



FLAME RETARDANT COMPOUNDS: NEW RECYCLING OPPORTUNITIES

Arese 17-18 Maggio 2023
Micaela Lorenzi, GREENCHEMICALS Srl
PALMAROLE AG

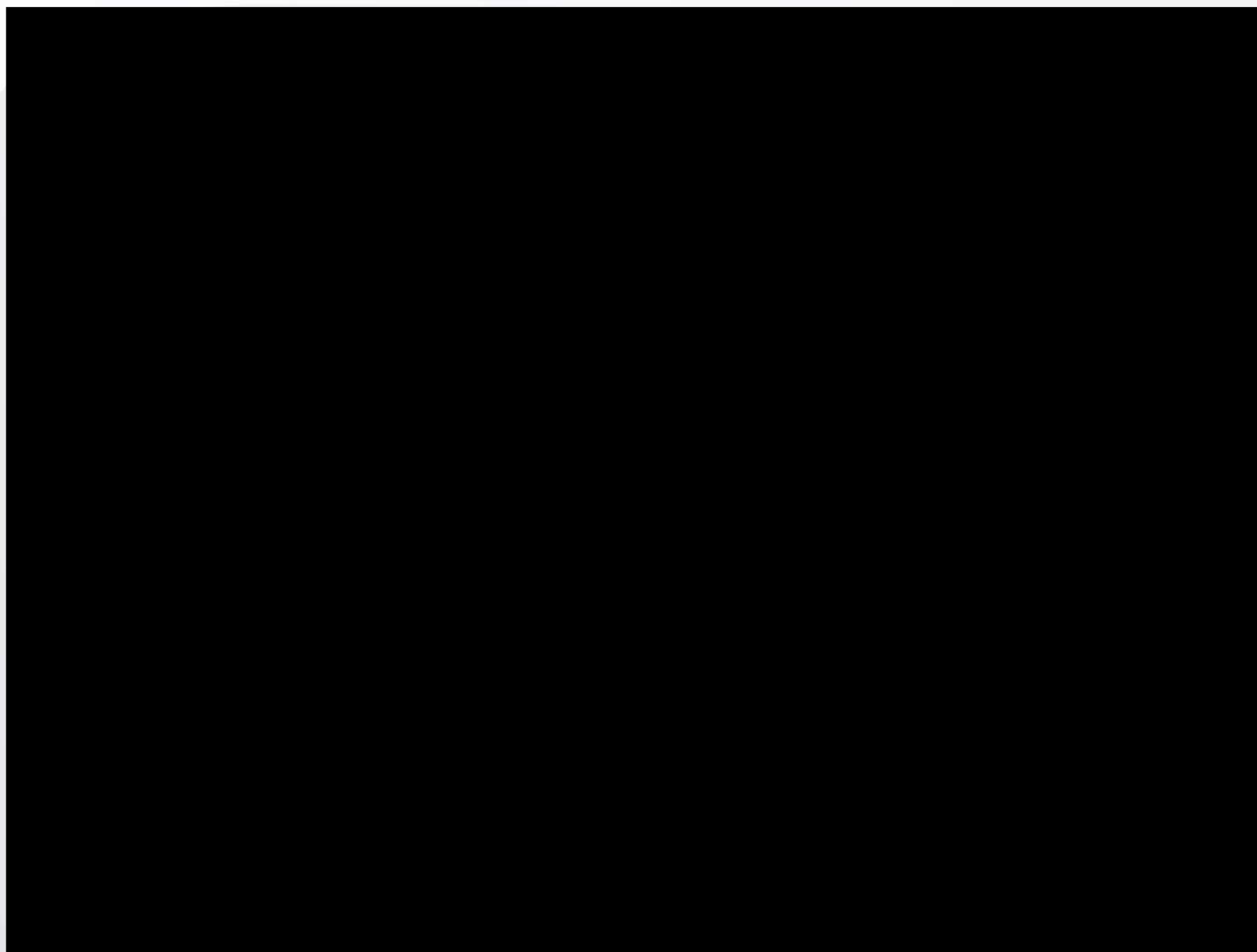
plast PLAST:DESIGN
COMPONENTI E PRODOTTI DI MATERIE PLASTICHE - PLASTIC PRODUCTS AND COMPONENTS



TABLE OF CONTENTS



- **FLAME RETARDANTS TODAY'S CONTEST**
- **HALOGENATED AND HALOGEN FREE: PRO AND CONTRO**
- **THERMAL STABILITY CONCEPT**
- **CHEMISTRY OF FR COMPOUND RECYCLING PROCESS**
- **WHAT CAN WE DO POLYMER BY POLYMER, PP, PA, PBT**
- **CONCLUSIONS**

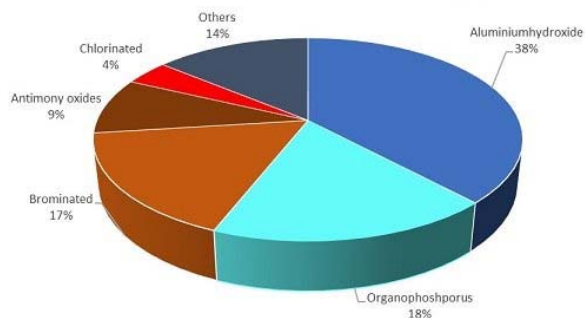


- **FR 2,2 MILLIONS MTs/YEAR, WITH GROWTH OF 3%/YEAR.**
- **1/3 ARE HALOGENATED WITH ANTIMONY TRIOXIDE AS SYNERGIST**

HALOGENS AND ANTIMONY TRIOXIDE CONCERNS

- Endocrine and systemthyroid disruption
- Impacts to the immune
- Reproductive toxicity
- Cancerogenic
- Adverse effects on fetal and child development
- Neurologic function

World consumption of flame retardants by type, 2019

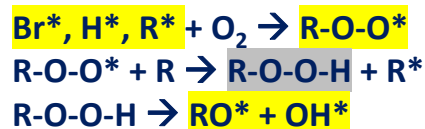


CRITICAL POINTS FOR HALOGEN FREE BROS

- 1) **MECHANICAL PROPERTIES**, due to higher loading level and low melting point;
- 2) **PRICE GAP**
- 3) **LOWER THERMAL STABILITY**

BROMINATED FR

R-Br



HBr/ HPO₄ IS CAUSING ACIDITY IN EXTRUDER, RUST AND CORROSION AND DEPOLIMERIZATION (MFI INCREASE WITH LOSS OF MECHANICAL PROPERTIES IN PA/PET/PBT/PC !

RADICALS ARE RESPONSIBLE FOR MFI INCREASE IN MANY POLYMERS, WITH BIG DECAY OF MECHANICAL PROPERTIES; THEY ARE ALSO CHANGING COLOR, PROMOTING OXIGEN REACTION ON POLYMER CHAIN; **PEROXIDES** ARE GENERATING VERY FAST NEW RADICALS, MAKING RADICAL GROWING CURVE, EXPONENTIAL.

RED P, PHOSPHATE AND PHOSPHINATES

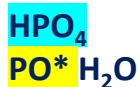
RED-P



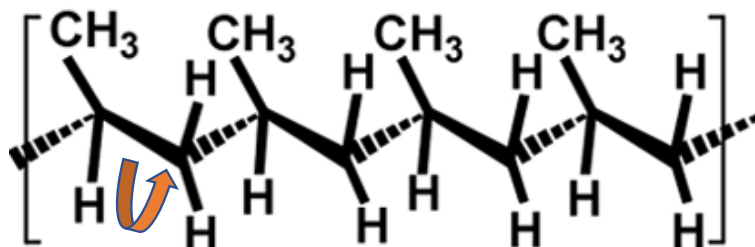
PHOSPHINATE



PHOSPHATE

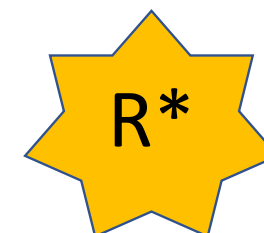


POLYPROPYLENE



LOI	
PS	17
ABS	18
PA	24
PC	27
PP	17

HIGH LOI	→	BAD FLAME RETARDANT RESISTANCE
N AND O IN CHAIN	→	ALL FLAMABLE GASES
LOW PROC. TEMP. 200°C-280°C	→	WIDE RANGE OF FR
NO PRESENCE OF N AND O	→	BAD CHAR
RADICAL POLYMERIZATION / ZIEGLER NATTA	→	DRIPPING
CROSS-LINKING ABILITY	→	VERY BAD



FR POLYPROPYLENE FORMULATIONS

FLAME RETARDANT PACKAGE	TEST	TYPE OF FR	DOSAGE
GC DPE 81+ Sb ₂ O ₃	UL94 V0	HALOGEN + Sb	22%
GC HF 1000 (intumescent)	UL94 V0	HALOGEN FREE	27%
GC BDDP 68+ Sb ₂ O ₃	UL94 V2	HALOGEN + Sb	4%
GC DRIPP HF 70 (low Halogen)	UL94 V2	HALOGEN FREE	2%
GC HF D 40 (Halogen free)	UL94 V2	HALOGEN FREE	6-8%

FR POLYPROPYLENE MECHANICS

TEST TYPE	IZOD ISO 180 (KJ/m ² with cut)	IZOD ISO 180 (KJ/m ² without cut)	YIELD STRENGTH (N/mm ²)	ELONGATION BREAK (%)
PPV2 LOW HALOGEN	2,25	47,9	32,85	11,43
PPV2 HALOGEN	1,88	38,7	34,22	13,81
PPV0 HALOGEN	1,94	38,13	29,44	17,99
PPV0 HALOGEN FREE	1,63	15,16	27,38	6,03

HALOGENATED PP V0 WITH AND WITHOUT STABILIZATION

X EDIZIONE
**SMART
PLASTICS**
'TECNOPOLIMERI A CONVEGNO'

17 | 18
MAY 23
MUSEO STORICO
ALFA ROMEO

GC
GreenChemicals
IMPROVE YOUR PERFORMANCE

PP HAL= PP + 22% MB PP DETO 31

Compound has been kept at 200 °C for different time.



0
h



1
h



2
h



4
h



PP HAL st = PP + 22% MB EVA DETO 31 + MB PO POX 20-4



0
h



1
h



2
h



4
h



**MUCH MORE
STABLE!**

plast PLAST:DESIGN

HALOGENATED PP V2 WITH AND WITHOUT STABILIZATION

X EDIZIONE
**SMART
PLASTICS**
'TECNOPOLIMERI A CONVEGNO'

17 | 18
MAY 23
MUSEO STORICO
ALFA ROMEO

GC
GreenChemicals
IMPROVE YOUR PERFORMANCE

PP HAL= PP + 6 % MB PP BATO 21

Compound has been kept at 200 °C for different time.



0
h



1
h



2
h



4
h



PP HAL= PP + 6 % MB PP BATO 21 + MB PO POX 20-4



0
h



1
h



2
h



4
h



**MUCH MORE
STABLE!**

plast PLAST:DESIGN
COMPONENTS & PRODUCTS TO DESIGN PLASTIC PARTS AND COMPONENTS

HAL FREE PP V0 WITH AND WITHOUT STABILIZATION



PPV0 HALOGEN FREE = PP + 27 % HF1000

Compound has been kept at 200 °C for different time.



1
h



2
h



3
h



4
h

PPV0 HALOGEN FREE = PP + 27 % HF1000 + MB PO POX 20-4



1
h



2
h



3
h



4
h



**HAL FREE PP V2
WITH AND WITHOUT
STABILIZATION**

X EDIZIONE
**SMART
PLASTICS**
'TECNOPOLIMERI A CONVEGNO'

17 | 18
MAY 23
MUSEO STORICO
ALFA ROMEO

GC
GreenChemicals
IMPROVE YOUR PERFORMANCE

PPV2 HALOGEN FREE = PP + 2% GC DRIPP HF 70

Compound has been kept at 220 °C for different time.



1
h



2
h



3
h



4
h



PPV2 HALOGEN FREE st= PP + 2% GC DRIPP HF 70 + MB PO POX 20-4



1
h



2
h



3
h



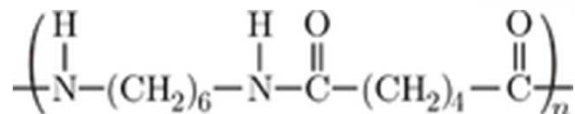
4
h



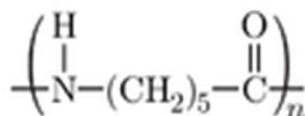
**MUCH MORE
STABLE!**

plast PLAST:DESIGN

POLYAMIDE



Nylon 66



Nylon 6

LOI

PE	17
ABS	18
PA	24
PC	27
PTFE	95

MAIN FR FEATURES

HIGH LOI	→	GOOD FLAME RESISTANCE
N AND O IN CHAIN	→	LESS FLAMMABLE GASES
HIGH PROCESSING T, 230°C – 280°C	→	FR MUST BE THERMAL RESISTANT
PRESENCE OF N AND O	→	CHAR
POLICONDENSATION	→	DRIPPING
CROSS-LINKING ABILITY	→	CROSS-LINK



FR POLYAMIDE FORMULATIONS

FLAME RETARDANT PACKAGE	TEST	FR TYPE	DOSAGE
GC DPE 81+ Sb₂O₃	UL94 V0, 30%GF	HALOGEN + Sb	20%
GC BPS 67+ Sb₂O₃	UL94 V0, 30%GF	HALOGEN + Sb	22%
GC PAP 12 (PHOSPHINATE)	UL94 V0, 30%GF	HALOGEN FREE	18%

HALOGENATED PA V0 WITH AND WITHOUT STABILIZATION

X EDIZIONE
**SMART
PLASTICS**
'TECNOPOLIMERI A CONVEGNO'

17 | 18
MAY 23
MUSEO STORICO
ALFA ROMEO

GC
GreenChemicals
IMPROVE YOUR PERFORMANCE

Compound has been kept at 220 °C for different time.

PA HAL= PA66 + 20% MB EVA DETO 31



PA HAL= PA66 + 20% MB EVA DETO 31 + MA PA POX ED71



**MUCH MORE
STABLE!**

plast PLAST:DESIGN
COMPONENTI E PRODOTTI DI MATERIE PLASTICHE PLASTICI, PRODOTTI E ACCESSORI

HAL FREE PA V0 WITH AND WITHOUT STABILIZATION

Compound has been kept at 220 °C for different time.

X EDIZIONE
**SMART
PLASTICS**
'TECNOPOLIMERI A CONVEGNO'

17 | 18
MAY 23
MUSEO STORICO
ALFA ROMEO

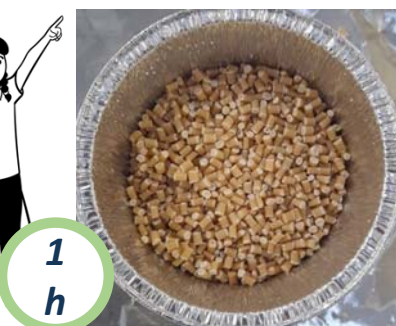
GC
GreenChemicals
IMPROVE YOUR PERFORMANCE



PAV0 HALOGEN FREE PA
+ 18 % GC PAP 12

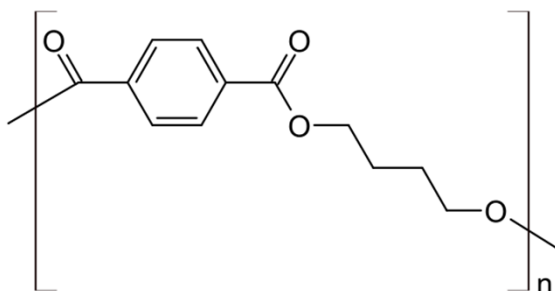


PAV0 HALOGEN FREE PA +
18 % GC PAP 12+
STANDARD STABILIZATION



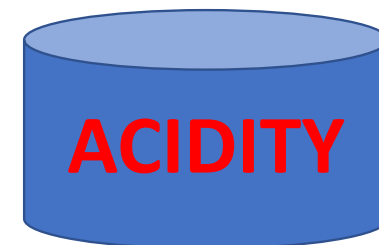
PAV0 HALOGEN FREE PA +
18 % GC PAP 12+
+ GC PA POX ED71

POLYBUTYLEN TEREPHTHALATE



LOI	
PE	17
ABS	18
PET	24
PBT	23
PC	27
PTFE	95

- HIGH LOI → GOOD FLAME RESISTANCE
- PRESENCE OF ETHEROATOMS → NOT FLAMABLE GASES
- T PROCESS PET 260°C – 290°C → FR MUST BE THERMAL RESISTANT
- PBT 230°C-270°C
- ETHEROATOMS IN CHAIN → CHAR
- POLYCONDENSATION → DRIPPING
- EASY TO CURE → CROSS-LINK





NOFIA HM1000

Phosphonate omopolymer, 10,5 % P, Tm= 110-120°C

- Polymeric, Hal free, P based flame retardants.
- GreenScreen 3, ChemFORWARD SAFER B. Oekotex 100 listed, RoHS, TCO – all compliant.
- Use in inherently FR Polyester fiber. Including rPET.
- Also use in molded and extruded PET. Including rPET.
- Replacement for KPFBS in thin PC sheet and molded compounds. Transparent and filled.
- Use in PC/ABS, and other PC blends, to get V0 at 0.8mm, with up to +30C HDT improvement.
- In PU used in Auto interior for Chinese quality low odor, and meet VDA 278.
- Also part of formulation to replace TCPP + Melamine in British Standard foam
- Use in graphite free PU formulae for “Under hood”, EVs and other.

PBT



GC DPE 81+ Sb ₂ O ₃	UL94 V0	HALOGEN + Sb	20%
GC BPS 67+ Sb ₂ O ₃	UL94 V0	HALOGEN + Sb	22%
NOFIA + MPP+PTFE	UL94 V0	HALOGEN FREE	25%
NOFIA + MPP+PTFE+GF30	UL94 V0	HALOGEN FREE	30%

TEST TYPE	IZOD ISO 180 (KJ/m ² with cut)	IZOD ISO 180 (KJ/m ² without cut)	YIELD STRENGTH (N/mm ²)	ELONGATION BREAK (%)
PBT GF 30%	9,5	36,00	55	2,7
PBT V0 HALOGEN FREE	2,18	16,18	46	1,6
PBT V0 GF 30% HALOGEN FREE	2,25	17,44	50,6	1,9

PBT

PBT HAL= PBT + 20% MB EVA DETO 31



1
h



2
h



3
h



4
h

Compound has been kept at 220 °C for different time.



PBT HAL= PBT + 20% MB EVA DETO 31 + MB EVA POX 900



1
h



2
h



3
h



4
h

**MUCH MORE
STABLE!**



HALOGEN FREE PBT V0



Compound has been kept at 220 °C for different time.

PBT HAL= PBT + 15% NOFIA HM1000 + 10% MPP



CONCLUSIONS



- IMPROVEMENT IN TECHNOLOGY AND ECONOMICAL CHANGE MAKE **HALOGEN FREE MORE INTERESTING**
- KNOWN HALOGEN FREE FORMULATIONS ARE GENERALLY **LESS RECYCLABLE**.
- IT'S CLEAR THAT **FLAME RETARDANT COMPOUND CAN BE RECYCLED**

