Metal hydrates for thermosets

APYRAL®

APYRAL® AOH

Metal Hydrates for thermosets

Product	D50 [µm]	D90 [µm]	BET [m^2/g]	Oil absorption	Applications
APYRAL® – Standard grade					Dispersions Cast resins Fillers/putty PUR foams Adhesives
APYRAL® 1E	50	100	0.2	21	
APYRAL® – Morphologically modified					
APYRAL® 2E	20	50	0.5	18	
APYRAL® – Ground					
APYRAL® 8	15	30	1.3	24	Dispersions & coatings Hand & spray lay-up SMC/BMC - RTM/RIM Pultrusion - winding/layering Laminates/prepregs PUR foams
APYRAL® 15	12	23	1.7	27	
APYRAL® 16	16	44	1.8	17	
APYRAL® 24	8	21	2.5	19	
APYRAL® – Viscosity-optimized					
APYRAL® 20X / 20HC	8	80	1.2	12	SMC - RTM/RIM Hand & spray lay-up Cast resins/sealing compounds/gap fillers
APYRAL® 30X	7	45	1.5	13	
APYRAL® 22	12	40	2	13	
APYRAL® 33	6	20	3	15	
APYRAL® 44	8	19	2.3	20	
APYRAL® – Fine-precipitated					
APYRAL® 40CD	1.5	3.3	3.5	22	Pultrusion Laminates/prepregs PUR foams Adhesives
APYRAL® 200SM	0.4	0.8	15	48	
APYRAL® AOH – Boehmite					
APYRAL® AOH 30	1.8	4.2	3	28	PCBs base laminate / prepregs (e. g. FR4, FR5, CEM3) Cast resins/sealing compounds Encapsulation compounds (EMC, EEC) Solder masks Rheology additives
APYRAL® AOH 60	0.9	1.7	6	30	
ACTILOX® 200SM	0.3	0.6	17	36	
NABALOX® – Aluminium oxide					
NABALOX® NO 325	3	7.2	1.5	19	Cast resins/sealing compounds PCBs base laminate / prepregs thermal interface materials (TIM)
NABALOX® HC 170	4	13	1.7	15	

All data listed in this brochure are reference values and subject to production tolerance. These values are exclusive to the product description and no guarantee is placed on the properties. It remains the responsibility of the users to test the suitability of the product for their application.

Content

01 Metal hydrates in thermosets

Halogen-free flame retardancy with metal hydrates 04
Metal hydrates in thermosets 04
Factors influencing ignitability of thermosets / composites 05
Ignitability of various resin systems 05
Influence of the reinforcing materials 06
Influence of the filler loading and other factors 06

02 APYRAL® grades based on aluminium hydroxide

Chemical and physical parameters 10
Rheological performance of **APYRAL®** 11
Sedimentation 13
Dispersion in liquid resins 14
Avoiding agglomeration 15
Filler mixtures 15

03 APYRAL® AOH grades based on aluminium oxide hydroxide

General chemical and physical parameters 17
Processing 18
Reliable thermal stability up to 340 °C 18
Low electrolyte content 19
Basicity and acid-resistance 19
Viscosity properties 20
Low-cost flame retardancy with **APYRAL® AOH** 21

04 Application processes and basic formulations for APYRAL®

Hand lamination 24
SMC and BMC compounds 25
Pultrusion 26
Cast resins on epoxy resin basis 28
Epoxy resins for building applications 29

05 Special applications in thermosets

Thermal conductivity of thermoset compounds 31
Application of **APYRAL® 44** in RTM 34
Combination of **APYRAL®** with ammonium polyphosphate (APP) 35

Halogen-free flame retardancy with metal hydrates

Mineral flame retardants based on metal hydrates, especially aluminium hydroxide, have established themselves over years as by far the most important flame retardants.

In the past few years, metal hydrates have experienced the highest growth among all flame retardants. In particular their good environmental compatibility and their favourable price-to-performance ratio make **APYRAL®** and **APYRAL® AOH** sustainable flame retardants. For a detailed introduction into mineral flame retardancy, please refer to our brochure „Mineral flame retardancy with metal hydrates".

Metal hydrates in thermosets

Nabaltec AG provides a number of functional mineral fillers for applications in thermosetting resins. Their primary purpose is the effective and low-cost flame retardant finish of the end products.

APYRAL® grades are used primarily to this effect. But there are also applications for **APYRAL® AOH**, mainly in combination as a synergist with **APYRAL®** or other halogen-free flame retardants. One successful example is application in basic materials for printed circuit-boards based on epoxy.

An overview of the two product lines available at Nabaltec AG which are recommended for thermosetting applications, as well as the appropriate designations of the substances used in literature and colloquial language are listed up in the table in the box below.

Due to the complexity of thermosetting systems and composite materials, this brochure deals primarily with flame retardancy in unreinforced resin types.

The general advantages of the application of mineral flame retardants are:

- low-cost
- environmentally compatible / halogen-free
- retardation of ignition and flame propagation
- significant smoke gas suppression
- no volatility (no VOC)
- no emission of toxic fire gases
- no emission of corrosive fire gases and thus
- reduction of consequential damage

Nomenclature and properties of aluminium hydroxide

APYRAL®	$Al(OH)_3$
Chemical	Aluminium hydroxide
Mineral	Gibbsite
Common name	Aluminium trihydrate (ATH)
Loss on ignition	34.6 %
Density	2.4 g/cm³
Mohs hardness	2.5 - 3
pH	8 - 9

Nomenclature and properties of aluminium oxide hydroxide

APYRAL® AOH	AlOOH
Chemical	Aluminium oxide hydroxide
Mineral	Boehmite
Common name	Aluminium monohydrate (AOH)
Loss on ignition	17 %
Density	3.0 g/cm³
Mohs hardness	3 - 4
pH	7 - 8

This brochure does not pretend to be exhaustive; it is instead intended to provide the user with an overview and assistance for starting formulation developments.

For further details, see our brochure „Mineral flame retardancy with metal hydrates“.

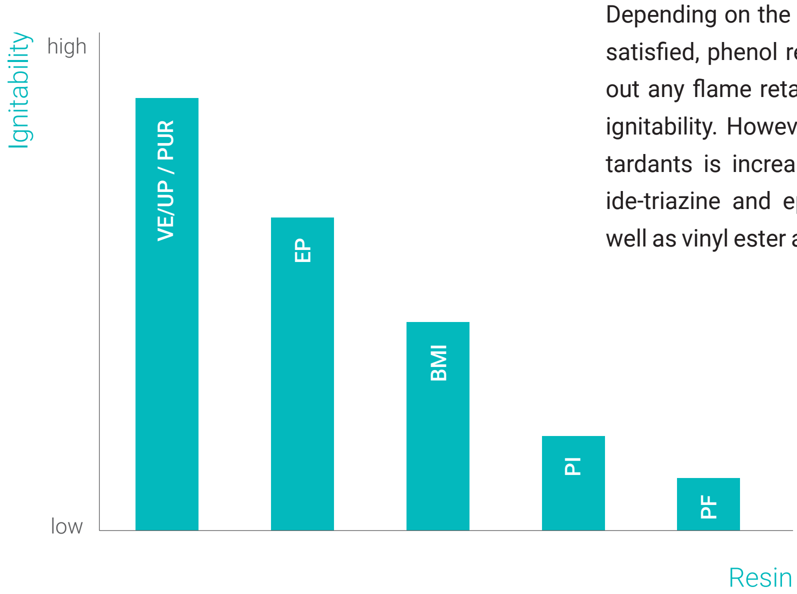
Factors influencing ignitability of thermosets / composites

Factors to be taken into account which influence ignitability for thermosets:

- inherent ignitability of resin
- with/without reinforcing materials
- product / composite thickness
- type of reinforcing material
- volume fraction of the reinforcing material
- fiber type within the reinforcement
- loadings depending on the fire standard to be satisfied
- arrangment of reinforcement (type of fabric and fiber orientation)

Ignitability of various resin systems

For mineral flame retardancy in thermosetting systems, the differences in the inherent ignitability of the various resin types must be taken into account. A rough classification of the most important resin types on the basis of their ignitability is shown in the below diagram.

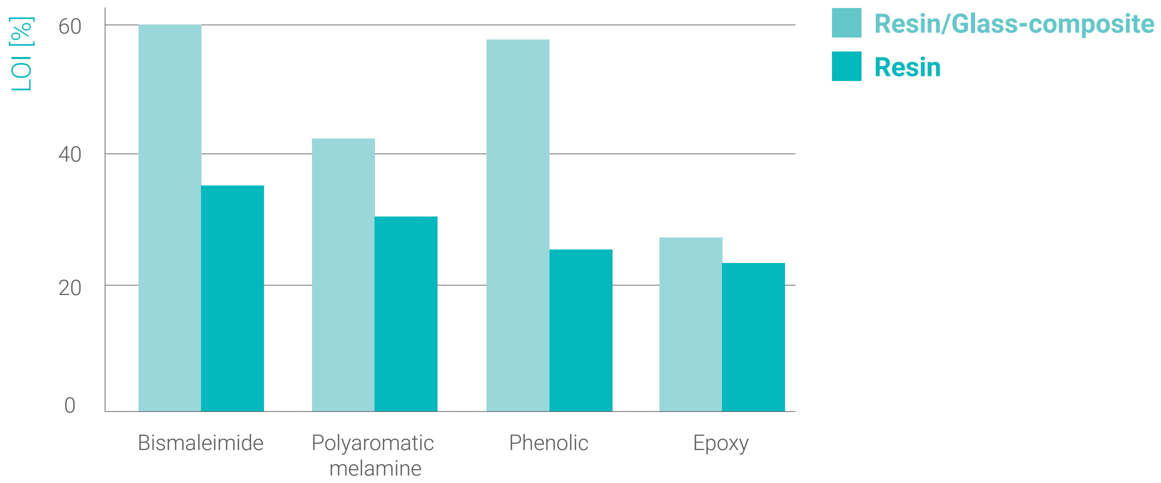


Rough classification of different resin types according to their inherent flammability [1]

Depending on the flame retardancy standard to be satisfied, phenol resins can be used partially without any flame retardants due to their low inherent ignitability. However, the filler loading of flame retardants is increasing for polyimides, bismaleimide-triazine and epoxy resins to polyurethane as well as vinyl ester and unsaturated polyester resins.

Influence of the reinforcing materials

Moreover, the influence of a possible reinforcement (e.g. long or short fiber, fabric, knitted fabric, etc.), must be taken into account. Here again, the various resin types differ greatly. This is illustrated using the example of the widespread glass fiber reinforcement in the below diagram based on the various oxygen indices for the various resins with and without glass fiber reinforcement. With the use of reinforcing materials, fibers could poke out at the cutting edges. In the event of a flammability test unwanted wicking may occur, which influences the results negatively. A careful deburring of the test specimens at the cutting edges is necessary.



Comparison of the influence of fiber glass reinforcement on the LOI of different resin types [1]

Influence of the filler loading and other factors

When developing a flame retardant thermoset resin the filling level of **APYRAL**® and **APYRAL**® **AOH** is the most decisive paramter.

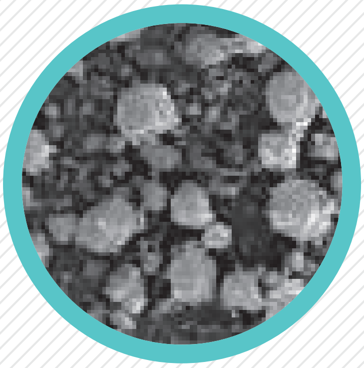
A rough overview of the loadings necessary to satisfy a special standard with aluminium hydroxide is shown as an example for UP resin systems in the table below. However, these loadings may vary depending on the used resin system and hardener.

Necessary loadings of aluminium hydroxide in unsaturated polyester resins (phr = parts ATH per 100 parts resin)

[phr]	[wt.-%]	Standard	Application
50	33	Does not satisfy any standard	
100	50	DIN 4102 B2	Buildings
150	60	DIN 5510 S4 UL94 V0	Railway E&E
200	66	–	
250	71	DIN 4102 B1	Buildings
300	75	NF 16-101 M1 F0	Railway
400	80	SBI, fire class B smoke class S1 BS6853; EN 45545-2	Buildings Railway

APYRAL® grades based on aluminium hydroxide

APYRAL® grades based on aluminium hydroxide



Subdivision of the **APYRAL®** grades into product classes

Product classes APYRAL®:

Standard	–	**APYRAL® 1E**
Morphologically modified	–	**APYRAL® 2E**
Ground	–	**APYRAL® 8, 15, 16, 24**
Viscosity-optimized	–	**APYRAL® 22, 33, 44, 20X, 30X**
Fine-precipitated*	–	**APYRAL® 40CD, 60CD, 120E, 200SM**

**fine-precipitated grades are only rarely used in thermosets*

The inner front cover contains an overview of the product grades of Nabaltec AG used in thermosets. Moreover, typical applications for each product class are specified. For more detailed information, please refer to the appropriate product data sheets (www.nabaltec.de).

Our **APYRAL®** products can be structured into five product classes based on different manufacturing processes and property profiles, as shown in the above box.

APYRAL® 1E – standard

With a mean grain diameter of 50 µm, the standard product **APYRAL® 1E** is the coarsest **APYRAL®** grade. It is used for example in the manufacture of cast resins, dispersion paints and putties. Due to its low specific surface area (BET), it is also used for adhesives, because high surface areas are known to lower the adhesive strength.

APYRAL® 2E – morphologically modified

A chemical process („etching") is used to transform an aluminium hydroxide with sharp-edged particles into rounded, scarcely agglomerated particles. The resulting product **APYRAL® 2E** is almost free from fines. It is predominately used for the production of flame-retardant cast resin compounds, especially in electronics. It has proved itself due to its relatively low viscosity in liquid resins and its very low specific electrical conductivity. Because of its low BET surface area it is often used in adhesives.

APYRAL® 8, 15, 16 and 24 – ground

APYRAL® 8 and **APYRAL® 15** are produced by grinding aluminium hydroxide. They have a narrow, symmetrical grain size distribution. The particle morphology is platetype with a high L/D ratio, up to splintery. In liquid systems, these products are especially characterized by a very low sedimentation. **APYRAL® 8** and **APYRAL® 15** are used in various applications, primarily in resins which are used in glass-fiber reinforced products manufactured via BMC, and in flame-protected coatings.

APYRAL® 16 and **APYRAL® 24** are produced by application of a special grinding process. These products have only a very low portion of splintery particles - their grain size distribution is relatively broad. Due to their good viscosity characteristics (see pp 11), these products permit high loadings and consequently good flame retardant properties of the filled resin. This feature is utilized, for example in components of glass-fiber reinforced plastics based on UP resin, which are manufactured via the SMC, BMC, RTM and pultrusion processes. Here, the ground products **APYRAL® 16** and **APYRAL® 24** have proved to be extremely effective.

If even higher loadings are required, these can only be achieved using the viscosity-optimized products.

APYRAL® 22, 33, 44, 20X and 30X – viscosity-optimized

The decisive parameter in the processing of highly filled resin compounds is their viscosity. This is illustrated in the figure on page 12 which shows the growth of the relative viscosity along with the increasing loading in an UP resin as an example. Thus, the distinct differences in the viscosity behavior of the individual **APYRAL®** grades are illustrated. Extremely high loadings can only be achieved using the viscosity-optimized products **APYRAL® 20X** and **APYRAL® 30X**, as well as **APYRAL® 22**, **APYRAL® 33** and **APYRAL® 44**. These products are specifically manufactured with the aim of achieving an extremely broad, but well-defined grain distribution. They also permit the attainment of very high packaging densities in finished molded parts. This leads to high loadings and therfore to high flame retardancy and high thermal conductivity levels (see p. 34).

The products **APYRAL® 20X** and **APYRAL® 30X** are optimized especially for high loadings alongside with a very low viscosity.

APYRAL® 22 and **APYRAL® 33**, on the other hand, combine two very important properties, i. e. a very low viscosity along with very low settling properties (see fig. p. 12).

Moreover, **APYRAL® 22** and **APYRAL® 33** are recommended if high loadings are to be achieved but a low top cut is required due to the surface quality of the end product (see D90 values on p. 2). Similarly, that also applies for **APYRAL® 44**. This was developed specifically for applications on resin-transfermoldings (RTM, etc.), where its high flowability in combination with its high fineness make a fast injection (short cycle time) possible and work against filtration effects (see p. 34).

APYRAL® 40CD, 60CD, 120E, 200SM – fine-precipitated

These **APYRAL®** products are made by controlled precipitation following complete dissolution of aluminium hydroxide. This process results in very fine, morphologically optimized types. These are used predominately in thermoplastics and elastomers, as here the relatively high viscosities produced by the fine-precipitated products can be controlled by the processing methods used which create extremely high shear rates (e. g. twin screw extruder, internal mixer, etc...).

In the case of liquid resin applications, only low to moderate loadings can be achieved. The requirements thermosets have to satisfy today regarding flame retardancy, however, can only be achieved through high loadings, which in turn is very difficult to achieve with fine-precipitated aluminium hydroxides. Thus, these products are practically not used any longer in thermosets today. Hence, this brochure does not dwell further on that **APYRAL®** line. For more detailed information, please refer to the brochures „Mineral flame retardancy with metal hydrates“ and „Metal hydrates in cable applications“.

Used in low quantities, however, **APYRAL® 200SM** can work as an antisettling agent without the negative side effects of an increase in viscosity or imparting thixotropy. To this effect, 10 – 20 phr of the main filler, e. g. aluminium hydroxide, are replaced by **APYRAL® 200SM.**

Chemical and physical parameters

APYRAL® products have a very high chemical purity of approx. 99.5 % $Al(OH)_3$. The residual constituent contains traces of iron and silicon compounds but is mainly sodium oxide which is present in two fractions. One part is integrated into the crystal lattice and the other part partially adheres to the crystal surface in hydrated form.

Aluminium hydroxide is a water-insoluble solid and has an amphoteric character. Due to its alkali oxide content, an aqueous **APYRAL**® suspension has a pH value of 8 – 9. This must be taken into account in applications involving aqueous alkali-sensitive solvents or dispersions, especially when utilizing other additives which can only be used within a certain pH range. In case of doubt, possible interactions must be verified.

Aluminium hydroxide is not hygroscopic. A shelf life of one year is guaranteed, as long **APYRAL**® is stored in the original packing material under dry conditione, e.g. under roof, protected from rain and splash water.

When used as a flame retardant, **APYRAL**® acts in many applications as white pigment. Due to its high whiteness, **APYRAL**® behaves neutral to color when dyeing plastics. The Mohs hardness of 2.5 – 3 does not cause any problems either when processing resins with a high loading, and does not result in abrasion phenomena in molds, such as may occur for example in the use of very hard fillers such as aluminium oxide or silicon carbide.

The relatively high thermal capacity (c_P = 1.65 J/gK at 127 °C) is beneficial for the dimensional heat stability of plastics using the filler **APYRAL**® and for some applications is even the dominant feature.

APYRAL® is a mineral filler tending to the low side with regard to density (2.4 g/cm^3). Unfortunately, as a consequence of the loadings required, the density of the flameprotected plastics is higher compared to unfilled polymers. However, all in all, **APYRAL**® also counts among the commercially most attractive flame retardants regarding the volume-related cost balance.

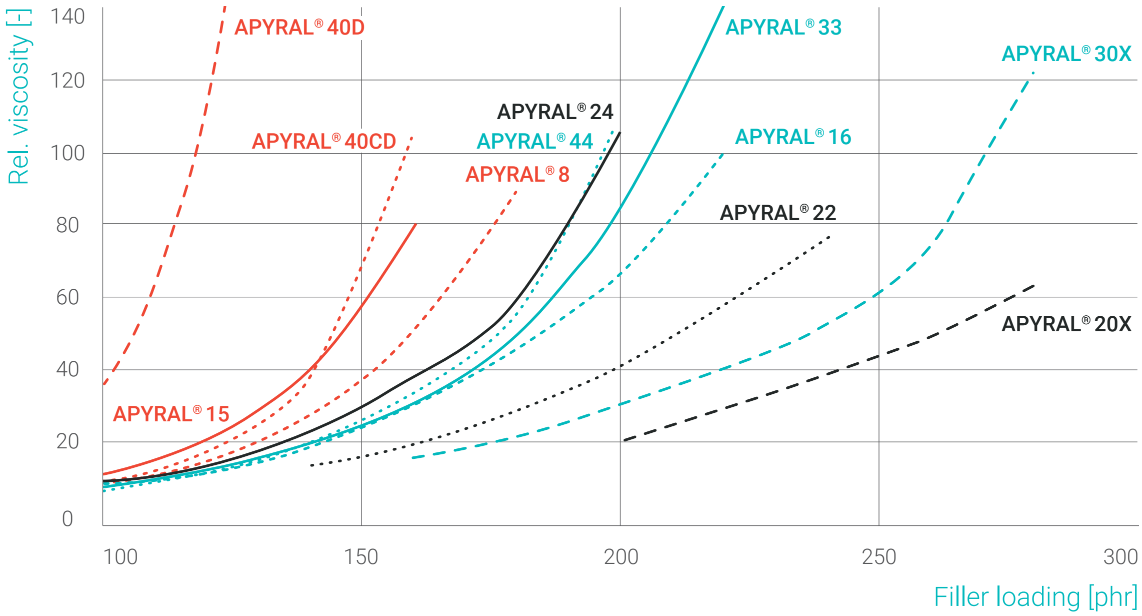
Product advantages APYRAL®:

- high chemical purity
- water-insoluble, pH 8-9
- high whiteness, neutral in color
- low hardness (Mohs 2.5 - 3)
- high thermal capacity (c_P = 1.65 J/gK)
- good thermal conductivity
- average density (2.4 g/cm^3)
- not hygroscopic (good storage stability)
- **APYRAL**® filled thermosets can be machined like wood or metal

The overall result is extremely positive due to the physical properties of the final parts. Resins filled with aluminium hydroxide, unlike calcium carbonate, can also be machined similar to wood (drilling, sanding, mill cutting). This effect is used in model making and rapid prototyping, where the exact adjustment of geometry is decisive.

Furthermore, high volume filler loadings and a significant increase of the thermal conductivity can be quite simply achieved, in particular with the viscosity-optimized grades of **APYRAL**® **20X** and **30X** (see p. 31 ff.).

Rheological performance of APYRAL®

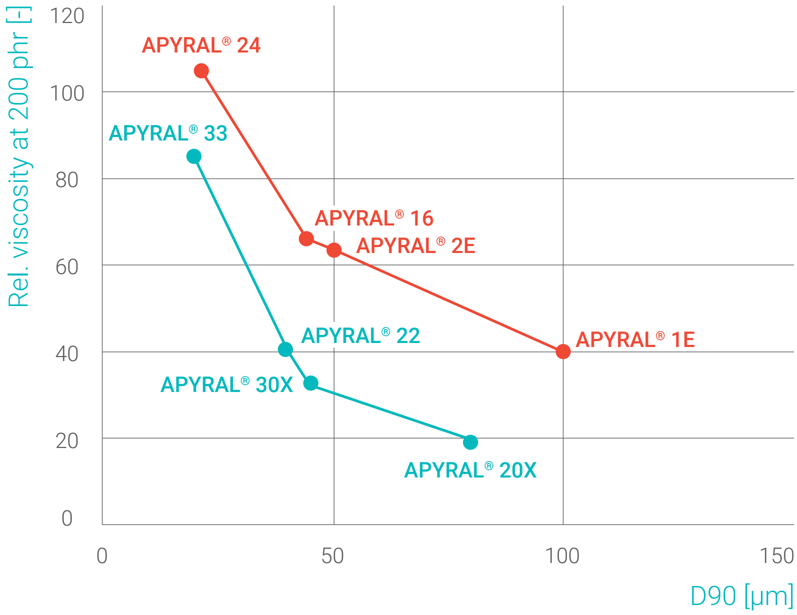


Comparison of the increase in viscosity of a UP resin filled with various ***APYRAL®*** *types at 23 °C (rel. viscosity = ratio of the viscosities of resin with fillers to resin without fillers; UP resin: Palapreg P17-02, Aliancys. Initial viscosity approx. 1800 mPa*s, shear rate 10 1/s; no use of any additives)*

One of the most important physical parameters with the use of mineral flame retardants is the influence of the filler on the viscosity of the resin formulation. Generally, by the addition of fillers a significant increase of the viscosity occurs. Fine precipitated grades like **APYRAL® 40D** already lead to a strong viscosity increase at relatively low filler loadings (approx. 100 phr). On the contrary, with the use of grades tailored for resin applications much higher filler loadings can be achieved, see the figure above.

With its state-of-the-art production processes, Nabaltec AG offers ATH grades, where different characteristics concerning fineness, particle size, particle size distribution and morphology are optimized for various processes in resin applications. Filler loadings of 300 – 400 phr or more are achievable when suitable resins systems are used together with viscosity optimized grades like **APYRAL® 20X** and **APYRAL® 30X**.

- strong increase of viscosity in the case of ground grades **APYRAL® 8** and **15** and fine-precipitated grades, such as **APYRAL® 40D**
- moderate increase of viscosity with **APYRAL® 16** and **24**
- highest loadings only with viscosity-optimized types **APYRAL® 44, 33, 22, 30X,** and **20X**
- **APYRAL® 44, 33,** and **22** with a high degree of fineness and good sedimentation properties (see p. 13)
- **APYRAL® 30X** and **20X** with the best viscosity performance



Viscosity in dependence of the D90 at 200 phr for different **APYRAL®** *grades (shear rate 10 1/s, 23 °C; UP resin: Palapreg P17-02, Aliancys, initial viscosity approx. 1800 mPa*s; no use of any additives)*

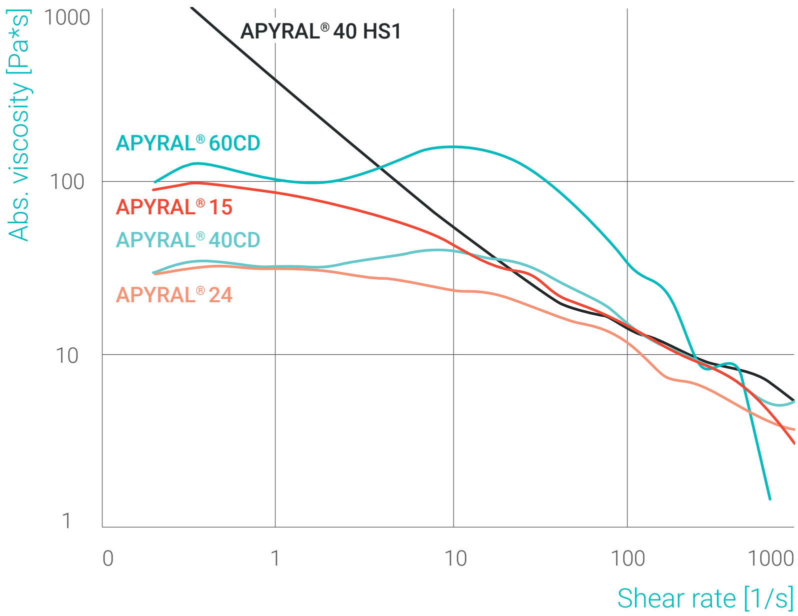
Generally the viscosity is a function of the grain size. Usually finer grades exhibit a clearly higher viscosity than coarser grades. However, the viscosity is not solely dependent on the mean particle size, in fact it is a function of the particle size distribution, the BET surface area, and the morphology of the particles. Since the width of the particle size distribution plays a very important role, these values are given on the technical data sheets of Nabaltec AG. Next to the parameters of the average grain size (D50) as well the D90 is given. This describes the coarse fraction in the particle size distribution. Its significance for the viscosity is represented in the illustration above.

It is also important to mention that the viscosity is not a onedimensional parameter, but next to the temperature it depends also on the shear rate. The shear rate varies strongly depending on the process and affects the resulting viscosity (see table on the right).

As shown in the figure below, the viscosity over a range of the shear rate can be quite different between the varying ATH grades. Generally, ground hydrates show a clear drop with the shear rate (shear thinning), while fine precipitated grades exhibit bellshaped curves. By means of a surface treatment of a hydrophobic silane (HS) the viscosity at lower shear rates can be strongly increased, so a filler stabilization and a lower sedimentation gradient are observed.

Shear rate by different processes

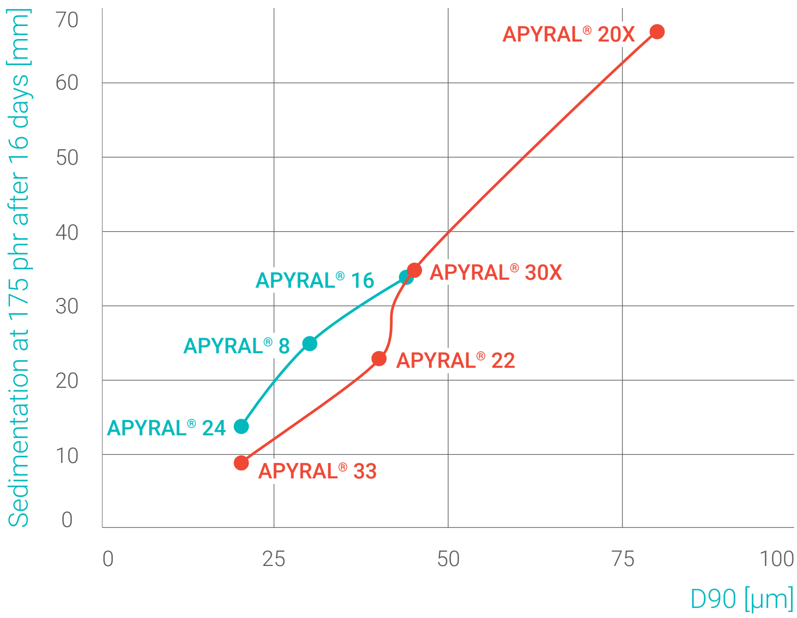
Process	Shear rate [1/s]
Sedimentation	< 0.0001 – 0.01
Leveling	0.01 – 0.1
Sagging	0.01 - 1
Grouting/pouring	1 - 10
Coating by dipping	1 - 100
Tube flow, pumping, filling	1 – 1,000
Mixing, stirring	10 – 10,000
Coloring, painting, brushing	100 – 10,000
Spraying	1,000 – 10,000



Shear rate in dependence of the viscosity at 140 phr for different ***APYRAL®*** *grades (23 °C; UP resin: Palapreg P17-02, Aliancys, initial viscosity approx. 1800 mPa*s; no use of additives)*

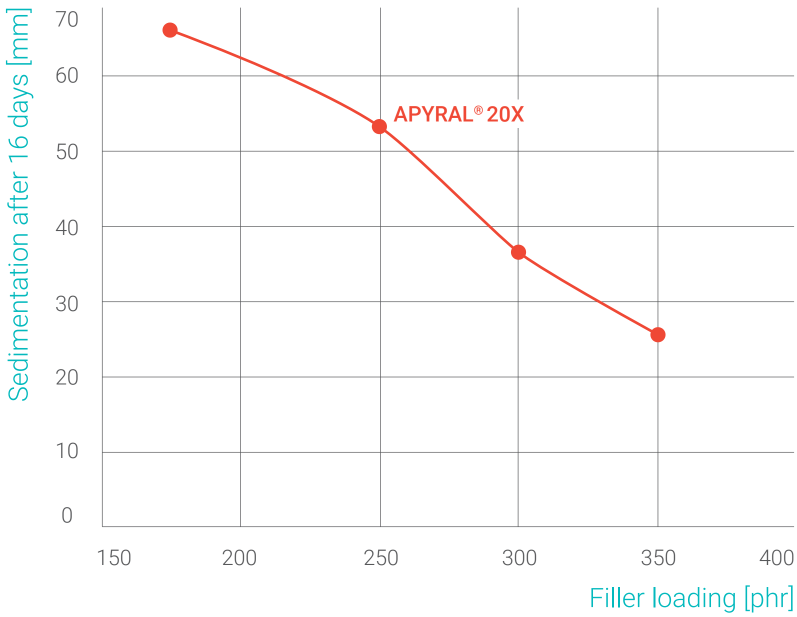
Sedimentation

A further important aspect is the sedimentation of the fillers, which is a complex function of the particle size, the particle size distribution, the filling grade and the viscosity of the resin mixture. The sedimentation generally increases with increasing particle size, but decreases with increasing filler loading and viscosity. By means of suitable additives (thixotropic agents) the shelf-life of a resin mixture can be regulated.



- clearly lower sedimentation gradient of **APYRAL® 33** with low top cut (D90 = 20 µm)
- higher sedimentation of **APYRAL® 20X** (D90 = 80 µm), optimized on viscosity

Sedimentation of different ***APYRAL®*** *types in a highly liquid UP resin at 175 phr (room temperature, UP resin: Palatal P80-02, Aliancys, initial viscosity approx. 600 mPa*s; no use of anti-settling agents)*



Sedimentation of ***APYRAL® 20X*** *as a function of the filler loading in a highly liquid UP resin (room temperature, UP resin: Palatal P80-02, Aliancys, initial viscosity approx. 600 mPa*s; no use of anti-settling agents)*

Dispersion in liquid resins

For the production of (reinforced) composites made from liquid prepolymers or uncrosslinked reactive resins in a first step a proper dispersion of the mineral filler has to be achieved. Only a good dispersion will tap the full potential of flame retardancy and mechanical properties of the final composite.

In principle, high shear mixers should be used. Better dispersion also improves the storage stability of the resin. Good results can already be achieved with standard dissolvers, utilizing a rotating chopper disc in high speed.

An efficient method is also the use of inline dissolver technologies which can achieve a highly efficient dispersion within a very short time.

Processing advantages of APYRAL®:

- good dispersion possible using standard dissolver technology and inline dispersion methods
- extremely good dispersion results in case of a high input of shearing energy and under vacuum
- in the case of viscosity-optimized **APYRAL®** types or low loadings, the pre-dispersion at higher loadings (and high shear) might be useful to avoid agglomeration

Avoiding agglomeration

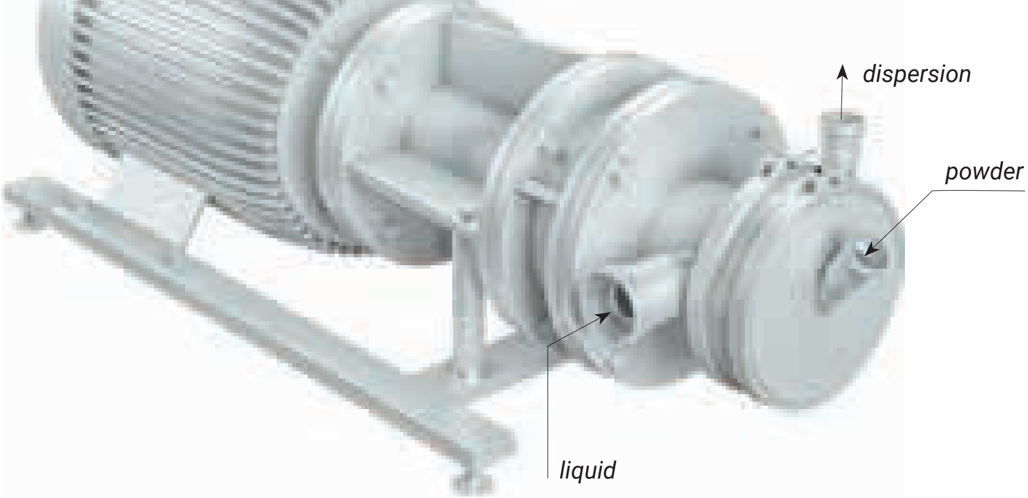
In the case of formulations with a relatively low loading, it may be advantageous to achieve a good dispersion in a preblend with high loading (which produces high shearing forces) and subsequently to dilute slowly, by adding resin, until the required final loading is reached. This method can also be used to prevent agglomeration if viscosity optimized **APYRAL**® types are used during the dispersion process.

Chopper disc of a dissolver to create maximum shear rates (based on Wilhelm Niemann GmbH & Co Maschinenfabrik, Melle, Germany)

Filler mixtures

If other fillers are used in addition to **APYRAL**® or if several **APYRAL**® types are contained in a blend, it may be advantageous to begin by adding the finest filler in order to rapidly generate high shear rates which should improve the dispersion of all ingredients. However, depending on the system (fillers, resin, additives, etc.), especially fine-particle fillers may in turn result in agglomeration and hence in poor dispersion. Thus, in this case, it may make sense to first add a coarser filler in order to increase the shear rates which will then aid the dispersion of the fine filler.

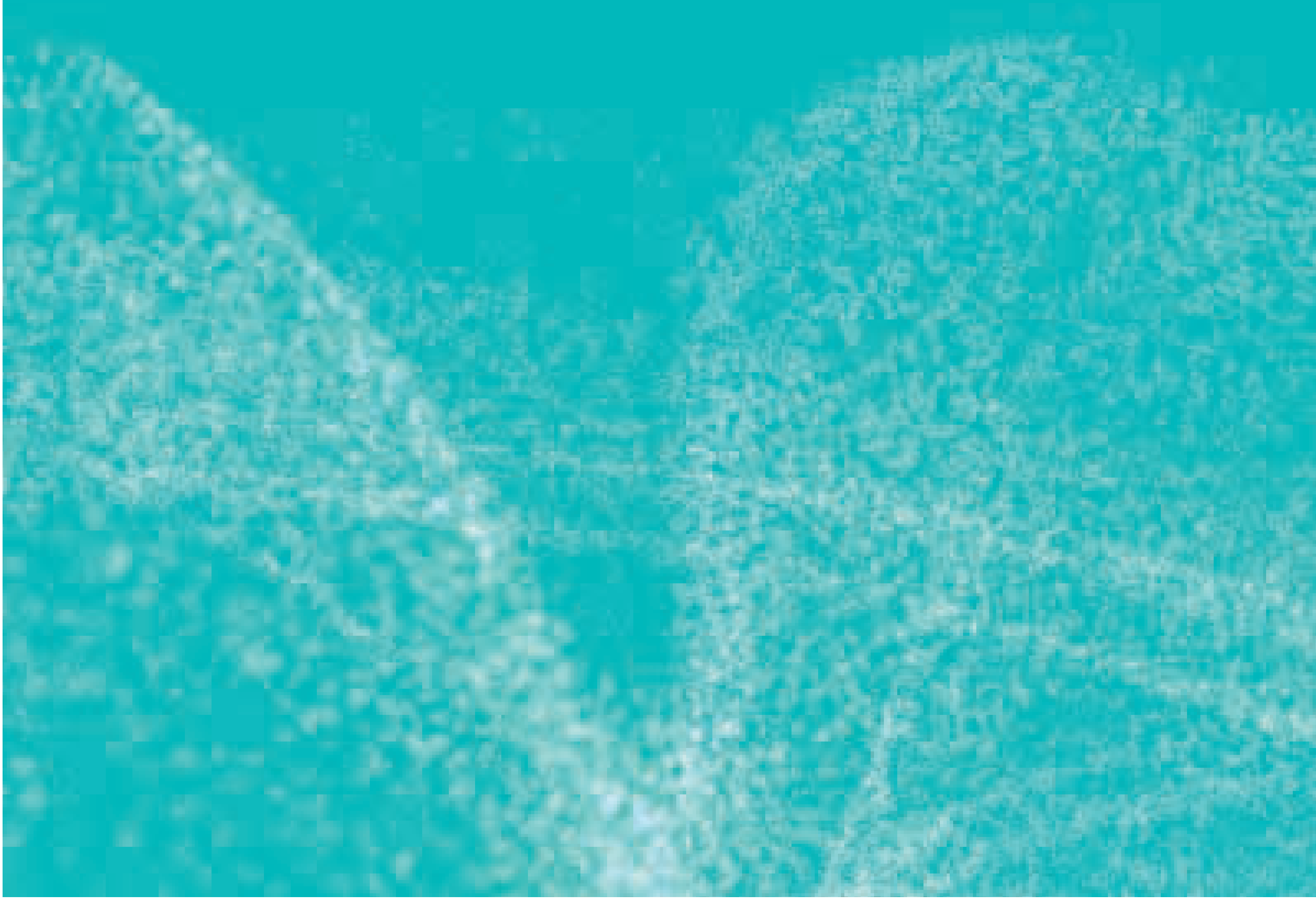
Ultimately the process engineer has to find out the optimum sequence of filler addition during mixing if a premix of the fillers cannot be applied.



Inline dispersion technology (based on Ystral GmbH, Ballrechten-Dottingen, Germany)

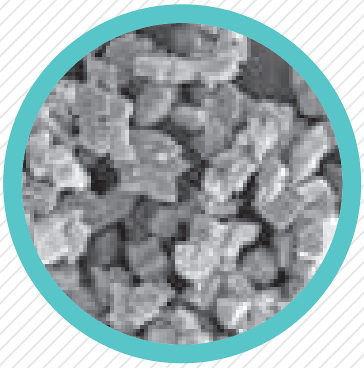
APYRAL® AOH grades

based on aluminium oxide hydroxide (AlOOH)



APYRAL® AOH grades based on aluminium oxide hydroxide (AlOOH)

The tradenames **APYRAL® AOH** and **ACTILOX®** encompass the different Boehmite grades of Nabaltec AG (carrying on in this brochure only **APYRAL® AOH** for both Boehmites will be used). **APYRAL® AOH** is used for an increasing number of applications, especially in areas requiring a high thermal stability and/or a synergistic use together with other halogen-free flame retardants.



Product advantages of APYRAL® AOH:

- high thermal stability, processing up to 340 °C
- decomposition only slow up to approx. 400 °C
- synergistic flame retarding effects with other halogen-free flame retardants
- excellent resin compatibility
- low viscosity due to special morphology
- very good settling properties
- low water adsorption in resin systems
- high purity
- low electrolyte content
- moderate alkalinity
- high acid-resistance
- high thermal conductivity
- high thermal capacity (c_P=1.54 J/gK at 227 °C)
- low Mohs hardness

General chemical and physical parameters

All **APYRAL® AOH** products are high-purity crystalline boehmites with a very low residual content of aluminium hydroxide and sodium oxide (purity min. 98 %). This ensures the extraordinarily high thermal stability and resin compatibility.

A high thermal capacity (c_P=1.54 J/gK at 227 °C), combined with the high thermal stability, predetermines **APYRAL® AOH** for utilization in electrically insulating heat sinks.

Its high whiteness combined with the extreme fineness and very good dispersion properties make **APYRAL® AOH** an interesting white pigment. **APYRAL® AOH** is characterized, thanks to its low alkalinity and residual moisture, by a good compatibility with reactive resin.

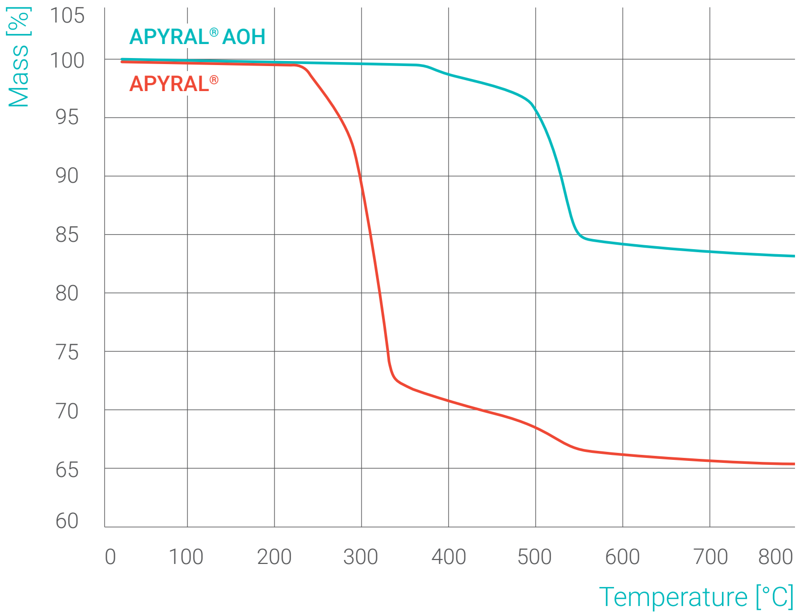
Like **APYRAL®**, **APYRAL® AOH** is not hygroscopic. A shelf life of one year is guaranteed, as long it is stored in the original packing material under dry conditione, e.g. under roof protected from rain and splash water.

Due to its good processing properties, it is possible to use boehmite as a filler, e.g. to adjust specific physical characteristics in the end product (e.g. thermal conductivity, coefficient of thermal expansion, mechanical characteristics) while reducing the amounts of other high-priced flame retardants required (see also p. 21 f).

Processing

As aluminium hydroxide, **APYRAL® AOH** can be processed without any problems by means of usual processes for liquid resin systems. In principle, the same processing information applies as for **APYRAL®** (see p.14 f), the processing window offering a much larger range of options with a compound temperature of up to 340 °C.

Reliable thermal stability up to 340 °C



Comparison of the thermal stability of Boehmite **(APYRAL® AOH 60)** *and aluminium hydroxide* **(APYRAL® 22)** *by thermogravimetric analysis (TGA, heating rate: 10 K/min)*

This prominent property is shown in the diagram above which represents a thermogravimetric analysis (TGA) of **APYRAL® AOH 60** compared to **APYRAL® 22**. While the decomposition of aluminium hydroxide commences relatively quickly at temperatures above 200 °C, decomposition of boehmite commences slowly and only as of 340 °C.

For a comparison of the thermal stability of flame retardants, the critical temperature is often specified at which a 1 % mass loss has occurred. With **APYRAL® AOH**, this low loss is not observed as of approx. 400 °C. On the other hand, aluminium hydroxide shows, at this temperature and under identical test conditions, a weight loss of 29 %, which corresponds to a water release of 85 %. Thus, the **APYRAL® AOH** is predestined for applications in which a higher thermal stability is required in the manufacturing process or in the final application. In the case of liquid resin applications, this is especially true in case epoxy resins are used.

Low electrolyte content

Another essential difference from aluminium hydroxide is also the considerably lower electrolyte content. This makes **APYRAL® AOH** ideal for utilization in electrically insulating plastic products, e.g. PCB laminates or cast resins. The electrolyte content is also an important factor influencing the viscosity properties and the hardening properties of resins.

In the manufacture of our **APYRAL® AOH** products, the electrolytes are depleted in the mineral. Thus, the total content of Na_2O of **APYRAL® AOH** is approx. 75 - 90 % lower than in aluminium hydroxide. Typical values are listed in the table on the right.

Typical values of the total [Na_2O(total)] and water-soluble sodium oxide content [Na_2O(ws)], and the corresponding value of water-soluble sodium ions [Na^+(ws)]

Product	Unit	Na_2O (total)	Na_2O (ws)	Na^+ (ws)
APYRAL® 2 E	[ppm]	1800	19	14
APYRAL® 20X	[ppm]	1600	47	35
APYRAL® 40CD	[ppm]	1200	117	87
APYRAL® AOH 30	[ppm]	200	10	7
APYRAL® AOH 60	[ppm]	300	35	25
ACTILOX® 200SM	[ppm]	250	90	66

Basicity and acid-resistance

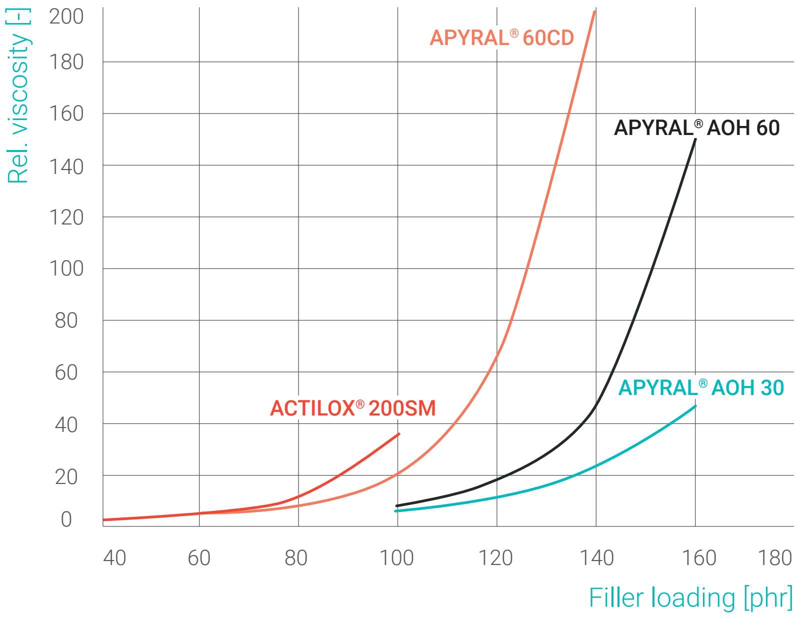
Among all the relevant metal hydrates, **APYRAL® AOH** has by far the highest acid resistance, as is shown by the results in the table on the right. This benefits all applications in which products are used in or near acid fluids (e.g. in the automotive sector, in the vicinity of batteries, etc.). Regarding PCB production, the high resistance to the usual etching techniques is already established. Nevertheless, no problems occur in the chemical throughhole deburring process („desmear“).

APYRAL® AOH - due to its amphoteric character (low alkalinity and acidity) – shows an excellent compatibility with epoxy resin.

Comparison of the resistance to battery acid (34 % H_2SO_4, D=1.25 g/cm³) at room temperature

Product	Chemical composition	Dissolved fraction [wt.-%]
APYRAL® AOH 30	AlOOH	0.2
APYRAL® 40CD	$Al(OH)_3$	8

Viscosity properties



Comparison of the viscosity increase of ***APYRAL®*** *and* ***APYRAL® AOH*** *grades in a UP resin at 23 °C (relative viscosity = viscosity ratio of resin with to resin without fillers; UP resin: Palapreg P17-02, Aliancys, initial viscosity approx. 1800 mPa*s, shear rate 10 1/s)*

APYRAL® AOH is, similary with aluminium hydroxide, compatible with practically all thermosetting resin systems.

Its excellent processing properties are especially advantageous for **APYRAL® AOH**. The morphological shape (orthorhombic crystalline structure) of our **APYRAL® AOH** grades results in very low viscosity increases in the resin start formulation. This is demonstrated in the illustration above, which shows the relative viscosity of the various **APYRAL® AOH** types and that of **APYRAL® 60CD**.

Due to the orthorhombic crystal habitus which is most distinct in **APYRAL® AOH 30**, this only medium-sized boehmite shows the best viscosity properties.

Comparison of the viscosity properties of **APYRAL® AOH 60** with aluminium hydroxide **APYRAL® 60CD**. These are two fillers with an almost identical fineness and BET surface area (both: 6 m²/g), clearly shows the viscosity advantages of **APYRAL® AOH** versus aluminium hydroxide.

Low-cost flame retardancy with APYRAL® AOH

APYRAL® AOH is utilized as co-flame retardant whenever the process temperature exeeds 200 °C or the long lasting temperature of the finished product does not allow the use of **APYRAL®** (aprox. > 125 - 150 °C).

As the flame retardant effectiveness of Boehmite is low compared to aluminium hydroxide (see brochure „Mineral flame retardancy with metal hydrates"), the Boehmite should be combined with other flame retardants.

It is recommended that other halogen-free flame retardants, e.g. those based on phosphorus and/or nitrogen are combined with the **APYRAL® AOH** to fulfill stringent flame retardancy classification, e.g. UL 94 V0. To this effect, the materials appearing in the below table can be used (examples).

APYRAL® AOH can be effectively combined with **APYRAL®** to exploit the synergistic flame retardancy effect of this combination. But the limitation of **APYRAL®** towards temperature stability and resin compatibility has to be considered in this approach, as well.

Due to its filler nature, considerable advantages in compounds can be achieved by the application of **APYRAL® AOH**, i.e:

- high temperature stability up to 340 °C
- increase of heat capacity and thermal conductivity
- reduction of the thermal expansion

Furthermore, by utilizing **APYRAL® AOH** the necessary amount of phosphorus organic flame retardants can be reduced. Simultaneously, the negative technical influence of organic phosphorus flame retardants on the finished product can be strongly reduced, i.e:

- decrease of migration effects
- reduction of water absorption
- decrease of corrosion features (smaller release and absorption of acid decomposition products of phosphorus organic flame retardant)
- stabilization of the glass transition temperature (T_g)
- reduction of brittleness

Different flame retardant resins or halogen free flame retardants that can be combined with ***APYRAL® AOH***

Type	Examples	Manufacturer
Inherently flame retardant resins	Phenol resins	diverse
	BT resins	Mitsubishi Gas Chemical
Additives	Metal phosphinates (i.e. DEPAL)	Clariant (Exolit® OP)
	Melamine polyphosphates	Budenheim, BASF
Flame retardant resins	DOPO-modified epoxy resins	DOW, NanYa
	Benzoxazine epoxy resins	Toto-Kasei, Huntsman
Hardeners with flame retardancy effect	ATN hardener	Dai Nippon Ink & Chemicals
	Oligomeric aryl phosphonates	ICL-IP (Fyrol® PMP)

Finally, Boehmite can reduce substantially the costs of the formulation. The tables on the right show formulation examples of flame retarded epoxy resin systems with a classification according to UL94 V0. Substantial quantities of expensive P-organic flame retardants can be replaced with **APYRAL® AOH**. Consequently, the application of boehmite makes considerable cost reductions possible.

An example for the excellent compatibility of **APYRAL® AOH** is the application together with the reactive P-organic flame retardant DOPO (see appendix A) in an epoxy novolak. In the example shown, the necessary quantity of DOPO could be reduced in around 39 %.

The compatibility with another halogen-free flame retardant metal phosphinate (DEPAL, Exolit® OP, Clariant) is visible in the following examples. Here, two epoxy resins based on bisphenol-A, with a higher flammability than the above-mentioned phenol novolak have been provided with a flame retardant mixture. In this case, relatively high loadings in the range of 60 - 69 % flame retardants are necessary. Indeed, the positive influence of the glass-fiber reinforcement on the ignitability is clearly visible.

Of course, combinations of different resins / hardeners and additives are also possible. Such combinations help formulators to optimize their epoxy resin formulation depending on the application in question. For example systems containing bismaleimidtriazine or cyanate ester are optimally suited for the production of low dielectric constants.

To summarize, the universal applicability of **APYRAL® AOH** in liquid resins provides users with new opportunities to optimize their products.

Required weight component in various halogen-free flame retardants in an epoxy novolak for classification in acc. with UL94 V0, the resulting glass transition temperatures (Resin: DOW DEN™438; Tg:180 °C, hardener: Dicyandiamide; accelerator: Fenuron; thickness: 4.0 mm; ***without glass fiber****)*

Flame retardant	Portion [wt.-%]	T_g (DSC) [°C]
DOPO-HQ	17.0	161
DOPO	11.2	158
DOPO + **APYRAL® AOH 30**	6.9 + 30.0	168

UL94V classification of an epoxy resin filled with ***APYRAL® AOH 30*** *and DEPAL (Exolit® OP 930) (DOW DER™330, DER™732, DEH™24,* ***without glass fiber***

Board thickness	APYRAL® AOH 30 [wt.-%]	DEPAL [wt.-%]	UL94
1.6 mm	64	5	V1
	59	10	V1
3.0 mm	59	10	V0
	0	25	V0

UL94V classification of an 8-layer laminate, based on an epoxy resin filled with ***APYRAL® AOH 30*** *and DEPAL (Exolit® OP 930) (DOW DER™663UE, DEH™81,* ***E-Glass*** *Hexcel® 7628)*

Laminate thickness	APYRAL® AOH 30 [wt.-%]	DEPAL [wt.-%]	UL94
1.8 mm	55	5	V1
	50	10	V1
2.9 mm	55	5	V0
	50	10	V0

Application processes and basic formulations for **APYRAL®**

Application processes and basic formulations for APYRAL®

APYRAL® products, especially the ground, morphologically modified and viscosity-optimized products, have proved themselves for many years in the production of flame retardant thermosets.

APYRAL® can be used in all common techniques of thermoset and composite production, no matter whether in hand lay-up, laminating processes, SMC, BMC, RTM or pultrusion.

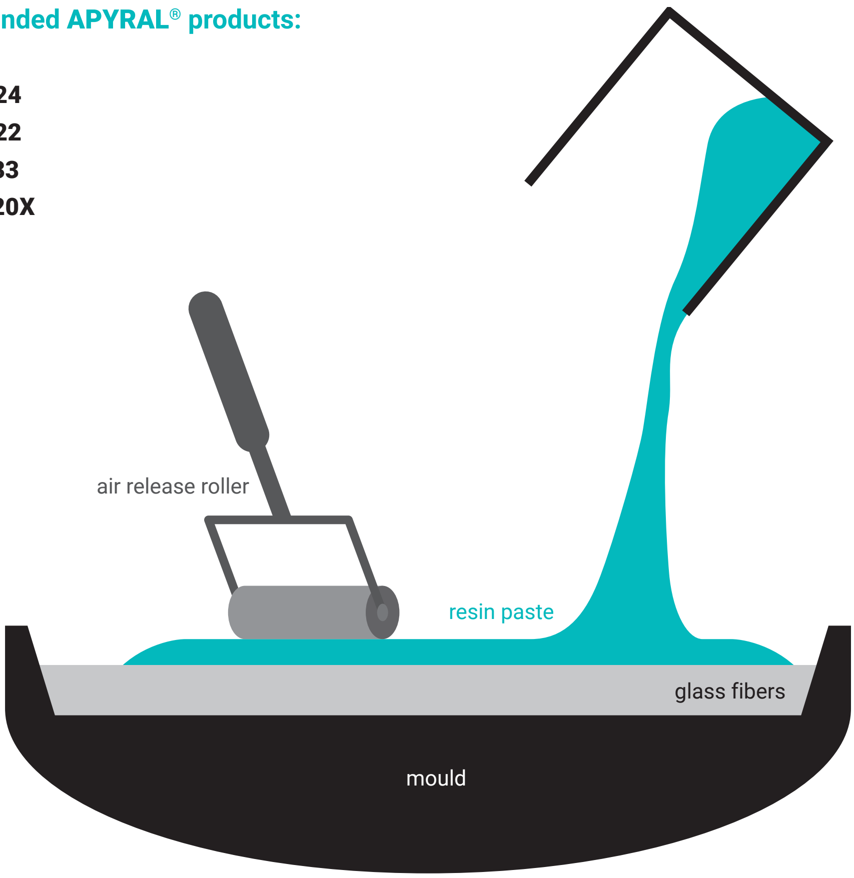
The commonly used resins are UP, EP, PUR, VE, acrylates, methacrylates and silicones.

The following chapters contain some reference formulations for various applications in terms of an example.

Hand lamination

Recommended APYRAL® products:

APYRAL® 24
APYRAL® 22
APYRAL® 33
APYRAL® 20X



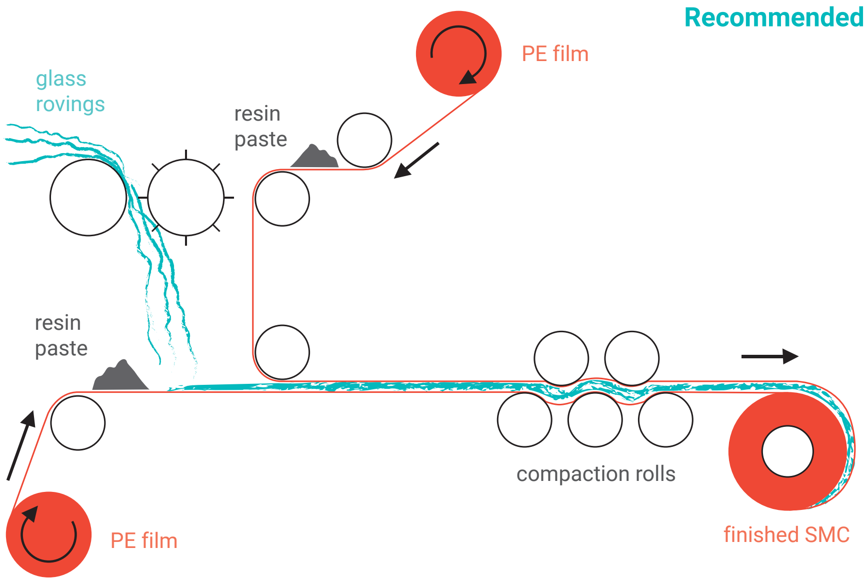
In this application, good processing properties and rapid venting by means of the manual roller are important. Thus, our viscosity-optimized **APYRAL®** grades have proved especially good for this application. They are used for example on a large scale in the field of plant engineering in wind power plants (rotor blades), in boat construction (hulls) and for the manufacture of components of passenger trains (wagon trim paneling, heads of train).

The tables below show two formulations based on UP resin in terms of example. The components manufactured from this material, incl. the applied gel coat, have passed the test in acc. with DIN 5510 S4.

Component	Trade name	Parts
UP resin	Palatal S340-01 KR	100
Aluminium hydroxide	**APYRAL® 22**	200
Viscosity (23 °C)	2.7	Pa*s
LOI [%]	52	O_2

Component	Trade name	Parts
UP resin	Palatal S340-01 KR	100
Aluminium hydroxide	**APYRAL® 33**	200
Viscosity (23 °C)	3.4	Pa*s
LOI [%]	55	O_2

SMC and BMC compounds



Recommended APYRAL® products:

SMC:
APYRAL® 8
APYRAL® 16
APYRAL® 22
APYRAL® 20X

BMC:
APYRAL® 8
APYRAL® 15
APYRAL® 22
APYRAL® 20X

APYRAL® products are used widely in the manufacture of moulding compounds in acc. with the SMC and BMC process. The compounds having the same name are almost exclusively based on UP resins and are used for the manufacture of halogen-free flame retardant, glass-fiber reinforced materials for the building, electrical engineering and automotive sectors.

If very smooth surfaces (Class A) are to be realized, the utilization of as-fine-as-possible grades such as **APYRAL® 22** or **APYRAL® 33** is recommended. If viscosity-optimized **APYRAL®** grades are used, very high loadings can be realized as shown in the formulation according to the table below.

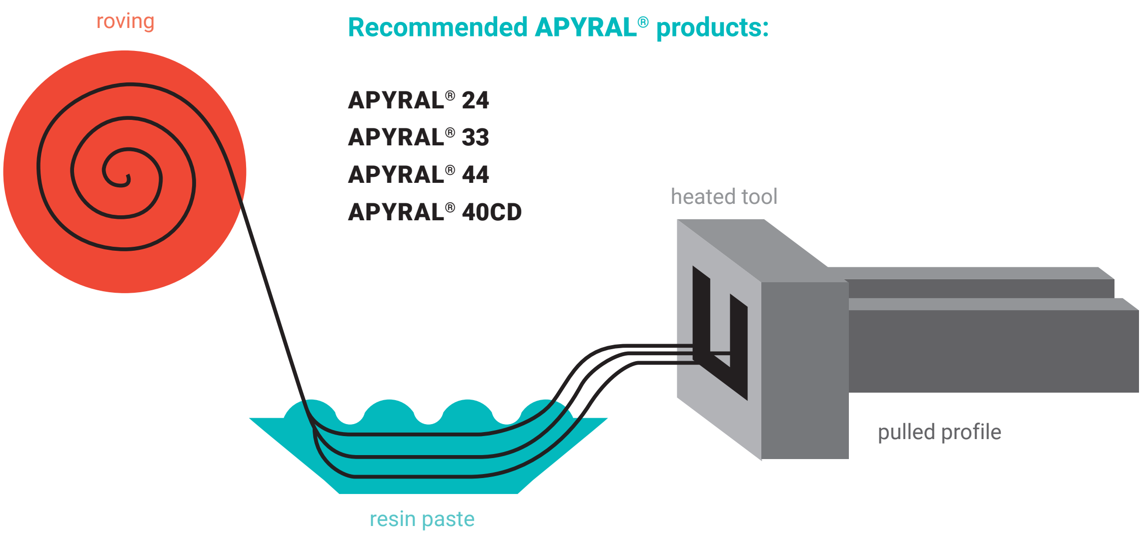
Example of a compound with a high filler loading for SMC applications

Component	Trade name	Parts	Properties	
UP resin	Palapreg P17-20	80.0		
UP resin	Palapreg H814-01	20.0	**Viscosity (30 °C)**	36 Pa*s
Styrene	not defined	5.0		
Dispersing additive	BYK-W 996	6.0	**GRP with 25 % glass fiber**	
Hardener (TBpB)	Trigonox C	1.5	Density [g/cm^3]	1.97
Inhibitor	p-Benzoquinone	0.3	Impact strength [kJ/m^2]	74
Demolding agent	Zn 101/6	4.0	Tensile strength [N/mm^2]	170
Thickener	Luvatol MK 35 nV	2.5	Flexural modulus [N/mm^2]	12300
Aluminium hydroxide	**APYRAL® 22**	320.0	LOI [% O_2]	82

Pultrusion

Recommended APYRAL® products:

APYRAL® 24
APYRAL® 33
APYRAL® 44
APYRAL® 40CD



The continuous process of pultrusion is increasingly used for the manufacture of flame retardant profiles. A glassfiber reinforcement is passed continuously through an impregnation bath; the composite material created is put into the required shape in a heated pulltruder head, and hardening started. Subsequent heating and cooling zones control the reaction rate. Due to the continuous process and the particular rheological conditions of pultrusion, the requirements to be satisfied by the impregnating compound and the resins, additives and fillers contained in it are especially high.

Modified methacrylic resins which in addition to a certain inherent flame retardancy have the advantage of very low initial viscosities have proved to be a very advantageous resin basis for filled systems which are produced following the pultrusion process.

The left table shows an example of a formulation based on PMMA containing. **APYRAL® 33** which, due to its optimized viscosity properties, has proved itself for the highly flame-protected profiles produced by the pultrusion process.This recipe satisfies the most important fire retardancy standards for the railway and building sector, such as the German DIN 5510 S4 and DIN 4102 B1 and the French classification M1 acc. to NF P92-501.

The second formulation based (right table) on an unsaturated polyester resin also fulfills these standards, however, in this case with a considerably higher loading. In any case, relatively fine **APYRAL®** grades are recommended to this effect, in order to prevent a filtration effect of the particles on the glass fibers.

Pultrusion compound based on PMMA resin

Component	Trade name	Parts
Modified PMMA in MMA	Modar 835S	100.0
Dispersing additive	BYK-W 996	3.0
Peroxide (TBpB)	Trigonox C	1.2
Demolding agent	Celec UN	1.0
Aluminium hydroxide	**APYRAL® 33**	150.0

Pultrusion compound based on UP resin

Component	Trade name	Parts
UP resin	Synolite 5001 T1	100.0
Dispersing additive	BYK-W 9010	3.0
Degassing agent	BYK-A 560	0.4
Wetting agent	BYK-9075	0.3
Peroxid (TBpB)	Trigonox C	1.5
Demolding agent	Celec UN	0.4
Aluminium hydroxide	**APYRAL® 33**	300.0

Cast resins on epoxy resin basis

Cast resins are often used in the electrical industry to encapsulate electrical components such as power supply units, transformers etc. in an epoxy resin. As in many electrical and electronic applications, a flame retardancy in acc. with the UL 94 standard (normally V0) is required. To this effect, loadings of at least 150 parts (related to the pure resin) are required. An example for this is indicated in the table below. However, considering the necessity of stoichiometric composition of resin and hardener for epoxy resins, and the fact that the phr value is only related to the A-component (pure epoxy resin without hardener), by varying the hardener type very different filler loadings may be necessary in the resin itself.

For example, utilizing cyclo-aliphatic polyamines as hardener loadings in the range around 180 parts of **APYRAL®** are necessary. These are characterised by a fast cold curing with the possibility of being able to reach high Tg values.

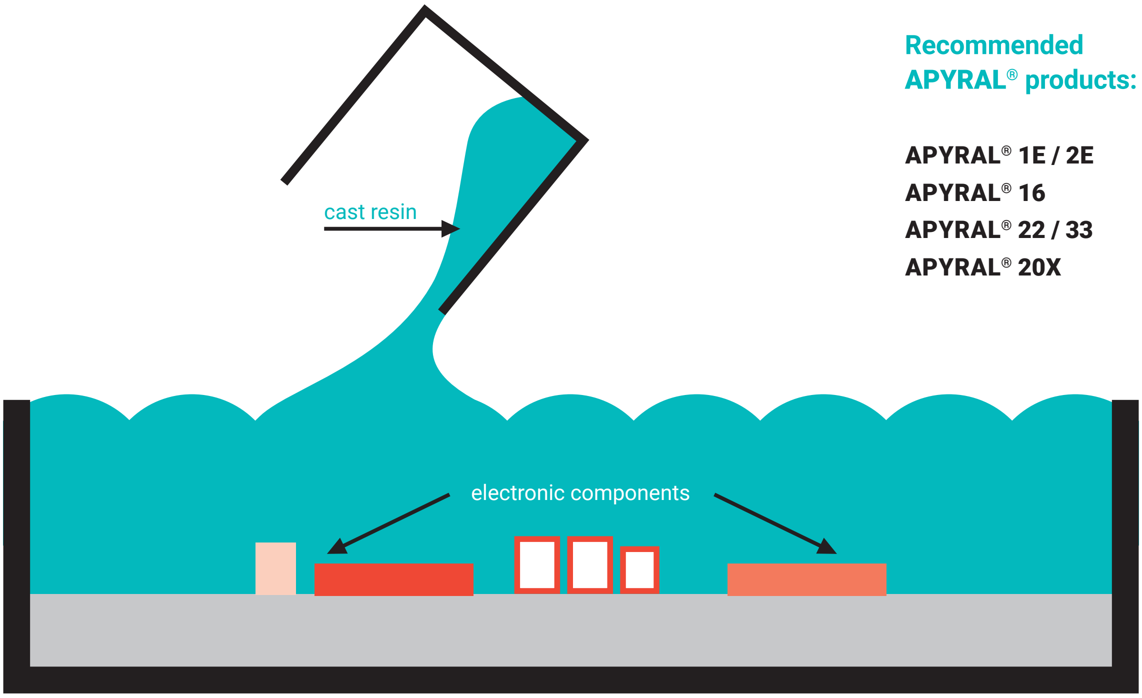
Alternatively, using anhydrides, loadings in the range around 250 parts of **APYRAL®** are necessary, which is easily achievable by viscosity-optimized **APYRAL®** grades. These types of hardeners will be used for hot curing.

However, in both cases the ATH content in the total formulation (epoxy + hardener) is on a similar level of about 57 wt.-% in total (similar like in the example given in the table).

Amine-hardened cast resin based on epoxy satisfies UL94 V0

Component	Trade name	Parts
Epoxy resin	Epikote 828	100.0
Amine hardener TETA*	–	13.5
Aluminium hydroxide	**APYRAL® 2E** **APYRAL® 33**	150.0

** Triethylentetramine*



Recommended APYRAL® products:

APYRAL® 1E / 2E
APYRAL® 16
APYRAL® 22 / 33
APYRAL® 20X

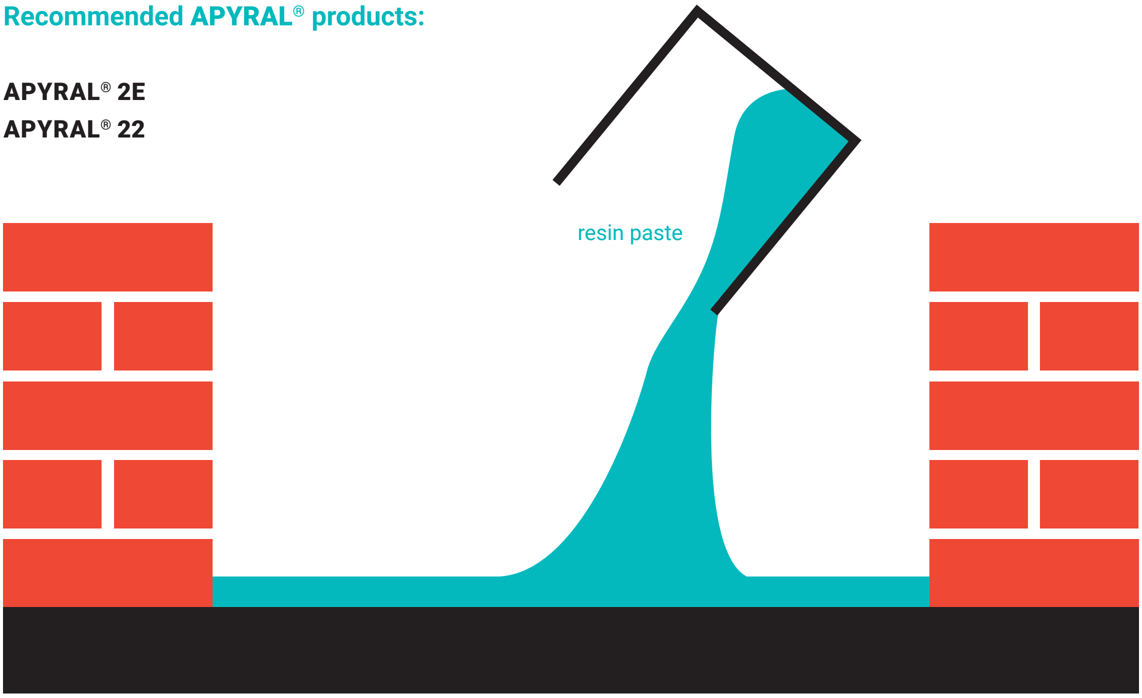
Epoxy resins for building applications

Epoxy resins are also used in building applications, such as floorings and adhesives.

For the flame retardant adjustment in acc. with the German construction standard DIN 4102 acc. to B1, 2 cases must be distinguished: amine-hardened systems require normally an **APYRAL®** content of 250 parts per 100 parts of resin, whereas anhydride-hardened systems usually require considerably higher loadings in the range of 300 parts. Two of such basic formulations are specified in the tables below as examples for this application (comp. p. 28).

Recommended APYRAL® products:

APYRAL® 2E
APYRAL® 22



Amine-hardened epoxy cast resin meets DIN 4102 acc. to B1

Component	Trade name	Parts
Epoxy resin	Epikote 828	100.0
Amine hardener TETA*	–	13.5
Aluminium hydroxide	**APYRAL® 2E** **APYRAL® 22**	250.0

**Triethylenetetramine*

Anhydride-hardened epoxy cast resin meets DIN 4102 acc. to B1

Component	Trade name	Parts
Epoxy resin	Epikote 828	100.0
Anhydride hardener MHPA* Accelerator BDMA**	–	85.0
Aluminium hydroxide	**APYRAL® 2E** **APYRAL® 22**	300.0

**Methyl hexahydrophthalic acid anhydride*
***Benzyldimethylamine*

Special applications in thermosets

Thermal conductivity of thermoset compounds

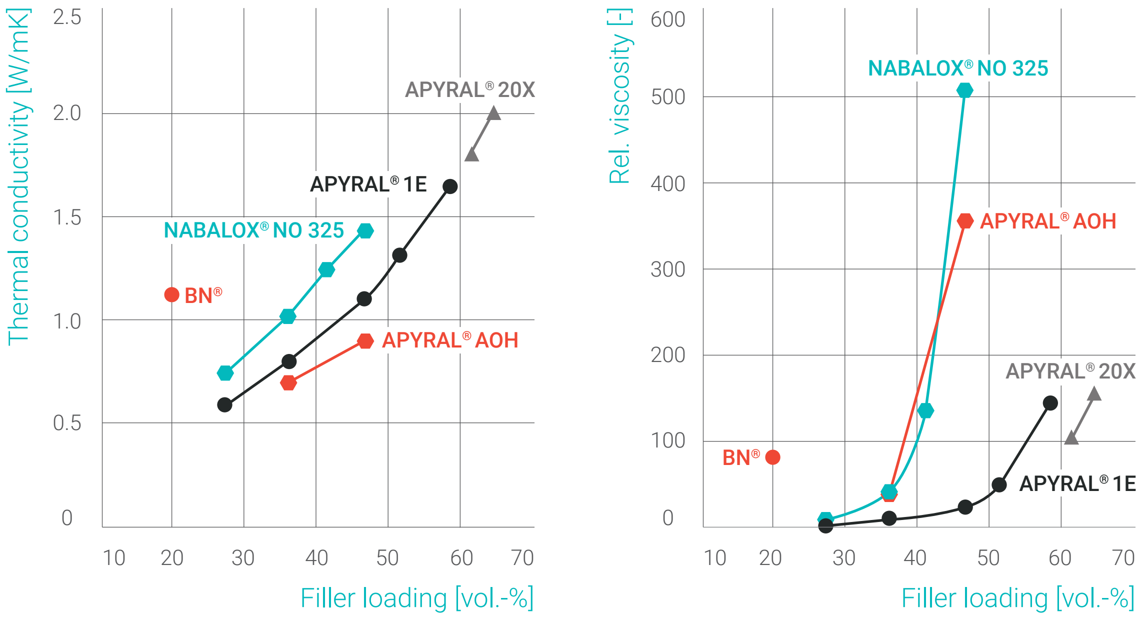
The efficient transfer of generated heat during operation always plays a crucial role in order to prevent material fatigue and loss of components, in particular within the field of E&E applications, for example in LED lighting, electronic parts and electric motors. In such applications thermal interface materials (TIM) and casting compounds with a high thermal conductivity (TC) are becoming more important.
The TC of thermally isolating thermoset materials (approx. 0.2 - 0.3 W/mK) has to be lifted by the addition of high quantities of thermally conductive fillers, such as graphite, hexagonal boron nitride (BN), silicon carbide (SiC) or aluminum nitride (AlN).
When utilizing graphite, not only the thermal but also the electrical conductivity is increased and this is often unwanted. In case of AlN, corrosion problems can occur by release of ammonia due to hydrolysis of the AlN. The abrasion of the extremely hard SiC limits its usage.
Utilizing BN, in fact a high thermal conductivity can be produced in the compound. However, due to its platy particle shape (similar to graphite) and the resulting parallel arrangement of the particles in the final product this usually leads to a strong anisotropic character of the resulting TC. Thus, the heat cannot be dissipated in all directions homogeneously, which must be considered in the final product design. Furthermore, the high cost in comparison to standard filler types make the industrial utilization of BN difficult.
Additionally, the platy BN produces a very high viscosity and exhibits a pronounced shear thinning effect. This makes the dispersion substantially more difficult and limits the maximum possible filler loadings. Hence, even with BN as a high performance filler the achievable TC is limited and hardly economically feasible.
In contrast, metal hydrates and aluminum oxide can be considered as economical alternatives. The table below shall demonstrate the advantages and disadvantages of each products to allow proper choice for each application.
It is important to emphasize that the properties of the resin will influence the final results strongly, as well.

Overview of Nabaltec grades for thermal conductivity

Property	APYRAL® 20X	NABALOX® HC 170	APYRAL® AOH	APYRAL® 20HC
Processability / Viscosity	++	++	-	++
Filler loading	++	+	-	++
Thermal conductivity	++	+	-	++
Abrasion	++	-	+	++
Cont. operation temperature	o	++	++	o
Fineness / Mechanical properties	-	+	+	-
Compatibility to MS / Silicon	++	++	++	+++

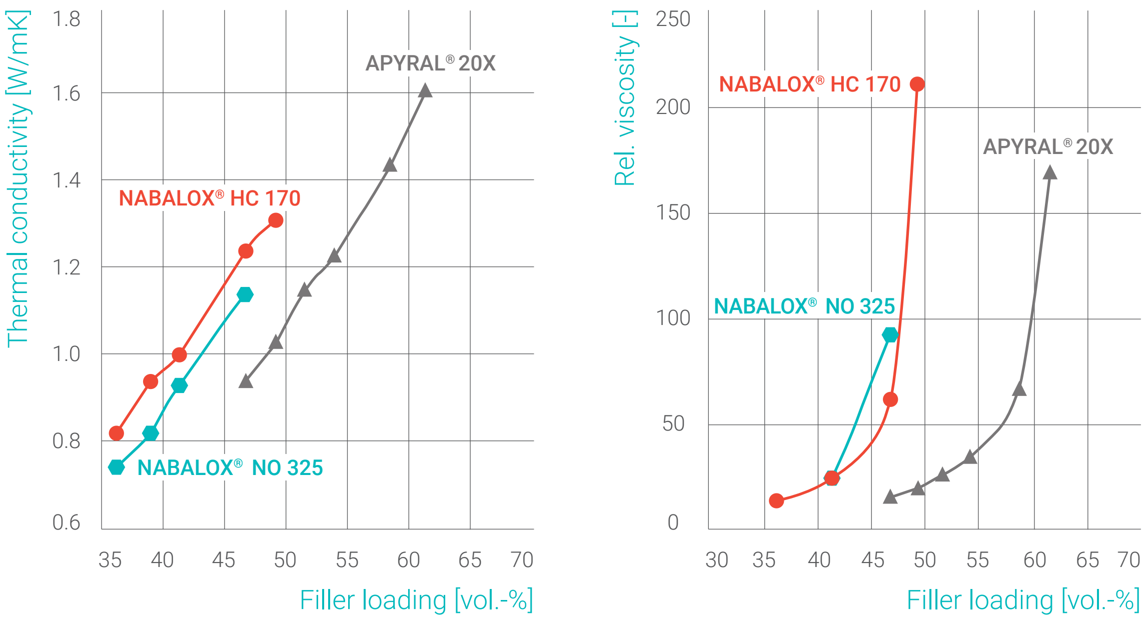
Despite the low intrinsic TC level of ATH, TC levels of up to 2 - 3 W/mK or higher can be obtained, e.g. in UP or EP, when very high loadings of viscosity optimized grades like **APYRAL® 20X** are utilized (comp. upper Graph on next page). This TC level is sufficient for many applications. However, because of the limited thermal stability of **APYRAL®** it cannot be used in all applications. In such cases aluminium oxide is preferable, e.g. **NABALOX® NO 325**.

- due to the better rheological characteristics of viscosity optimized **APYRAL®** grades, high volume filler loadings can be reached and thus final higher heat conductivity as with BN
- even the supposed more favorable aluminium oxide with its inherent higher heat conductivity can be outperformed, whereby with **APYRAL®** no abrasion has to be considered
- **APYRAL® 20HC** shows better wettability and pot life in extremely moister sensitive resins (e.g. MS polymer) and silicone



Comparison of the resulting heat conductivity and the viscosity of different fillers in an UP resin (Palatal P80-02, Alyancis; maximal possible filler loading of BN in this resin: 20 vol.-%; TC determined through the "Hot Disk method" on cured, polished test specimens)

- in comparison to stiff resins like UP (see above) or EP, lower TC levels in more flexible PUR are obtained
- optimized **NABALOX® HC 170** shows highest TC levels at lower filler loadings
- with viscosity optimized **APYRAL® 20X** higher filling and TC levels can be obtained (lower density of ATH)



Comparison of ***APYRAL® 20X*** *and* ***NABALOX®*** *grades; Left: resulting heat conductivity in cured PUR; right: corresponding viscosity increase in uncured polyol (Caradol®, Shell; TC determined through the Hot Disk method on cured, unpolished test specimens)*

As shown in the graph on the page before, in general, higher TC levels at the same volume filler loadings can be obtained with **NABALOX®** grades because of the higher intrinsic TC level of Aluminium Oxide. This may give more freedom to obtain formulations with improved mechanical properties in comparison to extremely highly filled compounds based on **APYRAL®**.

Due to its improved rheological characteristics in comparison to **NABALOX® NO 325** we recommend the use of our new optimized **NABALOX® HC 170**. It has a high intrinsic TC and best viscosity performance of all **NABALOX®** Grades, which allows the highest filler loadings for oxides. However, its viscosity level is still significantly higher than the one of **APYRAL® 20X** and the obtainable, maximum TC values may be lower.

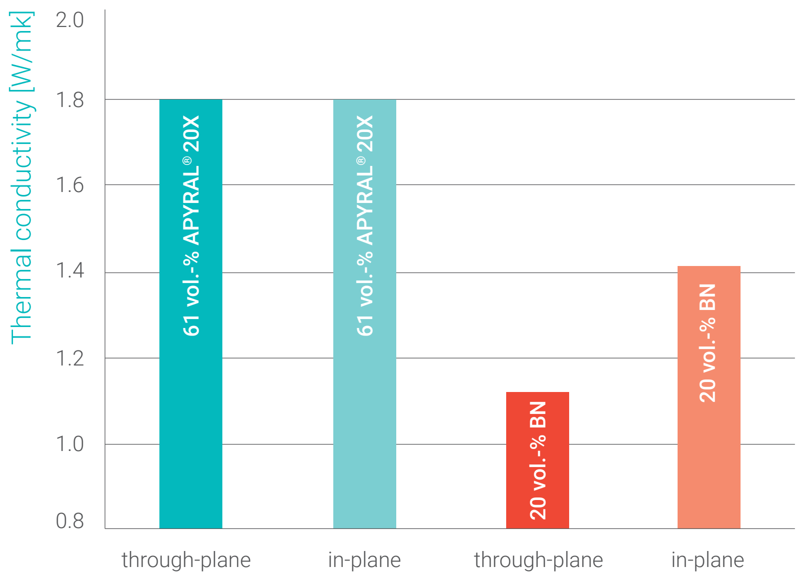
Naturally, **NABALOX®** does not exhibit any flame retardancy effect and due to its much higher hardness a higher abrasion on the tools (wear) has to be accounted for. On the other hand, no restriction of temperature has to be considered, as it is the case with **APYRAL®** (decomposition at 200 °C, long lasting usage < 125 - 150 °C).

Thus, **NABALOX®** grades are preferable especially when low filler loadings are decisive and / or high thermal stress resistance is required.

In case of higher thermal loads with demand for flame retardancy, the use of **APYRAL® AOH** is recommended (decomposition > 340 °C). Here the abrasion is on a similar low level as with **APYRAL®**.

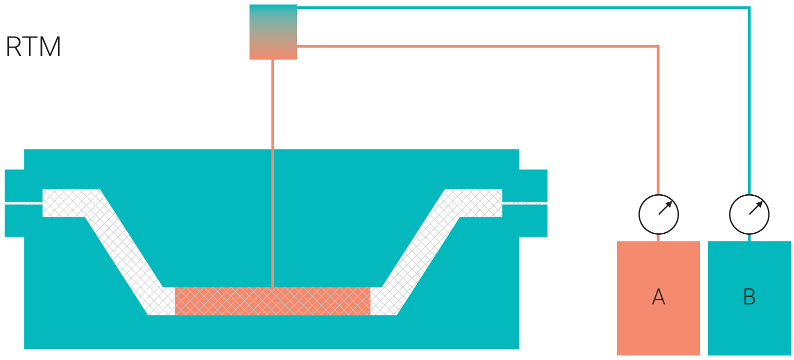
Anisotropy of thermal conductivity

Next to the better processability and a better cost efficiency the resulting TC of the final product does NOT show any anisotropic character if **APYRAL®** or **NABALOX®** is used, which is shown in the next illustration. Here no difference of the TC in-plane or through-plane is visible. This is due to the quasi-spherical crystal structure of **APYRAL®**. In contrary, in the case of the platy BN a substantial in-crease of the TC along the test specimens in comparison to the measurements across the test specimens exists. This occurs although the casting process should result only in a slight probability of orientation of the plates. In case of injection molded specimens this effect would probably be strongly pronounced, since the BN plates usually align in the direction of the melt flow.



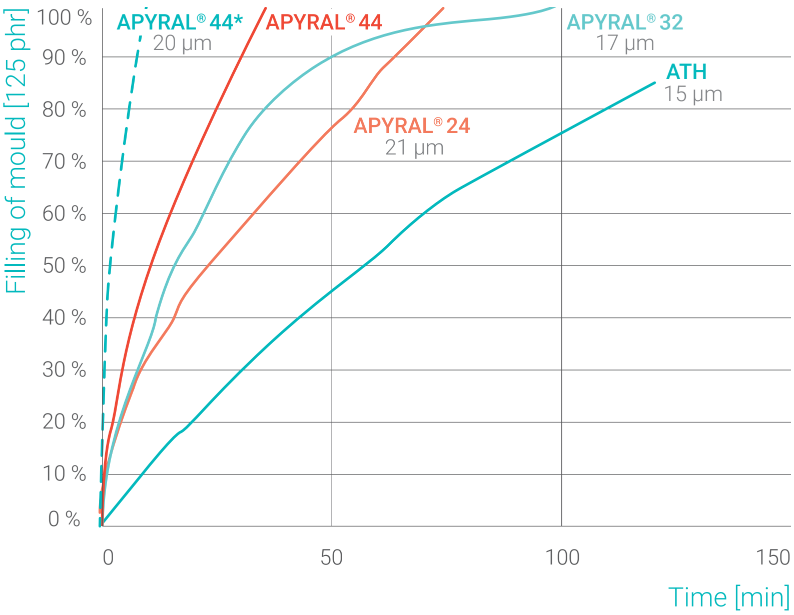
*Comparison of the resulting heat conductivity lengthwise and crosswise through an UP casting resin filled with **APYRAL® 20X** or BN (UP resin: Palatal P80-02, Alyancis)*

Application of APYRAL® 44 in RTM



Sketch of the resin transfer molding process where a resin mixture is filled into a closed mold containing the reinforcing material

The injection technology (RTM, Resin Transfer Moulding) continues to gain more and more significance due to it being a closed process resulting in the elimination of solvent emissions. **APYRAL® 44** is a grade with a distinctive high fineness and at the same time a good fluidity, which was optimized for the high requirements in the RTM process. The difficulty in this process consists of the fact that reinforcing materials are placed within a closed form. This may be a fiber reinforcement (glass, carbon, natural fiber, etc.) in the form of a roving, a fleece or a fabric. Cores with open cellular foam structure are also used. Resin is injected into this form which is filled by means of pressure or by application of vacuum. The form must be completely filled as fast as possible, free of bubbles or voids and with homogeneous distribution of resin and fillers. The reinforcing material acts as a substantial resistance against the resin flow (depending on the density with different reinforcements). A creeping separation of resin and filler (filtration effect) can occur, which can result in inhomogeneous filler distribution with corresponding negative effects on the mechanical characteristics and flame retardancy of the fiber reinforced plastic part. In the worst case a complete



*Filling times of the mold after vaccum infusion in Palatal P80-02, Aliancys (initial viscosity ~ 900 mPa*s) except **APYRAL® 44*** in Polylite 680-191, Reichhold (initial viscosity ~ 90 mPa*s); (Fiber content approx. 25 vol.-% of the mould; mould dimension: L x W x H = 94 x 6 x 0.5 cm; D90-values of the used fillers are indicated)* separation and blockade of the mold may occur. Hence, in this closed mold process a high fluidity (short cycle times) is required but at the same time a high fineness of the filler is desired - normally two diametrically opposite characteristics. **APYRAL® 44** with its optimized particle size distribution shows a very good injection ability in RTM experiments and thereby exceeds coarser products like **APYRAL® 24**, see figures above. In combination with ultra low viscosity resins very short injection times can be realized (see **APYRAL® 44*** in the photos below).

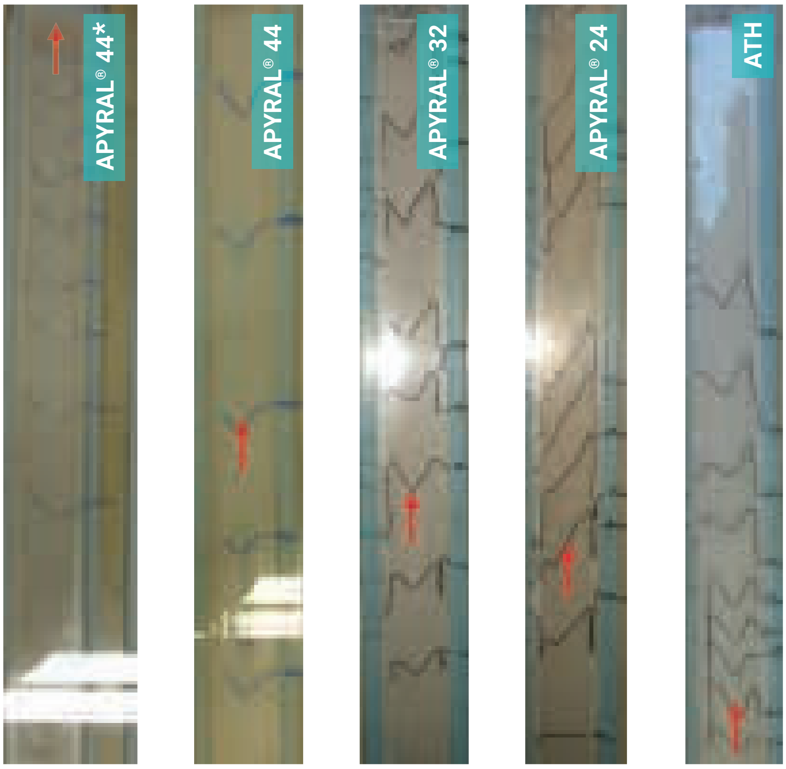


*Photo of the mould after vaccum infusion in Palatal P80-02, Aliancys (initial viscosity ~ 900 mPa*s) except "**APYRAL® 44***" in Polylite 680-191, Reichhold (initial viscosity ~90 mPa*s); (Fiber content approx. 25 vol.-% of the mold; mold dimension: L x W x H = 94 x 6 x 0.5 cm)*

Combination of APYRAL® with ammonium polyphosphate (APP)

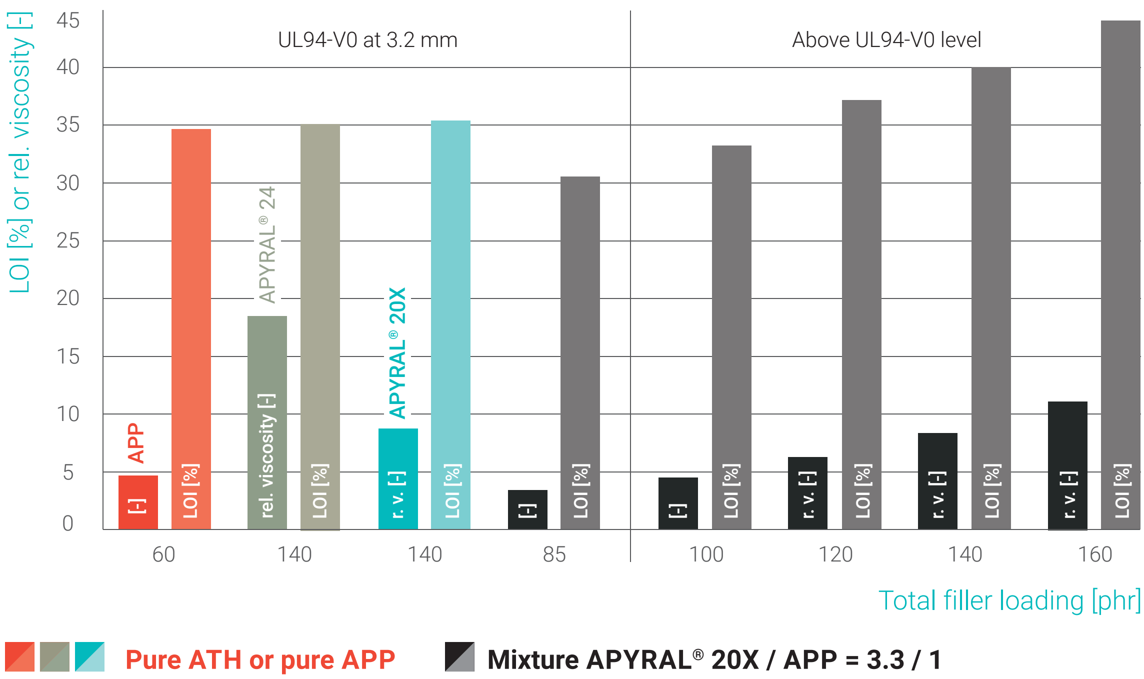
While in many cases the required flame retardancy characteristics can be realized exclusively by the use of **APYRAL®**, there are situations where its application is limited. In some cases the necessary flame protection cannot be achieved even with high quantities of the required **APYRAL®**, for example: with extremely high flame protection requirements, thin components or high portion of inflammable natural fiber reinforcement. The viscosity or the mechanical characteristics of the final products can be affected strongly with very high filler loadings. Thus, if the filler loading on **APYRAL®** is limited, one often uses alternative halogen-free flame retardants such as ammonium polyphosphate (APP). Due to their higher price these alternative flame retardants will clearly generate higher costs of the final products. In such a case the combination of **APYRAL®** (or **APYRAL® AOH**) with APP is recommended in order to be able to obtain both low filler loadings and higher flame protection characteristics, without a disproportionate rise in costs. This approach is demonstrated by an example with **APYRAL®**, which is outlined in the following section and on the illustration.

In a first test the minimum necessary filler loading for an UL94 V0 classification in an UP resin was realized by 2 systems, firstly with **APYRAL® 24** or **APYRAL® 20X** and secondly with APP (left side of graph). With APP a UL94 V0 classification was given at only 60 phr but with the **APYRAL®** grades a higher filler loading at 140 phr was necessary. In addition the relative viscosity and the resulting limiting oxygen index (LOI) of these formulations were determined. The resulting viscosity of the APP system was significantly lower at this filler loading than the **APYRAL®** system, even using the viscosity optimized **APYRAL® 20X**.

Next the optimal mixing proportion for **APYRAL®** with APP was determined. For reasons of cost optimization, the maximum possible quantity of **APYRAL®** was tried to be applied and the quantity of APP was tried to be kept as small as possible. The optimal ratio was determined to be 3.3 : 1 (UL94 V0 with 65 phr for **APYRAL® 20X** in combination with 20 phr of APP). In addition, other mixtures with higher APP content would be also feasible but would result in higher cost. The mixture of APP with **APYRAL® 20X** showed a significantly lower viscosity than the formulation using only APP. Due to the change of the flame protection mechanisms a lower LOI value resulted in the case of the combination of **APYRAL®** and APP. However it exhibited identical flame retardancy classification according to UL94 V0, which proves again that a direct correlation of the two flame tests is not possible.

This mixing ratio of 3.3 : 1 was now used, in order to achieve higher total filler loadings for higher flame retardancy standards (right side of graph). The latter was simulated by the LOI test, which consequently rose in relation to the original filler loading at 85 phr.

We emphasize that all formulations shown here, whether with **APYRAL®** alone or in combination with APP, are commercially more attractive than the formulation using only APP.



The resulting relative viscosity (left columns) and the limiting oxygen index (right columns) with the use of APP (Exolit® AP 422) or ATH as pure material or rather in case of a combination in an UP resin (Palatal - P80-02, Aliancys). All the shown formulations fulfill the UL94 V0 norm (with 3.2 mm).

Annex

Annex

List of abbreviations

Abbreviation	Meaning
BET	specific surface area according to Brunauer, Emmett, Teller
BMI	bismaleimide resin
BT	bismaleidtriazine resin
CTE	coefficient of thermal expansion
DGEBA	bisphenole A epoxy resin (diglycidyl ether of bisphenol A)
DOPO	dihydro-oxa-phosphaphenanthrene-oxide
DOPO-HQ	hydroquinone adduct of DOPO
EP	epoxy resin
LOI	limiting oxygen index (see brochure "mineral based flame retardancy with metal hydrates")
phr	parts per hundred parts of resin
PUR	polyurethane resin
TC	thermal conductivity
UL 94 V	vertical burning test according to UL 94 (Underwriter Laboratory)
UP	unsaturated polyester resin
VE	vinyl ester resin
VOC	volatile organic compounds

Products specified in the formulations

Product	Manufacturer
BYK-9075	BYK
BYK-A 560	BYK
BYK-W 996	BYK
BYK-W 9010	BYK
Celec UN	Akzo
DEH 24	DOW
DEH 81	DOW
DEN 438	DOW
DER 330	DOW
DER 663UE	DOW
DER 732	DOW
Epikote 828	Momentive

Product	Manufacturer
Exolit AP 422	Clariant
Exolit OP 930	Clariant
Hexcel 7628	Hexcel
Luvatol MK 35 nV	Lehmann & Voss
Modar 835S	Ashland
Palapreg H814-01	Aliancys
Palapreg P17-02	Aliancys
Palatal P80-02	Aliancys
Palatal S340-01-KR	Aliancys
Polylite 680-191	Reichhold
Synolite 5001 T1	Aliancys
Trigonox C	Akzo
Zn 101/6	Greven

List of references

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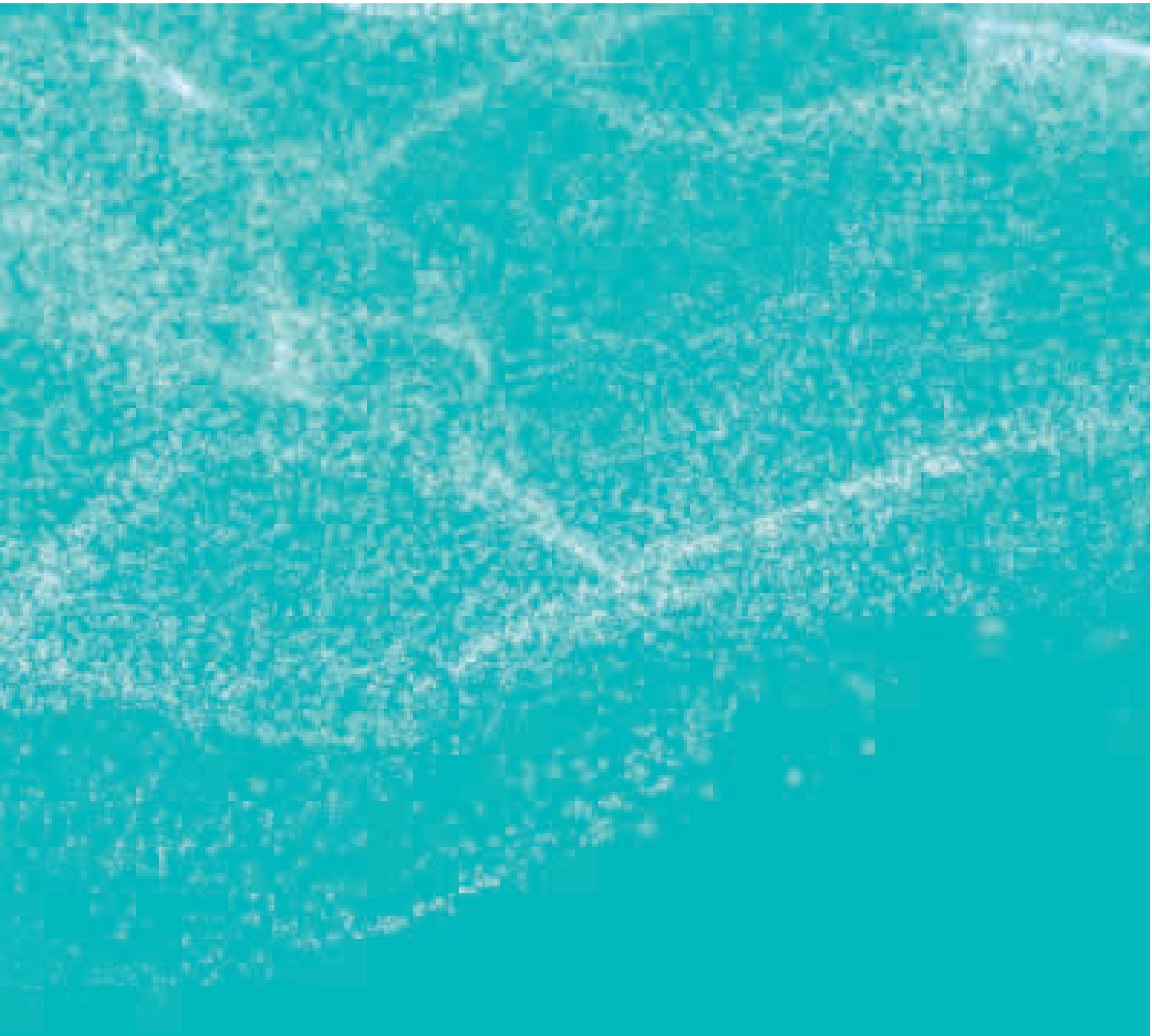
[2]	Brochure "Tipps and Tricks mit Joe Flow – Joe Flow steht Rede und Antwort", Anton Paar GmbH
[3]	Jutta Gehm, Brochure "Viskositätsmessung kosmetischer Produkte", proRheo GmbH http://www.prorheo.de/fileadmin/user_upload/pdfs/Viskositaetsmessung_kosmetischer_Produkte.pdf



Service for our customers

Service
for our customers

Technical service development / production

Nabaltec AG develops new products and refines innovative products in close cooperation with our customers and raw material suppliers.

Here we use our own lab facilities as well as our excellent contacts to external test institutes and laboratories to offer our customers a wide range of service to support them in formulation development and test procedures.

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Nabaltec
product portfolio

NABALOX®

Aluminium oxides, for the production of ceramic, refractory and polishing products

APYRAL®

Aluminium hydroxides, as flame retardant and functional filler

APYRAL® AOH

Boehmite, as flame retardant filler and functional filler

GRANALOX®

Ceramic bodies, for the production of engineering ceramics

NABACAST®

Hydraulic, cement-free binder, based on α-alumina

SYMULOX®

Synthetic sintered Mullite, for the production of e.g. refractory products

ACTILOX®

Boehmite, as flame retardant filler and catalyst carrier

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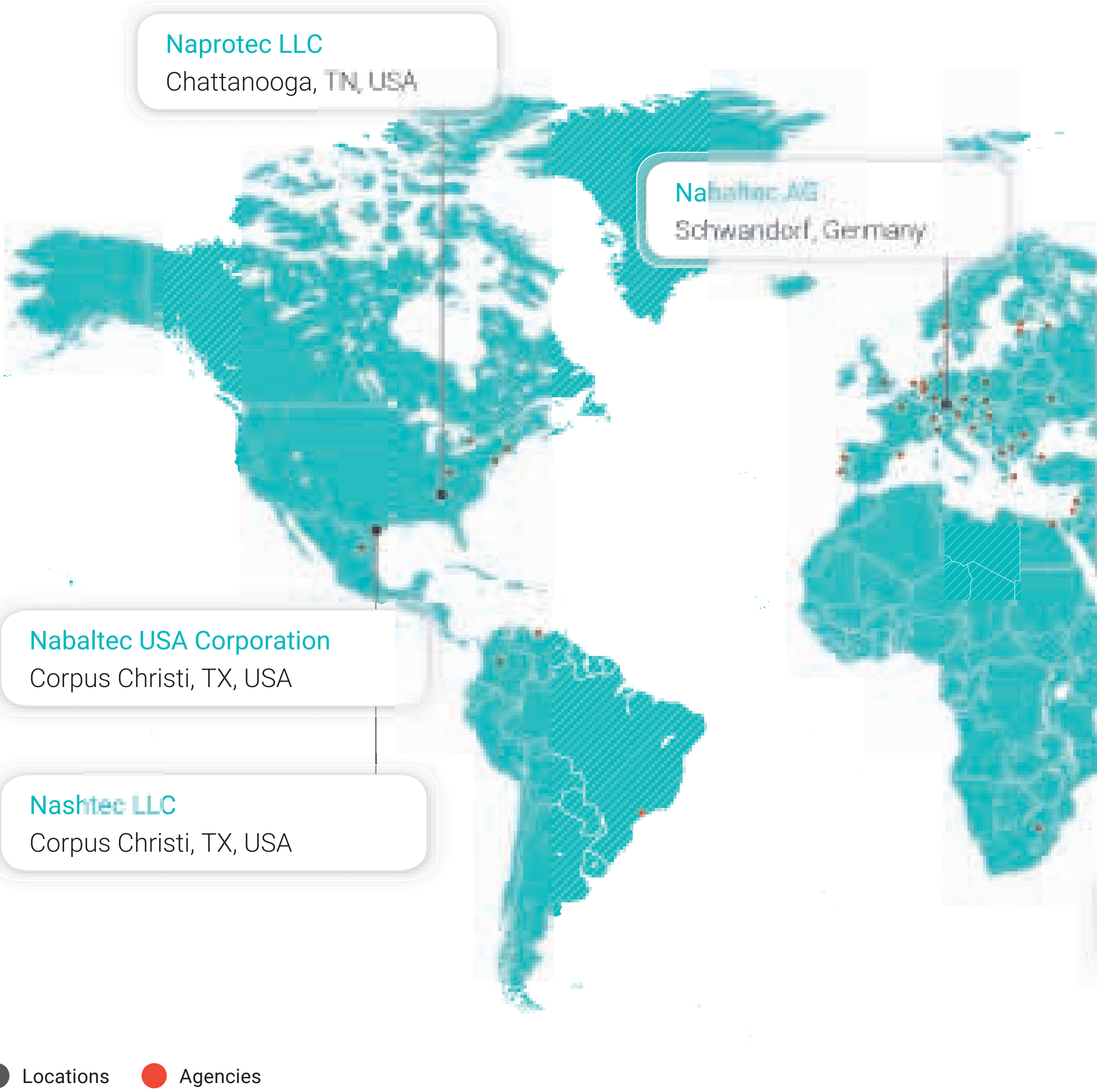

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All data listed in this brochure are reference values and subject to production tolerance. These values are exclusive to the product description and no guarantee is placed on the properties. It remains the responsibility of the users to test the suitability of the product for their application.

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