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Halogen-free polytriazinyl synergists for fire resistance beyond state-of-the-art fire & flame resistance technologies

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It is all about:
"*Chemistry-our life, our future”*

About us

MCA TECHNOLOGIES GmbH
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- **Co-sponsors of this conference, and co-exhibitors with Schmidt-Chemie; Brochures of our products and services available at the table top exhibition.**
- **Conducting/Supporting R&D & business development in environmentally friendly technologies (benign handprints) and products; Not just in words but in deeds, for example as supported by our novel, proprietary technologies for fire retardants, to be presented today.**
- **Bridging gaps between science and technology:**
  Making a new molecule or developing a new technology in a test tube for the sake of curiosity and publicity is not enough. Innovating its real need, creating its market, and finding ways and means of implementing it most economically and ecologically, to create new opportunities and jobs, is the focus of our activities.

Fire/Flame Retardants: Problems and opportunities

Fire & flame retardants, with almost 2 million tons annual consumption are the largest volume but the least developed and hence the most challenging of all polymer additives:

- Incredible loadings required compared to any other polymer additive, just to achieve even the bear minimum, are the fundamental cause of most problems, from processing over economy to ultimate environmental issues, now being debated even at governmental levels (the US Senate)
- The basic problem of fire safety namely the toxic smoke, smoke density & heat of glow for safe rescue & escape, and fire fighting, have yet to be properly resolved
- Compatibility/reactivity issues with polymer itself, the permanency of the effect (blooming/durability stability) and the synergism and antagonism with other polymer additives need to be addressed

Pointers towards improved fire retardance

- Plastics are basically <solidified> fossil fuels, hence the need of a common scientific approach, and not individual empirical methodology separately for each polymer and each application, for their fire resistance.

- We need a better understanding of the mechanisms of fire and flame retardance and aim at universal solutions. This knowledge may even help us develop more efficient combustion fuels.

- We should forget our prides and prejudices and mind-set, and make joint efforts to resolve the issues by returning back to the basics: Minerals, halogen and phosphorous chemistries may not be the only solutions.

- We also clearly need to focus on fire retardants (FR) rather than flame retardants (FMR). Burning tests (UL 94-Flammability) are only an eye-wash. We need to look at the complex whole

Definition and differentiation of fire retardants versus flame retardants

Fire Retardants (FR)

Prevent materials from burning, even before flaming: By quenching of fire; i.e. <Nip the fire in the bud>;

They, therefore, prevent the generation of the excessive heat of glow, and suppress formation of toxic smoke (aerosols);

<Intumescent systems>

Flame Retardants (FMR)

Act at advanced stage of fire in gas/condense phase by highly exothermic radical reactions, mainly as anti-flaming agents. Hence, usually the problems of high heat glow and smoke density associated with their use;

Excessive heat glow generates excessive N-oxides by burning of air, like burning of all fossil fuels, for example in engines/motors /heaters.

<Halogen & phosporous based>

Typical characteristics of a fire retardant vs. a flame retardant

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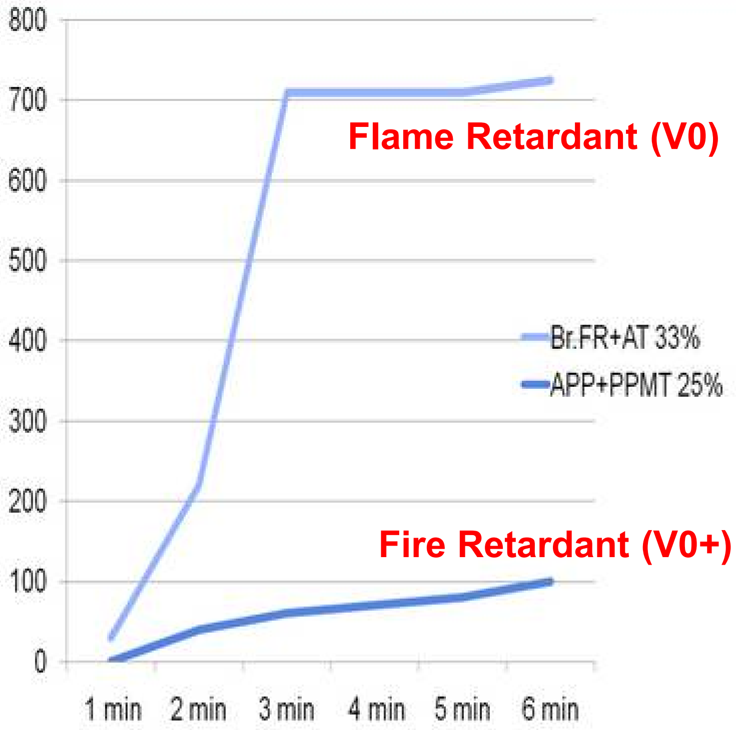
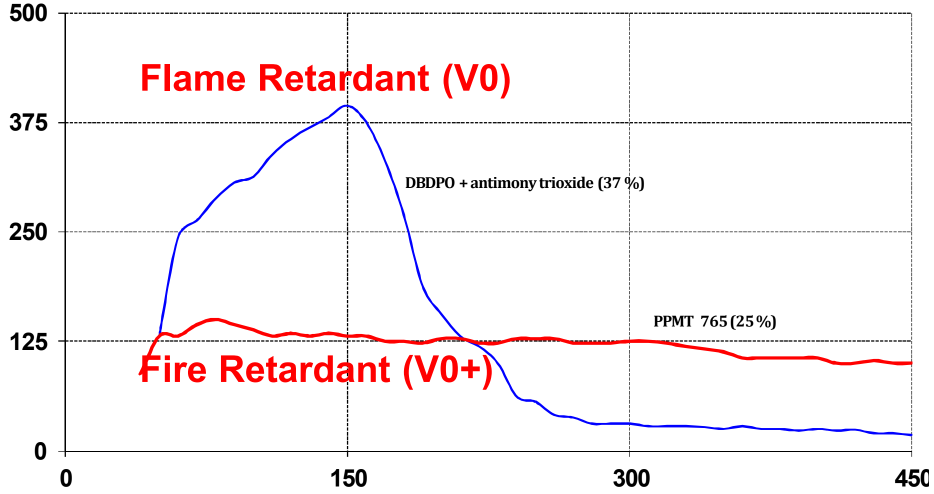
Specific Optical Smoke Density (Ds): Polypropylene; In spite of V0 Classification (1.6 mm)

Heat Release Rate [kW/m²]:PE; in spite of V0 Classification (1.6 mm)





Cone Calorimeter
Heat flux: 50 kW/m²
Orientation: horizontal

The most essential aspects of rescue, escape (++ classification)

Promising of all future FR-Technologies:

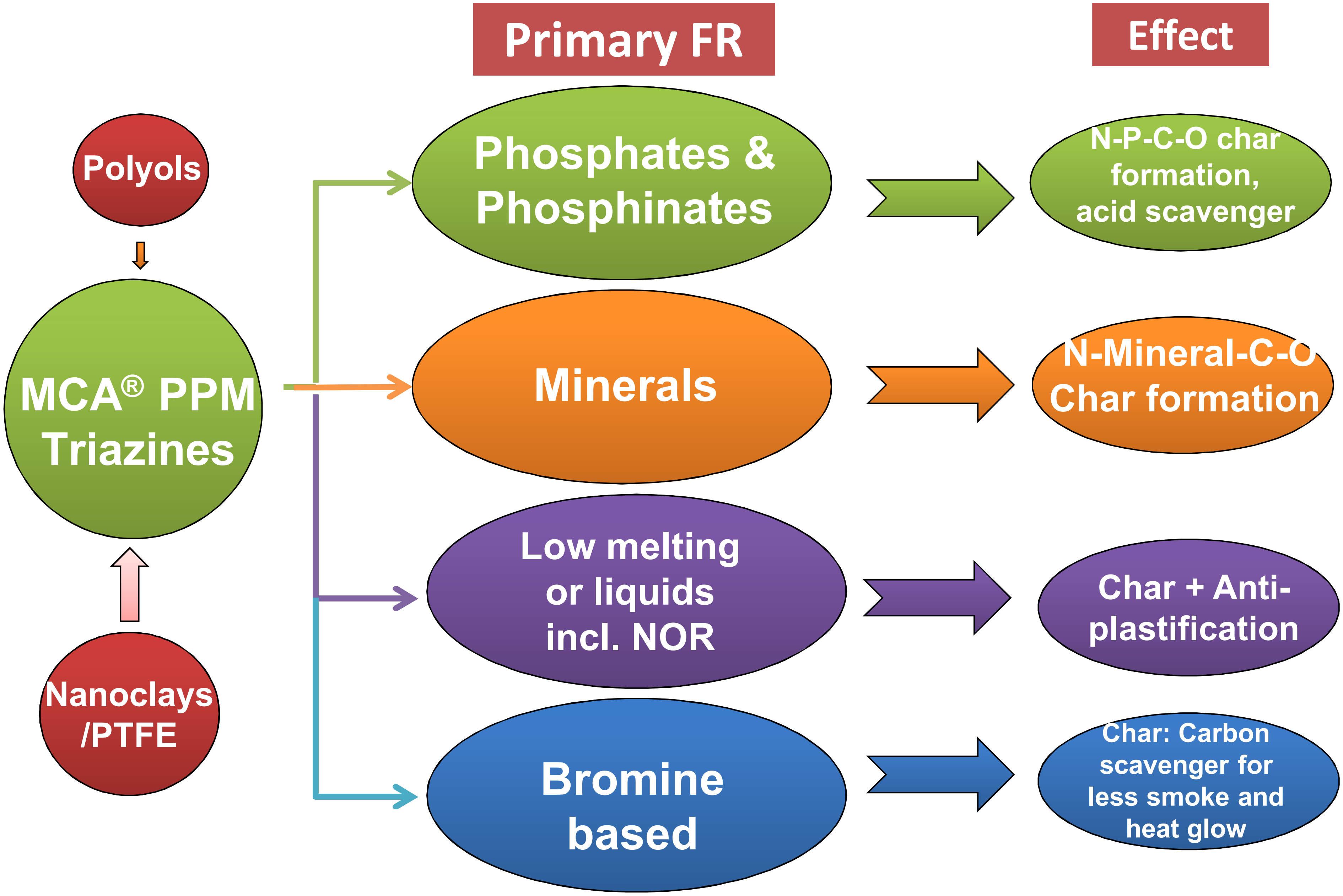
Intumescent or even ceramic fire shields in the event of fire: Fire retardancy of nature

Formation of a spongy char-barrier at the fire point;
Extinguishing and preventing the proliferation of fire
(with low heat of glow & almost no smoke)

**< Act both as fire and flame retardants:
Nipping the fire in the bud>**

“PPM Triazine-Synergism” approach, to be presented now, seems to be a viable pathway

Universal synergists of FRs and co-synergists



Primary FR

Effect

Polyols

MCA® PPM Triazines

Nanoclays /PTFE

Phosphates & Phosphinates

N-P-C-O char formation, acid scavenger

Minerals

N-Mineral-C-O Char formation

Low melting or liquids incl. NOR

Char + Anti-plastification

Bromine based

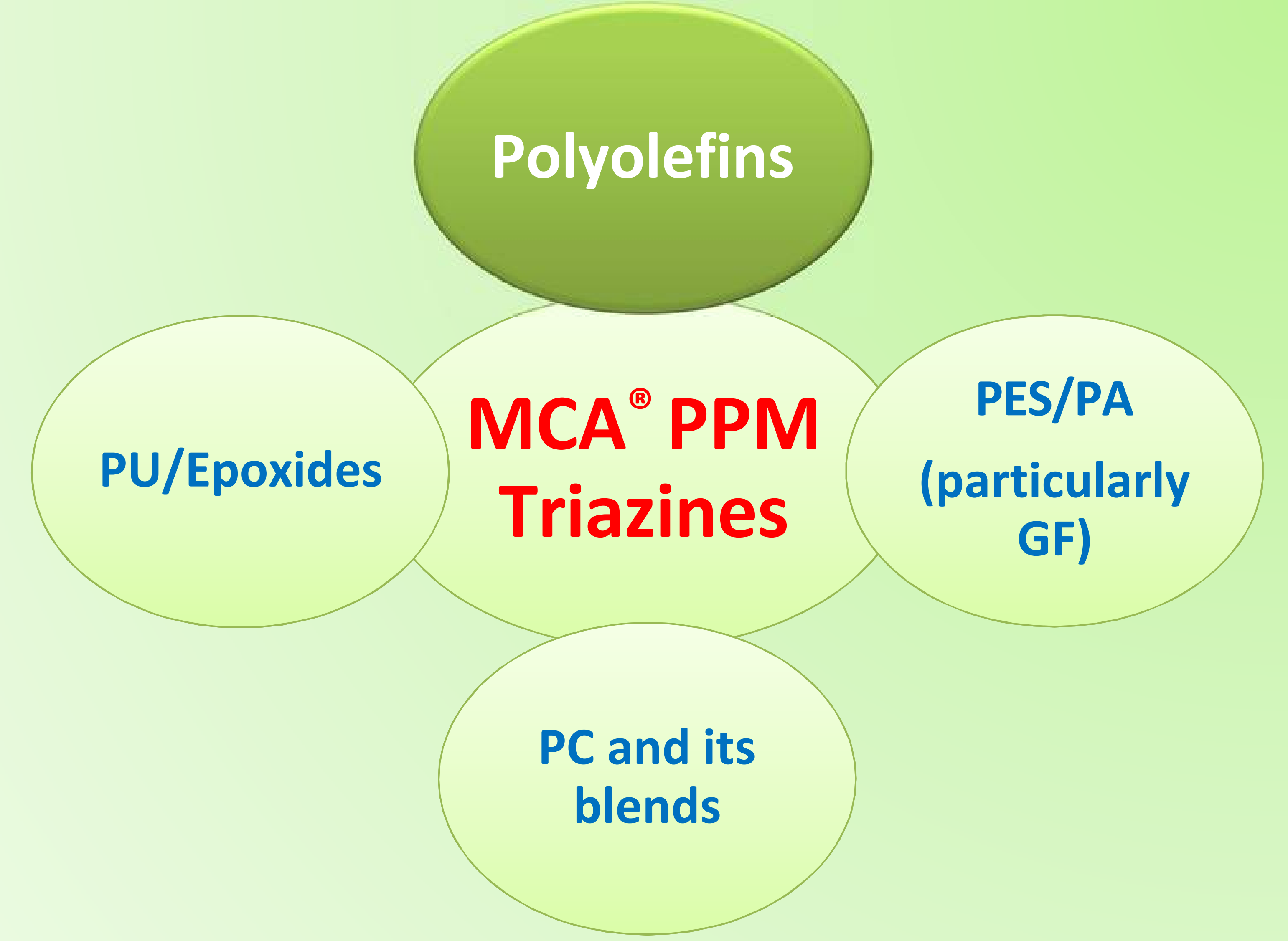
Char: Carbon scavenger for less smoke and heat glow

Why MCA® PPM Triazines as nitrogen-synergists?

PPM Triazines are particularly recommended where state-of-the-art nitrogen synergists, **based on melamine and/or its derivatives** have limitations due to **any or many** of the following reasons:

- **Sublimation and mould deposits**
- **Blooming** (particularly incompatibility in polyolefins)
- **Reactivity:** Self-condensation and **tridimensional** (dendrimer) reactivity towards the monomers (urethanes, epoxides); and **even** polymers (such as polyesters by **amidation**; polyamides by **cross-amidation** and with primary FRs (APP) by **"Pre–intumescent"** reaction ((in processing);
- **Heat stability**
- **Water solubility**
- **Hydrolytic & thermal stability/corrosivity** (i.e. Melamine polyphosphate: being rather a **weak acid-base salt,** can undergo **gradual** dissociation in the presence of water in the polar polymer itself).

MCA® PPM Triazines: Suitability for polymers & resins



MCA® PPM Triazines

Polyolefins

PU/Epoxides

PES/PA (particularly GF)

PC and its blends

Mechanism of polytriazinyl synergism for fire retardance: Mimicking of nature

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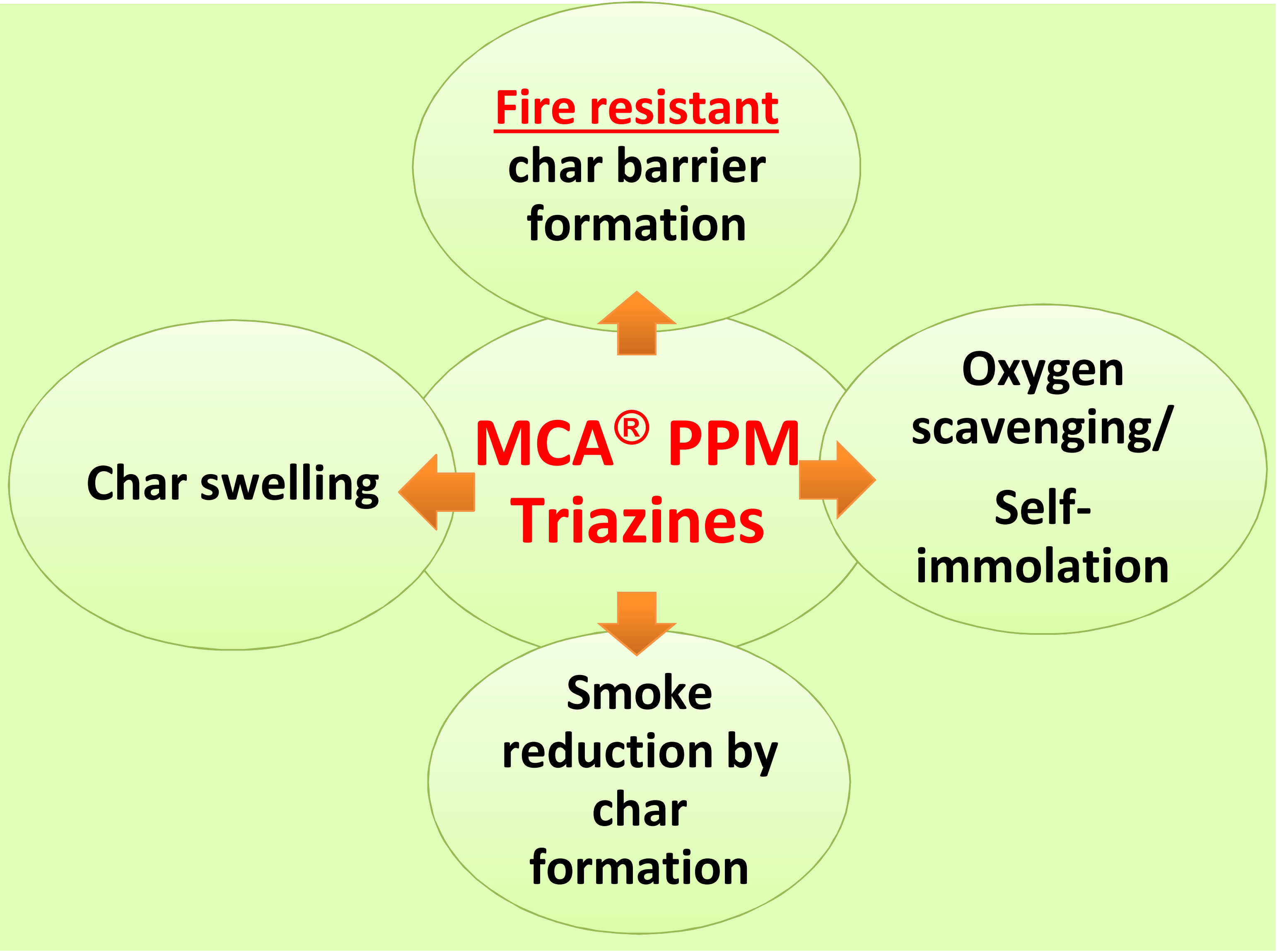

MCA® PPM Triazines

Fire resistant char barrier formation

Char swelling

Oxygen scavenging/ Self-immolation

Smoke reduction by char formation

MCA® PPM Triazine HF:

Novel, polymeric, halogen-free & chemically mostly inert nitrogen synergist

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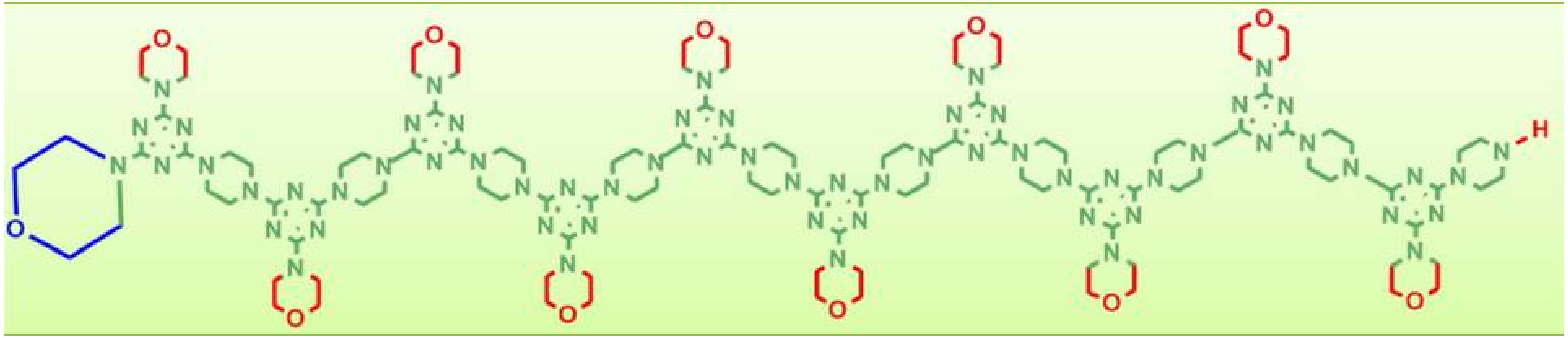

Chemical Formula: $C_{126}H_{212}N_{61}O_{11}$
Exact Mass: 2755.8
Molecular Weight: 2757.4

Elemental Analysis: C, 54.88; H, 7.75; N, 30.99; O, 6.38

MCA® Proprietary volatile-organic-solvent-free technology*

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Suspension polymerisation in the presence of catalysts

Examples: PVC made by suspension polymerisation
PP made using Ziegler-Natta process

Patent applications :
“Polytriazinyl compounds as flame retardants and light stabilizers”
European Patent application 2130854.
US patent application US 2009/0281215 A1
Also in China, India, Taiwan, JAPAN

Patent granted in the USA (Patent No. 8,202,924)

***The “handprint” of the technology**

MCA® PPM Triazines: Characteristics

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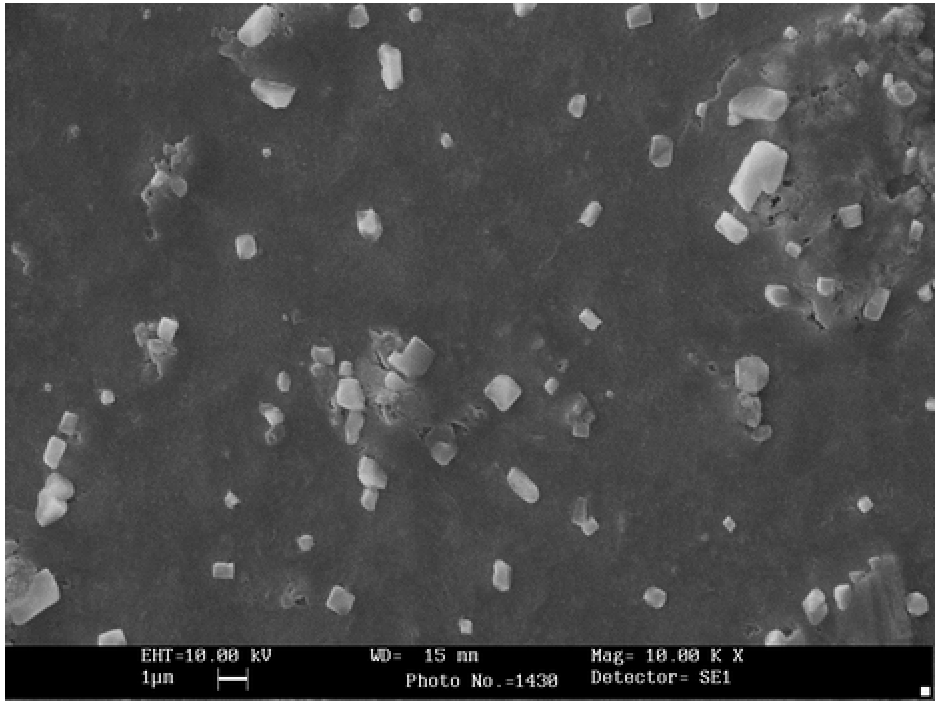
- White to off white powders
- Density: 1.01 (almost same as most of polymers)
- Melting point :> 290 ^{0}C / 555 ^{0}F;
- Chemically mostly inert: No self-condensation possible
- Heat stability in polymer itself: 280-320 ^{0}C/540-610 ^{0}F
- Insoluble in water and many other solvents;

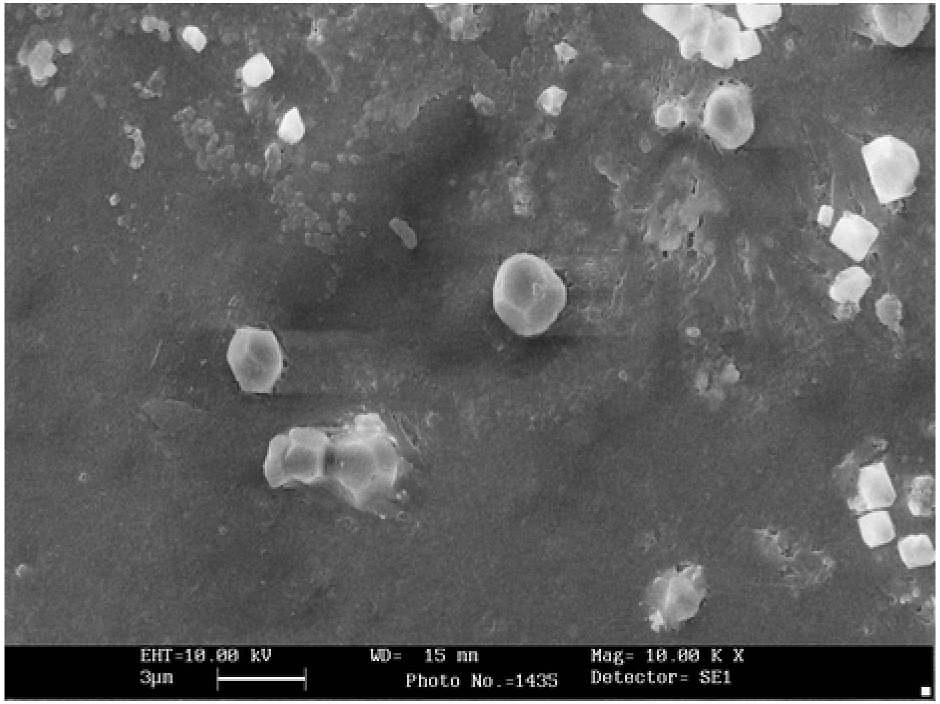
Particle size distribution (measured on powder, with ultrasonic dispersion in a liquid): d_{50} < 10 µm

Need not have relation to dispersion in a polymer

MCA® PPM Triazine HF ;
Scanning electron microscopic pictures (x10,000)



Individual particle ***size***:
< 1 µm



Individual particle ***shape***:
Diamond like

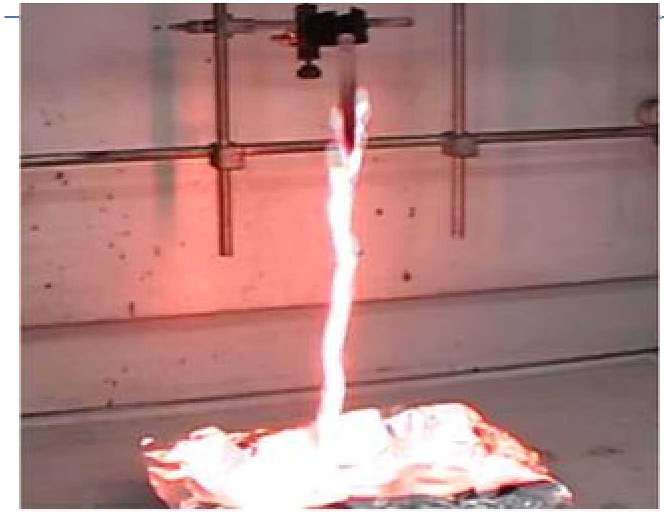
MCA® PPM Triazine-Synergism

Trends and pointers in various polymers and in combinations with various FRs and co-synergists

The Formulations are in no way optimum

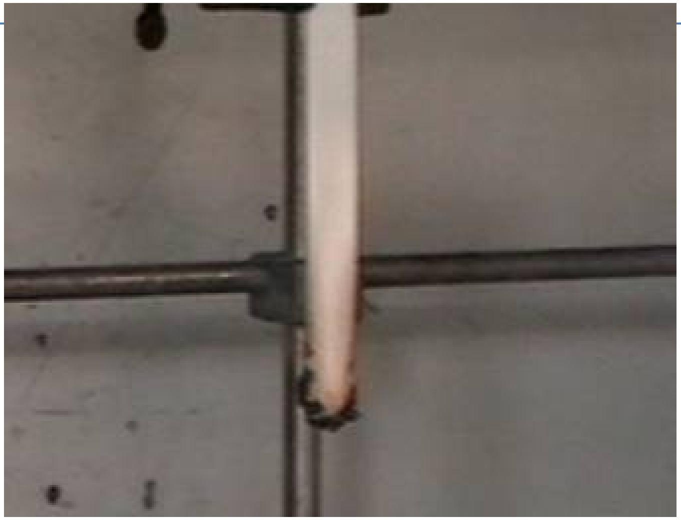
MCA® PPM Triazine HF-Ammonium polyphosphate combination: PPMT 765 (IS=intumescent system)

Polypropylene



80% Polypropylene + 20% PPMT 765

H



Almost no burning^{V-0} & no smoke^{+}, low heat release^{+}

Sample	t_1 (S)	t_2 (s)	Dripping/Ignition of Cotton	Time to dripping	UL 94 Rating
PP	70	-	Yes	6 (s)	No Rating
PP+20% PPMT 765 (5% HF)	**1**	**3**	No	**No dripping**	**V-0 (++)**

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SEM micrographs and elemental distribution from EDS mapping of the MCA® PPM Triazine 765 composite (20%) in PP before combustion

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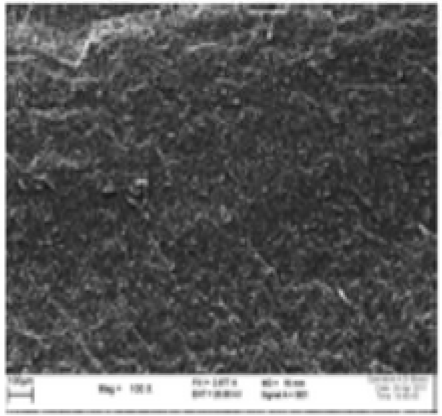

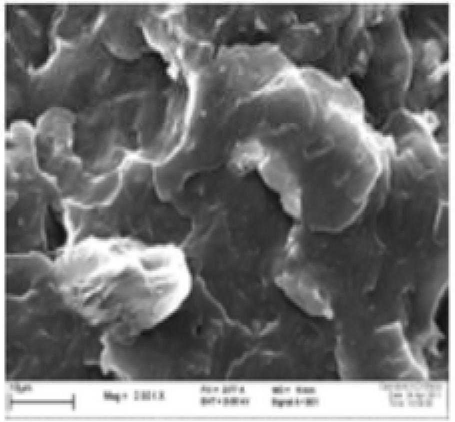

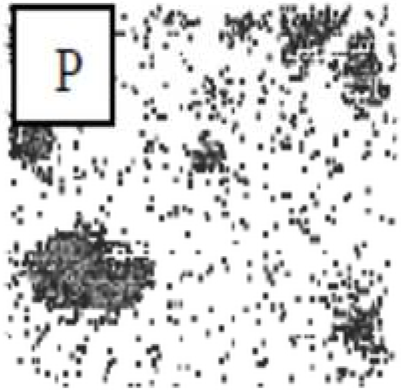

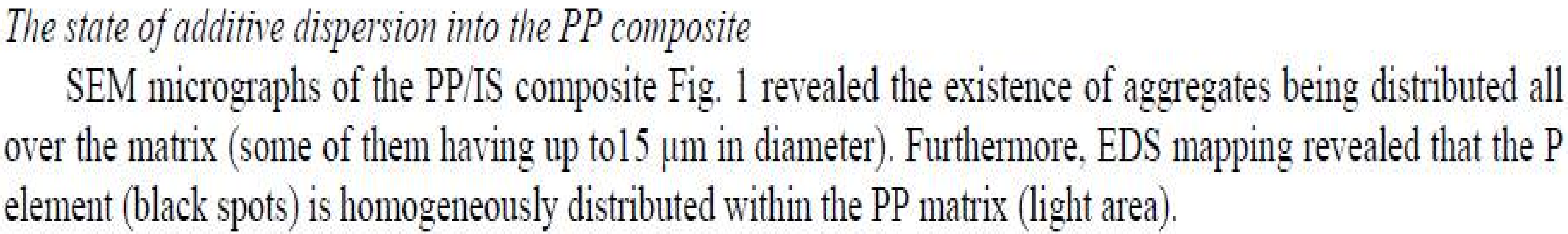

The state of additive dispersion into the PP composite

SEM micrographs of the PP/IS composite Fig. 1 revealed the existence of aggregates being distributed all over the matrix (some of them having up to15 µm in diameter). Furthermore, EDS mapping revealed that the P element (black spots) is homogeneously distributed within the PP matrix (light area).

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MCA® PPM Triazine 765 (IS) : Char formation after the fire test

PP

PP/10 % 765

PP/20 % 765

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Thermal stability in PP (TGA)

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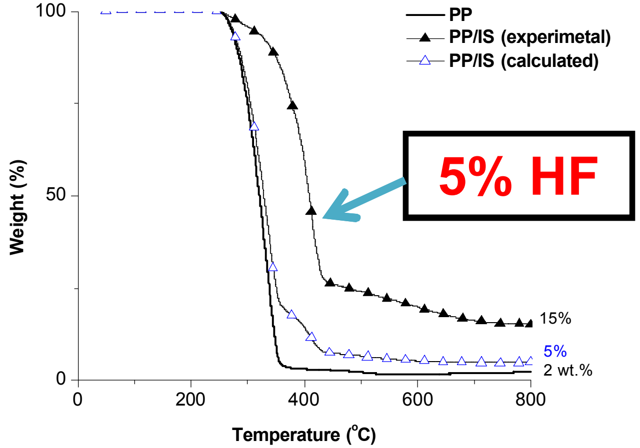

(Air atmosphere)

*** Versus 225-230°C for melamine based intumescent systems, due to the reaction of APP with melamine under processing conditions, thereby confirming the inertness of PPM Triazine towards APP**

Sample	T_{onset} (°C)	T_{max} (°C)	Residue at 800 °C (%)
PP	271	335	2
PP/20% 765 (5% HF)	306*	406	15 (Real)

T_{onset} (the temperature at which the sample has lost 5 wt% of its original mass);
T_{max} (the temperature at which the maximum rate of mass loss occurs).

Cone calorimeter test: Heat release

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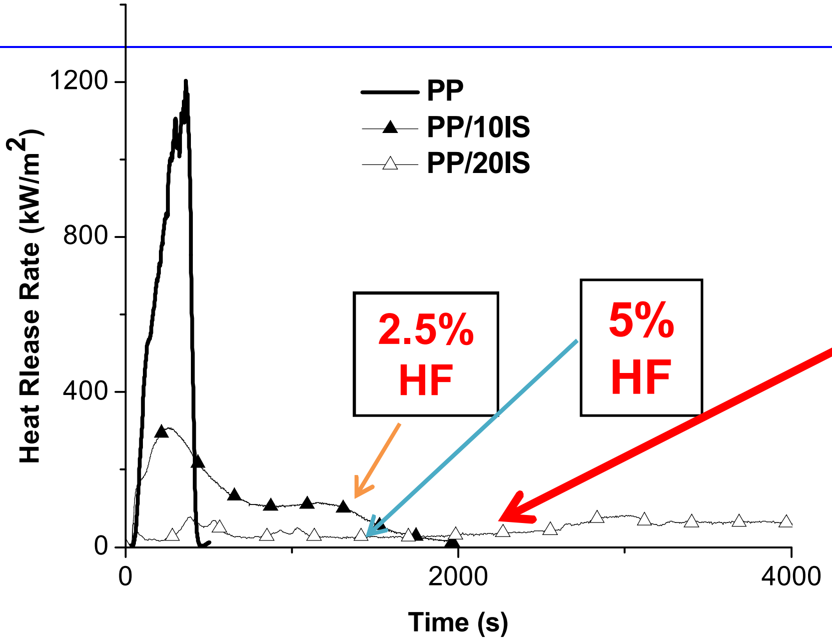

2.5% HF

5% HF

Heat release inhibitor

Sample	Peak heat release rate ($kW \cdot m^{-2}$)	Peak heat release rate %
PP	1221	100
PP/10% 765 <u>(2.5% HF)</u>	313	-75
PP/20% 765 <u>(5% HF)</u>	115	-90

Cone calorimeter test: Smoke release

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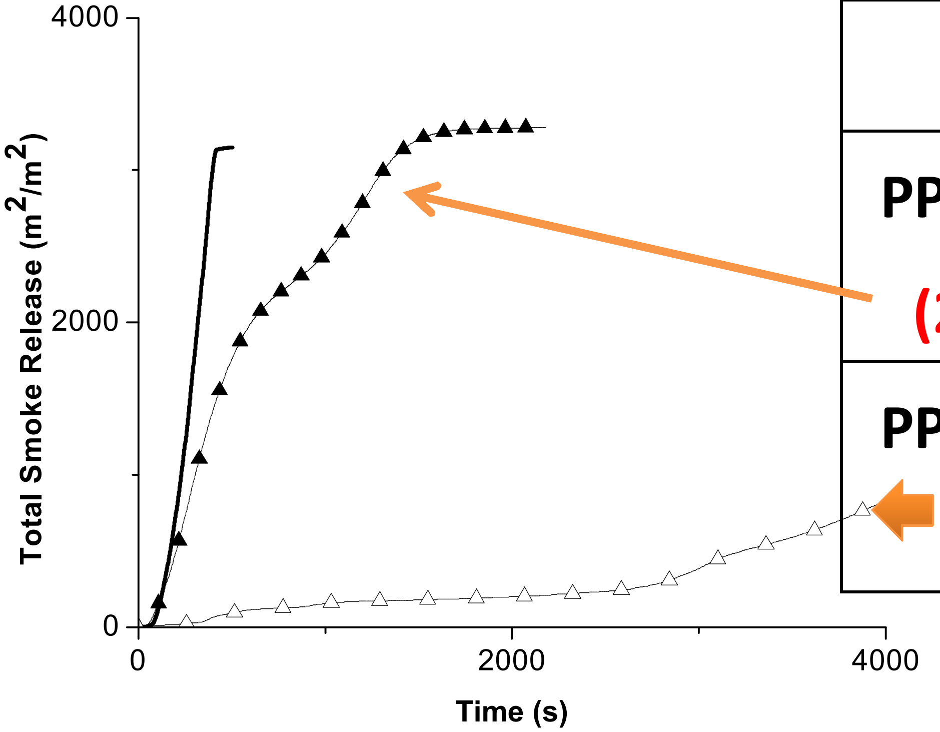
Smoke release inhibitor



Sample	ASEA± σ $(m^2 \cdot kg^{-1})$	TSR ± σ $(m^2 \cdot m^{-2})$
PP	638±29	3305±139
PP/10% 765 (2.5% HF)	604±27	3144±135
PP/20% 765 (5% HF)	313±8 (-50%)	1309±346 (-60%)

ASEA - the average specific extinction area;

TSR - total smoke release.

Cone calorimeter test; Time to ignition: Mechanism of HF fire retardancy in PP: Self-immolation of HF to protect PP

Sample	TTI ± σ (s)	pkHRR ± σ ($kW \cdot m^{-2}$)
PP	62±9	1221±28
PP/10% 765 (2.5% HF)	44±1 (-30%)	313±12 (-75%)
PP/20% 765 (5% HF)	43±4 (-30%)	115±8 (-90%)

TTI- time to ignition; pkHRR- peak heat release rate;

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MCA® PPM Triazine HF with ammonium polyphosphate & PTFE/Nanoclay/Pentaerythritol

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PP (%)	75	75		75		75	
APP (AP- 422)* (%)	25	20		20		15	
PPM Triazine HF (%)	0	5		5		5	
PTFE (%)			0.1				
Nanoclay (%) (Cloisite Na^+)					5		
Pentaerythritol							5
MFR (190C g/10 min)	5	4	4	N.A.	N.A.	N.A.	N.A
UL-94 (1/16") UL-94 (1/8")	Burn Burn	V-2 V-0	→ V-0	V-2 V-0	→ V-0	V-2 V-0	→ V-0
Oxygen Index	18	35	32				

MCA® PPM Triazine HF & a phosphinate combination in glass-filled PA 6

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Polyamide 6*	**54.5**	**54.5**	**59.5**	**54.5**
Additives	**0.5**	**0.5**	**0.5**	**0.5**
Glass fibers	**25**	**25**	**25**	**25**
Exolit OP 1230**	**15**	**10**	**7.5**	**0**
MCA® PPM Triazine HF	**5**	**10**	**7.5**	**0**
Melamine polyphosphate***	**0**	**0**	**0**	**20**
Average burning time(s)	**3**	**14**	**21**	**32**
UL 94 (1.6 mm)	**V-0**	**V-0/V-1**	**V-1/V-2**	**n.c.**

*(Ultramid B3S),** Clariant, ***Melapur 200 (BASF)

Dr. Rudolf Pfaendner

Fraunhofer-Institut Darmstadt

Cone calorimeter test: MCA® PPM Triazine HF & a phosphinate combination in glass-filled PA 6

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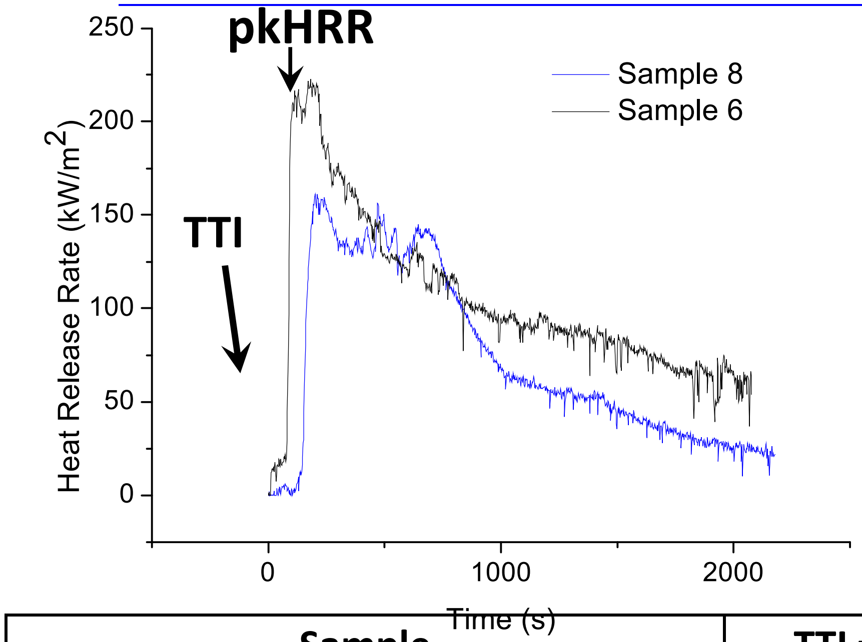

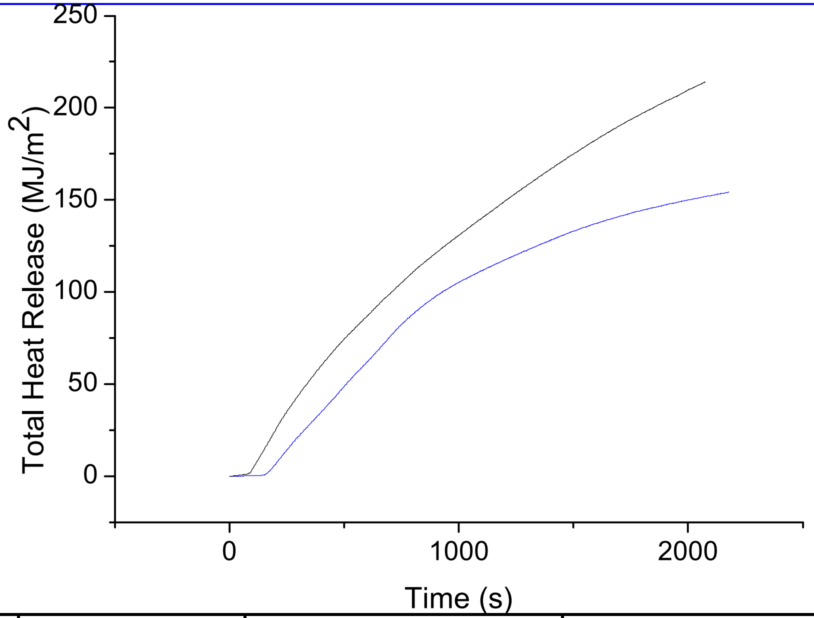

Sample	TTI ± σ (s)	pkHRR ± σ (kW·m^{-2})	THR± σ (MJ· m^{-2})	AMLR (g·s^{-1})
Sample 8 **(Exolit OP 1312+HF: 10+10 %)**	127±14	168±7	157±11	0.027±0.003
Sample 6 **(Exolit OP 1230+HF: 10+10 %)**	91±16	207±14	194±62	0.019±0.003

TTI- time of ignition; pkHRR- peak heat release rate; THR - total heat release; EHC - effective heat of combustion; AMLR - average mass loss rate.

Cone calorimeter test: MCA® PPM Triazine HF & a phosphinate combination in glass-filled PA 6

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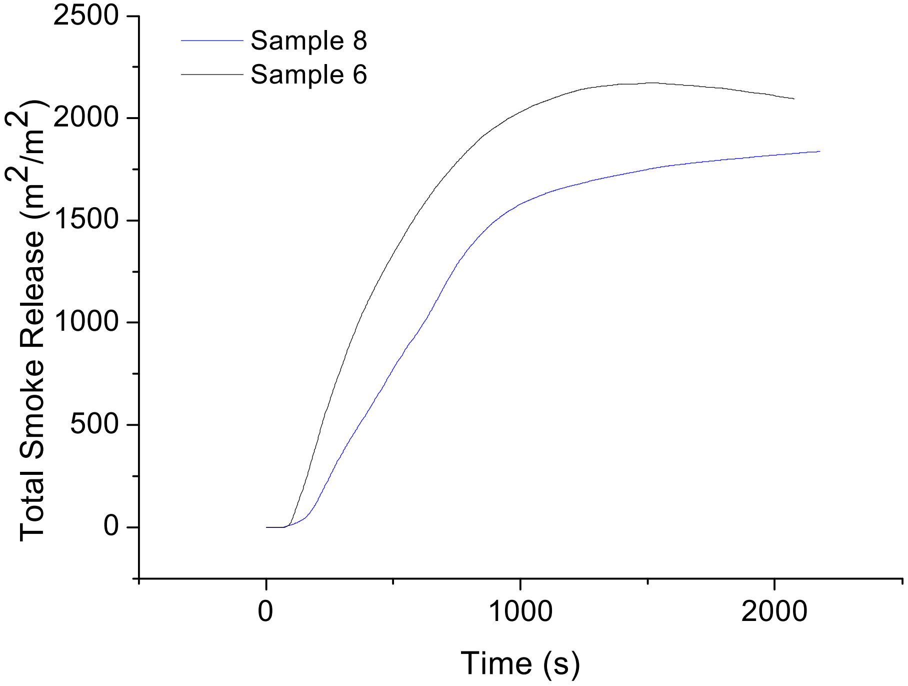
Sample	ASEA± σ ($m^2 \cdot kg^{-1}$)	TSR ± σ ($m^2 \cdot m^{-2}$)
Sample 8 **(Exolit OP 1312+HF)**	325±50	1611±213
Sample 6 **(Exolit OP 1230+HF)**	447±47	2158±146



ASEA - the average specific extinction area; TSR - total smoke release.

Cone calorimeter test: MCA® PPM Triazine HF & a phosphinate combination in glass-filled PA 6

Residue at the end of the combustion test

Sample 8

MCA® PPM Triazine HF & ATH Martinal OL-104 LEO in EVA Compound (19% VA) for a W&C Application*

(* Special courtesy of Albemarle-Martinswerk GmbH, Germany)

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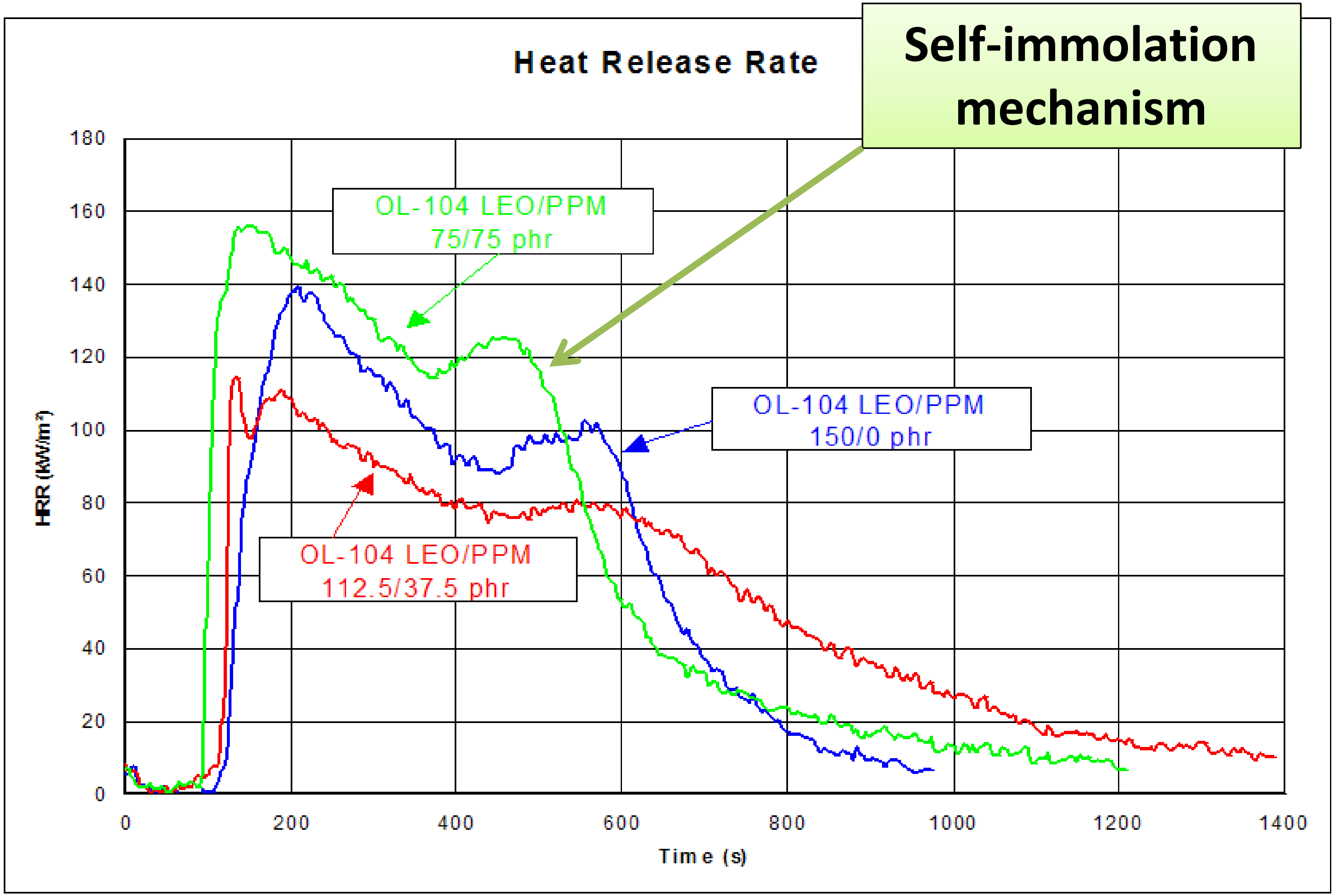

Self-immolation mechanism

“Self-immolation mechanism” of fire and flame retardancy

Self-sacrificing moth

“Self-immolation mechanism” of fire and flame retardancy also valid for NOR-Chemistry; because increase of the NOR-concentration in a polymer increases and not suppresses the flammability

Summary

- MCA® PPM Triazines: Universal synergist of most fire/flame retardants, and in many polymers.
- MCA® PPM Triazines should enable reduce the total loadings of many FR-systems, and therefore, the total cost of fire retardancy & processing, and thereby improve the quality of the plastic items and reduce the ultimate waste for environmental impact
- MCA® PPM Triazines should enable achieve halogen-free fire retardancy, at a reasonable cost if and wherever required or desired
- MCA® PPM Triazines should enable reduce heat release rate (HRR) & smoke density for better fire safety, particularly if combined with brominated or even halogen-free (phosphorous based) flame retardants associated with this problem. Such properties are perhaps more important than even the flame for fire fighting, and for rescue and escape.
- Ease of incineration at the disposal stage is an environmental plus.

Conclusions:

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It is all about:
"*Chemistry-our life, our future*"

Are universal solutions possible?

Yes, we can jointly do it!

Thank You

Current State of fire and flame retardants for polymers

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