Flame retardants for composites, trends and new developments

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BU Additives, BL Flame Retardants
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what is precious to you?

Clariant at a Glance – A Globally Leading Company in Specialty Chemicals

3 860
Sales 2020 (CHF m)
from continuing operations

578
EBITDA 2020 (CHF m)
from continuing operations

3
Core Business Areas

13 235
Total staff 2020 (FTE) [2]

799
Net result 2020 (CHF m)
of total Group[1]

15.0%
EBITDA margin 2020
from continuing operations

85
Production sites worldwide
in 2020 [2, 3]

[1] Including discontinued operations [2] Total Group incl. discontinued operations (excl. Business Unit Masterbatches) [3] Shared production sites with Business Unit Pigments are split as separate sites

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We are globally present …

CENTRAL FUNCTIONS

- Headquarter
- 7 Production Sites
- 3 Technology & 3 Innovation Centers
- Various Key offices (sales, others)
- Other BU sites

… and more to come

Trends and challenges also influencing composite industry

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Addressing global megatrends – composites are especially important for transportation sector

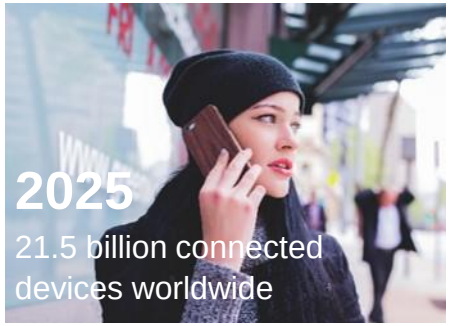
URBANIZATION
More and more people live in urban areas giving rise to the development of megacities.

Source: United Nations (2018)

MOBILITY
Transportation is a non-separable part of society.

Source: Business Insider (2016)

CONNECTIVITY
Technology has become an increasing part of everyday lives.



Source: IoT Analytics (2018)

NUTRITION
The world's population continues to grow while, at the same time, arable land is diminishing.

Source: Food and Agriculture Organization of the United Nations (2014)

DEMOGRAPHIC CHANGE
The world population is undergoing an unprecedented process of aging.

Source: United Nations (2017)

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Trends and Challenges in Composite Materials

Lightweighting

- Use of more polymer based high-performance solution instead of metal
- Reduction of fuel consumption and CO_2 emissions

Transportation

- Structural parts and interior for trains, aviation, automotive
- New applications, i.e. e-mobility (battery box etc.)

Advanced processes

- Advanced processes for optimized production, more complex parts, mass production
- New challenges for resin formulation and its components (resin, hardener, flame retardant...)

Regulatory Changes

- More demanding tests like EN 45545 preferring non-halogenated flame retardants due to tox and smoke demands

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Thermosets composites for weight reduction and decreased energy consumption; big difference in demands for FR's

- Thermosets like epoxy resin are for example used for composites, addressing the need for weight reduction in transportation and for safe advanced electronic materials like FCCL and PCB
- Flame retardants help to control:
  - Flame spread
  - Heat release
  - Smoke & Smoke toxicity
- FR-regulations are more severe if its not easy to escape

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Different flame test requirements and regulations in certain application areas; main focus on transportation, B&C and E&E

Application area	Test	Country	Test parameters, description	Performance rating, comments
TRANSPORTATION – RAILWAY	DIN EN 45545	EU	Smoke density & toxicity, spread of flame, heat release (Cone)	HL3 > HL2 > HL1
	ASTM E 162	USA	Surface flammability	A > B > C
	ASTM E 662	USA	Smoke box	Smoke density (Ds) value
TRANSPORTATION – AVIATION	FAR 25.853	Worldwide	Smoke density & toxicity, spread of flame, heat release (OSU)	Requirements for materials in crew and passenger compartments are given in FAR 25.853, methods described in Appendix F
	ABD 0031	Airbus	Smoke density & toxicity	Limit concentration for 6 toxic gases: HF, HCl, HCN, SO_2, NOx, CO
TRANSPORTATION – ELECTRICAL VEHICLE SAFETY REQUIREMENTS AND TEST METHODS FOR ELECTRIC VEHICLES	GB 18384-2020	PRC	Safety requirements and test methods for electric vehicles	Defines general requirements for E-Vehicles
TRANSPORTATION – ELECTRICAL VEHICLE – ELECTRIC VEHICLES TRACTION BATTERY SAFETY REQUIREMENTS	GB 38031-2020	PRC	Battery package, external burning test; thermal shock/cycle test, physically compression test, needle penetration test...	Defines battery requirements for E-Vehicles
TRANSPORTATION – ELECTRICAL VEHICLE – ELECTRIC BUSES SAFETY REQUIREMENTS	GB 38032-2020	PRC	Electrical bus safety requirement	Defines requirements for E-Vehicles, busses
TRANSPORTATION – BATTERY ELECTRIC VEHICLE SAFETY	ECE R-100	Europe	External Fire Exposure Test, UL 2580	Lithium battery test, flaming conditions for 70 seconds
BUILDING AND CONSTRUCTION (B&C)	EN 13501	EU	Heat release, Fire, flame spread and smoke	Class A1, A2, B, C, D, E and F, depending on class different tests required: EN ISO1182, EN ISO 1716 and EN 13823; EN ISO 11925-2
	E 84	USA	Steiner tunnel	Flame spread & smoke density
ELECTRIC AND ELECTRONIC (E&E)	UL 94	International	Flammability test, small scale	5V; V-0 > V-1 > V-2; HB; VTM

Our solutions and selected examples
FOKUS ON SUSTAINABILITY

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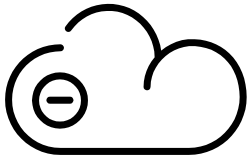
Planet – Setting out ambitious 2030 Sustainability Targets

SCIENCE-BASED CLIMATE TARGETS SET OUT ABSOLUTE REDUCTIONS IN GREENHOUSE GAS EMISSIONS*



- 40%

Scope 1+2 greenhouse gas emissions

- 14%

Scope 3 greenhouse gas emissions

SUSTAINABLE OPERATIONS TARGETS SET OUT INTENSITY REDUCTIONS FOR KEY ENVIRONMENTAL ASPECTS*

- 20

Water intake

- 25

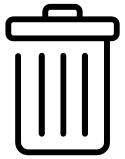
Waste water volume

100%

of sites in areas of high water stress with advanced water management

- 40%

Landfilled non-hazardous waste



- 25%

Hazardous waste

- 35%

Nitrogen oxide (NOx) emissions

* From 2019 to 2030

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The Portfolio Value Program: Home for discovering EcoTain® products

The Portfolio Value Program implements tools and processes to screen and move Clariant's product portfolio towards **increased sustainability performance**.

The PVP is developed with the Collaborating Centre on Sustainable Consumption and Production (CSCP), a renowned »think and do tank« founded by the UNEP and the Wuppertal Institute.

It takes a **two-sided look at product sustainability** assessing:

the sustainability performance **against the market**, and

the **absolute** sustainability **risks and benefits** of the product

PEOPLE	PLANET	PERFORMANCE
Safe use, transparency and information	Raw materials and sustainable sourcing	Integrated sustainable business
Addressing megatrends and social needs	Resource efficiency and environmental protection	Performance advantages

With a focus on **holistic and life cycle thinking** and the identification of EcoTain® products and solutions.

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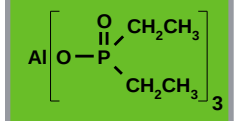
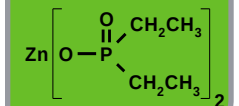
Clariant's Exolit® portfolio offers a variety of non-halogenated phosphorus-based flame retardants for thermoset applications

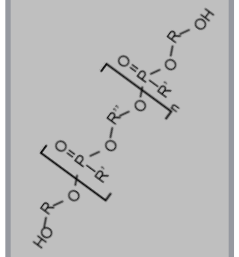
Feedstock

Exolit OP (DEPAL)





Exolit OP 550 / OP 560

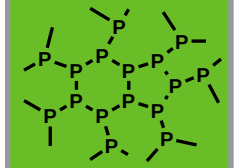


Exolit 5060

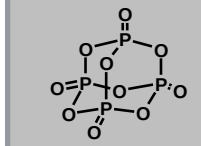
Exolit EP

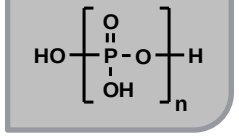
New!

Exolit RP
Red Phosphorus

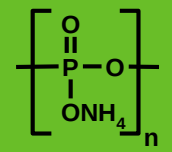


P_2O_5 / PPA

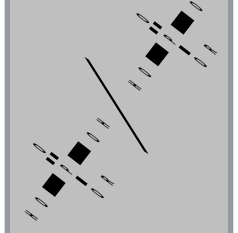




Exolit AP (APP)



Hordaphos



Core markets for Clariant's sustainable FRs are thermoplastics (E&E), Thermosets and intumescent coatings (construction).

These products are produced at three manufacturing sites: Hürth-Knapsack (near Cologne, Germany), Muttenz (Switzerland) + Lufeng (Kunming, China; JV since June 2010).

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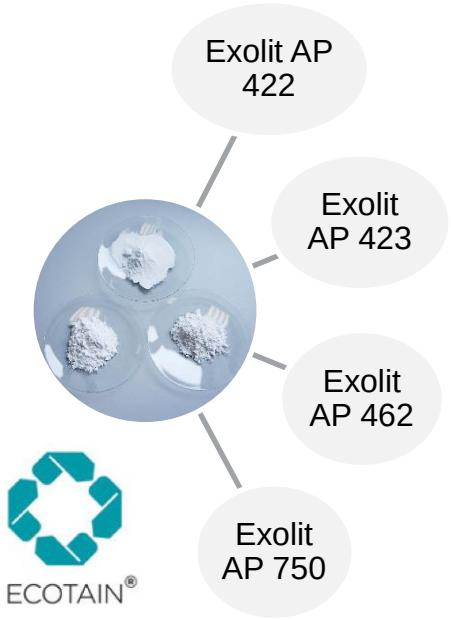
Exolit AP: Highly Efficient FR based on Ammonium Polyphosphate



Chemistry
- Long-chain inorganic polymer (phase II APP)
- High P-content
- Lowest acid number

Properties
- Fine grained white powder
- Lowest solubility in water and organics
- Different particle sizes available
- Encapsulated grades available for maximized water resistance

Sustainability
- Non-halogenated
- Ecotain® Product
- (Bio)-degradable

Benefits
- High P-content for high effectiveness
- Two flame retardancy mechanisms in action
- No contribution to emissions due to low vapor pressure

$(NH_4PO_3)_n \xrightarrow{> 250\ °C} (HPO_3)_n + n\ NH_3$

solid-phase >> **char formation**

gas-phase >> **displacement of oxygen**

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Exolit AP products are awarded with the Ecotain® label

- **Exolit AP-products are part of Clariant's Ecotain product range**
- Flame retardant for intumescent coatings, thermosets, adhesives, sealants and plastics
- Halogen-free
- low water solubility
- biodegradable

Sustainability

EcoTain®

Products that offer outstanding sustainability advantages are awarded Clariant's EcoTain® label. EcoTain® products significantly exceed sustainability market standards, have best-in-class performance and contribute overall to sustainability efforts of the company and our customers. Find out more about: EcoTain®.

PEOPLE

SAFE USE, TRANSPARENCY AND INFORMATION
- Non hazardous, studies on life cycle data available

ADDRESSING MEGATRENDS AND SOCIETAL NEEDS
- Saves lives and assets as a (halogen free) flame retardant

PLANET

RAW MATERIALS AND SUSTAINABLE SOURCING
- Phosphorus is on the EU list of critical raw materials, however, recycling is possible and actively investigated

RESOURCE EFFICIENCY AND ENVIRONMENTAL PROTECTION
- High material efficiency and minimized waste in production through recycling of raw materials

PERFORMANCE

INTEGRATED SUSTAINABLE BUSINESS
- Joint developments with customers on formulations

PERFORMANCE ADVANTAGES
- Constant high quality and hydrolytic stability
- Supports the attainability of eco-labels for customer products

ECOTAIN®

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Exolit® EP 360 and EP 390 –our new flame retardants for liquid processing (development products, samples and data under NDA)

KEY PRODUCT FEATURES

- Lower viscosity compared to alternative solutions
- Non halogenated flame retardant with epoxy functionality (Exolit EP 360)
- High phosphorus content
- Broad epoxy resin compatibility
- Transparent components possible due to excellent compatibility with epoxy base resin

TARGET MARKET, FOCUS CUSTOMERS

- Composite producers with focus on transportation and where particle free processing is needed → Aviation, Railway, Automotive but also E&E under investigation

Epoxy sample containing Exolit EP 360, 3 wt% P

Epoxy sample containing ATH, 40 phr

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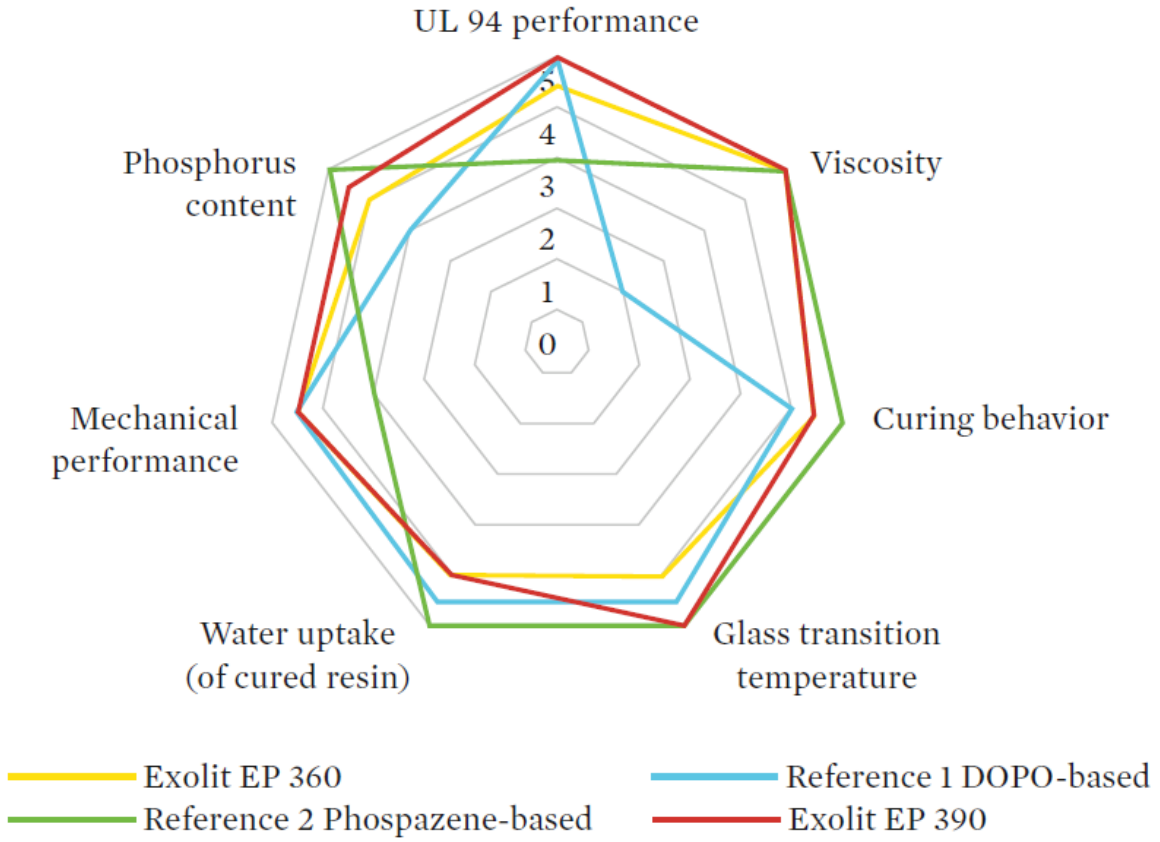
Exolit® EP 360 and EP 390 –our new flame retardants for liquid processing showing clear advantages compared to alternative products

CUSTOMER BENEFITS

- Favorable environmental health profile
- Ideal solution for all solvent-free processes like infusion and resin transfer molding processing
- Enabling to fulfill the required flame retardant performance at a low dosage
- Combination with other synergistic flame retardants possible
- Excellent curing performance
- Shows outstanding performance according to UL 94 standard



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Viscosity of Exolit EP 360 & EP 390 with DGEBA resin; Exolit EP 390 offering at same phosphorus content excellent viscosity

Components	Unit	# 1	# 2	# 3	# 4	# 5(1)
Exolit EP 360	g	31.7		62.5		
Exolit EP 390	g		22.8		43.5	
DOPO-resin (2)	g					100
DGEBA (3)	g	68.3	77.2	37.5	56.5	
Ingredients total	g	100	100	100	100	100
Phosphorus	% (w/w)	2.0	2.0	4.0	4.0	4.0
Viscosity (45 °C, 5 s^{-1})	mPa*s	1000	5800	1 x 10^5	41000	1 x 10^9
Viscosity (80 °C, 5 s^{-1})	mPa*s	370	250	1900	900	1 x 10^5

(1) Reference system
(2) Commercially available , solvent free DOPO-modified epoxy resin
(3) DGEBA epoxy resin with 1200 mPa*s at 45 °C and 80 mPa*s at 80 °C

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Epoxy composites for transportation

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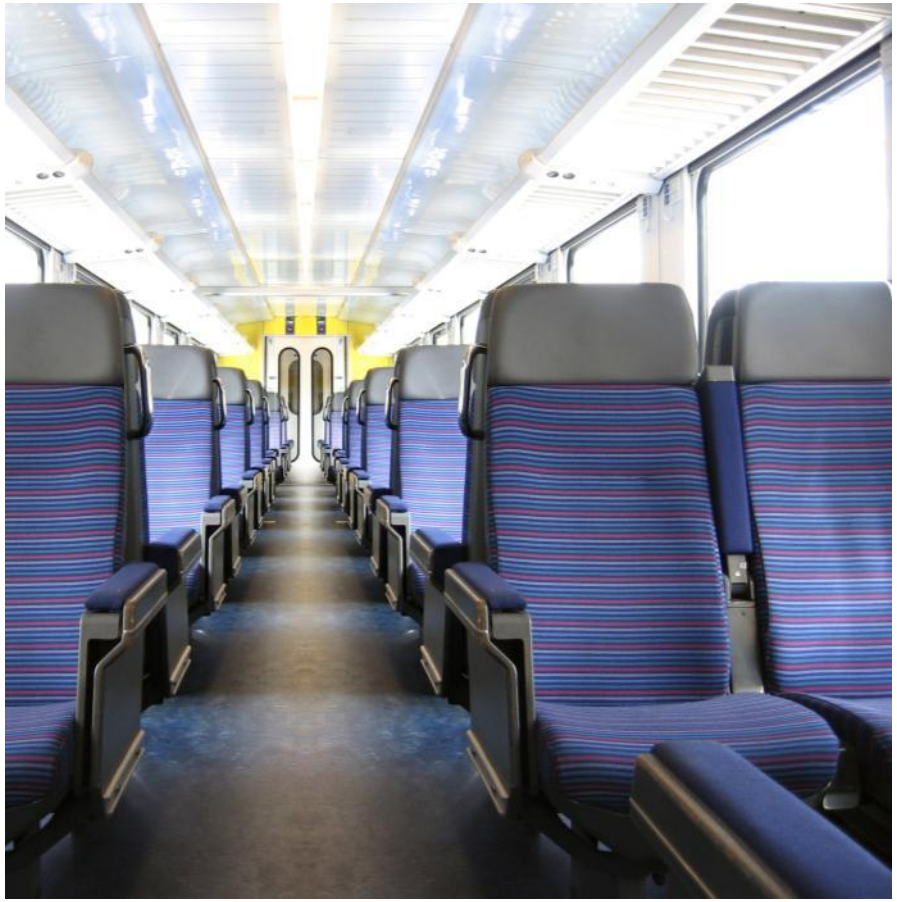
Epoxy composites for railway, optimized system allowing passing high demanding norm EN 45545-2, HL 3, R1

- In Europe the EN 45545-2 (“Fire protection of railway vehicles: requirements for fire behaviour of materials and components”) describes the required testing for the railway in detail. The components are grouped in R-classes and hazard levels (HL 1, 2 and 3).
- The level of fire safety required (Hazard level: HL) depends on the category of operation and design.
- The complex and demanding European Railway Standard favours halogen-free FRs, particularly due to challenging smoke requirements (toxicity and density).
- Parameters like spread of flame (CFE), smoke density (DS 4, VOF 4) and toxicity (CIT) and maximum of average rate of heat emission (MARHE) must be controlled.



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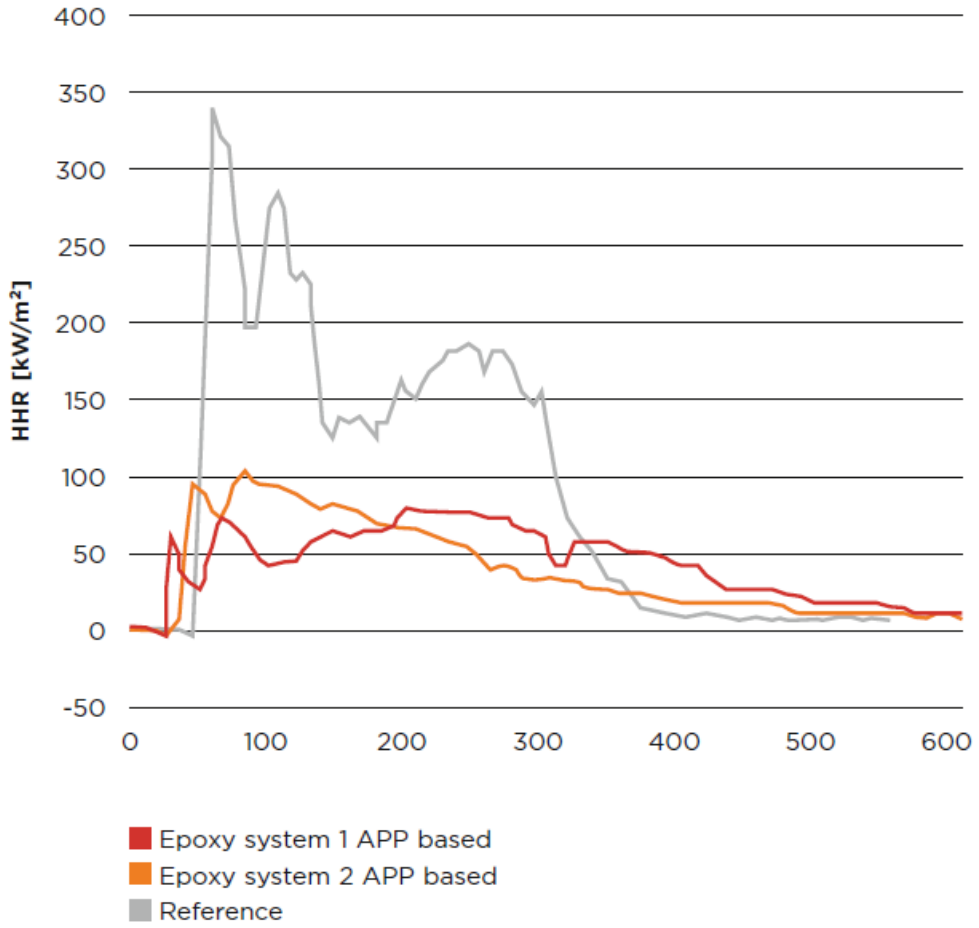
Optimizing MARHE performance of epoxy formulations by Cone Calorimetry: HRR Comparison of composites with different flame retardants



- Epoxy composites with different flame retardants (40 phr), measured at 50 kW/m^2
- APP I and APP II (red, orange) show an increased effect on HRR curve (heat release rate)
- Formulation APP II (orange) shows best effect as HRR is furthermore reduced

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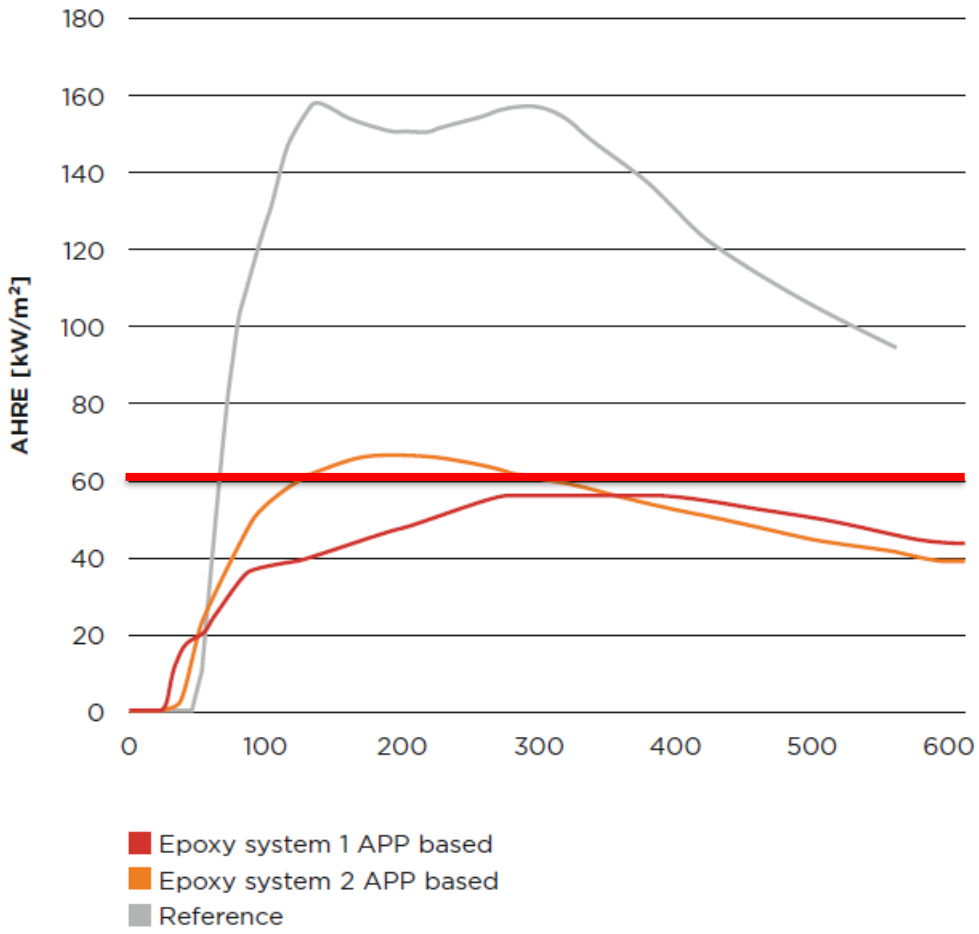
By using APP-based systems, already HL 2 can be reached; For passing HL 3, R1, intumescent system was optimized, formulation available



- ARHE curve of measured samples
- Maximum (MARHE) determines which hazard level in class R1 can be passed
- Formulation APP II (red) shows best performance, passing HL3 (AHRE < 60 kW/m^3)

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PINFA/Crepim: Smoke Toxicity Test Campaign, information on epoxy samples from Clariant passing UL-94 V-0 and EN 45545-2, R1, HL3

PROJECT BACKGROUND

- Lack of studies available on the influence of PIN FR on smoke toxicity
- Literature review (CREPIM, 2017) could not reveal clear adverse effect regarding the addition of PIN FRs or synergist on smoke toxicity

CREPIM tested samples chosen and provided by PINFA members to determine:

- Smoke toxicity determined by NF X 70-100 (short term)
- Smoke density determined by ISO 5659-2 + Annex C of EN 45545-2 at 50 kW/m^2 (for density)

SELECTED CLARIANT EPOXY SAMPLES

- Five epoxy composite samples containing flame retardants were tested and compared with a reference sample not containing flame retardants
- Four samples containing Clariant's flame retardants and formulations passing UL-94 V-0 and one also EN 45545-2, R1, HL3
- One sample containing a halogenated FR, passing UL-94 V-0

More details on test campaign, 94 representative commercial samples from 12 companies, tomorrow by Mr. Hervé Feuchter, CREPIM, France

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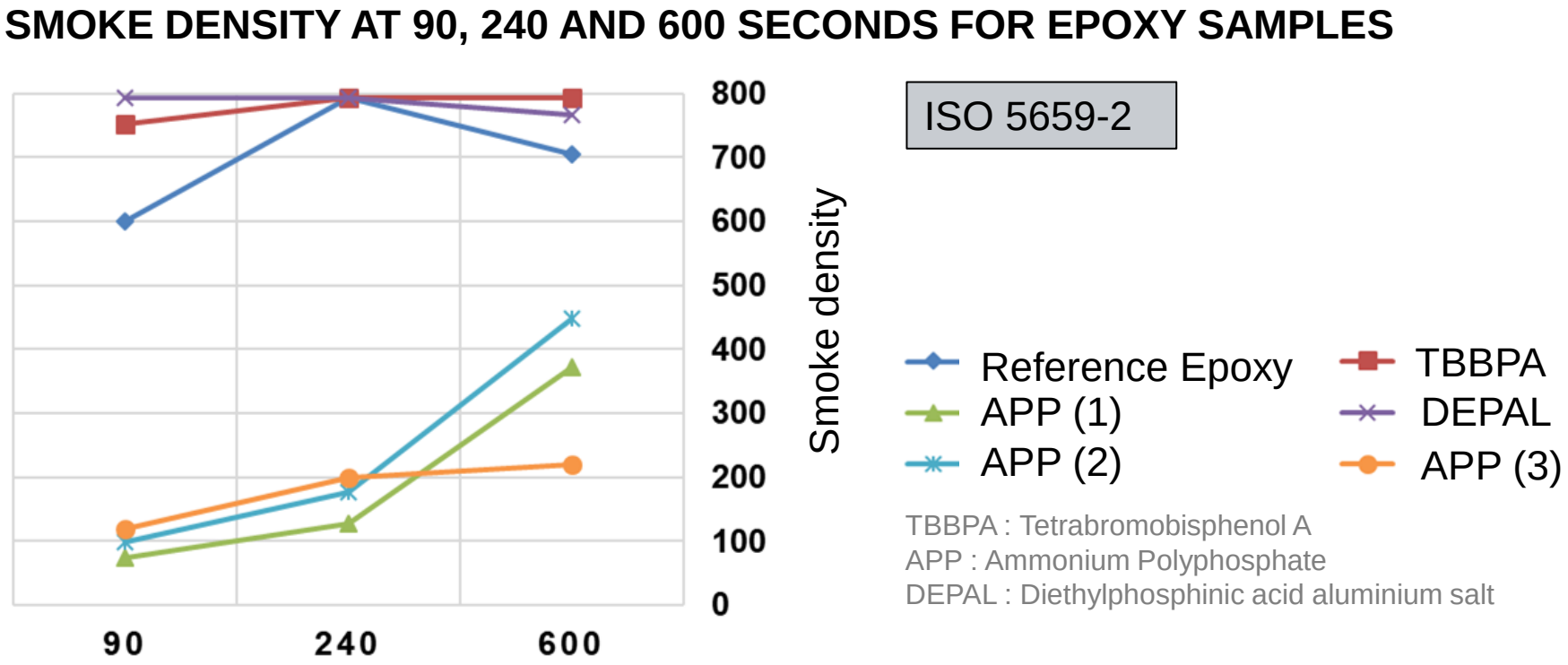
Smoke density: Especially APP based systems showing excellent performance



- Two different behaviors in smoke emission
- High smoke densities with DEPAL and TBBPA
- Very low smoke density with APP

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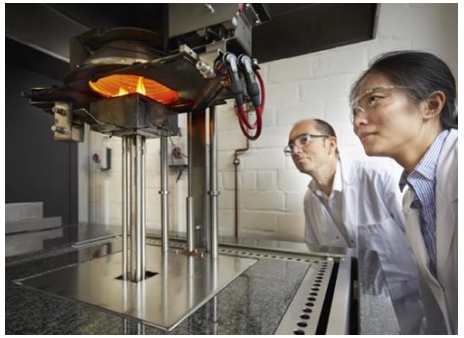
Conclusion

- Our dedicated technical service offers support regarding individual recipe development and optimization of flame retardant and additive packages.
- Guiding formulations with the focus on unsaturated polyesters or epoxy resin based composites for different applications available.
- Flammability tests (UL 94, Cone Calorimeter, LOI, GWFI/ GWIT, DIN 4102 B2, CTI, FMVSS 302) and standard methods to characterize plastics properties (e.g. mechanical and rheological data).
- Exolit® EP 360 and EP 390 for liquid processing available.



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