GC SAM

ALTERNATIVE TO HBCD for XPS

Micaela Lorenzi
Ethel Garlaschi

POPRC 9

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SAM PROJECT PARTNERSHIP

GREENCHEMICALS

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SUMMARY

- GREENCHEMICALS
- KEY CRITERIA FOR SELECTING A HBCD REPLACEMENT
- HOW WE GOT TO GC SAM
- REGULATORY, ARTICLE END OF LIFE
- INTELLECTUAL PROPERTY, AVAILABILITY
- POSITIVES & NEGATIVES ON GC SAM
- SOLUTIONS TO NEGATIVE ASPECTS
- SAM COMMERCIAL EXPERIENCE
- CONCLUSIONS

established in 2010.
We are Flame Retardants and Plastic Additives formulators.
Powder blends, compacted, masterbatches.

Our intention is reducing enviromental impact of exsisting FR formulations!

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) .

Proposed to ban HBCD from August 2015 for EPS and XPS application!

www.greenchemicalsrl.it

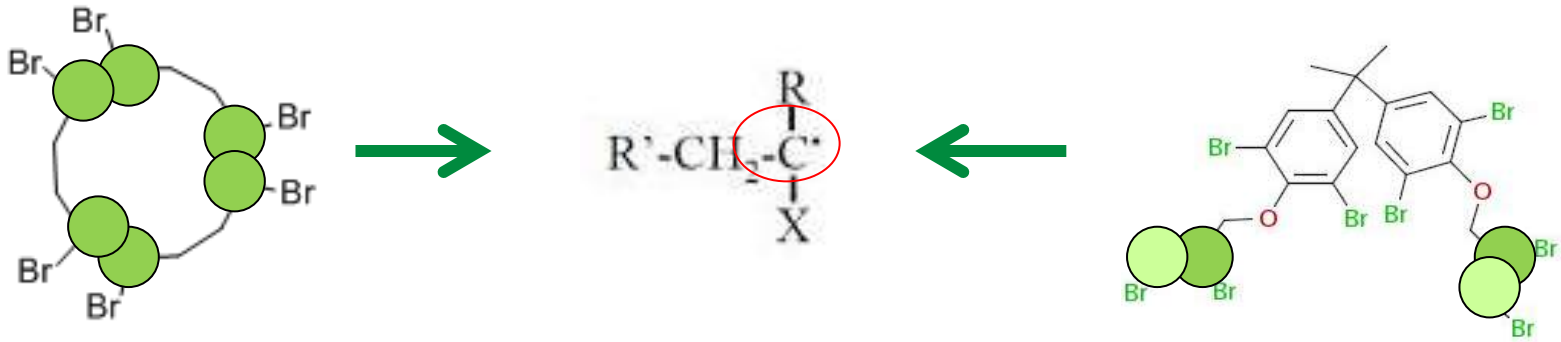
KEY CRITERIA SELECTION FOR HBCD REPLACEMENT

- FIRE PERFORMANCE
- SUPERIOR ENVIRONMENTAL AND HEALTH PROFILE
- REACH COMPLIANCE
- THERMAL STABILITY (TGA) FOR " FR – PS SECOND LIFE"
- COMPATIBLE WITH BASE POLYMER SYSTEMS
- EXISTING TECHNOLOGY. IMMEDIATE AVAILABILITY
- COST EFFECTIVE SOLUTION!

PS AND PP

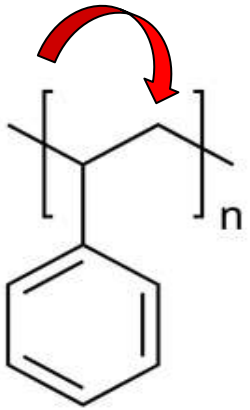
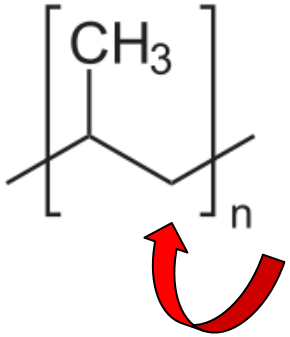
DRIPPING MECHANISM

In PS, as in PP, aliphatic or Br radicals in the melt cause rapid polymer breakdown.
The material drips away from the flame front , taking heat with it.



HBCD + DICUMENE + HEAT STAB.

BDDP + DICUMENE + ANTIMONY TRIOXIDE

PS 		PP 
Test	**EUROCLASS E** **DIN 4102 B1-B2**	**UL 94 V2**

Comparison PS and PP

DRIPPING MECHANISM

In PS, as in PP, aliphatic or Br radicals in the melt cause rapid polymer breakdown.
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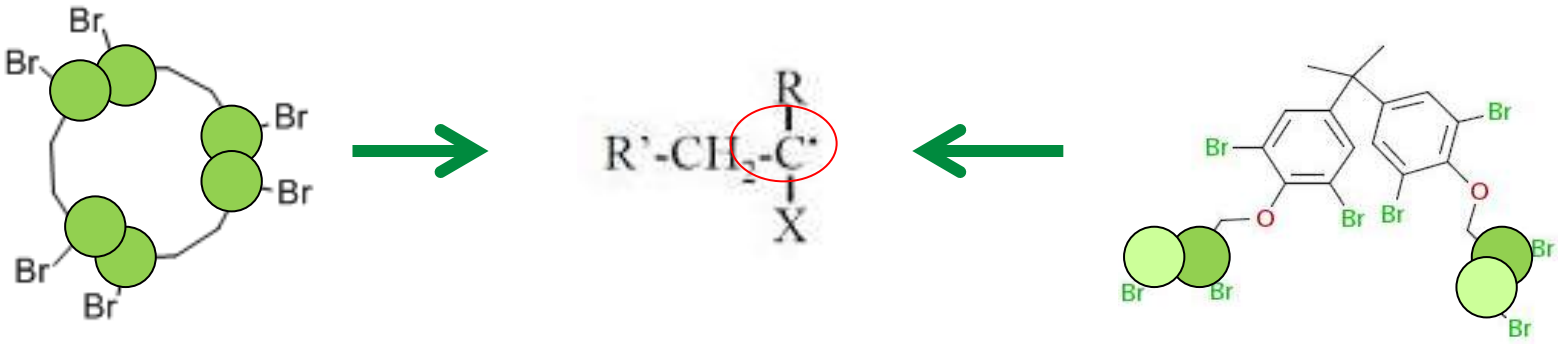

HBCD + DICUMENE + HEAT STAB.

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Test	EUROCLASS E DIN 4102 B1-B2	UL 94 V2

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Due to similarities between PS and PP, we supposed BDDP could have good performance in PS.

Removal of the Sb_2O_3 and **optimizing of BDDP/DICUMENE ratio**

has given unexpected result of remarkeble **drop of extinguishing times.**

Spring 2011: development of lab tests and formulation.

Test performed: UL 94 V2

PS		*100*	*100*	*100*	*100*	*100*
BDDP			*3*	*3.4*	*0.6*	*0.8*
Dicumene			*0.16*	*0.2*	*0.06*	*0.08*
Sb_2O_3			*0.8*	*0.9*	-	-
Rating V-2	1.6 mm 3.2 mm	Fail Fail	Fail Fail	Pass Pass	Pass Pass	Pass Pass

All values are in %w/w
HB: Horizontal Burning
V-2: Formulations that meets UL94 V-2 criteria
BDDP: Tetrabromobisphenol A bis (2,3-dibromopropyl ether)
Sb_2O_3: Antominy Trioxide
Dicumene: 2,3-dimetyl-2,3-diphenylbutane

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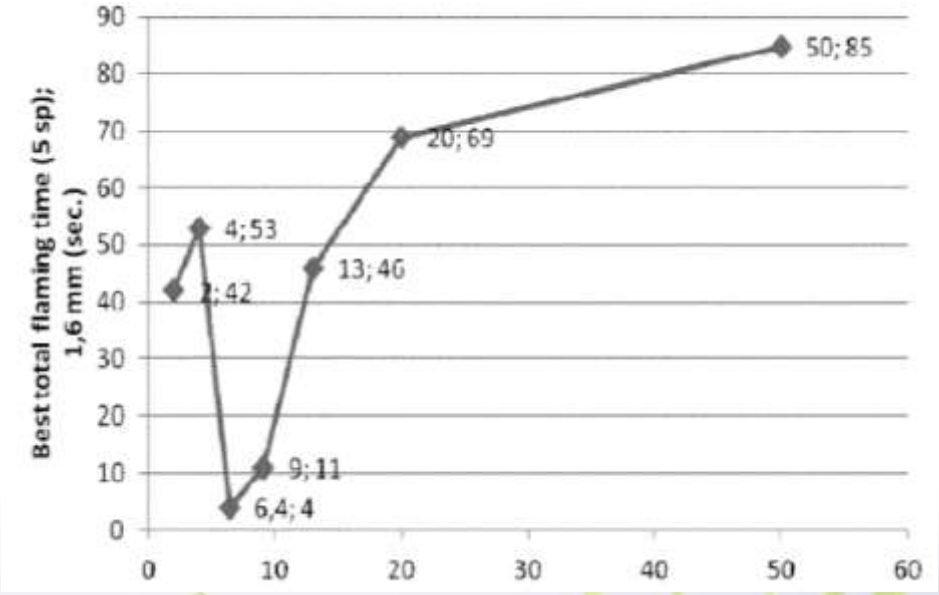
UNEXPECTED SYNERGISTIC EFFECT OF BDDP AND DICUMENE

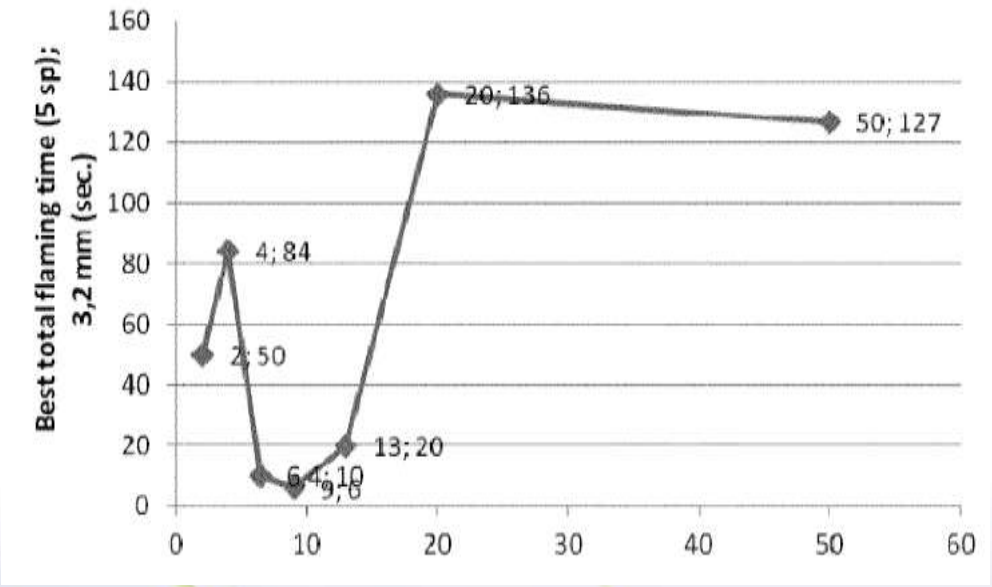
% R2 / R1+R2	R1:R2	Best total flaming time (5 sp); 1,6 mm (sec.)
2	50:1	42
4	25:1	53
6,4	15,625:1	4
9	11,1:1	11
13	7,7:1	46
20	5:1	69
50	1:1	85

%R2 / R1+R2	R1:R2	Best total flaming time (5 sp); 3,2 mm (sec.)
2	50:1	50
4	25:1	84
6,4	15,625:1	10
9	11,1:1	6
13	7,7:1	20
20	5:1	136
50	1:1	127

Range of concentration of the best total flaming time: 0,9-1,7%



% Dicumene on the total amount of Flame Retardant



% Dicumene on the total amount of Flame Retardant

LAB TRIALS

TEST performed: UL 94 V-2

TESTS TO CATCH BEST BDDP/DICUMENE RATIO

		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
PS		94.6	99.2	99.0	99.5	99.25	99.05	99.54	99.08	98.62	**99.34**	**99.12**	**98.72**	**98.3**	99.06	99.08	98.88	98.67
BDDP		0.3	0.4	0.5	0.4	0.6	0.8	0.4	0.8	1.2	**0.6**	**0.8**	**1.2**	**1.6**	0.9	0.9	1.1	1.3
Dicumene		0.3	0.4	0.5	0.1	0.15	0.2	0.06	0.12	0.18	**0.06**	**0.08**	**0.08**	**0.1**	0.04	0.02	0.02	0.03
% Dicumene su totale FR		**50%**	**50%**	**50%**	**20%**	**20%**	**20%**	**13%**	**13%**	**13%**	**9%**	**9%**	**6%**	**6%**	**4%**	**2%**	**2%**	**2%**
Max Flaming Time (sec.)	**1.6 mm**	> 60	22	20	17	22	30	20	18	10	**19**	**3**	**19**	**1**	15	20	20	15
	3.2 mm	26	20	16	17	17	17	16	13	8	**25**	**3**	**10**	**2**	10	>30	20	17
Total Flaming Time for 5 Spec. (sec.)	**1.6 mm**	> 300	85	92	69	147	165	62	91	46	**86**	**11**	**60**	**4**	53	95	78	42
	3.2 mm	145	127	84	136	95	59	100	91	20	**115**	**6**	**34**	**10**	84	>300	90	50
Specimens Dripped	**1.6 mm**	All	All	All	All	All	All	All	All	All	**All**	**All**	**All**	**All**	All	All	All	All
	3.2 mm	All	All	All	All	All	All	All	All	All	**All**	**All**	**All**	**All**	All	All	All	All
Cotton Ignition	**1.6 mm**	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	**Yes**	**Yes**	**Yes**	**Yes**	Yes	Yes	Yes	Yes
	3.2 mm	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	**Yes**	**Yes**	**Yes**	**Yes**	Yes	Yes	Yes	Yes
Rating	**1.6 mm**	HB	V-2	V-2	V-2	V-2	V-2	V-2	V-2	V-2	**V-2**	**V-2**	**V-2**	**V-2**	V-2	V-2	V-2	V-2
	3.2 mm	V-2	V-2	V-2	V-2	V-2	V-2	V-2	V-2	V-2	**V-2**	**V-2**	**V-2**	**V-2**	V-2	V-2	V-2	V-2

INTELLECTUAL PROPERTY

REGULATORY

	BDDP	DICUMENE
Cas N°	21850-44-2	1889-67-4
Reg. 1272/2008 (CLP) C&L	Not classified	Skin Sens. Cat. 1
Reg. 1907/2006 (REACH)	REACH compliant Registered in 2013 No SVHC	REACH compliant Registered in 2013 No SVHC
Dir. 2002/95/CE and s.m.i. (RoHS)	Compliant	Compliant

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(71) Applicants:
- Lorenzi, Micaela
20900 Monza (MB) (IT)
- Zambotti, Sabrina Francesca
20090 Cusago (MI) (IT)

(72) Inventors:
- Lorenzi, Micaela
20900 Monza (MB) (IT)
- Zambotti, Sabrina Francesca
20090 Cusago (MI) (IT)

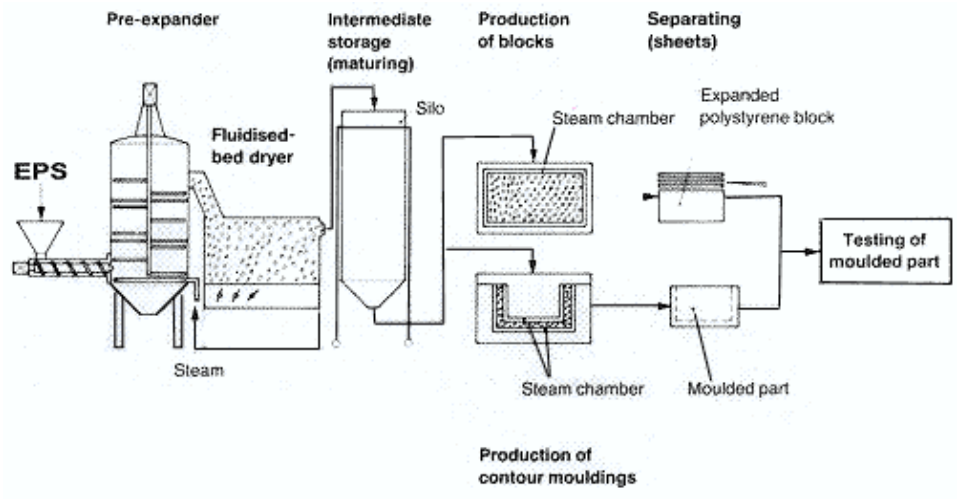
(74) Representative: Autuori, Angelo et al
EUREKA IP Consulting
Borgo Santa Lucia, 31
36100 Vicenza (IT)

(54) Novel flame-retardant composition for polystyrenic compounds

GC SAM is patent pending in EU, waiting for the grant.

Greenchemicals is evaluating partnership.

XPS and EPS



EPS

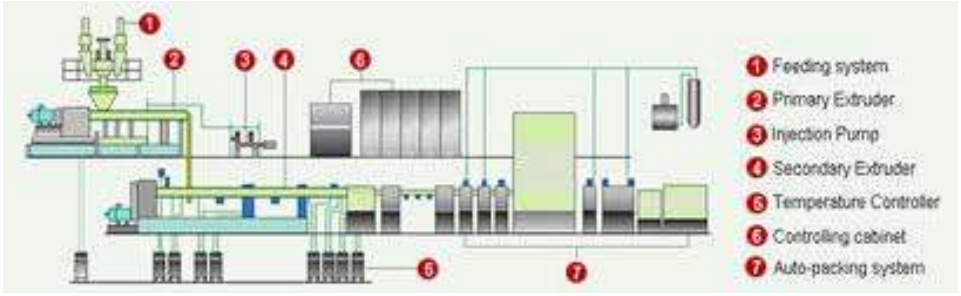
STYRENE,

FR, OTHER ADDITIVES IN POWDER,

PENTANE,

MIXED IN WATER BEFORE POLYMERIZATION

MAX TEMPERATURE REACHED 150° C



XPS

POLYSYRENE

FR OTHER ADDITIVES IN MASTERBATCHES

BLOWING AGENTS

T REACHED > 220° C

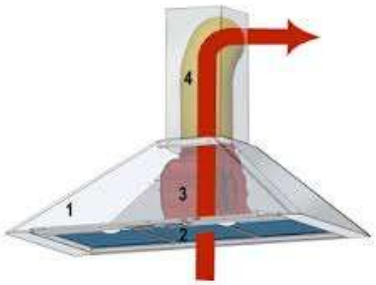
POSITIVES & NEGATIVES

POSITIVE	NEEDS IMPROVEMENTS	NEGATIVE	HBCD + DICUMENE	BDDP + DICUMENE
FIRE PERFORMANCE			0,8 – 1,5 %	2 – 3 %
REGULATORY **Reg. 1272/2008 (CLP)** **Classifing & Labelling** **Reg. 1907/2006 (Reach)** **Reg. RoHS**			*Repr.2/Lact./Aq.Acute1/Aq.Chronic1; H362;H400;H410* Registered in 2010 SVHC Substance	<u>Not Classified.</u> *Registered in 2013.* *No SVHC substaces.* **Reach Compliant.**
AVAILABILITY			PROPOSED TO BE BANNED	AVAILABLE: Raw materials are commodities. Existing plants.
COST			Fluctuating: 3Q 2013: 5 USD/Kg 2Q 2012: 12 USD/Kg	Stable: 5,50 – 6,50 USD/Kg
THERMAL STABILITY			5% @ 228˚ C	5% @ 305˚ C
RECYCLING PROP			Unstable, no possible to recycle.	Thermal stable. Possible to reprocess!
MELTING POINT			180 – 190 ˚ C	105 – 115 ˚ C
PROCESSABILITY			Good	Very Good
COMPATIBILITY WITH PS			Good	Very Good

END PRODUCT SECOND LIFE

	HBCD	BDDP
THERMAL STABILITY	**5% @ 228° C**	**5% @ 305° C**
RECYCLING PROP	Unstable, no possible to recycle.	Thermal stable. Possible to reprocess!

PP + BDDP + Dicumene + Sb_2O_3 → Re-processable, renewable



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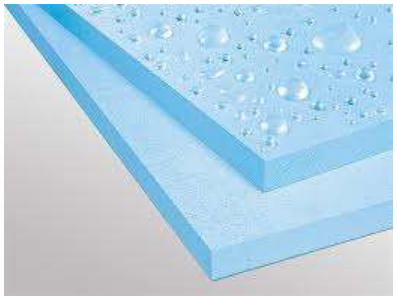
PS + BDDP + Dicumene → Re-processable, Ok for rubber!



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GREENCHEMICALS STARTED A PROJECT TO STUDY THE REGENERATION CYCLE OF ARTICLES CONTAINING GC SAM

AVAILABILITY

	HBCD	BDDP
AVAILABILITY	**PROPOSED TO BE BANNED**	**AVAILABLE: Raw materials are commodities. Existing plants.**

- **RAW MATERIALS ARE WORLDWIDE COMMODITIES, MAIN PRODUCTION SITES IN CHINA**
- **ALL THE RAW MATERIALS OF GC SAM ARE FLAME RETARDANT ADDITIVES COMING FROM PP (V2).**
- **FORMULATION IS IMMEDIATELY AND FULLY AVAILABLE ON A COMMERCIAL SCALE**

LOW MELTING POINT SOLUTION

	HBCD	BDDP
MELTING POINT	180 – 190 ° C	105 – 115 ° C

MASTERBATCH EXTRUSION DIFFICULTIES

SOLUTION

MASTERBATCH WITH PS-TALC OR POLIOLEFINS

2011 **MB PS SAM 54, MB PS SAM 55**:
BDDP/DICUMENE, PS AND TALC.
PROBLEMS: TALC MAY GIVE NUCLEATION EFFECTS.

2012 **MB PO SAM 54, MB PO SAM 55:**
BDDP/DICUMENE, LDPE AND/OR EVA

REACTIVITY SOLUTIONS

	HBCD	BDDP
FIRE PERFORMANCE	**0,8 – 1,5 %**	**2 – 3 %**

BDDP HALF REACTIVITY THAN HBCD

SOLUTION

HIGHLY CONCENTRATED PHYSICAL FORMS

2012 ***GC SAM 54 COMPACTED***
GC SAM 55 COMPACTED:
100% BDDP/DICUMENE

2012 ***GC PO SAM 54 DROPS***
GC PO SAM 55 DROPS:
80-85% ACTIVE BDDP/DICUMENE IN15-20% PE WAX.
MELTED AND DROPPED.

THESE TWO SOLUTIONS CAN REPLACE 1:1 A 50% ACTIVE HBCD MASTERBATCH STABILIZED AND SYNERGIZED.

TECHNICAL COMMERCIAL DATA

WE HAVE GOT APPROVALS IN 13 DIFFERENT XPS PRODUCERS

CUSTOMER	TEST PERFORMED	2012 LONG PRODUCTION RUN	BEST PRODUCT SOLUTION	NOTES	LOADING LEVEL COMPARED TO 50% HBCD MB
1 2	Euroclass E DIN4102 B1-B2	***MB PS SAM 54***	***MB PS SAM 54***	XPS BOARD KEEPS SAME MECHANICAL PARAMETERS THAN WITH HBCD	FROM SAME TO 50% MORE
3-4 5- 6-7	Euroclass E	***MB PS SAM 54*** ↓ PRODUCTION PROBLEM NUCLEATING EFFECTS DUE TO TALC IN MB	***MB PO SAM 55*** ***GC PO SAM 55 DROPS***	PROCESSING AID EFFECT THAT ALLOWS LOWER P AND TP OF THE PROCESS	FROM SAME TO 50% MORE
8-9 10-11 12-13	DIN4102 B1- B2		***MB PO SAM 55*** ***GCSAM 55 COMP.*** ***GC PO SAM 55 DROPS***	BEST PERMARMANCE HIGHER THICKNESS BOARDS	FROM SAME TO 50% MORE

SAM COMMERCIAL EXPERIENCE

REGULAR CUSTOMERS

WE HAVE BEEN AUTHORIZED TO MENTION:

SELIT-TEC DÄMMSYSTEME GMBH	GERMANY
SSF PRODUCTION, LLC	STATE OF NY, US Y
DGSA ITALIA SRL	ITALY
SECTOR 2	ITALY

THE ALTERNATIVE GC SAM IS AVAILABLE, IT WORKS AND XPS FOAM REMAINS A COST EFFECTIVE PRODUCT FOR B&C!

GREENCHEMICALS PRODUCTION PARTNERS

3A Mcom S.r.l.

Amedeo Brasca S.r.l.

Guzzetti Master S.r.l.

SAP Europa S.r.l.

VIBA S.p.A.

CONCLUSIONS

- **A NEW FLAME RETARDANT FORMULATION IS DEVELOPED TO REPLACE HBCD IN XPS APPLICATION:**

- **BDDP + DICUMENE**

  FIRE PERFORMANCE
  GOOD ENVIRONMENTAL AND HEALTH PROFILE
  IMPROVED PROPERTIES TO RE-USE THE END PRODUCT!
  COMPATIBILITY WITH BASE POLYMER SYSTEMS
  COMPETITIVE COST
  AVAILABILITY
  THERMAL STABILITY

- **FORMULATION IS ALREADY AVAILABLE ON A COMMERCIAL SCALE LEVEL.**

…….to be continued

GREENCHEMICALS

WE ARE WORKING FOR

CATCHING

HALOGEN FREE SOLUTION

THANKS TO

MR. TIMO SEPPÄLÄ
MR. PETER DAWSON
CUSTOMERS THAT HELP US DEVELOPING SAM
OUR COMMERCIAL AND PRODUCTION PARTNERS

ALL OF YOU FOR YOUR ATTENTION