI and simultaneously low smokes.
- All the above solution are simultaneously used in PVC compounds for *plenum cables* in USA, the globally safest cables in case of fire.

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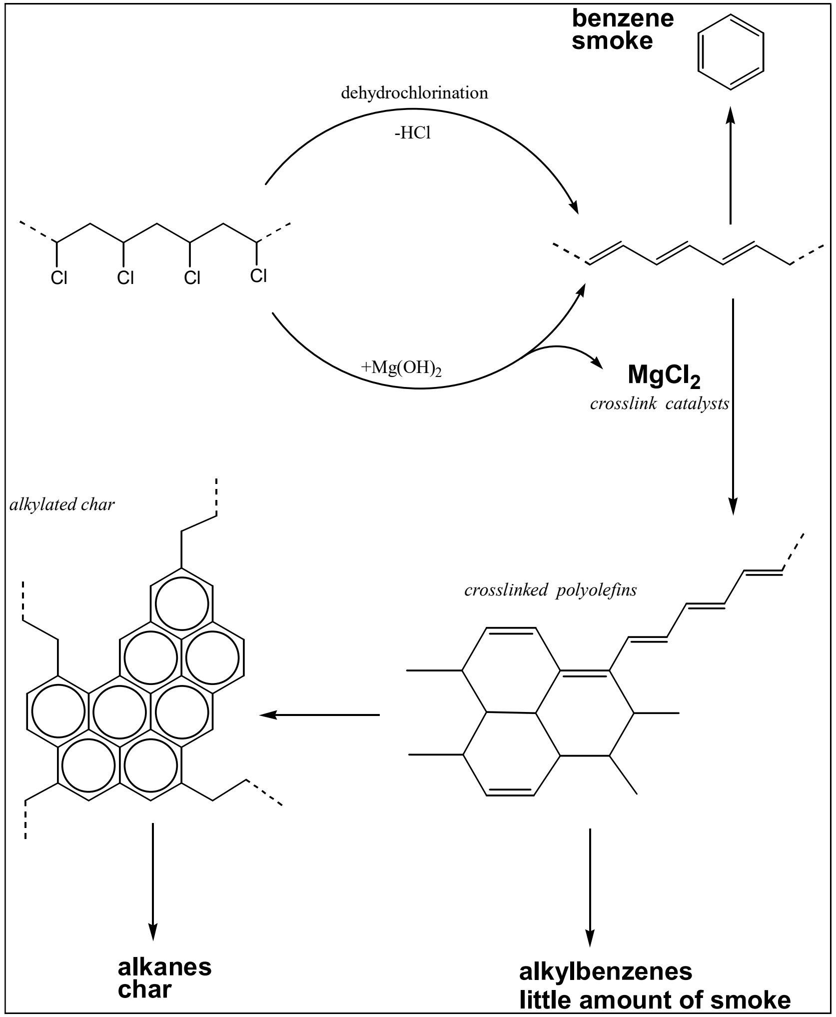

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Conclusions

✓PVC is self-extinguishing and has intrinsically a high potential to resist ignition sources: it does not contribute, or only minimally contributes, to the generation and spread of a fire (it 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 material: if properly formulated with additives and FR fillers, it allows to produce cables complying with Euroclass B2ca-s1-d0, the safest class in European standard (CPR), and complying with specification for *plenum cables* in USA.

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Special thanks to:

Cable Group Italy of PVC forum Italy, associated to **PVC4Cables** which intends to act as a driver for environmentally responsible innovations in the PVC cables sector and as a focal point for dialogue and communications with all stakeholders, and composed by some of the biggest Italian PVC Compounders, focusing to R&D for new formulations for cables with better performances in term of flame retardancy, smoke suppressant properties and smoke acidity.

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Thank you for the kind attention!

Questions are welcome

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