Fire Retardants in Plastics 2019

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« GREEN AND COMPETITIVE SOLUTIONS FOR FLAME-RETARDANT PP »

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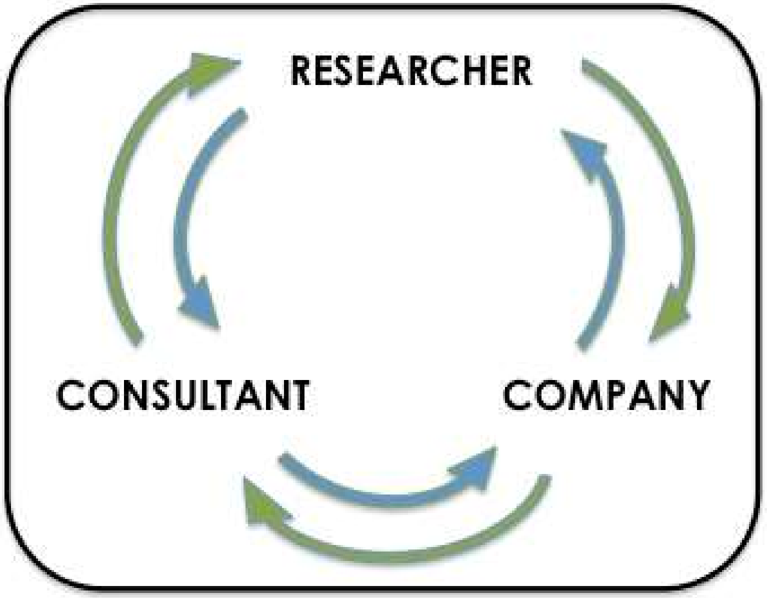
spin-off company of National Council of Research institute (CNR) of Italy. It has been established in July 2011 and it is founded on the strictly connected work of researchers, professionals and industrial companies.



Mission

Scientific and industrial development of know-how and applications regarding chemical and physical properties of materials and specific measurements methods and instruments.

Technical consulting about design, industrialization, and marketing of raw materials and compounds with
high performances and low environmental impact.

Specialized services of Applicative Research and Technological Development for companies operating in safe-materials (flame retardant and low smokes) and recycling materials (circular economy).

Comparison amongst common polymers during burning

Polymer	Self-ignition T (°C)	Tendency to drip	LOI (%)	Morphology
Polyethylene	350	High	18	Semi crystalline, very wide range of grades
Polypropylene	350	Very high	18	Semi crystalline, very wide range of grades
Polystyrene	490	Very high	18	Rigid amorphous
Polyvinyl chloride	450	No	42	Rigid amorphous and Flexible amorphous
Poly(ethylenevinylacetate)	320	Moderate	19	Semi crystalline, flexible
Polyamide 6 (and 6,6)	450 (530)	Moderate	25 (24)	Semi crystalline, very rigid

⇒ Only flexible amorphous phases of polymeric materials are suitable to accept solid flame-retardant additives

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

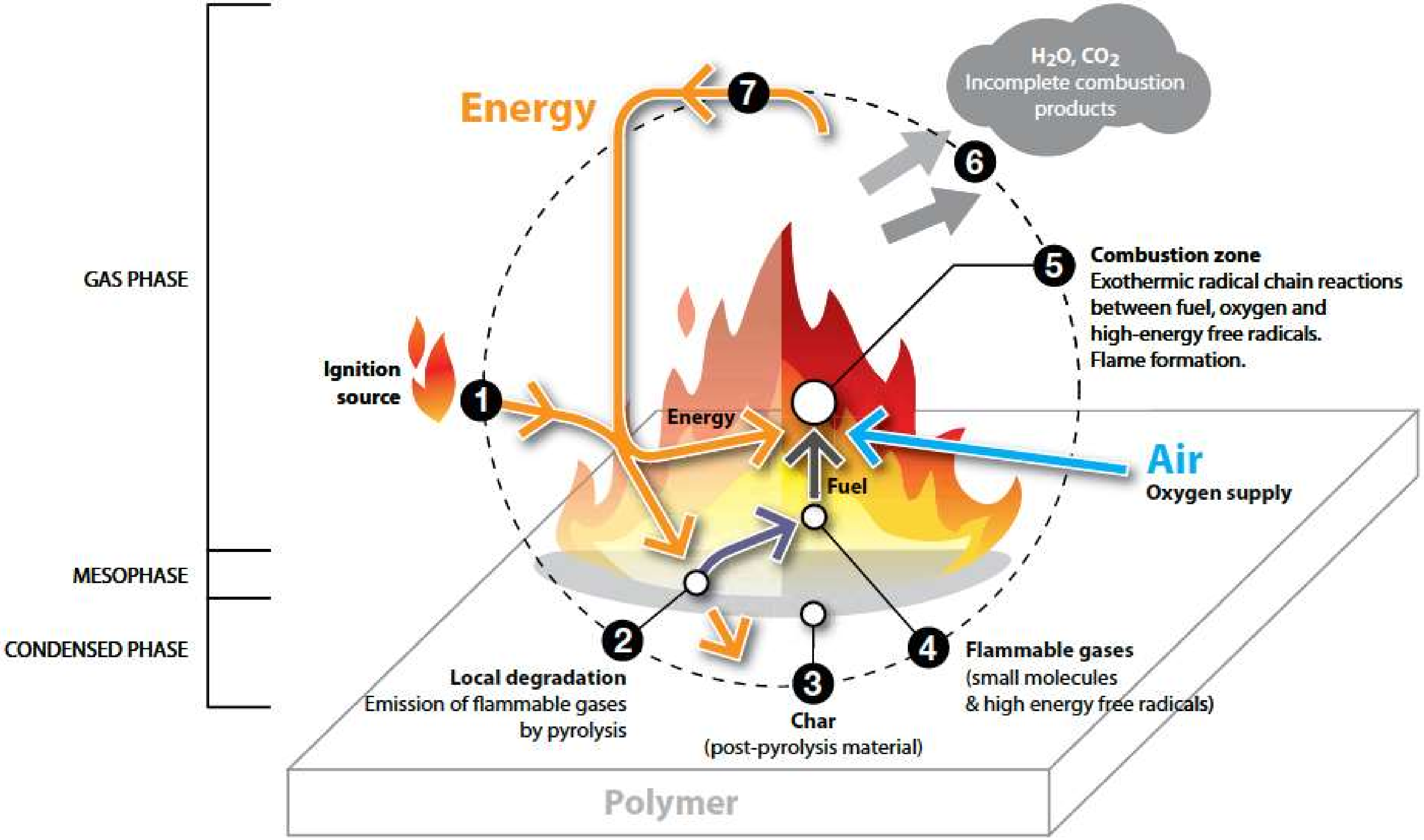
Comparison amongst PP grades

PP type	Crystallinity	T_m (°C)	Flexural Modulus	FR Applications
Homopolymer	High	>160	1400 - 2100	Pipes, fittings, conduits, fibers, textiles, electrical parts, stadium seats, sheets
Random copolymer	Medium	145-155	900 - 1200	
High Impact copolymer	High	>160	1200 - 1800	
Heterophasic reactor blend	Low	140 - 160	80 - 900	Water proofing membranes, cables
High ethylene copolymer	Low	60 - 130	10 - 300	

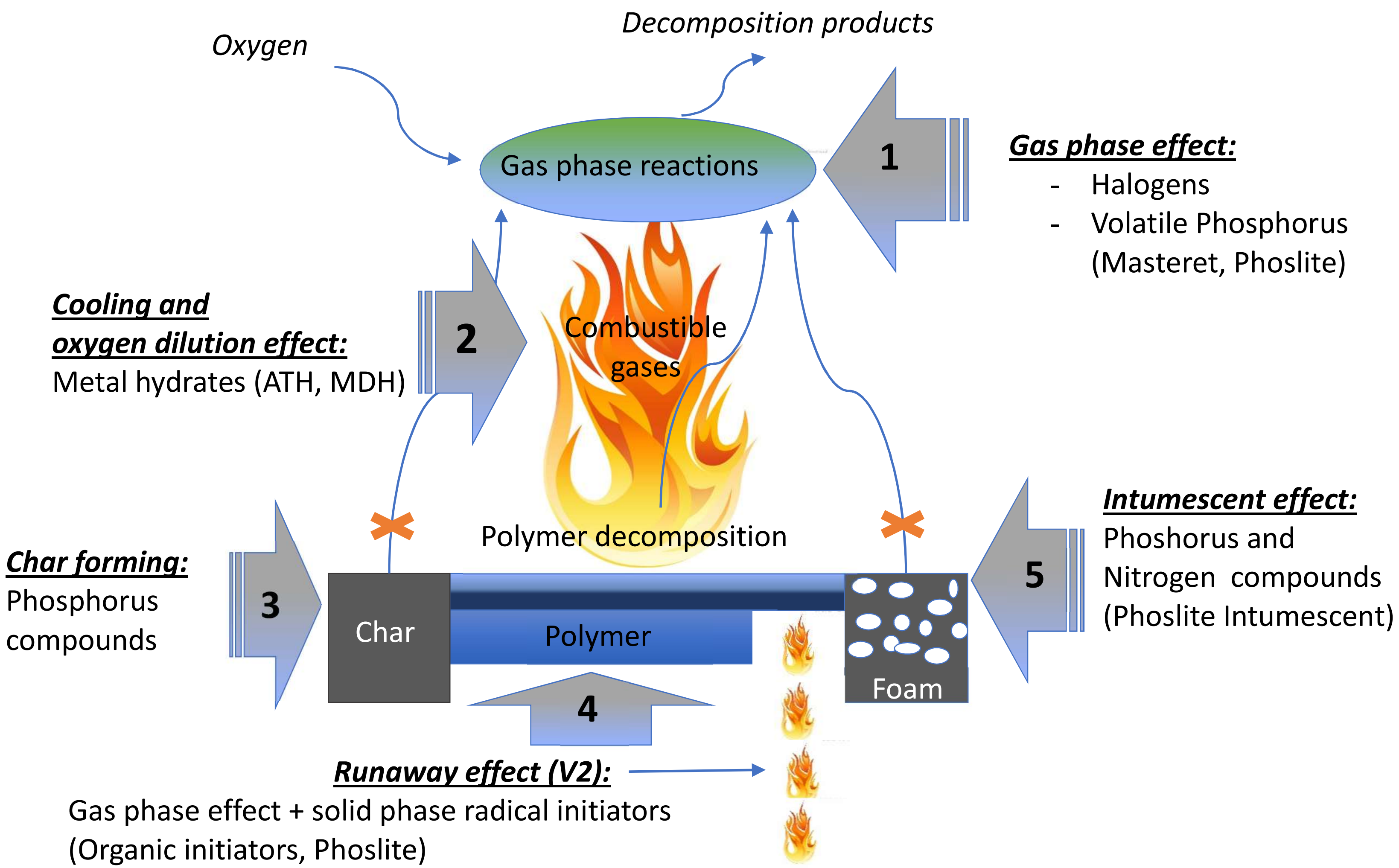
Any type of Polypropylene shows the following burning properties:

- ✓ High flammability
- ✓ High heat release of combustion
- ✓ High tendency of dripping of burning material

Schematic description of combustion of polymers



Flame Retardant mechanisms of action: *the 5 effects*



Why Halogen free?

- Globally growing interest on toxicity and bioaccumulation problems of flame retardants containing halogen.
- The main reason for fatalities is the emission of dense and poisonous gases like the acid gaseous emissions during combustion in real fires of halogens containing materials synergized with Antimony trioxide
- corrosive gases damage the concrete reinforcement as well as electronic devices like PCs, alarms, servers, elevators

⇒ Need of NO toxic, no asphyxiant, no acidic, no corrosive, and LOW smoke FR-PP

What's "Halogen free" compound?

Technical and legal references indicated by international norms:

IEC 61249-2-21 (electronics) < 1500 ppm (< 0.15%wt)
based on determination of **content** of halogen by EN 14582 (= analyse by Ion-Chromatography of halogens adsorbed in water after combustion with O_2).

IEC 60754-1 (= EN50267-2-1) and IEC 60754-2 (= EN50267-2-2) (Cables) Based on determination of halogens **emission** and the degree of acidity and conductivity of gases evolved during combustion. Strictly speaking, the IEC 60754-1 is fulfilled if halogens emission is < 5000 ppm (<0.5%wt), but, to pass both the norms, halogens content has to be < 3000 ppm (<0.3%wt).

Halogen Free Flame Retardant (HFFR) additives used for PP based compounds

- *mineral fillers;*
- *boron-based (B-based) flame retardants;*
- *phosphorus-based (P-based) flame retardants;*
- *nitrogen-based (N-based) flame retardants;*
- *silicon-based (Si-based) flame retardants;*
- *nanoparticles*
- *intumescent (forming agent + catalyst to char formation + spumific agent)*

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

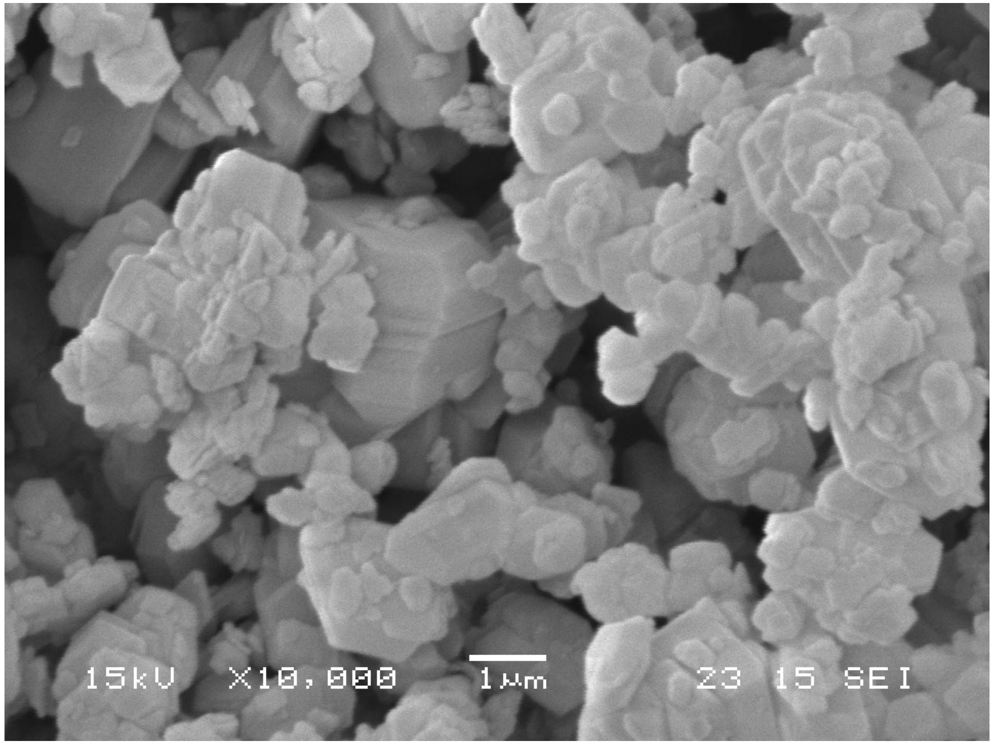
General effects of fillers on polymer ignition and combustion:	Main additional effects of Flame-Retardant fillers:
a) dilution, reducing the amount of fuel available for combustion; **b)** change of the heat capacity and thermal conductivity of material; **c)** thermal effects such as reflectivity and 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).

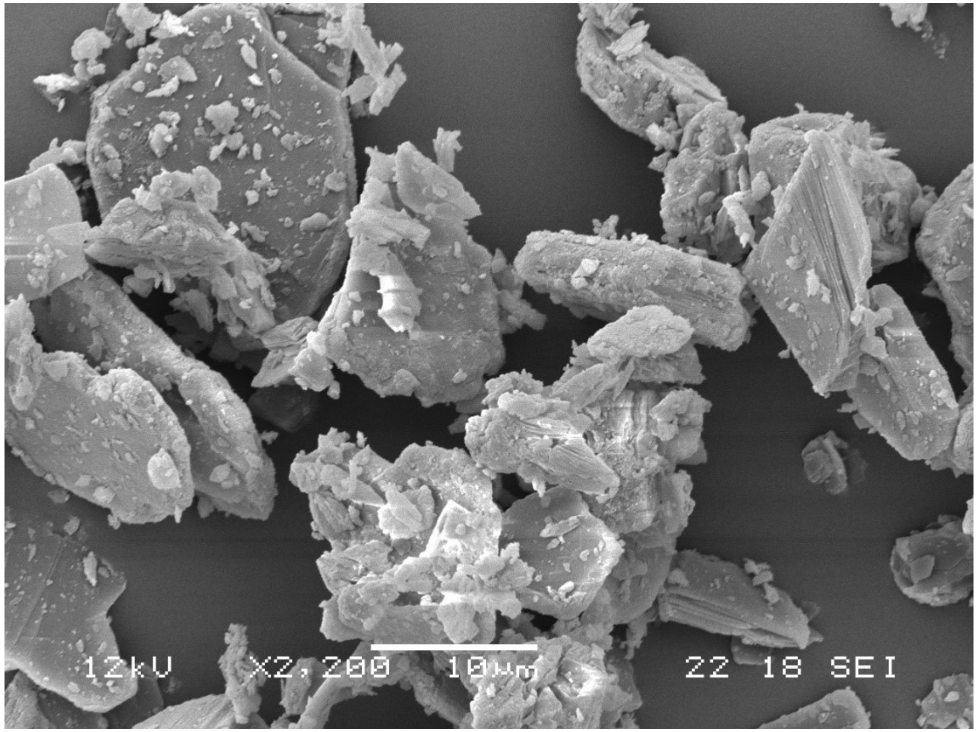
Properties of most used flame-retardant fillers

Name	**Aluminum Hydroxide (ATH)**	**Magnesium Hydroxide (MDH)**	**Hydromagnesite** [a]	**Huntite** [a]
Origin	Synthetic	Synthetic/Natural	Natural	Natural
Chemical formula	$Al(OH)_3$	$Mg(OH)_2$	$Mg_5(CO_3)_4(OH)_2{\cdot}4H_2O$	$Mg_3Ca(CO_3)_4$
Onset of decomposition (°C)	180-220	300-340	220-240	~ 400
Enthalpy of decomp. ($J\ g^{-1}$)	1300	1450	1300	980
Market price (U$D/lb)	0.20 – 0.50	0.20 – 1.20	0.25 – 0.40	
Volatile content by mass (%)				
Water	35	31	19	0
Carbon dioxide	0	0	38	50
Residue content (%)				
Al_2O_3	65	-	-	-
MgO	-	69	43	34
CaO	-	-	-	16

[a] *In nature there is mixed mineral, approx. 70:30 Hydromagnesite:Huntite.*

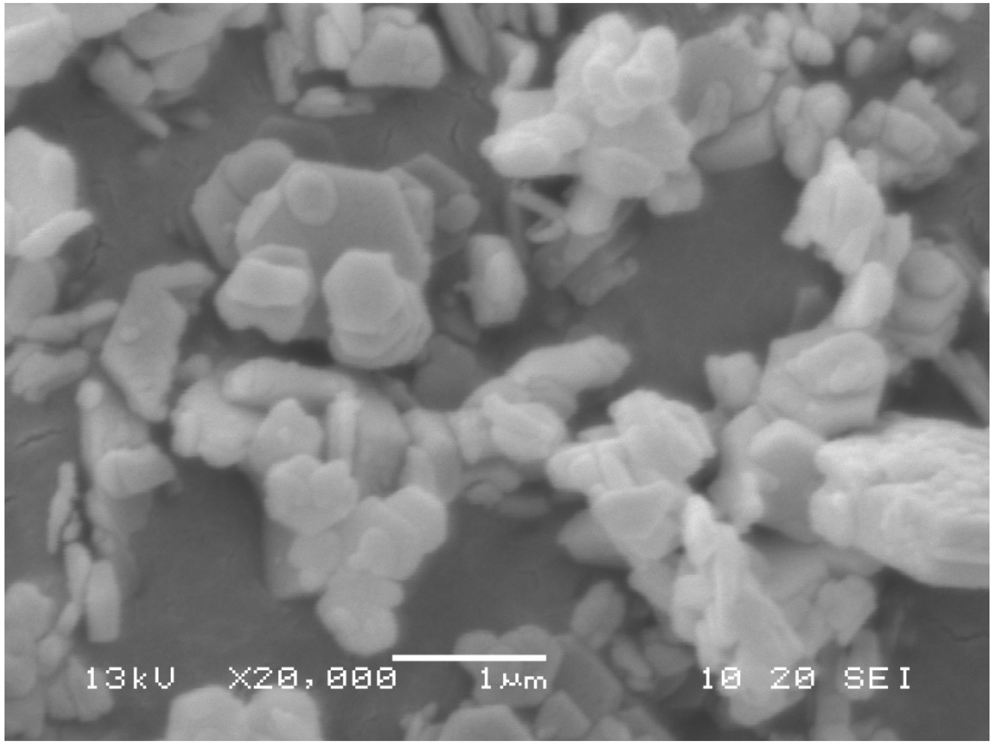
Fine precipitated ATH (left) and milled ATH (right)





⇒ **Due to low decomposition temperature, ATH not suitable for most of PP compounds**

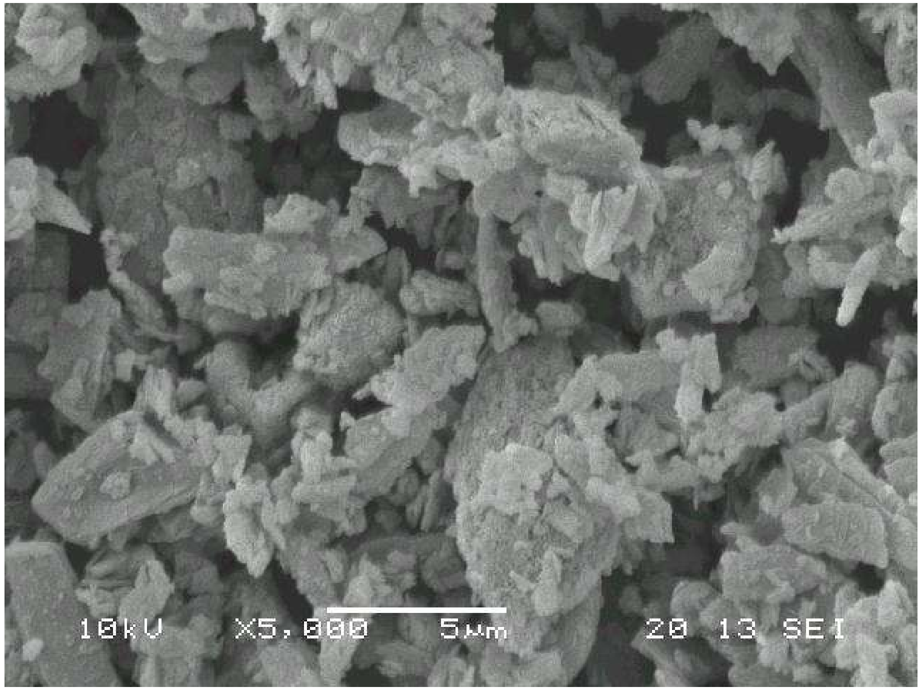
Synthetic MDH grades

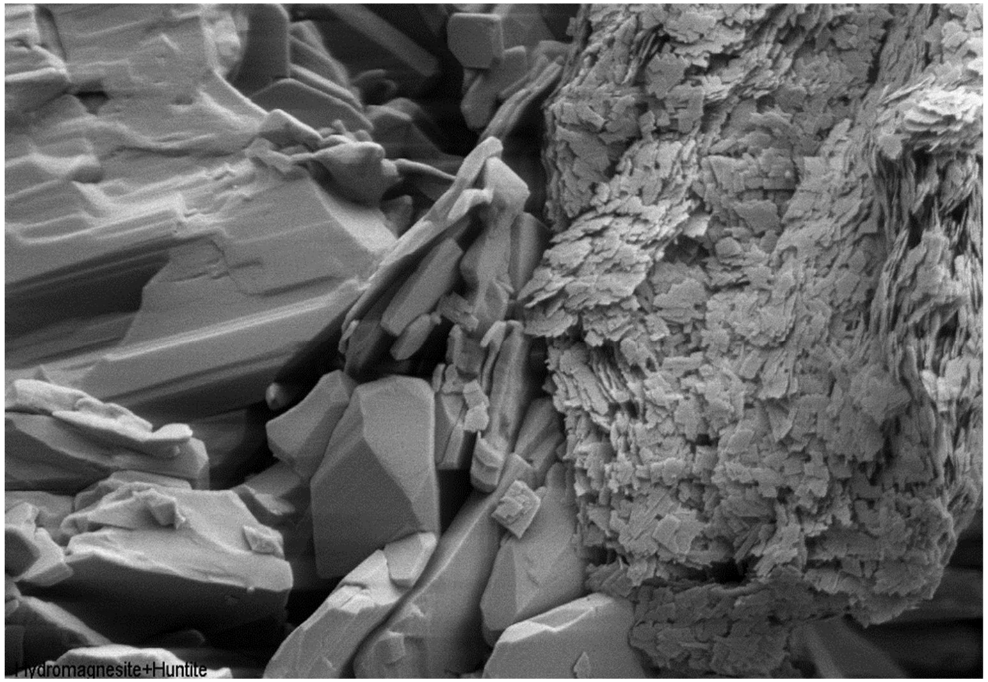


Precipitated and crystallized MDH

Precipitated MDH

Natural MDH (brucite, *left*) and Huntite/Hydromagnesite (*right*)





TPO roofing membranes

- Flexible PP are used:
  - Reactor blend grade (Hifax)
  - PP plastomers (Versify, Vistamaxx) in combination with PP homo or copo

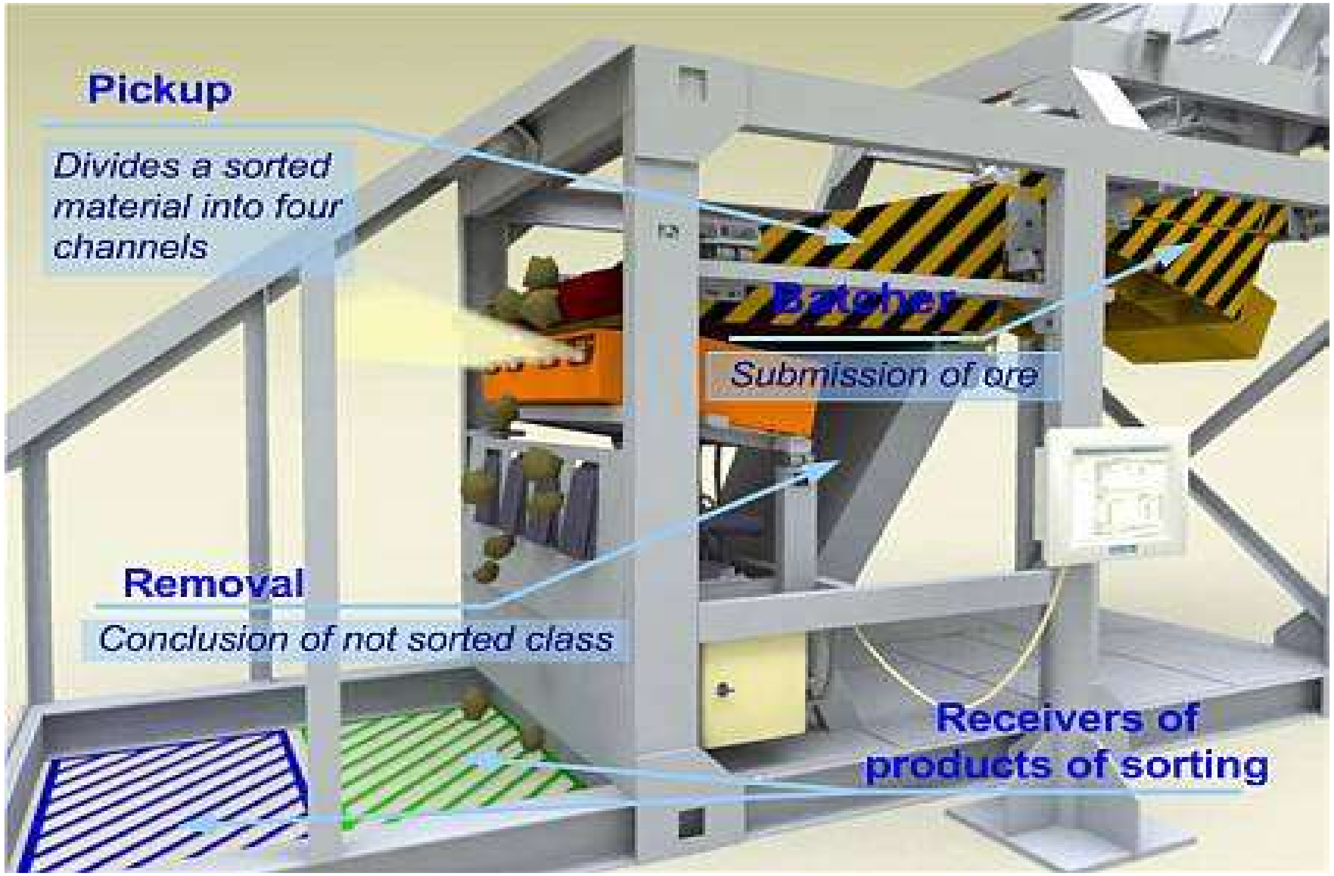
- MDH is the preferred FR filler due to high processing temperature allowing production of high concentrated compounds (masterbatches) to add during extrusion.
- Most common FIRE tests require dosage in the range 35 – 45% of MDH
- Long term ageing test required to guarantee long life in outdoor conditions
- Extremely cost-competitive application, especially in USA

- Due to the high requirements for ageing resistance under outdoor conditions, presence of impurities such as compounds of iron, copper, manganese and others must be strictly controlled and certified.

⇒ High quality natural MDH (brucite) offers the best solution

High quality natural MDH (Ecopiren®)

- ✓ Ecopiren® 5,5C is made from specially selected brucite ore of high purity and thanks to use of new separation technologies, the content of impurities is reduced and monitored.
- ✓ Sorting is done strictly in accordance with certain limits for Mg, Ca, Si and Fe compounds.



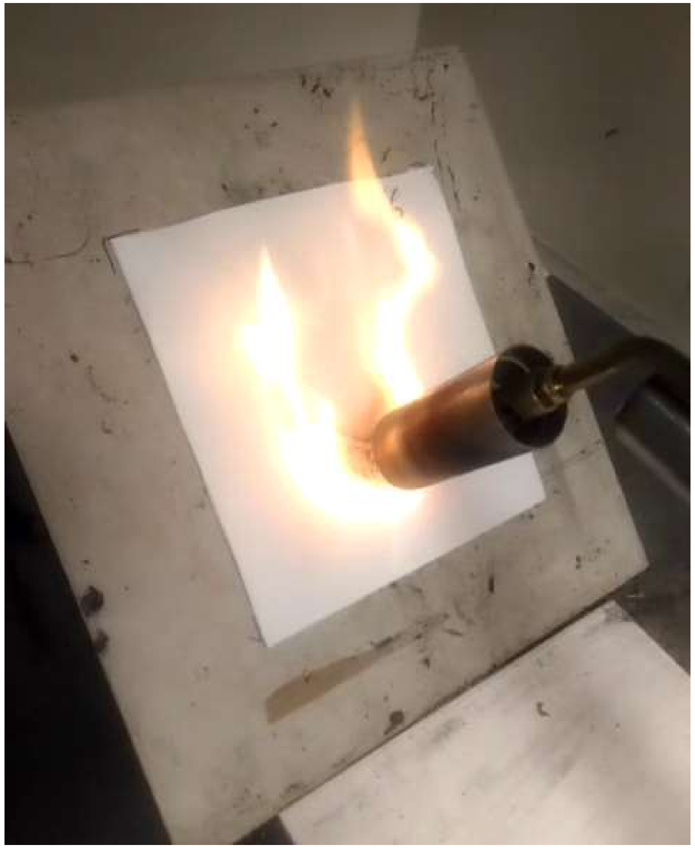
High quality natural MDH vs synthetic fillers in TPO compounds

- ✓ Fire performances are the same for all compounds
- ✓ Compounds with Brucite with high amount of iron have shown weak thermal aging resistance.
- ✓ High quality Ecopiren 5.5C, with low amount of iron, shows the same results as synthetic (more expensive) fillers.

Ingredients	%			
PP copolymer	56	56	56	56
Stabilizer pack	1,5	1,5	1,5	1,5
Grey Color MB	2,5	2,5	2,5	2,5
Ecopiren 5,5C (<0.13% Fe_2O_3)	40			
Competitor Brucite (>0.26% Fe_2O_3)		40		
Synthetic MDH, D50 – 1,5 μm			40	
Synthetic ATH, D50 – 1,5 μm				40
Properties				
Tensile strength, PSI	1,770	1,600	1,680	1,830
Elongation at break, %	581	513	597	525
Oxygen Induction Time (OIT) mins	148	85	78	147
Weeks* till Elongation drops of 50%	9	6	7	7
Weeks* till OIT drops to zero	>9	6	7	>9

**Mechanical properties and properties after aging at 285°F*

Flame retardant properties



Surface internal test

The fire behavior of TPO compounds for roofing application was evaluated in an internal test in order to simulate the fire application in roofing membrane.

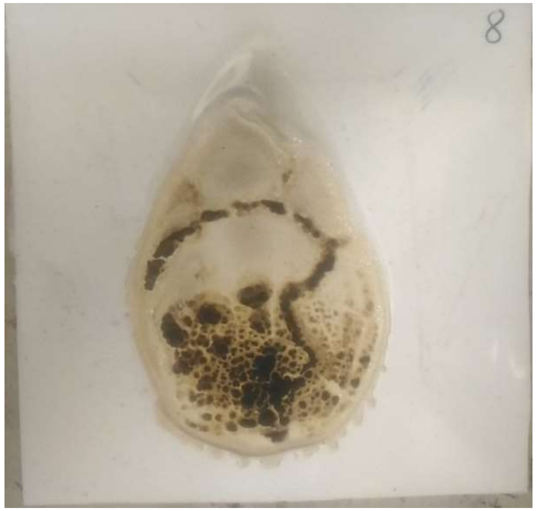
The orientation of the specimen was set with inclination of 45° from the ground, what is higher of any roofing application.

Parameters of the test:

- Sample dimensions: 8 x 8 x 0,06 inch
- Sample inclination is 45° from ground
- Burner: gas burner (29 mbar) with head diameter of 1,6 inch
- Distance between burner and sample surface: 1,5 inch
- **Flame application time: 2 min**
- **Compound filling level 50%.**

Results of lab scale burning test

Filler	**Ecopiren 5,5C**	**Synthetic MDH**	**Synthetic ATH**
Self-extinction (YES/NO)	YES	YES	YES
Time to self-extinction (s)	15	30	73
Dripping	NO	NO	NO
Flame propagation	standard	standard	standard



Automotive cable compounds (under hood)

PVC based:

- Very traditional and still >90% of the market.
- No FR additives necessary (easy fire test).
- Simple process at high speed, diffused know-how in all five continents.
- Suitable till Class T3 = -40°C/125 °C, thin layer (0.25mm wall thickness) for electrical limitations.

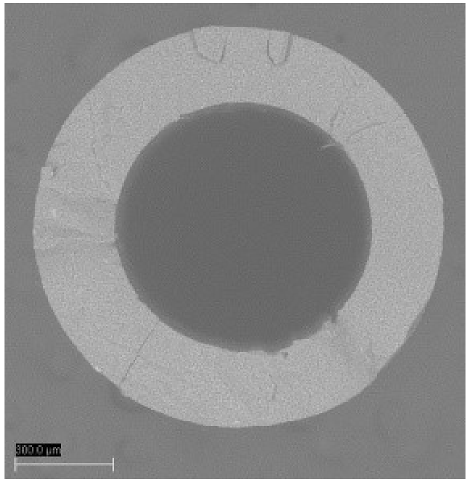
XLPE (peroxide, radiation, silan) based:

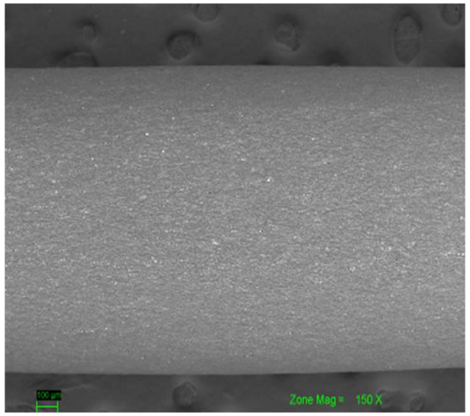
- High performances in ageing test at high T for long t (3000h@150°C, Class T4 = -40°C/150°C).
- Medium-low performances in abrasion resistance if more than 40% of mineral fillers.
- Only "low-halogen" solutions fulfilled all standards (<12% Br), with some MDH as synergist.
- **NOT** recyclable (crosslinked).

PP based:

- Good performances in ageing test at high temperature for long time (3000h@125°C).
- High performances in abrasion resistance also with 50% of fillers.
- Halogen-free solutions fulfilled all standards (with high quality, surface coated MDH).
- Recyclable (thermoplastic).
- Suitable till Class T3 = -40°C/125°C
- Suitable for **ultra**thin layer (**0.20**mm wall thickness)

Automotive cable PP compound (MDH-based)



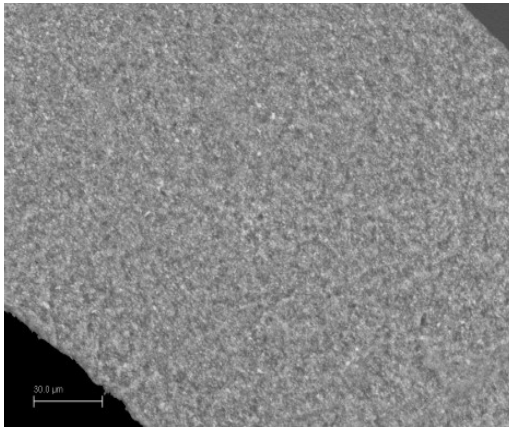


- Fire test in automotive cable is at 45°C, and around 50% of MDH is required inside PP to pass the fire test.
- Due to very thin insulation layer, perfectly dispersed very fine MDH is required with excellent electrical properties (= low water absorption).
- Due to very high production speed of these cables (>500 meters/minute), low viscosity is required with minimal interaction between PP and filler
- Due to high abrasion resistance required, very hard grade of PP is applied, but at the same time >200% elongation is also required

⇓

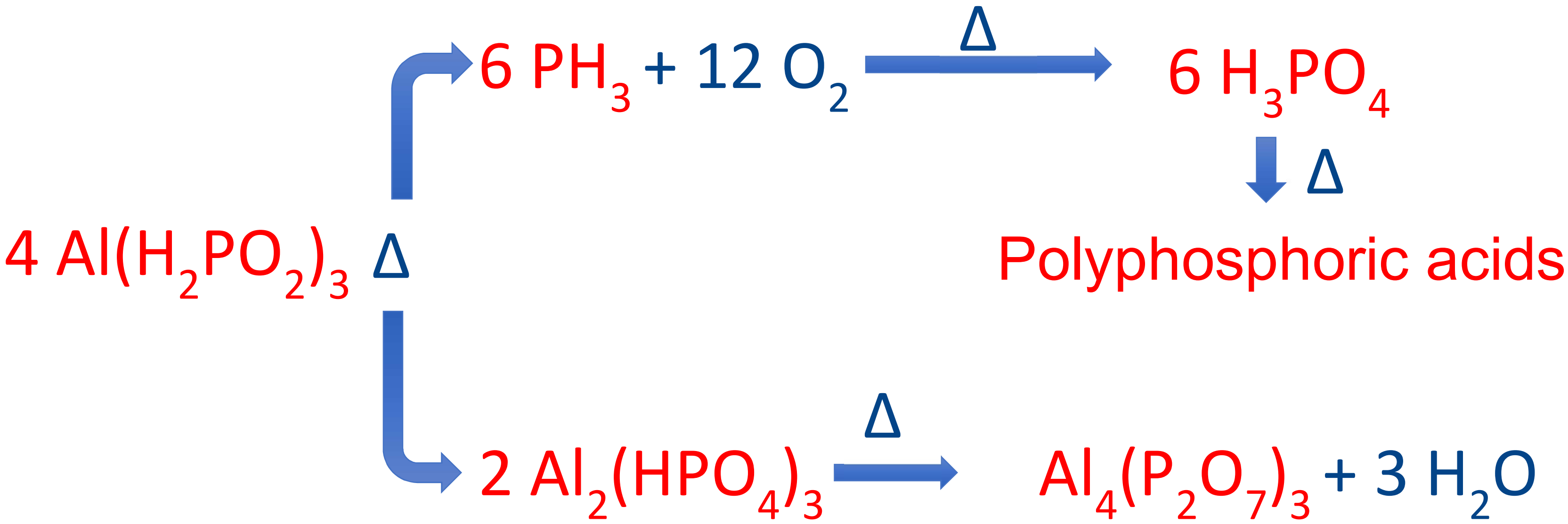
Surface coated fine synthetic MDH

(Ref. patent of Borealis)



"Green" solution for self-extinguish rigid PP

Phoslite ™ Technology: Inorganic Phosphorus Salts produced by Italmatch Chemicals



Inorganic phosphinate proposed FR mechanism

⇒ Char Forming + Runaway effect + Gas Phase (Multifunctional FR)

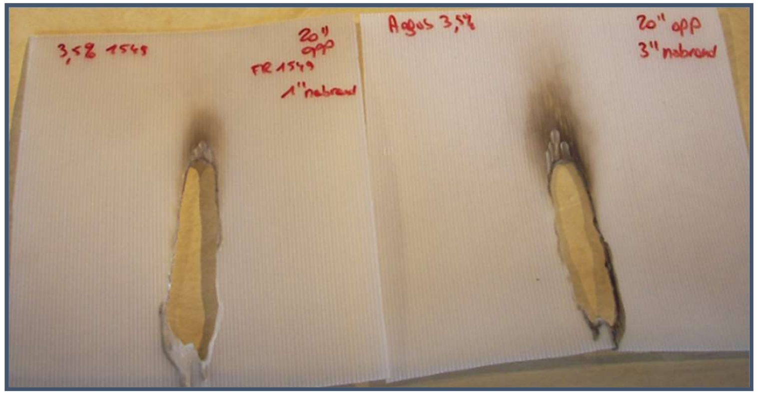
Italmatch Chemicals

Silmaflame: the new generation of FR MB for PP based on Phoslite

- ✓ Odorless and colorless
- ✓ NOT volatile
- ✓ NOT migrating
- ✓ Water insoluble
- ✓ Thermally stable until 270°C
- ✓ Antimony free (= heavy metal free)
- ✓ High specific efficiency = low dosage (from only 2%)
- ✓ Low interference into mechanical properties
- ✓ NO interference with most of UV-stabilizers
- ✓ NO increase of Toxicity Index of polymers
- ✓ NO increase of acid smoke emission in case of fire
- ✓ Fully comply with REACH
- ✓ Without any forbidden substance listed in RoHS
- ✓ NOT classified as dangerous according to international transport regulations

Silmaflame MB for halogen free, low smoke rigid PP

FR system	Dosage	Halogen free (IEC 61249)	Heavy Metals (ATO)*	Smoke density and toxicity	Impact on rheological and mechanical FR-PP properties
Brominated FR MB*	2.5-5%	NO	YES	HIGH	NONE
Magnesium Hydroxide	>55%	YES	NO	LOW	VERY HIGH
Polyphosphate salts	>20%	YES	NO	MEDIUM-HIGH	MEDIUM
Silmaflame	2.5-5%	YES	NO	Lower than pure PP	NONE



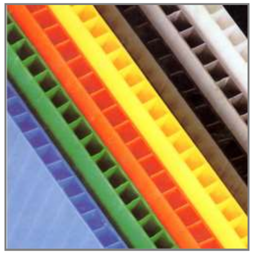
** Based on Tetrabromobisphenol A bis(2,3-dibromopropyl ether)* ***(TBBPA-DBPE)*** *[CAS: 21850-44-2]*

Green FR with performances/cost like Br-FR

FR masterbatch	Dosage %wt. in PPH	Halogen content (ppm)	Halogen content (%wt.)	Relative Cost vs pure PP
Silmaflame AP1770	5% (V2)	0	0	+35%
Silmaflame Grey BP2344	2.75% (V2)	< 1500	< 0.15%	+20%
Silmaflame neutral AP1372	2.5% (V2)	< 1500	< 0.15%	+25%
Typical halogenated MB*	2.5% (V2)	**> 8500**	**> 0.85%**	+15%

* *Based on Tetrabromobisphenol A bis(2,3-dibromopropyl ether)* ***(TBBPA-DBPE)*** *[CAS: 21850-44-2]*

Application of Silmaflame



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Dr. Ugo Zucchelli, Technical Manager of Italmatch (www.italmatch.com), producer of special halogen-free, phosphorous-based flame retardant for polypropylene and polyamide.

Dr. Alexander Kulichenko, Technical Manager of Europiren BV (www.europiren.com), producer of high quality, fine milled, natural magnesium hydroxide.

SILMA masterbatches (www.silmaster.com), Italian company producing special halogen-free, phosphorous-based flame retardant masterbatches for polypropylene and engineering polymers.