

***Nabaltec***



# Halogen-Free Flame Retardant Systems for EP-Based PWB's

Dr. M. Dietz, Clariant Produkte (D) GmbH, Germany  
Dr. C. W. Ihmels, Nabaltec AG, Schwandorf, Germany

# Content

- ▶ Short overview on halogen free FR's for EP
- ▶ Technical challenge to use filler type FR's
- ▶ Example: Apyral<sup>®</sup> AOH as highly temperature stable mineral filler with FR functionality
- ▶ Example: Exolit<sup>®</sup> OP as highly effective P-based FR
- ▶ Conclusions

# Content

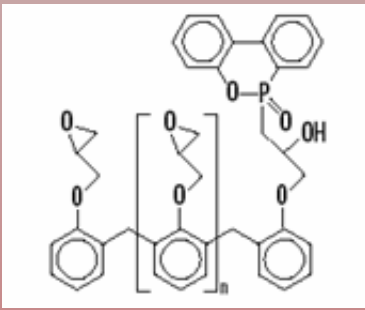
- ▶ Short overview on halogen free FR's for EP
- ▶ Technical challenge to use filler type FR's
- ▶ Example: Apyral<sup>®</sup> AOH as highly temperature stable mineral filler with FR functionality
- ▶ Example: Exolit<sup>®</sup> OP as highly effective P-based FR
- ▶ Conclusions

# *Ways of Incorporating FR in EP*

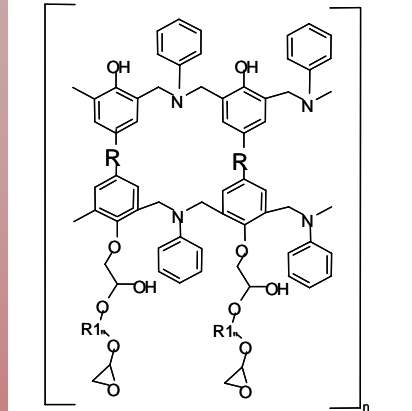
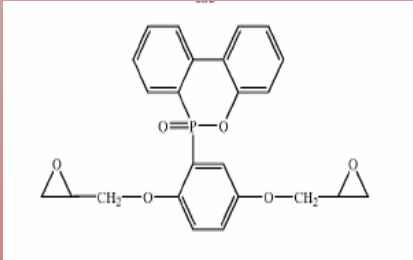


# Possible Combinations of HFFR

## Modified resins

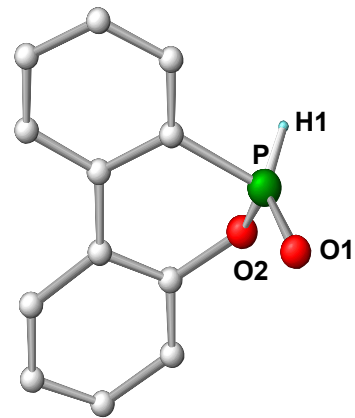


**DOPO - modifications**



**Benzoxazine/epoxy**

e.g.  
 Dow Chemical,  
 Tohto Kasei,  
 Nan Ya,  
 Huntsmann,  
 Hexion Chemical



„Phosphaphene-anthrene-oxide“

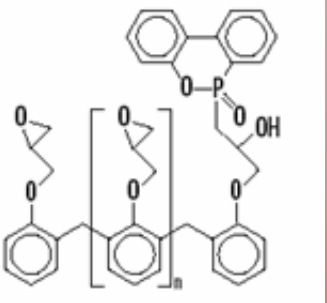
14% Phosphorous

- + P in polymer chain
- high price
- influence on resin prop., e.g.
  - lowers  $T_g$
  - increases water uptake

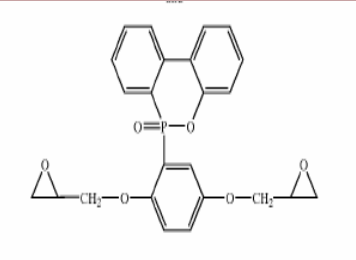
**Reasons why DOPO often used in combination with other HFFR**

# Possible Combinations of HFFR

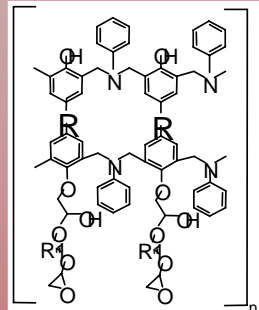
## Modified resins



**DOPO - modifications**

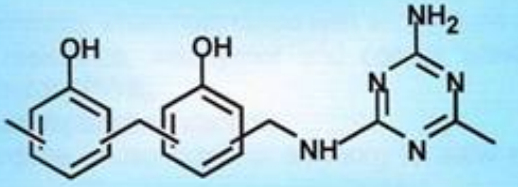


**Benzoxazine/epoxy**

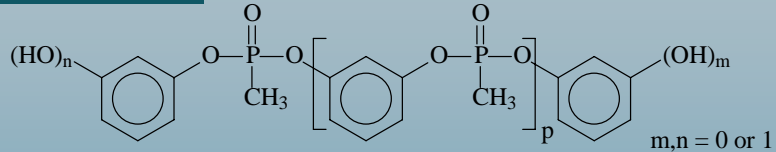


e.g.  
**Dow Chemical,**  
**Tohto Kasei,**  
**Nan Ya,**  
**Huntsmann,**  
**Hexion Chemicals**

## Hardeners



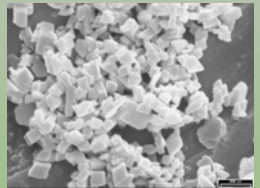
**ATN-hardener**



**Fyrol PMP**

e.g.  
**DIC**  
 (Dai -Nippon Ink & Chemicals),  
**Supresta**  
 (ICL)

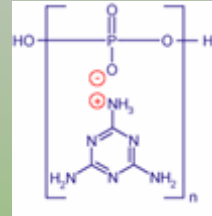
## Fillers



**AlOOH or ATH**



**Metal phosphinate**



**Melamine Polyphosphate**

e.g.  
**Nabaltec,**  
**Clariant,**  
**Budenheim,**  
**Ciba**

**Combination of these HFFR's give a wide range of possibilities to optimize base material for each application**

## Technical requirements to FR system and base laminate

Thermal properties	Mechanical properties
No bubbles or delamination after PCT	High Copper peel strength
No decomposition or delamination during soldering	High inner laminate adhesion
low CTE	
High Tg-level of base laminate	
Electrical properties	Processing
Good electrical properties (Dk, Df)	Good chemical resistance against acid, alkali and oxidative substances
No propensity for migration (CAF testing)	Suitable resin flow of prepregs
Low water uptake	Acceptable prepreg surface

# Content

- ▶ Short overview on halogen free FR's for EP
- ▶ **Technical challenge to use filler type FR's**
- ▶ Example: Apyral<sup>®</sup> AOH as highly temperature stable mineral filler with FR functionality
- ▶ Example: Exolit<sup>®</sup> OP as highly effective P-based FR
- ▶ Conclusions



# Halogen-Free FR for PCB 's

Technical Challenge: Usually, a combination of different compounds is necessary to match the requested properties.

## Traditional varnish composition

4 component system:

- epoxy resin (brominated)
- curing agent
- Accelerator
- solvent

## Varnish bath (halogen-free)

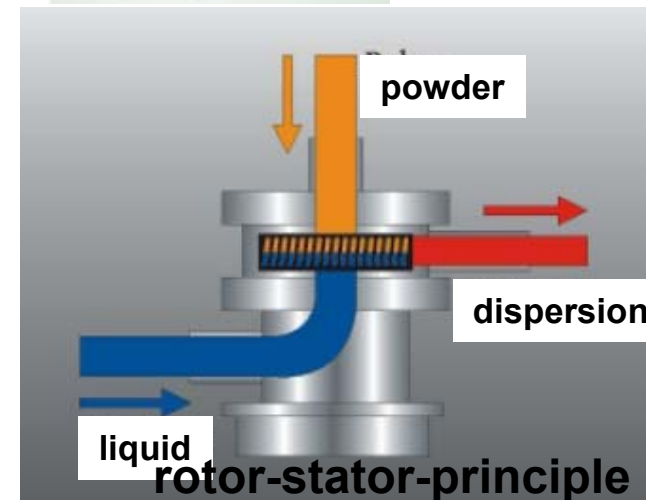
> 6 components system

- **new epoxy resin ?**
- **new curing agent ?**
- **new accelerator ?**
- **flame retardants ?**
- **fillers ?**
- **processing additives?**
- solvent

Challenge - the varnish bath must be completely reformulated, and individual components optimized to customer requirements.  
No industry standards - Each customer with own recipe, tests & requirements

# Processing of Filler Type FR

- ➔ Incorporation into acetone, MEK, etc. as solvent is preferred
- ➔ use a high-speed dissolver for good dispersion
- ➔ Additives can improve dispersion, air release, and stability (anti-settling)
- ➔ State of the art :  
Inline dispersion machines, eg.  
YSTRAL Conti-TDS,  
NETZSCH Psi Mix, ...  
for dust-free induction, wetting  
and dispersing  
of powders into a liquid.

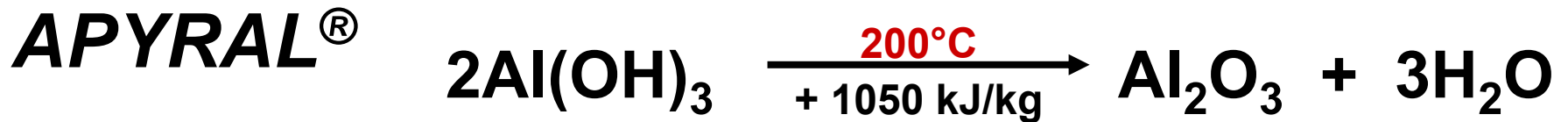


# Content

- ▶ Short overview on halogen free FR's for EP
- ▶ Technical challenge to use filler type FR's
- ▶ **Example: Apyral<sup>®</sup> AOH as highly temperature stable mineral filler with FR functionality**
- ▶ Example: Exolit<sup>®</sup> OP as highly effective P-based FR
- ▶ Conclusions

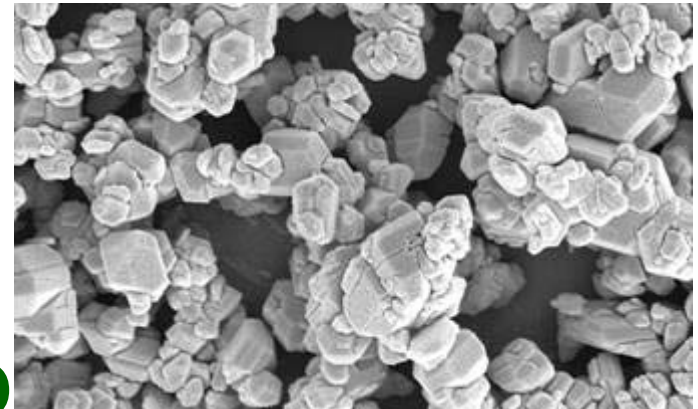
# ATH as FR Filler ?

Aluminium hydroxide :  $\text{Al}(\text{OH})_3$  or “ATH”



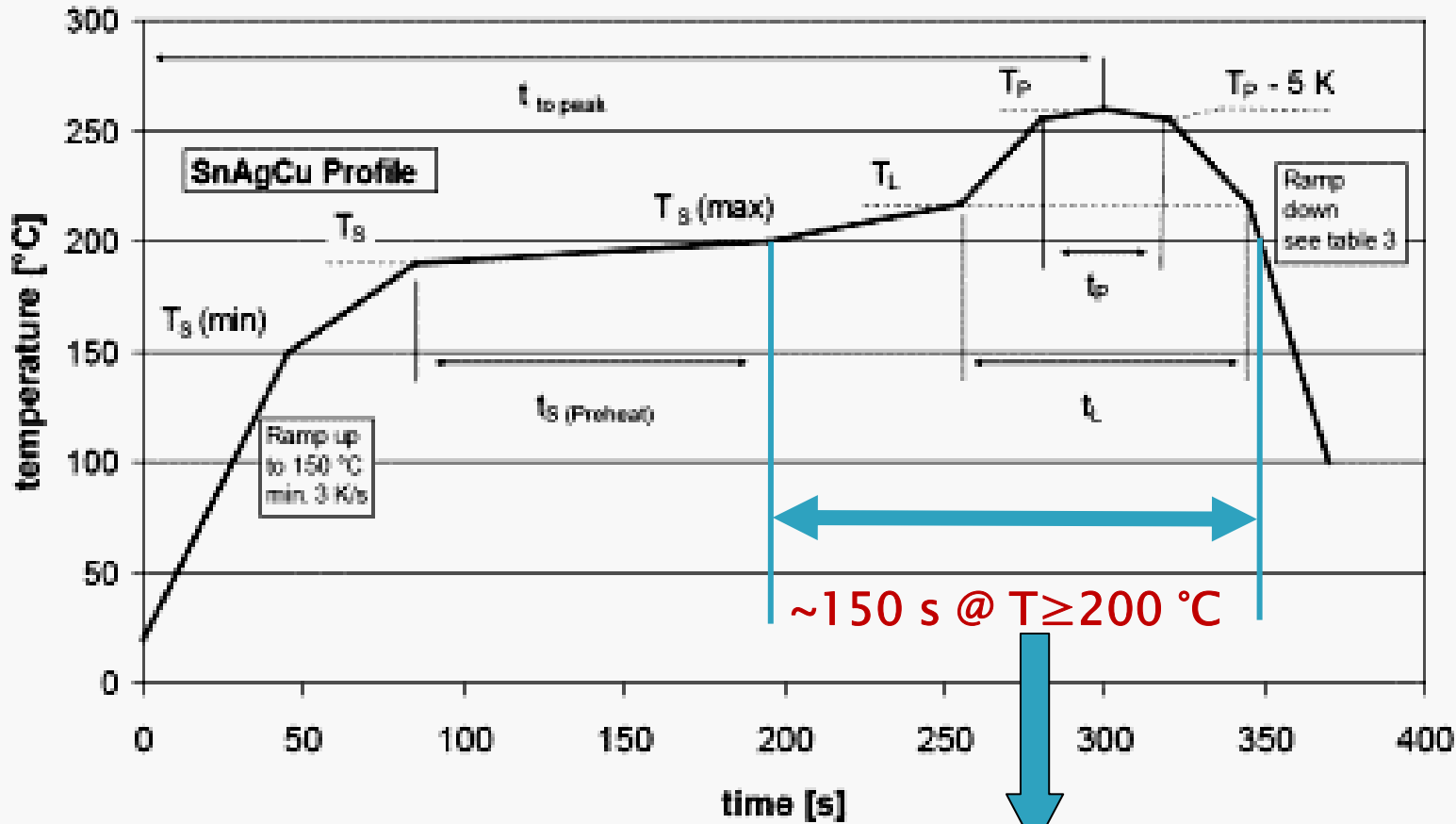
High heat resistance is required for modern lead free soldering !!!!

Aluminium oxide hydroxide :  
 $\text{AlO}(\text{OH})$  or “AOH”



**APYRAL<sup>®</sup> AOH**

# Temp.- Profile of Lead Free Soldering



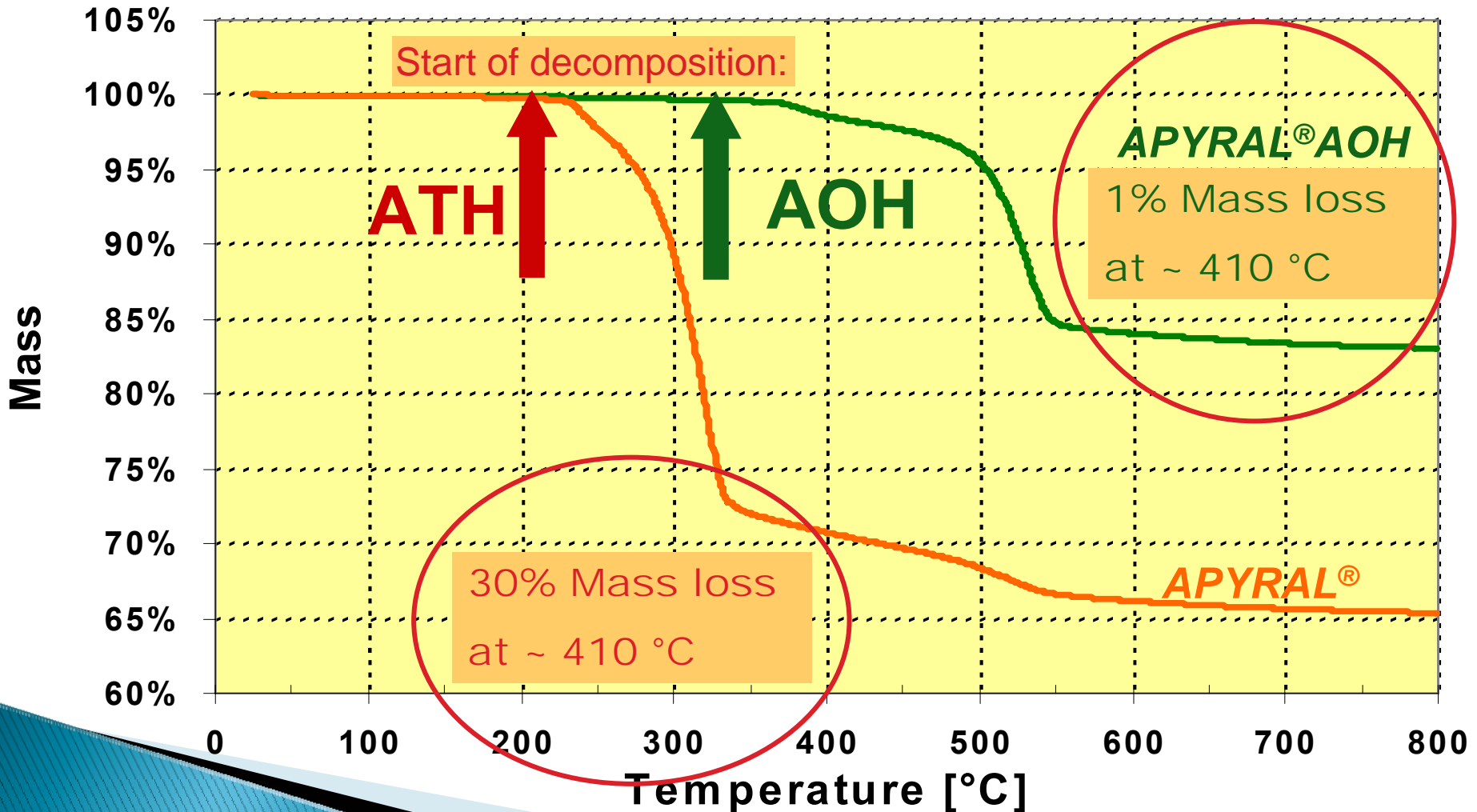
Temp.-profile used by automobile industry for prototyp qualification

**Under such conditions ATH will partially decompose:**

- Loss of flame retardance efficiency
- Release of water → CAF + delamination

# TGA-Diagramms : T-Stability of ATH vs AOH

## TGA : ATH vs AOH



# APYRAL® AOH - Synergist for P-Containing FRs

*Necessary amount of FR to fulfill UL94 V0 in novolak epoxy*

Flame retardant	Content [% w/w]	T <sub>g</sub> (DSC) [°C]
Metal phosphinate	16,7	167
Oligomeric Aryl phosphonate	23,5	165
DOPO-HQ	17,0	161
DOPO	6,5	158
DOPO + <b>APYRAL® AOH 30</b>	2,9 + 30	168

*resin: DOW DEN 438*

*hardener:  
dicyandiamide*

*accelerator: fenuron*

*thickness: 4,0 mm*

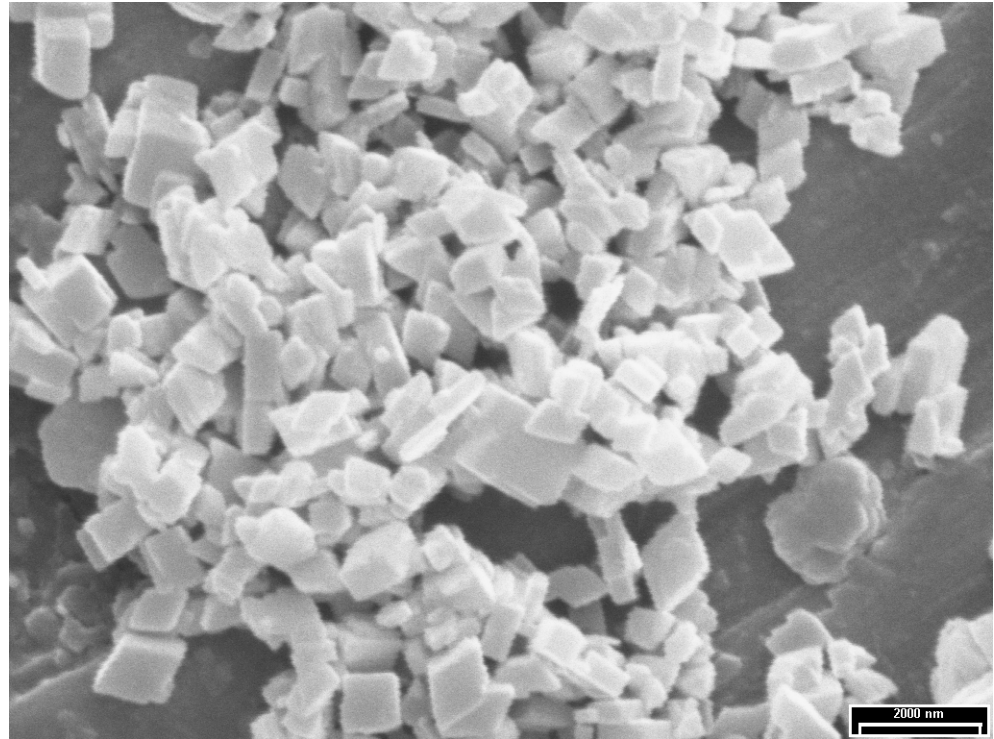
*no glass fiber*

*T<sub>g</sub> 180 °C*

- Significant reduction of expensive DOPO
- Significant Increase of T<sub>g</sub>

# Advantages of APYRAL® AOH

- Positive influence on
  - $T_g$
  - copper peel strength,
  - laminate adhesion
  - extremely low CTE reported ( 36 ppm (RT- $T_g$ ) !)
- T-stable up to 340 °C !!
- No corrosive & toxic gases
- Smoke reduction effect
- Low price
- high load for FR necessary, better to use as synergist to P-/N-based FR



APYRAL® AOH available from

7  $\mu\text{m}$  to 300 nm  
(typically 1  $\mu\text{m}$ )  
(mean diameter)



*Ultra-thin applications possible*

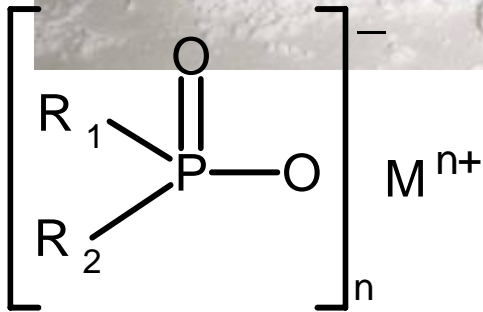


# Content

- ▶ Short overview on halogen free FR's for EP
- ▶ Technical challenge to use filler type FR's
- ▶ Example: Apyral<sup>®</sup> AOH as highly temperature stable mineral filler with FR functionality
- ▶ **Example: Exolit<sup>®</sup> OP as highly effective P-based FR**
- ▶ Conclusions

# Exolit® OP 930/OP 935 – Product characteristics

Exolit® OP 935



- New class of flame retardants
- based on phosphinate chemistry
- Additive flame retardant (not reactive)
  - fine grained white powder
  - high P-content (23-24%)
  - non toxic, no hazard labels
  - behaves like a filler
  - Mohs hardness: < 3
  - good thermostability (decomposition above 300°C)

# *Exolit<sup>®</sup> OP 930/935 - Toxicological and Ecotoxicological Properties*

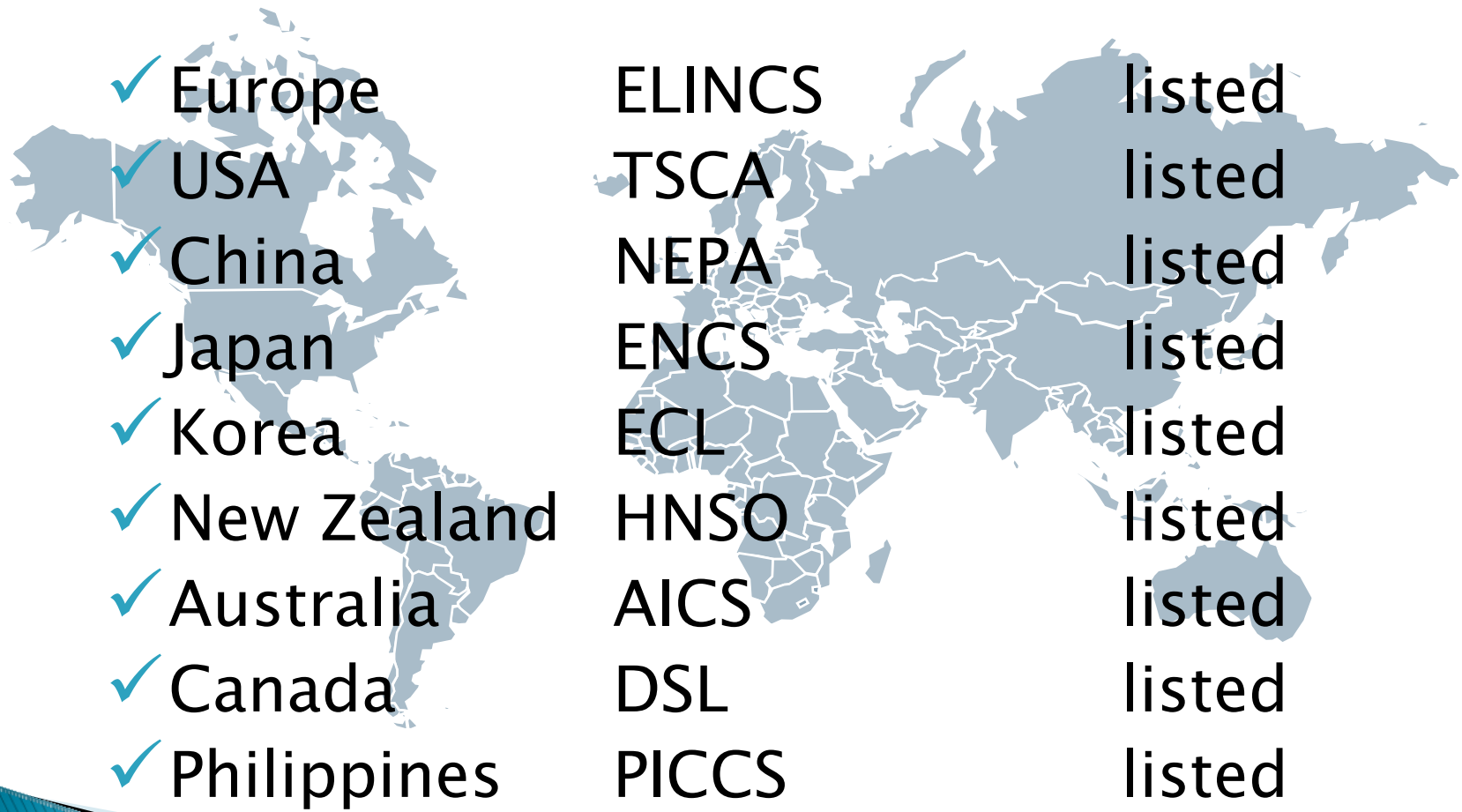
Exolit<sup>®</sup> OP :

- is **non-toxic**
- there is **no need for labelling it as a hazardous substance**  
(threshold LD<sub>50</sub> = 2000 mg/kg)
- **has no potential for bioaccumulation**
- has a very low aquatic toxicity and does **not have to be labelled for ecotoxic effects** ! (threshold LD50 = 100 mg/L)



# Exolit<sup>®</sup> OP 930/935 – Registration Status\*

*(in countries with chemical inventories)*



✓ Europe	ELINCS	listed
✓ USA	TSCA	listed
✓ China	NEPA	listed
✓ Japan	ENCS	listed
✓ Korea	ECL	listed
✓ New Zealand	HNSO	listed
✓ Australia	AICS	listed
✓ Canada	DSL	listed
✓ Philippines	PICCS	listed

\* = A number of countries like Taiwan and India do not have chemical inventories

# Exolit®OP – Efficiency as FR material

Flame retardant	Content [% w/w]	P-Content [% w/w]	T <sub>g</sub> (DSC) [°C]
Metal-phosphinate	10.0	2.4	168
MPP + P-synergist (1:1)	8.0	0.8	179
DOPO-HQ	17.0	1.4	161
DOPO	6.5	0.90	158
DOPO + APYRAL® AOH 30	2.9 + 30	0.40	168

*Exolit®OP more effective like DOPO-HQ*

Necessary weight content of different halogen-free flame retardants in an epoxy novolac for the classification according to UL94-V0

(resin: DOW DEN 438; hardener: dicyandiamide; accelerator: fenuron; thickness: 4,0 mm; no glass fiber)

# Role of Exolit® OP 930 in rigid base material manufacturing



using Exolit® OP 930 as synergist in combination with N or P containing resins or other halogen free FR additives

# Exolit® OP 930 for halogen free rigid FR-4 boards

- first formulations have been successfully developed and positively tested throughout the supply chain
- halogen free laminates containing Exolit OP 930 are already available on the market or are currently being introduced.

*Environmentally Friendly, Lead-Free Compatible, FR-4 Epoxy with a Tg of 165°C*



OP 930  
inside

Property	
Tg (DSC)	165°C
Td (TGA 5% weight loss)	425°C
T260	> 30 min
Z-Axis Expansion (50°C-Tg)	65 ppm/°C
Z-Axis Expansion (Tg-260°C)	250 ppm/°C
Dk @ 10 GHz	3.8
Df @ 10 GHz	0.016
Flammability (UL 94)	V-0

# Exolit® OP 935 in non rigid FR-4 applications

Exolit OP 935 has been also released for

- a) adhesive formulations used in flexible printed circuits based on polyimide-copper
- b) formulations used in epoxy moulding compounds (EMC) and resist inks

## *Environmentally friendly adhesive formulation*

Property	
Adhesive thickness	18 µm
Peel Strength (after solder float)	1.4 kN/m
Solder resistance (288°C, 10 min)	pass
Dk @ 1 GHz	3.2
Df @ 1 MHz	0.02
Flammability (UL 94)	VTM-0





# Conclusions

- ▶ Halogen-free FR can be used as additive, resin or hardener in a varnish formulation
- ▶ A wide range of materials of halogen-free technologies are currently available and further research is expected to result into new raw materials
- ▶ This include FR additives, as well as resin backbones
- ▶ Both additives and resins have different mechanical and electrical properties
- ▶ This offers an increasing wide range of CCL properties, which makes it easier to find suitable halogen-free alternatives for different applications and markets segments.
- ▶ *Apyral*<sup>®</sup> AOH and *Exolit*<sup>®</sup> OP filled base laminates are available or are being currently introduced into the market

# Invitation

- ▶ Please visit us at our booth
- ▶ Free HFFR-brochure available !!!



**Budenheim**  
 Budenheim Iberica Extramuros,  
 S/N 50784 La Zaida/Zaragoza Spain  
 Phone: + 34 976 1784 12  
 Email: budenheim@budenheim.es  
 www.budenheim.es

ammonium polyphosphates (FR CROS<sup>®</sup>)  
 melamine phosphates (Budite<sup>®</sup>)  
 melamine polyphosphates (Budite<sup>®</sup>)  
 melamine cyanurates (Budite<sup>®</sup>)  
 intumescent systems (Budite<sup>®</sup>)

**Ciba Inc.**  
 CH - 4002 Basel Switzerland  
 Phone: + 41 61 63 64 000  
 Email: melapur@ciba.com

melamine phosphate (Melapur<sup>®</sup> MP)  
 melamine polyphosphate (Melapur<sup>®</sup> 200)  
 melamine cyanurate (Melapur<sup>®</sup> MC)  
 NOR HALS (Flamestab<sup>®</sup> NOR<sup>TM</sup> 116)

**Clariant International Ltd.**  
 MS Flame Retardants  
 Rothausr. 61, CH - 4132 Muttenz 1  
 Phone: +41 61 469 7974  
 Fax: +41 61 469 7577  
 e-mail: adrian.beard@clariant.com  
 www.exolit.com

metal phosphinates (Exolit<sup>®</sup> OP)  
 ammonium polyphosphate (Exolit<sup>®</sup> AP)  
 red phosphorus (Exolit<sup>®</sup> RP)

**Karlsruhe Research Centre**  
 Institute for Technical Chemistry (ITC-CPV)  
 PO-Box 3640, 76021 Karlsruhe Germany  
 Phone: +49 7247 82 4385  
 Fax: +49 7247 82 2244  
 Email: manfred.doering@itc-cpv.fzk.de  
 www.fzk.de/itc-cpv.de

Research and Development halogen-free  
 flame retardants

**LANXESS Deutschland GmbH**  
 BU Functional Chemicals  
 41538 Dormagen Germany  
 Phone: +49 2133 51 23788  
 Fax: +49 2133 51 23323  
 www.phosphorous-chemicals.com

triphenyl phosphate (Disflamoll TP<sup>®</sup>)  
 cresyl diphenyl phosphate (Disflamoll DPK<sup>®</sup>)

**Nabaltec AG**  
 Alustraße 50 - 52, 92421 Schwandorf  
 Phone: +49 9431 53-458 /-462/-467  
 Fax: +49 9431 61557  
 E-Mail: fillers@nabaltec.de

aluminium hydroxide (Apyral<sup>®</sup>)  
 boehmite (Apyral<sup>®</sup> AOH)  
 magnesium hydroxide (Apymag<sup>®</sup>)  
 blend of aluminium & magnesium hydroxides  
 (Apymag<sup>®</sup> AOH)

**Supresta LLC**  
 Hoefseweg 1, 3821 AE Amersfoort  
 The Netherlands  
 www.supresta.com

poly(1,3-phenylene methylphosphonate)  
 (Fyrol PMP<sup>®</sup>)  
 resorcinol bis (diphenyl phosphate)  
 (Fyrolflex RDP<sup>®</sup>)  
 bis-phenol A-bis (diphenyl phosphate)  
 (Fyrolflex BDP<sup>®</sup>)



*Thank you!*