Mineral filler solutions

for E-Mobility

Nabaltec

Mineral Fillers used for E-Mobility

Product	D50* [µm]	D90* [µm]	BET [m^2/g]	Oil absorption [ml/100 g]	Thermal conductivity [W/mk]	Specific gravity [g/cm^3]	Mohs hardness
APYRAL® HC – optimized aluminium hydroxide for thermal conductivity							
APYRAL® HC 500	30	110	1.2	11	~20	2.4	3
APYRAL® HC 600	20	66	1.5	12			
APYRAL® HC 700	20	55	1.8	13			
APYRAL® HC 800	5	23	2.5	16			
APYRAL® HC – surface coated grades							
APYRAL® HC 501P	30	110	0.5	–	~20	2.4	3
APYRAL® HC 502H	30	110	1.2	–			
APYRAL® HC 503H	30	110	1.5	10			
ACTILOX® HTB – ACTILOX® for high temperature barrier							
ACTILOX® HTB PA	under development						
ACTILOX® HTB PP	under development						
ACTILOX® HTB UP	under development						
APYRAL® AOH / ACTILOX® – boehmite for LIBS & electrode edge coating							
APYRAL® AOH 30	2.2	4	3.2	28	n. d.**	3	3 - 4
APYRAL® AOH 60	0.7	1.4	5	30			
APYRAL® AOH 70	0.5	0.8	7.5	31			
ACTILOX® 200 SM	0.3	0.6	18	36			

*Laser diffraction, Microtrac S3500
**not defined

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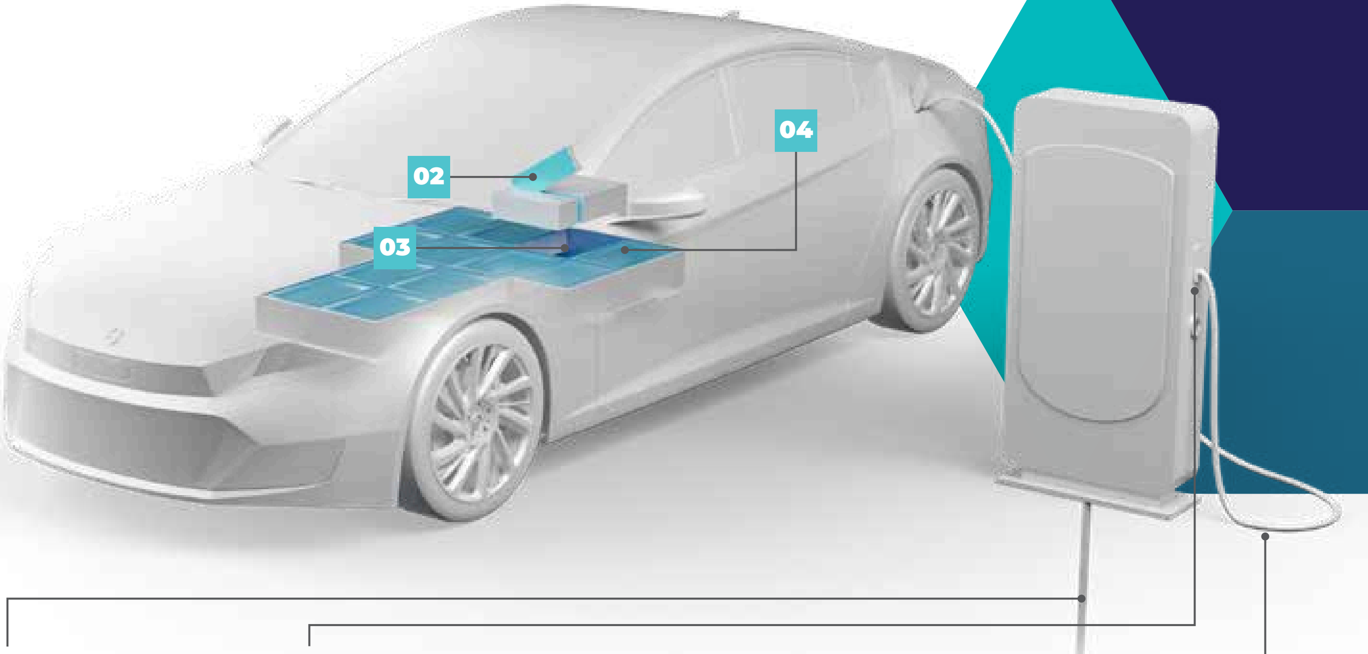


Flame retardants for engineering plastics
ACTILOX®,
ACTILOX® B

Metal hydrates for thermosets
APYRAL®,
APYRAL® AOH

Metal hydrates for cables
APYRAL®,
ACTILOX® B

Preamble

The storage of electrical energy is a major challenge when it comes to implementing national and international energy policy goals. Without effective storage technology, the energy transition toward carbon neutrality would not be realizable. The Lithium ion battery (LIB) has a prominent position in this context due to its power and energy density. LIB technology is of central importance for the growth of electromobility and the progressive development of stationary storage for renewable energies worldwide.

Nabaltec AG supports these developments in the battery industry with aluminium hydroxide (**APYRAL**®), aluminium oxides (**NABALOX**®) and boehmite **APYRAL**® **AOH** product family. Thanks to the close cooperation between Nabaltec and key customers, a large number of innovative products tailored to the respective application have been developed. By increasing product safety while reducing overall costs at the same time, Nabaltec is making an active contribution to the breakthrough of Lithium ion battery technology in safety-relevant application areas.

Thermal Runaway – a most discussed safety issue

Thermal runaway is the uncontrolled generation of heat within the battery. Thermal runaway specifically in Li ion battery often leads to a total failure of battery with devastating consequences, an overview is shown in figure 1.

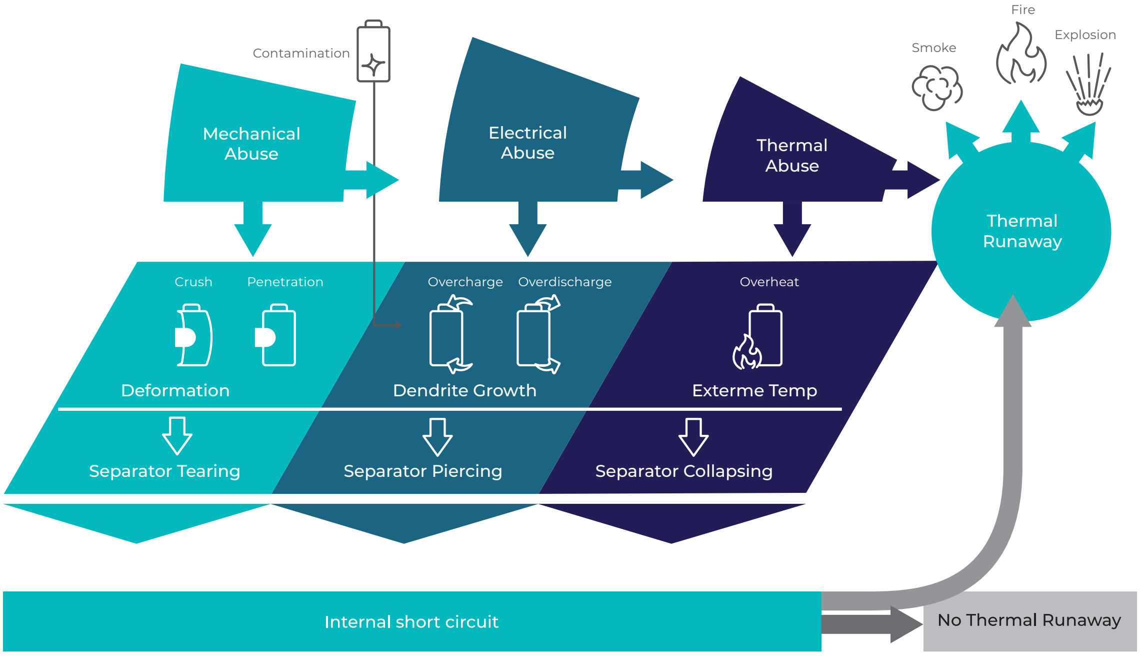


Figure 1: Abuse conditions leading to thermal runaway.

After: Feng, X.; Ouyang, M.; Liu, X.; Lu, L.; Xia, Y.; He, X. Thermal runaway mechanism of lithium ion battery for electric vehicles: A review. Energy Storage Mater. 2018,10, 246–267. [CrossRef].

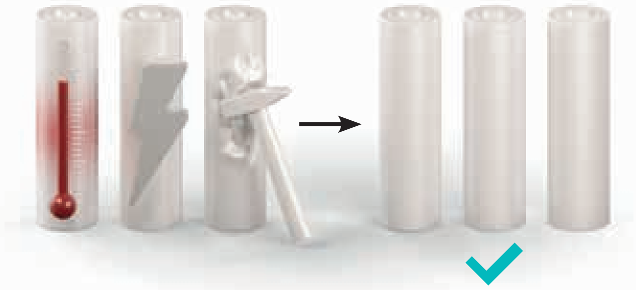
The most common cause of a thermal runaway is failure of the separator. In this brochure we will show how Nabaltec's products enable longevity and safety of LIB, by strengthening the separator against failure, protecting the electrodes, and by conducting heat out of the battery packs.

Nabaltec's product portfolio for LIB safety is completed by designated functional filler blends preventing heat propagation on LIB pack level.

Inside cell

APYRAL® AOH, ACTILOX®

- Boehmite for LIB separator coating
- Boehmite for LIB electrode edge coating

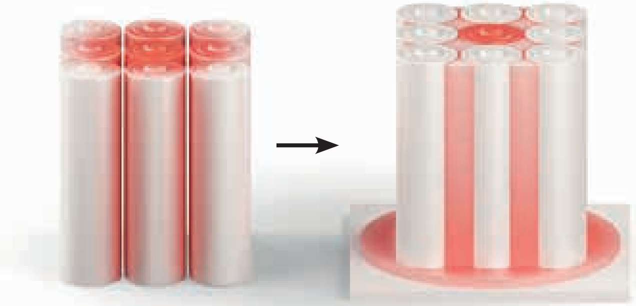


Prevention of short circuit

Inside battery

APYRAL® HC

- Aluminium hydrates for high thermal conductive gap filler/ adhesive and sealant



Prevention of thermal overload

Battery casing

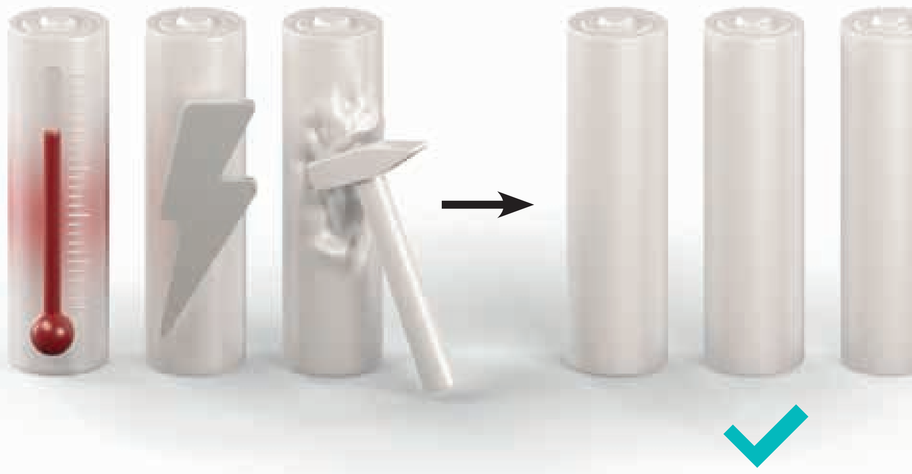
ACTILOX® HTB

- High temperature barrier functional fillers in battery covers

Prevention of fire propagation

Inside cell

LIB separator coating



- **General explanation of the LIB separator coating**

Each battery cell is built up in several different layers. The energy source is hidden in these layers. A porous separator acts as an electrically isolating layer between the positively charged cathode and its negative counterpart the anode but allows the free move of Lithium ions (s. figure 2).

However, if there is an overload or an external short circuit within the system or thermal stress the plain polypropylene (PP), or polyethylene (PE) based separator in former generation without protection coating will shrink due to the sudden heat development. At some points the direct contact between the cathode and the anode will happen. This results in an internal short circuit and continuous in a thermal runaway in the battery. The entire system starts to burn or may even explode.

Such failure can be prevented by an inorganic ceramic coating applied on the separator. Boehmite has become the preferred material for such coatings.

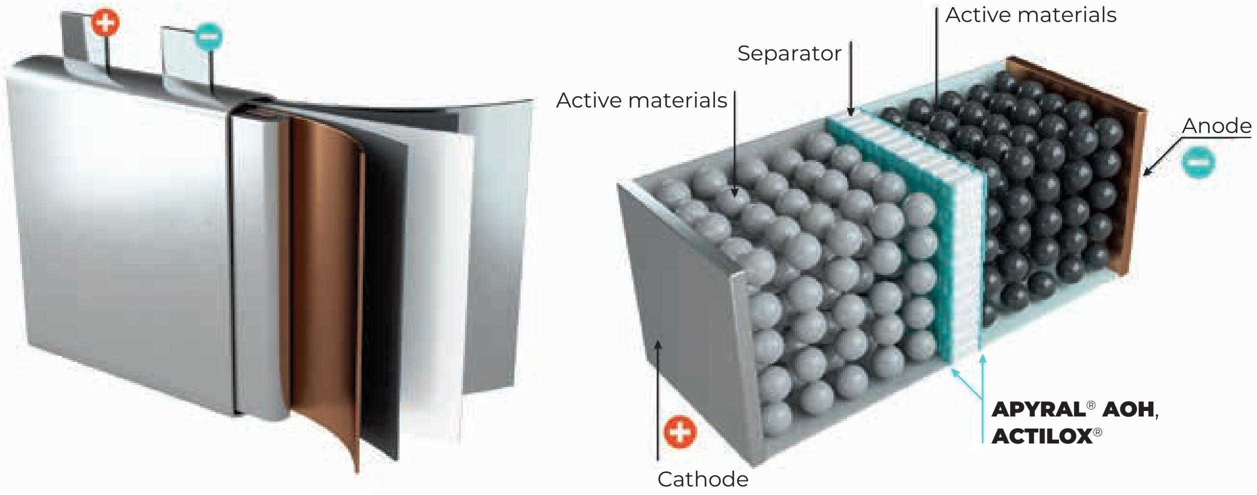


Figure 2: Three-dimensional structure illustration of a Lithium ion battery cell.

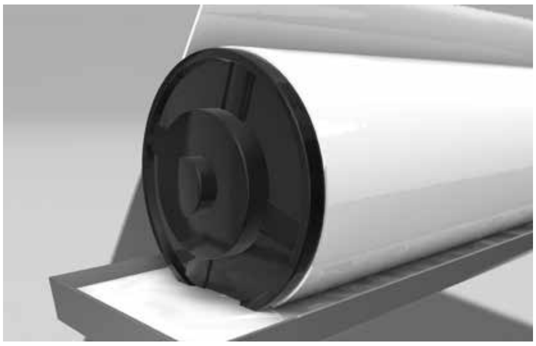


Figure 3: A gravure roller coating sytem in which the boehmite dispesion is applied on a separator.

Boehmite is produced by hydrothermal conversion of aluminium hydroxide (ATH). Nabaltec's boehmite products **APYRAL® AOH**, **ACTILOX®** are extremely pure crystalline boehmites with a very low ATH and electrolyte residue (purity min. 99 %). This guarantees an extraordinary high temperature stability up to 340 °C. Additionally boehmites have a very good chemical resistance (s. figure 3).

The white boehmite powders are processed into a dispersion which is applied to the separator either on one side or on both sides, e.g. by using of a gravure roller coating or slot die system.

The separator coated in this way gains heat-resistance and prevents shrinkage of the polymer membrane. It is crucial that the coating is still permeable and has a high porosity. Thanks to this ceramic coating the separator can withstand a temperature of up to 250 °C, depending on the substrate. In comparison, untreated separators already shrink at around 90 °C. Additionally the coated separator is reinforced against dangerous dendrites which may form during charge-discharge cycles and pierce the non-coated separator causing short circuit by contacting the cathode.

The heat stable coating with **APYRAL® AOH**, **ACTILOX®** makes the battery much safer and more resistant to short-circuit reactions and prevents possible fires and explosion.

- **Advantage of boehmite over high pure alumina (HPA) and low soda aluminium oxide**

Due to the increasing energy density of Lithium ion batteries, the use of safe separators with ceramic coatings is becoming more and more important.

High pure alumina (HPA) was developed as a first-generation commercial solution at the beginning of the 2010 decade. However, prices of HPA did not allow ceramic coating technology to leave the status of a niche product.

HPA was therefore quickly replaced by the second generation based on low soda aluminium oxide.

As a new coating material for the third generation, boehmite has the strongest growth rate. Technically boehmite is characterized by the following advantages:

- high chemical purity
- narrow particle size distribution
- uniform morphology
- good dispersibility
- low moisture content
- low hardness compared to alumina
- moderate physical density

Important powder parameters of boehmite & low soda aluminium oxide and application benefits of **APYRAL® AOH.**

Materials	Mohs hardness	Density [g/m^2]	BET [m^2/g]	Na$_2$O$_{total}$ [%]	Na$_2$OH$_2$O$_{-soluble}$ [%]
α-Al$_2$O$_3$ typical commercial grade	9	3.9	6.3	0.037	0.036
APYRAL® AOH 60	3 - 4	3.0	5	0.020	0.002
	reduced abriasion and total weight		reduced moisture uptake		

In comparison to alumina, the powder parameters shown in table above (light gray backgrounds) result in the following benefits of the LIB-Separator coating:

Reduced abrasion

Aluminium oxide is one of the hardest materials with a value of around 9 on the Mohs hardness scale. In contrast, boehmite with a Mohs hardness of 3 - 4 is a rather soft mineral. This difference is clearly noticeable in the abrasiveness of the slurry during preparation and coating process. Finally, the ceramic separators itself are less abrasive, making coiling and further processing easier.

Reduced moisture uptake

Because of its moderate surface area according to BET when comparing with alumina of similar fineness, and it's very low level of water-soluble soda, boehmite shows low water uptake. Consequently, separators coated with **APYRAL® AOH** have a very low moisture uptake.

Lower Density

Furthermore, the lower density of **APYRAL® AOH** enable separator with lower specific weight and cells with higher energy density.

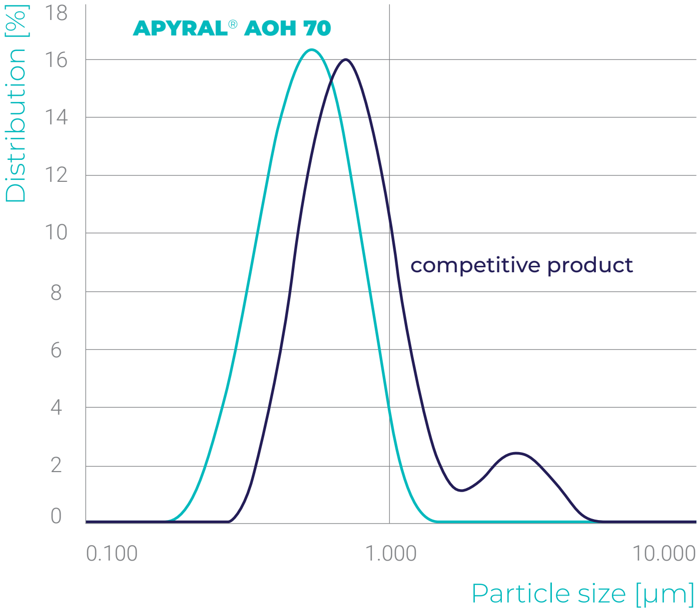
Tailor-made particle size distribution (PSD)

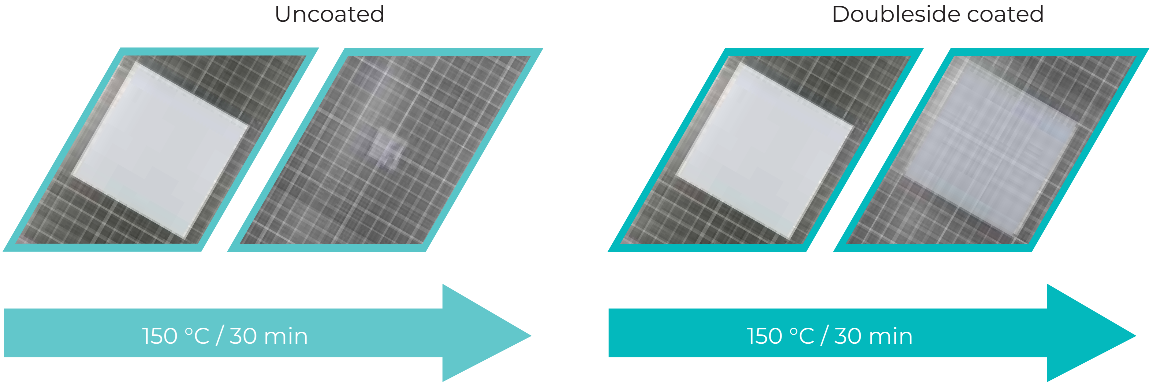
Last but not least, the most important parameter in powder production and application is the tailor-made PSD. Less coarse particle and an excellent Top Cut serves not only a perfect appearance of coating layer but also avoid defect structure or inconsistent thickness of coating layer. Special matched PSD offered the best performance in different coating formulation in particular in terms of anti-heat shrinkage and ion permability. Following example shows application data, see the following page (9).

Water based test formulation:

Wet type PE separator
0.5 % - 1.5 % Dispersant
1 % - 2 % Wetting agent
2 % - 5 % Binder system
Dosage based on boehmite content

No milling!



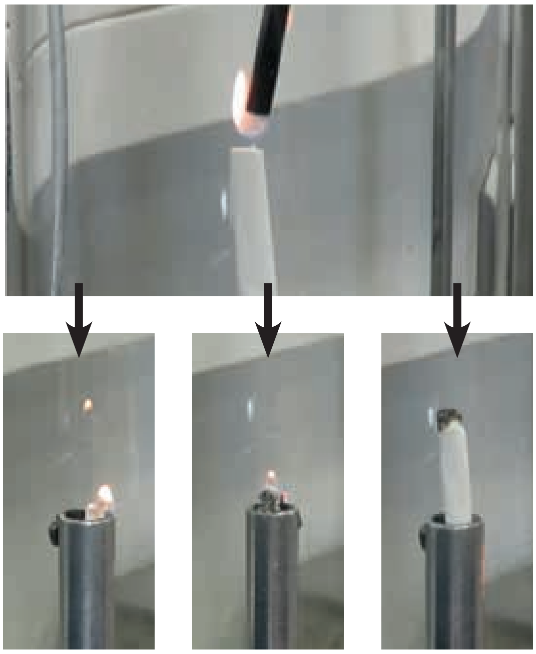


Result of powder dispersing (top) and oven shrinkage test of coated / uncoated separator (bottom).

PE-Separator (12 µm)				
150 °C / 30 min	**D50**	**Coated layer**	**Shrinkage of MD & TD**	**Gurley**
	[nm]	[µm]	[%]	[s/100 ml]
Reference PE	–	–	> 70	140
APYRAL® AOH 70	500	2 + 2	1 - 3	200

Flame retardancy

Furthermore boehmite coated LIB separator shows effective flame resistance in comparison with aluminium oxide coating LIB separator as shown in the following burning test (s. page 10).



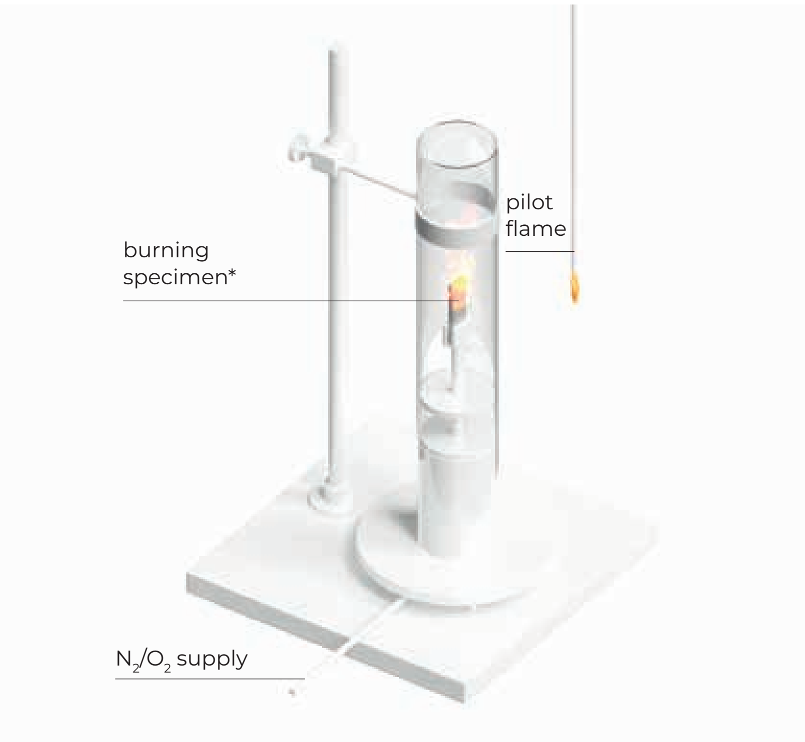
Uncoated

Al_2O_3 coated

APYRAL® AOH 60 coated

Burning test

In LOI (limited oxygen index) test, the test specimen of Al_2O_3 coated separator burned through, while the specimen of boehmite coated separator self-extinguished.



*specimen is an interfolded coated / uncoated LIBS

LIB Electrode edge coating

An additional protection against internal short circuit besides separator coating is the electrode edge coating (e.g. via die coating, figure 4). The main functions of the electrode edge coating are:

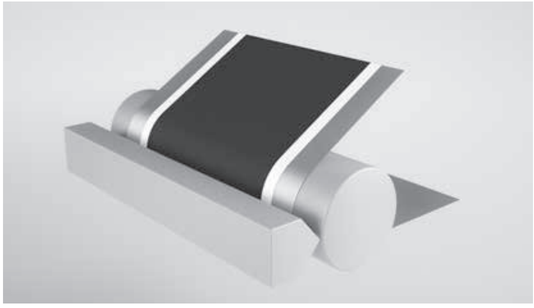


Figure 4: A die coating system in which the boehmite dispersion is applied to the cathode edge.

1. Prevention of cutting burrs caused issues

The boehmite covered current collector (Al- or Cu-foil) reduces the occurence of cutting burrs and the risk of such burrs to puncture through the separator, touching the counter electrode and causing a short circuit.

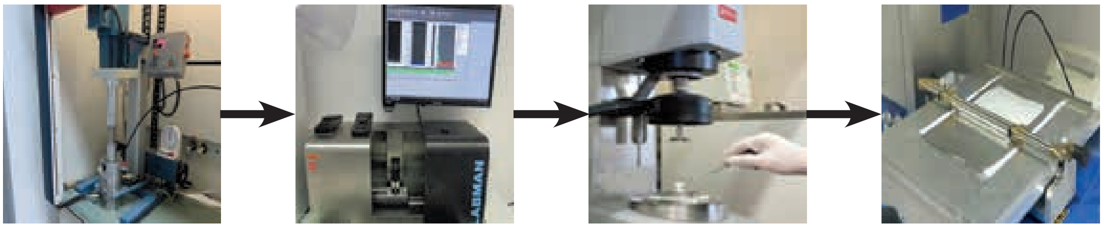
2. Isolation to avoid an internal short circuit caused by possible devition of cell assembling.

Other than for separator coating the industry chooses boehmite for this application right from the start. The determining metric to use boehmite is the low hardness compared to alumina. Boehmite coating improves the overall

performance of the electrode cutting process and it avoids a secondary contamination through abrasion of cutting tools.
All these positive effects on processing performance and battery cell safety can only be deployed when the production process from slurry production via slurry handling and coating is properly designed. Dispersibility of the boehmite powder, sedimentation and agglomeration and viscosity of the coating slurry are essential for a successful coating and need a detailed evaluation.
Following picture shows every step in figurative presentation and result and figure 5 displays details of viscosity measurement.

Formulation and flow chart of lab test

Boehmite / **APYRAL® AOH**, Dispersant / DISPERBYK® -180, PVDF / HSV 900, NMP



Dispersion
- Mix of AOH
- Add PVDF

PSD measurement
- Via Grindomether

Viscosity measurement
- Via Rheometer

Coating
- Via bar coater

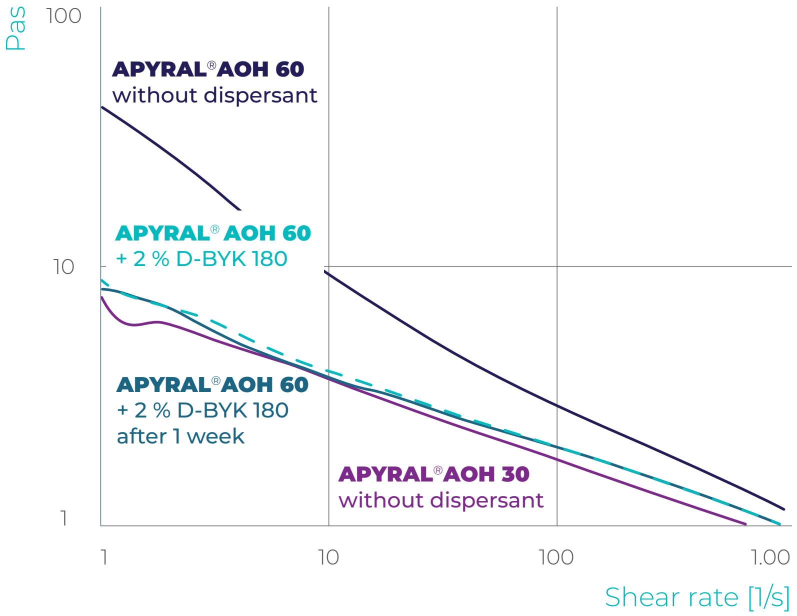
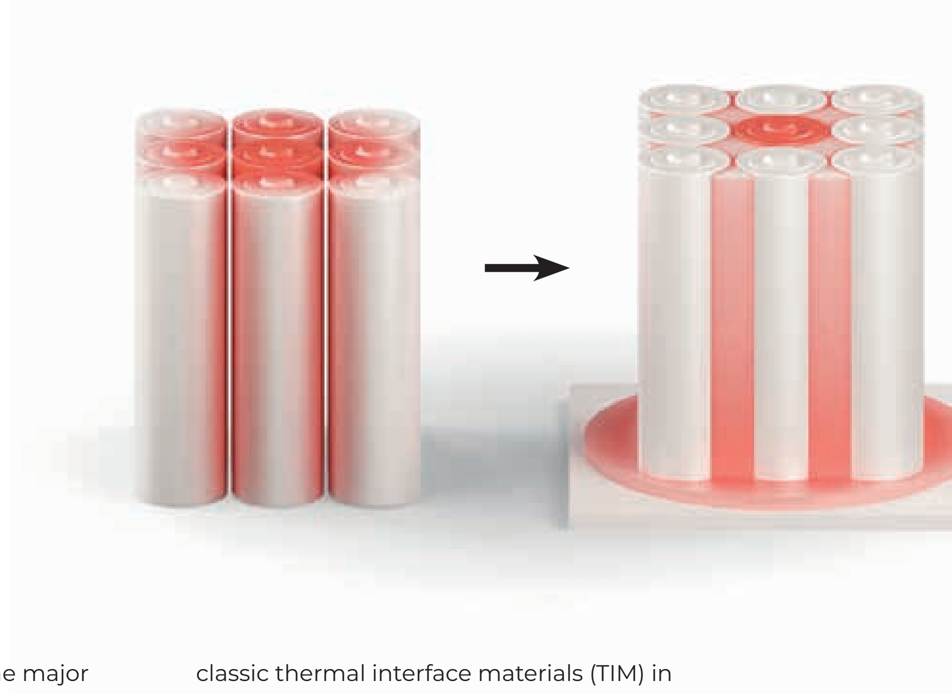


Figure 5: Viscosity as a function of shear rate for edge-coating slurries. Influence of boehmite choice (**APYRAL® AOH 30** vs. **APYRAL® AOH 60**), effect of dispersant (+2 % D-BYK) and slurry ageing (after 1 week) are demonstrated.

Inside battery

Thermal conductive compounds



Regarding thermal management the major components which need consideration are electrical motors, power electronics (e.g. inverter and converters) and last but not least the Lithium ion batteries (LIBs).

To keep the battery from overheating during fast charging the heat has to be conducted out of the battery stacks through the battery enclosure to an external (active) cooling system. Here the adhesive attaching the stacks to the enclosure and especially the gap filler between the single stacks of the battery module (s. figure 6) play key roles.

For gap fillers usually a thermal conductivity (TC) of 2.5 – 3 W/mK is demanded, which requires filling levels often significantly above 80 wt.-%. While gap fillers and classic thermal interface materials (TIM) in the electronic industry are used in scale of some grams per unit, a modern LIB for EVs require kilograms of a gap filler. In this regard, easy and fast dispensing plays a critical role to enable short assembly times.

Nabaltec AG has developed high performance fillers based on aluminium-tri-hydroxide (ATH) – **APYRAL® HC**. Their optimized particle size distributions simultaneously allow high packaging densities (resulting in high TC values) and extremely low viscosity levels.

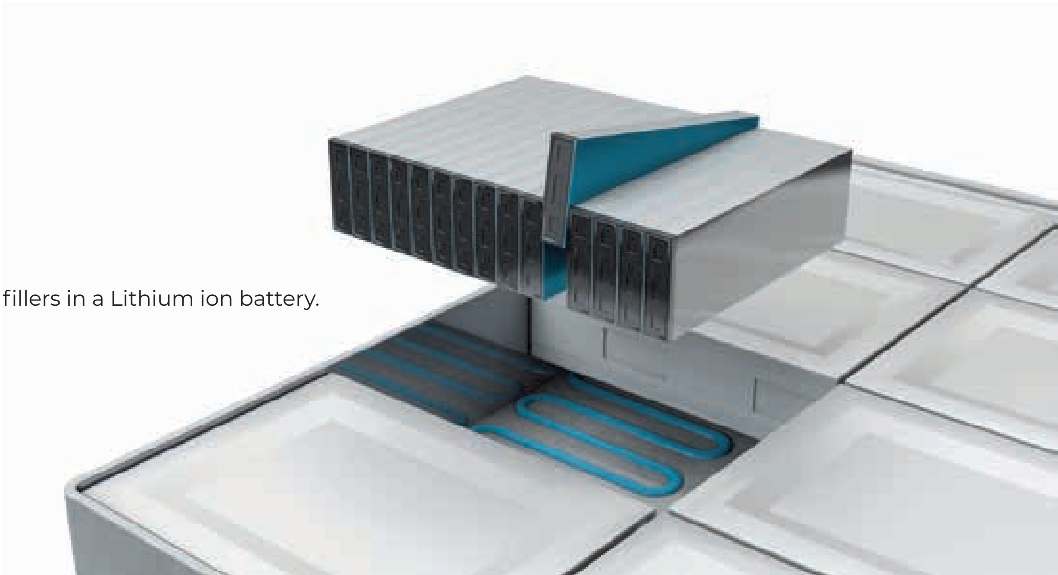


Figure 6: Adhesives and gap fillers in a Lithium ion battery.

With the help of optimized **APYRAL® HC** fillers, formulators obtain a toolbox to reach required thermal conductivity levels in an easy way. Depending on the applications the maximum particle size may be limited. Therefore finer grades are offered, as displayed by the d90-value:

APYRAL® HC 500	d90 = 110 µm
APYRAL® HC 600	d90 = 66 µm
APYRAL® HC 700	d90 = 55 µm
APYRAL® HC 800	d90 = 23 µm

With the fine grades like **APYRAL® HC 700** & **800** even thin applications like conductive coatings or tapes can be realized.

The highly favorable product properties of APYRAL® HC grades, like

- optimized particle size distribution,
- unique morphology,
- high packaging density,
- improved sedimentation stability,
- low hardness and abrasion,
- low cost in comparison to high performance thermal conductive fillers,
- very low density.

→

finally lead to very attractive compound properties:

- extremely low viscosity,
- extremely high filler loads,
- good dispensing properties,
- high flame retardancy,
- good thermal conductivity (isotropic),
- good value,
- very low density & weight.

Parameters influencing thermal conductivity

When trying to improve the TC of a polymer compound a set of parameters of the compound ingredients have to be considered. Figure 7 gives a simple overview on these parameters. First and foremost, one usually considers the thermal conductivity of the resin and of the mineral filler.

The TC of most resins is very low, consequently TC of the mineral filler is in the focus. Naturally the formulator seeks fillers with high intrinsic TC values, like boron nitride (BN), aluminium nitride (AlN), alumina (Al_2O_3, AO) or magnesia (MgO). For an overview of selected mineral fillers for polymer applications including their TC values, please compare table below.

However a high intrinsic TC of the filler is not a necessity. A high filler loading can be more important, which the following chapters shall demonstrate.

Important powder parameters of common thermal conductive fillers.

Name, abbreviation	**Formula**	**T_{decomp} [°C]**	**TC [W/mK]**	**Density [g/cm³]**	**Mohs hardness**
APYRAL® HC, aluminium hydroxide, ATH	$Al(OH)_3$	200	20 - 25	2.4	3
APYRAL® AOH, boehmite, AOH	AlOOH	340	n. d.*	3.0	3 - 4
Alumina, AO	Al_2O_3	>> polymer	20 - 40	3.9	9
Magnesium hydroxide, MDH	$Mg(OH)_2$	320	10	2.4	3
Magnesia	MgO	>> polymer	40 - 60	3.6	6
Hexagonal boron nitride	BN	>> polymer	15 - 400	2.2	1
Aluminium nitride	AlN	>> polymer	180 - 220	3.2	9
Silica	SiO_2	>> polymer	1 - 12	2.2 - 2.6	6 - 7
Calcium carbonate	$CaCO_3$	>> polymer	4 - 6	2.7	3
Polymers	–	> 350	0.2 - 0.5	–	–

*not determined

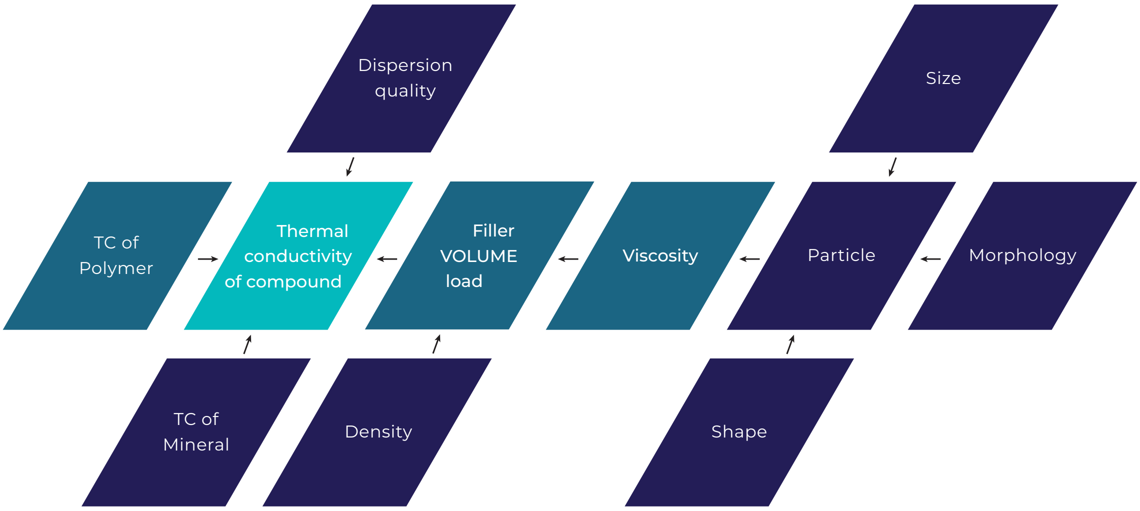


Figure 7: Important parameters to influence the thermal conductivity of a polymer compound.

Filler load

When filling a compound one quickly realizes that filler loading level is a very crucial parameter. This is understandable as one tries to replace as much of the insulating polymer by the better conducting mineral. With low loading levels the TC is affected only little, while with increasing load the incremental increase of TC becomes higher. Such an effect is well known when trying to increase the electrical conductivity (EC). Only when the particles start to touch each other, the conductivity rises strongly. This point is called the percolation threshold, see figure 8 (next page). For EC this point is very sharp, while for TC the steepness of the slope changes more slowly. But both parameters, TC and EC, have in common that a minimum filling level is required to gain an adequate level of conductivity. The percolation threshold explains why it is better to plot the TC versus volume based filling level (vol.-%) rather than filler loading based on weight percent (wt.-%).

Ultimately, the formulator has to gain as high filling levels as possible. These levels may be limited by mechanical properties and processing factors during compounding. Such an important factor is the viscosity performance of the filler, as a low viscosity is crucial to gain high filler loadings.

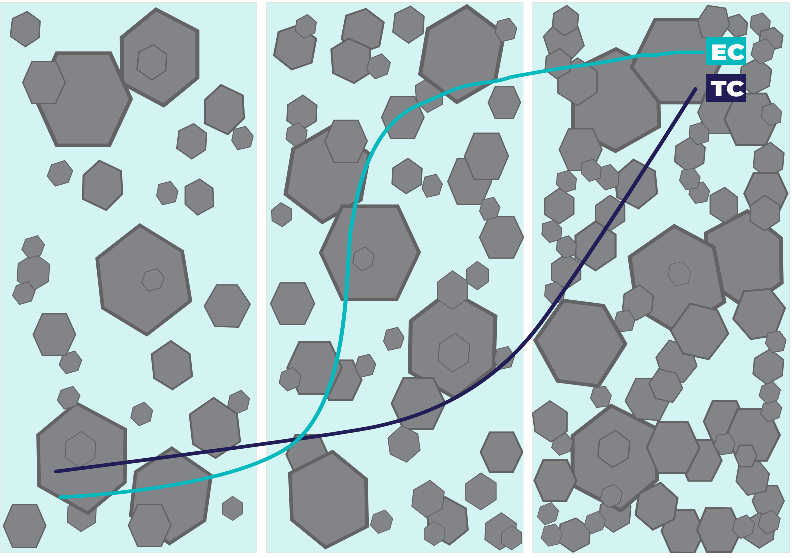


Figure 8: Percolation threshold for the electrical (EC) and thermal conductivity (TC) of a compound.

Viscosity

As indicated above the viscosity effect of the filler cannot be underestimated. Actually this is the dominating factor to obtain high filling levels necessary for high TC values. The upper graph in figure 9 shows the influence of the filler loading to the resulting viscosity increase of an unfilled unsaturated polyester resin (UP) by various mineral fillers. The fillers have been dispersed by a high speed dissolver into the resin, which featured a low viscosity of about 0.9 Pa·s only. Step by step the filling level was increased until the maximum filling level with a visible good dispersion was reached (indicated by the sign T in figure 9).

Subsequently after dispersion each resin compound was measured in a rotational rheometer. The viscosity value was determined at a shear rate of 10-s at 22 °C. The plotted relative viscosity represents the quotient of the viscosity of the filled resin to the viscosity of the neat, unfilled resin at same measuring conditions. After measuring the viscosity, the compounds have been cured and the specimens where polished to obtain a plain surface necessary for measuring the thermal conductivity by Hot Disk method at 22 °C, according to ISO 22007-2.
The TC of these cured compounds are plotted in the lower graph of figure 9.

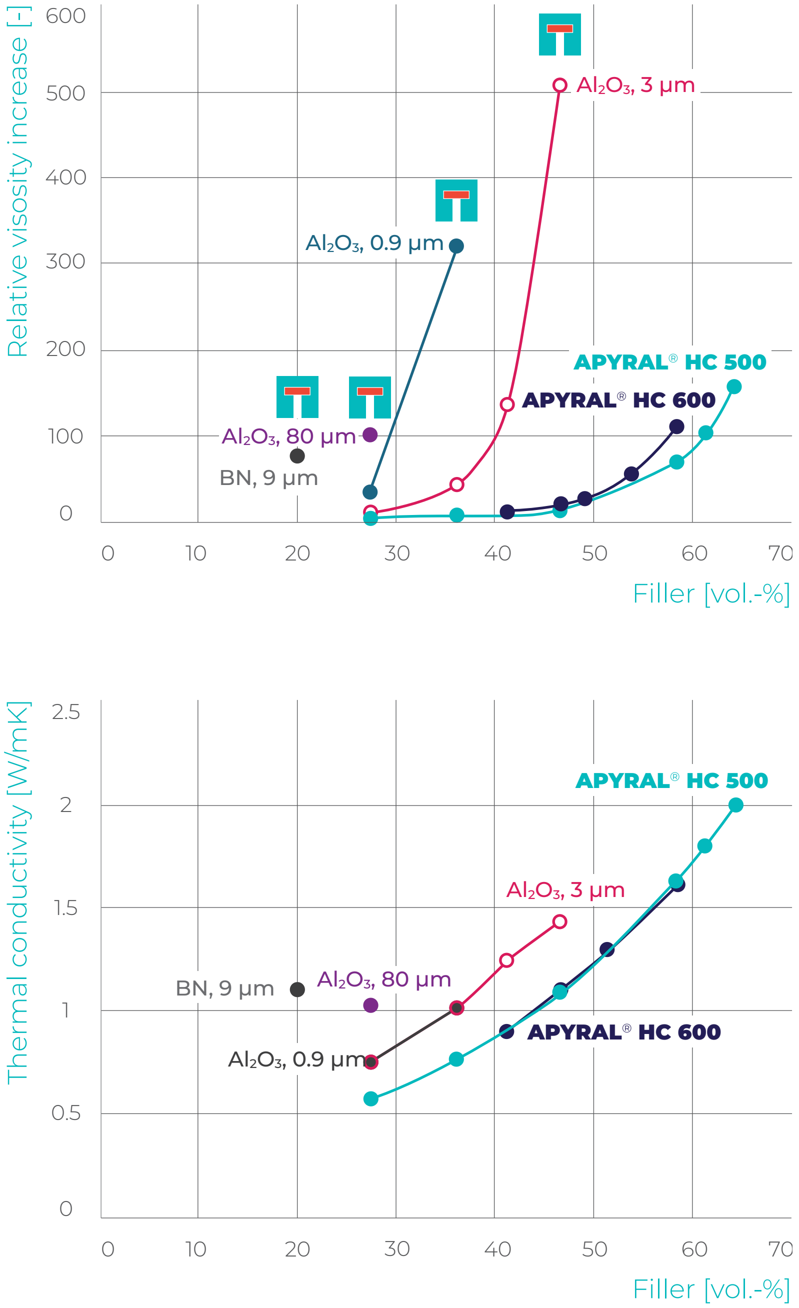


Figure 9: Relative viscosity of **APYRAL® HC** in comparison to calcined Al$_2$O$_3$, and BN in UP resin at shear rate 10 s-1 at 22 °C (above) and the corresponding TC values obtained by Hot Disk method after curing (below).

Similarly to the conductivity, the viscosity is rising strongly with increasing filler loads. However, the rheological performance of BN and alumina is lacking far behind the one of optimized **APYRAL® HC**.

These discrepancies can be explained when considering the differences in particle size and morphology of the individual minerals, displayed in figure 10 (next page).

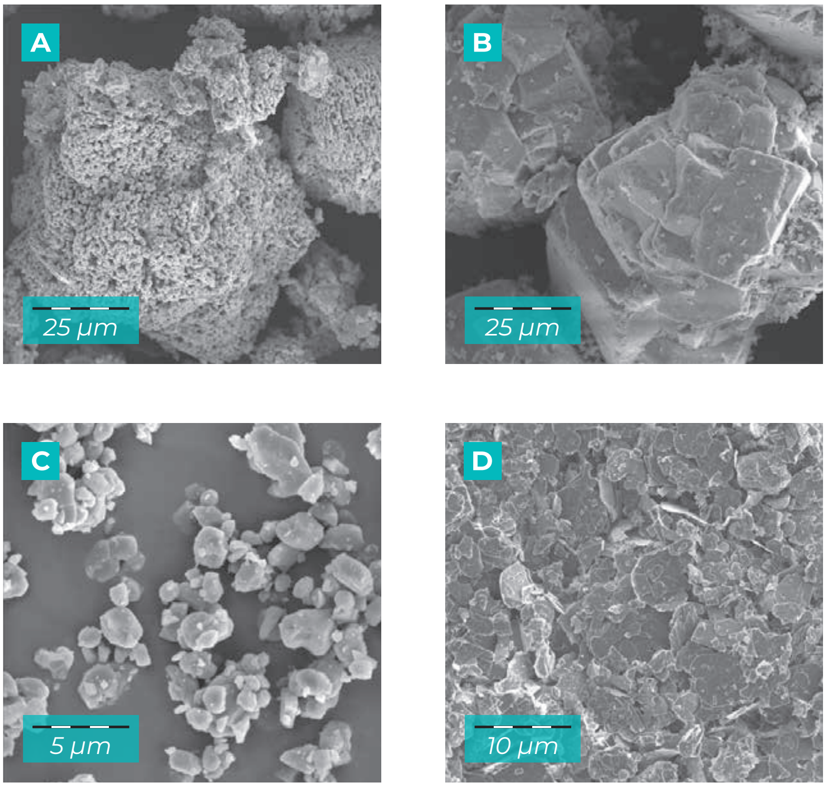


Figure 10: SEM-images of calcined alumina (80 µm, A), **APYRAL® HC 500** (B), calcined alumina (3 µm, C), and BN (9 µm, D).

Particle size

Very often formulators seek for fillers with big particle size as they expect to gain not only lower viscosity enabling higher filling level, but also higher TC levels in comparison to small particles. In theory this is truly the case when one compares particles of the same chemistry and morphology which feature low porosity. However, this is not easy to obtain in every kind of mineral.

For example, **APYRAL® HC** and the coarse calcined alumina have similar particle size, but their viscosity is very different. **APYRAL® HC** (figure 10 B) consists of single grown, compact crystals, while the coarse alumina (figure 10 A) is revealed as a hard agglomerate of small primary crystals with many internal macro pores. This raises oil absorption and viscosity. Thus, only one, low filling level could be obtained no higher filling was possible, limiting the obtainable TC (s. figure 9).

In case of calcined alumina the optimum viscosity is gained when the primary particles (figure 10 C) are set free by gentle grinding without further destroying them. This is usually the case at mean particle sizes between 1 and 10 µm, depending on the calcination state. When grinding is enforced to smaller particle sizes, then the primary particles are destroyed and more micropores generated which leads to high oil absorption and viscosity (s. Al_2O_3, 0.9 µm in figure 9). However, even alumina in ideal primary crystals state do not feature the viscosity performance of the unique crystals of **APYRAL® HC**.

Particle shape

The distinct platy nature of the BN crystals (figure 10 D) lead to very strong shear thinning effect in fluids.

In the reported experiments a filler load of 20 vol.-% BN could be generated only, leading to a low TC level. When trying to disperse a higher loading of 27 vol.-%, the BN could not be dispersed. During addition of the filler the compound was clogging at the wall of the container, (s. figure. 11), a region of low shear where the viscosity is several orders of magnitude higher than in the near of the dispersion blade (high shear region).

This makes the dispersion of platy BN very difficult and leads to low to moderate filling levels only. The high intrinsic TC level of this mineral could not be fully utilized as the rheology was limiting the filler loading.

Another aspect influenced by the particle shape is the 3-dimensional flux of the conducted heat. Ideally the heat shall be conducted in equal measure in all dimensions (isotropy) and not directed in one direction only (anisotropy).

The graphite-like molecular structure of BN does not only lead to a platy shape, but also to the fact that within the plates the heat is conducted much faster in plane than through plane. Thus, BN has a strong intrinsic anisotropy in its particles. However, due to the rheological properties plates often align into the same direction during flow, e.g. during injection molding. Therefore in a lot of applications where BN is utilized as a filler, a strong anisotropy of TC in the final component needs to be considered.

Figure 11: Aborted experiment trying to disperse 27 vol.-% of BN in UP-resin. All material clogs to the wall while the dissolver blade (not shown) is mixing only air.

To check for anisotropy a simple experiment was made. The two specimens from the viscosity/TC-experiment described above were cut into stripes, each stripe turned by 90 degrees and glued together with same uncured resin compound. The TC of these specimens was measured again after hardening and polishing of the former cut stripes.

Although the original specimen have been prepared by a simple casting, which should not evoke a high degree of alignment of the BN particles, a significant higher in-plane-TC could be determined for the BN compound (s. figure 12 , next page) in contrast absolutely no difference of TC, was observed for **APYRAL® HC** whether measured in plane or through plane. This is confirming the expected isotropy of ATH, demonstrating that parts made by **APYRAL® HC** filled resins are free from geometrical design restrictions.

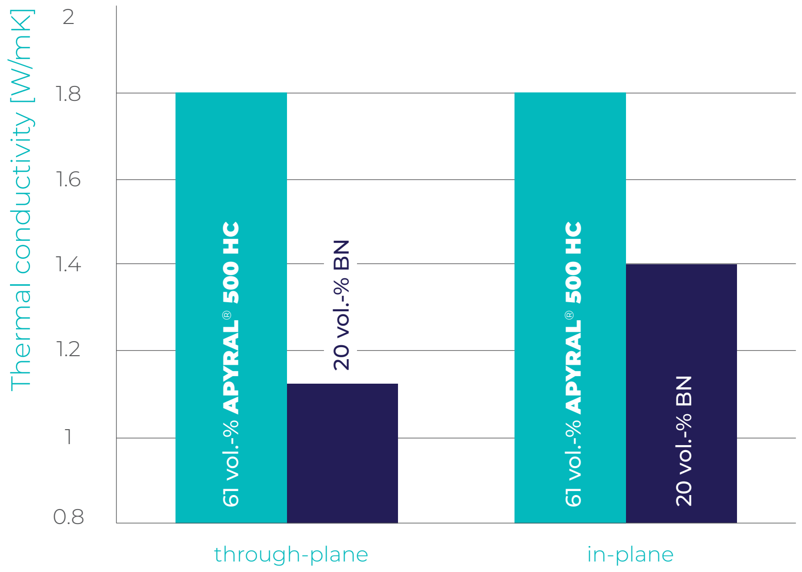


Figure 12: Thermal conductivity of an UP resin filled with BN or **APYRAL® 500 HC**, measured in- (right) and through-plane (left).

Density (specific gravity)

Considering the model of touching particles to generate a high TC it is better to plot the TC versus volume based filling level rather than filler loading based on weight percent. Therefore the density (specific gravity) of the filler plays an important role. Low density fillers will gain a higher volume loading at the same loading level by weight.

APYRAL® HC exhibits a very low density (2.4 g/ml). This is a very important point when calculating the mass based formulation cost versus the volume based application cost, where a certain volume has to be filled.

Finally, using **APYRAL® HC** with its unique rheological properties allows highest filler loadings resulting in even higher TC levels in comparison to calcined alumina or even BN.

The obtained TC of the maximum filling levels of the UP compounds are plotted in figure 13 in two ways, by volume fraction (vol.-%) and weight fraction (wt.-%) of the same compound.

Again one can see the strong effect of the low density of **APYRAL® HC**: The alumina with best viscosity features (3 µm) can be filled up to 76 wt.-% but results in a lower TC than **APYRAL® HC 600** which reaches only 75 wt.-% loading. The higher TC value can only be explained when taking the volume based filling level into account, displayed as green bars. When utilizing **APYRAL® HC 500** with its outstanding viscosity performance an even higher volume loading and a TC of 2 W/mK can be obtained.

The unique properties of **APYRAL® HC 500** were demonstrated in several resins with varying viscosity and intrinsic TC levels. The results are displayed in figure 14. Depending on the viscosity level and the mechanical properties (e.g. cross linking degree) of the resin, different loadings and TC levels close to 3 W/mK can be gained. This makes **APYRAL® HC 500** and **600** ideal candidates for modern TIM and especially gap fillers for EV batteries.

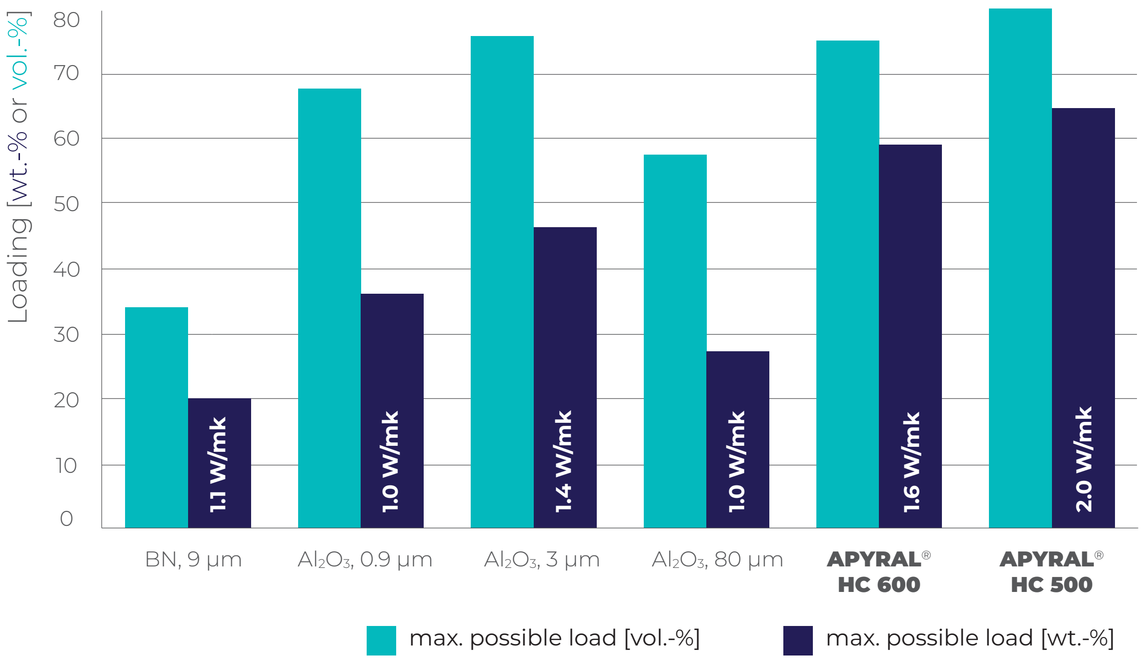


Figure 13: TC of **APYRAL® HC** in comparison to calcined alumina, and BN in UP-resin at 22 °C (Hot Disk method).

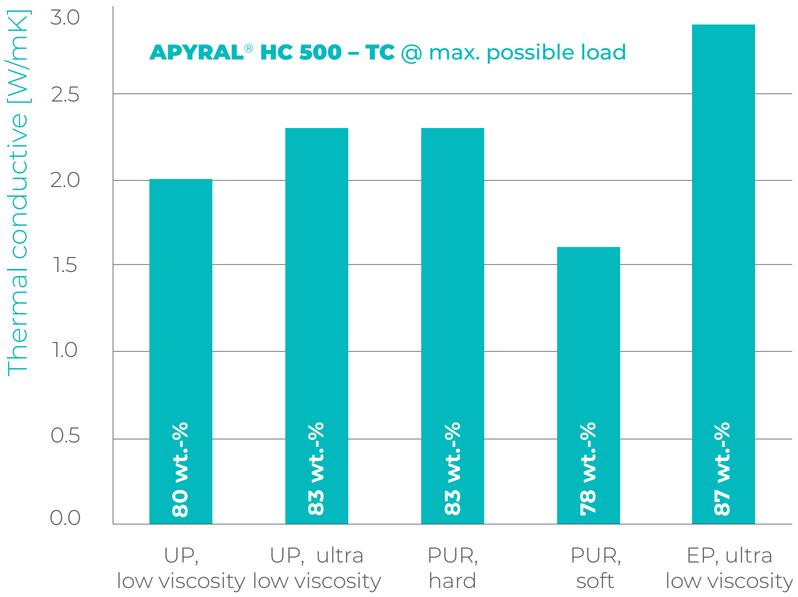


Figure 14: Thermal conductivity of selected resins of various chemistry and cross linking density filled with **APYRAL® 500 HC** to the maximum possible load in each resin.

Abrasion

Thermal conductive compounds used in EV parts, especially gap fillers for LIB packs and modules, are to be consumed in big volumes so far not known from TIM in classical electronic applications. In large scale industrial applications abrasion and wear of tools during production and dispensing of HC compounds becomes an extremely important quality and cost factor.

Because of Mohs hardness 9 (only diamond is harder) Al_2O_3 particles are excellent abrasive materials – and it is known that abrasiveness increases strongly with particle size. This is another reason why it is not a good idea to use big alumina particles at high loadings. Materials with low Mohs hardness and low abrasion, like **APYRAL® HC** (Mohs 3) are to be preferred.

In figure 15 the color of a PU resin compound filled with **APYRAL® HC 500**, a fine ground alumina and a coarse spherical alumina is shown. The differences of abrasion from a common high speed dissolver disk during a 10 minute dispersion are very obvious. Practically no abrasion occurs when utilizing **APYRAL® HC**, while alumina will always cause additional cost due to abrasion.

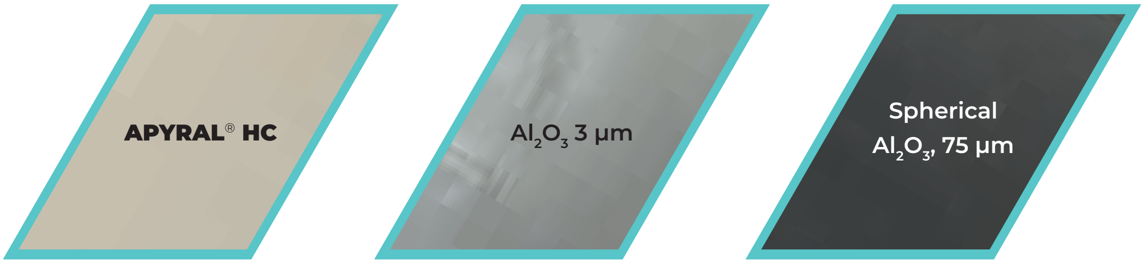
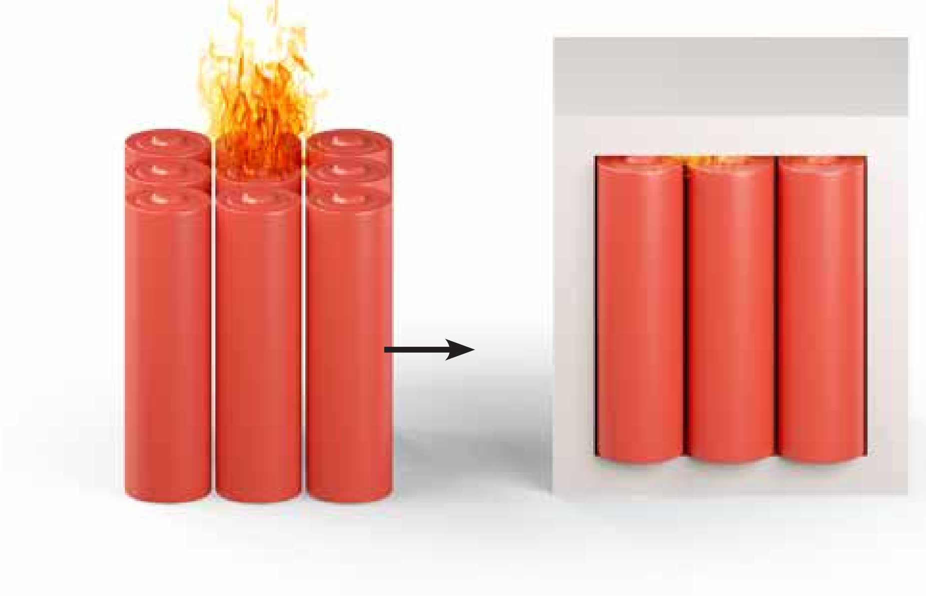


Figure 15: Color change of a PUR compound due to abrasion from dissolver disk when utilizing Al_2O_3.

Battery casing

Flame retardancy & Heat barrier



Flame retardancy

Likewise other electric components, LIBs belong to the safety sensitive components of an EV. Such components need to fulfil fire safety requirements. While final standardization is still in progress, materials in use are commonly requested to fulfill flame retardancy classification according the UL 94 V0 (similar to E&E applications). Even when using BN or alumina at high filling levels which fulfil the required 3 W/mK, an UL94 V0 classification is not easy to achieve. Therefore additional flame retardants have to be used, which lead to higher cost and even higher viscosity.

This is not the case with **APYRAL® HC** as it is based solely on ATH, a well-known mineral flame retardant. In many resins a UL94 V0 classification is already achieved with filler loadings of 60 – 65 wt.-%. When it is used at loadings enabling 2.5 - 3 W/mK reported above, often very stringent flame retardancy classifications like e.g. lined out in EN 45545 (European railway standard) or CPR can be achieved.

Exemplarily, figure 16 (next page) shows the results of the cone calorimetry measurement of PUR, unfilled as well as with high filler loading of **APYRAL® HC 500**. It can be easily seen that the addition of **APYRAL® HC 500** leads to a significant reduction of the peak heat release rate which means in effect a considerably improved flame retardancy.

Such highly filled glass fiber reinforced plastics (e.g. SMC / BMC) are already in use, when such severe flame retardancy classifications are required. This makes **APYRAL® HC** grades also an ideal solution for glass fiber reinforced battery housings in an EV.

Hence **APYRAL® HC** is not only a filler enabling required thermal conductivity but features also excellently as flame retardant and smoke suppressor, enabling additional value and performance for a broad use in EV applications.

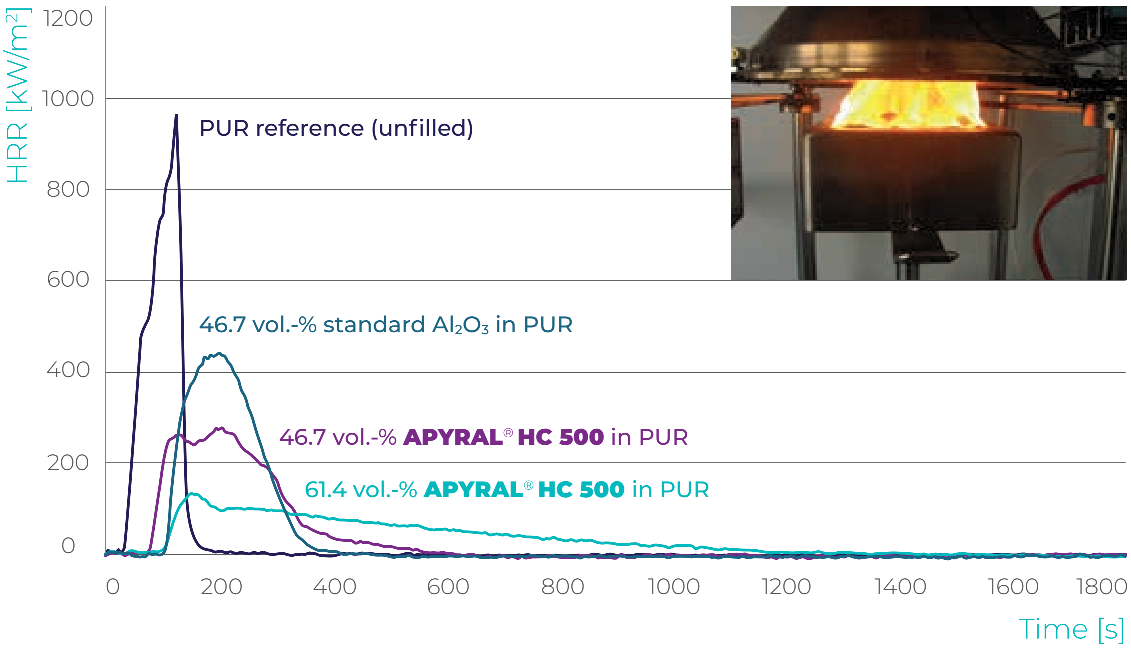


Figure 16: Cone measurement of PUR. Heat release rate of unfilled PUR in comparison with **APYRAL® HC 500** and standard Al_2O_3 filled PUR.

Heat barrier

As the number of EVs is increasing strongly, fire safety of the battery casings becomes more and more important. Herein, the trend goes far beyond the well-known UL 94 V0 classification but towards a real heat barrier which can enclose the thermal runaway of a battery for a certain time. Since first of January 2021 China as pioneer in electromobility has already defined a new standard (GB 38031- 2020) which demands a thermal propagation test. It is described that after the thermal runaway of an individual cell, there must be at least 5 minutes until thermal propagation leads to battery ignition or explosion. This requirement shall allow passengers to have enough time to escape the EV. It is expected that new standards all around the world will be implemented to tackle this thermal propagation issue of the battery module in EVs.

Lightweight materials like aluminum or fiber reinforced composites are preferred for the construction of battery casings. These materials per se do not withstand torch flame tests which are requested by OEMs to evaluate thermal propagation in case of a thermal runaway scenario. Nabaltec AG has developed innovative filler systems called **ACTILOX® HTB** to meet this new and demanding requirement. **ACTILOX® HTB** are mineral based flame retardant filler blends, which together with the polymer matrix form hard ceramic-like layers during torch testing. These ceramic like residues guarantee physical strength and a strong heat barrier for battery casings in a thermal runway event.

Figure 17: Torch Flame Test

Coating of Aluminum sheets

As a non-corrosive light metal, aluminum is a well-established automotive material and therefore also broadly used for the construction of battery enclosures. But its low melting temperature of 660°C hinders the use of pure Aluminum. Mica-sheets are used as additional heat barriers applied on battery modules. But this requires an extra assembly step.

More preferred are heat barrier coatings applied on the inner side of the Al-sheet. With an **ACTILOX® HTB** blend optimized for an epoxy-resin coating, a stable ceramic-like ash crust is formed during the torch flame test (see figure 18). The Al-sheet keeps faultless on the backside, and the backside temperature stays below 140 °C for the 20 min test duration (see figure 19).

Figure 18: Al-sheet coated with EP-resin with 300 phr **ACTILOX® HTB** after torch flame test.
Left: exposed (coated) side showing ceramic like residue, right: backside showing intact Al.

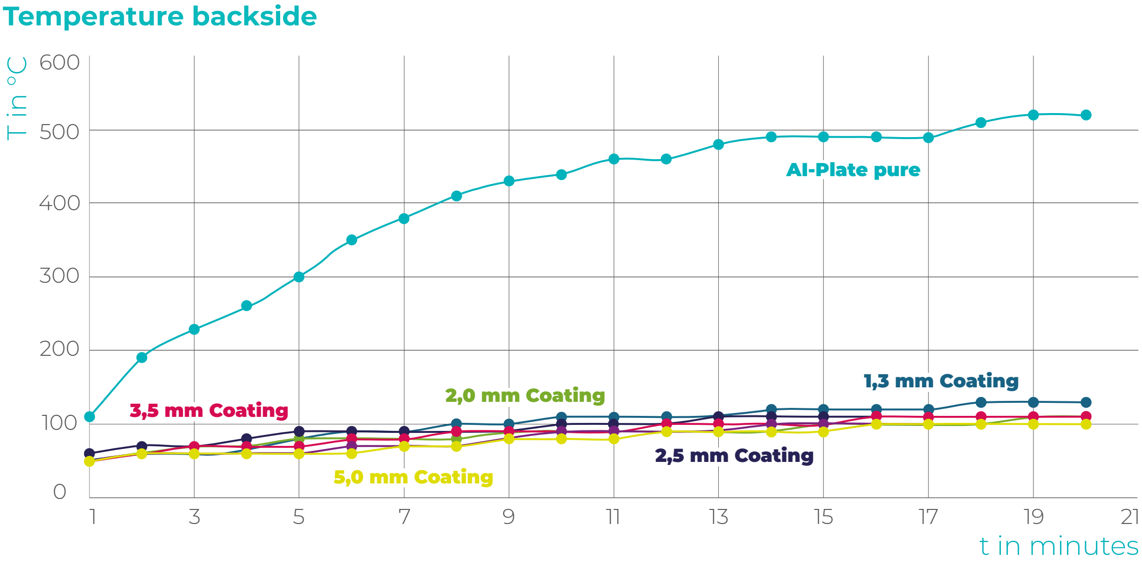


Figure 19: Temperature on backside during 20 min torch-flame test procedure. Upper curve: pure Al-Plate (no coating). All other Al-Plate specimens are coated with EP, containing 300 phr **ACTILOX® HTB** at different thicknesses. While non-coated reference reaches > 500 °C on backside, even the thinnest coated specimen (1.3 mm) stays < 140 °C.

SMC (Sheet Moulding Compounds)

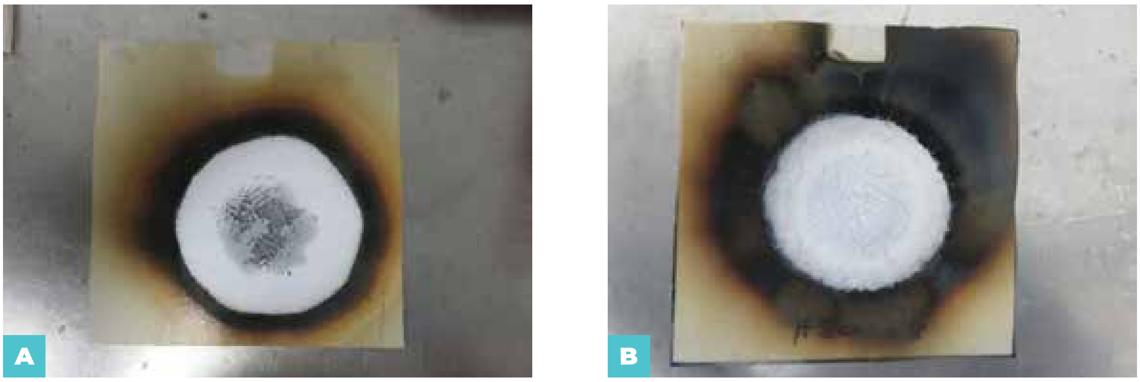


Figure 20: UP-laminate (15 wt.-% GF) after torch test: A) 300 phr **APYRAL® HC 500** and B) 200 phr **ACTILOX® HTB**.

Glass-fiber reinforced thermosets like UP-resins highly filled with ATH **APYRAL® HC** are already used for battery covers made of SMC. But to fulfil the heat barrier requirements against thermal runaway scenario, mica sheets must be glued onto the inner side of the SMC battery lid in addition. Again, this is a non-favored extra assembly step.

When using **ACTILOX® HTB** as specialty mineral flame-retardant filler during SMC production, this additional assembly step is no longer needed. **ACTILOX® HTB** can easily be mixed into the reactive resin blend with standard process equipment. The two specimens shown in figure 20 are hand laminates based on UP-resin and 15 wt.-% glass fiber matts after 30 min exposure to the torch flame.

One specimen is highly filled with pure ATH **APYRAL® HC 500** at 300 phr (specimen A), left). The other one (specimen B), right) is filled with 200 phr **ACTILOX® HTB**.
Both specimens keep intact after the torch flame test, but the specimen filled only with ATH is relative fragile. Figure 21 compares the cross-section of specimens A) and B). While the ATH filled laminate A) results in a soft ash with loose fibers (area exposed to the torch), the **ACTILOX® HTB** containing laminate builds a very strong ceramic like residue. This residue builds an excellent heat barrier proven by the temperature recording shown in figure 22. The temperature difference between torch-flame exposed front side and backside does not undercut 600°C and backside temperature does not exceed 400°C.

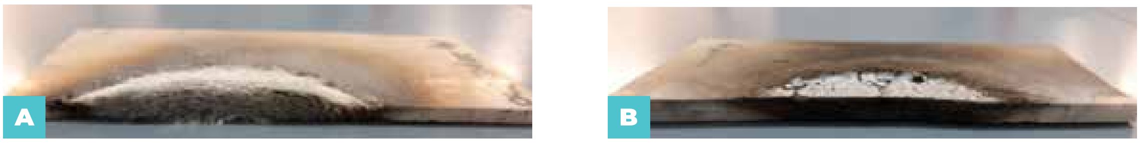


Figure 21: cross-section of specimen A) = 300 phr **APYRAL® HC 500** on left side and specimen B) = 200 phr **ACTILOX® HTB** on right side.

Temperature front/back

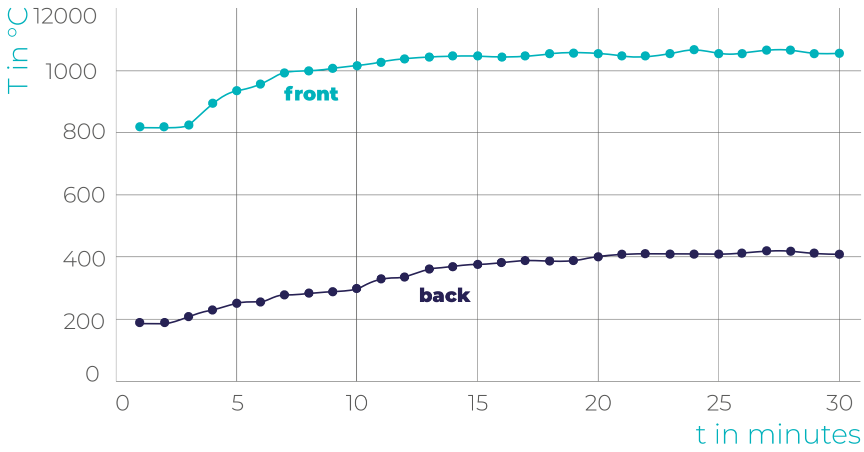


Figure 22: Temperature recording over 30 min torch-test on **ACTILOX® HTB** containing laminate B) for front side (blue, exposed to flame) and back side (orange).

GFRP (Glass Fiber Reinforced Plastic)

GFRP based on PP or engineering plastics like e.g. PA6, PA6.6, are further light-weight material options under investigation for battery covers. Other than crosslinked thermosets used for SMC, thermoplastics soften and start to flow when exposed to heat. This effect is lessened with GF reinforcement, but it is still existent. Crosslinking is doable, but non-desirable, because then GFRP materials lose their benefit of being recyclable by thermo-forming.

To make a thermoplastic GFRP pass the torch test, compound melt flow should not be too high and solidification kinetic of burnt compound needs to fit to the melt flow in the areas surrounding the spot exposed to the torch flame. In other words, the composite needs to be balanced between ceramification reaction of flame-retardant component with polymer / glass fiber matrix – which is induced by the direct contact of the torch flame – and the plastification of the composite under the influence of the heat.

Parameters influencing melt flow and plastification are the glass fiber content, the composition of the flame-retardant blend and its addition level. The flame-retardant composition as such is the key for the formation of a stable crust.
Figure 23 shows three examples based on PA6. For the specimen on top, the flame retardant – boehmite **APYRAL® AOH 30** – did not form a stable char during torch-flame test. A hole was burnt into the plate within 4 min, the test failed. The specimen in the middle shows a composite containing an **ACTILOX® HTB** variant (-a) which formed a stable, ceramic like crust. But the non-burned compound plasticized too quickly. The solidified crust broke out of the test plate after 15 min and test failed. The specimen on bottom passed the test in all criteria. One reason is the glass fiber content, which was increased up to 20 wt.-%. An optimized **ACTILOX® HTB** variant (-b) was used at 40 wt.-%. Backside temperature stays below 400 °C for the 20 min test duration and the residue is a very solid and mechanically integer plate.

PA6_5%GF_50% **APYRAL**® **AOH 30** 4 min until sample burns through

PA6_5%GF_50% **ACTILOX**® **HTB** -a
15 min until solid, ceramic like residue breaks out

PA6_20%GF_40% **ACTILOX**® **HBT** -b
No burn through within 20 min; very solid, ceramic like residue; backside temperature < 400 °C

Figure 23: PA6-plates with varying glass fiber (GF) and flame-retardant contents (all values in wt.-%) after torch-flame test.
Top: pure boehmite **APYARAL**® **AOH 30**
Middle: non-optimized flame-retardant **ACTILOX**® **HTB** (-a) blend
Bottom: GF-content increase to 20 % and 40 wt.-% of an optimized **ACTILOX**® **HTB** (-b)

Annex

Abbreviation	Meaning
α-Al_2O_3	Alpha-alumina
AlN	Aluminium nitride
AO	Aluminium oxide
AOH	Aluminium oxide hydroxide
ATH	Aluminium trihydroxide (aluminium hydroxide)
BET	Specific surface area according to Brunauer, Emmett, Teller
BN	Boron nitride
BMC	Bulk moulding compound
d50	Median particle diameter/size
d90	90 % of particles have a smaller particle diameter/size
D-BYK 180	DISPERBYK® -180, BYK-Chemie GmbH, Wesel, Germany
E&E	Electrical and electronics
EC	Electrical conductivity
EV	Electric vehicle
EP	Epoxy
GFRP	GLASS FIBER REINFORCED PLASTIC
HC	Heat / thermal conductivity
HPA	High purity alumina
HSV 900	Kynar® HSV 900, fluorinated thermoplastic homopolymers, ARKEMA
HTB	High temperature barrier
LIB	Lithium ion battery
LOI	Limiting oxygen index
MD	Machine direction
MDH	Magnesium dihydroxide (magnesium hydroxide)
MgO	Magnesia, magnesium oxide
NMP	N-Methyl-2-pyrrolidone
PE	Polyethylene
PP	Polypropylene
PSD	Particle size distribution
PUR	Polyurethane
PVDF	Polyvinyliden fluoride
SEM	Scanning electron microscope
SMC	Sheet moulding compound
TC	Thermal conductivity
Tdecomp	Decomposition temperature
TD	Transverse direction
TIM	Thermal interface material
UP	Unsaturated polyester resin
GB 38031-2020	Electric vehicles traction battery safety requirements
Class H	NEMA insulation classes for motors (180 °C)
CPR	Contruction product regulation (July 1, 2017)
EN 45545	European railway standard
ISO 22007-2	Plastics – Determination of thermal conductivity and thermal diffusivity – Part 2: … Transient plane heat source (hot disc) method…
UL 94	Vertical burning test according to UL 94 (Underwriter Laboratory)

Nabaltec
product portfolio

ACTILOX®

Boehmite, as flame retardant filler and catalyst carrier

GRANALOX®

Ceramic bodies, for the production of engineering ceramics

APYRAL® AOH

Boehmite, as flame retardant filler and functional filler

NABALOX®

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

APYRAL®

Aluminium hydroxides, as flame retardant and functional filler

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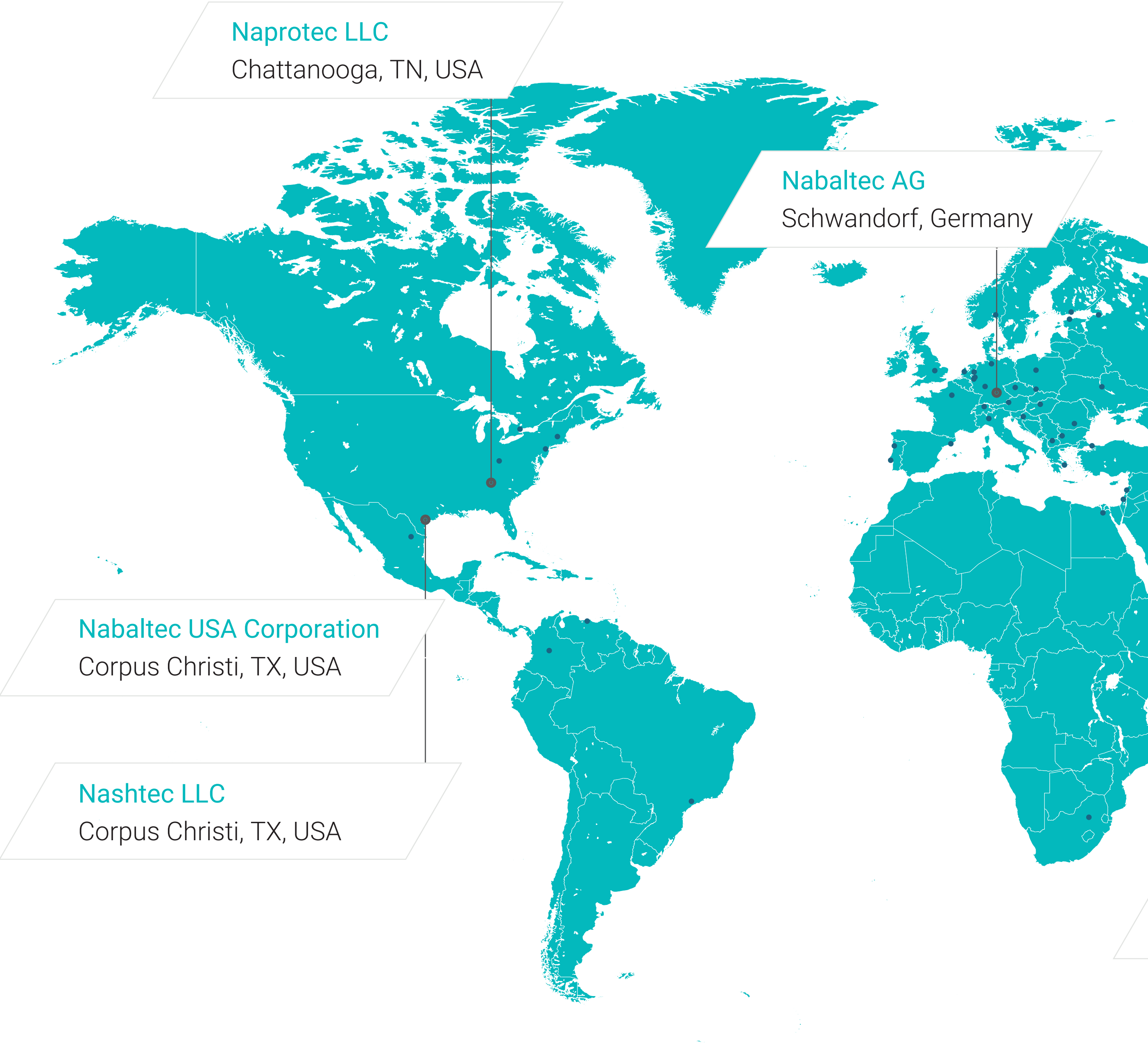


Naprotec LLC
Chattanooga, TN, USA

Nabaltec AG
Schwandorf, Germany

Nabaltec USA Corporation
Corpus Christi, TX, USA

Nashtec LLC
Corpus Christi, TX, USA

● Locations ● Agencies

Nabaltec (Shanghai) Trading Co., Ltd.
Shanghai, China

Further information:

Nabaltec AG

P.O. Box 1860 · 92409 Schwandorf
Phone +49 9431 53-0
www.nabaltec.de
info@nabaltec.de

Customer Service

Phone +49 9431 53 910
sales@nabaltec.de

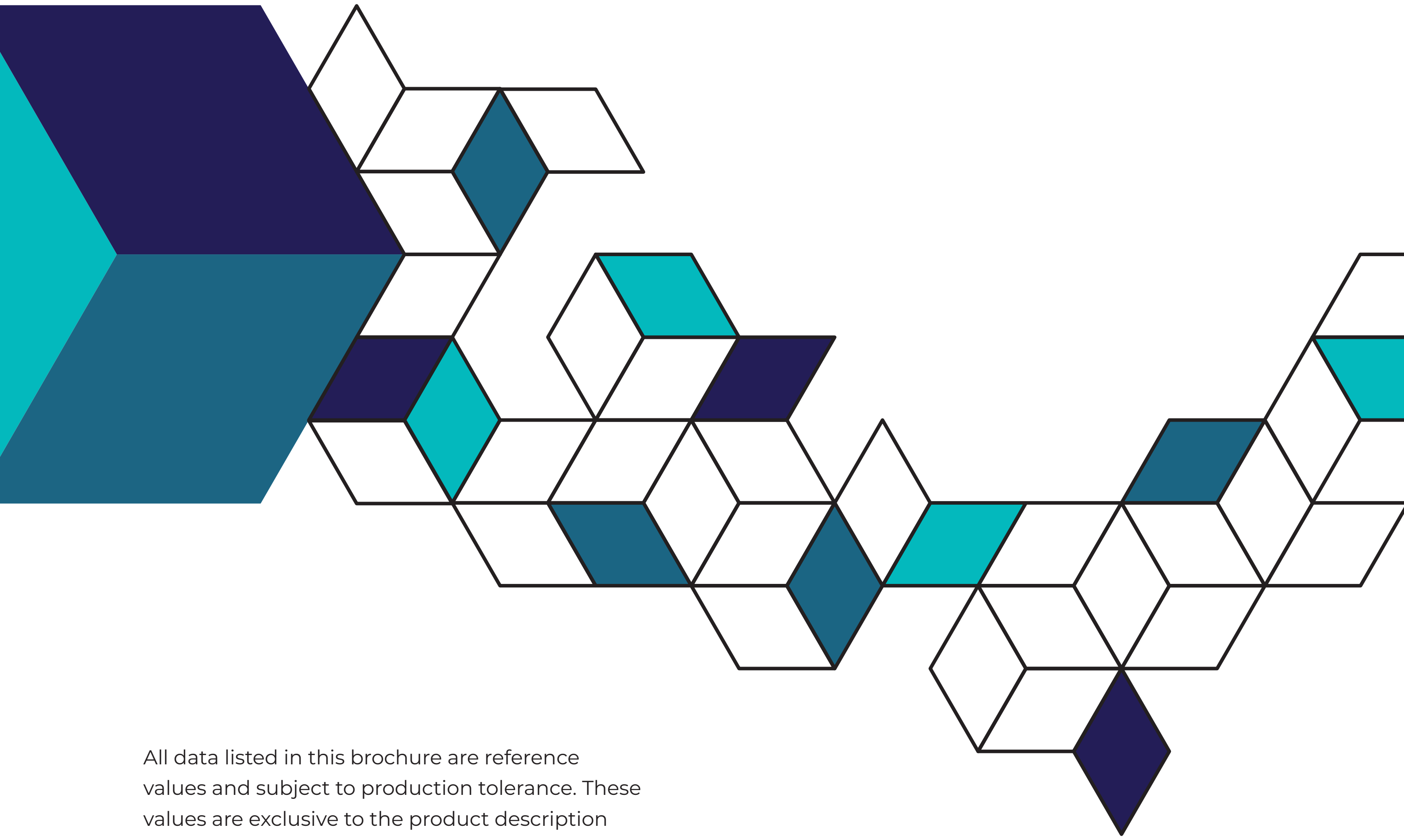
Technical Service

Phone +49 9431 53 920
tec-service@nabaltec.de

Nabaltec AG
P.O. Box 1860 · 92409 Schwandorf

Tel +49 9431 53-0
Fax +49 9431 61 557

www.nabaltec.de
info@nabaltec.de



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