Metal hydrates for elastomers

APYRAL®

APYRAL® AOH

ACTILOX®

Metal hydrates for elastomers

Product	D50* [µm]	BET [m²/g]	Oil absorption [ml/100g]	Main application
APYRAL® – Ground				
APYRAL® 1E	60	0.5	21	**Carpet backing,** e.g. EPDM **Cable bedding compounds** **Roofing sheets,** e.g. EPDM, Bitumen **Flooring,** e.g. EPDM
APYRAL® 8	20	1.3	24	
APYRAL® 16	21	1.8	17	
APYRAL® – Fine-precipitated				
APYRAL® 40CD	1.8	3.5	22	**Cable Insulation and Jacketing Compounds, for:** offshore cables, specialties, e.g. EVA, EVM, EPDM, Silicone, TPU **Sealing, for:** Railcar windows, compartments, e.g. EVM, EPDM, Public Building, e.g. EPDM, Offshore-Installations, e.g. EVM **High Voltage Insulators,** e.g. Silicone, EPDM **Mining belts,** e.g. EPDM **Materials for Offshore-Installations,** e.g. EVM. **Insulation Foams,** e.g. for Building & Construction, e.g. PVC / NBR, Air condition pipes, e.g. EPDM, Water pipes, e.g. EPDM
APYRAL® 60CD	1.0	6	28	
APYRAL® 120E	0.9	11	37	
APYRAL® 40VS	1.5	4.0	26	
APYRAL® 40 VS1	1.6	3.5	33	
APYRAL® 40H1	1.3	4.0	24	
APYRAL® 40 HS1	1.5	3.5	26	
APYRAL® 40T1	1.4	4.0	27	
ACTILOX® – Aluminium oxide hydroxide				
ACTILOX® B30	2.2	3	28	Additives for **Diverse applications**
ACTILOX® B60	0.7	5	30	
ACTILOX® 200SM	0.3	18	36	

**Laser granulometer Microtrac S 3500*

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

Introduction

Elastomers are polymer materials which are unique due to their special mechanical properties.

The crosslinking of the polymer chains after moulding and their low glass transition temperature enable those materials to gain back their original shape, even after mechanical deformation.

This characteristic clearly distinguishes elastomers from other polymer types such as thermoplastics (re-meltable and re-mouldable but hardly elastic) and liquid resin based thermosets (not re-meltable and not elastic).

Different types of elastomers are classified according to the chemistry of their backbone structure. The last letter of the polymer designation indicates to which class this material belongs.
Selected examples are given in the table below [1].

Samples of polymer designations.

Group	Backbone structure	Example
M	Saturated backbone, Methylene-type	EPDM, EVM
R	Double bonds, Rubber-type	NR, CR
U	Urethane-group	AU, EU
Q	Siloxane-group	MQ
O	Oxygen	PO

The abbreviations of the monomers which were used to form the polymer are put in front of the class designation to form the polymer's name. Selected examples are given in the following table [2].

According to this, styrene butadiene rubber for example is designated as SBR.

Monomer abbreviations.

Monomer abbreviation	Monomer	Rubber example	
B	Butadiene	NBR	nitrile butadiene r.*
C	Chloroprene	CR	chloroprene r.*
D	Diene	EPDM	ethylene propylene diene r.*
E	Ethylene	EPDM	ethylene propylene diene r.*
M	Methyl-siloxane	MQ	methyl polysiloxane r*
N	Nitrile	NBR	nitrile butadiene r.*
P	Propylene	EPDM	ethylene propylene diene r.*
S	Styrene	SBR	styrene butadiene r.*

r. rubber*

Elastomer compounds offer an optimal property profile for several applications, for example where mechanical impact must be absorbed or where flexibility and sealing must be guaranteed.

Thus, elastomeric compounds are used for the production of very special parts, but also for products which we use every day.

In all areas where people or goods must be specially protected from harm and damage from fire, the resistance of a compound against ignition as well as a slow rate of flame spread and smoke development are decisive factors. Application areas for such materials are public transport and building products.

For this purpose Nabaltec offers manufacturers of elastomeric materials a broad range of different grades of metal hydrates.

In particular, their environmental friendliness and their favourable cost performance ratio make **APYRAL®** (aluminum tri hydroxide / ATH) and **ACTILOX®** (aluminum oxide hydroxide / AOH) important sustainable flame retardants.

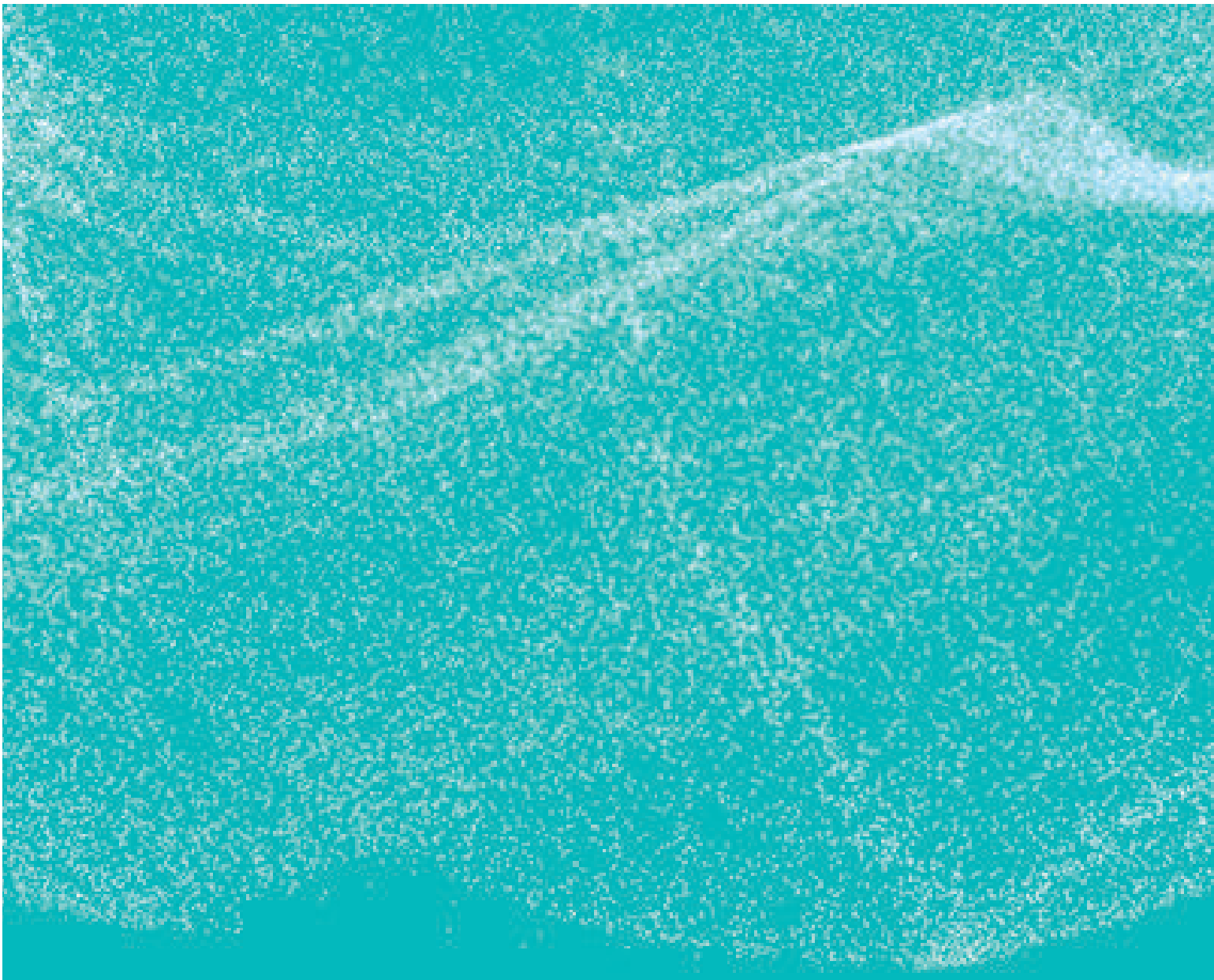
In the following table those mineral flame retardant product groups of Nabaltec are shown. Listed are chemical composition, mineral structure and the commonly used synonyms.

This brochure shall offer the reader an insight into the broad possibilities to develop an elastomeric compound formulation with mineral flame retardants. It complements our brochures „Mineral Based Flame Retardancy with Metal Hydrates“, „Metal Hydrates for Thermosets”, „Metal Hydrates for Cables“, and “Metal Hydrates for PVC”.

Due to the diversity of available resins, processing methods, additives, and fillers for the production of elastomeric compounds, this brochure cannot be exhaustive. It is intended to give an overview and hints for own formulation developments.

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

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



APYRAL®

APYRAL®

Our **APYRAL®** products for elastomers can be divided into two classes, on the basis of their property profiles:

- Ground grades
- Fine precipitated grades

Fine precipitated **APYRAL®** products are broadly used in elastomeric compounds for fire protection of materials which have to fulfill special mechanical and flammability requirements like in cables, seals, and many other products used e.g. for applications in public buildings, on ships, or oil rigs.

Of particular importance for use in halogen free flame retardant (HFFR) compounds are **APYRAL® 40CD**, **APYRAL® 60CD** and **APYRAL® 120E**.

To further improve the mechanical properties and surface characteristics of the final compound, **APYRAL®** can be surface treated with organic substances to enhance the coupling between the polymer matrix and the surface of the mineral. Relevant modified **APYRAL®** grades for elastomeric applications are given in next table.

APYRAL® 40 VS1 and **APYRAL® 40VS** have a vinyl functionalization and are especially used in cross-linked LSOH (low smoke zero halogen) compounds,

*Relevant modified **APYRAL®** grades for elastomeric applications.*

Coated product	Production plant
APYRAL® 40CD	Nabaltec, Germany / Nashtec, USA
APYRAL® 40 VS1	Nabaltec, Germany
APYRAL® 40VS	Naprotec, USA
APYRAL® 40 HS1	Nabaltec, Germany
APYRAL® 40H1	Naprotec, USA
APYRAL® 40T1	Naprotec, USA

e.g. on silicone rubber (SiR) basis. **APYRAL® 40 HS1** and **APYRAL® 40H1** contain a special hydrophobic surface modification. **APYRAL® 40T1** carries a non-reactive surface treatment. These three products are used in specialty silicone elastomers and TPU compounds. Other surface treatments of our **APYRAL®** grades are also available depending on the specific requirements of the users.

For compounds in which the mechanical properties and the surface characteristics are not the main focus, e.g. in cable bedding compounds or certain roofing materials, ground **APYRAL®** grades are recommended, like **APYRAL® 8** and **APYRAL® 16**.

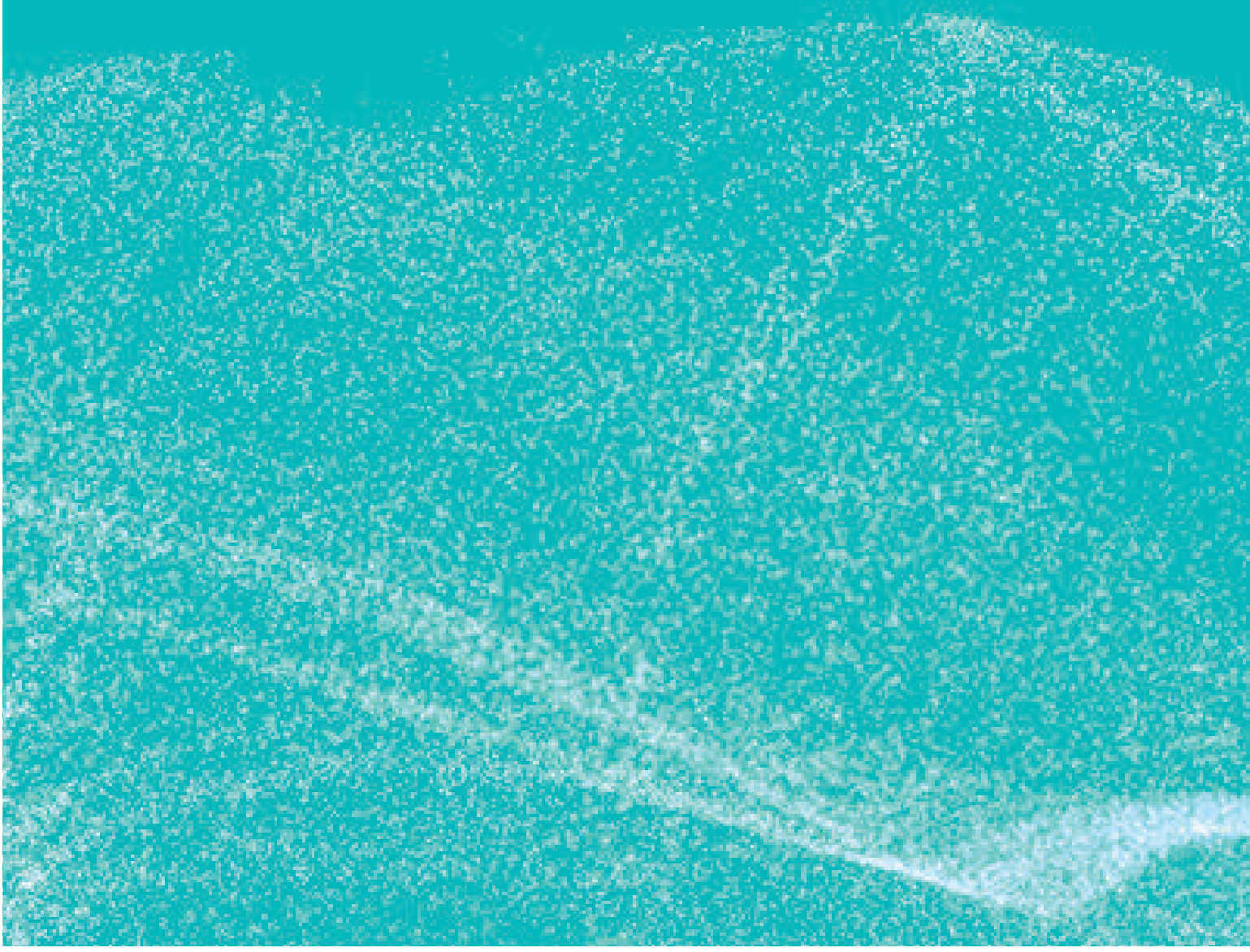
Chemical and physical parameters

APYRAL® products have a very high chemical purity of approx. 99.5 %. The remaining constituents are mainly sodium oxide, which is part of the crystal lattice and partly adhering to the **APYRAL®** surface in hydrated form, as well as traces of iron and silicon compounds. Due to its whiteness **APYRAL®** behaves neutral to the colouring of polymers.

Its Mohs hardness of 2.5 – 3 causes no tool abrasion problems even in highly filled molten masses. Its relatively high heat capacity c_p of 1.65 J/gK at 400 K (127 °C) has a beneficial effect on the dimensional stability under heat for **APYRAL®** filled polymers.

With a specific density of 2.4 g/cm³, **APYRAL®** is a medium dense mineral filler. As a result of the required filling ratios, the density of the flame retardant plastics is increased compared to the virgin polymer. **APYRAL®** is one of the most attractive flame retardants, even on the basis of a volume specific cost balance.

ACTILOX®



ACTILOX®

Boehmite grades produced by Nabaltec are finding a new range of application as functional fillers within the polymer industry, particularly due to their high temperature stability up to 340 °C (613 K). These grades are sold under the trade names **APYRAL® AOH** and **ACTILOX® B**.

Currently, three products of this range are available in different grades of fineness for application in elastomers: **ACTILOX® B30**, **ACTILOX® B60**, and **ACTILOX® 200SM**. Among them, **ACTILOX® 200SM** with its high fineness and optimised processing behaviour shows advantages for melt compounding processes which are used for the production of elastomeric compounds.

The flame retardancy efficiency of boehmite is lower, compared to aluminium hydroxide and magnesium hydroxide (see also our brochure „Mineral Based Flame Retardancy with Metal Hydrates"). **ACTILOX® B** and **ACTILOX® 200SM** should therefore be used in combination with other flame retardants to comply with most severe flame resistance standards. In thermoplastic and elastomeric compounds, synergistic effects can be observed if **ACTILOX® B** or **ACTILOX® 200SM** are combined with aluminium hydroxide, magnesium hydroxide, or metal phosphinates, for example.

When **ACTILOX® B** and **ACTILOX® 200SM** are used as co-additives to **APYRAL®** the remaining char after combustion forms a very homogeneous, nearly fully closed surface. During the start of a fire, the char forms a protective shield against heat and it retards the release of volatile and flammable decomposition products and the incipient thermal breakdown of the polymer.
This is even more successful if the char layer is more closed and stable.

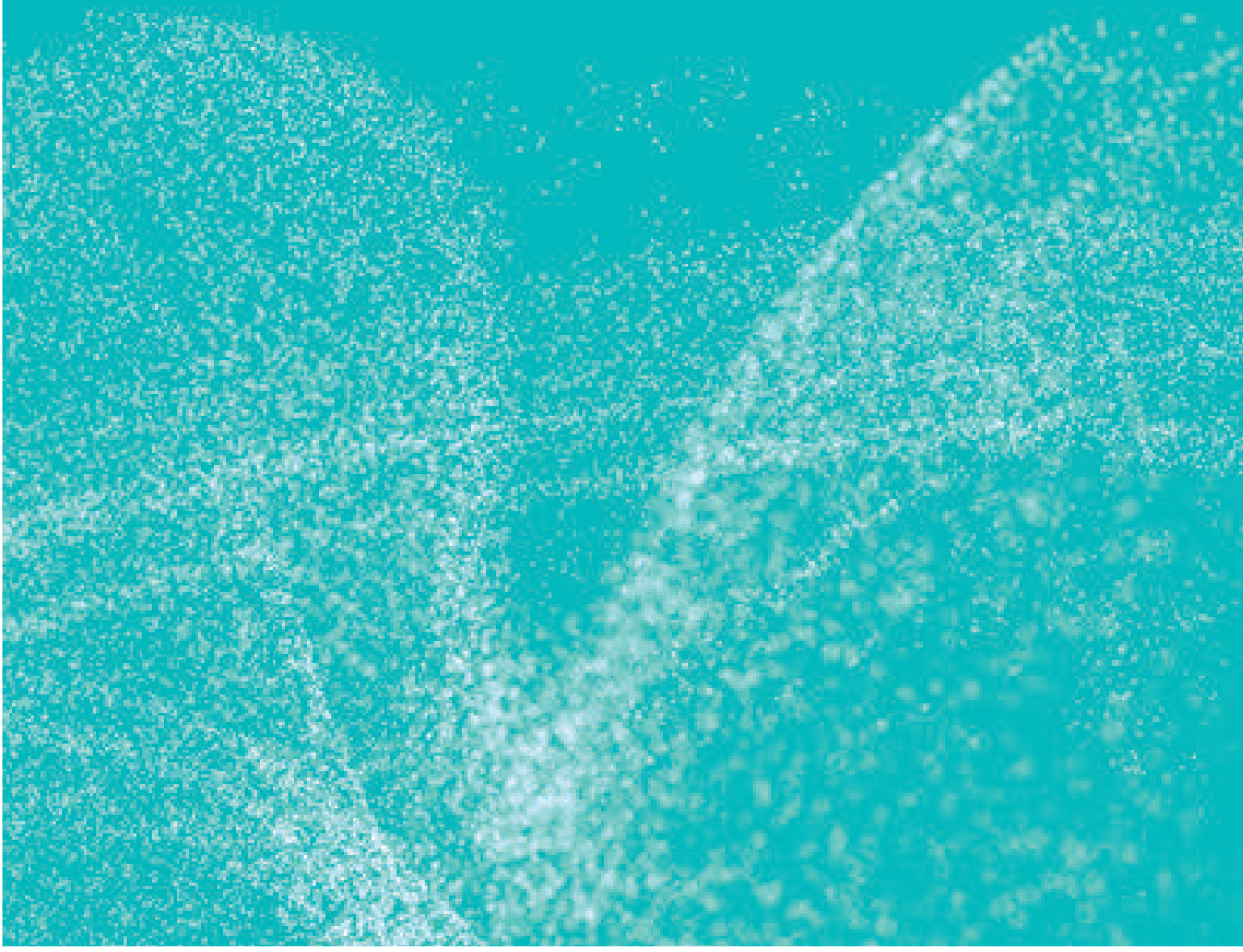
Chemical and physical parameters

All **ACTILOX® B** grades and **ACTILOX® 200SM** are extremely pure (ca. 99 %) crystalline boehmite products with a very low aluminium hydroxide content. This ensures extraordinary temperature stability. **ACTILOX® B** and **ACTILOX® 200SM** can be easily processed up to 340 °C. Their very low electrolyte content is crucial for the application of **ACTILOX® B** and **ACTILOX® 200SM** in electrically insulating products.

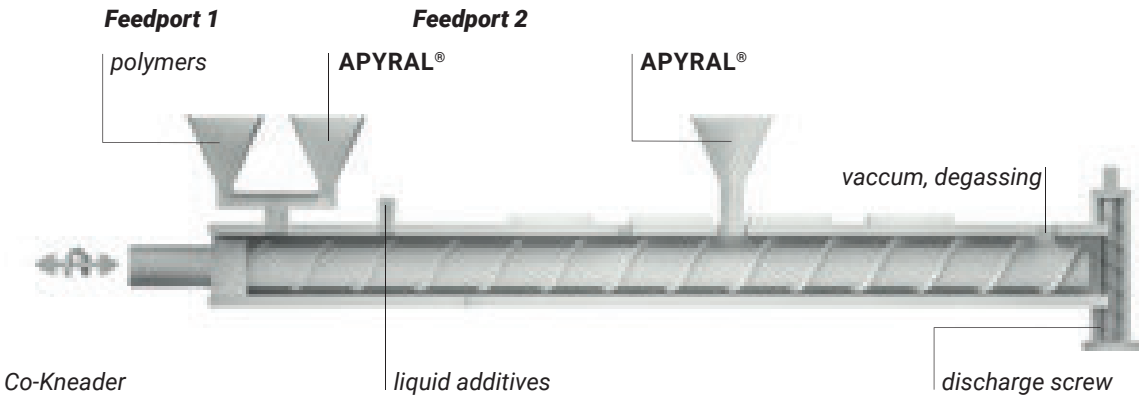
ACTILOX® B and **ACTILOX® 200SM** are ideal for the use in electrically insulating heat sinks due to their high heat capacity (c_p = 1.54 J/gK at 500 K, 227 °C) combined with high temperature stability.

In addition, **ACTILOX® B** and **ACTILOX® 200SM** can be used as white pigments due to their high whiteness in conjunction with extreme fineness and good dispersion properties.

Processing guidelines



Processing guidelines



There are several possibilities for the production of elastomeric compounds which are filled with **APYRAL®**, **ACTILOX® B** or **ACTILOX® 200SM**.

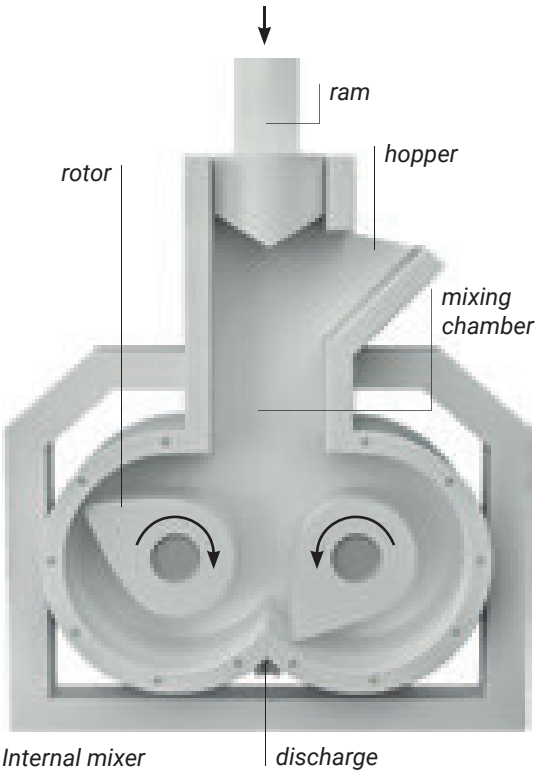
Batch processing in internal mixers (see right sketch) and/or on two roll mills are often used if good dispersion of large amounts of fillers is necessary and if regular product changes occur.

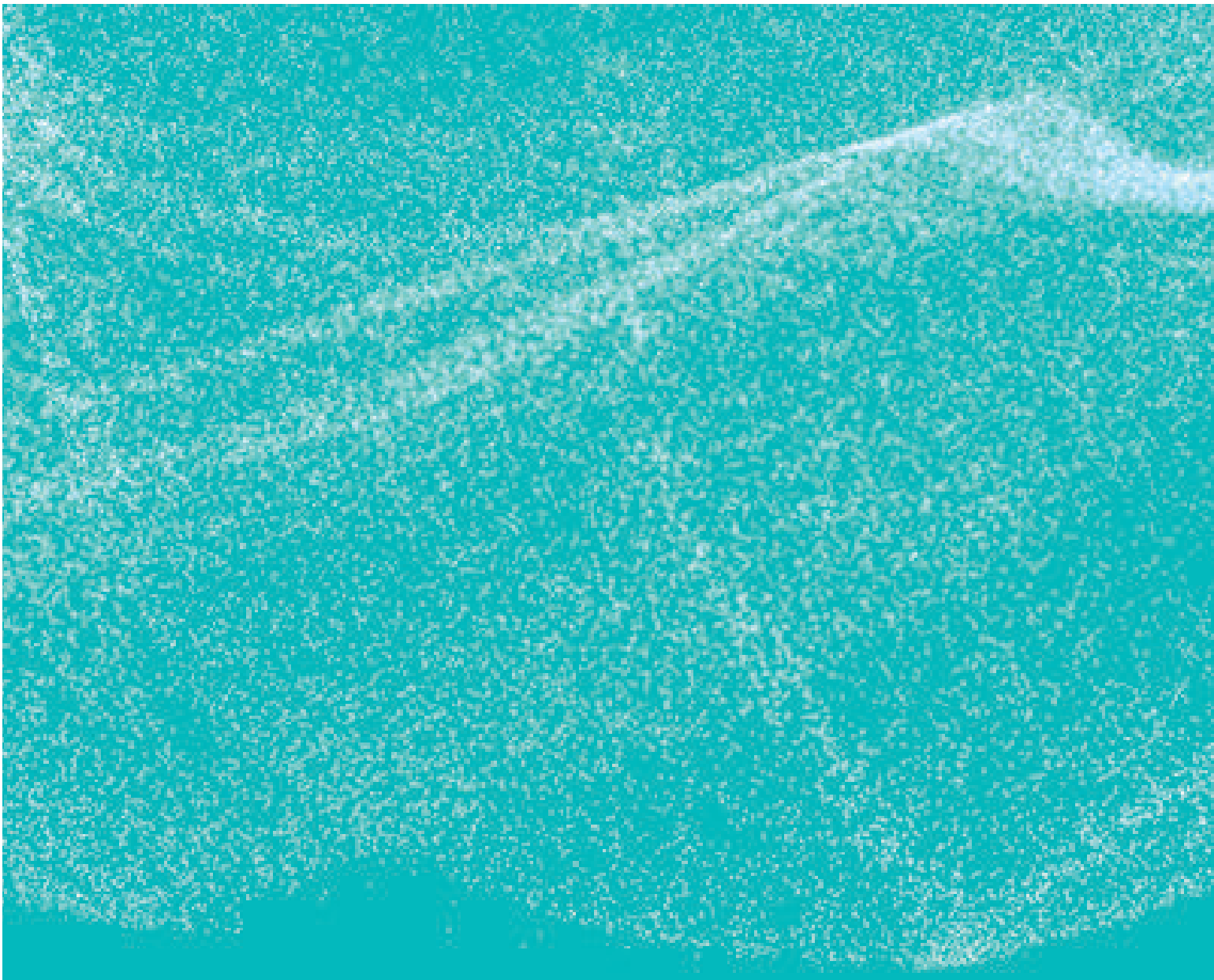
Continuous extrusion via twin screw extruders or co-kneaders (see sketch above) is recommended for large volume products and if the dispersion of the filler can be guaranteed during the residence time of the melt in the extruder without overheating the materials.

To garantee a sufficient dispersion and to ease the incorporation of the metal hydrates into the polymer, the twin screw extruder or co-kneader should have at least two feedports.

Subsequently, the compounds are shaped, for example via extrusion, and crosslinked. The crosslinking can be initiated chemically, such as for sulphur or peroxide crosslinking or energetically like in E-beam crosslinking.

The temperature limits for **APYRAL®** (200 °C) and for **ACTILOX® B** and **ACTILOX® 200SM** (340 °C) must be considered. It is recommended to keep the temperature of the molten mass below 190 °C while producing **APYRAL®** filled elastomers via batch compounding, for example. In the case of continuous processing, higher temperatures are possible for short residence times. But this must be tested depending on the individual process conditions.





Application examples

Application examples

The following chapters will demonstrate the performance of **APYRAL®** and **ACTILOX®** in different elastomeric compounds.

The influence of a certain type of mineral flame retardant on the properties of the final compound shall be demonstrated. Mechanical properties and flame retardancy performance of the materials will be compared.

EPDM based compounds

EPDM (Ethylene-propylene-diene-elastomer) is a versatile polymer which combines high elasticity and good resistancy against moisture, ozone and other media. Thus, it can be used for the production of a broad range of compounds which can be adjusted to diverse requirements and applications using additives and fillers.

EPDM is recommended as base polymer for the production of HFFR compounds with mineral flame retardants as EPDM can hold even large amounts of minerals and still retains good mechanical properties and processing behaviour.

High filling levels are necessary for mineral based flame retardant compounds as the flame resistance of a compound increases with growing amounts of minerals (see also our brochure „Mineral Based Flame Retardancy with Metal Hydrates“).

Two examples for EPDM based formulations are shown on the following pages. One of them is a black sulphur cured EPDM compound and the second example is a bright peroxide crosslinked material.

Fine precipitated minerals were used as flame retardant fillers. These were **APYRAL® 40CD**, **APYRAL® 60CD**, **APYRAL® 120E** and **APYRAL® 200SM** with a median particle size (D50) ranging from 1.8 down to 0.6 µm. Additionally, the submicron sized boehmite **ACTILOX® 200SM** was used as filler.

The compounds were produced on a laboratory scale two roll mill according to the formulations in the following tables. Subsequently, plaques were pressed out of these masses and they were cured at 180 °C. The specimens for mechanical analyses and flame retardant tests were cut out of these cured plaques.

Black, sulphur cured EPDM compounds

Black, sulphur cured EPDM compound examples.

Component [phr]		APYRAL® 60CD	APYRAL® 120E	APYRAL® 200SM
EPDM, Keltan® 8340		100	100	100
Additives		7	7	7
Curing		14.55	14.55	14.55
Plasticiser		65	65	65
Carbon black		60	60	60
APYRAL® 60CD		155	–	–
APYRAL® 120E		–	155	–
APYRAL® 200SM		–	–	155
Total		401.55	401.55	401.55
Characteristic data		**APYRAL® 60CD**	**APYRAL® 120E**	**APYRAL® 200SM**
Mooney viscosity (MU) (ML (1+4) 100 °C)		64	75	80
Tensile Strength	[MPa]	9	8.2	8.1
M 500	[MPa]	6.7	6.5	6.2
Elongation at Break	[%]	616	641	654
Shore A, 23 °C	(dimensionless)	56	63	63
LOI (Limiting Oxigen Index)	[% O_2]	26	27	27

Compounding on laboratory scale two roll mill, specimens made of compression moulded and cured (180 °C) plaques.

The compound above represents a starting formulation for an electrical insulating sealing profile with a mineral content of 155 phr.
The Mooney viscosity of these mixtures increases if finer **APYRAL®** particles with a higher specific surface area are used. Concurrently, tensile strength is decreasing with higher surface area of the filling material as it is illustrated in figure 1.

However, LOI values are only slightly affected by the type of **APYRAL®** at this moderate filling level.

The user can easily adjust the mechanical characteristics of the compound to the requirements for a certain application by the choice of an appropriate **APYRAL®** product with rather stable flame retardancy properties.

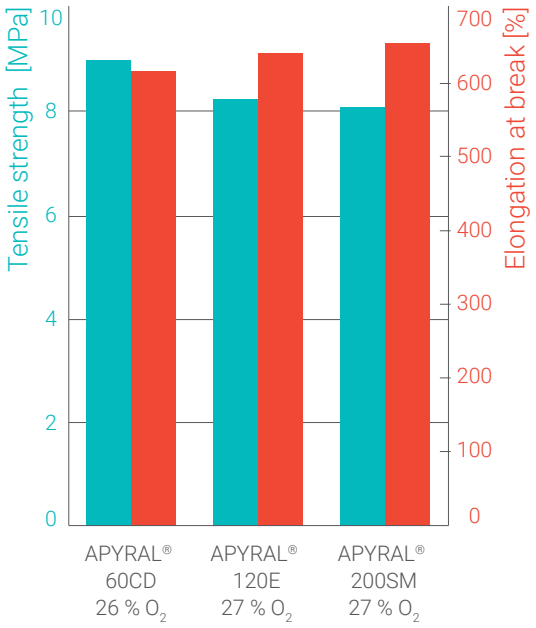


Figure 1: *Mechanical properties and LOI of the* ***black*** *EPDM compounds.*

Bright, peroxide cured EPDM compounds

A bright peroxide cured EPDM formulation with a higher filling level of 250 phr is exemplary for the application building profile (s. table on following page).

For the given compound, the use of **APYRAL® 40CD** gives only poor results, as one can see in the right chart. **APYRAL® 40CD** has the lowest specific surface area of all products compared here and and, as the mechanical results show, it is not the appropriate product for this kind of compound. **APYRAL® 120E** by contrast results in an optimal balance of tensile strength and elongation at break. The use of **APYRAL® 200SM** leads to similar values in tensile strength and shows a higher shore hardness, but the elongation at break decreases significantly when using a submicron sized filler.

The LOI values of the compounds which contain **APYRAL®** as mineral flame retardant are around 30 % O_2.

When using the boehmite and **ACTILOX® 200SM** a very good balance of tensile strength and elongation at break combined with a relatively low Mooney viscosity can be achieved. Unfortunately at the cost of flame retardancy. The LOI drops to only 25 % O_2.

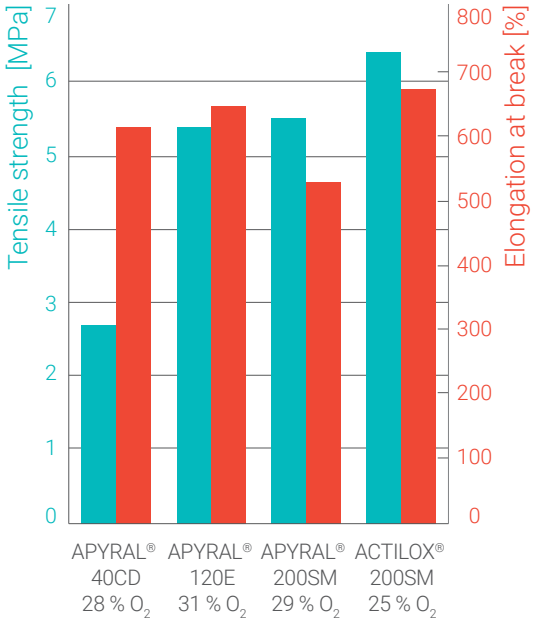


Figure 2: *Mechanical properties and LOI of the* ***brigth*** *EPDM compounds.*

If the mechanical properties of the compound are most important, **ACTILOX® 200SM** is superior to the aluminium hydroxide products in this compound. But if a certain level of flame retardancy is required, **APYRAL®** should be used or boehmite should be combined with aluminium hydroxide or other flame retardants. (See also our brochure „Mineral Based Flame Retardancy with Metal Hydrates“).

Bright, peroxide cured EPDM compound examples

Component [phr]	APYRAL® 40CD	APYRAL® 120E	APYRAL® 200SM	ACTILOX®200SM
EPDM, Vistalon™ 7500 [A]	100	100	100	100
Additives [A]	12	12	21	21
Curing [A]	16	16	16	16
Plasticiser [A]	60	60	60	60
APYRAL® 40CD	250	–	–	–
APYRAL® 120E	–	250	–	–
APYRAL® 200SM	–	–	250	–
ACTILOX® 200SM	–	–	–	250
Total	438	438	438	438

Characteristic data		APYRAL® 40CD	APYRAL® 120E	APYRAL® 200SM	ACTILOX® 200SM
Mooney viscosity (MU) (ML (1+4) 100 °C)		52	126	133	92
Tensile strength	[MPa]	2.7	5.4	5.5	6.4
M 500	[MPa]	1.4	3.7	4.5	3.8
Elongation at break	[%]	615	648	530	675
Shore A, 23 °C	(dimensionless)	51	64	67	62
LOI	[% O_2]	28	31	29	25

Compounding on laboratory scale two roll mill, specimens made of compression moulded and cured (180 °C) plaques.

Heat release rate (HRR) and smoke density (rate of smoke release, RSR) of EPDM compounds have been measured by Cone Calorimeter at a heat irradiation of 50 kW/m² (for more information on Cone Calorimetry see brochure „Mineral Based Flame Retardancy with metal hydrates"). The ratio at which heat is released is a good indication whether a fire will grow and how quickly. Keeping smoke density as low as possible during the infant state of a fire is critical for people to escape. Hence, both rates (HRR and RSR) should grow as slowly as possible and their peak values PHRR (Peak of Heat Release) and PRSR (Peak Rate of Smoke Release) should be as small as possible.

In the following diagrams (figure 3, 4) the HRR and the RSR for the bright EPDM compounds are shown as an example. The test results differ depending on the mineral flame retardant used. In general, the compounds with the finest aluminium hydroxide products and the highest specific surface areas (BET), **APYRAL® 120E** and **APYRAL® 200SM**, lead to a significantly less intense heat release and smoke emission compared to the reference compound with **APYRAL® 40CD**.

The EPDM compound containing the boehmite **ACTILOX® 200SM**, even though it has the highest BET surface area of all fillers compared, releases

more heat and smoke. HRR and RSR curves for this compound are between the **APYRAL® 40CD** containing compound and the best performing materials based on **APYRAL® 120E** and **APYRAL® 200SM**. This results due to the lower amount of crystal water released from boehmite compared to aluminium hydroxide.

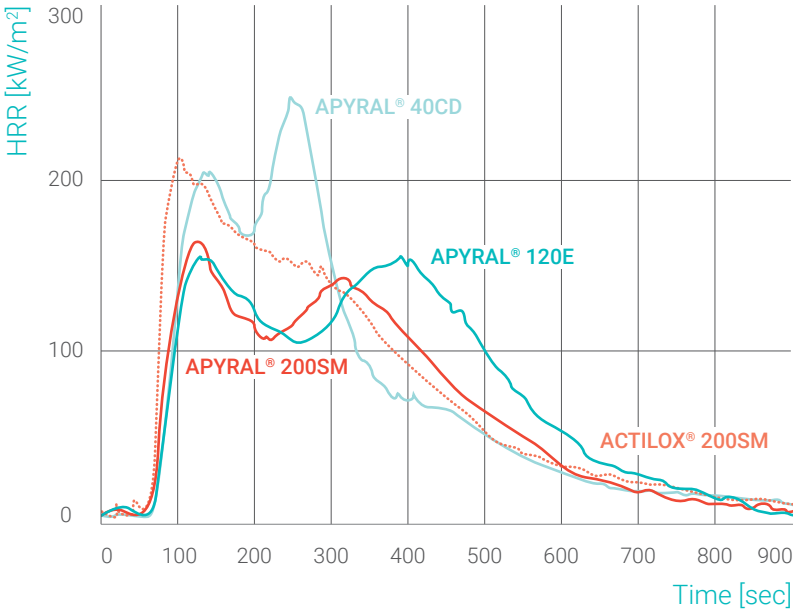


Figure 3: *Heat release rate (HRR) of bright EPDM compounds filled with 250 phr of different Nabaltec flame retardants.*

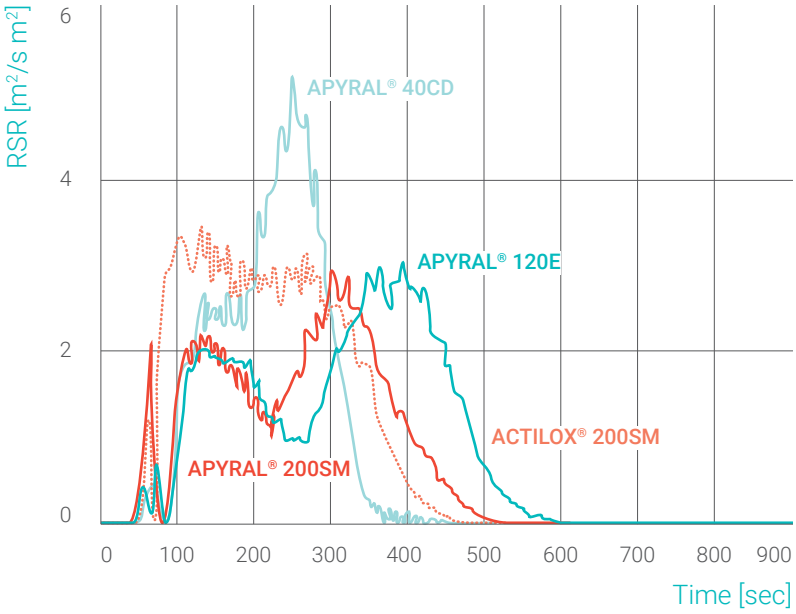


Figure 4: *Heat release rate (HRR) of bright EPDM compounds filled with 250 phr of different Nabaltec flame retardants.*

Ageing of EPDM compounds

Compounds which are used for transport or building applications have to stay functional over long periods of time. Therefore, tests are done to evaluate the influences of ageing on the compound properties according to national and international standards. Depending on the application of the compound, different test media and temperatures are used to accelerate possible ageing processes of the material. This is necessary for an estimation and evaluation of the lifetime of a material under specific environmental conditions.

The effects of hot air ageing were investigated for the earlier described black and bright EPDM compounds. The specimens were stored at 100 °C for 168 hours (7 days) and after that the mechanical properties tensile strength and elongation at break were determined again. Due to the hot air ageing, the mechanical properties of the compounds are influenced, as demonstrated in the diagrams on the next page (s. figure 5, 6).

The mechanical characteristics of the black, sulphur cured compounds with 155 phr mineral content are reduced after hot air ageing, the use of the submicron sized **APYRAL® 200SM** results in a better stability against ageing.

APYRAL® 120E in the bright peroxide cured compounds gives in a better retention of the mechanical properties of the compound after ageing, compared to the other mineral flame retardants in these tests. This effect has an even stronger impact because the mechanical characteristics of the compound containing **APYRAL® 120E** had already been better before the ageing.

The suitability of fine precipitated **APYRAL®** products for the use in EPDM is supported by this data.

A good balance of all properties of a compound is required. Its mechanics, flame retardancy, and ageing resistance must be adjusted according to the requirements for the intended use.

The broad range of available **APYRAL®** and **ACTILOX®** products offers the user flexibility for the formulation of an appropriate compound.

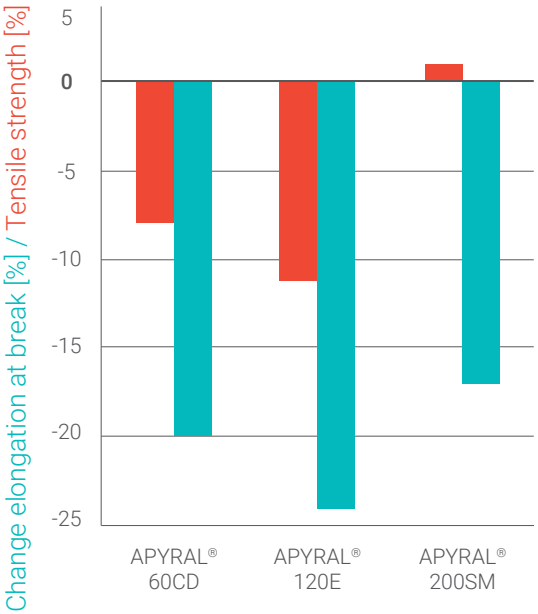


Figure 5: *Change of the mechanical properties of the **black** EPDM conpounds after ageing (100 °C, 7 days).*

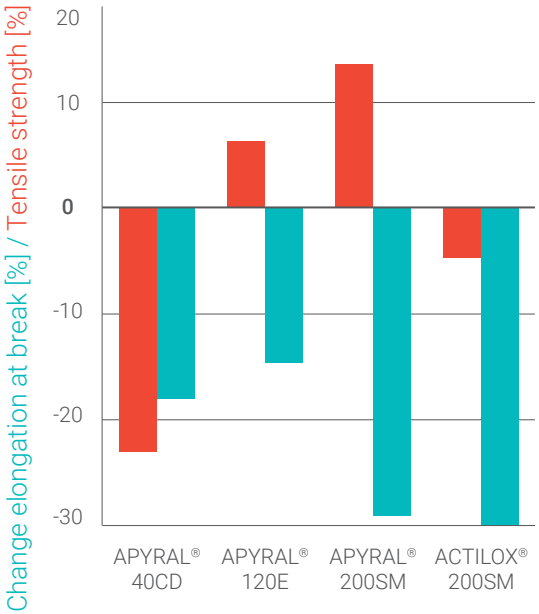


Figure 6: *Change of the mechanical properties of the **bright** EPDM compounds after ageing (100 °C, 7 days).*

EVM based compounds

Ethylene-vinylacetate-co-polymers are a diverse group of materials. They can either be used as thermoplastic materials (EVA), or those grades with a high vinyl acetate content (VA) (> 40 %) can be crosslinked to form elastomeric polymers (EVM, LEVAPREN®, ARLANXEO Deutschland GmbH).

As described in the introduction of this brochure, the M in the polymer description indicates the saturated polymer backbone of the molecules, the Methylene type of EVM. EVM based materials combine extraordinary ageing and media resistance with good flame resistance. This property profile makes them suitable polymers for a wide variety of applications. EVM based compounds are used for the production of cable sheathings or sealings. End uses are in public transport, the building sector or in oil rings and e.g. marine applications. In those sectors, ever increasing demands for fire safety have to be met.

In the following, some effects of mineral flame retardants shall be demonstrated on the basis of EVM compound formulations.The focus shall not only be on high flame resistance of the resulting compounds, but the balance of all compound properties must be considered, depending on the intended use.

In the following chapter data of different EVM compounds are shown. The data is sorted in dependence on the VA content of the EVM type, and on the fineness and the specific surface area of the **APYRAL®** products.

Formulation examples with EVM

The flame retardancy can be improved with increasing surface area (BET) of **APYRAL®** or by using EVM with increasing VA content. To show these effects in particular, the following EVM formulations were used.

Three EVM types from Arlanxeo (Deutschland GmbH, tradename: LEVAPREN®) were used for this investigation: EVM 500, EVM 600 and EVM 700 with VA contents of 50, 60 and 70 %.

As mineral flame retardants fine precipitated **APYRAL®** products were chosen: **APYRAL® 60CD** and **APYRAL® 120E**.

The other components of the compound were not changed.

EVM formulations.

Component \ Compound ID		L500-6	L500-11	L600-6	L600-11	L700-6	L700-11
LEVAPREN® 500 (VA = 50 %)	[phr]	100	100	–	–	–	–
LEVAPREN® 600 (VA = 60 %)	[phr]	–	–	100	100	–	–
LEVAPREN® 700 (VA = 70 %)	[phr]	–	–	–	–	100	100
APYRAL® 60CD (BET = 6 m^2/g)	[phr]	160	–	160	–	160	–
APYRAL® 120E (BET = 11 m^2/g)	[phr]	–	160	–	160	–	160
MAGLITE® DE (MgO)	[phr]	3	3	3	3	3	3
EDENOL® 888 (DOS)	[phr]	6	6	6	6	6	6
EDENOR® C 18 98-100	[phr]	1	1	1	1	1	1
AFLUX® 18	[phr]	1.5	1.5	1.5	1.5	1.5	1.5
GENIOSIL® GF 31	[phr]	1.6	1.6	1.6	1.6	1.6	1.6
RHENOFIT® TRIM/S	[phr]	1	1	1	1	1	1
PERKADOX® 14-40 B-PD	[phr]	6	6	6	6	6	6

Within a certain VA (vinyl acetate) content of the polymer, the tensile strength increases with increasing specific surface area of the used **APYRAL®**.

By using a constant specific surface area, the tensile strenght decreases with increasing VA content oft the polymer.

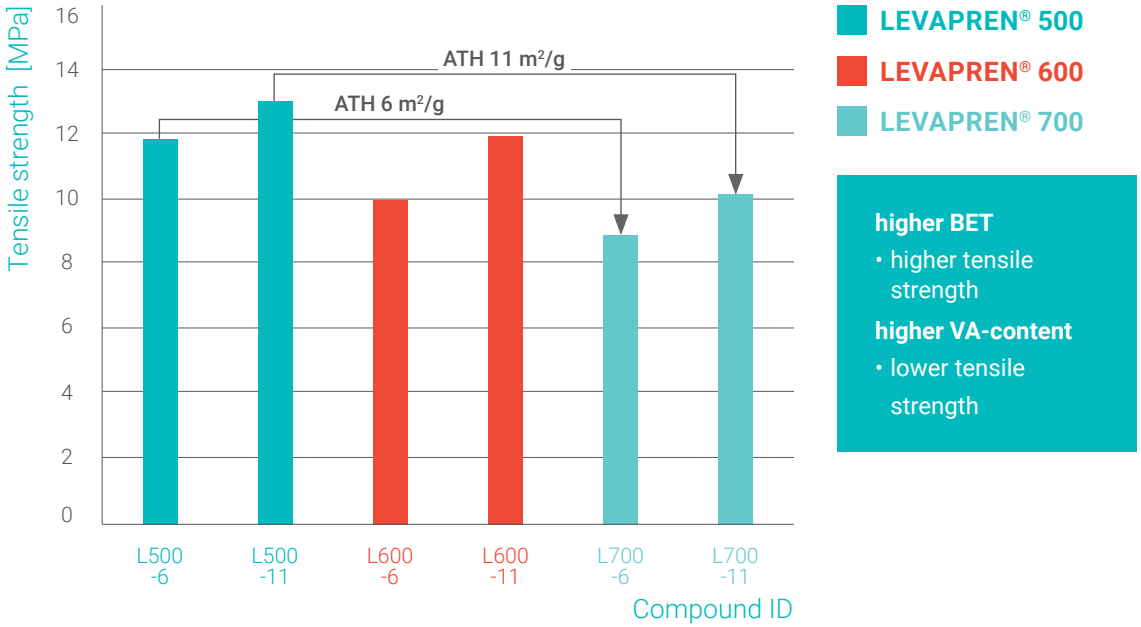


Figure 7: *Tensile strength of EVM compounds containing different VA-contents as well as 160 phr of the fine precipitated grades* **APYRAL® 60CD** *and* **APYRAL® 120E**.

Regarding the LOI as indicator for the resistance against ignitability of the compound, the following chart shows interesting interrelations between BET and VA-content.

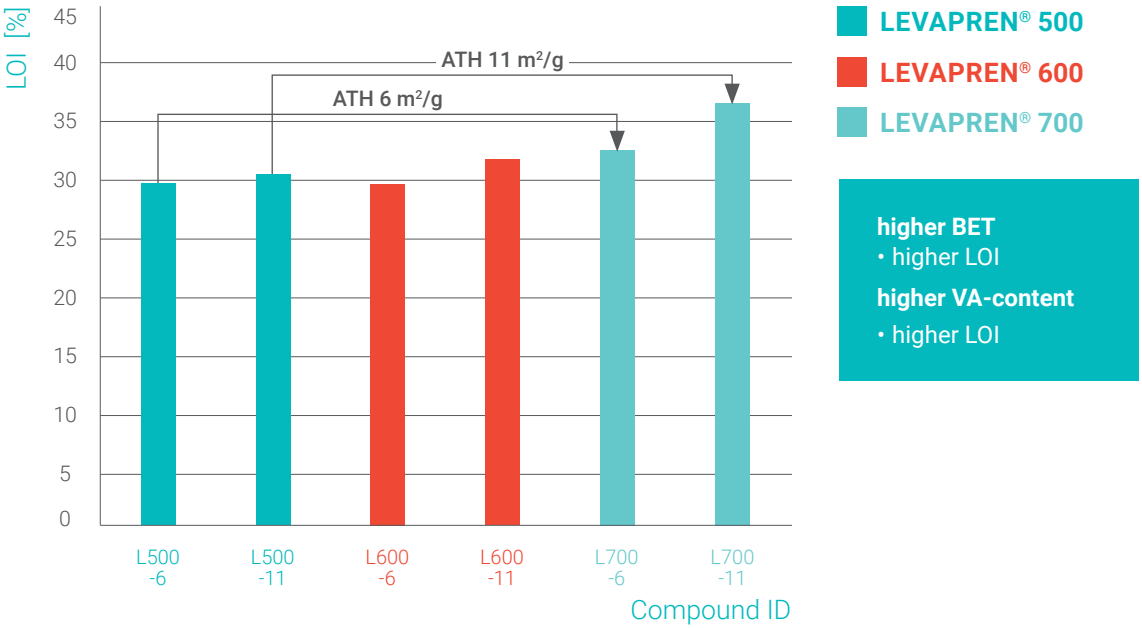


Figure 8: *Limiting oxigen index (LOI) of EVM compounds containing different VA-contents as well as 160 phr of the fine precipitated grades* **APYRAL® 60CD** *and* **APYRAL® 120E**.

Using the same **APYRAL®** grade but different VA contents, it is shown that the inherent flame retardancy of EVM is improved, if the VA content of the polymer is higher. The same effect can be observed by increasing the specific surface area of the mineral filler. With both, increasing VA content or specific surface area of the used **APYRAL®**, the LOI can be increased.

An important fact is that even if the specific surface area of **APYRAL®** increases, the media resistance of the compound will be unaffected.
The following chart shows that the specific surface area of **APYRAL®** has no negative influence on the oil swelling (IRM 902*, IRM 903* FUCHS Lubritech GmbH, Germany). To further reduce the swelling a polymer with higher VA content can be used.

Considering these correlations, it is easy to create tailor made compounds to balance the compound costs and the media resistance at given mechanical properties.

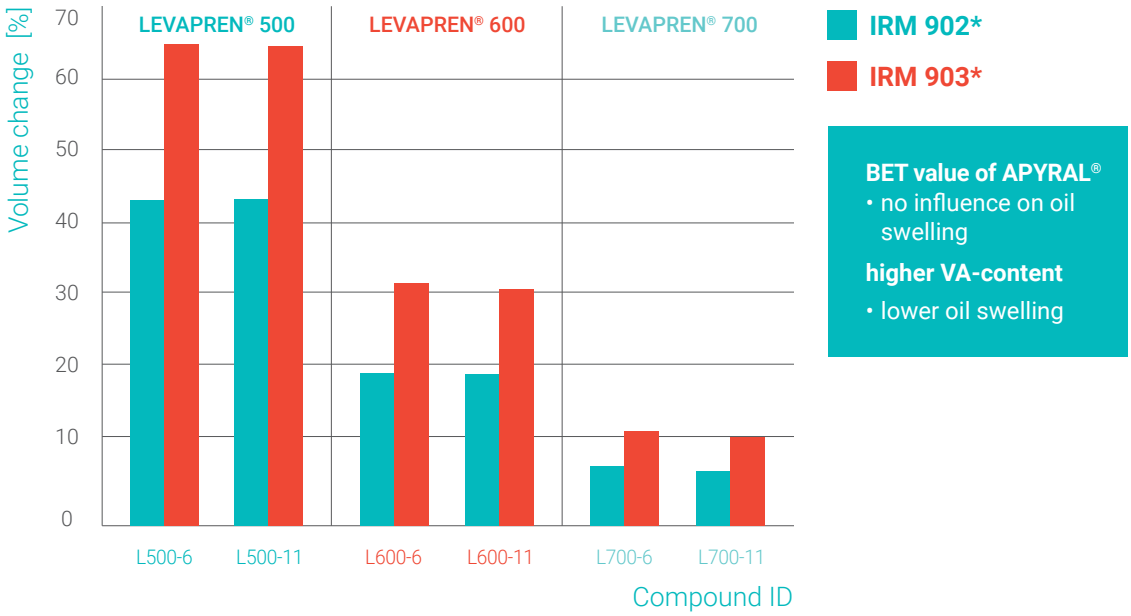


Figure 9: *Heat release rate (HRR) of bright EPDM compounds filled with 250 phr of different Nabaltec flame retardants.*

Combination of various NABALTEC products

The previous results in this brochure show that especially the very fine to nanosized Nabaltec products achieve improved properties in rubber compounds. The following chapter shall demonstrate how combinations of different Nabaltec products like **APYRAL® 120E** and **APYRAL® 60CD** as well as the nanosized boehmite **ACTILOX® 200SM** can be combined and even be replaced by each other without any losses in compound performance.

For the tests an EVM compound with 60 wt.-% VA and 140 phr of various filler combinations was used.

*Formulations with combination of various **APYRAL®** and **ACTILOX® 200SM***

	Unit	APYRAL® 60CD APYRAL® 200SM	APYRAL® 60CD APYRAL® 120E	APYRAL® 120E ACTILOX® 200SM	APYRAL® 120E ACTILOX® 200SM
LEVAPREN® 600	[phr]	100	100	100	100
APYRAL® 60CD	[phr]	**80**	**80**	**–**	**–**
APYRAL® 200SM	[phr]	**60**	**–**	**–**	**–**
APYRAL® 120E	[phr]	**–**	**60**	**120**	**100**
ACTILOX® 200SM	[phr]	**–**	**–**	**20**	**40**
Uniplex DOS	[phr]	20	20	20	20
Firebrake® ZB	[phr]	10	10	10	10
CORAX® N 550/30	[phr]	3.0	3.0	3.0	3.0
GENIOSIL® XL 33	[phr]	2.0	2.0	2.0	2.0
Maglite® DE	[phr]	3.0	3.0	3.0	3.0
RHENOFIT® DDA-70	[phr]	1.4	1.4	1.4	1.4
STABAXOL® P-powder	[phr]	0.5	0.5	0.5	0.5
AFLUX® 18	[phr]	1.5	1.5	1.5	1.5
Palmera® A9818	[phr]	1.0	1.0	1.0	1.0
RHENOFIT® TRIM/S	[phr]	2.0	2.0	2.0	2.0
PERKADOX® 14-40 B-PD	[phr]	6.5	6.5	6.5	6.5

Mechanical properties

As it is depicted in the charts next page, there are only minor differences in elongation at break, tensile strength and hardness Shore A when comparing all compositions. Opposite to this, modulus at 100 % elongation is higher with a combination of **APYRAL® 120E** and **ACTILOX® 200SM**.

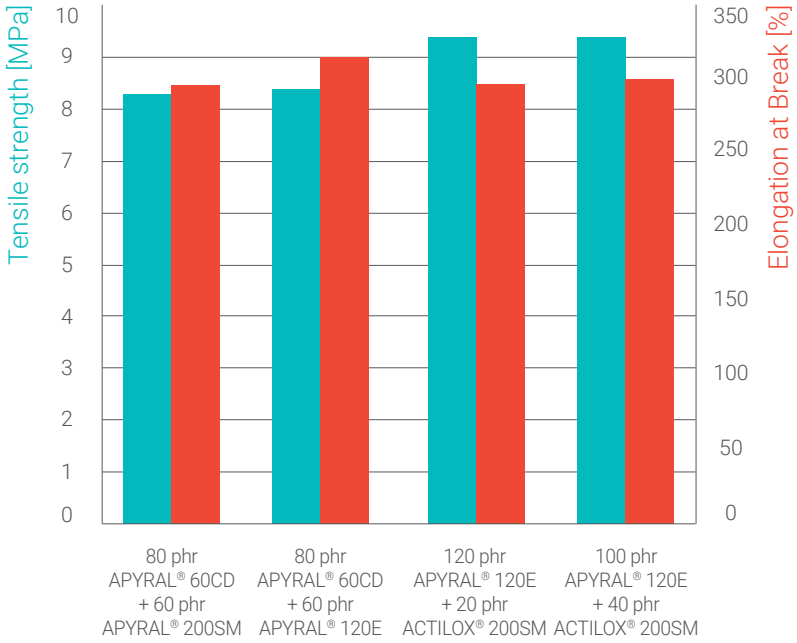


Figure 10: *Tensile strength and elongation at break of EVM compounds (60 wt.-% VA) filled with 140 phr of various filler combinations.*

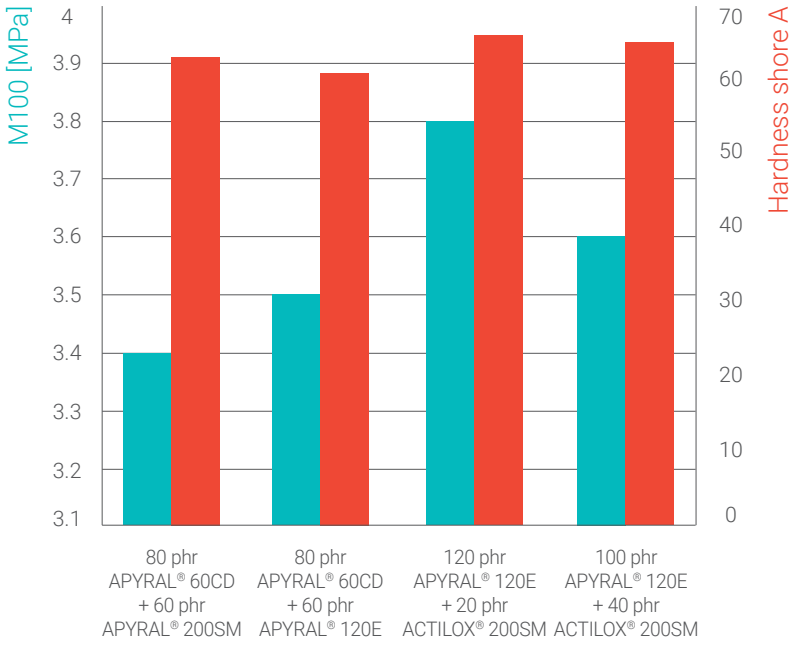


Figure 11: *Modulus and Shore A durometer of EVM compounds (60 wt.-% VA) filled with 140 phr of various filler combinations.*

Flame Retardancy

Cone calorimeter measurements were performed at 50 kW/m². As can be seen from the data in the table (below), there are likewise only minor differences between the compounds. Especially formulation 1 with **APYRAL® 200SM** and formulation 2 with **APYRAL® 120E** achieve almost equal values.

Interestingly, the combination of **APYRAL® 120E** and 20 wt.-% of Nabaltec's nanosized boehmite **ACTILOX® 200SM** brings improved results, especially the smoke production (TSR) is significantly reduced. All combinations reach a LOI of around 32 % O_2 and an UL 94 V-0 classification at 1.5 mm except the formulation with 40 phr **APYRAL® 200SM** (UL 94 V-1).

*Results of Cone calorimeter measurements of formulations with **APYRAL® 200SM** and **APYRAL® 60CD**.*

50 kW/m²	80 phr APYRAL® 60CD + 60 phr APYRAL® 200SM	80 phr APYRAL® 60CD + 60 phr APYRAL® 120E	120 phr APYRAL® 120E + 20 phr ACTILOX® 200SM	100 phr APYRAL® 120E + 40 phr ACTILOX® 200SM
PHRR [kW/m²]	133	133	128	135
MARHE [kW/m²]	88	86	82	85
THR [MJ/m²]	39	39	37	36
TSR [m²/m²]	261	267	222	235
tti [s]	45	46	45	44

Aging of EVM compounds

The retention of the mechanical property profile, even after long time use, is a decisive criterion for the selection of a certain compound. The required lifetime of cables, e.g. offshore cables for windmills or oil rigs, amounts to many years and the harsh environmental conditions (heat, cold, salt water) pose an additional challenge. Stringent tests are necessary to evaluate the suitability of a compound for such applications.

The aging behaviour of above mentioned compounds were analysed by means of hot air- and hot water test. The specimens were stored for 168 hours (7 days) at 175 °C in hot air and for 72 hours at 70 °C in water. After that, the mechanical characteristics were determined again and the changes compared to the data of the virgin compound were calculated in %. The results are given on the next two pages.

The hot air ageing shows that there is a wide spectrum in Nabaltec product combinations that can be used in EVM and can be replaced by each other without any losses in compound performance.

Immersion in water shows less alteration with all combinations not using **APYRAL® 200SM**. Especially the compound with **APYRAL® 60CD** and **APYRAL® 120E** achieves a great stability.

Hot air aging at 175 °C for 168 h.

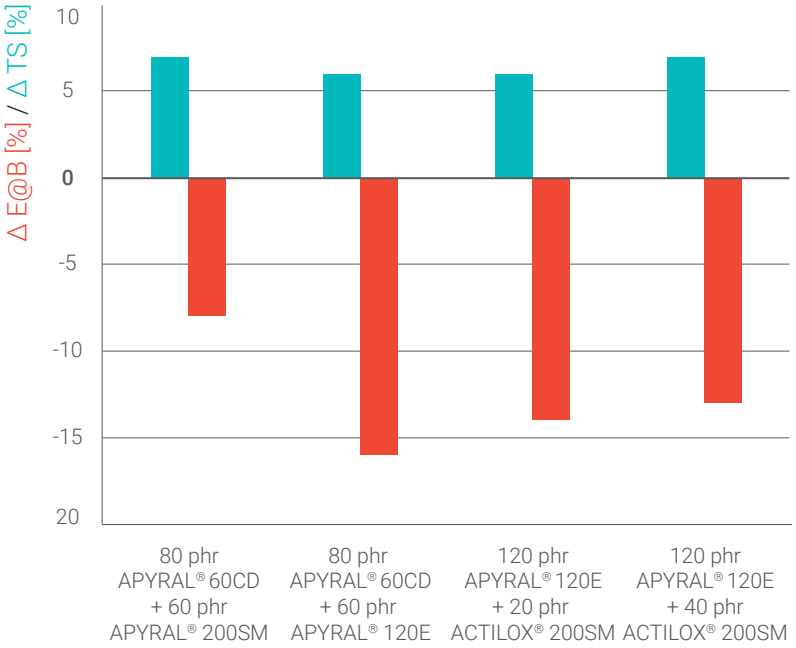


Figure 12: *Change of mechanical values of EVM compounds (60 wt.-% VA, 140 phr filler load)* ***after hot air aging (175 °C, 168 h).***

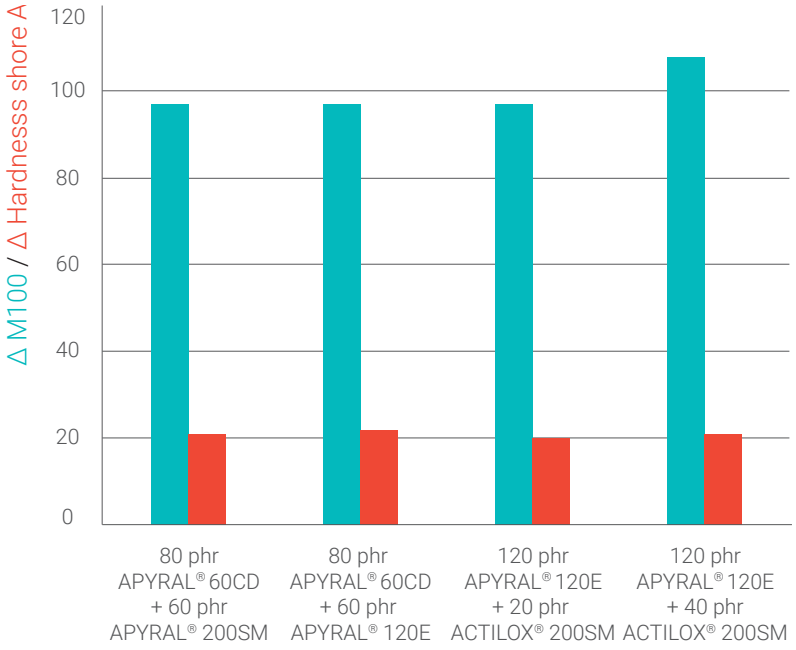


Figure 13: *Change of modulus and hardness of EVM compounds (60 wt.-% VA, 140 phr filler load) after* ***hot air aging (175 °C, 168 h).***

Immersion in water at 70°C for 72 h.

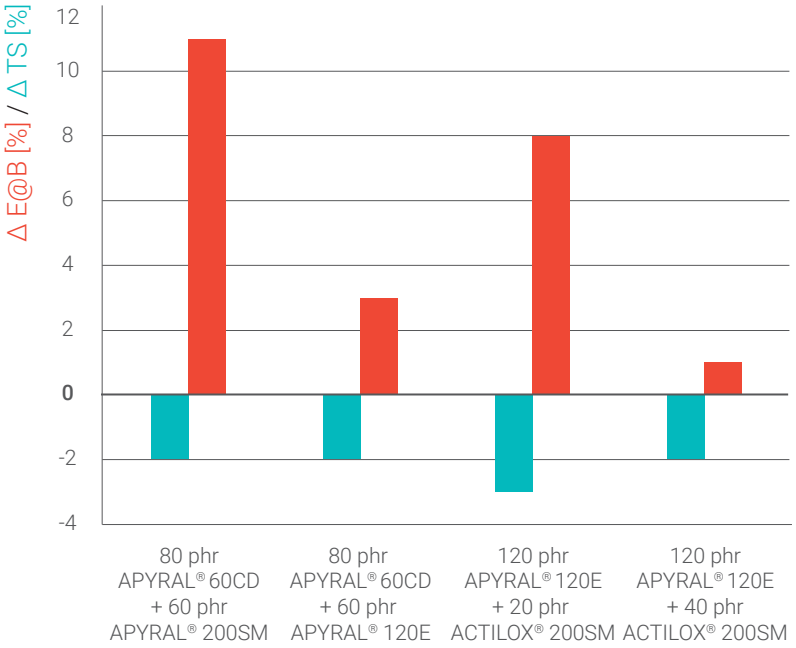


Figure 14: *Change of mechanical values of EVM compounds (60 wt.-% VA, 140 phr filler load) after* ***immersion in water (70 °C, 72 h).***

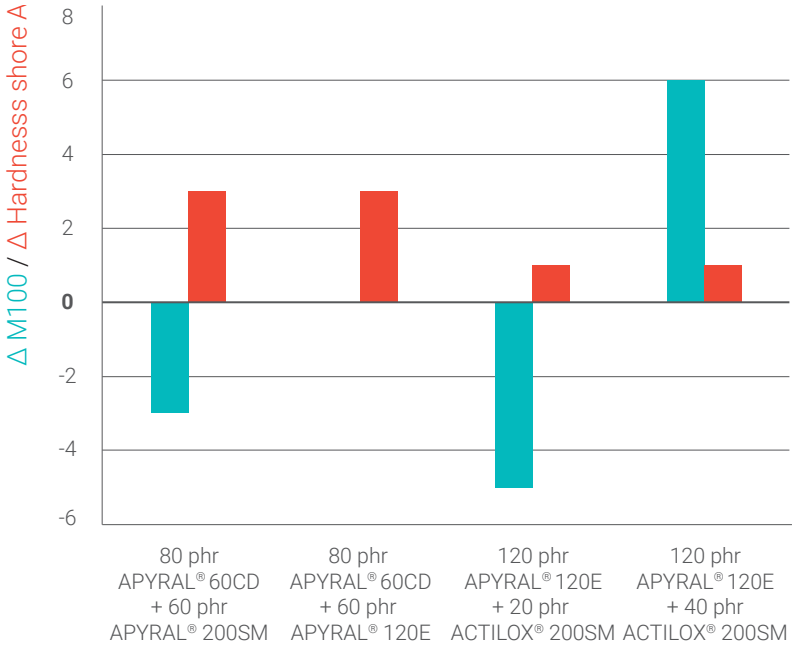


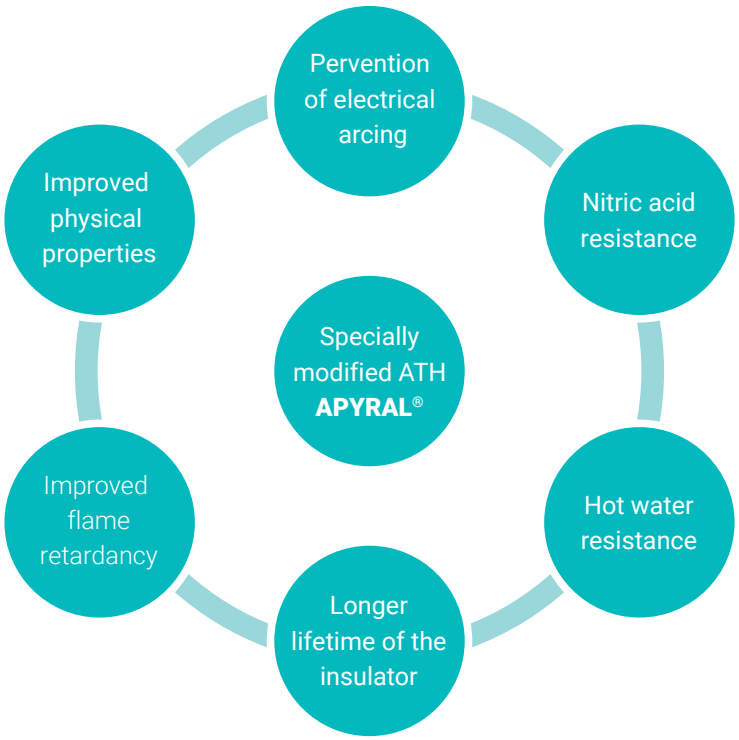
Figure 15: *Change of modulus and hardness of EVM compounds (60 wt.-% VA, 140 phr filler load) after* ***immersion in water (70 °C, 72 h).***

Silicone based compounds

Silicone rubber is a specialty elastomer that is used when its specific properties are necessary and offer an advantage for the user. This is true for example for special fire resistant cables in building applications which must stay functional even during and after a fire. Such cables are used for applications in elevators, alarming or fire exit lighting. To achieve the required properties, special ceramifying minerals need to be added.

Another application field of silicone rubber compounds is high voltage insulators. In these compounds, aluminium hydroxide is used to increase the life time of the insulator by reducing the impact of overvoltage [3]. Surface modification of fine precipitated **APYRAL**® grades from Nabaltec can be applied to further improve the mechanical and electrical properties of the silicone compounds.

In the following, it will be demonstrated why these optimized ATH grades are ideally suited for high voltage silicone rubber applications. The electrical performance was evaluated by testing arc resistance as well as resistance to tracking an erosion. To simulate acid rain, the resistance against nitric acid has been tested in a special test procedure.



Summarized visualization of the benefits offered by **APYRAL**® *grades in silicone rubber.*

The following table shows suitable Nabaltec grades to improve resistivity properties of silicone compounds.

Each tested silicone compound contain 120 phr of the different **APYRAL®** products. Silicone rubber with a durometer Shore A of 50 was used and the compounding was done on a lab two roll mill at room temperature. Vulcanization was performed at 170 °C for 10 minutes. Afterwards, the specimen were cured at 200 °C for 4 hours. In the following tables and diagrams some properties of the silicone compounds are shown.

*Nabaltec`s **APYRAL®** grades for use in silicone rubber.*

Product	Production plant
APYRAL® 40CD	Nabaltec, Germany / Nashtec, USA
APYRAL® 40 VS1	Nabaltec, Germany
APYRAL® 40VS	Naprotec, USA
APYRAL® 40 HS1	Nabaltec, Germany
APYRAL® 40H1	Naprotec, USA
APYRAL® 40T1	Naprotec, USA

Resistance against high voltage low current arcs

Due to a constant electric current travelling across an insulator's surface, the surface will eventually be damaged and become conductive. Arc resistance is the measure of time that is required to make an insulating surface conductive under high voltage low current arcs under carefully controlled laboratory conditions. With this test, the ability of the polymeric material to withstand an impact of a high voltage electrical arc for a certain time is determined [4].

In figure 16 it is shown, that the minimum requirement of 180 seconds of arc resistance according to IEC 62217:2012 (red line) is fulfilled with all used **APYRAL®** grades [5]. All specimen failed through a conductive path, no specimen ignited. It can also be seen, that all modified **APYRAL® 40** variants show a significant better arc resistance compared to unmodified **APYRAL®**. The blue vertical line marks the highest possible arc resistance using unmodified ATH.

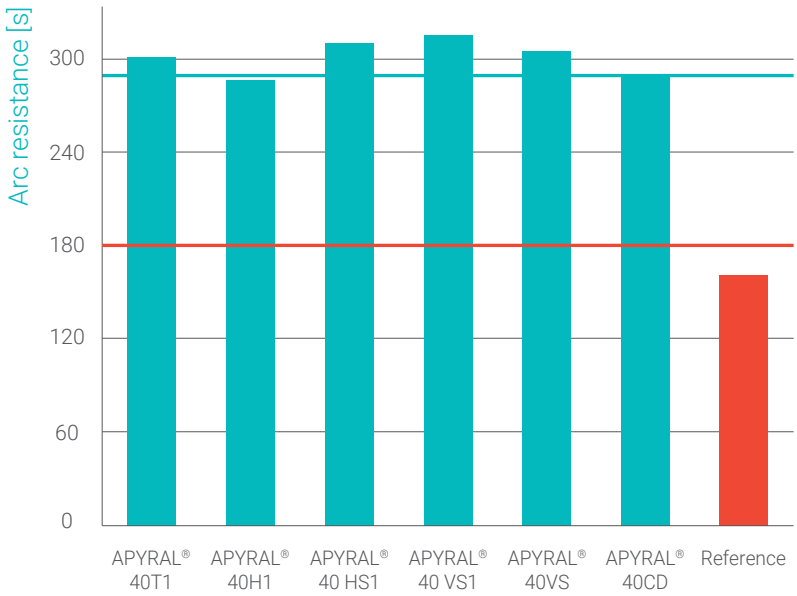


***Figure 16:** Arc resistance of silicone rubber filled with different ATH types.*

With **APYRAL® 40 VS1** an increase of 27 seconds in arc resistance is possible compared to unmodified **APYRAL® 40CD**. Due to a slower electrical aging using the special modified **APYRAL®** grades, the service life of the insulator can be significantly prolonged.

General performance of tested silicone compounds

Elasticity and tear strength for all tested materials are shown in figure 17. The results show that all ATH filled compounds guarantee a good rebound elasticity and only minor deterioration compared to an unfilled silicone compound. The minimum requirement for tear strength of materials that is used in HV insulators of 10 N/mm is met by all materials. Nevertheless the results show, that the tear strength can be significantly improved by using a hydrophobic coated **APYRAL®** grade like **APYRAL® 40H1**.

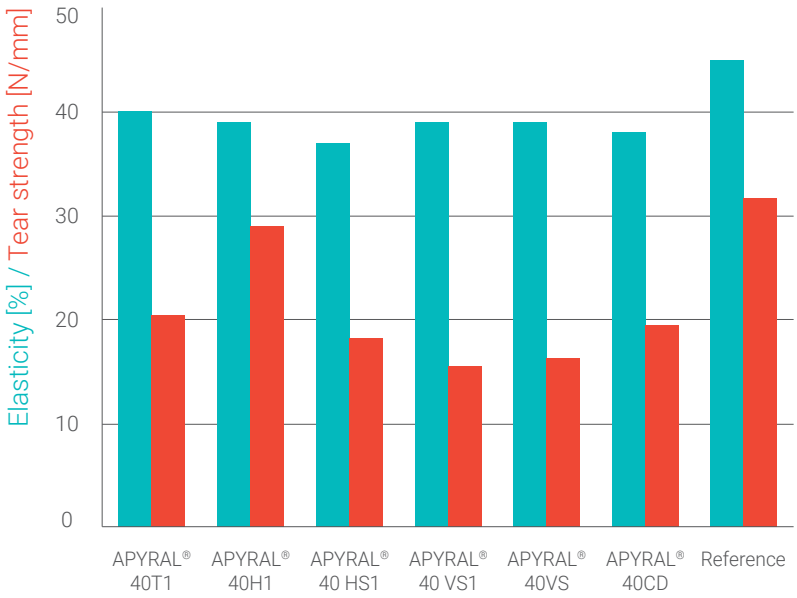


Figure 17: *Results of rebound elasticity and tear strength of cured silicone compounds filled with several* ***APYRAL®*** *grades.*

The results of compression set at different temperatures are shown in figure 18. It can be clearly seen, that very low compression set can be achieved even at high temperatures by using modified **APYRAL®** grades that bear a vinyl-moiety like **APYRAL® 40VS** or **APYRAL® 40 VS1**.

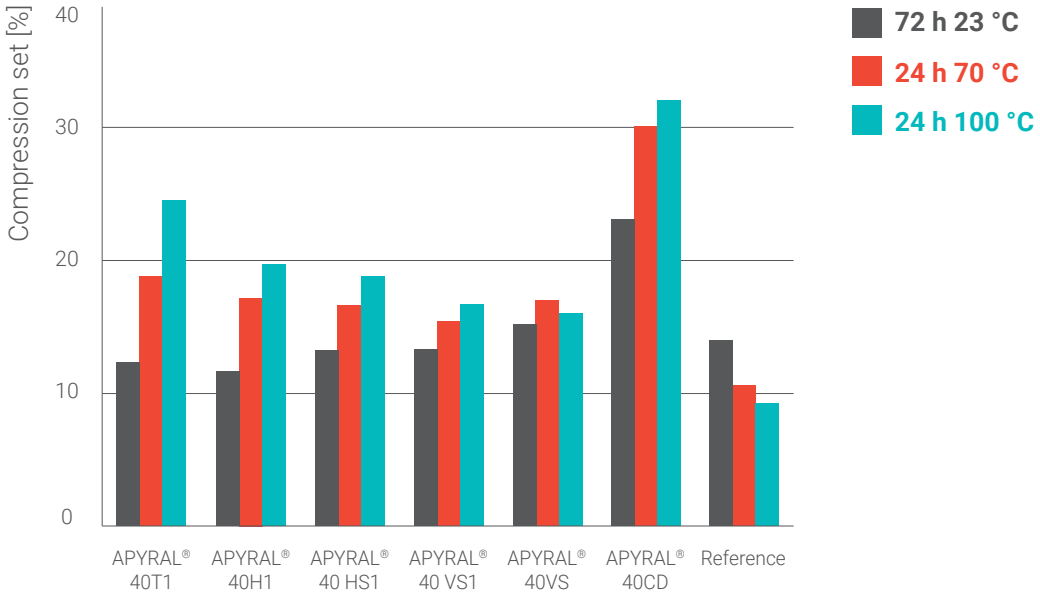


Figure 18: *Results of compression set of cured silicone compounds filled with different* ***APYRAL®*** *grades.*

Flame retardancy

The minimum requirements for overhead line insulators in outdoor use according to IEC 62217 in terms of resistance to flammability is a UL 94 V-0 classification [5]. All aluminum hydroxide filled materials easily passed the UL 94 V-0 classification and also showed high LOI values of around 45 % oxygen.

Nitric acid resistance

Resistance against nitric acid is another aspect that is required and needs to be improved. In general, aluminum hydroxide used as filler in a polymeric insulator is able to absorb energy from corona discharges and is therefore used to increase the resistance to tracking and erosion of the polymeric compound [3, 6]. During the process of corona discharges, ozone can be formed [7]. Together with nitrogen and water from the atmosphere, the formation of nitric acid is facilitated. The nitric acid will attack the ATH that is incorporated in the silicone based HV insulator. ATH will easily dissolve in the acidic medium which again negatively affects its ability to absorb energy. That will lead to an impairment of the insulator itself caused by an increase in surface discharge currents and finally results in a shorter lifetime of the material [8].

Therefore, the physical properties have been analyzed through the determination of fluid absorption during nitric acid test. In figure 19 the volume change of vulcanizates after treatment durations from 24 hours to 100 hours in 1M nitric acid is shown. As can be seen, the lowest volume change under harsh conditions is given using Nabaltec`s hydrophobic grades **APYRAL® 40 HS1** and **H1** as well as grade **APYRAL® 40T1**.

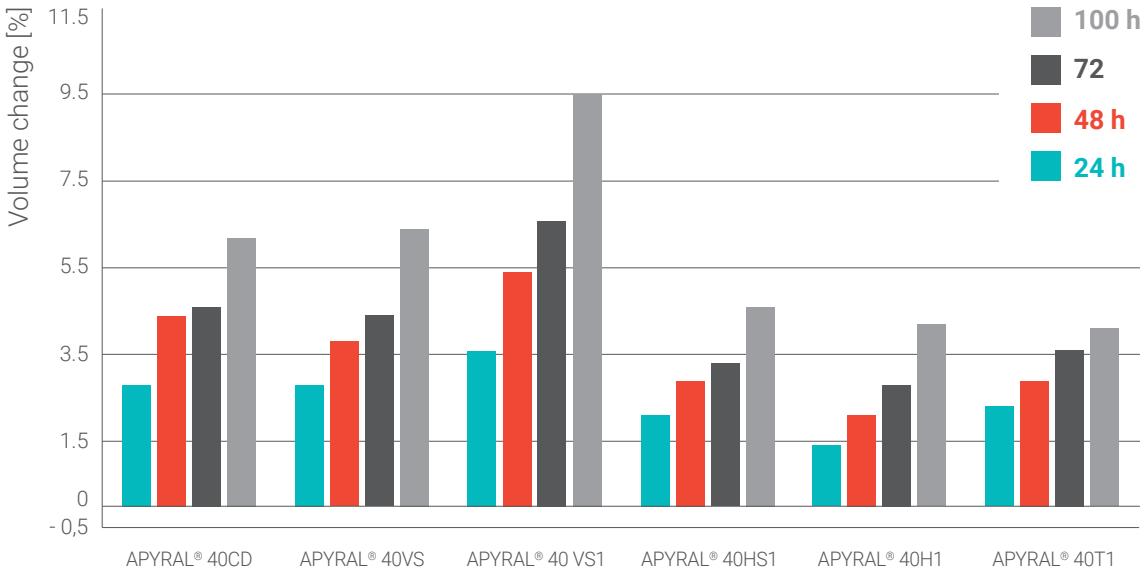


Figure 19: *Results of volume change after storage in 1M nitric acid for 100 hours in total.*

All modified **APYRAL®** grades developed by Nabaltec for the use in high voltage insulating applications show an improved nitric acid resistance compared to unmodified ATH or competitor products. Besides, with the right modification the resistance to corona ageing can be improved. These enhanced properties are key requirement to prolong the lifetime of a polymeric high voltage insulator. Due to the outstanding material properties, Nabaltec´s **APYRAL®** products can also be used in other silicone applications.

The final choice of product will always depend on the basic requirements of the end application and end product.

For more detailed information regarding Nabaltec´s **APYRAL®** products suitable for HV-insulation please refer to our whitepaper on our website.

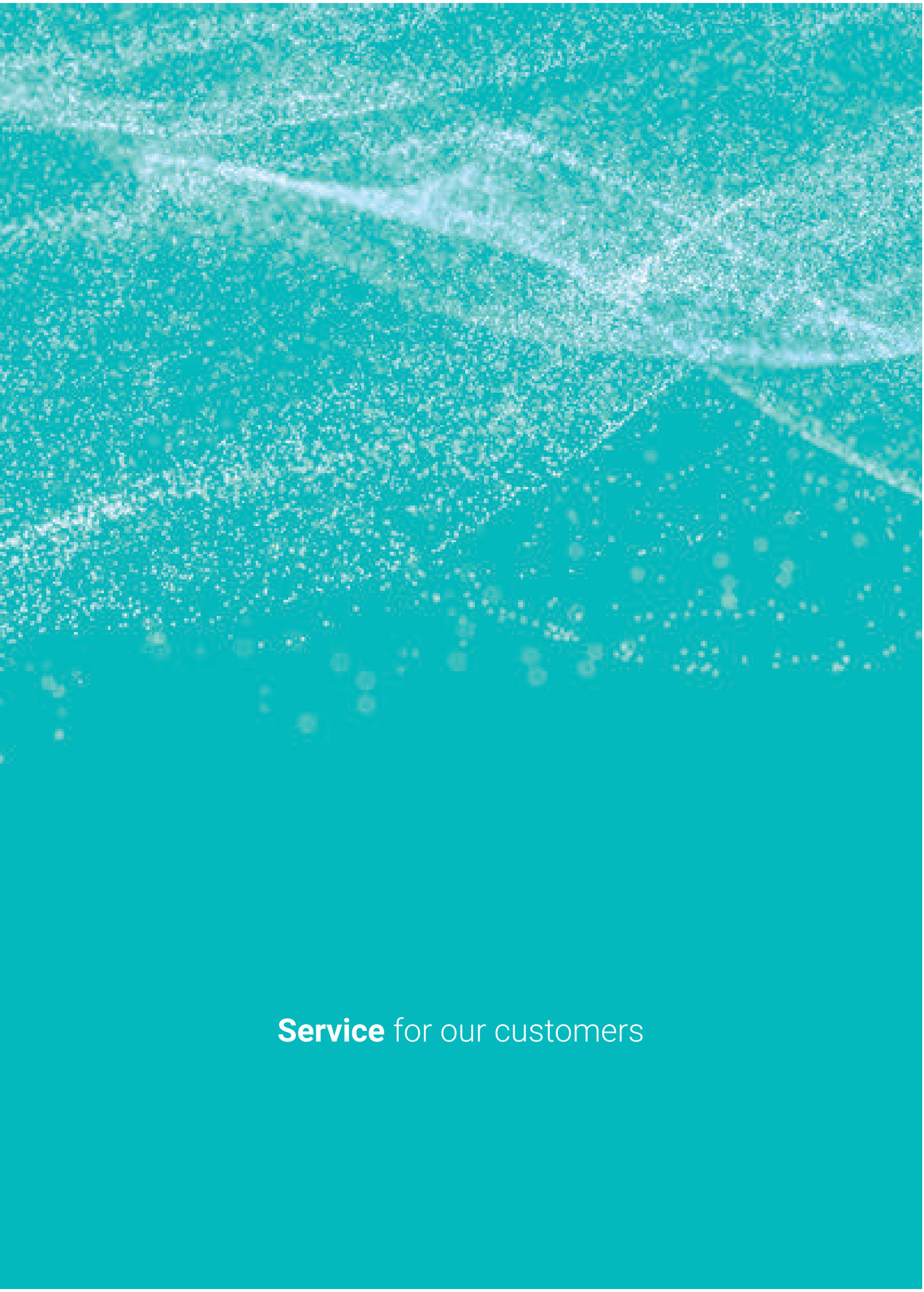
Annex

List of abbreviations

Abbreviation	Meaning
AOH	Aluminium oxide hydroxide, aluminium monohydrate, boehmite
ATH	Aluminium trihydrate, aluminium hydroxide, gibbsite
BET	Specific surface area according to Brunauer, Emmett, Teller
c_p	Thermal / heat capacity
CR	Chloroprene rubber
D50	Median particle diameter/size
EPDM	Ethylene-propylene-diene-elastomer
EPD	Ethylene propylene diene
EVA	Polyethylene-co-Vinylacetate
EVM	Polyethylene-co-Vinylacetate with a high VA-content
HFFR	Halogen free flame retardant
HRR	Heat release rate
LOI	Limiting oxygen index
LSOH	Low smoke zero halogen
M 500	Modulus at 500 % elongation
MAHRE	Maximum of average rate of heat emission
MQ	Methyl polysiloxane rubber
ML (1 + 4) 100 °C	Final torque at 100 °C after 4 min. testing
MU	Mooney viscosity
NBR	Nitril butadiene rubber
phr	Parts per hundred parts of resin
PHRR	Peak of heat release
PRSR	Peak rate of smoke release
PVC	Polyvinil chloride
RSR	Reat of snoke release
SBR	Styrene butadiene rubber
SiR	Silicone rubber
THR	Total heat release
TPU	Thermoplastic polyurethane
TSR	Total smoke release
tti	Time to ignition
UL 94 V	Underwriters Laboratories widely used flammability test standard for determining relative flammability for plastic materials
VA	Vinyl acetate

List of references

[1]	Ehrenstein, G.W., Pongratz, S., „Beständigkeit von Kunststoffen“, Hanser-Verlag, 2007.
[2]	Schnetger J., „Lexikon Kautschuktechnik“, Hüthig-Verlag, 2004.
[3]	D. Meng, B. -Y. Zhang, J. Chen, S. C. Lee, J. -Y. Lim, Tracking and erosion properties evaluation of polymeric insulating materials, IEEE Int. Conf. High Voltage Eng. and Appl. (ICHVE), 2016, pp.1-4. DOI: 10.1109 ICHVE.2016.7800616.
[4]	IEC 61621:1997, Dry, solid insulating materials - Resistance test to high-voltage, low-current arc discharges, 1997-09.
[5]	IEC 62217:2012, Polymeric HV insulators for indoor and outdoor use - General definitions, test methods and acceptance criteria, 2012-2009.
[6]	S. Kumagai, N. Yoshimura, Tracking and erosion of HTV silicone rubber and suppression mechanism of ATH. IEEE Trans. Dielectr. Electr. Insul. 2001, 8, (2), pp. 203-211. DOI: 10.1109/94.919930.
[7]	J. Chen, J.H. Davidson, Ozone Production in the Positive DC Corona Discharge: Model and Comparison to Experiments. Plasma Chem. Plasma Proc. 2002, 22, pp. 495 522. DOI: org/10.1023/A:1021315412208.
[8]	X. Wang, S. Kumagai, N. Yoshimura, Contamination performances of silicone rubber insulator subjected to acid rain. IEEE Trans. Dielectr. Electr. Insul. 1998, 5, (6), pp. 909-916. DOI: 10.1109/94.740775.



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.

The successful implementation of this development and the intensive customer consultations enable Nabaltec AG an interaction with our customers in a cooperative, responsible and innovative manner. This culminates in the development of high performance products at the customer as well as in our facility.

Additionally, we have the capacity to fashion tailor made products for special customer requirements and their highly sophisticated and demanding markets.

Laboratory services

Our analysis centre is responsible for independent production and quality control. It offers laboratory services for customers intending to use our large analytical equipment.

With this excellent equipment we are able to execute analytic tests in the area of inorganic solids, trace elements and water quality.

The certification in accordance with DIN EN ISO 17025 confirms the high service standards of our lab.

We will gladly inform you about our capabilities.

Nabaltec
product portfolio

ACTILOX®

Boehmite, as flame retardant filler and catalyst carrier

APYRAL® AOH

Boehmite, as flame retardant and functional filler

APYRAL®

Aluminium hydroxides, as flame retardant and functional filler

GRANALOX®

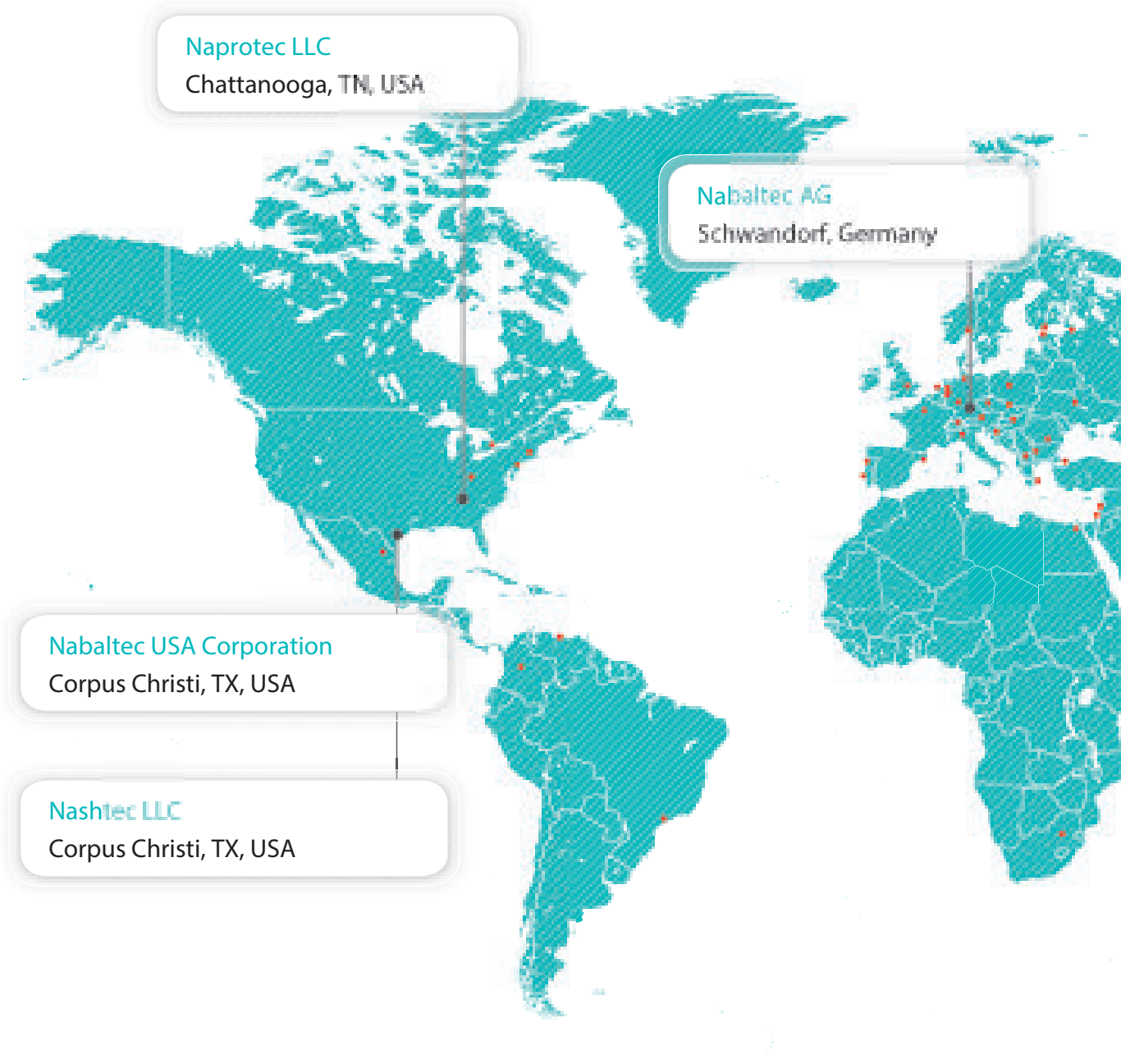
Ceramic bodies, for the production of engineering ceramics

NABALOX®

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

Nabaltec
worldwide

Visit us at our website www.nabaltec.de where you will find the latest company updates and recent versions of all available certificates free for download as PDF-documents.



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

09 / 2022