33rd Cotton Conference

Polyphosphazenes as halogen free flame retardants for textiles

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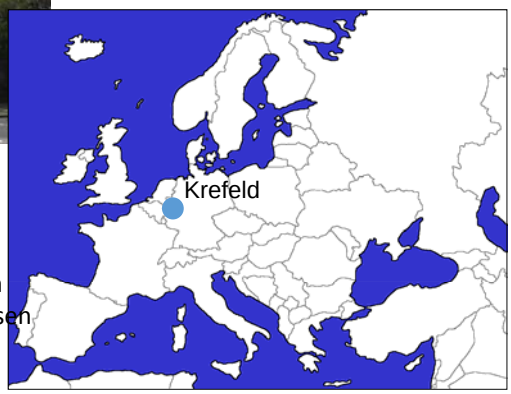
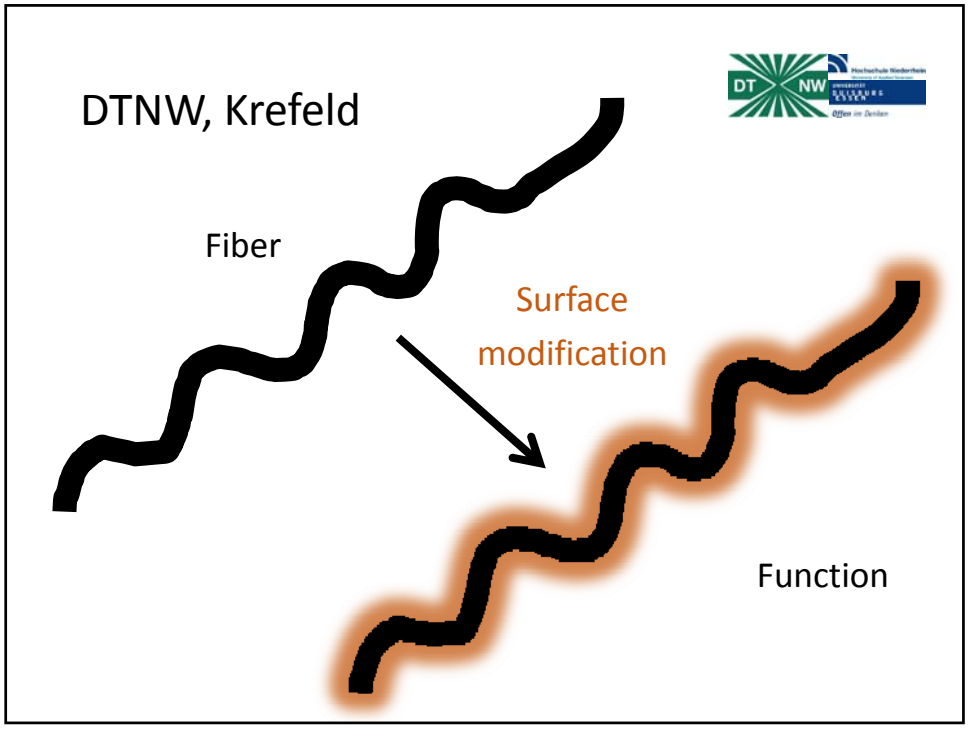
DTNW

Deutsches Textilforschungszentrum Nord-West



- Research institute
- Associated Member:
  - Hochschule Niederrhein
  - Universität Duisburg-Essen

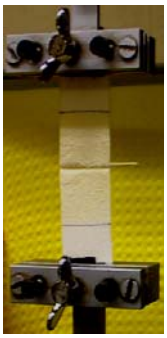


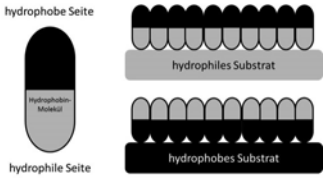
Methods

- thermal
- wet chemical
- sol-gel process
- super-critical fluids
- physical
- photo-chemical
- laser
- …

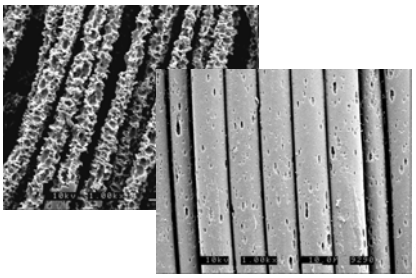
Wettability, adhesion

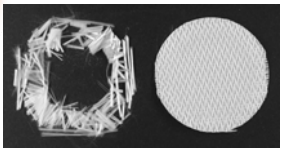
hydrophil
hydrophob
oleophob





Barrier-layers



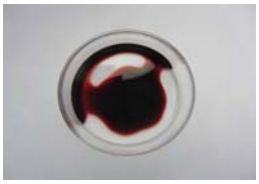


Protection againts:
-chemistry
-abrasion/wear
-light (UV or IR)

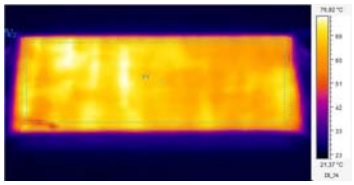
New green dyeing solvents

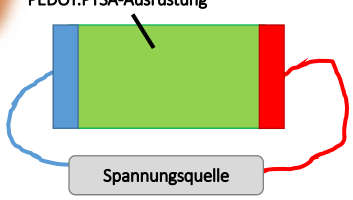
$scCO_2$

Ionic Liquids

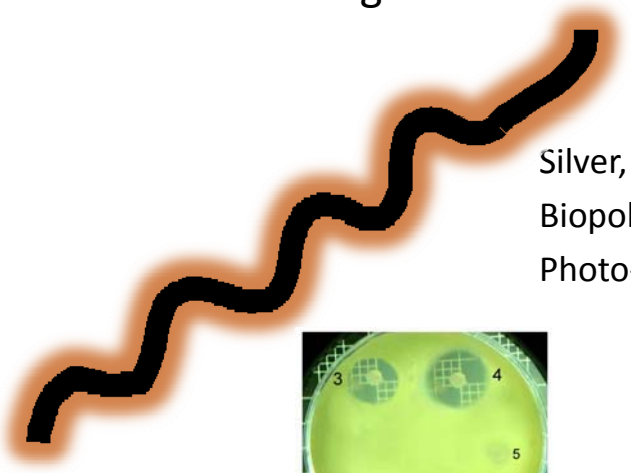


Conductive Texiles



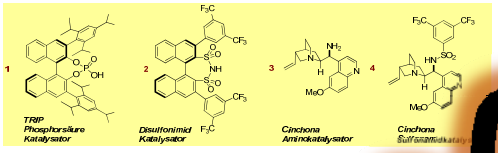


Antimicrobial Textiles
Antifouling Textiles



- Silver, Copper, Zinc
- Biopolymere
- Photo-catalytic surfaces

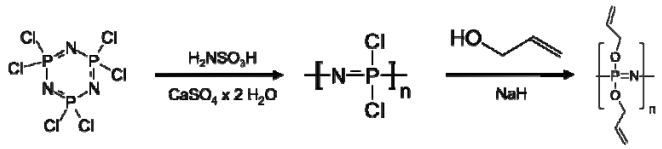
Organotextile Catalysis



Environmental Remediation - Urban-Mining

Ausgezeichnet mit dem Deutschen Rohstoffeffizienz-Preis 2014

Flammschutz



Why flame retardants?
Why halogene free?

- World: 300.000 dead by fire
  + serious burns/deformation
- Europe: 25.000 dead at 2.5 million fire
- 1 % economical damage
- 80 % dead at house fire

Why no halogens?

- Environmental problem
- Toxicity, persistent, bioaccumulation, cancerogenice
- REACH / Ban of use

Why flame retardant textiles?

Cotton

Cotton/PET
50:50

PET

Cotton/PET
50:50

Why flame retardant textiles?

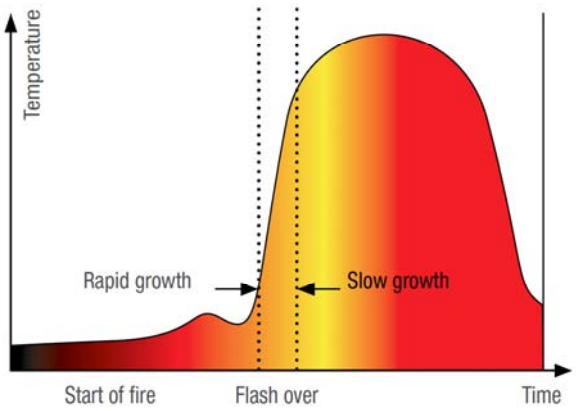
Cotton

Cotton/PET
50:50

PET

Cotton/PET
50:50

Task of a flame retardant



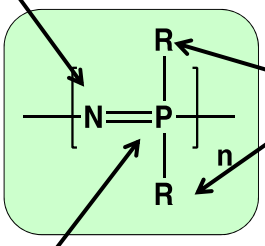
US National Fire Protection Association

Functions of Flame retardants

- Dilution of the gas phase by
  - Nitrogen
  - Water
- Radical Scavenger
  - Bromine or Chlorine compounds
- Formation of a barrier layer
  - Char formation (phosphor compounds/nanoclays)
  - Intumescent layer

Why polyphosphazenes?

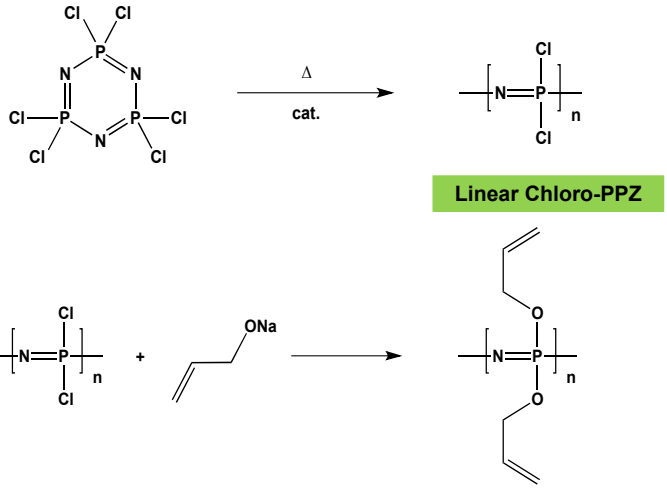
Nitrogen:
- dilution of gas phase



- Anchor Groups
  - properties modification
- further flame retardant function

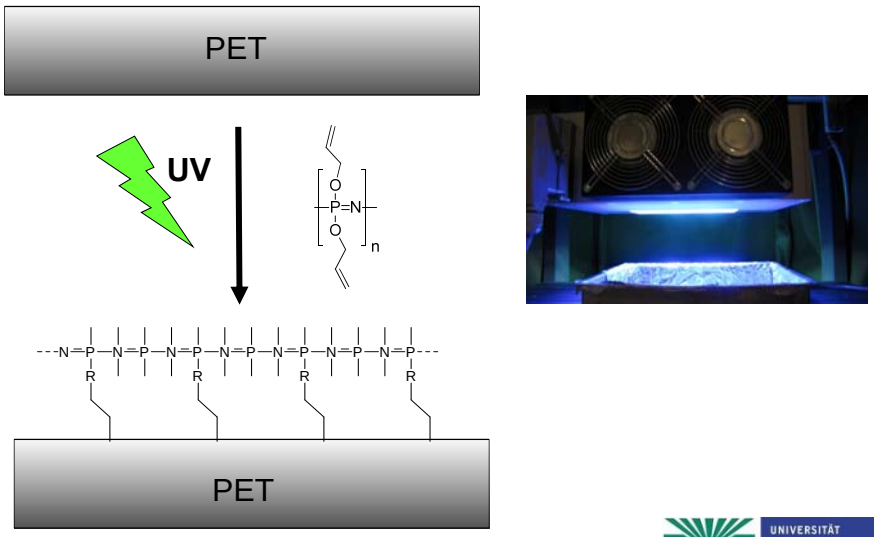
Phosphor:
- Char and
- Barrier layer formation

Solvent-based synthesis of polyphosphazenes



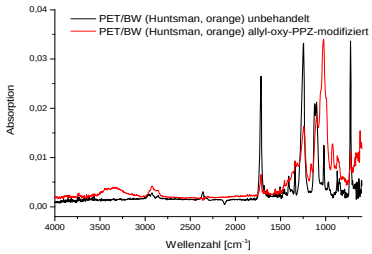
Mujumdar, A. N.; Young, S. G.; Merker, R. L.; Magill, J. H. Macromolecules 1990, 23, 14–21., DOI: 10.1021/ma00203a004

Next step: Photo-induced immobilization



Characterization Cotton/PET (50/50)

FT-IR (ATR)



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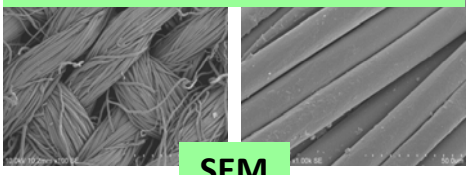
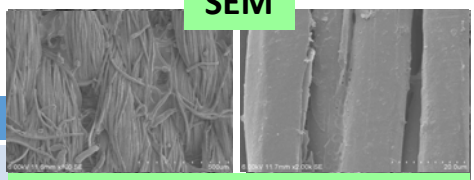


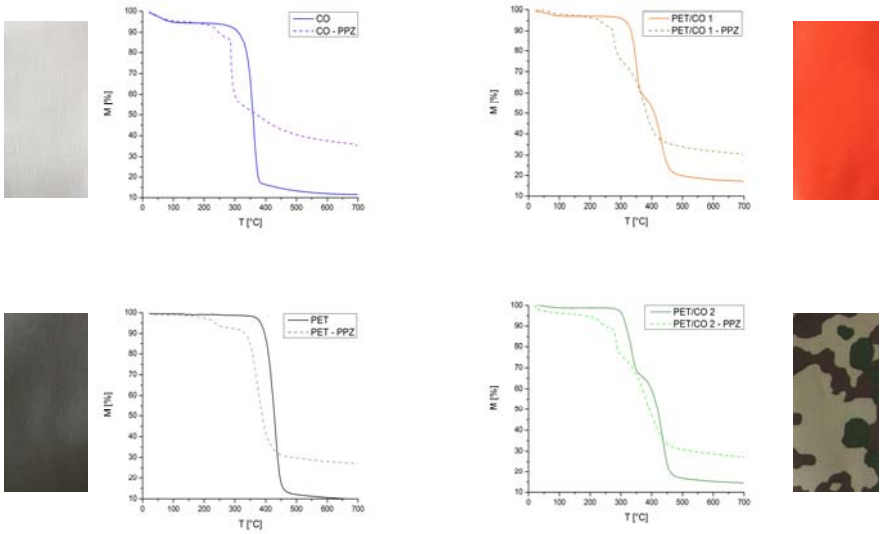
SEM



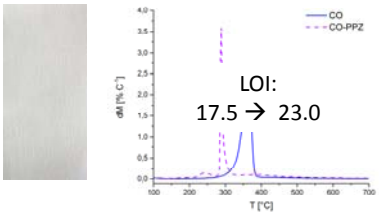
PPZ-modified

Analyses			
Add-on	22.3 wt.-%		
P-content (ICP-OES)	3.06 wt-%		
EDX (surface composition)	C	O	P
Blank	50.2 %	49.8 %	0
Allyl-oxy-PPZ modified	49.9 %	31.6 %	18.5 %

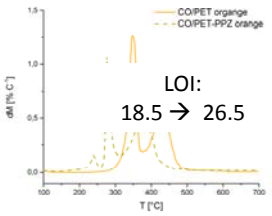
Flame retardant performance pre-testing by TGA



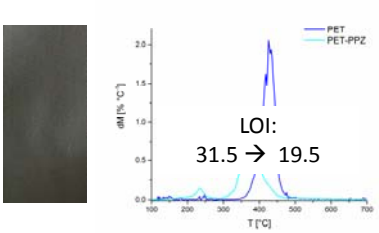
Flame retardant performance
Pre-testing by TGA



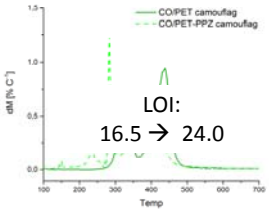
LOI:
17.5 → 23.0



LOI:
18.5 → 26.5



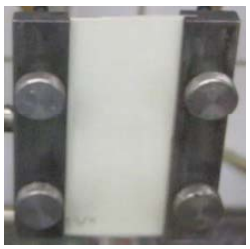
LOI:
31.5 → 19.5

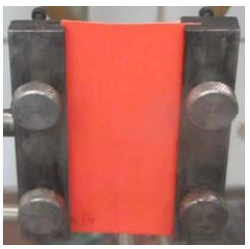


LOI:
16.5 → 24.0

Flame retardant performance
"DIN EN ISO 15025"

Cotton



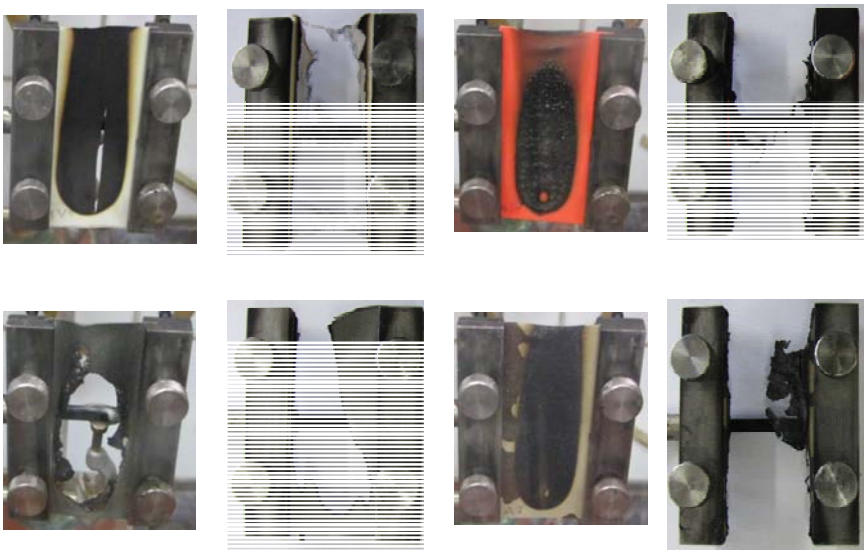


Cotton/PET
50:50

PET

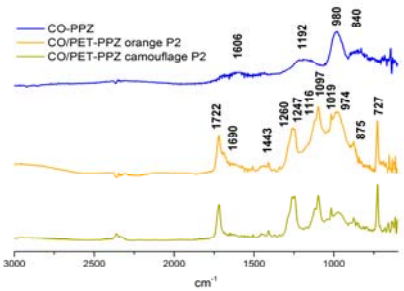
Cotton/PET
50:50

Flame retardant performance
"DIN EN ISO 15025"

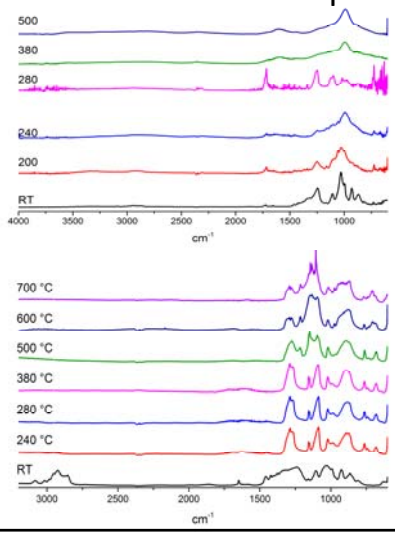


Mechanism: Char Analysis - Thermal decomposition

IR - Char



IR – thermal decomp.



Washing resistance
Example: Cotton/PET Blend (50/50)

untreated

1 Washing Cycle
Add-on 26.7 %

2 Washing Cycles
Add-on 26.7 %

6 Washing Cycles
Add-on 25.8 %

No significant loss of weight
No significant loss of flame retardant performance

Abrasion resistance
Example: Cotton/PET Blend (50/50)

5 k rounds

10 k rounds

50 k rounds

No significant loss of weight
No significant loss of flame retardant performance

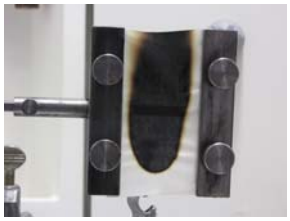
Summary

- polyphosphazenes are suitable halogen-free flame retardants
- permanent and resistant finishing of textiles
- curing of AllylPPZ by UV-irradiation
- Adjustable loading in the range of 10 - 50 wt.-%
- Ideal flame retardant for Cotton/PET blends and pure cotton
- Significantly change in melting behavior of PET by PPZ finishing

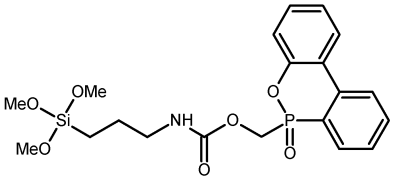
Outlook – Sol-Gel

N-P-Silane – Flame retardant test

+14.5 %



+6.3 %



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Permanent Flame Retardant Finishing of Textiles by Allyl-Functionalized Polyphosphazenes

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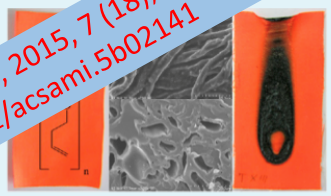
Supporting Information

ABSTRACT: Despite their excellent flame retardant properties, polyphosphazenes are currently not used as flame retardant agents for textile finishing, because a permanent fixation on the substrate surface has failed so far. Here, we present the succe[illegible] synthesis and characterization of a noncombustible [illegible] forming polyphosphazene derivative, that can b[illegible] durably on cotton and different cotton/polye[illegible] using photoinduced grafting reaction[illegible] properties are improved, a higher l[illegible] and the modified textiles pa[illegible] tests. As flame retardant[illegible] the immobilized p[illegible] observed. Th[illegible] decomp[illegible] the[illegible] ...ubstrate was ...duces an earlier ...reduced mass loss in ...mposition of cotton and polyester leads to the formation of phosphorus oxynitride, which ...on the fiber surface. In addition, the permanence of the flame retardant finishing was proven by [illegible]



[illegible]on, polyester/cotton blends, textiles, polyphosphazenes, permanent flame retardant finishing, ph[illegible]mmobilization

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Thank you for your attention!!!

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