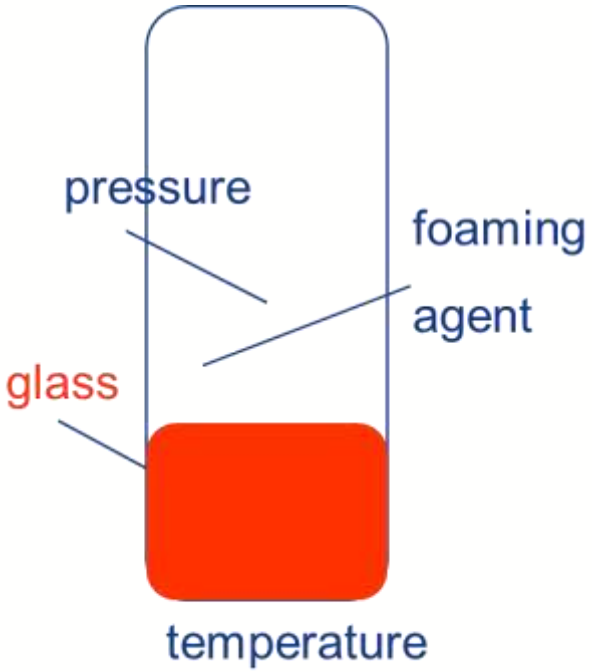
TROVOtech
functional inorganic additives

The long way from invention to commercialization – development, drawbacks and introduction of the synergist TROVO®powder B

- The Invention
- Trovotech´s Technology and Foaming Process
- Characteristics of the Glass Powder
- Synergistic Behavior of TROVOpowder B
- Results of TROVOpowder B in PA ,PBT and PET Applications
- Experience with Compounder and Trovopowder B Application Developments



glass foam is created by sudden relaxation

If you make something new something new will be coming out.

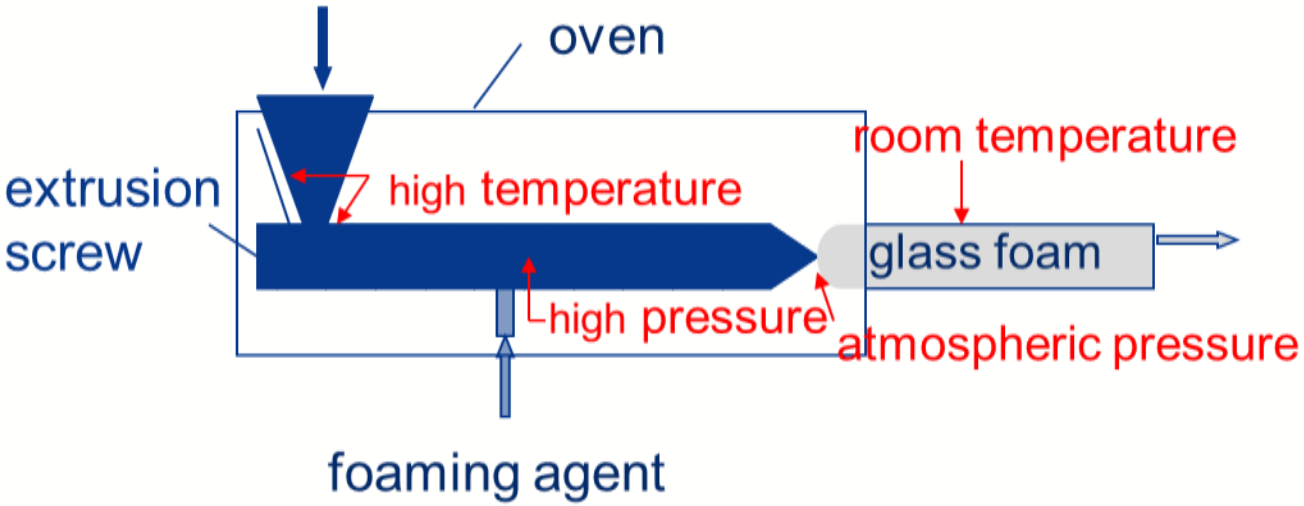
Free according to Joseph Schumpeter
(National Economist and Politician 1883 – 1950)

Patent application for "the production of foamed glass by a high temperature extrusion process"

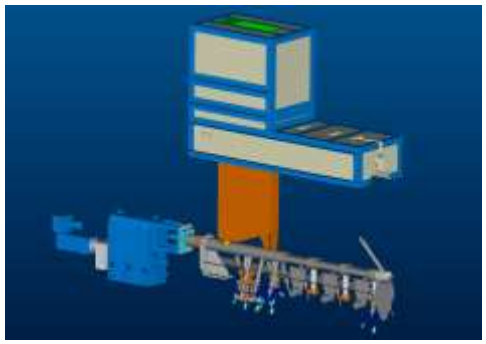
Grant of the German patent

1995 → 09/1995 → 11/1997

To develop a world novel production technology – producing foam glass by a high temperature extrusion process to be used as insulation material.



2000 2000 2000



Period of constructing the extruder

Completion of the extruder

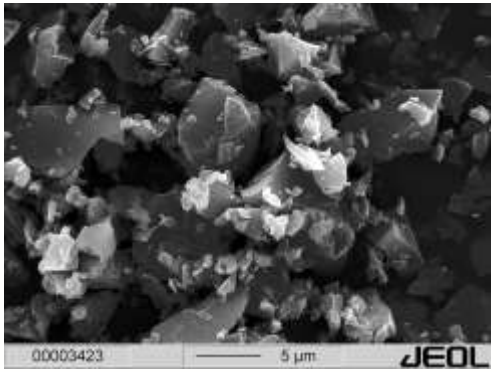
1/2000 — 12/2000 — 2003

First Glass Foam

Fracture of the Screw

Continous Production

2003 — 2004 — 2006

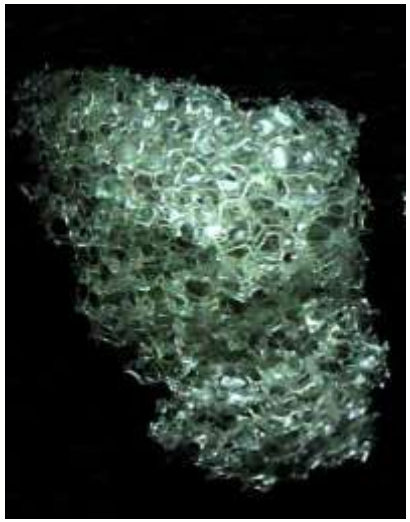


High temperature extrusion

Crushing

Modifying

2003 → 2005 → 2006 → 2017



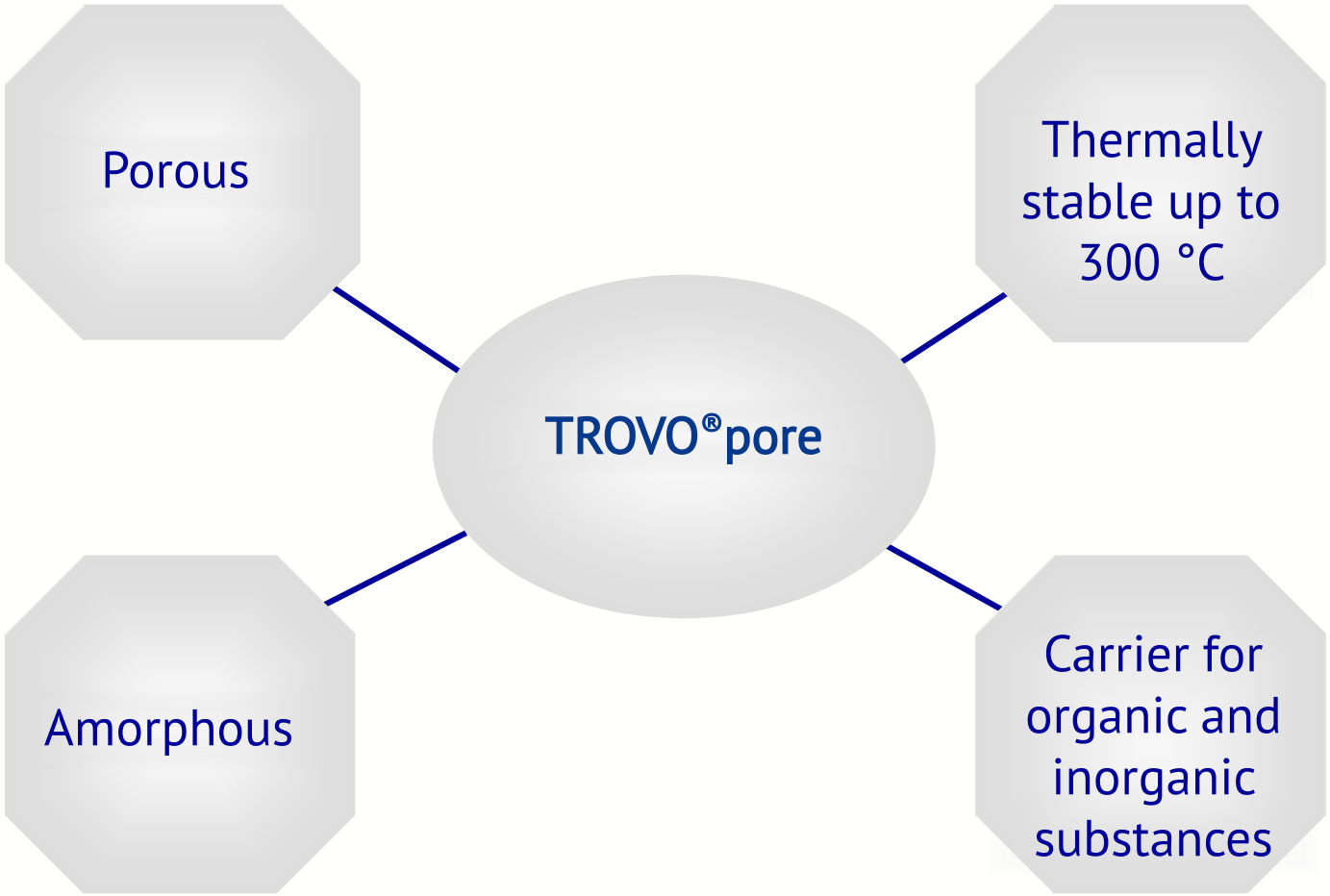
- density: > 0,3 g/cm³
- coarse-pored
- inhomogeneous
- recycled glass

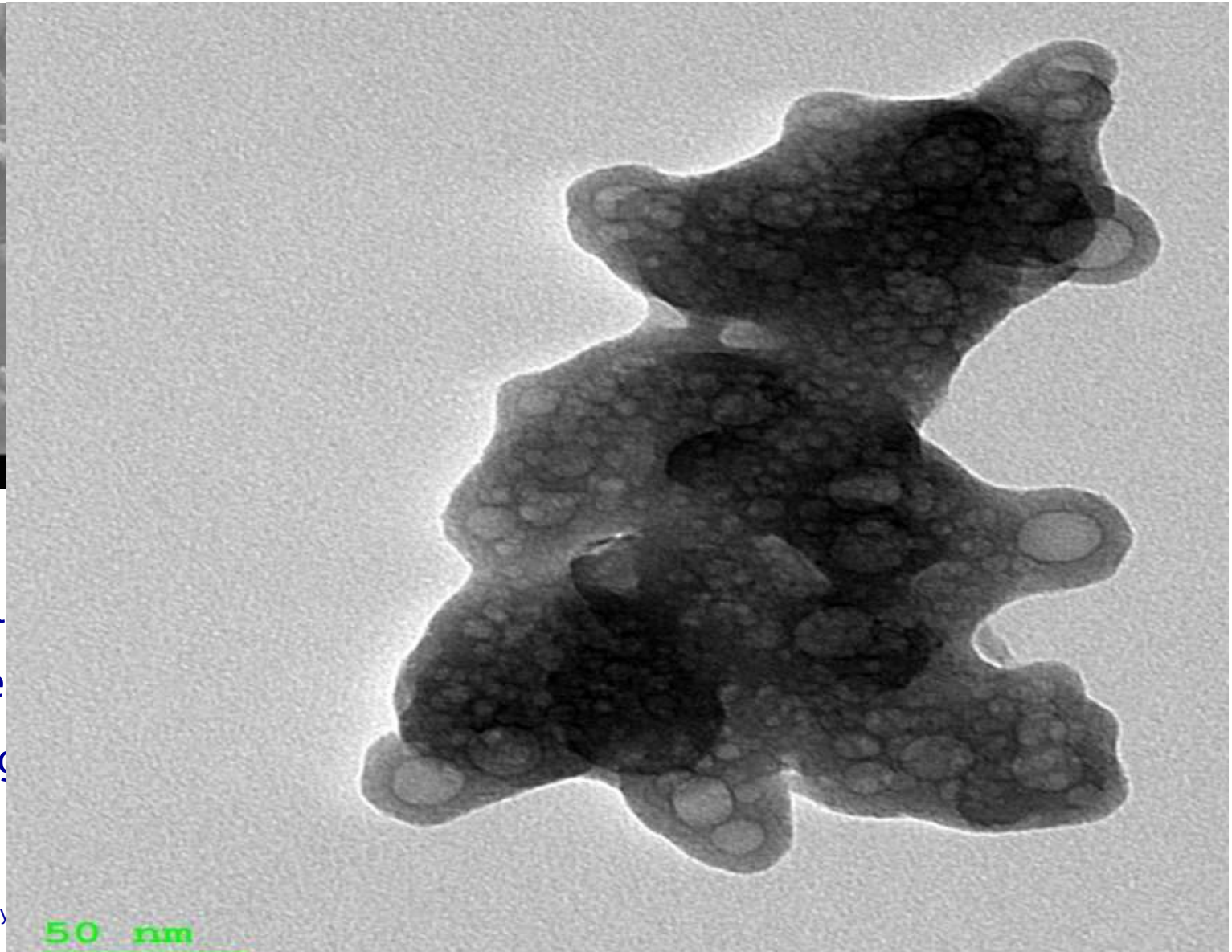
- density: 0,3 g/cm³
- coarse-pored
- inhomogeneous
- glass pellets

- density: 0,2 g/cm³
- fine-pored
- inhomogeneous
- soda lime glass

-density: ⩽ 0,13 g/cm³
- finest-pored
- homogeneous
- borosilicate glass

2003 2004 2005 2006


Porous
Thermally stable up to 300 °C
TROVO®pore
Amorphous
Carrier for organic and inorganic substances



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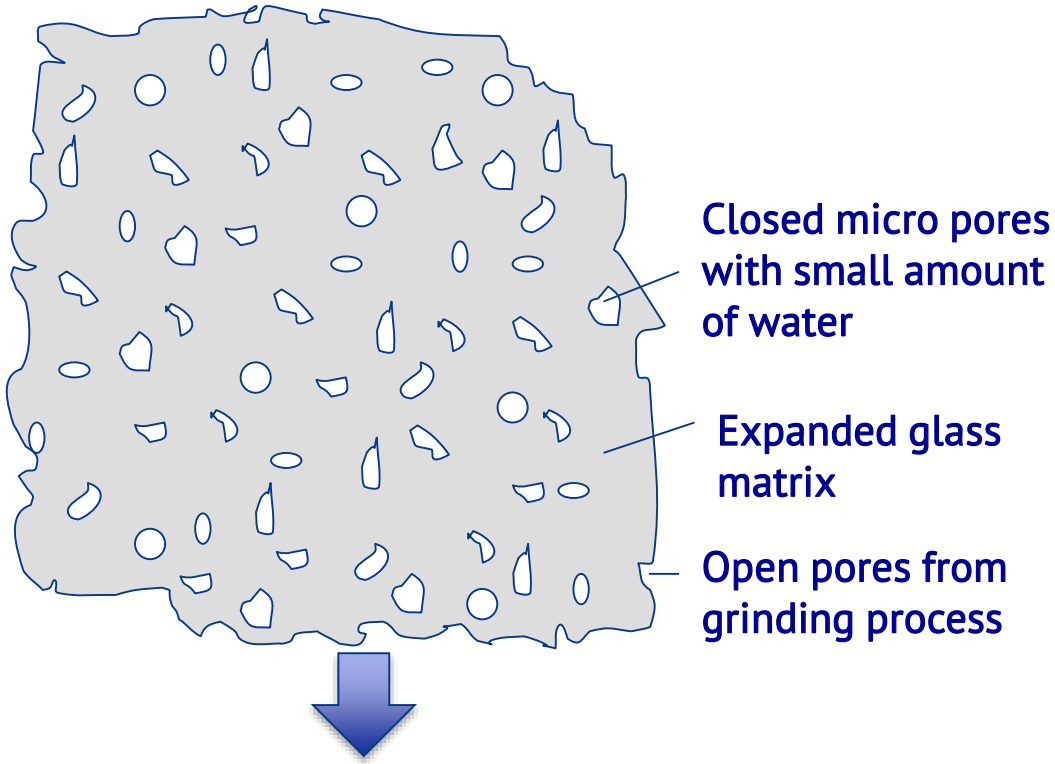
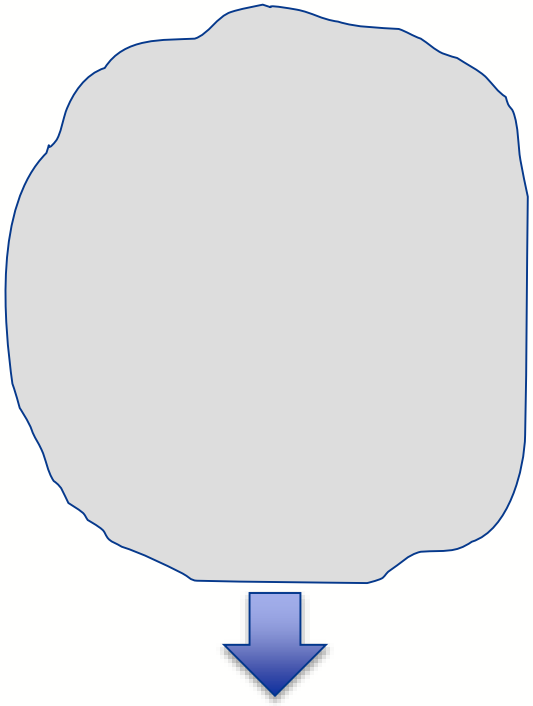
Physically modified glass particles made out of foam glass



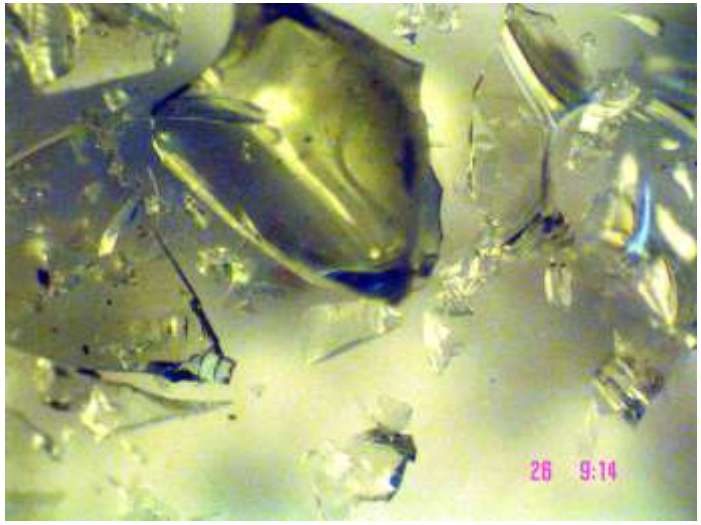
Glass particles from non-foamed glass



5 – 50 nm	Pore diameter	---
1,3 g/cm³ (including closed micro pores)	Bulk density	2,5 g/cm³

The Glass Alliance Europe (former CPIV) is the European Alliance of Glass Industries. It gives the following information on the nature of glass on their web site:

Glass is an inorganic material obtained from different inorganic raw materials which react at high temperature to form a new random network, where different elements are linked together, typically by oxygen bridges. Under the REACH Regulation glass is considered as a UVCB substance (substance of unknown or variable composition, complex reaction products or biological materials).

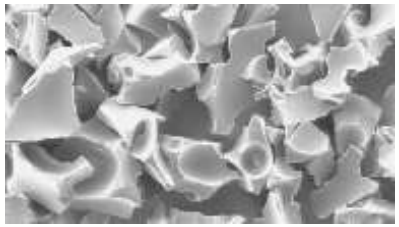


Glass and Registration: CAS no.: 308066-74-2; EC / List no.: 920-837-3
Based on the nature of the substance glass and its specific generic inertness, the Commission added glass to the list of substances exempted from the "obligation to register" (REACH Regulation Annex V (11)).

2007 2010 2013 2018

Product grades 	d_{50} in µm	d_{99} in µm
TROVO®powder B-K2	2.0	< 10
TROVO®powder B-K3	3.0	< 12
TROVO®powder B-K6	6.0	< 20
TROVO®powder B-K8	8.0	< 32

TROVO®powder



Improving mechanical properties

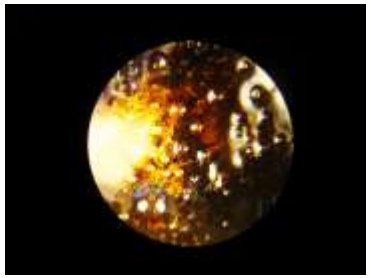
Grinding wheels

TROVO®guard

Protecting against germs

Silicon sealants

TROVO®powder B



Reducing flammability

First development of flame retardant

2006 2009 2011

IQ–Innovation Competition Central Germany

Innovation Competition Bitterfeld

Saint-Gobain Innovation Competition

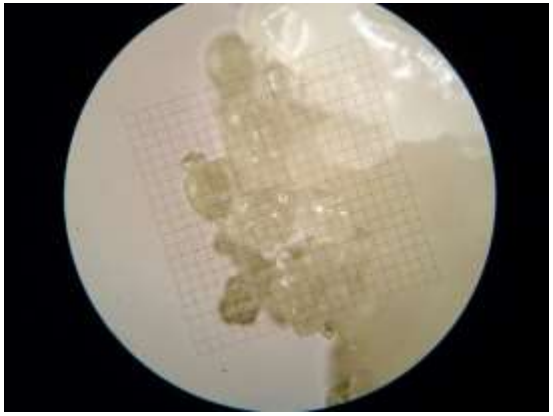
2005 → 2006 → 2011

- 1997 Patent „Extrusion process“
- 2010 Patent „TROVOguard“
- 2016 Patent „Flame retardant“
- 2016 US-Patent „Flame retardant“

US-Patent
No.: US 9,487,645 B2 - „Flame retardant“
Abstract: A flame retardant composition for thermoplastics molding materials, and also moldings, fibers or films that can be prepared from the flame retardant modling materials. The composition includes 30 to 70 % by weight of melamine cyanuarate and of 30 to 70 % by weight of porous amorphous glass particles. The composition is prepared from foam glass produced continuously in a high-temperature extruder. The sum of the components is 100 % by weight.

1997 2010 2016

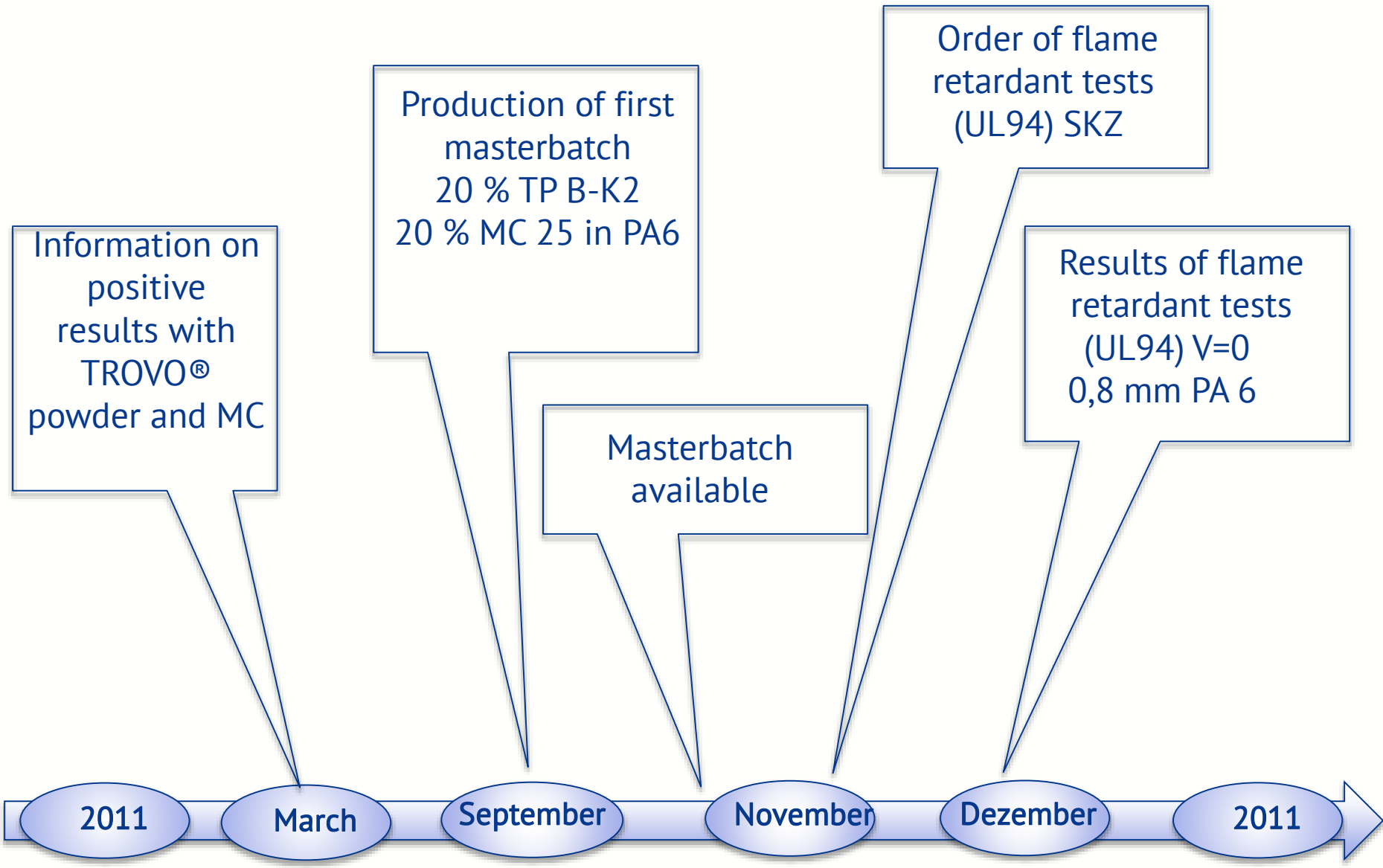
TROVO®powder B-K2 after exposure to flames:
Foaming of glass particles creates intumescent surface



Surface of a piece of wood protected with water glass and TROVO®powder B-K3 after 40 seconds of direct exposure to flames

2011 2011

2011 – First Developments with Flame Retardant Masterbatch



Sample with 10 wt % flame-retardant masterbatch (2.0% MC, 2.0 % TP B-K2; results from 11/2011)

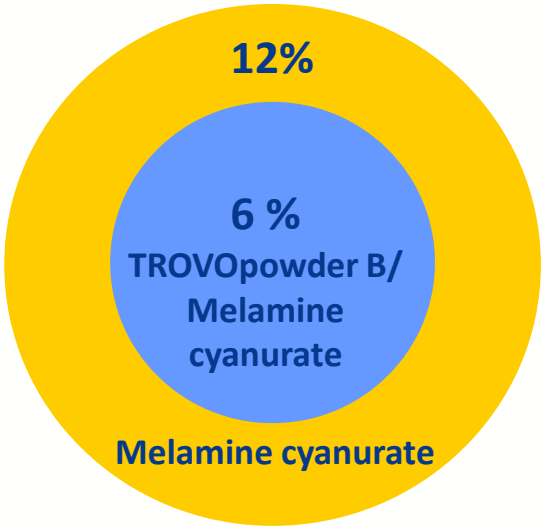
Spec. Nr.	Thickness [mm]	t_1 [s]	Burning cotton?	t_2 [s]	Burning cotton?	Classification
1	0.80	0.9	no	0.4	no	94 V-0
2	0.80	1.3	no	1.4	no	
3	0.80	0.6	no	0.5	no	
4	0.80	1.4	no	0.8	no	
5	0.80	0.4	no	0.6	no	

2011

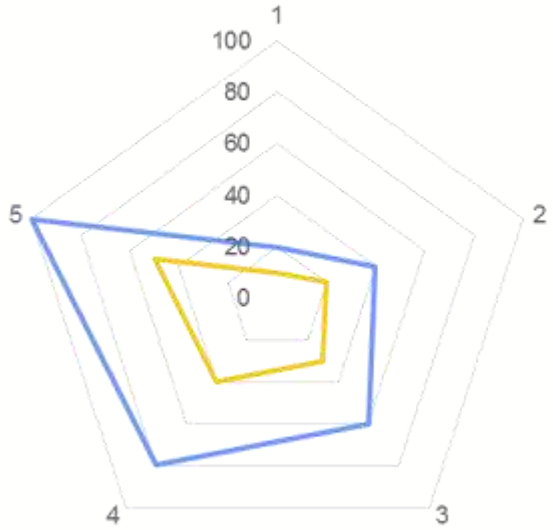
Advantage of TROVO®powder B

Less flame retardant additives leading to better polymer properties.

50 % saving in materials



Much better properties



2011 2013 2015 2017

Results PA6.6 (Ultramid A27), 30 % glass fibres

Specimen thickness	TP B-K3-Si-1.5	EXOLIT 1312	Afterburning time, total	UL94 class	GWIT/ GWFI
0.8 mm		20 %	39 s	V0	775/ 960
0.8 mm	5 %	15 %	41 s	V0	775/ 960

→ mechanical properties didn‘t change significantly
→ Results have been worked out by Dr. Sebastian Hörold, Clariant

Prüfergebnis / Test result

Das Material erfüllt den Anforderungssatz R22 und R23 für die Gefährdungsstufe:	The material complies with requirement set R22 and R23 for hazard level:
HL1 - HL2 - HL3	

CURRENTA Brandtechnologie

→ Similiar formulation with TP-K3-Si-1.5
→ HL 1 , HL 2, HL 3 for R22 and R23
→ Results have been worked out by Mr. Schwendinger, PolyOne

2012 2015 2017

Results combination of TROVOpowder B-K2 + FR halogen-free according to UL94 VTM.
Total active substance concentration: 4.5%

CLARIANT

Jürgen Wolf
Product Development Additives RBL Europe

Clariant Plastics and Coatings (Deutschland) GmbH

Gesamtkonzentration aktive Substanz: 4,5%

Preparation date:	
Thickness:	**150 MICRONS**
Polymer:	PET
MB dosage:	15%

SAMPLE NAME:S1

	FIRST IGNITION			SECOND IGNITION			
N° TEST	t1 (seconds)	DRIPPING	BURN COTTON	t2 (seconds)	t3 (seconds)	DRIPPING	BURN COTTON
1	1	Y	N	1	0	N	N
2	1	Y	N	1	0	Y	N
3	1	Y	N	1	0	Y	N
4	1	Y	N	1	0	Y	N
5	1	Y	N	1	0	Y	N
UL 94 classification:			**VTM-0**				

Results:

-> More stable UL94 / VTM = 0
-> Lower drippings
-> Cost reduction compared to pure HFFR solution.

Preparation date:	
Thickness:	**150 MICRONS**
Polymer:	PET
MB dosage:	

SAMPLE NAME:S7

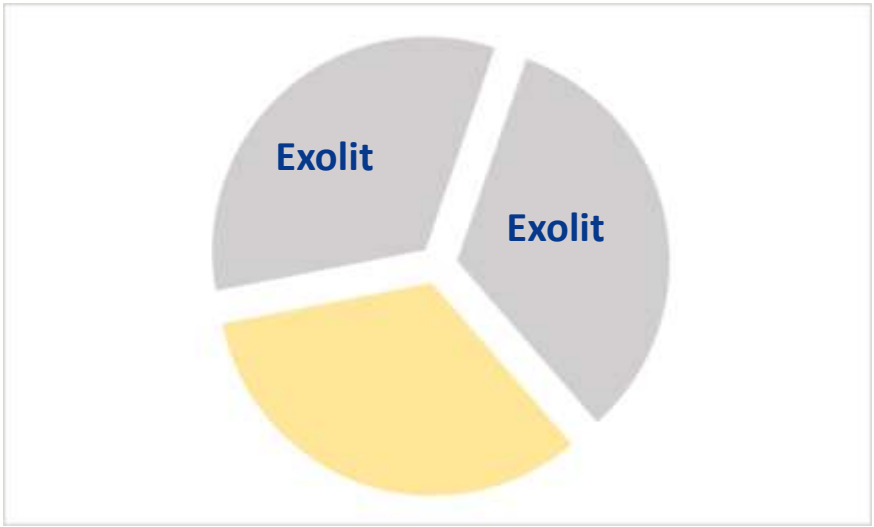
	FIRST IGNITION			SECOND IGNITION			
N° TEST	t1 (seconds)	DRIPPING	BURN COTTON	t2 (seconds)	t3 (seconds)	DRIPPING	BURN COTTON
1	1	Y	NO	1	0	Y	NO
2	1	Y	NO	1	0	Y	NO
3	1	Y	NO	1	0	Y	NO
4	1	Y	Y	1	0	Y	Y
5	1	Y	NO	1	0	Y	NO
UL 94 classification:			**V-0**	**limit**			

2015 2016 2017

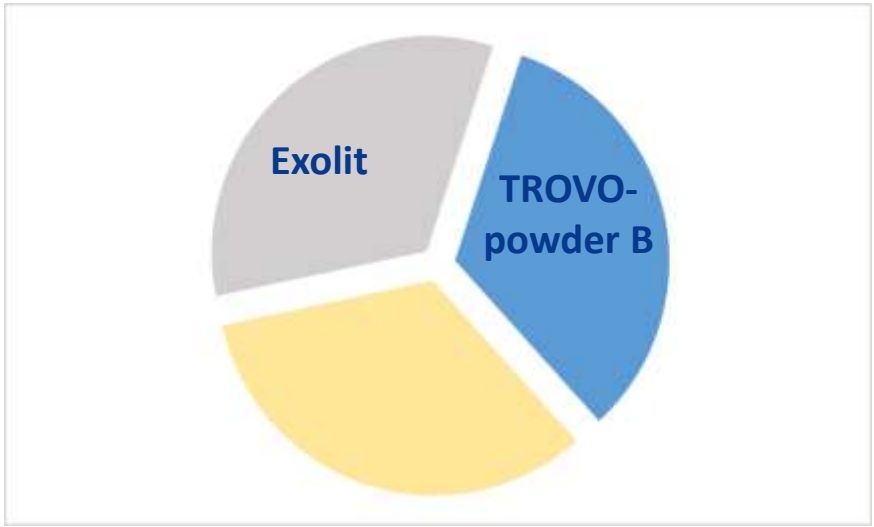
Advantage of TROVO® powder B

Substitution is reducing the costs of flame retardant equipment.

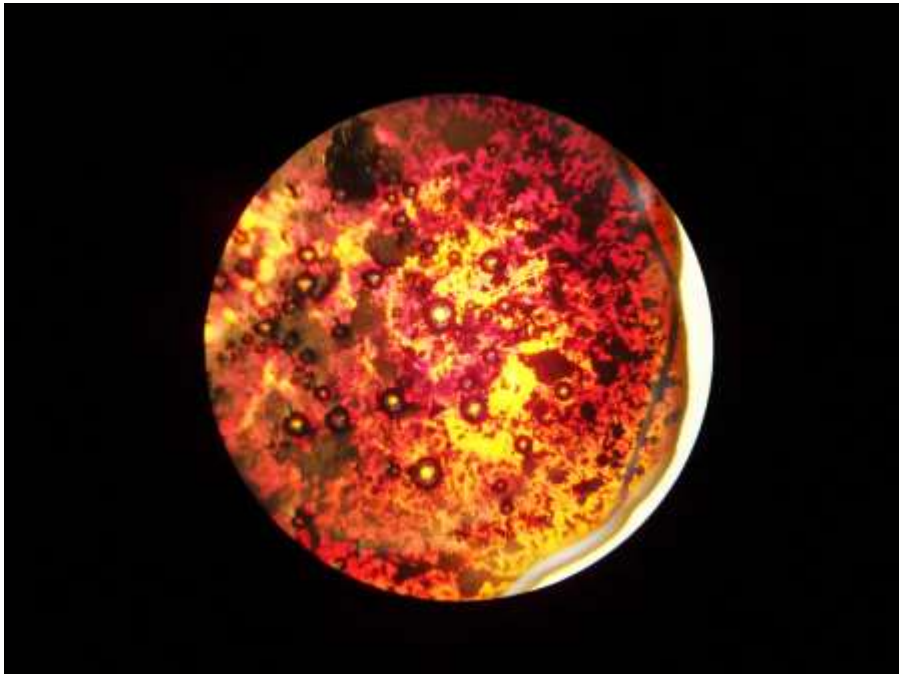
Only Exolit – Costs 100 %

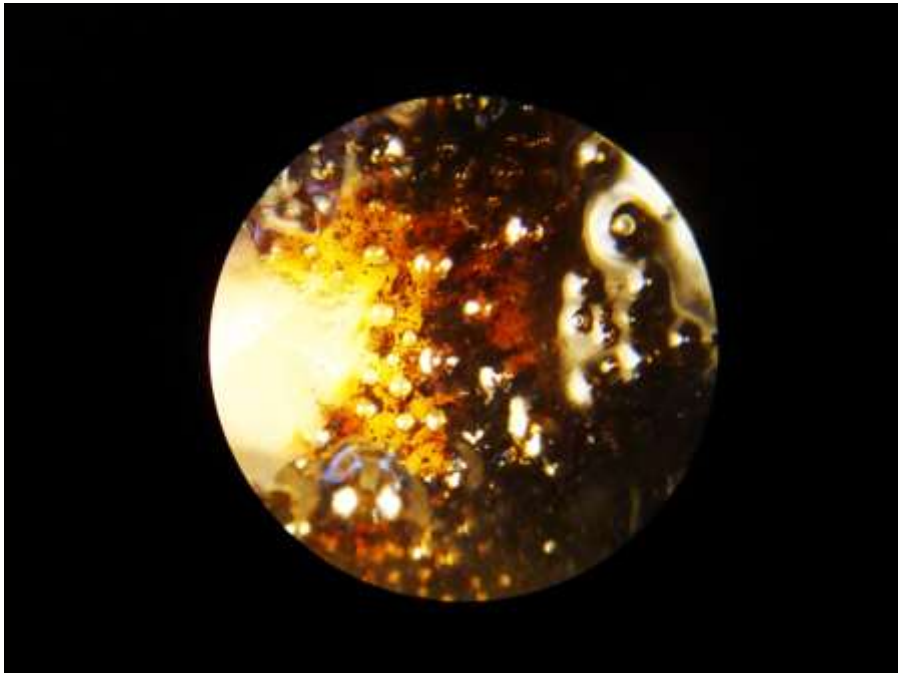


With TROVOpowder B – Costs 85 %



2012 2013 2017

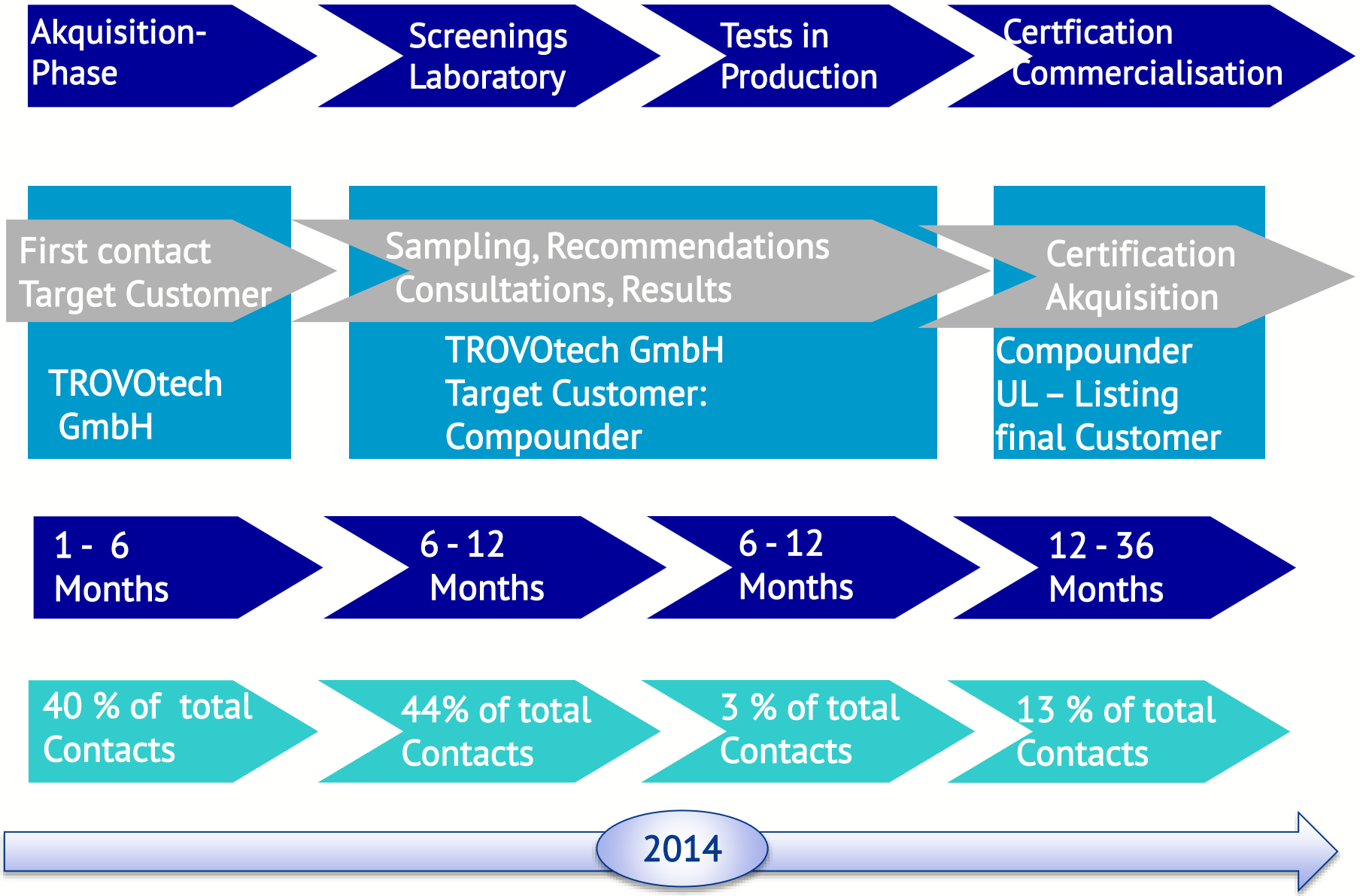




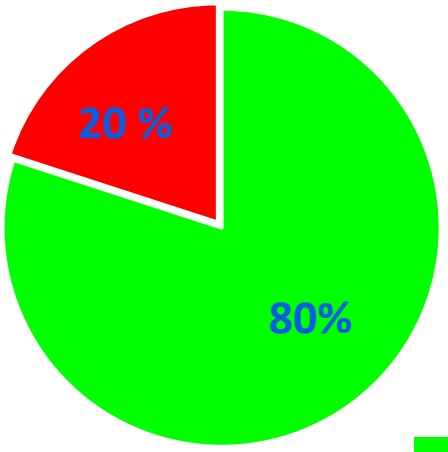
Microscope image of flame front of test specimen:

94 wt % PA6, 3.0 wt % TROVO®powder B-K2 and 3.0 wt % MC
confirmation of UL94 V0 results and good mechanical properties

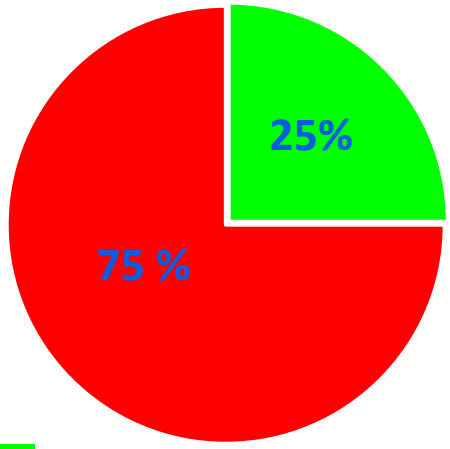
2013


Akquisition-Phase
Screenings Laboratory
Tests in Production
Certfication Commercialisation
First contact Target Customer
Sampling, Recommendations Consultations, Results
Certification Akquisition
TROVOtech GmbH
TROVOtech GmbH Target Customer: Compounder
Compounder UL – Listing final Customer
1 - 6 Months
6 - 12 Months
6 - 12 Months
12 - 36 Months
40 % of total Contacts
44% of total Contacts
3 % of total Contacts
13 % of total Contacts
2014

Results of target customers with 20 % TP, 20 % MC in PA 6 Masterbatch 10 % -15 % weight percentages in PA 6, PA 66:



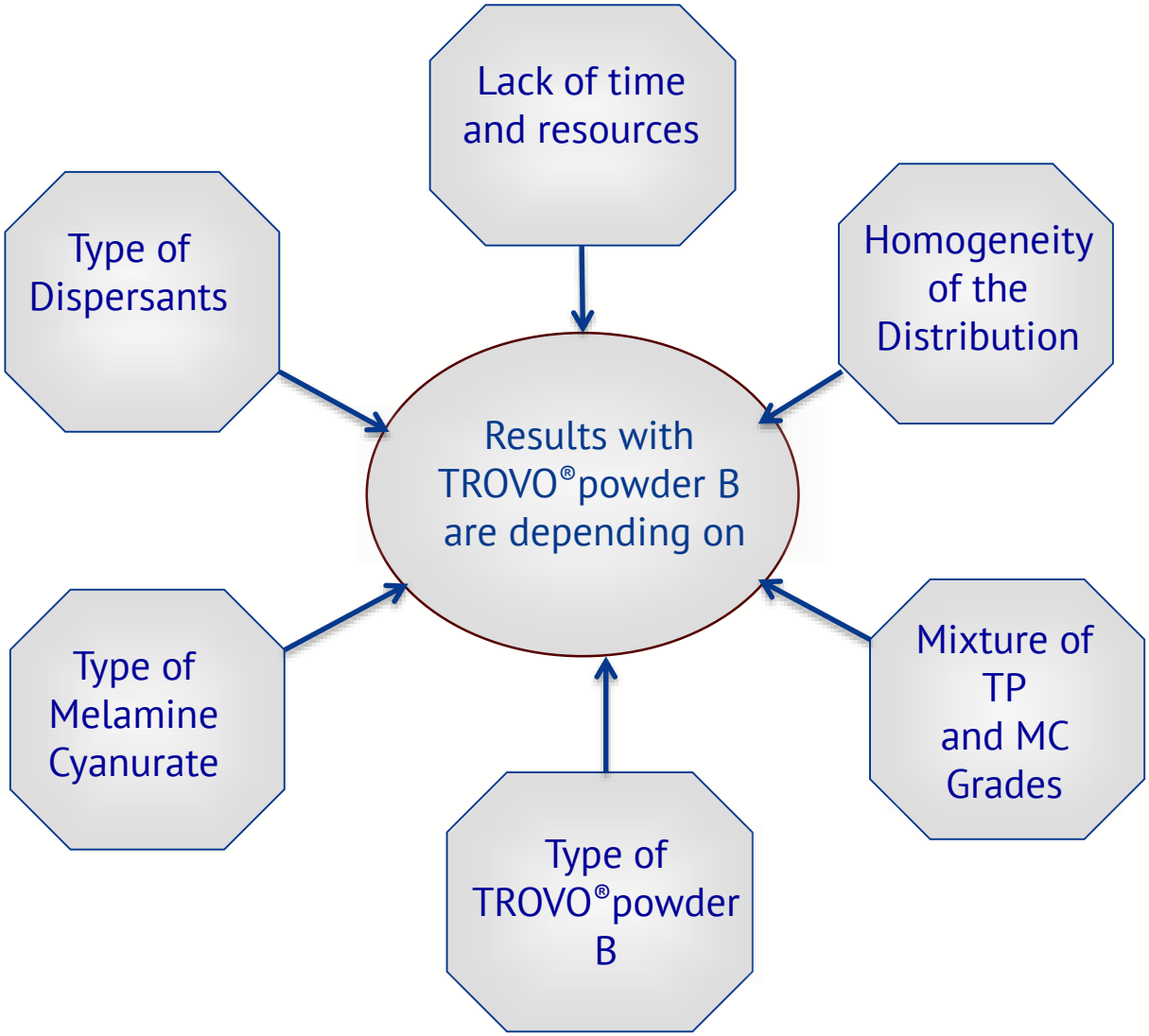
Results of target customers with 3 % TP and 3 % in PA 6, PA 66:



UL94 = V-0

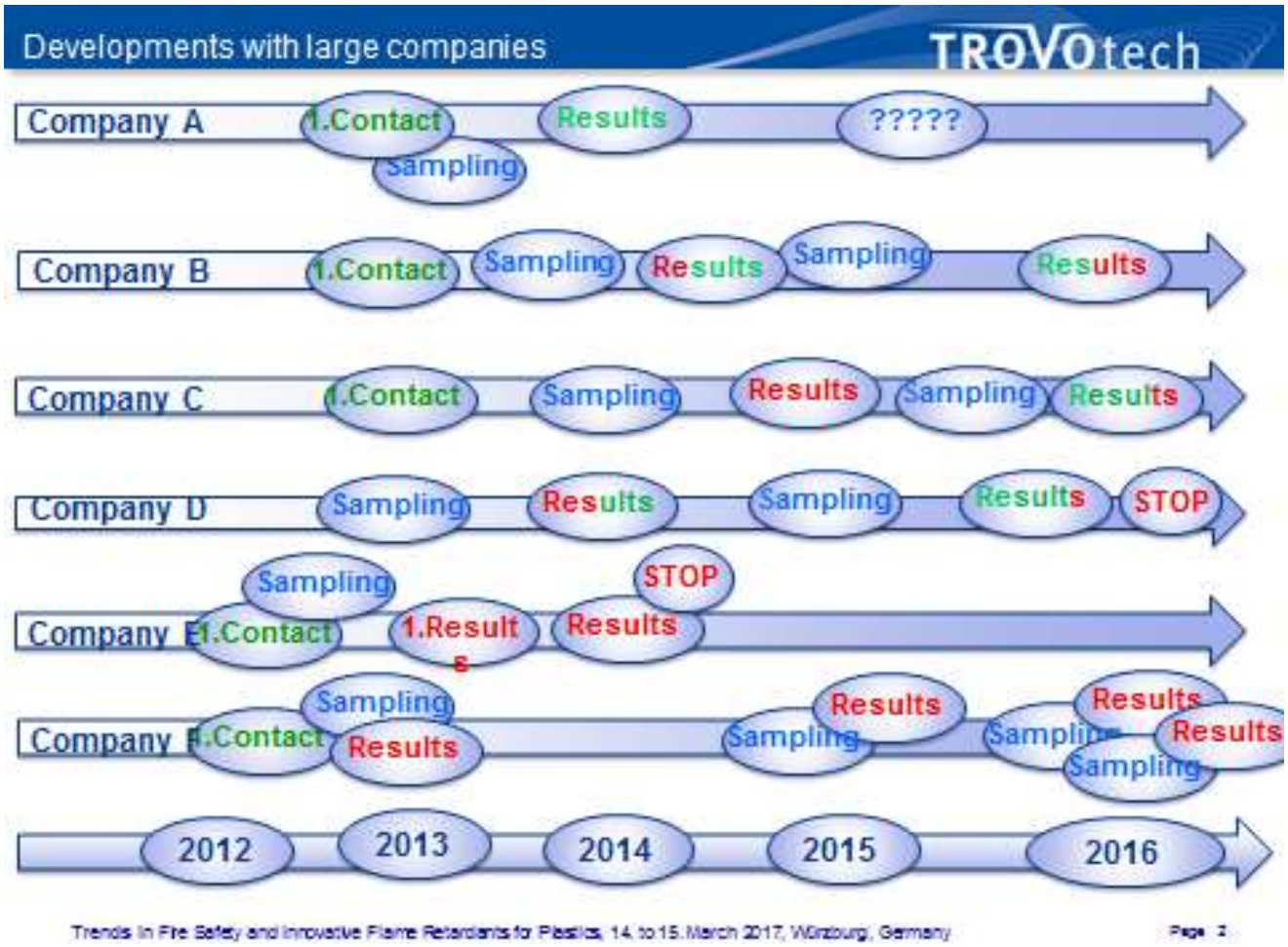
UL94 = V-2

2014

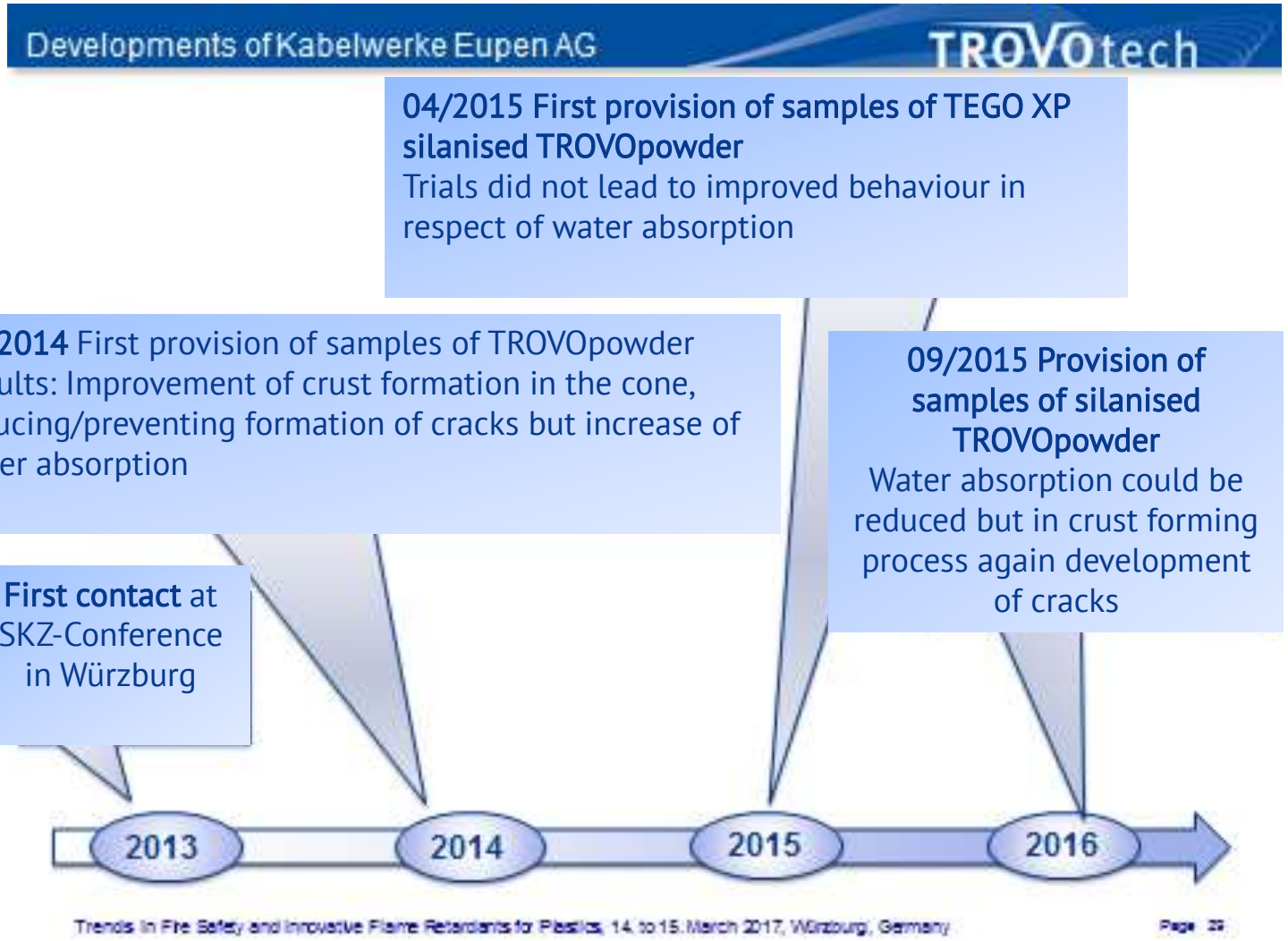

Lack of time and resources
Type of Dispersants
Homogeneity of the Distribution
Results with TROVO®powder B are depending on
Type of Melamine Cyanurate
Mixture of TP and MC Grades
Type of TROVO®powder B

Lack of time and resources

From sampling to initial results, large companies often need one year.



Lack of time and resources



Solution with TROVO®powder

No Cracks in coating

Current problem of cable surfaces

Cracks in coating

Access first shot

Total cracks reduction, but increase of water absorption

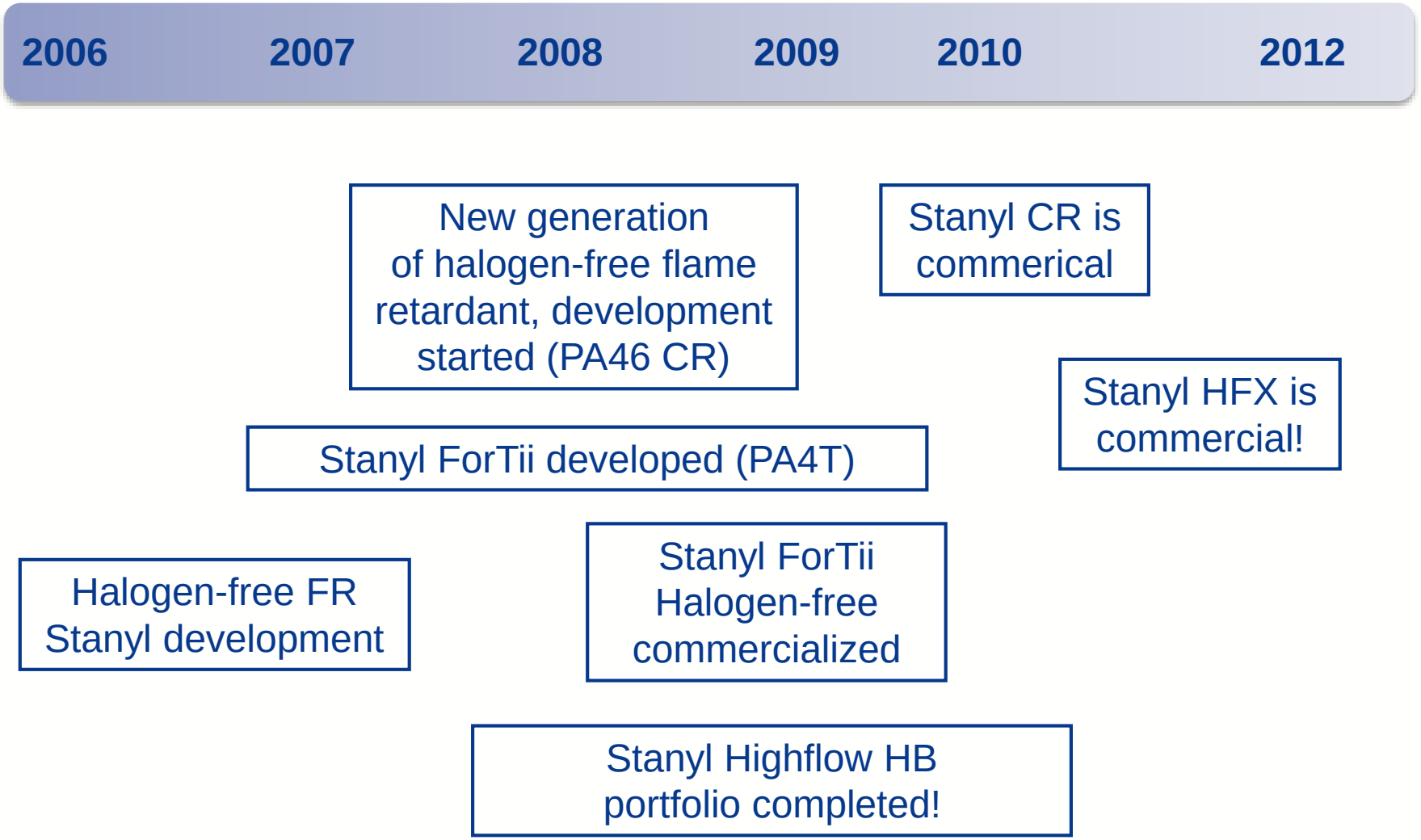
Results second shot

Reduction of water absorption, cracks present

Third shot

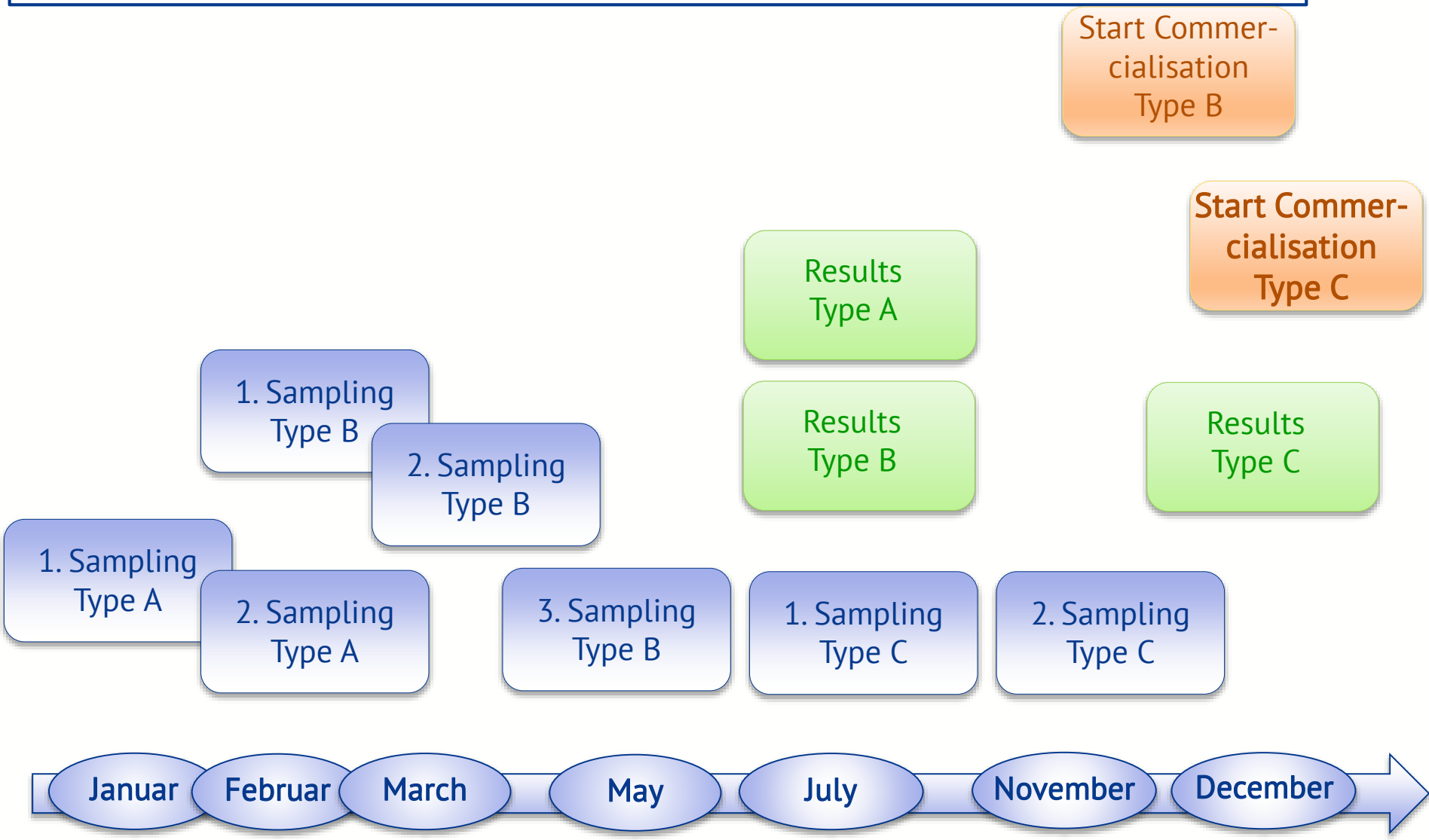
Results are expected at the end of March 2017

2014 → 2015 → 2016



Source: Patrick Duis, content of siide 7 of the presentation: Challenges for flame retardants posed by high temperature polyamides used in the lead-free solderable connector market; AMI confernece: Fire Resistance in Plastic 2014,

Company F - Developments 2016 with 3 types of TROVO®powder B



4. SITZUNG DES ARBEITSKREISES "FLAMMSCHUTZ“
UND
3. SITZUNG DES PROJEKTBEGLEITENDEN AUSSCHUSSES "DURCH DISPERGIERMITTEL OPTIMIERTE FLAMMSCHUTZFORMULIERUNGEN FÜR KUNSTSTOFFE"

18. Februar 2016

Markus Mazurowski
Fraunhofer-Institut für Betriebsfestigkeit und SystemzuverlässigkeitLBF
www.lbf.fraunhofer.de

Type of Dispersants

Different dispersants lead to different results - but in general it can be said they reduce the flame retardancy for plastics.

Einfluss der Dispergiermittel auf die Flammeigenschaften nach UL94

PA6 mit 8% MC15

Probe	Dispergiermittel		UL94 (1.6mm) Summe der Brennzeit	UL94 (1.6mm) Klassifizierung	UL94 (0.8mm) Summe der Brennzeit	UL94 (0.8mm) Klassifizierung
PA6-3	-	-	0	V-0	0	V-0
PA6-4	0,40%	CeasitAV/PA	0	V-0	0	V-0
PA6-17	0,40%	BYK-P 4102	0	V-0	1,4	3*V-0, 2*V-2
PA6-18	0,40%	Ceramer 1608	48,6	V-2	-	-
PA6-19	0,40%	Ken-React KR 12	0	V-0	0	2*V-0, 3*V-2
PA6-20	0,40%	TEGOMER H-Si 6440 P	12,3	V-2	-	-
PA6-21	0,40%	Tegomer V-Si 4042	0	V-0	0	V-2
PA6-22	0,40%	Tegomer E-Si 2330	8,2	4*V-0, 1*V-2	2,1	1*V-0, 4*V-2
PA6-23	0,40%	Tegopren 6875	5,4	V-2	0	V-2
PA6-24	0,40%	Dynasylan 6598	8,3	1*V-0, 4*V-2	-	-
PA6-25	0,40%	Dynasylan 1146	24,7	V-2	-	-

Dispergiermittel führen zu einer Verringerung der Flammschutzwirkung

PA6 = Durethan B30S

4. SITZUNG DES ARBEITSKREISES "FLAMMSCHUTZ“
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18. Februar 2016

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www.lbf.fraunhofer.de

Type of Melamine Cyanurate

MC with irregular form and wide particle size distribution shows a better flame retardant effect than platelet-/flake-shaped MC with a narrow particle size distribution.

Einfluss der Partikelgröße und -form auf die Flammeigenschaften nach UL94

PA6 mit 8% MC

Probe	MC-Typ	Dispergiermittel		UL94 (1.6mm) Summe der Brennzeit	UL94 (1.6mm) Klassifizierung	UL94 (0.8mm) Summe der Brennzeit	UL94 (0.8mm) Klassifizierung
PA6-1	MC50	-		0	V-0	0	V-0
PA6-2	MC50	0,40%	Caesit AV/PA	0	V-0	0	V-0
PA6-3	MC15	-		0	V-0	0	V-0
PA6-4	MC15	0,40%	Caesit AV/PA	0	V-0	0	V-0
PA6-5	MC20	-		0	V-0	0	3*V-0, 2*V-2
PA6-6	MC20	0,40%	Caesit AV/PA	0	V-0	0	V-2
PA6-7	MC3	-		0	3*V-0, 2*V-2	0	3*V-0, 2*V-2
PA6-8	MC3	0,40%	Caesit AV/PA	0	3*V-0, 2*V-2	0	2*V-0, 3*V-2

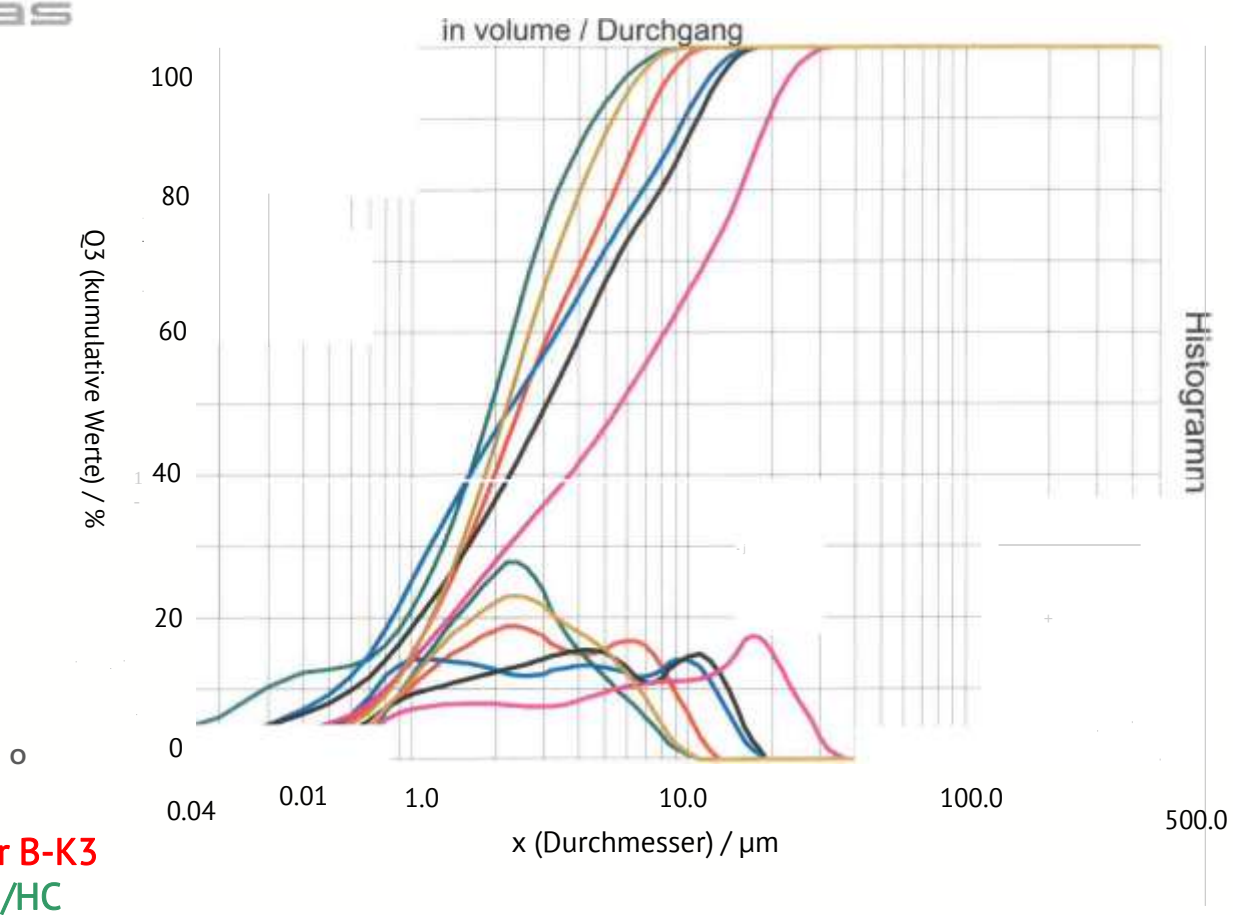
MC mit irreguläre Form und breiter Größenv erteilung zeigt eine bes sere Flamms chutzw irkung als plättchenförmiges MC mit enger Größenv erteilung

12

© Fraunhofer LBF

PA6 = Durethan B30S

Fraunhofer LBF



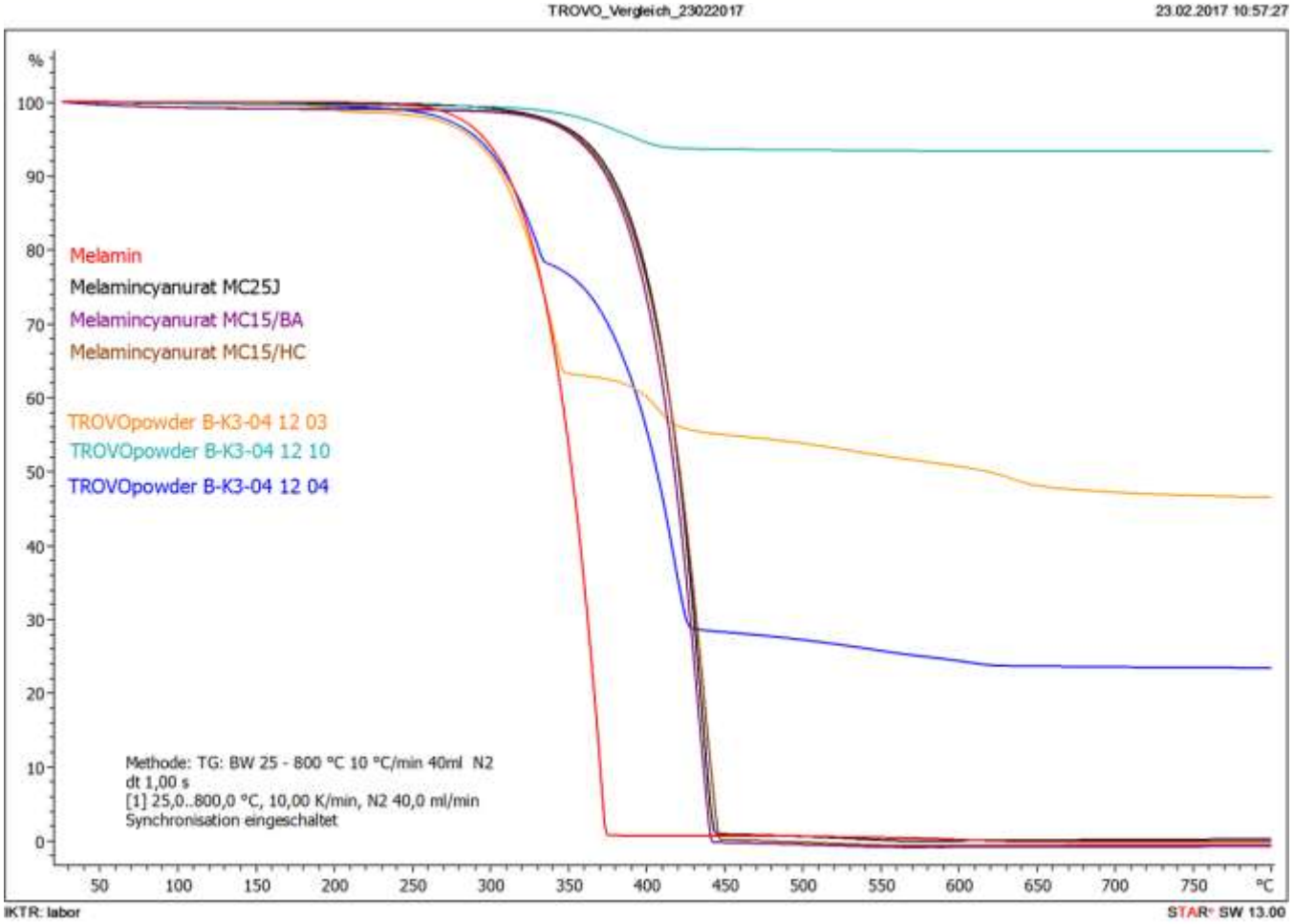
Mixture of TP and MC Grades

TROVO®powder B-K3
Melamin MC15/HC
Melamin MC15/BA
Melamin NORD-MIN MC-25J
Melamin NORD-MIN MC-50J
TROVO®powder B-K2

The same grain sizes of MC and TROVO®powder B leads to better flame retardancy results.

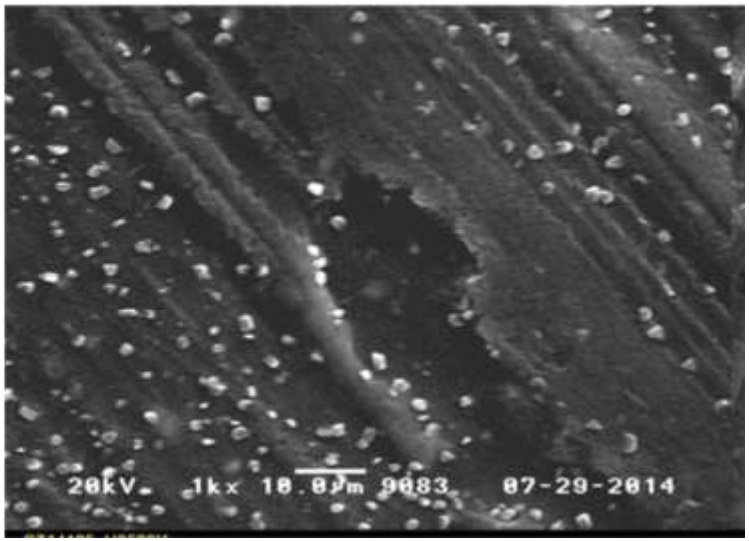
2016

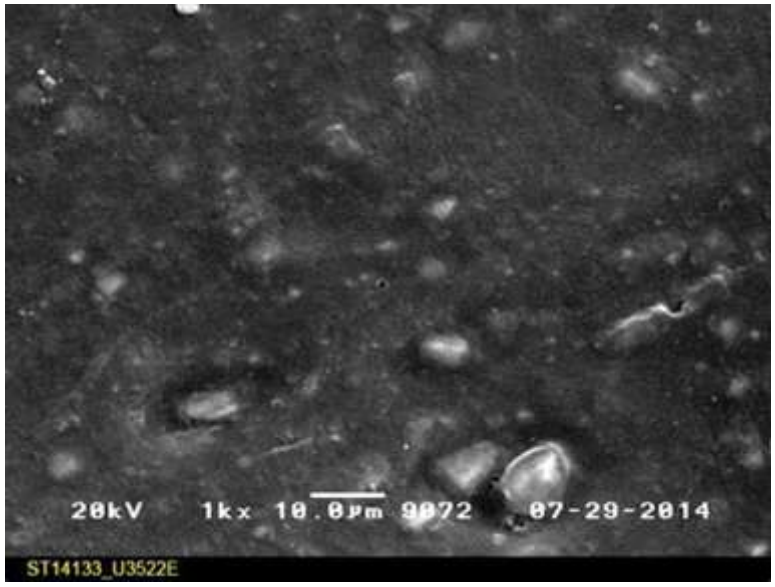
Thermogravimetric Analysis



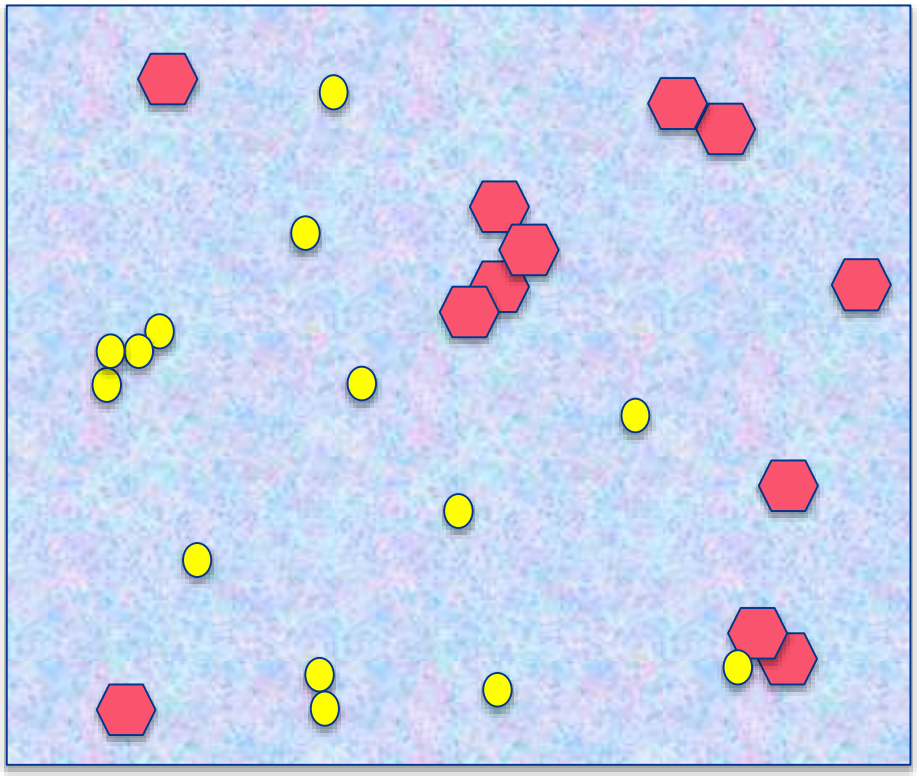
2016

Homogeneity of the Distribution

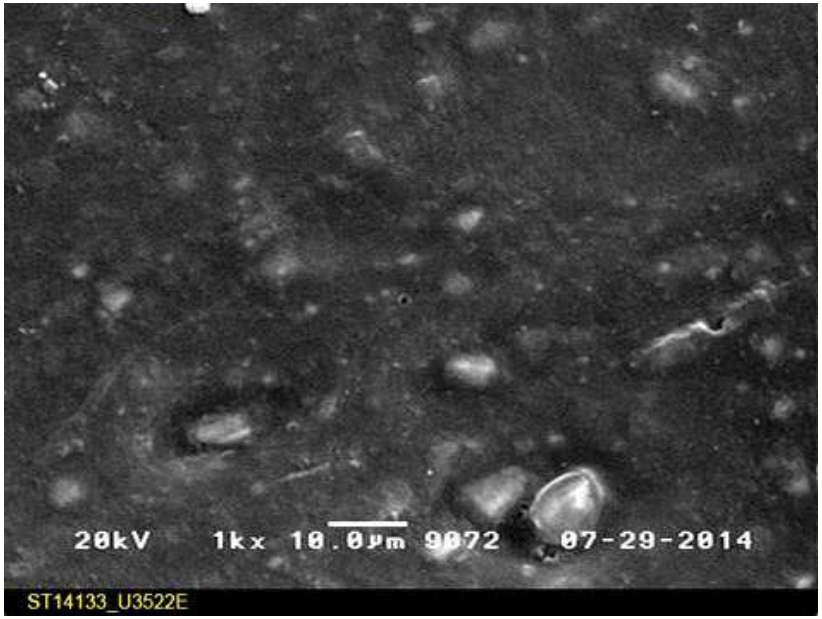




Inhomogeneities and agglomerates lead to poor flame retardancy.

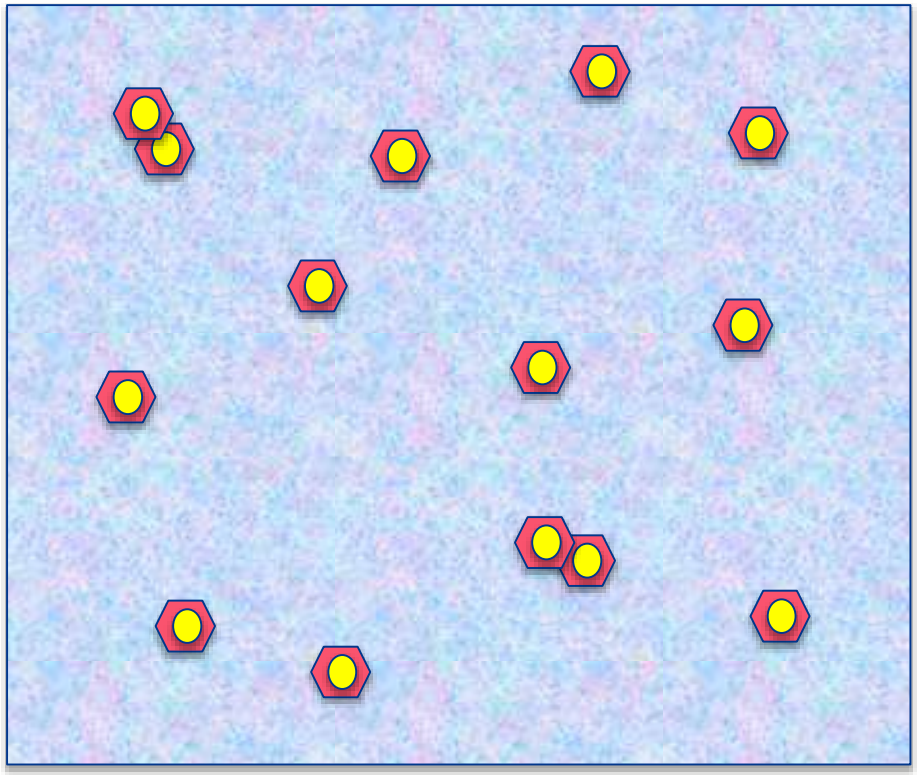


- Polymers like PA or PBT
- TROVO®powder B
- Flame Retardants like EXOLIT or Melamine or Melamine Cyanurate



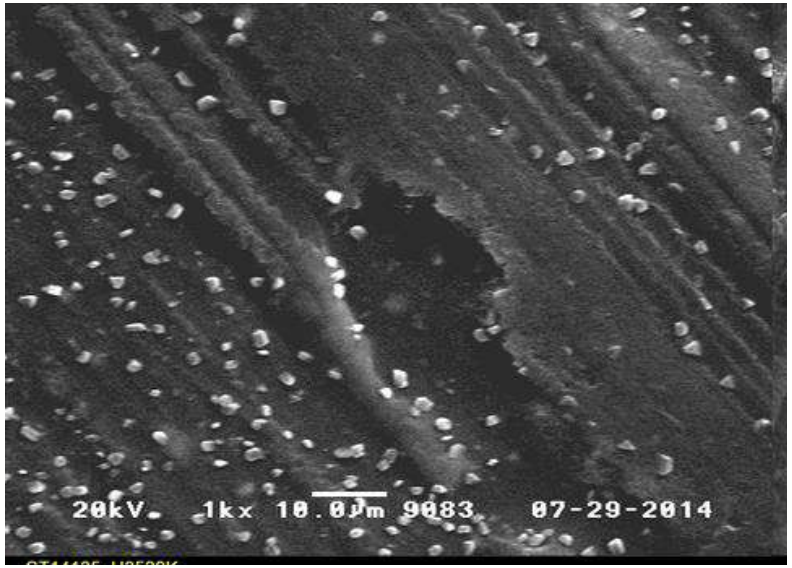
- Inhomogeneous Distribution
- Agglomerations

→ worse or not constant UL94-results



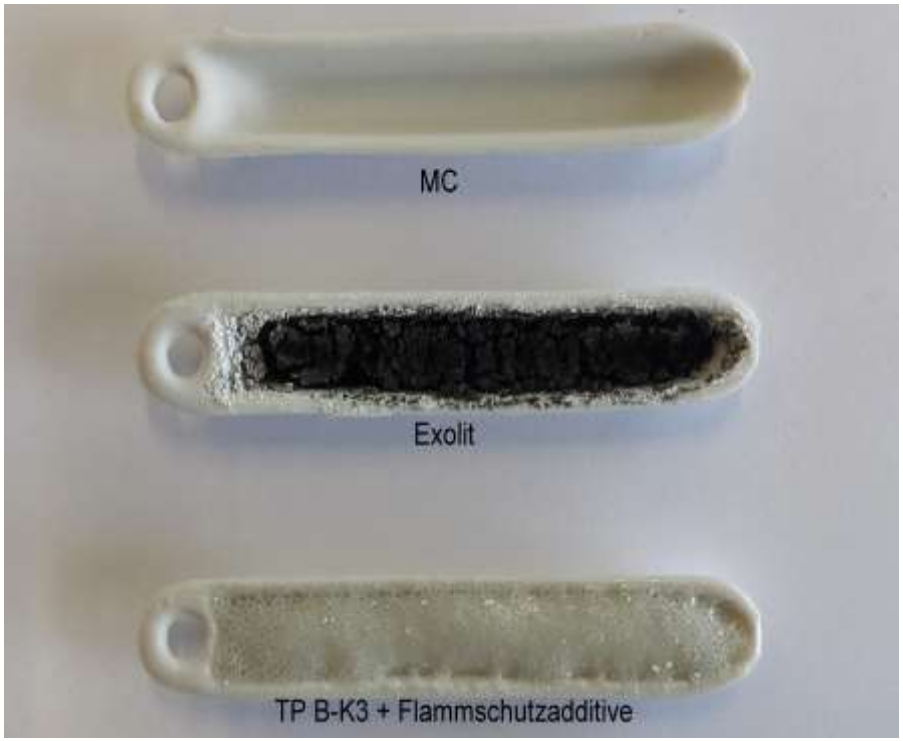
- Polymers like PA or PBT
- Doped TROVO®powder B
  With Flame Retardants like
  Melamine
  Melamine Cyanurate or
  Antidripping-Agents

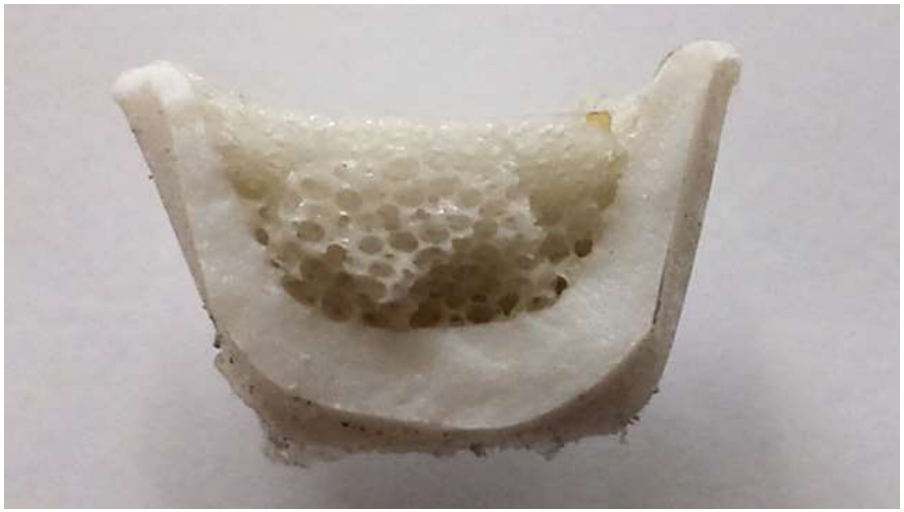
- Homogeneous Distribution
- Reduction of Agglomerations
- Easier Distribution in the Polymer



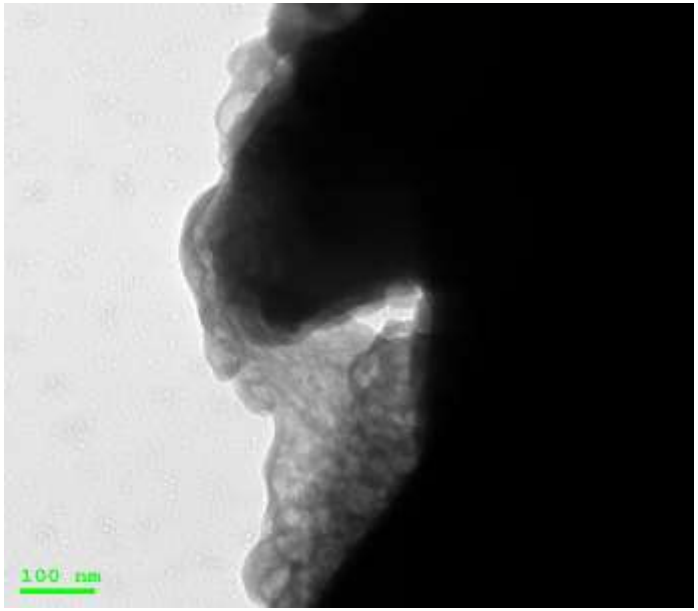
constant UL94-results
less quantity of FR necessary
better properties of the polymer

Doped TROVO®powder B with Flame Retardants like Melamine, Melamine Cyanurate or Phosphorus leads to different foam and char properties





cross-section of the ceramic mold with TP B K3 + HFFR temperted at 800 ° C



Sample with PA6 and 6% TROVO®powder B-K3-M-WI; results from 09/2015)

168 h, 70 °C, 50 % humidity

Spec. No.	Thickness [mm]	t_1 [s]	Burning cotton?	t_2 [s]	Burning cotton?	Classification
1	1.6	2	no	0	no	94 V-0
2	1.6	1	no	0	no	
3	1.6	2	no	0	no	
4	1.6	3	no	0	no	
5	1.6	0	no	1	no	

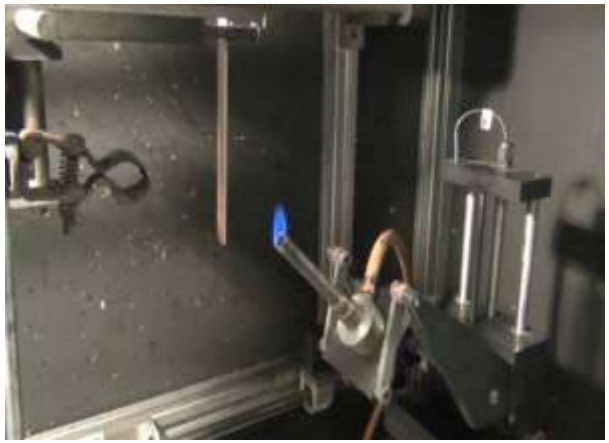
Sample with PA6 and 6% TROVO®powder B-K3-M-WI; results from 09/2015)

48 h, 23 °C, 50 % humidity

Spec. No.	Thickness [mm]	t_1 [s]	Burning cotton?	t_2 [s]	Burning cotton?	Classification
1	0.8	0	no	0	no	94 V-0
2	0.8	1	no	0	no	
3	0.8	1	no	0	no	
4	0.8	0	no	0	no	
5	0.8	0	no	0	no	

PBT – GF25
(0,3% PTFE)

6 % TP B-K3-M-WI 14 % EXOLIT OP 1240	6 % TP B-K3-M-WI 14 % EXOLIT OP 1240	6 % TP B-K3-M-WI 14 % EXOLIT OP 1240
UL 94 (48 /168h; 0,8 mm) **V0/V1**	UL 94 (48/168 h; 1,6 mm) **V0**	UL 94 (48/168 h; 3,0 mm) **V0**
GWFI: 960 °C GWIT: 800 °C	GWFI: 960 °C GWIT: 800 °C	GWFI: 960 °C GWIT: 800 °C
Burning time: 46 / 68 s Single value max.: 15 s	Burning time: 11 / 39 s Single value: max. 8 s	Burning time: 3 / 4 s Single value: max. 1 s

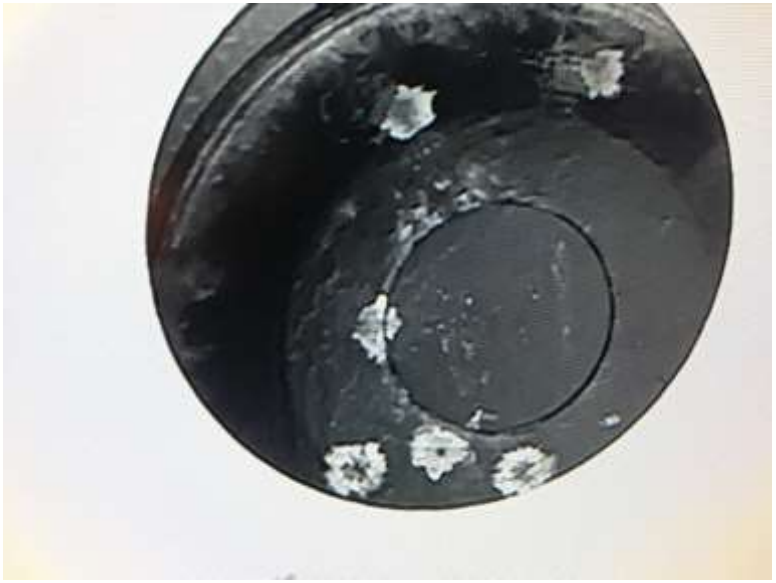


On the basis of the mechanical values achieved, further optimization is required

PBT – GF25
6% TP B-K3-M-WI + 14 % EXOLIT OP 1240 + 0,3 % PTFE

Elongation at break (ETP)	1,7 %
Charpy impact strength	4,06 kJ/m²
Notched Charpy impact strength	28,93 kJ/m²
Modulus (ETP)	9419 MPa

Being successful as Laura Dahlmeier means: a few shots are not enough.



Thank you very much for your attention!

Acknowledgement
to

Team Trovotech GmbH and his Shareholders

Support from

Hans-Jürgen Voss; General Manager, Trovotech GmbH, Bitterfeld-Wolfen