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Supporting R&D & Business Development in Life Sciences, Personal Care and Specialty Chemicals Industries

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Some novel polytriazinyl flame retardants and synergists of the state-of-the-art flame retardants for better value-in-use

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Primary Reference

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Update of the Chapter

Plastics, Additives

Rainer Wolf , Bansi Lal Kaul
Ullmann's Encyclopedia of Industrial Chemistry
Vol. A20, 459-507

Why Plastics?

- Plastics are the materials of choice over metals, wood, paper & ceramics etc. due to their:
  - Light weight for the sake of energy and fuel saving (particularly in the transportation industry)
  - Ease and low cost of processing
  - Service properties
  - Ability to be easily disposed of by incineration, after their service life
- Growth of plastics also due to increased consumption in growing economies, for very obvious economical/ecological advantages
- Requirement of plastics (and coatings), therefore, expected to continue, not only in spite of, but <u>because</u> of recession

Why Fire Resistance of Plastics?

- Plastics (and coatings) to be classified as solid fuels, and hence the need, and even the legal requirement, of their fire resistance for safer service life
- Imparting fire resistance could even be an opportunity to reduce cost of goods and add value
- Flame retardants are expected to reach almost 2.2 billion tonnes in 2011 (2006-2011E CAGR 4.7%)
- With every occurrence of major fire accident co-related to plastics, and the consequences thereof, regulations regarding the fire resistance and fire retardants are expected to get more stringent

Requirements of Fire Retardants

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- Efficacy and effectiveness
- Processibility, e.g. ease and economy of compounding
- Performance during the intended service life of the finished goods,
- Non-toxicity of gases in case of accidental fire
- Environmental compatibility recyclability and/or ability to be safely disposed of after the service life of the products
- Over-all value in use = Cost + processing cost + value of the end-product

Inherent Efficacy and Effectiveness beyond LOI and UL 94

- Nature and characteristics of the flame: Such as colour, the microgravity, the turbulence and speed of propagation,
- Maximum heat of combustion
- Maximum smoke density concentration
- Maximum concentration of the lethal carbon monoxide, formed under any and every circumstance
- Nature of other gases and volatile components formed

Mechanism of Fire Resistance

- Ideal functioning of a fire retardant is provided by the formation of the spongy porous fire resistant barrier (shield) at the point of fire, thereby preventing or retarding the propagation of the fire, occurrence of the flame, and reduction of smoke emission.
    - Inorganic metal hydroxides, additionally undergo endothermic dehydration to the corresponding metal oxides in the event of fire.
    - Phosphorus based fire retardants generate polyphosphoric acid , accelerating the formation of the required chary material for fire extinguishing.

Compounding and Ultimate Processing

- Considering the loadings required to achieve the required fire resistance, not only the nature and the chemistries of the fire retardants are important, but also their incorporation into the substrate (compounding) and ultimate processing could be even more important
- Optimum dispersion needs to be achieved and the methods to verify the same need to be established, if not already existing

Main draw-backs of state-of-the-art fire retardants for plastics

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- Usually high loadings required, negatively influencing the properties of the plastic materials, and defeating the very purpose of the use of plastics; namely their light weight , ease of processing and ultimate disposal of
- Mineral fire retardants, which currently account for almost two-third of the world consumption of fire retardants, even need to be added in amounts far exceeding the weight of the resin itself
- Low melting fire retardants greatly influence the mechanical properties of the plastics
- Halogenated fire retardants have an inherent potential of causing collateral damage by generating corrosive and toxic gases and other volatile components in the event of fire

Thumb-Rule Principal of the Efficacy and Effectiveness of FRs

Irrespective of the chemistry

- High density means poor efficacy
- Small specific surface area (however needs to be determined correctly) means poor efficacy
- Larger individual particle size means poor efficacy

And last but not least

- Poor dispersion means poor efficacy

Improving State-of-the-Art FRs through synergists/secondary FRs

To achieve fire retardancy at lower loadings, synergists or secondary fire retardants are used in combination with the primary fire retardants. Such cocktails usually facilitate and support the so-called intumescent process of fire retardancy

What is the Intumescence Process?

Mimicking of nature: The burning behavior of cotton versus silk

1. Softening/melting of the substrate/polymer
2. Release of an inorganic acid (ammonium polyphosphate)
3. Carbonization of the polymer and the synergist
4. Gas production through expanding agent (the synergist)
5. Swelling out of the mixture
6. Solidification through crosslinking reactions

Basic Requirement of Intumescence Cocktail

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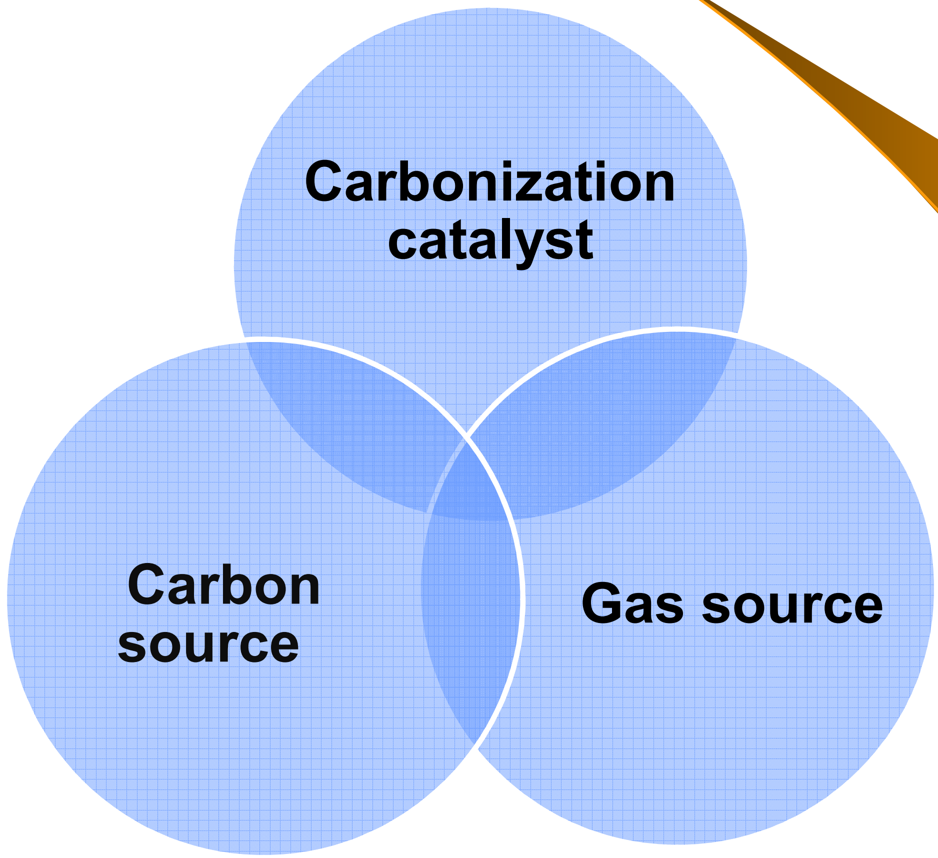

PPM Triazin: Synergist of APP for Intumescence

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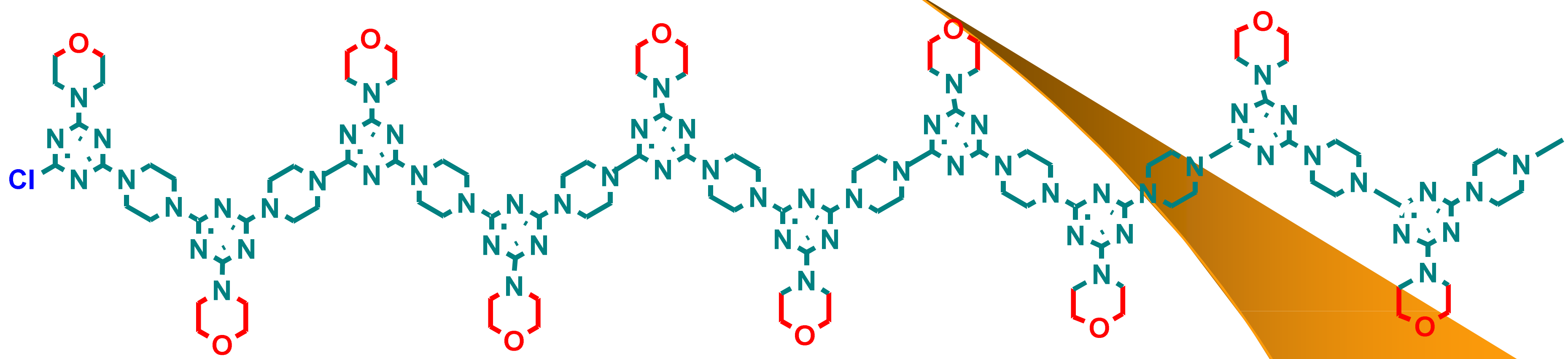

Chemical Formula: $C_{122}H_{204}ClN_{60}O_{10}$
Exact Mass: 2705
Molecular Weight: 2707
Elemental Analysis: C, 54.13; H, 7.60; Cl, 1.31; N, 31.05; O, 5.91

Mechanism: Air-bag principle/oxygen scavenging, and carbon source; two-in-one

State-of-the-Art Volatile Organic Solvent (VOS) Based Technology of PPMTs

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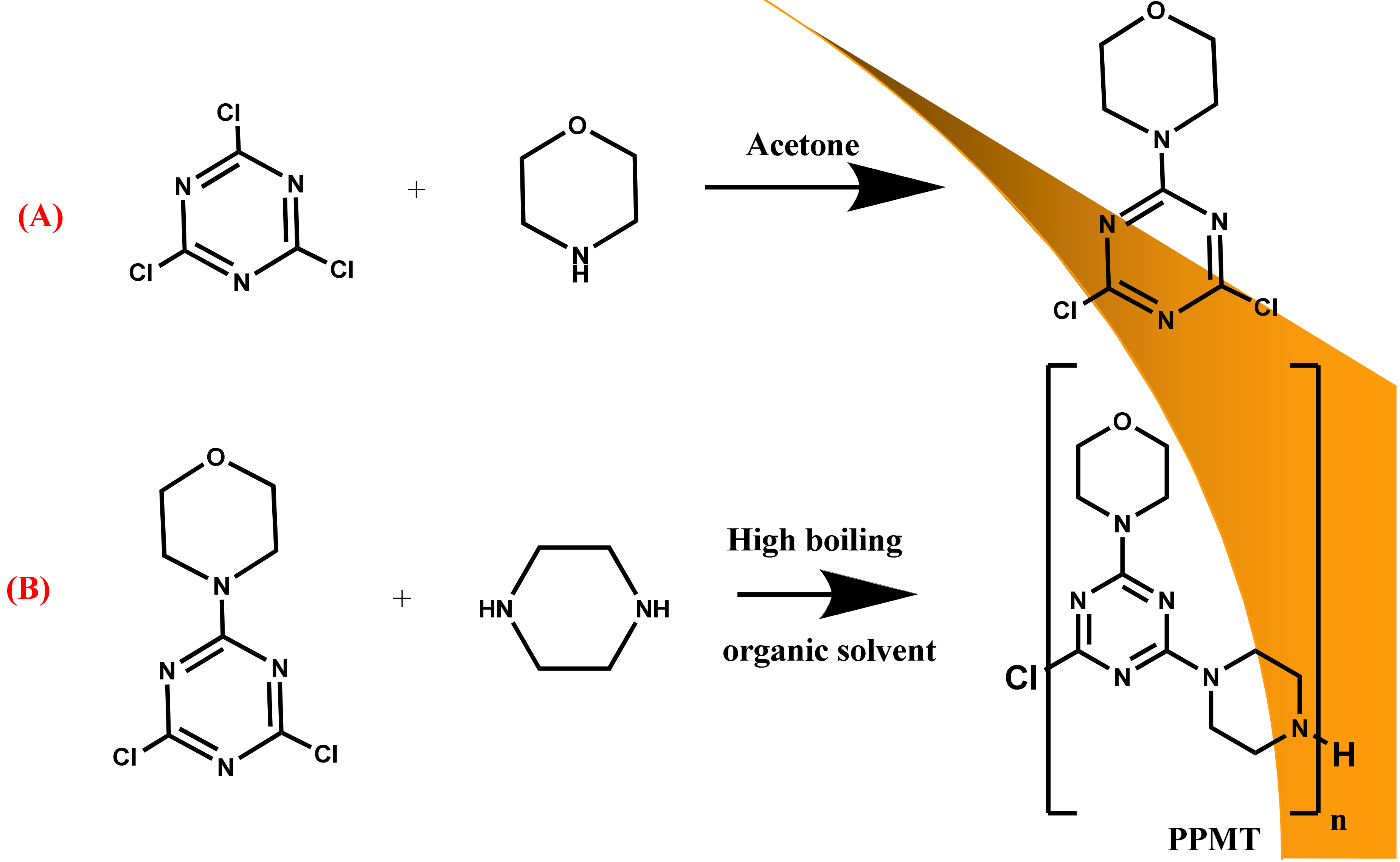

MCAT's Proprietary Volatile-Organic-Solvent-Free Technology

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Suspension polymerisation in the presence of catalysts

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

Novel environmentally friendly VOS-free technologies

(European Patent Application Nrs. EP 08008717.4 and EP 08015381 & more to come; also applied for the Japanese, Taiwanese, Chinese and the US patents)

PPM Triazin special: Novel Halogen-Free Secondary FR

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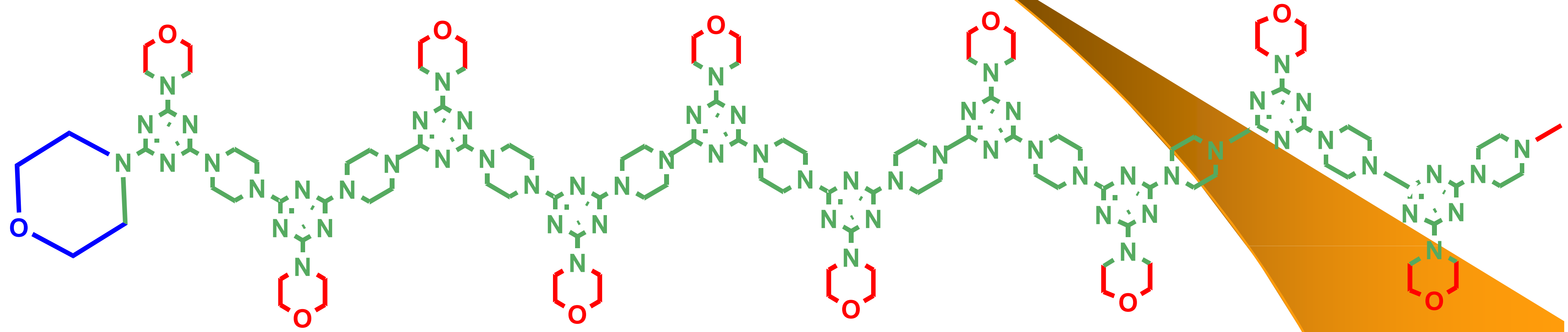

Chemical Formula: $C_{126}H_{212}N_{61}O_{11}$
Exact Mass: 2755.8
Molecular Weight: 2757.4
Elemental Analysis: C, 54.88; H, 7.75; N, 30.99; O, 6.38

<u>Mechanism:</u> Air-bag principle/oxygen scavenging, and carbon source; <u>two-in-one &</u> <u>halogen-free</u>

PPM Triazins: Physical Characteristics

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- White to off white powders
- Density: 1.01 (almost same as most of polymers)
- Melting point : > 290 C
- Particle size (measured on powder, without dispersion):
    a. Smallest individual particle: 0.2 µm
    b. 10 % aggregates: 2.672 µm
    c. 50 % aggregates 11.06 µm
    d. 90 % 28.35 µm

PPM Triazin special, scanning electron microscope (x 10,000)

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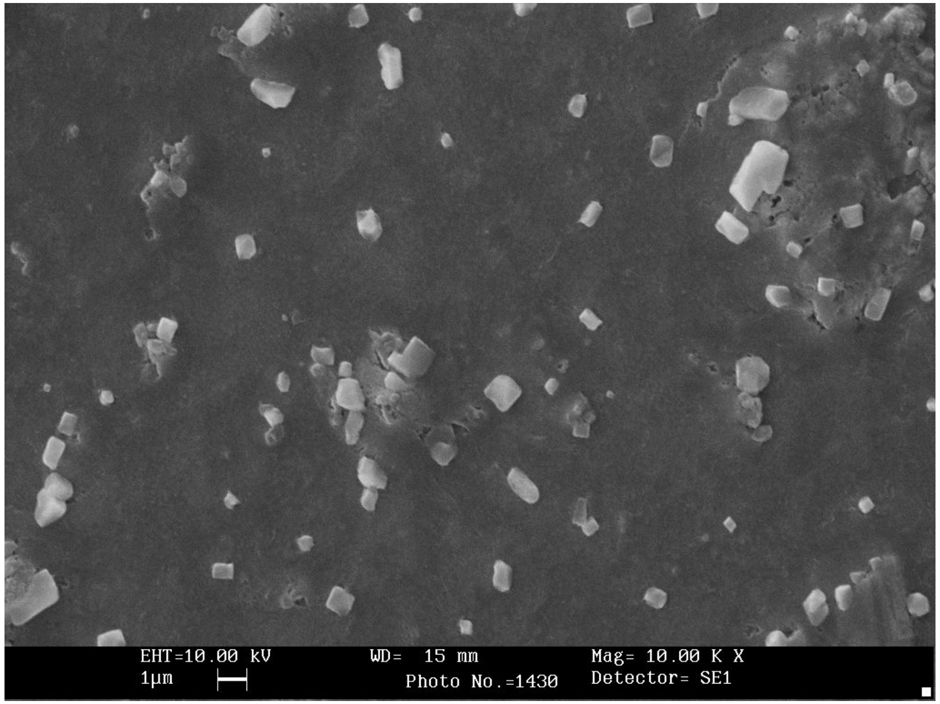

Individual particle size:
< 1 µm

Individual particle shape:
Diamond like

PPM Triazins: Application properties

- Heat stable up to 280 °C (536 °F), and beyond (MP > 290 °C) in most polymers, particularly the polyolefins
- Low density, much larger specific surface area at same weight of other FRs
- Non-migrating/non-blooming, insoluble in almost all common organic solvents, behave like pigments
- Chemically inert & neutral; absolutely hydrolysis resistant
- Compatible with HALS light stabilizers
- Non-abrasive to ensure longer life of the processing equipment
- Synergistically blendable with almost all cheaper flame retardants (such as APP and inorganics) for a better cost and value-in-use, such as higher productivity in compounding and production of end-products than with cheaper inorganics alone
- Light-weight plastics and thinner walled cables with reduced consumption of compound per meter of the cable compared to inorganics and some organic flame retardants

Polytriazins as Secondary FRs for Fire Retardation beyond LOI (Limiting Oxygen Index) and UL 94

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- Enhanced intumescence (two-in-one synergist)
- Retardation of the rate of combustion
- Reduced maximum heat of combustion
- Reduced maximum smoke density
- Scavenging of toxic acidic fumes (in combination with halogenated flame retardants)
- Reduced maximum concentration of toxic gases
- Easy to dispose of (by incineration)

Specific Optical Smoke Density (Ds) of Fire-Retarded Polypropylenes: V-0 Formulations 1.6 mm

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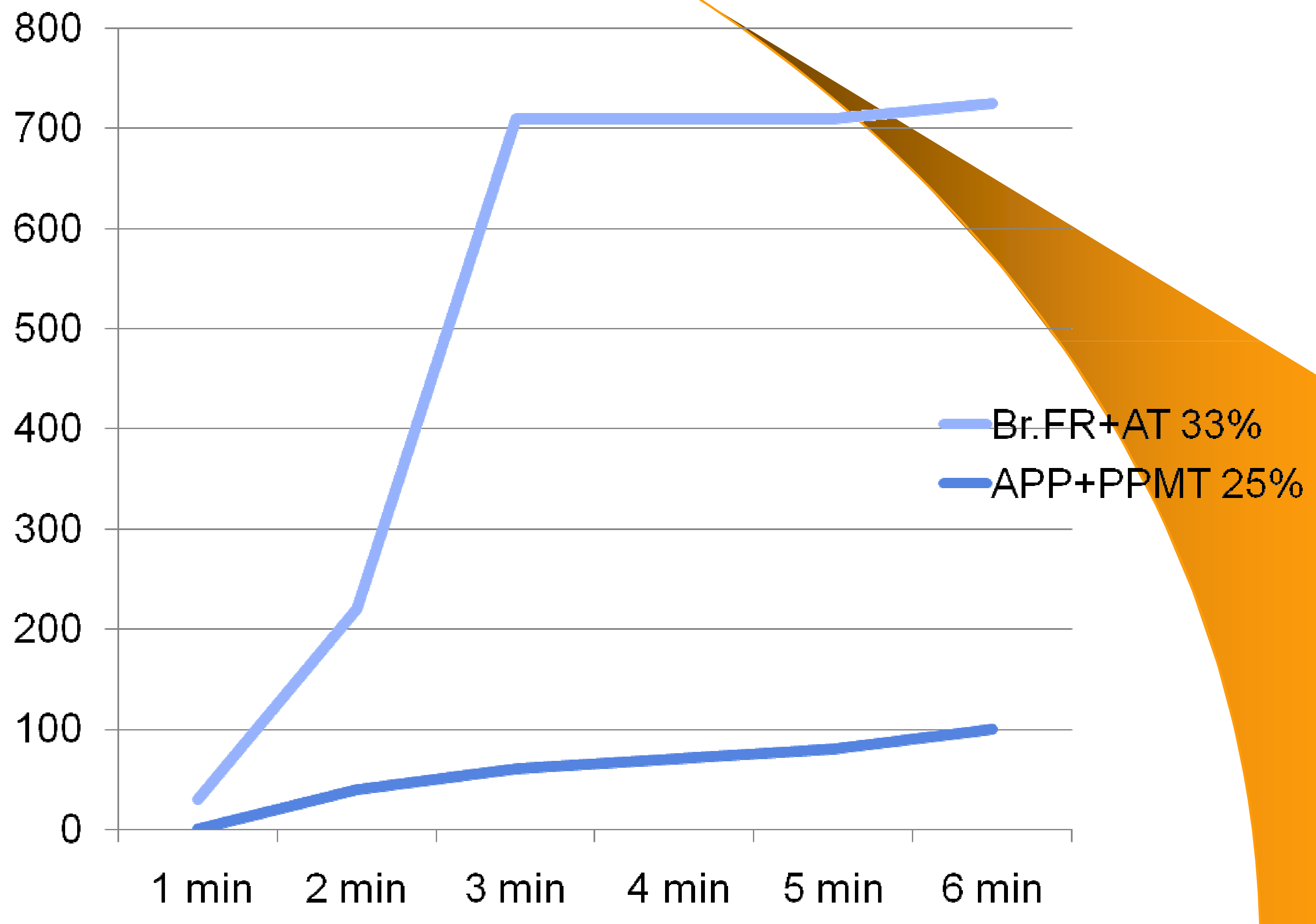

Typical Dosages of PPM Triazins as Secondary Flame Retardants

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- Combination with primary ammonium polyphosphate:

  Replacement of 25-50% of the primary FR; total concentration 20-35%
- Combination with primary mineral FRs:

  Replacement of 10-15% of the primary FR; total concentration 50-60%
- Combination with other flame retardants:

  Replacement of 5-10% of the primary FR; total concentration?

PPM Triazins: Registration Status

Chemical Name:

"Poly[[6-(4-morpholinyl)-1,3,5-triazine-2,4-diyl]-1,4-piperazinediyl]"

- REACH pre-registered (as a polymer)
- TSCA registered
- MITI registered

Summary and Conclusion

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- Fire resistance desired of all and required of many plastics items
- High loadings of fire retardants required, defeat the very purpose of the using of plastics as: a) Light-weight materials for energy saving b) easy and energy saving processing materials
- Use of secondary flame retardants in combination with primary flame retardants should enable to reduce the required loadings. However, more needs to done.
- Fire resistance need to be defined beyond LOI or UL 94 classifications, such as rate , maximum heat nature of combustion; And the nature and maximum concentration of the toxic gases in the event of fire.
- Non-hazardous, non-polluting (particularly in the event of fire) and more efficient fire retardant systems are required
- Imparting fire resistance need not always mean added cost, but it can certainly be an added value-in-use

Future Outlook

No single thing abides;

But all things flow;

Fragment to fragment clings;

The things thus grow;

Until we know them and name them;

By degrees they melt;

And are no more the things we know.

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in Life Sciences & Specialty Chemicals Industries

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