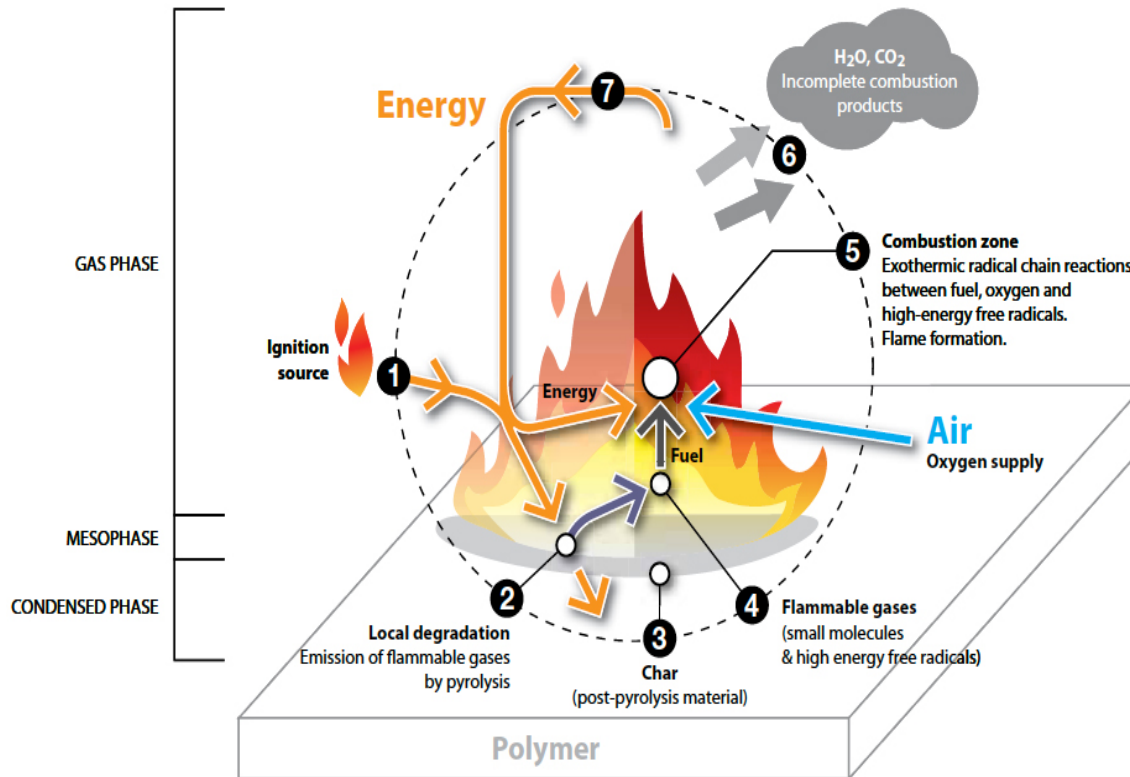


# FIRE RESISTANCE vs ENVIROMENTAL CONCERNS IN ENGINEERING THERMOPLASTIC POLYMERS

**Micaela Lorenzi**  
**Ethel Garlaschi**  
**15-May-2019**  
**ARESE- ITALY**

- POLYMERS THERMAL DEGRADATION MECHANISM
- FLAME RETARDANT MECHANISMS: 1) WATER DEVELOPMENT *HF*, 2) GAS PHASE *Br-Sb* vs *HF*, 3) DRIPPING *Br* vs *HF*, 4) CHAR *HF*, 5) INTUMESCENT *HF*
- ENGINEERING POLYMERS FR: PA, PBT-PET, PC, PC/ABS, PPO/HIPS, ABS, HIPS.
- CHOICE CRITERIA
- CONCLUSIONS

# COMBUSTION



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## OXIDATION CHEMICAL REACTION

Development: **HEAT**  
**FLAMES**  
**SMOKE AND GAS**

## STEPS OF COMBUSTION:

**HEATING**  
**DECOMPOSITION**  
**IGNITION**  
**COMBUSTION**  
**PROPAGATION**

## RADICAL REACTION

Oxygen is used by H• for radical chain degradation:



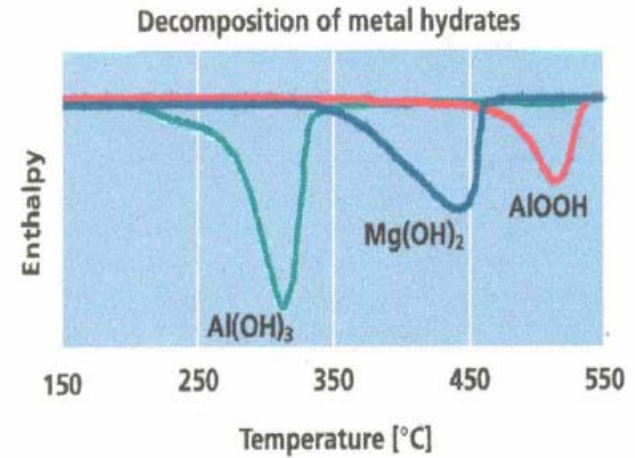
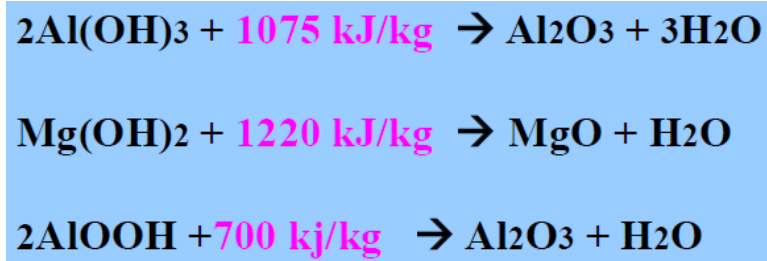
## LOI: Limiting Oxygen Index

**LOI: It is the minimum oxygen percentage needed to make a polymer burning**

Polymer	Oxygen Index(% O <sub>2</sub> )
PMMA	17.3
PP	17.5
PS	17.8
Paper	18.2
ABS	18.8
PET	20.0
NORYL	24.3
PA 6,6	24.3
PC	24.9
Polifenilen ossido	30.0
Polisolfone	38.0
PVC	40.3
PTFE	95.0

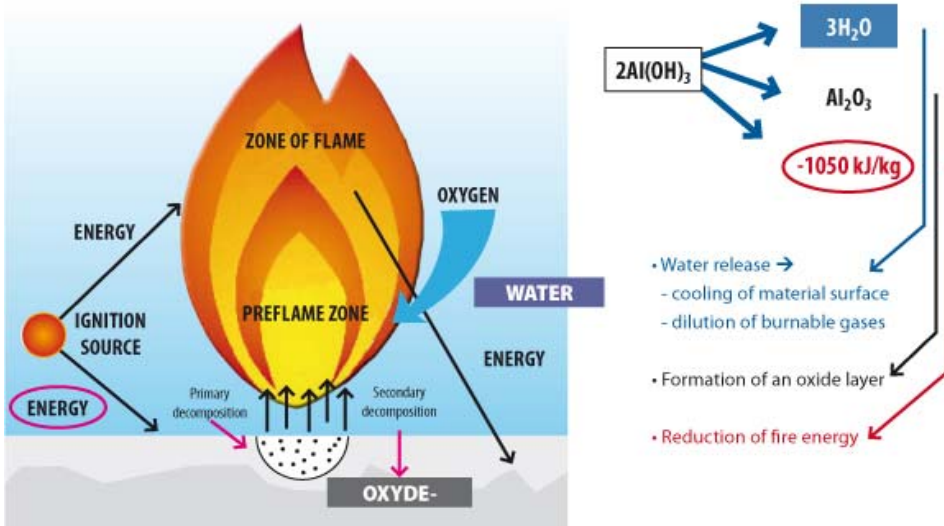


# 1) WATER DEVELOPMENT MECHANISM



PHISYCAL MECHANISM IN  
CONDENSED PHASE AND GAS  
PHASE

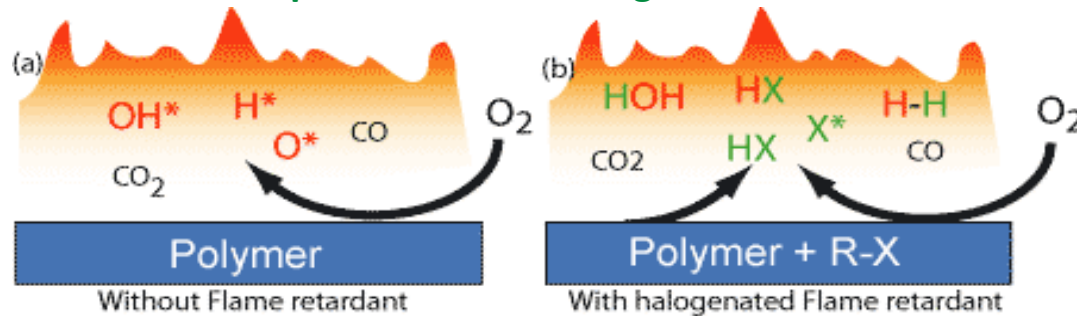
Cooling down  
Dilution of oxygen, LOI  
decreasing





## 2) MECHANISM GAS PHASE with bromide and Antimony

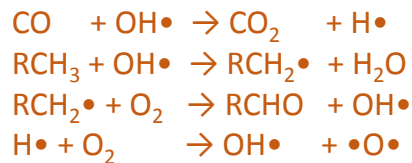
Brominated flame retardants, with help of antimony trioxide, generate HBr and radicals, which block radical chain degradation of polymer during fire. HBr developed, dilute also oxygen and inhibits fire.



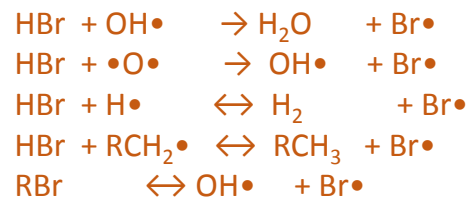
Gas phase radical Br mechanism

Example:  
Br-FR + Sb<sub>2</sub>O<sub>3</sub>

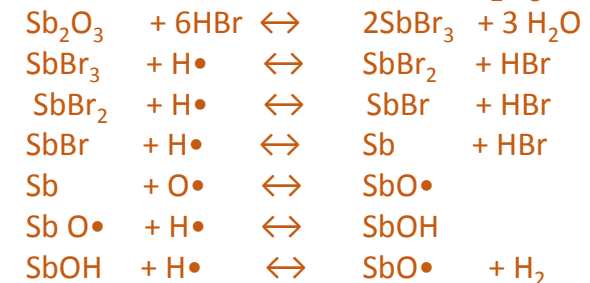
### Hydrocarbons burning



### Br Flame retardant action



### Flame retardant with Sb<sub>2</sub>O<sub>3</sub>



## 2) MECHANISM GAS PHASE HALOGEN FREE With Phosphorus

### P Flame retardant action in gas phase



Not all P molecules are able to react in the gas phase.

Suitable P compounds must be volatile during polymer pyrolysis.

In addition to this, ability of P to act in gas phase is higher, as lower is the oxidation number.

Phosphate>Phosponate>Phosphinate>Pred

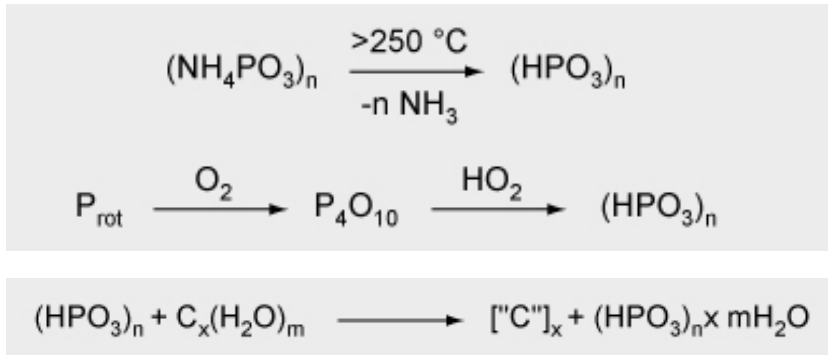
## GAS PHASE: BrSb vs HF-SbF

BrSb +	BrSb -	HF +	- HF -
<b>DOSAGE LEVEL</b>	<b>BROMIDE CONCERN</b>	<b>ENVIROMENTAL FRIENDLY</b>	<b>LOW THERMAL STABILITY</b>
<b>COST</b>	<b>ANTIMONY CONCERN</b>	<b>LOW SMOKE TOXICITY</b>	<b>LOW COMPATIBILITY</b>
<b>AVAILABILY</b>	<b>LONG TERM AVAILABILITY</b>	<b>EASIER RECYCLING</b>	<b>HIGHER COST AND DOSAGE</b>
<b>DEEP KNOWLEDGE FOR LONG USE</b>	<b>RECYCLING ISSUES</b>		<b>DIFFICUL PHYSICAL FORM</b>

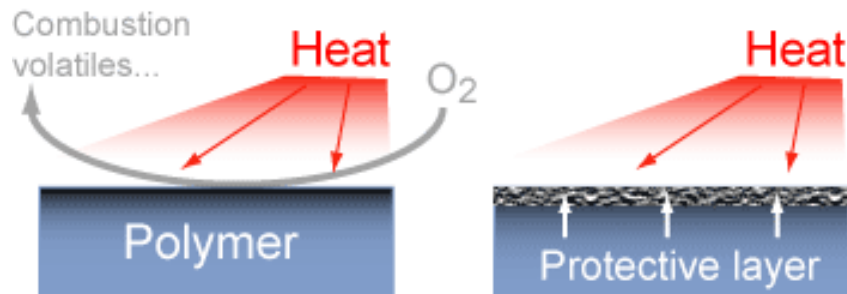
### 3) MECCANISMO CHAR CONDENSED PHASE

#### CHEMICAL AND PHYSICAL REACTION IN SOLID PHASE

Polymer char, who inhibits pyrolysis and reduce oxygen flux to fresh polymer.  
P based products dehydrates polymer and create char layers.

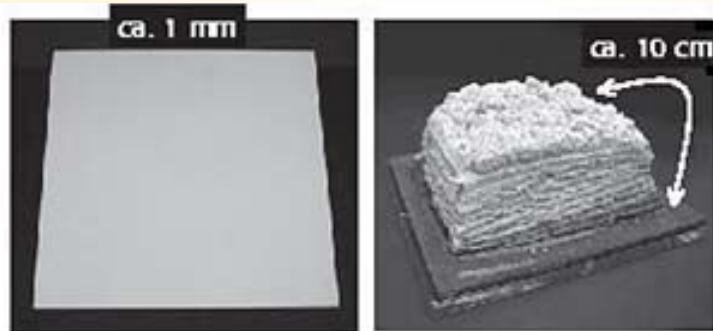
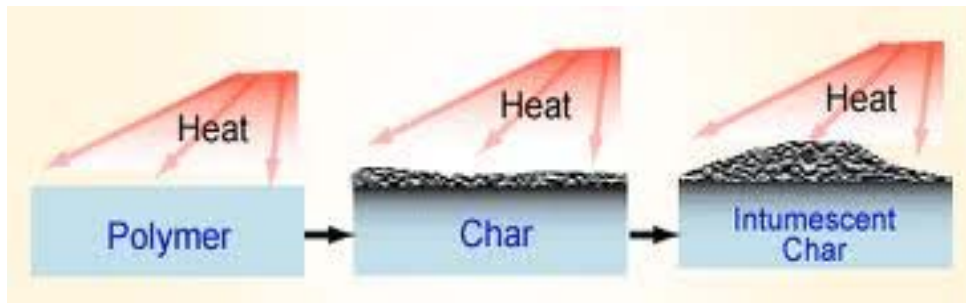


**REACTIVE SYSTEM:  
P BASED PRODUCTS  
BETTER WITH POLYMERS WITH  
HETEROATOMS**



## 4) INTUMESCENT MECHANISM

Example of reactive syste:  
**CHARING AGENT**  
**P BASED INORGANIC ACID**  
**N BASED FOAMING AGENT**



The thickness of the intumescent foam increases 10 to 100 fold that of the originally applied coating and insulates the substrate by its low thermal conductivity.

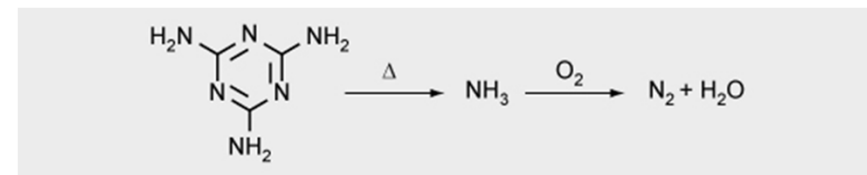
### CHEMICAL ACTION

#### SOLID PHASE REACTION

Dehydration and degradation of polymer with char formation.  
 Protective layer swelling.

#### GAS PHASE ACTION

Not flammable gas formation.

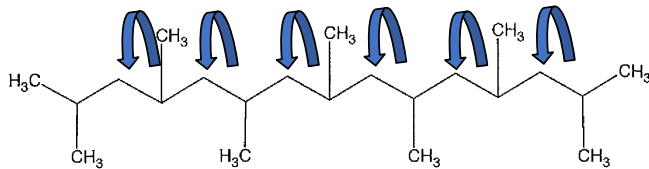
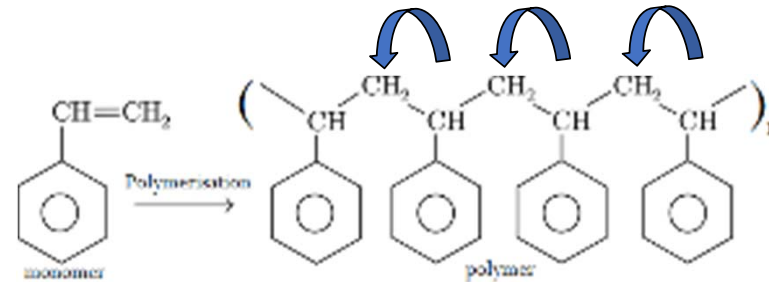
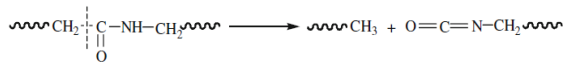
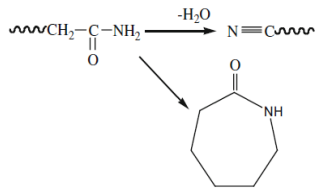
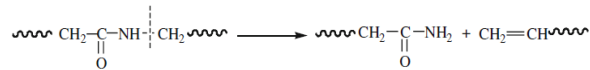




# 5) DRIPPING OR CHAIN SCISSION MECHANISM

## CHEMICAL ACTION IN GAS PHASE

Flame retardant, after heating, generates active radicals, which cut polymer chains, making the polymer from solid to liquid, which is an endothermic reaction.



## GC HF 693 PHOSPHONATE

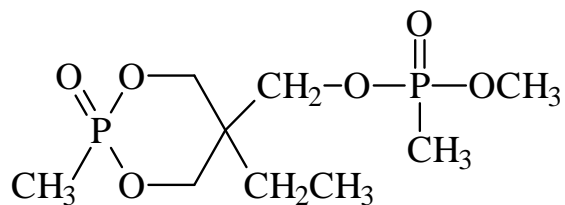
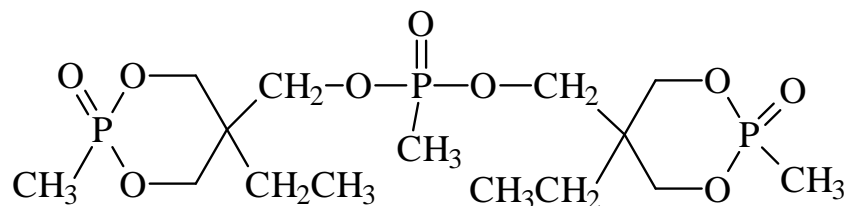
GC HF 693 works with char/intumescent mechanism. It's 20% more active than a phosphate. Extremely thermal stable (1% 350°C). Solid at room T, but easy melting into the polymer.

PROPERTY	VALUE
P	14%
N	7
Density	1,72-1,75 g/cm <sup>3</sup>
TgA (1% loss)	300°C
Melting point °C	110-117°C

## GC CPP1 and GC CPP2 CYCLIC PHOSPHONATES

PROPERTY	VALUE
P	> 20%
Apparence	Colorless liquid
Density	1,25-1,27 g/cm <sup>3</sup>
TgA (1% loss)	300°C
Avarage particle size, μm	5

CPP1 and CPP2 work with char mechanism at lower loading level than phosphate. They can offer very good FR and high thermal stability. This is due to high P content and dehydrogenation. It promotes very thick char at low loading level.

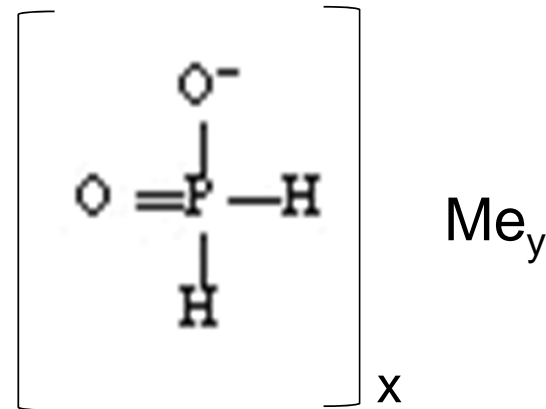


# METAL PHOSPHINATES

## Al, Ca, Zn.

MeP1, as well as other hypophosphites, works in gas phase. Thermal stability is high, and P level is highest in P molecules. Acidity level depends from metal.

PROPERTY	VALUE
P	>19 %
N	>0
Density	1,80 – 1,90 g/cm <sup>3</sup>
TgA (1% loss)	320°C
TgA (5% loss)	360°C
Average particle size, μm	5



## MELAMINE PYROPHOSPHATE

MPYR is stable phosphate product. Less sensitive to moisture, ideal for intumescent/char formulations.

PROPERTY	VALUE
P	19
N	14
Density	1,80 – 1,90 g/cm <sup>3</sup>
TgA (1% loss)	300°C
TgA (5% loss)	360°C
Average particle size, μm	5 μm
pH (10% susp. @ 20°C)	5-6

## GC PIPERAZINE INT

GC PIPER is a very active P/N flame retardant. When good formulated shows activity at low loading level. Stable and less igroscopic.

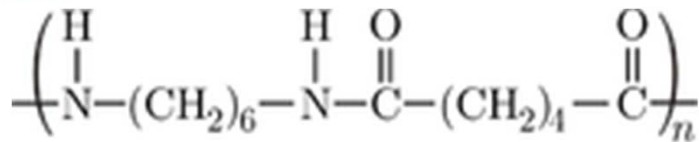
PROPERTY	VALUE
P	22
N	21
Density	1,80 – 1,90 g/cm <sup>3</sup>
TgA (1% loss)	250°C
TgA (5% loss)	280°C
Avarage particle size, μm	10 μm
Loss on drying	0,5 max

# GC MELAMINE IPOPHOSPHITE

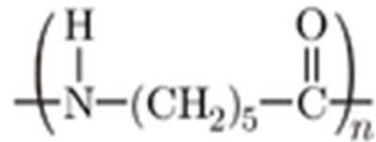
GC MIPO has together properties of ipophosphite and melamine. It very good and active, specially in PO.

PROPERTY	VALUE
P	19
content	99%
Melting range	128 – 133 °C
TgA (1% loss)	250°C
TgA (5% loss)	280°C
Avarage particle size, µm	10 µm
Loss on drying	0,5 max

# POLYAMIDE



Nylon 66



Nylon 6

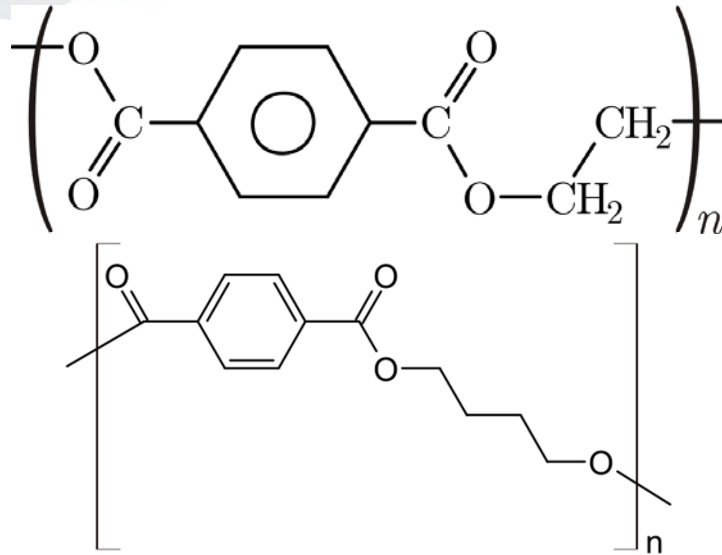
## LOI

PE	17
ABS	18
PA	24
PC	27
PTFE	95

HIGH LOI	GOOD FLAME RESISTENCE
<u>N</u> AND <u>O</u> 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

<b>POLYAMIDE</b>	TEST	+	-	<b>GREENCHEMICALS PURE PRODUCT</b>	<b>GREENCHEMICALS BLENDS OR MASTERBATCHES</b>
<b>METAL HYDROXIDE</b>	-	<b>NO HEALTHY AND ENVIROMENTAL PROBLEMS</b>	<b>HIGH DOSAGE</b>	GC Mg(OH) <sub>2</sub>	MB EVA MGOH
<b>DECA-OXIDE/ Sb<sub>2</sub>O<sub>3</sub> {ZnBO<sub>3</sub>}</b>	UL94 V0	<b>LOW DOSAGE LOW COST</b>	<b>KILLED FOR HEALTHY AND ENVIROMENTAL PROBLEMS</b>	GC DECA 83 Antimony trioxide,	MB EVA DATO 41 MB EMBA DATO 41
<b>DECA ETHANE /Sb<sub>2</sub>O<sub>3</sub> {ZnBO<sub>3</sub>}</b>	UL94 V0	<b>LOW DOSAGE LOW COST GOOD COLOR</b>	<b>BROMINE ANTIMONY POOR THERMAL STABILITY</b>	GC DPE 81 AntimonyTrioxide	MB EVA DETO 41 MB EMBA DETO 41
<b>PBS/Sb<sub>2</sub>O<sub>3</sub> {ZnBO<sub>3</sub>} {BEO}</b>	UL94 V0	<b>LOW DOSAGE LOW COST GOOD THERMAL STABILITY GOOD MECHANICAL PROPERTIES</b>	<b>COST BROMINE ANTIMONY</b>	GC BPS 67, GC BPS 310 Antymomy trioxide GC Zinc Borate GC FR 3100	Compacted version EVA TRIX 90-80
<b>P red</b>	UL 94 V0	<b>LOW COST HALOGEN FREE LOW DOSAGE</b>	<b>RED COLOR EXPLOSIVE</b>		MB PA P RED 50/60
<b>PHOSPHINATE/MC/MPP /ZnBO<sub>3</sub></b>	UL94 V0	<b>HALOGEN FREE WHITE COLOR GOOD MECHANICAL PROPERTIES</b>	<b>COST HEAT STABILITY DOSAGE PROCESSABILITY</b>	GC MC25 GC MPP GC HF 693, GC MPYR GC ZINC BORATE GC ME PHOSPHINATE	<b>GC HF V0 PAP1 GC HF V0 PAP6 GC HF EP 730 C</b>
<b>MELAMINE CYANURATE</b>	UL94 V2 (V0)	<b>LOW COST LOW DOSAGE HALOGEN FREE</b>	<b>NO Vo IF FG FILLED</b>	GC MCA SERIES	MB PA MC25 40
<b>REACTIVE HF</b>	UL94 V2 V0	<b>LOW DOSAGE VERY HIGH MECHANICS HIGH RECYCLE</b>	<b>ONLY IN POLIMERIZATIO NOT ALWAYS POSSIBLE OR LIMITED</b>	GC CEPPA GC RE DDP	

## POLY ETHYLEN TEREPHTALATE POLY BUTYLEN TEREPHTALATE



### LOI

PE	17
ABS	18
PET	25
PBT	23
PC	27
PTFE	95

% O < PET

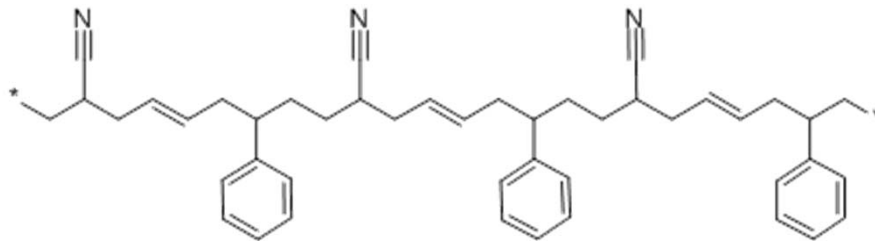
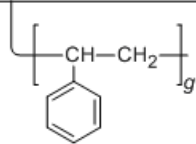
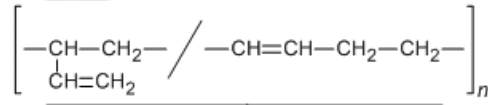
HIGH LOI	BUONA RESISTENZA ALLA FIAMMA
HETEROATOMS IN CHAIN	SVILUPPA GAS MENO INFIAMMABILI
EXTRUSION T PET 260°C – 290°C PBT 230°C-270°C	II FR DEVE ESSERE RESISTENTE ALLA T
PRESENCE OF HETEROATOMS	CHAR
POLY CONDENSATION	DRIPPING <b>acids</b>
CURING ABILITY	CROSS-LINK

PET PBT	TEST	+	-	GREENCHEMICALS PURE PRODUCT	GREENCHEMICALS BLENDS OR MASTERBATCHES
METAL HYDROXIDE	-	NO HEALTHY AND ENVIORNENTAL PROBLEMS	HIGH DOSAGE	GC Mg(OH)2	MB PE MGOH SETABOND
DECA-OXIDE/ $Sb_2O_3$ ( $ZnBO_3$ )	UL94 V0	LOW DOSAGE LOW COST	KILLED FOR HEALTHY AND ENVIORNENTAL PROBLEMS	GC DECA 83 Antimony trioxide,	MB PE DATO 41 MB EVA DATO 41 SETABOND
DECA ETHANE / $Sb_2O_3$ ( $ZnBO_3$ )	UL94 V0	LOW DOSAGE LOW COST GOOD COLOR	BROMINE ANTIMONY POOR THERMAL STABILITY	GC DPE 81 AntimonyTrioxide	MB EVA DETO 41 MB EMBA DETO 41 SETABOND
GC BPS / $Sb_2O_3$ ( $ZnBO_3$ )	UL94 V0	LOW DOSAGE LOW COST GOOD DISPERSION GOOD MECHANICAL PROPERTIES GOOD COLOR	COST BROMINE ANTIMONY	GC BPS 67 GC BPS 310 Antymomy trioxide GC Zinc Borate	EVA TRIX 80 and 90
P red	UL 94 V0	LOW COST HALOGEN FREE LOW DOSAGE	RED COLOR EXPLOSIVE	Acidity	MB PET P RED 50/60
PHOSPHINATE PHOSPHONATE MC $ZnBO_3$	UL94 V0	HALOGEN FREE WHITE COLOR	DISPERSION * HEAT STABILITY DOSAGE PROCESSABILITY MECHANICA PROPERTIES ACIDITY	GC MC25 GC HF 693 GC ZnBO3M ME PHOSPHINATE	MB HF EP 730 C GC HF 693



POLYPROPYLENE	TEST	+	-	GREENCHEMICALS PURE PRODUCT	GREENCHEMICALS BLENDS OR MASTERBATCHES
METAL HYDROXIDE	-	NO HEALTHY AND ENVIROMENTAL PROBLEMS	HIGH DOSAGE	GC Mg(OH)2	MB PE MGOH Compatibilizer
DECA-OXIDE/ Sb <sub>2</sub> O <sub>3</sub> {ZnBO <sub>3</sub> }	UL94 V0	LOW DOSAGE LOW COST	KILLED FOR HEALTHY AND ENVIROMENTAL PROBLEMS	GC DECA 83 Antimony trioxide,	MB PE DATO 41 MB EVA DATO 41 Compatibilizers
DECA ETHANE /Sb <sub>2</sub> O <sub>3</sub> {ZnBO <sub>3</sub> }	UL94 V0	LOW DOSAGE LOW COST GOOD COLOR	BROMINE ANTIMONY POOR THERMAL STABILITY	GC DPE 81 AntimonyTrioxide	MB EVA DETO 41 MB EMBA DETO 41 Compatibilizers
GC BDDP 68/Sb <sub>2</sub> O <sub>3</sub> {ZnBO <sub>3</sub> }	UL94 V0	LOW DOSAGE LOW COST GOOD DISPERSION GOOD MECHANICAL PROPERTIES GOOD COLOR	COST BROMINE ANTIMONY	GC BDDP 68 GC BDMP 66 Antymomy trioxide GC Zinc Borate GC DICUMENE	PE TRIX 80 and 90 ISODRIPP BR 69 MB PE BDDP 68 AF
P red	UL 94 V0	LOW COST HALOGEN FREE LOW DOSAGE	RED COLOR EXPLOSIVE		MB PE P RED 50/60
APP PIPERAZINE PYROPHOSPHATE MC	UL94 V0	HALOGEN FREE WHITE COLOR	DISPERSION * HEAT STABILITY DOSAGE PROCESSABILITY MECHANICA PROPERTIES	GC MC25 GC APP GC PIPER compatibilizer	GC HF 2000 GC FLAM V0
ME PHOSPHINATE M-Br-Hydrate	UL94 V2 (V0)	LOW COST LOW DOSAGE HALOGEN FREE	VERY SENSITIVE TO POISONS. ONLY VERGIN PP	GC DRIPP HF 70	MB PP DRIPP HF 70

# ABS / HIPS

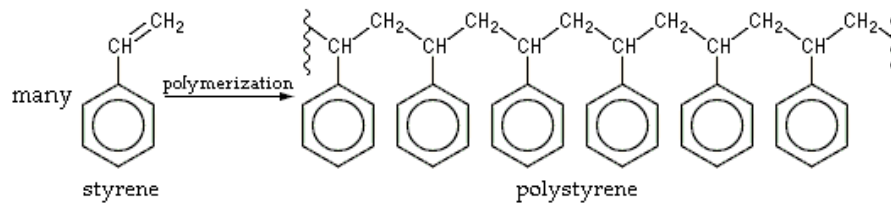


## LOI

HIPS	17
ABS	18
PET	25
PBT	23
PC	27
PTFE	95

LOI BASSO	SCARSA RESISTENZA ALLA FIAMMA
NON HA ETEROATOMI	SVILUPPANO GAS INFIAMMABILI
T DI LAVORAZIONE > 200°C	RESISTE QUASI TUTTI GLI FR
NON HANNO ETEROATOMI IN CATENA	SCARSO CHAR
POLIMERIZZAZIONE RADICALICA	DRIPPING <span style="color: red;">attenzione alle temperature di processo</span>
NON RETICOLANO	NO CROSS-LINK

# POLYSTYRENE



## LOI

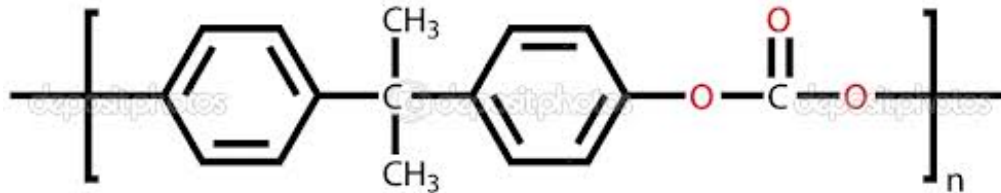
PE	17
ABS	18
PA	24
PC	27
PS	18

HIGH LOI	BAD FLAME RETARDANT RESISTANCE
<u>N</u> AND <u>O</u> IN CHAIN	ALL FLAMABLE GASES
LOW PROC. TEMP. 180°C-280°C	WIDE RANGE OF FR
NO PRESENCE OF N AND O	BAD CHAR
RADICAL POLYMERIZATION	HARD DRIPPING
CROSS-LINKING ABILITY	VERY BAD

ABS, HIPS	TEST	+	-	GREENCHEMICALS PURE PRODUCT	GREENCHEMICALS BLENDS OR MASTERBATCHES
METAL HYDROXIDE	-	NO HEALTHY AND ENVIROMENTAL PROBLEMS	HIGH DOSAGE	GC Mg(OH) <sub>2</sub>	MB PE MGOH SETABOND
DECA-OXIDE/ Sb <sub>2</sub> O <sub>3</sub> (ZnBO <sub>3</sub> )	UL94 V0	LOW DOSAGE LOW COST	KILLED FOR HEALTHY AND ENVIROMENTAL PROBLEMS	GC DECA 83 Antimony trioxide,	MB PE DATO 41 MB EVA DATO 41 SETABOND
DECA ETHANE FR 245 /Sb <sub>2</sub> O <sub>3</sub> (ZnBO <sub>3</sub> )	UL94 V0	LOW DOSAGE LOW COST GOOD COLOR	BROMINE ANTIMONY POOR THERMAL STABILITY	GC DPE 81 AntimonyTrioxide GC FR 245 66	MB EVA DETO 41 MB PE DETO 41 SETABOND GC FR 245 compacted
GC BDDP 68/Sb <sub>2</sub> O <sub>3</sub> (ZnBO <sub>3</sub> ) Even without Sb <sub>2</sub> O <sub>3</sub>	UL94 V0,V2	LOW DOSAGE LOW COST GOOD DISPERSION GOOD MECHANICAL PROPERTIES GOOD COLOR	COST BROMINE ANTIMONY	GC BDDP 68 GC BDMP 66 Antymomy trioxide GC Zinc Borate GC DICUMENE	PE TRIX 80 and 90 ISODRIPP BR 69 MB PS SAM series MB PS DRIPP 69
GC HF 693 GC ME PHOSPHINATE	UL 94 V0	LOW COST HALOGEN FREE LOW DOSAGE	RED COLOR EXPLOSIVE	GC HF 693 GC ME PHOSPHINATE GC Zinc Borate	GC EP HF 730
MODIFIED POLYMER CEPPA/DOPO GC HF 693	UL94 V0	HALOGEN FREE WHITE COLOR	DISPERSION * HEAT STABILITY DOSAGE PROCESSABILITY MECHANICA PROPERTIES	GC HF 693 GC ME PHOSPHINATE GC Zinc Borate GC CEPPA, GC DOPO	GC HF40 series

COMPONENTE PRODOTTI IN MATERIE PLASTICHE - PLASTIC PRODUCTS AND COMPONENTS

# POLYCARBONATE



## LOI

PE	17
ABS	18
PET	25
PBT	23
PC	27
PTFE	95

VERY HIGH LOI	GOOD FLAME RESISTANCE
HETEROATOMS	LESS FLAMABLE GASES
PROCESSING T 240°C – 280°C	FR MUST HAVE HIGH FR RESISTANCE
HETEROATOMS	CHAR
POLYCONDENSATION	DRIPPING <b>ACIDS</b>
CURING ABILITY	CROSS-LINK

<b>PC</b>	TEST	+	-	GREENCHEMICALS PURE PRODUCT	GREENCHEMICALS BLENDS OR MASTERBATCHES
<b>DECA ETHANE</b> /Sb <sub>2</sub> O <sub>3</sub> (ZnBO <sub>3</sub> )	UL94 V0	<b>LOW DOSAGE</b> <b>LOW COST</b> <b>GOOD COLOR</b>	<b>BROMINE</b> <b>ANTIMONY</b> <b>POOR THERMAL STABILITY</b>	GC DPE 81 Antimony sin GC BC58 GC FR3100	
<b>Br-PC</b> oligomeri/Sb <sub>2</sub> O <sub>3</sub> , Na antimoniato (BEO, BT <sub>93</sub> , BPS)	UL94 V0	<b>LOW DOSAGE</b> <b>LOW COST</b> <b>GOOD COLOR</b>	<b>BROMINE</b> <b>ANTIMONY</b> <b>POOR THERMAL STABILITY</b>	GC BC58 GC FR3100 GC BT67 GC BPS67	
<b>RDP</b> <b>BDP</b> FH <sub>693</sub>	UL94 V0	<b>HALOGEN FREE</b> <b>OPALESCENT</b>	<b>HIGH DOSAGE</b> <b>DIFFICULT FOR LOW THICKENSS</b>	GC BDP GC RDP GC 693 GC PTFE	
<b>KSS</b> <b>PBSK</b> HF <sub>693</sub> PTFE	UL 94 V0	<b>HALOGEN FREE</b> <b>TRASPARENT</b> <b>LOW DOSAGE</b>		GC KSS GC PBSK GC 693 GC PTFE	<b>NACHFLAME PC-HF</b>

## **PC/ABS**

<b>RDP</b> <b>BDP</b> FH <sub>693</sub> PTFE	UL 94 V0	<b>HALOGEN FREE</b> <b>TRASPARENT</b> <b>LOW DOSAGE</b>	<b>RELATIVELY HIGH DOSAGE</b>	GC BDP GC RDP GC 693 GC PTFE	
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## COMMERCIAL NAME

## PRODUCT DESCRIPTION

**GC HF V0 PAP1**

It's a mixture which can be powder or compacted, for white polyamide GF reinforced.

**GC HF V0 PAP6**

It's a mixture, which can be powder or compacted, for white GF polyamide compound. Particularly suitable with high GF level.

**GC HF EP 730 c**

It's a mixture (powder or compacted), with low acidity, which is particularly suitable for PET/PBT compounds. White color.

**NACHFLAM PC HF**

It's a mixture, ideal for transparent PC low thickness.

**GC HF 2000**

Intumescent mixture, in powder/compacted with compatibilizer, ideal for low loading needs.

**GC DRIPP HF 70**

< 900 ppm bromine blend, ideal for PPV2

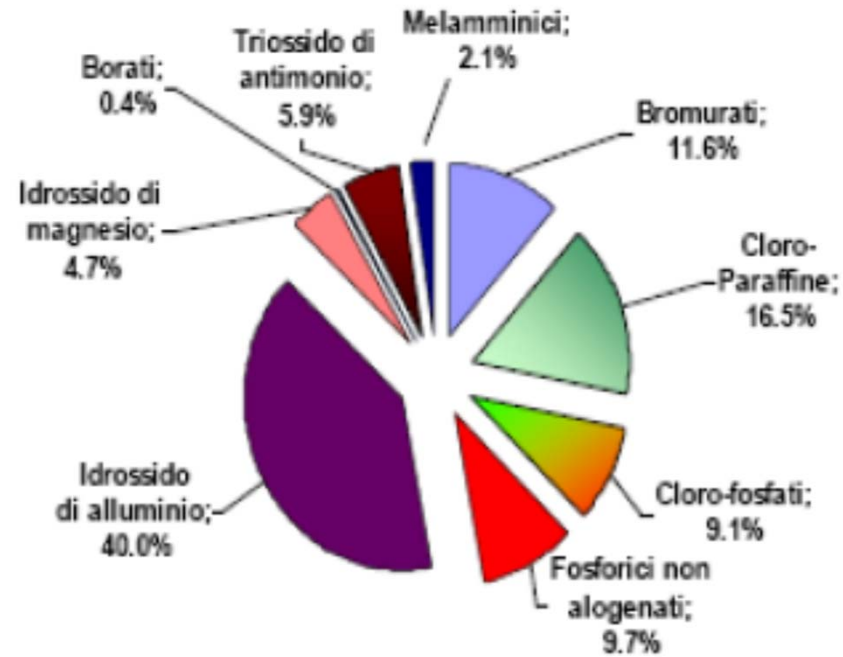
**GC HF40**

Powder or compacted blend, ideal for GPPS/HIPS V2 or classE application

**GC ABS P169**

Powder or compacted blend for ABS, V1 and V0.

- TOSSICITÀ
- BIODEGRADABILITÀ E BIOACCUMULAZIONE
- STABILITÀ ALLA TEMPERATURA DI TRASFORMAZIONE
- COMPATIBILITÀ CON IL POLIMERO
- COSTO/ATTIVITÀ



*Mercato dei ritardanti di fiamma*

- SI CERCANO FR HALOGEN FREE O A BASSO IMPATTO PER LA SALUTE E AMBIENTALE
- CHIMICA DEL P E' QUELLA CHE SI STA SVILUPPANDO
- ETP SI PRESTANO A FR INNOVATIVI
- ANTIFIAMMA REATTIVI
- POLIMERI SUPER FR PER LEGHE

