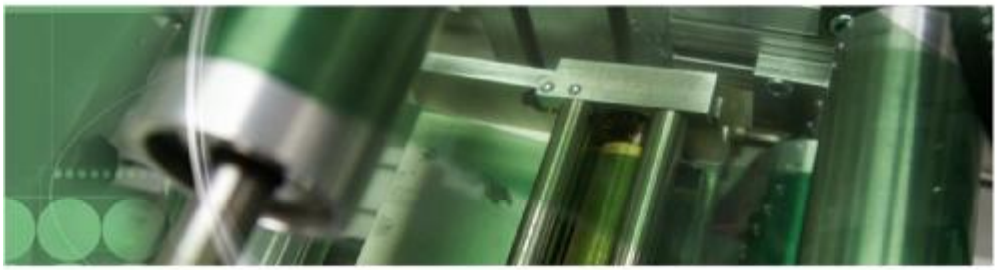

Development of new environmentally friendly and multifunctional flame retardants

Mélanie Aubert, Teija Tirri, Weronika Pawelec, Carl-Eric Wilén

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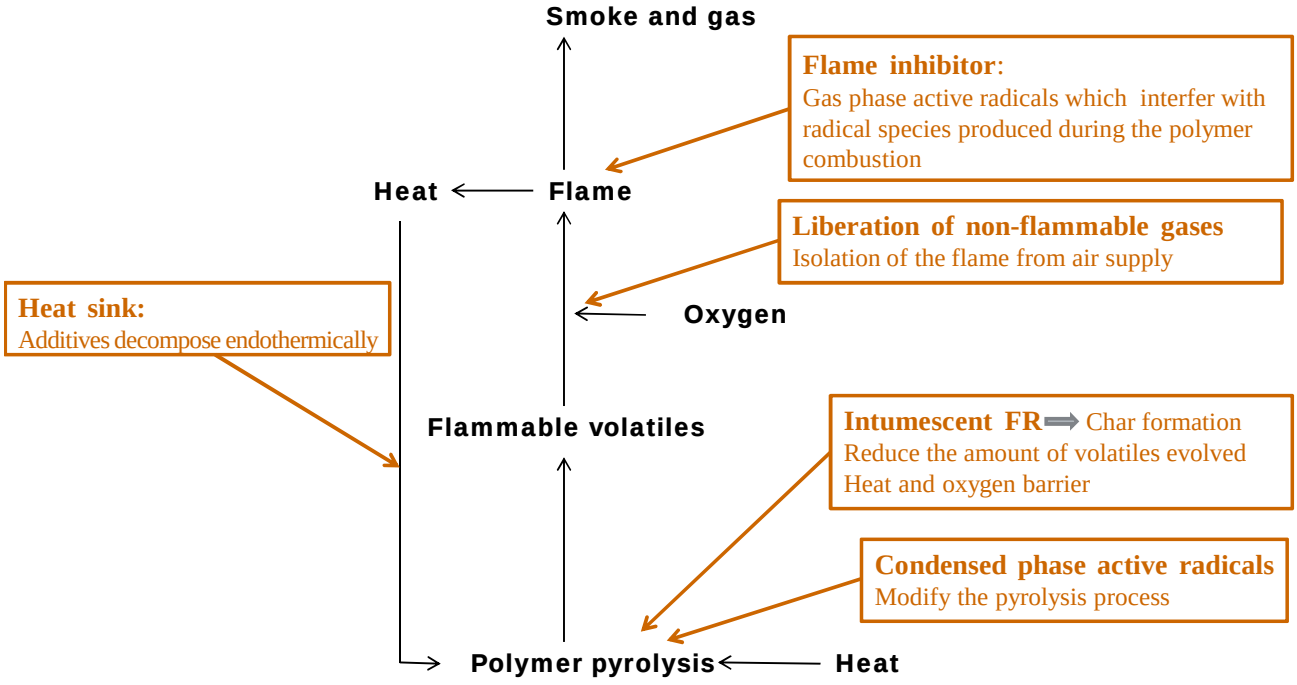
melanie.aubert@abo.fi

Funmat seminar 23.05.2012

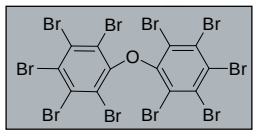
Introduction to flame retardants

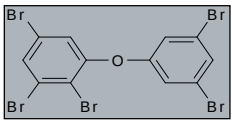


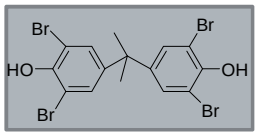
Common flame inhibitors : Halogenated flame retardants

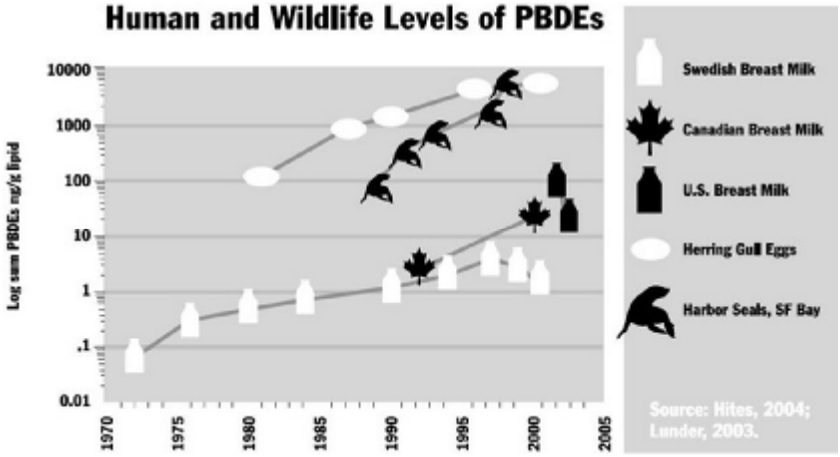
Disadvantages of halogenated FR´s

- Processing Problems (Odour, Corrosion, etc.)
- Loss of Physical/Mechanical Properties
- Decrease in UV Stability
- Environmental Concerns (bioaccumulation...)







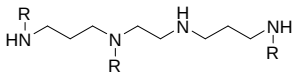


Certain polybrominated flame retardants have been banned by 2006.

Nitrogen based flame retardants

- no heavy metals or halogens
  - › environmentally friendly
- good flame retardancy at low concentrations of 0.5 -1 wt%.
- do not notably affect the mechanical properties or processing behavior of the product
- functions also as an efficient light stabilizer

NOR 116



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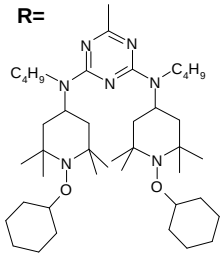
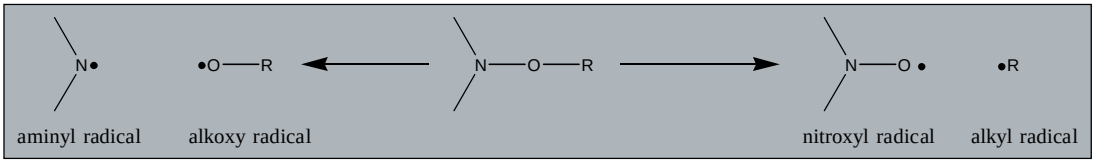
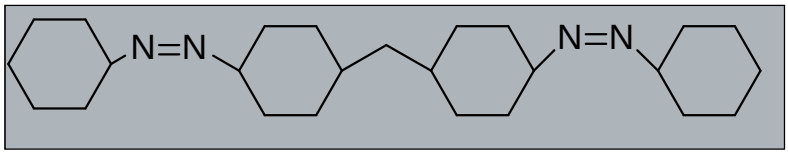


During the thermolysis of N-alkoxyamines, two cleavage processes may take place



Azoalkanes

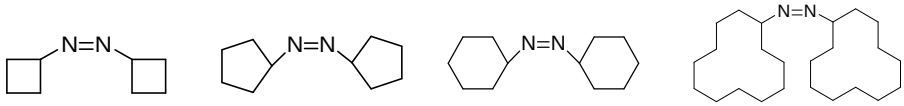
Novel flame retardants and their structure-property relationship



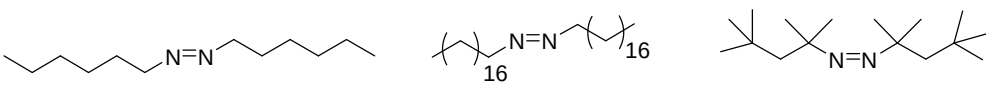
M. Aubert *et al.,* Polym. Adv. Tech., 2011, 22 (5)

Structure- Property Relationship

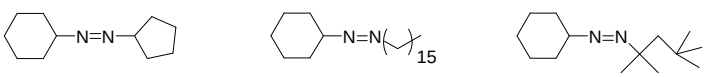
Variation of ring size: symmetrical 1,1'-biscycloazos



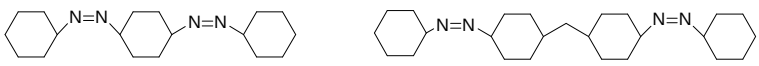
Linear symmetrical 1,1'-bisalkylazos



Unsymmetrical 1,1'-bisalkylazos

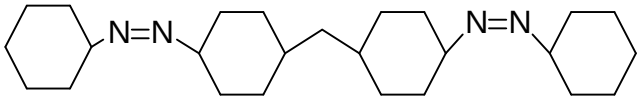


High molecular weight azos



Structure- Property Relationship: Conclusion

- Azoalkanes are an important and effective FR family
- Chemical structure is a key factor for the thermostability and therefore the FR activity
- Best candidate of this series:



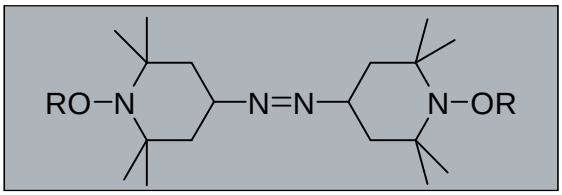
  - › Effective at concentration as low as 0.25-0.5 wt.%
  - › Low volatility
  - › No polymer discoloration
  - › No effect on polymer mechanical properties and processability
  - › As effective as NOR116 in thin polypropylene films (200 µm)
  - › More effective than NOR116 in thick polypropylene plaques (1 mm)
  - › Non dripping behavior
  - › Homogeneous burning

  - › Doesn't have any effect on light stability

Multifunctionnal Additives

Multifunctional Additives for Polypropylene combining

Flame Retardancy and Light Stability properties

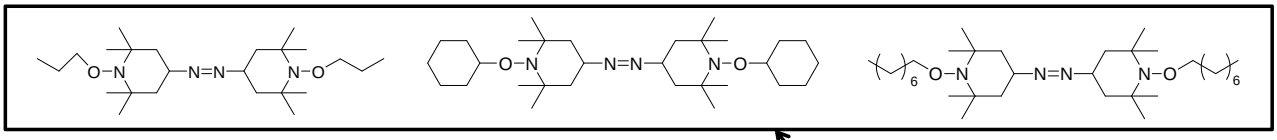


M. Aubert et al., Polym. Degrad. Stab., 2011, 96, 328
M. Aubert et al., " Synthesis of versatile bis(1-alkoxy-2,2,6,6-tetramethylpiperidin-4-yl)-diazenes and related structures and their utilization as multifunctional flame retardants forPP, LDPE and HIPS", submitted

Series of multifunctional AZONORs additives tested in PP films and plaques

All the compounds passed successfully the FR test

Most effective AZONORs
Shortest burning length and time



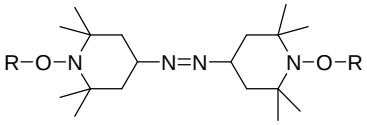
Their poorer FR activity could be attributed to the **lower thermal stability of NOR moiety** in comparison to the more effective AZONORs

Multifunctionnal Additives and their efficacy as FRs after and before artificial weathering

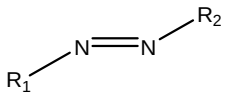
Additive	Thin section (200 µm)				Thick section (1 mm)						
	Burn. Length (mm)	Weight loss (%)	Burn. drips	FR Test	Burn. Length (mm)	Weight loss (%)	Burn. drips	FR Test	Artificial weathering Burn Length	Weight Loss	FR test
Control	190	100	yes	fail	100	100	yes	fail	Test failed before 400h		
NOR116 (0.5 wt%)	90	4.0	yes	pass	80	49.4	yes	fail	Test failed before 400h		
Cyclohexane azo (0.5 wt%)	92	3.8	yes	pass	47	12.9	yes	pass	Test failed after 800h		
NOR116 (0.25 wt%) + Azo (0.25 wt%)	92	3.8	yes	pass	44	14.5	yes	pass	Test failed after 1200h		
AZONO-propyl (0.5 wt%)	85	4.8	no	pass	27	5.2	yes	pass	30	7	pass
AZONO-me (0.5 wt%)	58	n.d.	no	pass	31	n.d.	yes	pass	70	n.d	pass

All the AZONORs passed successfully the FR tests
- in polypropylene thick section
- After 2000h of artificial weathering in polypropylene thick section

Multifunctionnal Additives: Conclusion



- With appropriate R group:
  - Superior FR efficacy in both thin and thick PP section Vs. AZO and NOR116
  - Multifunctional and excellent FR properties even after prolonged exposure to light and heat



Advantages
- High FR efficacy in thin and thick PP section at low loading 0.25-1 wt%
- No discoloration of PP
- No burning drips in PP films
- Excellent synergistic effect with ATH

Disadvantages
- Does not contribute to heat or light stability

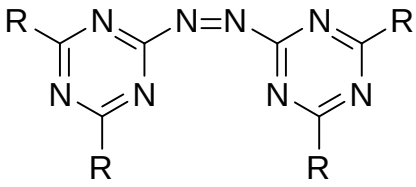
NOR116

Advantages
- High FR activity in thin PP section at low loading 0.5 wt%
- Multifunctional
- Excellent synergistic effect withbrominated FR

Disadvantages
- Limited FR efficacy in thick PP section
- Slight discoloration
- Burning drips

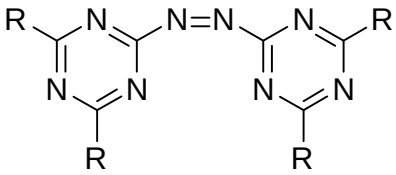
Bis-1,3,5-triazinyl azos

Heterocyclic Azos as Flame Retardants for Polypropylene



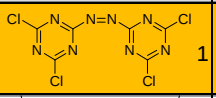
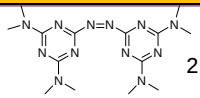
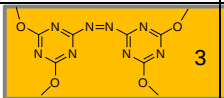
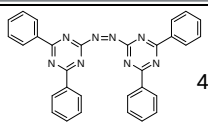
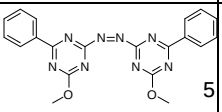
M. Aubert et al ” Bis-1,3,5-triazinyl azos: Heterocyclic azos as flame retardants for PP”, submitted

Heterocyclic azos: Bis-1,3,5-triazinyl azos



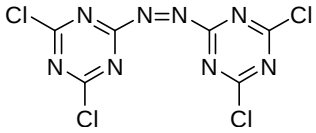
- Aromatic azos (mostly azobenzenes) represent the biggest tonnage and monetary value of all classes of dyestuffs.
- Aromatic azos are thermally and photochemically more stable than azo alkanes
- Toxicity issues: aromatic amines which are azobenzene metabolites and intermediates in manufacturing processes, are potentially carcinogenic and mutagenic depending on their molecular structure
- Bis-1,3,5-triazinyl azos metabolites and intermediates (amino-s-triazine) have low toxicity .

Bis-1,3,5-triazinyl azos

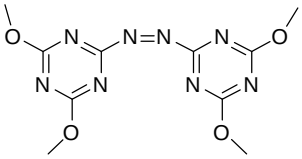
Compounds 0.5 w%	Tdec. (ºC)	Weight loss (%)	Av. damaged length (mm)	DIN4102-B2
 1	289	3.28	79	pass
 2	242	100	190	fail
 3	238	8.8	96	pass
 4	350	n.d.	152	fail
 5	270	n.d.	190	fail
3-$Zn(OAc)_2$ Metal complex 6	320	n.d.	155	fail
3-$Cu(OAc)_2$ 7 Metal complex	320	n.d.	80	pass

- Compounds 1 and 3 successfully pass the flammability test
- 7 is an active flame retardant and exhibits even shorter damaged length than 3 whereas 6 didn't pass the test.

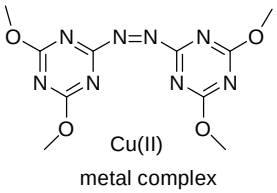
Bis-1,3,5-triazinyl azos: Conclusion



1



3

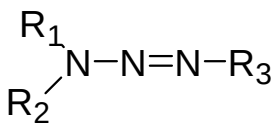


7

•We have been able to successfully synthesize a series of bis-1,3,5-triazinyl azos and to prove 1,3 and 7 are effective flame retardants for thin polypropylene films

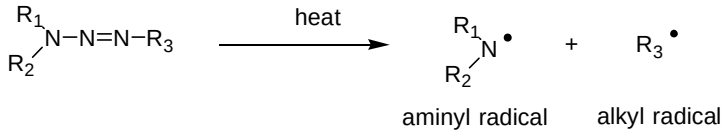
•For the first time we demonstrated that azo copper complexes could have good flame retardancy activity

Triazene compounds as a novel and effective class of flame retardants for polypropylene

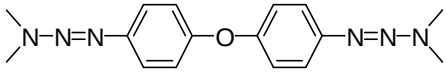


W. Pawelec et al, Polymer Degradation and stability, 2012

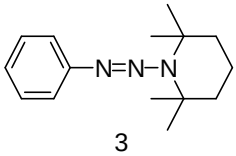
Series of synthesized and tested triazenes



•Like azos they are thermally unstable and their thermal stability can be tuned by tailoring of the molecular structure
•Unlike diazenes, the liberate aminyl radicals, alkyl radicals and nitrogen
•the following 4 structures have appropriate thermal stabiltiy for this application



1



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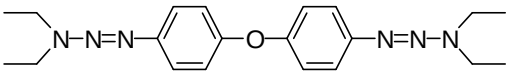

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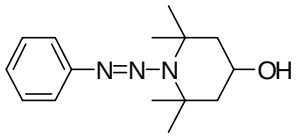
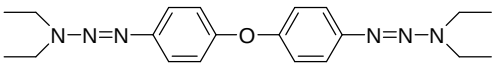


4

Flame retardancy activity of triazenes

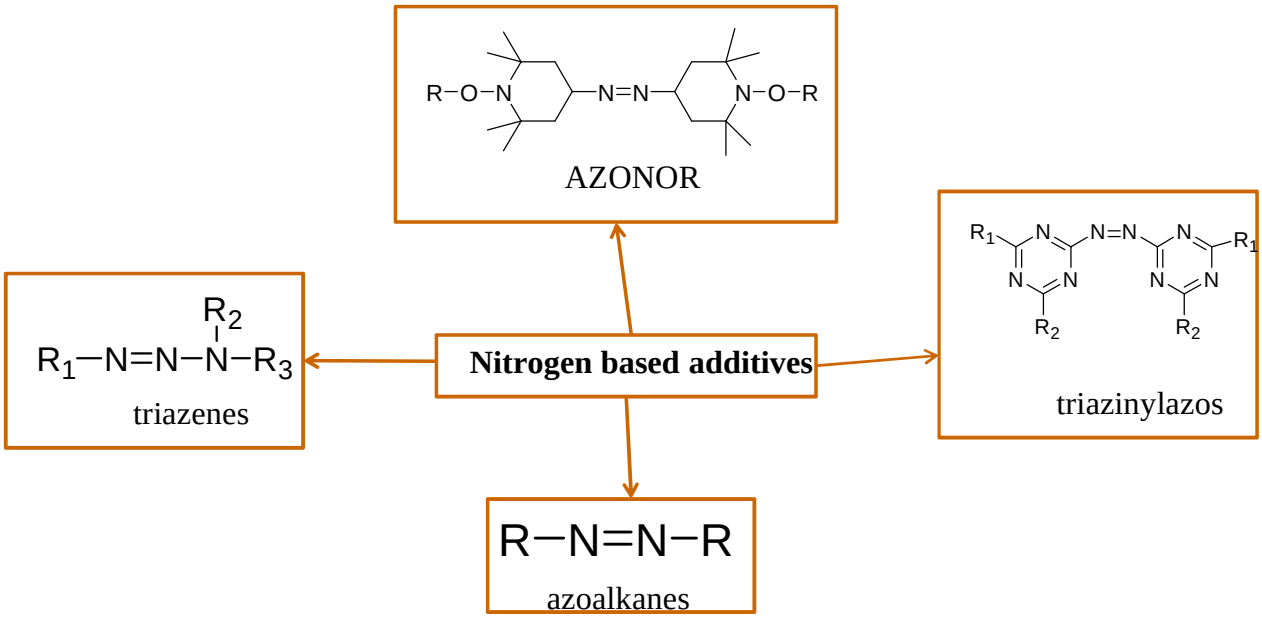
Formulation (0.5 Wt.%)	Av. Burn. Length (mm)	Av. Burn. Time (s)	Weight loss (%)	Paper ignition	DIN 4102-B2
Blank	190	33.3	100	yes	fail
NOR116	78	11	6.0	yes	pass
1	80	8.7	6.2	no	pass
2	77	7.0	4.4	no	pass
3	85	7.3	5.6	no	pass
4	89	8.3	3.7	no	pass



•No alteration of the physical or aesthetic properties of the polymer
•All the tested triazenes passed the flammability test successfully
•Unlike NOR116, no paper ignition was observed

⇨ New interesting radical generators for flame retarding of polymeric materials

Conclusion



Thank you for your attention

List of publications

- Articles
  - Azoalakanes: a novel class of flame retardants
    - Nicolas, R. *et al*. Rapid Comm. **2006**, 27(12), 976
  - Azoalkanes:Novel flame retardants and their structure-property relationship
    - M. Aubert ***et al.,*** Polym. Adv. Tech., **2011**, 22 (11), 1529
  - Azoalkanes: A Novel Class of Additives for Cross-linking and Controlled Degradation of Polyoefines
    - M. Aubert ***et al.,*** Macromol. Mater. Eng., **2007**, 292(6), 707
  - Bis(1-propyloxy-2,2,6,6-tetramethylpiperidin-4-yl)-diazene: An innovative multifunctional radical generator providing flame retardancy to polypropylene even after extended artificial weathering
    - M. Aubert ***et al.***, Polym. Degrad. Stab., **2011**, 96(3), 328
  - Synthesis of versatile bis(1-alkoxy-2,2,6,6-tetramethylpiperidin-4-yl)-diazenes and related structures and their utilization as multifunctional flame retardants for PP, LDPE and HIPS",
    - M. Aubert ***et al***., Polym. Degrad. Stab., **2012**, accepted
  - Triazene compounds as a novel and effective class of flame retardants for polypropylene
    - Pawelec, W ***et al***. Polym. Deg. Stab. **2012**, 97(6), 948.
  - Novel tetrapotassium azo diphosphonate (INAZO) as flame retardant for polyurethane adhesives
    - Tirri, T. ***et al.*** Polym. Deg. Stab. **2012**, 97(3), 375
  - Bis-[1,3,5]triazinyl diazenes: Heterocyclic diazenes as Flame Retardants in Polypropylene Films
    - T. Tirri ***et al***. **2012**, submitted
- Patents
  - Azo compound flame retardant compositions
    - Nicolas, R.; Wilén, C. **2005**, WO 2005030852
  - Symmetric azo compounds in flame retardant compositions
    - Roth, M.; Pfaendner, R.; Wilen, C.-E.; Aubert, M., **2008**, WO 2008101845
  - Phosphinic acid hydrazide flame retardant polymer compositions
    - Kniesel, S.; Hoppe, H.; Pfaendner, R.; Xalter, R.; Wilen, C.-E.; Pawelec, W.; Aubert, M.,**2012,** WO 2012013565