



PPM Triazines

Epoxy – Liquides

Soutenance/contacts

**P**olyFlame est une newsletter à destination des chercheurs et des industriels du domaine du «comportement au feu des matériaux organiques». Cette newsletter périodique est publiée via la Société Chimique de France (SCF).

A travers cette newsletter, vous découvrirez les nouveautés et les dernières avancées

dans le domaine du comportement au feu en matière de recherche et développement, la synthèse et la production de nouveaux systèmes de retardateurs de flamme, les besoins industriels. Pour faire avancer la connaissance et l'expertise, une partie de cette newsletter est consacrée à l'écoute des chercheurs et des industriels reconnus dans ce domaine.

Bonne Lecture,

### *PPM Triazines: Light-weight organo-polymeric universal fire and flame retardant synergists*

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#### **A**bstract

Plastics are being increasingly used in transportation industry as lightweight materials, in building and construction, and as insulating and construction materials in the electronics including cable. Plastics, however, are basically solid fuels susceptible to fire hazard and, therefore, need to be made fire resistant for safety reasons required of many of their applications.

The fundamental challenge on one hand is the required high loadings of the use of fire and flame retardants, many times far exceeding even the weight of the polymers themselves, and on the other hand the controversy about the potential hazard of certain types of materials, such as halogenic and many inorganic synergists such as antimony trioxide.

It is intended to present a novel proprietary fire retardant technology to alleviate the said deficiencies associated with the use of the state-of-the-art fire and flame retardants. It is also intended to propose novel pathways and mechanisms of fire retardancy for future research.

With the current world production of almost 300 million metric tonnes [1], plastics are the most important materials-in-use of modern times. Plastics are easy to process, light-weight, materials mostly resistant to increasingly corrosive atmospheric conditions. But for plastics the modern electric and electronics industry, the transportation including aviation, and many other industries would not even survive, let alone exist. Plastics are also used in building and construction for insulation to save the energy costs. Plastics-insulation materials for wires and cables are essential to the transmission, distribution and consumption of power, voice and data. Assurance of longevity, efficiency, ease of installation and protection of wire and cable are becoming increasingly important because of the remotely produced renewable energy, such as in solar parks and with wind-turbines, requiring transportation over long distances, with least losses, that could be caused by the inefficient insulation materials.

## Introduction:

Plastics are also used in agricultural films to enhance the agricultural productivity.

Plastics, however, are basically solid fuels susceptible to fire hazard. For many applications, therefore, the plastics need to be made fire resistant, usually prescribed by national and international standards. Almost 2 million tons of fire and flame retardants (FRs) are produced annually [2] and are, therefore the largest volume, but unfortunately the most problematic of all plastic additives.

First and foremost one needs to differentiate between fire and flame retardants. Whereas fire retardants such as intumescent systems nip the fire in the bud, flame retardants such as the halogenic materials quench the flame after the outbreak of fire. Therefore, there is mostly the production of excessive smoke and toxic gases associated with the use of halogenic flame retardants. However, in many cases halogenated flame retardants are very effective, notwithstanding the said drawbacks and the environmental issues.

There are many types of fire and flame retardants and synergists available [3]. The most commonly used are the inorganic substances, the halogenated organic compounds, the organophosphorus compounds, or other organic substances. The commonly encountered problems known of the state-of-the-art fire and are enumerated as following;

- Halogen-containing are no more desired or even allowed in the electronic industry, not only because of their potential of forming toxic dioxins in the event of fire or even at the disposal stage by incineration, but also because of their persistence in the environment due to their non-biodegradability.
- Inefficiency & the collateral effects such as excessive use of energy in their production and processing, and dead-weight & poor quality of the resulting plastic items, particularly with the use of the largest volume metal hydroxides.
- Hydrolytic (water) instability, of the much more efficient intumescent systems based on phosphate salts such as ammonium and piperazine and melamine (as halogen-free replacements).
- Instability of melamine polyphosphates.
- Increasingly stringent conformity of the ICE regulations for electric and electronic applications.
- Reactivity towards the polymers, such as that of melamine & melamine polyphosphates with polyamides and polyesters.
- Mobility particularly of small molecules, leading to slow release and environmental pollution. Some fire retardants, such as halogenic and melamine, have even been found in human body, picked-up from the environment.

- Safety beyond fire protection, i.e. smoke release & heat flux in the event of fire.
- Disposal of, after the service-life <waste-to-energy/Wilkie> [14].
- Last but not least, the dispersion/processing, because of high loadings.

**MCA Technologies GmbH** has developed novel proprietary polymeric universal synergists to alleviate many known technical deficiencies, including environmental issues, associated with the use of the most currently used fire and flame retardants for plastics and coatings [4, 5].

The primary purpose of MCA® PPM Triazines (PPMT) is to enable replacement of environmentally undesired halogen-containing fire retardants and reduce the total requirements of all fire retardants to alleviate the collateral problems associated with their use, such as waste of materials and energy, and improve both the performance and economics of the resulting plastic items. Specifically, this could mean a major breakthrough for light-weight plastics in transportation, cable, electric & electronic industries.

Moreover, we have also developed an environmentally friendly industry-scale MCA® proprietary volatile-organic-solvent-free technology for their manufacture [6].

## History and background of PPM Triazines (PPMT):

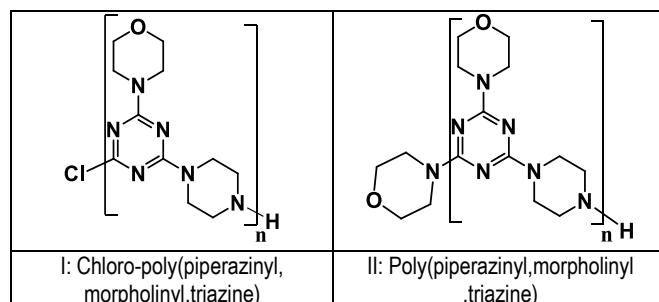


Figure 1: Chemical structures of PPM Triazines

PPM Triazines of formula I (chloro-poly(piperazinyl, morpholinyl, triazine) with halogen containing end-group were patented by Montedison in 1984/1985 [7], and later on produced by Degussa (now AlzChem). The Established use has been mainly for “intumescent systems” in combination with ammonium polyphosphate for polyolefins. Limitations of many intumescent systems based on PPM Triazines I are that by definition they are not truly halogen-free and that the phosphate salts (ammonium, melamine, piperazine etc.) based intumescent systems are not suitable for certain applications, requiring high water resistance.

With this background we have developed novel MCA® PPM Triazines (PPMT) of the formula II as light-weight H-C-N-O based organo-polymeric universal fire and flame retardant synergists, with following peculiarities beyond state-of-the-art PPM Triazines of Formula I:

- Chemistry: First and foremost, halogen-free with correct chemical composition “poly(piperazinyl,morpholinyl, triazine” as described in all chemical inventories (TSCA, REACH, MITI) for the required registrations of chemicals world-wide. The halogen element is not mentioned in many chemical inventories.
- Environmentally friendly because of solvent-free synthesis.
- More C & N content due to additional morpholine end-group for better char/residue formation.
- Many new applications, far-beyond “classical acid-induced” intumescence of charring.
- Intellectual property: World-wide patents/applications, including Europe, USA, Japan China, India etc.

The purpose of this article is to elaborate these features.

#### Combinations with metal hydroxides:

The largest volume and the most widely used mineral filler fire retardants, such as aluminium trihydroxide and magnesium dihydroxide, have one major drawback as flame retardants that large loadings of materials are required to obtain the desired fire resistance performance. Typically, the required loading levels of 60% or more cause significant detrimental effects in the physical properties of the base polymer [8, 9]. Moreover because of their basic character, the resulting composites are susceptible to acidic atmospheric conditions including carbon dioxide if not adequately encapsulated by the polymer. The degradation and the corrosion can occur not only on the surface but throughout the polymer by way of diffusion and uncontrolled proliferation. Therefore, by reducing the required loading of the fire retardant both the physical properties as well as the durability can be improved, by enabling better protection of the FR by the polymer.

With these objectives we have studied the combinations of MCA® PPM Triazines with metal hydroxides and carbonates with the belief that in fire conditions one should be able to generate metal nitrides or metal oxynitrides (for example of formula III with aluminium hydroxides) as fire barriers in situ [10, 11]. With other metal hydroxides and carbonates similar compounds could be generated.

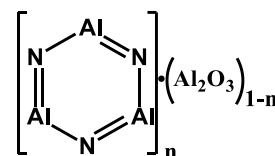


Figure 2: Formula III: Aluminium oxynitride:  $(AlN)_n.(Al_2O_3)_{1-n}$

It has been found that MCA® PPM Triazines do indeed exhibit exceptional properties as fire retardant synergists in combination with inorganic filler fire retardants such as metal hydroxides and carbonates (huntite/hydromyagnesite) [12]. Thus, in cone calorimetry test even at high heat flux of 50 kW/m<sup>2</sup>, FR composites with MCA® PPM Triazines undergo only low/slow burning due to immediate char formation by so-called “self-immolation” principle, as evidenced by rather short time to ignition but very low peak heat release rate, right from the very beginning. Thereafter, under continued heat flux required of the cone calorimetry test, they then seem to generate metal nitrides and/or oxynitrides (such as III with aluminium trihydroxide) in situ, as ceramic fire shields. Thus, in spite of almost 800°C end-temperature at the end of the cone test there is a 15-20 % more robust greyish (ceramic type) rather than blackish (char-type) residue formation in case of FR composites containing MCA® PPM Triazines than in case of the samples not containing these compounds.

Figure 3 underlines the effectiveness of the compounds of MCA® PPM Triazines as fire and flame retardant synergists in a typical cable polymer composition such as EVA (19%). Thus in spite of replacing 50 parts of aluminium trihydroxide (ATH) with just 2.5-5 parts of the compound of Formula II, all critical parameters of fire and flame retardancy such as flame out time, heat release rate (HRR), peak heat release rate (pkHRR), total heat release (THR) remain the same, in spite of almost 15% more incinerable organic material present in the samples with II (due to same wall-thickness as required of the test procedure).

Moreover, the resulting polymer compositions when used for cable applications show the following advantages:

- a) For the same amount (100%) of base polymer/resin required to be used for insulation-jacketing of the same length of cable, almost 18% less requirement (in weight) of the corresponding fire retardant (FR) compound.
- b) Ease of processing, more productivity, less energy demand
- c) Better E&E (IEC) conformity of insulating materials

- d) Less abrasion of the processing equipment
- j) Lighter-weight, better-quality, and eco (disposable) cable (LW-0LH-HQ-E= Light weight-zero/low halogen-high-quality eco cable)

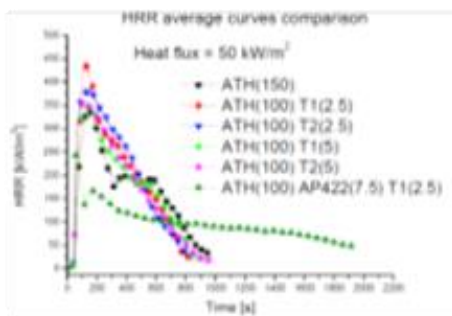


Figure 3: MCA® PPM Triazine HF (T1, T2: coated, non-coated) & aluminium hydroxide (ATH: Apyra® 40CD, Nabaltec) combinations in EVA (ELVAX® 470 DuPont, VA19%): Replacing 50 phr of ATH with 2.5 & 5 phr of PPMT HF, or 10 phr PPMT 765 (AP422+T1)

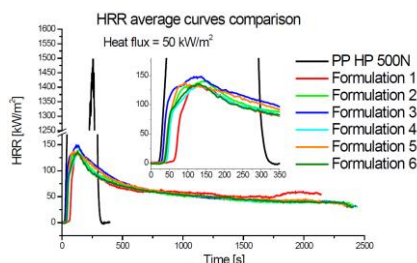


Figure 4: MCA® PPM Triazine HF & magnesium dihydroxide (MDH; APYMAG 60 (Nabaltec) combinations in polypropylene (PP; Mopen HP 500N, Basell), replacing 50 phr of MDH with 2.5 & 5 phr of HF (for weight reduction)

Figure 4 displays the cone calorimetry test results of MCA® PPM Triazine HF in combination with magnesium dihydroxide in polypropylene. Again here 50 parts of magnesium dihydroxide in Formulation 1 (150 phr) could be replaced with 2.5-5 phr of MCA® PPM Triazine HF (Formulations 2-6) to achieve the same average heat release rate (HRR) curves. Moreover, in UL 94 V test the formulation 4 (with 2.5 phr and 0.1 phr polytetrafluoroethylene, PTFE) and Formulation 6 (5 phr MCA® PPM Triazine HF) provided V-0 at 1.6 mm.

To be noted is that none of these compositions represent optimal formulations, and could be and should be further optimized for specific requirements.

Based on these results and the proposed mechanism we expect similar effects of MCA® PPM Triazines with other inorganic fire retardants and synergists such as borates, halloysite, huntite/hydromyagnesite (UltraCarb®, LKAB) and silicone compounds; the mechanism being the formation of the corresponding metal oxynitrides as fire barriers, in situ.

Sometimes nanocomposites are used as synergists to achieve

some of the said objectives to a limited extent [14]. They are mostly inorganic materials with the following advantages for the compounds of formula II:

- Light-weight purely organic materials of high efficacy.
- Formation of ceramic fire barriers in the event of fire.
- Non-ionic, for better E&E (IEC) conformity of insulating materials
- Better heat stability versus organo-clays
- Light stabilizing effect due to chemical relationship with light stabilizers
- Universal applications

#### Combinations with phosphates:

As an alternative to inorganic mineral flame retardants such as metal hydroxides and even carbonates for the replacement of halogen containing flame retardants the so-called intumescent systems based on phosphate salts such as ammonium polyphosphate (Clariant) and piperazine polyphosphate (Adeka) are mostly used in polyolefins.

Intumescent systems require lower dosages compared to metal hydroxides and other inorganic fillers, but are susceptible to hydrolysis (instability towards water) under humid conditions if not properly dispersed in and protected by the polymer.

However, as said above, proper dispersion and protection in the polymer are equally essential, and even more so, in the case of metal hydroxides because of high loadings required and their susceptibility towards the ever increasing acidic atmospheric conditions, and particularly towards carbon dioxide.

It has been generally assumed that for intumescence the presence of phosphates as acid source for the formation of fire resistant char is absolutely necessary [15].

We have now found that non-ionic MCA® PPM Triazine HF can be used in place of phosphates for the char formation. However, it has also been found that combining phosphates with MCA® PPM Triazine HF improves over-all stability of the former, both towards hydrolysis as well as thermal degradation, and their efficacy thereby enabling to considerably reduce the loadings and facilitate better protection-in-use by the polymer [16]. Moreover, the coating of such blends with siloxane (silicone wax) provides better hydrophobicity (water repellency), easy dispersibility, better mechanical properties of the plastic items and enables further reduce the loading for same fire retardancy.

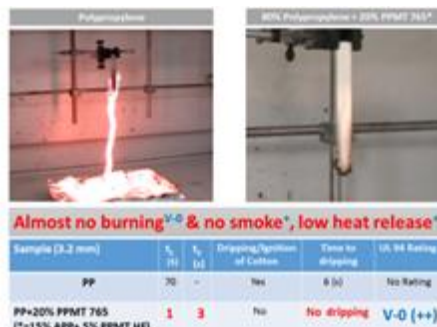


Figure 5: MCA® PPM Triazine HF-Ammonium polyphosphate combination (PPMT 765 is a blend of APP+PPMT HF)

Figure 5 demonstrates a typical test of an intumescent system based on MCA® PPM Triazine HF and ammonium polyphosphate in polypropylene. Of particular interest is the fact that for some results, on one hand one would have to use up to

300 % (or even more) by weight of a metal hydroxide, and on the other hand almost 140-150% by weight of the resulting FR compound for same wall-thickness in end-application (“double peak disadvantage”).

UL 94V in Polypropylene (M.I. = 8): 1.6 mm				0.8 mm	
PP (%)	74.4(63*)	74.4	74.4	74.4	71.4
APP**	25 (37*)	22.5	20.0	18.75	19.6
MCA® PPM Triazine HF	0	2.5	5.0	6.25	8.4
FR Total	25 (37*)	25	25	25	28
Additives	0.4 (0*)	0.6.	0.6	0.6	0.6
Burning time t1(s)	> 70	5	0	0	0
Burning time t2(s)	N.E.	5.5	2	0	0
UL 94	N.E. (*V-0)	V-2	V-2	V-0	V-0

\*\*AP 422 (Clariant); \*S. Levchik, AMI, FR conference Denver (USA), 2012; N.E.: not evaluated

Table 1: MCA® PPM Triazine HF with ammonium polyphosphate in polypropylene

Tables 1 give examples of how the combinations can be tailored/optimised to meet the specific requirements. Similar combinations and optimisations are also possible with

piperazine polyphosphates to improve their overall performance [17].

**Mechanism of the mistry of phosphorous-nitrogen synergism for fire retardancy:**

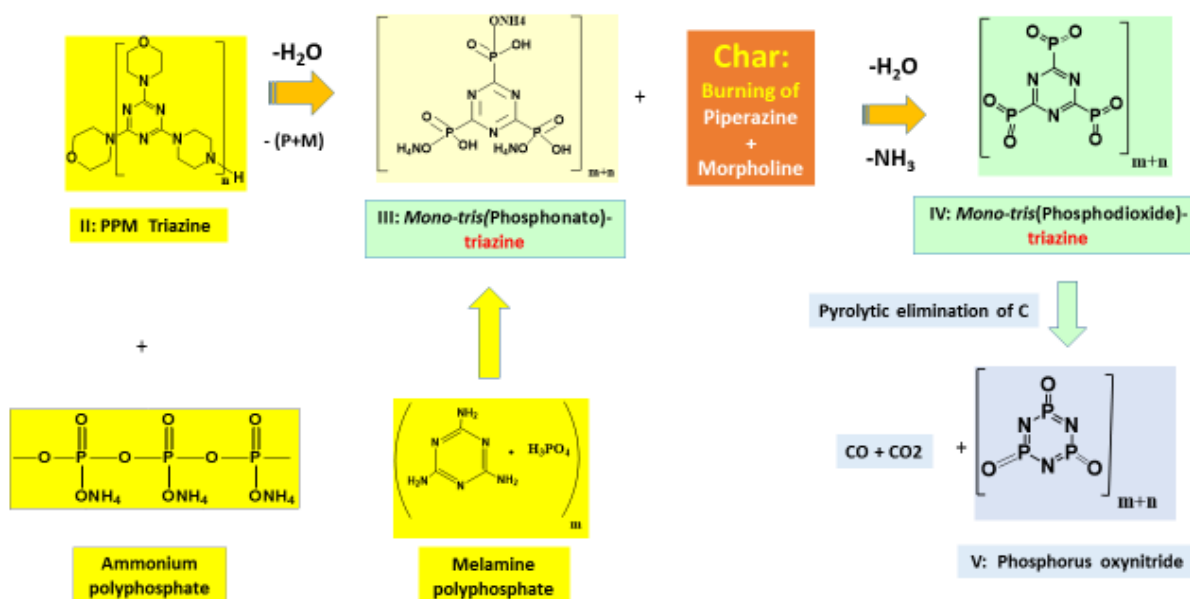


Figure 6: Mechanism of the fire retardancy of MCA® PPM Triazine HF with phosphates

It is assumed that in the event of fire the protection is provided by the ultimate formation of phosphorus oxynitride V. In case of MCA® PPM Triazine HF with phosphates (including their esters), or in case of melamine polyphosphate alone, the intermediary steps III and IV are perhaps involved. Most importantly, the use of triazines as nitrogen synergists perhaps facilitates the formation of V by way of acting as “molecular recognition” template for the formation of the stable cyclic triazine structure of V. The proof is provided by the fact that ammonium polyphosphate alone is not very effective as a fire retardant, in spite of its self-containing P & N elements. Also other nitrogen synergists do not seem to be as effective as triazines. Moreover, the residue in cone test of the experiment displayed in figure 5 was found to be 4-5%, corresponding to almost expected formation of V (phosphorus oxynitride).

Important conclusion is that incorporating P & N in the same molecule is not the right approach for the future fire retardant research.

Phosphorus oxynitrides, like most oxynitrides have been proved to be high-temperature resistant materials [18].

Polyamide 6* (%)	54.5	54.6	59.7	54.6
Glass fibres (%)	25	25	25	25
Exolite OP 1230** (%)	15	10	7.5	0
MCA® PPM Triazine HF (%)	5	10	7.5	0
Melamine polyphosphate*** (%)	0	0	0	20
Additives (%)	0.5	0.5	0.5	0.5
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 (BASF), \*\*Clariant, \*\*\*Melapur 200 (BASF), n.c: no classification

Table 2: MCA® PPM Triazine HF & a phosphinate combination in glass-filled PA 6

Table 2 gives an example of the use of PPM triazine in glass filled polyamide 6. Again here the formulations do have room for optimization.

#### Combinations with halogenated fire retardants:

Halogenic fire retardants include a broad range of chemical compounds mostly containing multiple halogen elements. Aromatic bromine compounds are frequently used where higher stability against dehalogenation at processing temperatures is required.

Notwithstanding the controversy of their use due to perceived environmental problems [21], halogenated fire retardants are still used for many applications mostly with antimony trioxide as a synergist. Halogenated fire retardants are rather very effective

#### Combinations with phosphinates:

Metal phosphinates such as aluminium diethylphosphinates (such as DEPAL of Clariant) are extensively used as fire retardants in polyamides and polyesters. However, the phosphinates need to be combined with a nitrogen synergist for proper efficacy. The most commonly used nitrogen synergist for such applications is melamine polyphosphate [19]. Considering the nature and appearance of the residue in cone calorimeter test we believe that the fire protection is provided by the formation oxynitrides such as the compounds of formula III & V as fire barriers in situ in the event of fire.

MCA® PPM Triazine HF is particularly recommended to be used in place of or in combination with melamine polyphosphate to resolve the issues of corrosion, resistivity/conductivity (electrical properties), reaction with the polymer itself [20], hydrolytic instability, water pick-up & longevity, and last but not least the weight reduction (density reduction, 1 against 1.85) compared to the use of melamine polyphosphates alone.

and yet they may slowly bloom out of some polymers, causing much debated environmental problems. Also the corrosive gases and toxic chemicals could be generated in the event of fire. Brominated compounds are also antagonistic towards the light stabilizers.

The known drawbacks of halogenated flame retardants also seem to be that they always generate more smoke and carbon monoxide during burning and they can be ineffective in high heat flux fires, due to their escaping from the polymer under the influence of heat.

With the objective of combining the advantage of intumescent systems (fire retardants) with the benefits of high efficacy of the halogenated flame retardants, thereby reducing the loadings for

somewhat safer use of the later, we have studied the combinations of the two systems. Thus it has now been found that MCA<sup>®</sup> PPM Triazines are also suitable as synergists of halogen containing flame retardants, on one hand to reduce their loading and on the other hand to partially or totally replace

antimony oxides. Antimony oxides are no more desired as flame retardant synergists because of their potential toxicity. Table 3 gives the example of such application. Here by reducing the loading of decabromodiphenyl ethane its observed blooming problem could perhaps be eliminated.

Decabromodiphenyl ethane (ICL) (%)	10	26*
Antimony trioxide (%)	0	11*
MCA <sup>®</sup> PPM Triazine 765 (%)	15	0*
Ammonium polyphosphate**		
Total FR	25	37*
Burning time t1	0	?*
t2	12	
UL 94 (1.6mm)	V-2	
+ PTFE (0.1-0.4 %)	V-0 (?)	V-0*
Blooming	No	Slight (!)*

\*S. Levchik, AMI FR conference 2012, Denver (USA) \*\*AP 422 Clariant

Table 3: Combination of MCA<sup>®</sup> PPM triazine with decabromodiphenyl ethane

#### Combinations with nitrogen-based radical generators:

This new class of nitrogen based flame retardants [22] has been developed for thin film polyolefins. In thick films and at higher concentrations they do not seem to perform well. Moreover, because of their limited heat stability and low melting points their use in PP is rather limited.

It has now been found that Flamestab<sup>®</sup> NOR 116 (BASF) can advantageously be combined with MCA<sup>®</sup> PPM Triazines to partially alleviate the deficiencies of the former and particularly enable further reduction of the loadings of MCA<sup>®</sup> PPM Triazines for critical applications such as polyolefin foams and films. The results of our studies are summarized in Table 4.

PP (%)	0	85	85
PE (%)	98	0	0
MCA <sup>®</sup> PPM Triazine HF (%)	1	0	
MCA <sup>®</sup> PPM Triazine 765 (%)		15	15
Flamestab NOR <sup>®</sup> 116* (%)	1	0	0
0.2 mm	B-2 (fire test)		
Total Burning time (s)		> 260	40
UL 94 (3.2 mm)			V-2
UL 94 (1.6 mm)+ Nanoclays/PTFE			V-0 (?)

Table 4: Combinations of MCA<sup>®</sup> PPM Triazines with Flamestab<sup>®</sup> NOR 116 (BASF)

#### Economics and cost-in-use of fire and flame retardants:

First and foremost, both for the fire resistance testing (such as UL or cone etc.) as well as the actual end-applications of the plastics mostly the wall-thickness (i.e. the volume) and not the weight of a plastic item matters [23]. Therefore, for the economics and their actual cost-in-use mostly the cost-in-use/liter (or gallon) and not the cost-in-use/kg (or lb.) of a fire retardant or the fire retardant compound should matter. For example: The cost factor in cable is not the weight but the length of the cable that can be made out of a given weight of the cable compound. Even for any plastic item it is how many individual items (of same wall- thickness) one can

make out of a given weight of the compound, and not the individual weight of the each plastic item itself. The actual cost-in-use, therefore, would be the weight multiplied by the density of the FR or the corresponding FR compound.

Table 5 gives the densities of the most important FRs and synergists in use versus for example base polymer such as polyolefins.

Table 6 gives the relative weight requirement for cost-in-use considerations of various FR compounds and the %age volume of the protecting polymer for the same wall-thickness

Materials	Specific gravity (density)	
	Absolute	Relative %
Polymer (PE/PP)	0.9	100
MCA® PPM Triazine HF	1.0	110
Melamine polyphosphate	1.85	203
Ammonium polyphosphate	2.0	220
Metal hydroxides	2.42	265
Decabromodiphenyl ethane (DCBE)	3.25	357
Antimony trioxide	5.25	5.77
Zinc borate	2.67	293
Nanoclays	2.62	286
Calcium carbonate	2.62	286

 Table 5: Densities of fire retardants and synergists versus polyolefins $\mu$ 

FR Compound Type	Specific gravity (compound)	Relative weight %age demand (compound) (cost-in-use)	Volume %age of polymer (Functionality + Protection of FR)
PPMT-Intumescent halogen-free	1	100	89 +5*
MDH, 200 phr	1.55	155	58
MDH, 150 phr + PPMT HF 5 phr	1.41	141	63 +3*
ATO/Halogen(DCBE)**	1.27	127	69
PPMT/Halogen(DCBE***)	1.07	107	89+4*

\*Polymeric HF, \*\*S. Levchik, AMI, FR Conference 2012, Denver (USA), \*\*\*ICL

Table 6: Theoretical relative weight-demand and the %age volume of the protecting polymer of some typical FR compounds for same volume of the end-plastic item (example: 3.2 mm PP/PE; UL 94 V-0)

## Conclusions:

- Based on current and on-going investigations, we believe that metal hydroxides (ATH and MDH) or combinations thereof with calcium carbonate can be partially replaced with MCA® PPM Triazine HF or MCA® PPM Triazine 765, in any and every existing formulation for weight reduction and better performance of the plastics.
- For the replacement of up to 50 parts ATH/MDH or combinations thereof with calcium carbonate, 5-2.5 parts of MCA® PPM Triazine HF, or 10-5 parts of MCA® PPM Triazine 765, to be individually optimized, should be sufficient.
- Processing aids may further enable to reduce the required loadings of MCA® PPM Triazines.
- MCA® PPM Triazine HF can be used in most engineering polymers in combination with metal dialkylphosphinates (DEPAL) with or in place of melamine polyphosphates, to avoid corrosion, hydrolysis, failure of mechanical properties, for weight reduction, and particularly to ensure longevity.
- Flamestab® NOR 116 (BASF) can be combined with HF for better performance and cost savings.
- Combination with halogenated flame retardants to reduce their loading and alleviate the blooming problems associated with the use of some brominated flame retardants; and partial or total replacement of antimony trioxide to further reduce the weight, peak heat release rate and smoke density.

## Pointers and pathways of future research:

Formation of stable expanded & spongy (zeolite like) fire resistant ceramic barriers in the event of fire, by way of the use of a cocktail of organo-inorganic materials. Neither organics nor inorganics alone can do it. Release of expanding gases and

simultaneous organo-inorganic ceramification is perhaps the pathway. Rather than permutations and combinations, well-thought concepts based on sound mechanisms should be investigated.

## Acknowledgements:

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Dr. Bansil L. Kaul

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*Still a globetrotter knowing almost all regions and markets of the world, Dr. Kaul has also given lectures at many scientific and technical conferences world-wide. He has also made numerous research publications and is author of chapters in many handbooks, such as Pigment Handbook; High -Performance Pigments; Ullmann's encyclopedia of industrial chemistry; Synthetic fiber dyeing etc.*

## Résines époxy intrinsèquement ignifuges à base de liquides ioniques phosphorés

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Les résines époxy sont utilisées dans de nombreuses applications pour lesquelles les matériaux doivent être ignifugés. C'est le cas par exemple des composites époxy-fibres de carbone utilisés dans le domaine aéronautique. L'incorporation de retardateurs de flamme non liés au réseau therm durcissable (appelée voie additive) est la solution la plus courante mais elle souffre de certains inconvénients : diminution des propriétés mécaniques, répartition inhomogène des retardateurs de flamme lors de la préparation du composite, risque de migration des retardateurs de flamme au cours du temps, associé à une réduction du niveau d'ignifugation. L'utilisation d'une résine intrinsèquement ignifuge (voie réactive) doit permettre d'éviter ces problèmes. De plus certaines études ont montré qu'à taux de phosphore équivalent, la voie réactive est plus efficace que la voie additive.

Il a été démontré récemment au laboratoire d'Ingénierie des Matériaux Polymères de l'INSA de Lyon que les liquides ioniques phosphonium combinés à des anions plus ou moins basiques pouvaient amorcer la polymérisation anionique du prépolymère DGEBA (bisphénol-A-diglycidyl ether) et s'intégrer au réseau therm durcissable. C'est le cas en particulier du liquide ionique dénoté tributyl(éthyl)phosphonium diéthylphosphate (Figure 1). Ce liquide ionique contenant du phosphore, on peut s'attendre à ce qu'il participe à l'ignifugation de la résine.

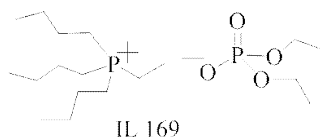


Figure 1 – Structure du liquide ionique IL169

Des résines époxy DGEBA contenant 10 à 30 parts de IL169 (soit 1,45 à 3,69% de phosphore) ont été préparées et leurs propriétés comparées à celles d'un réseau époxy-amine composé également du prépolymère epoxy DGEBA et d'une amine aliphatique (Jeffamine D230). Concernant les propriétés thermiques des matériaux préparés, l'augmentation du taux de liquide ionique dans le réseau époxyde conduit à une diminution de la température de transition vitreuse passant de 114 °C avec 10 parts d'IL169 à 93 °C avec 30 parts d'IL169.

L'analyse thermogravimétrique en atmosphère inerte a montré que la présence d'IL169 ne réduit pas la stabilité thermique de la résine, alors que les retardateurs de flamme phosphorés conduisent souvent à une dégradation anticipée (à plus basse température) du matériau. Le taux de résidu en pyrolyse anaérobie augmente légèrement de 10 à 20% en présence d'IL169.

Le comportement au feu a été évalué par calorimétrie au cône à une irradiance de 35 kW/m<sup>2</sup> (Figure 2). Le temps d'ignition reste constant, en bon accord avec les analyses thermogravimétriques. L'ajout d'IL169 conduit à une diminution significative du pic de débit calorifique (pHRR) et de l'énergie totale libérée (THR), associée à une forte expansion du résidu (Figure 3). Le pHRR diminue de 1100 kW/m<sup>2</sup> pour la résine DGEBA-D230 à 300 kW/m<sup>2</sup> pour la résine contenant 30 parts d'IL169 tandis que le THR chute d'environ 50%.

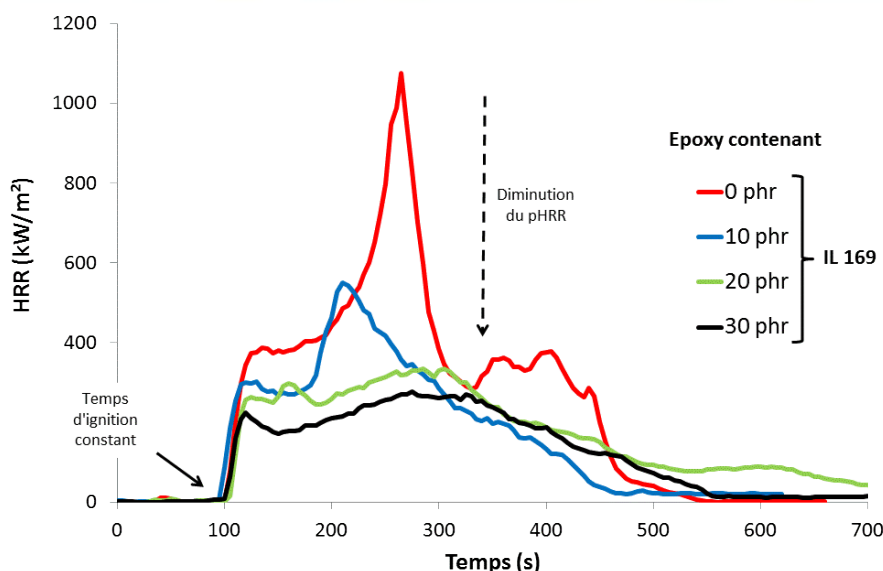


Figure 2 – Courbes de débit calorifique des résines étudiées (irradiance 35 kW/m<sup>2</sup>)

L'expansion est progressive (non instantanée) après ignition. Le taux de résidu est très élevé (40%) pour la résine la plus chargée en phosphore et correspond à une fraction de résine non pyrolysée car protégée par la couche de char expansée. Le phosphore promeut le charbonnement de la résine époxy et

augmente la stabilité thermo-oxydative du résidu, mais près de 65% du phosphore est libéré en phase gazeuse, et les données semblent indiquer qu'il agit aussi comme inhibiteur de flamme, ralentissant la combustion.

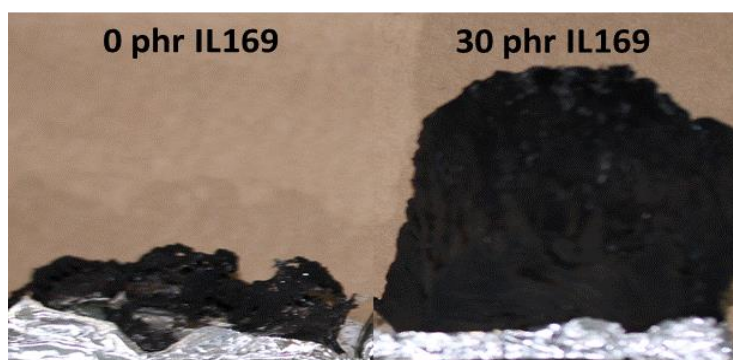


Figure 3 – Résidus après essai au cône calorimètre de la résine référence et de la résine contenant 30 parts d'IL169

L'analyse par tomographie de rayons X a permis de visualiser la structure interne du résidu expansé. Celle-ci est constituée de cellules ouvertes dont la taille augmente avec le taux d'expansion (donc avec le taux d'IL169). Les résidus les plus expansés sont constitués de cellules de grande taille (plusieurs centimètres carrés). Une telle structure ne semble pas optimale et pourrait encore être améliorée pour une protection accrue de la résine sous-jacente.

Ces premiers résultats montrent le potentiel des liquides ioniques phosphorés pour ignifuger les résines époxy, afin d'éviter ou de réduire l'ajout de retardateurs de flamme non liés au réseau thermodurcissable. En raison de la variété des liquides ioniques porteurs de groupements phosphorés, il doit être possible de

modifier à façon la réaction au feu de ces résines époxy en adaptant les modes d'action du phosphore. Des essais préliminaires ont ainsi montré que les effets d'un autre liquide ionique phosphoré (IL104) sont sensiblement différents de ceux de l'IL169. Enfin, il reste à élucider les relations entre les propriétés du réseau thermodurcissable et l'aptitude à l'expansion du matériau en cours de pyrolyse.

Les résultats déjà publiés sont disponibles ici :

R. Sonnier, L. Dumazert, S. Livi, T.K.L. Nguyen, J. Duchet-Rumeau, H. Vahabi, P. Laheurte, Flame retardancy of phosphorus-containing ionic liquid based epoxy networks, *Polymer Degradation and Stability* 134 (2016), 186-193 - <http://dx.doi.org/10.1016/j.polymdegradstab.2016.10.009>

## Avis de Soutenance

Louis DECOSTER soutiendra publiquement ses travaux de thèse intitulés

**"Contribution à l'étude et à la modélisation du dépôt des suies lors d'un incendie"**

dirigés par Messieurs Olivier VAUQUELIN et Fabien CANDELIER.

Soutenance prévue le jeudi **12 janvier 2017 à 10h00 à la Préfecture de Paris** et d'Île de France- salle Frochot  
- 5, rue Leblanc - 75015 Paris

Ce travail est consacré à l'étude du dépôt des particules de suie transportées par des fumées d'incendie. L'étude de la littérature donne une synthèse des propriétés connues des particules de suie produites par un incendie ainsi qu'une revue de l'état de l'art des outils disponibles pour modéliser leur dépôt. Le code Fire Dynamics Simulator, outil numérique utilisé dans ce travail, permet depuis sa version 6 de simuler le dépôt de suie mais aucune étude expérimentale à échelle réelle ne fournit de données quantitatives de dépôt qui permettraient de valider les performances de l'outil dans ce domaine. Une première campagne expérimentale a donc été réalisée pour pouvoir évaluer FDS et les modèles fournis par la littérature dans le cas du dépôt à échelle réelle de particules de suie produite par la combustion d'heptane. Ces essais ont été suivis d'une seconde campagne expérimentale à échelle réelle avec pour objectif la prise en compte de l'écoulement des fumées le long de la paroi de dépôt et de sa vitesse. Les deux campagnes d'essais à échelle réelle ont enfin été complétées par le montage d'un banc expérimental à petite échelle permettant d'étudier l'influence de la vitesse d'écoulement sur le dépôt à l'intérieur d'une conduite de particules produites par un petit foyer.

*Merci de bien vouloir confirmer votre venue avant le 5 janvier 2017 à l'adresse suivante : [marie-christine.bonenfant@interieur.gouv.fr](mailto:marie-christine.bonenfant@interieur.gouv.fr), afin que nous puissions établir une liste de présence que nous transmettrons à la préfecture. Plans d'accès : <http://www.prefectures-regions.gouv.fr/ile-de-france/Outils/Horaires-et-coordonnees/Plans-d-acces>*

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*Bonnes fêtes de fin d'année*