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AGENDA

- INTRODUCTION: PLASTIC RECYCLING IN EUROPE AND ITALY
- FLAME RETARDANT PLASTICS RECYCLING
- WHICH POLYMERS AND WHICH FLAME RETARDANTS
- FLAME RETARDANT BANNED
- FLAME RETARDANTS THERMAL STABILITY, TgA
- FLAME RETARDANT DEGRADATION: BROKEN PIECES
- CHEMICAL OVERVIEW OF UNDESIRED RECTIONS AND CONSEQUENCES
- ADDITIVES PACKAGES FOR SAVING FR-POLYMERS DURING RECYCLING
- ADDITIVE AND TECHNOLOGY FOR DESTROYING BANNED-FR-POLYMERS;
- EXAMPLES, CASES
- CONCLUSIONS

PLASTIC RECYCLING EU&ITALY

EUROPE

LAST 50 YEARS EUROPEN PLASTIC PRODUCTION INCREASED FROM 50000 MT TO 400 MMT/YEAR. IT GROWS 10%/YEAR.
UNTIL 2015 EUROPE USED TO SHIP MOST OF USED PLASTICS TO ASIA, BUT FROM 2015 EU STOPPED WITH EVERY SYSTEM THIS PROCESS.

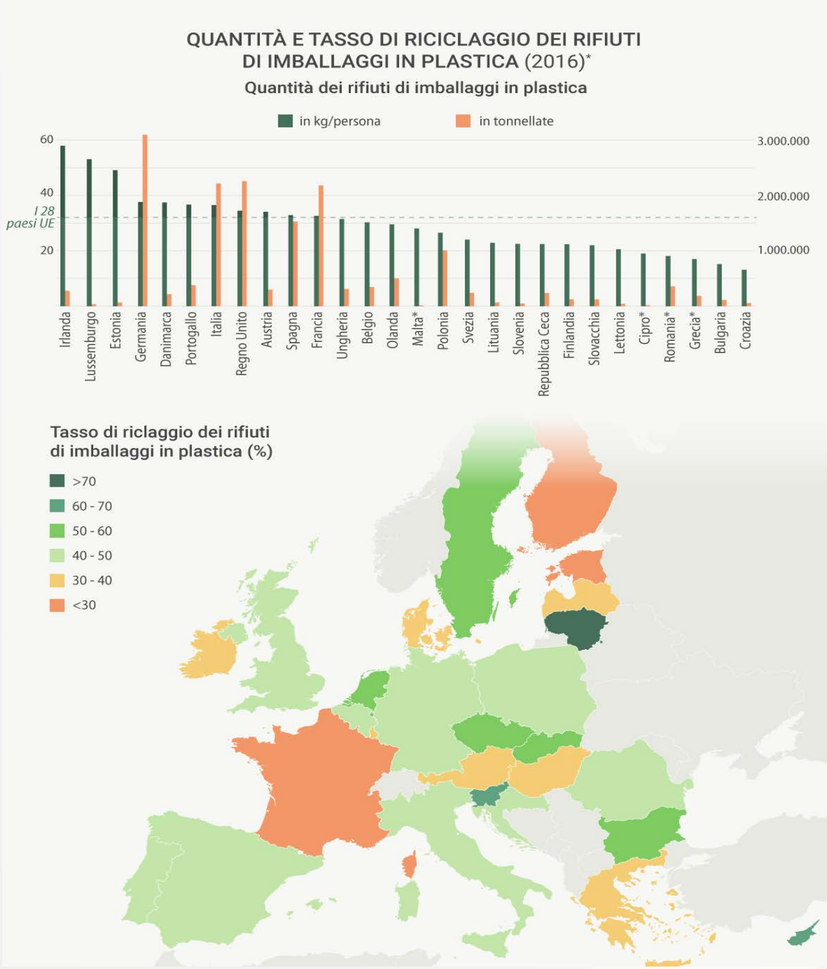
IN EUROPE WE RECYCLE 33% OF PLASTIC WITH A LOT OF DIFFERENCE BETWEEN THE COUNTRIES.

ITALY

IN ITALY WE RECYCLE 45% OF PLASCTIC (2016 DATAS)
NATIONAL ASSOCIATION IN CHARGE FOR COLLECTING AND RECYCLING WASTE ARE:

COREPLA
CORIPET

PLASTIC LOSES UP TO 95% OF ITS VALUE, AFTER BEING USED.



PLASTIC RECYCLING: PROBLEMS

- PLASTIC R[illegible]CLING [illegible]LY EXPENSIVE AND MO[illegible] THE TIME, SECOND[illegible]E POLYMER IS LE[illegible]ORMANT AND [illegible]PENSIVE OF V[illegible]NE
- SO[illegible]LAST[illegible]E DEMAND IS ONLY[illegible]D I[illegible]HE TIME IT'S DRIVE[illegible]S GI[illegible]N BY LAW.

THAT'S WHY EU IS ACTING THIS WAY

6. BANNING PLASTIC BAGS;
7. HELPING PROJECTS FOR RECYCLING PLASTICS
8. HELPING PROJECTS FOR MICROPLASTICS;

PRE-USE (companies waste)
COLLECTION, directly from factories to recyclers;
PRE-TREATMENT, sometimes alredy prepared by factories;
CONFERMENT OF REFUSAL, inside the factory, to recyclers or wasting area/incenerition plants;

POST-USE (public waste), much more difficult
COLLECTION, really difficult because fragmented and heavily contaminated;;
PRE-TREATMENT, really important to separate different materials as much as possible.
CONFERMENT OF REFUSAL, it's working well only for some refusals, very good for PET
RECYCLE: possible only in small percentage of cases.

FLAME RETARDANT PLASTICS

TODAY ALL FIRE EXTINGUISHING PLASTICS, CANNOT BE RECYCLED; THEY MUST BE BURNED OR STORED IN RUBBISH DUMP, AS SPECIAL WASTE.

PARTICULARLY, PLASTICS CONTAINING BANNED FLAME RETARDANT ARE GENERATING EVEN MORE CONCERN AND THEIR DISPOSAL IS EVEN MORE EXPENSIVE.

AFTER FIRST PHYSICAL SEPARATION BETWEEN PLASTICS WITH OTHER MATERIALS, LIGHT PLASTICS (WITHOUT FLAME RETARDANTS) ARE SEPARATE FROM HEAVY ONES (WITH FR) BY FLOTING WATER DENSITY.

FIRE EXTINGUISHING PLASTICS

PLASTICS FROM RAEE WASTE
PLASTICS FROM BUILDING AND COSTRUCTION INDUSTRY
PLASTICS FROM AUTOMOTIVE
PLASTICS FROM WIRE&CABLES INDUSTRI

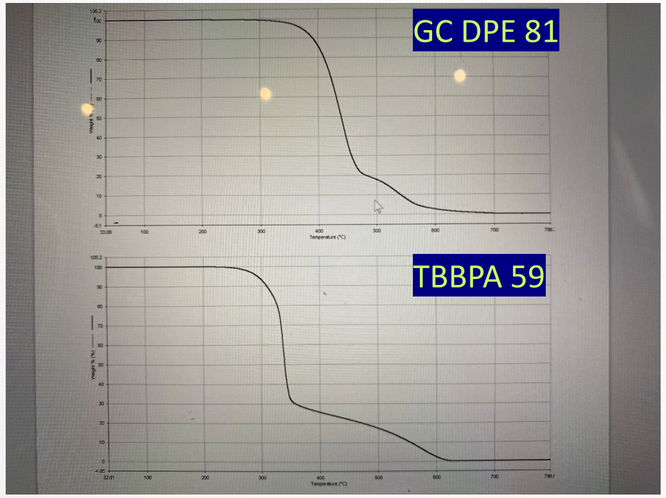
FLAME RETARDANTS TYPE

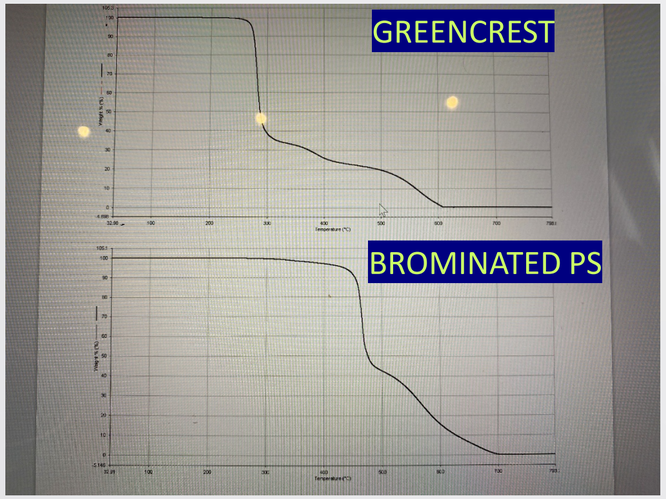
TYPE	CLASSIFICATION	FLAME RETARDANT	PP	PA	PET/PBT	PE	PC	ABS/HIPS	PS
BROMINATED	NOT DANGEROUS	GC DPE 81	●	●	●	●	●	●	●
BROMINATED	NOT DANGEROUS, BANNED by RoHS norm	GC DECA 83	●	●	●	●	●	●	●
BROMINATED	NOT DANGEROUS	GC BDDP 68	●			●			●
BROMINATED	NOT DANGEROUS	GC BPS 67		●	●				
BROMINATED	NOT DANGEROUS	GC BT 93			●	●	●		●
BROMINATED	NOT DANGEROUS	GC BC 52/58					●		
BROMINATED	NOT DANGEROUS	GC FR 245						●	
BROMINATED	H400/H410	GC TBBPA						●	
BROMINATED	NOT DANGEROUS	GC FF680						●	
BROMINATED	NOT DANGEROUS	GC PBR							●
BROMINATED	NOT DANGEROUS	GC BDMP 66							●
BROMINATED	SVHC (PBT H317) H361/H362/H410	GC HBCD							●
HALOGEN FREE	H317	DICUMENE	●			●			●
HALOGEN FREE	H242, H315, H319, H411	PEROXIDES				●			●
HALOGEN FREE	THEY CAN BE H302	PHOSPHATES		●	●	●	●	●	●
HALOGEN FREE	THEY CAN BE H228, H302, H319	PHOSPHITES	●	●	●	●			●
HALOGEN FREE	H373	MELAMINE CYANURATE	●	●	●	●		●	●
HALOGEN FREE	H228, H412	P RED	●	●	●	●		●	●
HALOGEN FREE	H351	ANTIMONY TRIOXIDE	●	●	●	●		●	●

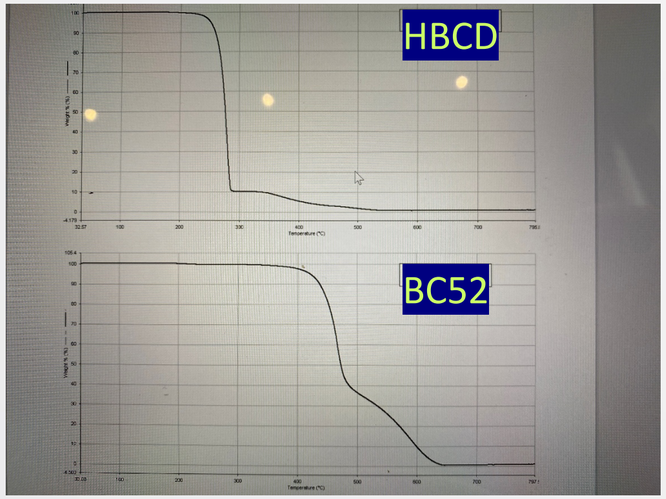
THERMOGRAVIMETRIC ANALYSIS

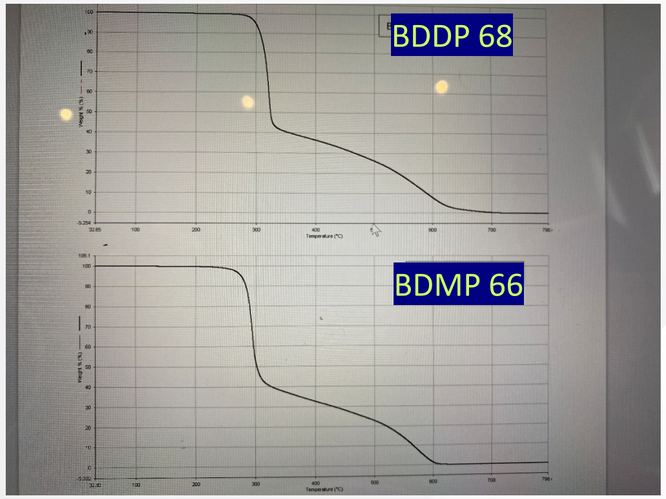
THERMOGRAVIMETRIC ANALYSIS

Thermogravimetric analysis or thermal gravimetric analysis (TGA) is a method of thermal analysis in which the mass of a sample is measured over time as the temperature changes. This measurement provides information about physical phenomena, such as phase transitions, absorption, adsorption and desorption; as well as chemical phenomena including chemisorptions, thermal decomposition.

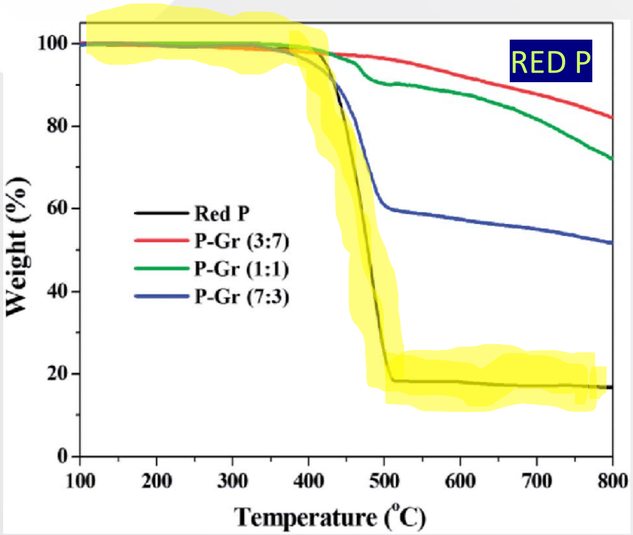


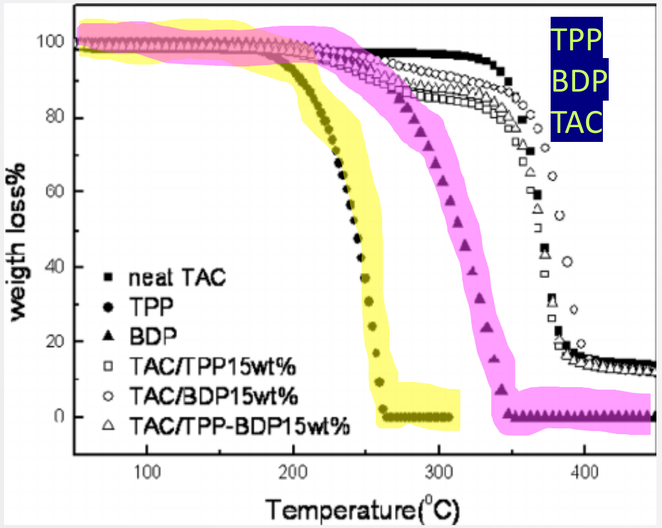


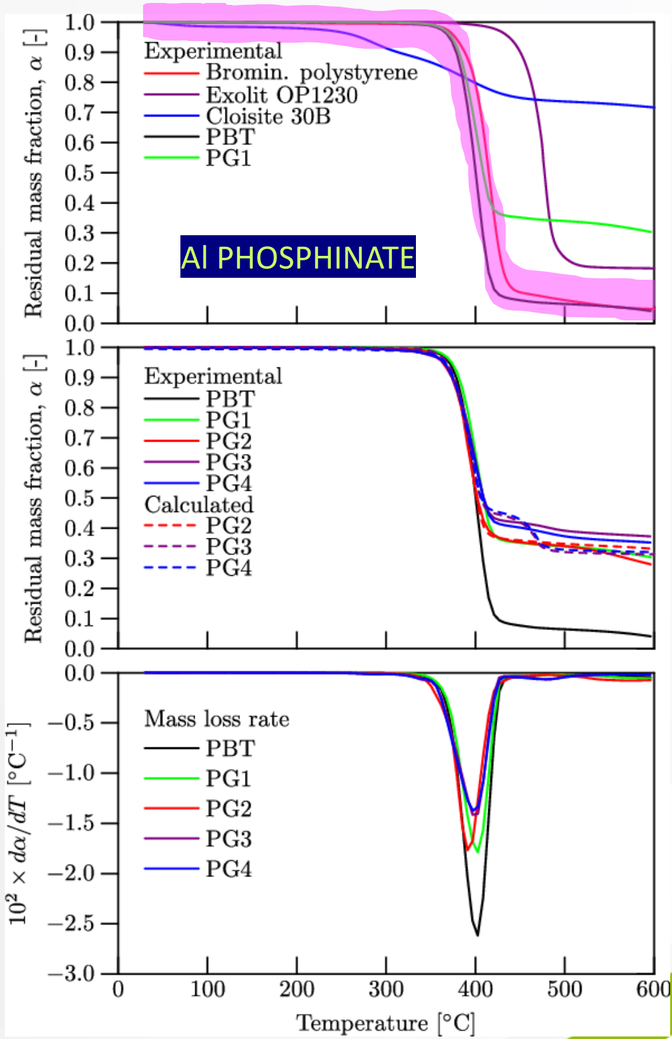




THERMOGRAVIMETRIC ANALYSIS







FR THERMAL STABILITY

POLYMER	FLAME RETARDANT	T ΔW= 1%	T ΔW= 2%	T ΔW= 5%	T ΔW= 50%
PS	HBCD 75	231,02	240,23	251,19	277
PS	BDMP 66	244,63	260,76	275,07	302
PS	GREENCREST	256,22	264,2	272,05	288
ABS	TBBPA59	259,74	273,57	292,75	340
PP, PE	BDDP 68 PW	279,9	289,07	298,96	325
PP, PA, PET, PBT	DPE81/DECA 83	318,55	340,69	367,5	440
PBT, PET, PE	BT 67	330,72	367,46	433,45	476
PC	B52	359,19	392,05	420,42	473

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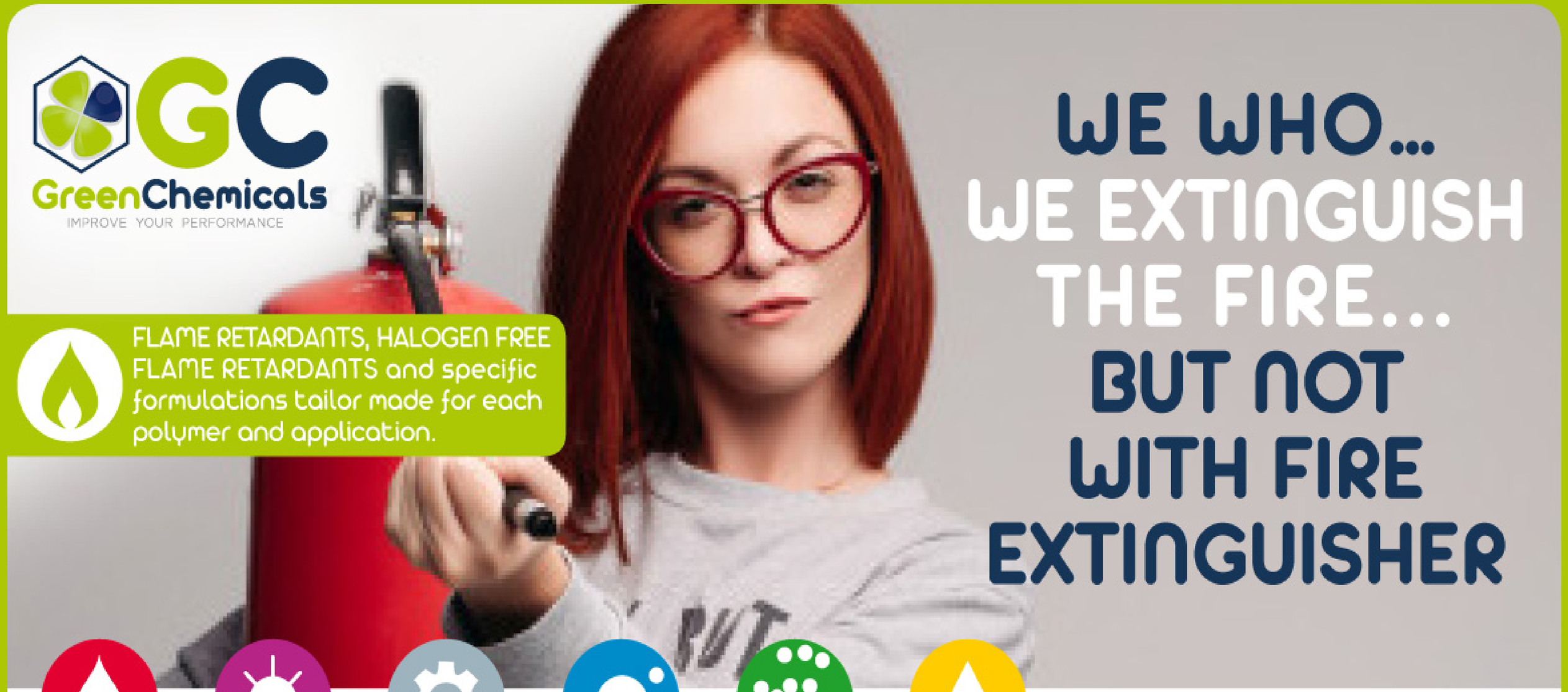

FLAME RETARDANTS, HALOGEN FREE FLAME RETARDANTS and specific formulations tailor made for each polymer and application.

WE WHO... WE EXTINGUISH THE FIRE... BUT NOT WITH FIRE EXTINGUISHER

FLAME RETARDANTS

UV ABSORBERS & HALS

PROCESS AID & PEROXIDES

ANTIOXIDANTS

ANTISTATICS

LUBRICANTS

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FR BROKEN PIECES

BROMINATED FR

R-Br

Br* → HBr

Br*, H*, R* + O_2 → R-O-O*
R-O-O* + R → R-O-O-H + R*
R-O-O-H → RO* + OH*

RED P, PHOSPHATE AND PHOSPHINATES

RED-P

P → PO*

PHOSPHINATE

HPO_4
PO*

PHOSPHATE

HPO_4
PO* H_2O

HBr/ HPO_4 IS CAUSING ACIDITY IN EXTRUDER, RUST AND CORROSION AND DEPOLIMERIZATION (MFI INCREASE WITH LOST OF MECHANICAL PROPERTIES IN PA/PET/PBT/PC !

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

AGAINST BROKEN PIECES

ACIDS can be neutralized with specific acid scavengers:
HT4, BASE, EPOXY RESINS, **AS4**

A-H + B-OH → AB + H_2O
A-H + Epoxy → Epoxy-Br + H_2O

AS4

+

RADICALS can be neutralized with specific to polymer:
HYNDRED PHENOLS **AOX1**

R*, OH*, H*, RO*, PO* + AOX1 → R, H_2O, RH, RO, PO

AOX1

+

PEROXIDES can be neutralized with specific to polymer:
PHOSPHINATES **AOX2**

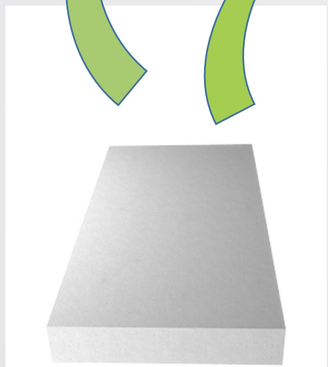
R-O-O-H + AOX2 → R-OH + PHOSPHATE

AOX2

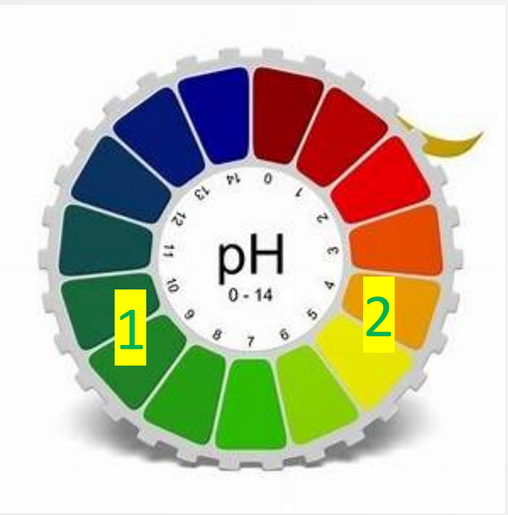
THIS ADDITIVES PACKAGE, SPECIFIC FOR EACH POLYMER, WILL GUARANTEE TO MANTAIN A GOOD COLOR AND LOW MFI, DURING RECYCLING !

EXAMPLES 1 - ACIDITY

1	FR-PS RECYCLED AT 250°C + MB PS POX 126
2	FR-PS RECYCLED AT 250°C

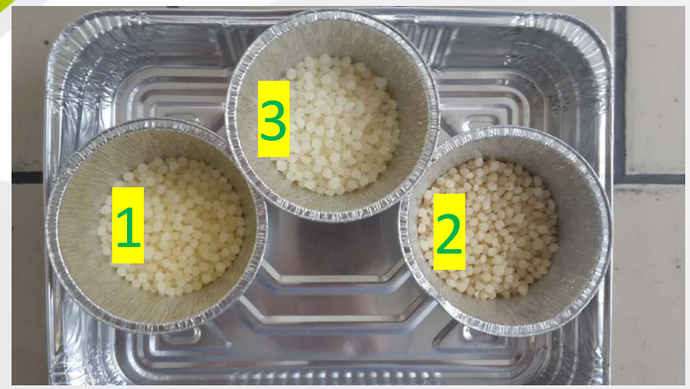


GPPS + 2% FR
$MFI_{180°C / 325 gr}$:5
BUILDING

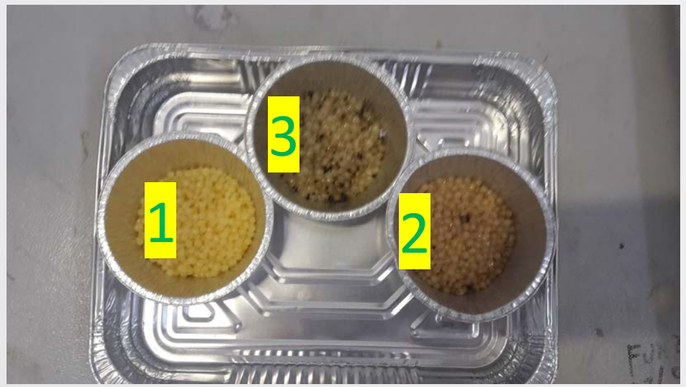


	1	2
COLOR	WHITE	BROWN
MFI 180°C / 325 gr	7	35
pH	7-8	4-5

EXAMPLES 2 – THERMAL OXIDATION



A



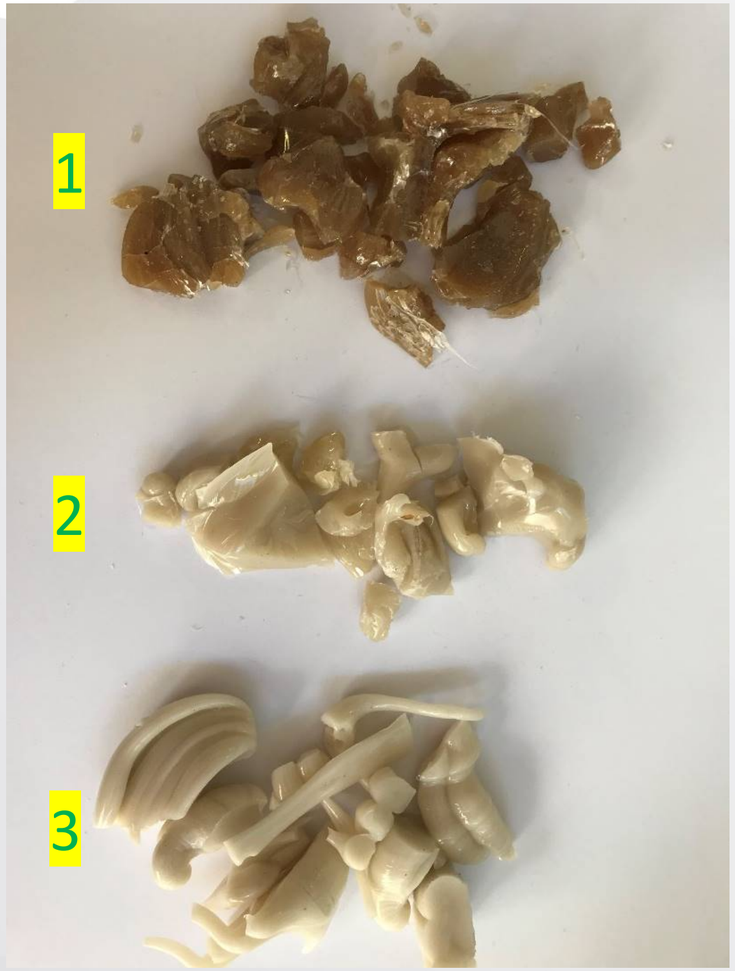
B

C

1	FR-PS RECYCLED + MB PS POX 126 3%
2	FR-PS RECYCLED + MB PS POX 126 1%
3	FR-PS RECYCLED + STANDARD STABILIZATION

A	B	C
1 EXTRUSION 220°C	1 EXTRUSION 220°C	1 EXTRUSION 220°C
	1 HOUR @ 205°C	1 HOUR @ 205°C
		2 HOURS @ 205°C

EXAMPLES 3 MULTIPLE EXTRUSIONS



1	2	3
FR – PS EXTRUDED AT 220°C FOR 3 TIMES	FR – PS EXTRUDED AT 220°C FOR 3 TIMES	FR – PS EXTRUDED AT 220°C FOR 3 TIMES
STANDARD STABILIZATION	3% MB PS POX 126	5% MB POX 126
MFI: 50 180°C / 325 gr	MFI: 16 180°C / 325 gr	MFI: 7 180°C / 325 gr

BANNED FR - GC HBCD CHILLER

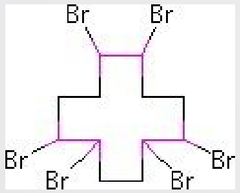
2008 HBCD has been declared PBT product, toxic for the enviroment.

October 2008: HBCD in annex XIV, Reg. 1907/2006 very high concern substance (SVHC) .

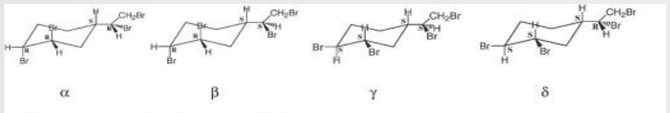
It has been banned from August 2015 for EPS and XPS application!

→ BIG CONCERN WHEN IT COMES TO WASTE PLASTICS, MAINLY PS, CONTAINING HBCD, BECAUSE IT'S SVHC, H361, H362, H410

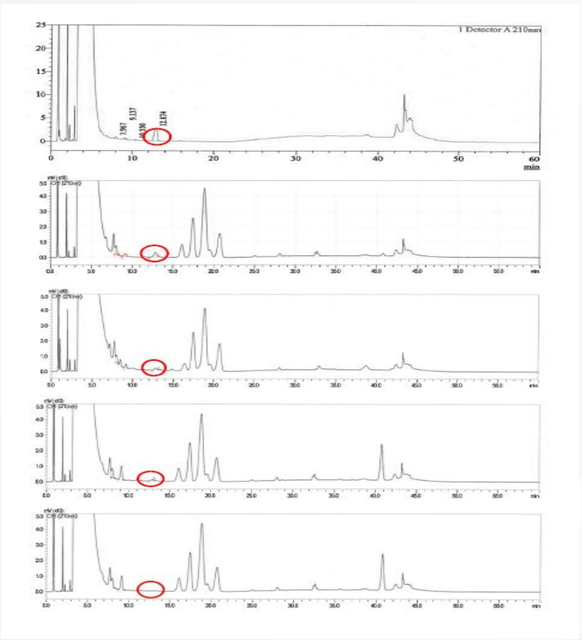
THERMAL STABILITY OF HBCD: T50= 277°C / 260°C + **GC HBCD CHILLER**, strong base → POLYMER + INORGANIC SALT

PS+ 

+ **GC HBCD CHILLER** → R+ H_2O + SALT



T: 280°C + 5% **GC HBCD CHILLER**
No more HBCD detected →



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WE WHO...
WE PROTECT FROM THE SUN...
BUT NOT WITH SUNGLASSES

UV ABSORBERS, HALS and specific formulations to protect plastic polymers from sun light.

- FLAME RETARDANTS
- UV ABSORBERS & HALS
- PROCESS AID & PEROXIDES
- ANTIOXIDANTS
- ANTISTATICS
- LUBRICANTS

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GREENCHEMICALS PACKAGES

PE, PP, PS

MB PO HT4 40
- It's a heat stabilizer, acid scavenger, polyolefines carried masterbatch
- It's particularly suitable for recycling plastics containing flame retardants.
- MB PO HT4 neutralizes bromidric acid, which is creating during recycling extrusion and guarantee good color of final compound.

MB PO POX 20
- It's a polyolefine carried antioxidants masterbatch.
- It prevents radical polymer degradation and polymer oxidation, during polymer recycling. Mainly for PE, PP, PS
- It guarantees to preserve MFI and color, during recycling

MB PS POX 126
- It's a PS carried antioxidants masterbatch.
- It prevents radical polymer degradation and polymer oxidation, during polymer recycling. Mainly for PS
- It guarantees to preserve MFI and color, during recycling

ETP, ETP fibers, PC, ABS

MB PA AS4 31
- It's a heat stabilizer, acid scavenger, PA6 carried masterbatch
- It's particularly suitable for recycling PA/PET/PBT containing flame retardants.
- MB PO AS431 strongly neutralizes acidity, which is creating during recycling extrusion and guarantee good color of final compound and guarantees to preserve MFI and color, during recycling

MB PAF AS4 94
- It's a heat stabilizer, acid scavenger, PA6 carried masterbatch
- It's particularly suitable for recycling PA/PET fibers containing flame retardants.
- MB PO AS431 strongly neutralizes acidity, which is creating during recycling extrusion and guarantee good color of final compound. It's really active against peroxides.

MB PC AS4 9
- It's a PC carried antioxidants masterbatch, containing chemical acid scavenger.
- It prevents radical polymer degradation and polymer oxidation, during polymer recycling. It has been developed for PC, PC/ABS.
- It guarantees to preserve MFI and color, during recycling.

CONCLUSION

- PLASTIC RECYCLING IS A VERY SENSITIVE TOPIC
- FLAME RETARDANT PLASTICS IS PROBLEMATIC BUT POSSIBLE
- IT'S POSSIBLE TO RECYCLE FR-PLASTIC WITH SPECIFIC PACKAGES
- IT IS POSSIBLE TO DESTROY SPECIFIC MOLECULES BY EXTRUSION WITH SPECIFIC PACKAGES
- VIA EXTRUSION IT'S POSSIBLE TO SOLVE A LOT OF RECYCLE PROBLEMS

THANKS A LOT FOR THE ATTENTION