Casico[™] Novel flame retardant technology



About Borealis

Borealis is a leading provider of innovative solutions in the fields of polyolefins, base chemicals and fertilizers. With headquarters in Vienna, Austria, Borealis currently employs around 6,400 and operates in over 120 countries. It generated EUR 8.1 billion in sales revenue in 2013. The International Petroleum Investment Company (IPIC) of Abu Dhabi owns 64% of the company, with the remaining 36% owned by OMV, the leading energy group in the European growth belt. Borealis provides services and products to customers around the world in collaboration with Borouge, a joint venture with the Abu Dhabi National Oil Company (ADNOC).

Building on its proprietary Borstar® and Borlink[™] technologies and 50 years of experience in polyolefins, Borealis and Borouge support key industries including infrastructure, automotive and advanced packaging.

The Borouge 3 plant expansion in Abu Dhabi will be fully operational in 2014. Borouge 3 will deliver an additional 2.5 million tonnes of capacity when fully ramped up, bringing the total Borouge capacity to 4.5 million tonnes. Borealis and Borouge will then have approximately 8 million tonnes of polyolefin capacity. Borealis offers a wide range of base chemicals, including melamine, phenol, acetone, ethylene, propylene, butadiene and pygas, servicing a wide range of industries. Together with Borouge the two companies will produce approximately 6 million tonnes of Base Chemicals in 2014.

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Borealis and Borouge aim to proactively benefit society by taking on real societal challenges and offering real solutions. Both companies are committed to the principles of Responsible Care®, an initiative to improve safety performance within the chemical industry, and contribute to solve the world's water and sanitation challenges through product innovation and their Water for the World[™] programme.

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Fire test safety

Material safety in Wire & Cable

Following the invention of polyethylene (PE) in 1936, the value of its excellent electrical properties was quickly recognised and became the main focus for its rapid development. Almost from the outset it was adopted as insulation in communication cables. With the invention of the peroxide crosslinking technique in the 1950's, PE also became the preferred material for the insulation of Medium and High Voltage cables. Then with the later development of silane grafting technologies and the arrival of ethylenevinylsilane copolymers, competitive techniques were also developed for Low Voltage cables. As a result, cables with crosslinked polyethylene (XLPE) insulation and PE jackets have gradually become the material of choice for energy distribution networks.



Cable mounting for large scale fire test

If infrastructure cabling is predominantly polyolefin, building and equipment cables, which make up the largest percentage of all wiring and cabling, are usually PVCbased. Due to these systems being installed within buildings and therefore close to the consumer, flame retardancy is an issue.

Flame retardancy is of concern in respect of all materials used in domestic, commercial and industrial environments. From the fabric of buildings and vehicles to their furniture and fittings, minimising or eliminating materials that potentially cause fire or contribute to its spread is a fundamental necessity to ensure the safety of people and the protection of property. Electrical wires and cables are essential to the functioning of virtually every aspect of modern life, in the home, transportation, communications and in the workplace, and therefore their composition is of critical importance in controlling fire risks.

Flame retardant (FR) issues are complex. While it is true that PVC has relatively low calorific value and therefore low burning potential, when exposed to fire it generates dense smoke, toxic gases and corrosive combustion products (hydrochloric acid), which may inhibit evacuation, damage equipment and even building structures. On the other hand, polyolefin compounds have an inherently higher calorific value and have difficulty matching the properties of PVC in terms of combustibility. Nevertheless, it can be claimed with good justification that in every other respect polyolefin products have superior combustion properties to those of PVC.

Why polyolefin?

- Excellent dielectric properties
- Balance of physical and barrier performance
- No plasticiser to give migration and embrittlement problems
- Combustion properties:
- Reduced smoke, effluent corrosivity & toxicity
 High heat release can be compensated by downsizing
- Excellent processing characteristics
- End of life/environment
- Same building blocks as nature carbon, hydrogen, silicon and oxygen
- Disposal by reprocessing or as fuel substitute with heat recovery

In order to enable cable makers to capitalise on the broader advantages offered by polyolefins, developments in the 1980's to reduce their flamability resulted in compounds heavily loaded with aluminium hydroxide. These compounds perform well in fire situations and are therefore used for



Preparation for large scale fire test

special cables intended for critical installations such as public buildings, subways, ships and nuclear power stations. However, they are costly and their processing requires investment in extrusion equipment with low compression screws and optimised crossheads.

Furthermore, the low extrusion temperature and highly viscous melt of these compounds results in a significant reduction in cable production speed compared with ordinary PVC or PE. These drawbacks make this technology impracticable as an alternative to PVC for standard cables.

Flame retardant technologies

Polyolefins have good combustion properties with regard to smoke, corrosiveness and toxicity. Flame retardant additives in polyolefins have the effect of slowing the rate of combustion as well as reducing their calorific value.

The usual technique for making flame retardant polyolefin compounds for Wire & Cable applications is by high loadings (50–65%) of aluminium hydroxide (Table 1). Two alternative flame retardant fillers, chalk and magnesium hydroxide are also shown. Flame retardancy is achieved through combination with the correct polymer system (Table 2).



Large scale fire test

Note: the synergy between Silicon Gum and PE copolymers is a patented technology of Borealis.

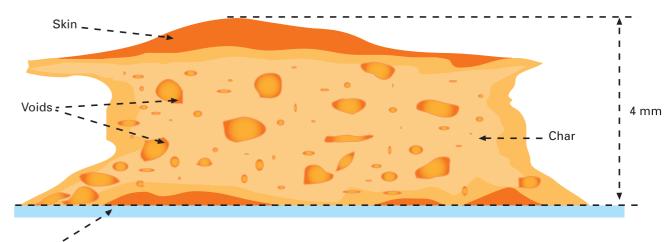
Туре	Temp. Dec. [°C]	Addition [%]
CaCO ₃	± 700	20-40
Al(OH) ₃	± 200	50-65
Mg(OH) ₂	± 300	50-65

Table 1: Inorganic additives used as flame retardants for W&C applications

Filler	Polymer
CaCO ₃	PE-copolymers, silicon elastomer PP
Al(OH) ₃	EVA/HDPE
Mg(OH) ₂	PE-copolymers PP

Table 2: Optimal combinations filler/polymer

Aluminium hydroxide starts to decompose at 200°C. This limits extrusion temperature to about 160°C, which is below optimum for a high viscosity material. The alternative flame retardants do not have this limitation. Moreover, Borealis flame retardant compounds have a melt viscosity similar to unfilled PE. Consequently they can be processed on standard PVC and PE extruders, without any major modifications, with a similar extrusion speed to that of unfilled PE and PVC. The Borealis patented technology is called Casico[™]. During burning, Casico forms a physically and thermally stable charred layer that protects the polymer from further burning (Figure 1). This effect is achieved with a relatively small amount of chalk combined with an oxygen containing ethylene copolymer and a minor fraction of silicon elastomer. The properties and cost structure of this technology make it most interesting for the replacement of PVC in standard building cables.



Surface of the cone calorimeter sample holder

Novel char forming system (Casico) – mechanism

Active parts for the char formation are:

- 1. Polar ethylene copolymers
- 2. Filler e.g. $CaCO_3$
- 3. Silicon elastomer
- a. The decomposition products of the copolymer effervesce and generate a cellular structure.
- b. The polar decomposition part of the copolymer is at an early stage of the burning process reacting with the chalk, binding it to the char. At the same time water and carbondioxide are formed, diluting the burnable gases.
- c. The char is stable, due to the decomposition of the silicon gum which is forming a glasslike layer.

Figure 1: Cross section of ash from FR4807 burned on the Cone calorimeter

Establishing flame retardant performance

Flame retardant products can be compared using a cone calorimeter. The equipment is based on the principle of oxygen consumption calorimetry. The heat of combustion of any organic material is directly related to the amount of oxygen required for combustion - 13.1 MJ of heat is released per kg oxygen consumed.

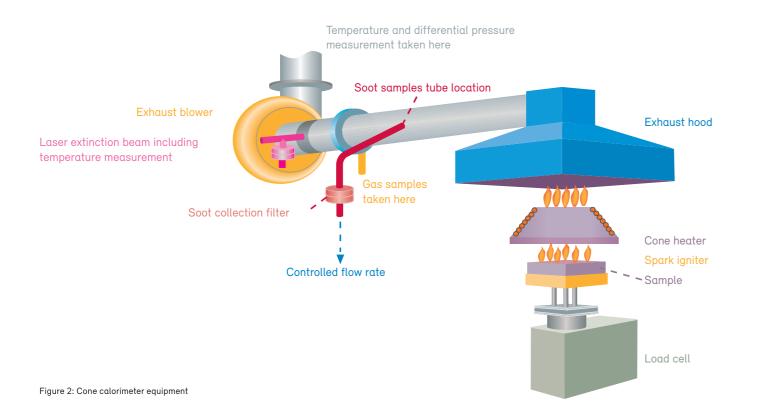
In the cone calorimeter (Figure 2), the specimen is exposed to a specific irradiance. It is placed on a load cell and weight loss is monitored during the test. The combustion gases are collected in a hood and the rate of heat release is estimated by measuring the oxygen consumption and gas flow rate in the duct. Levels of carbon monoxide (CO), carbon dioxide (CO₂) and light obscuration due to smoke are measured. Much data can be derived from the parameters measured by the cone calorimeter.

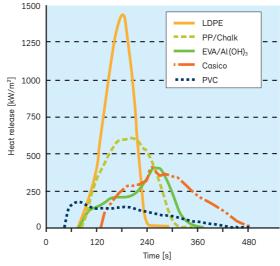
Cone calorimeter

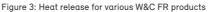
Ignition time [s]

- Burning time [s]
- \cdot Rate of heat release, RHR, (ave or max) $[kW/m^2]$
- \cdot Heat of combustion, HC, [MJ/dm³]
- \cdot Smoke extinction area, SEA [m²/dm³]
- CO and CO₂ concentrations [kg/dm³]

Various flame retardant systems of interest for Wire & Cable applications have been measured using a cone calorimeter (35 kW/m², 3 mm plaques) according to ISO 5660-1.







Cone calorime Comparison o	eter f combustion behavior
Product	Description
Casico	Chalk filled, Polysiloxane modified, Copolymer
LDPE	Low density polyethylene
PP/Chalk	Chalk filled, polypropylene
EVA/Al(OH)3	Aluminium trihydrate filled, EVA
PVC	General jacketing compound building wire

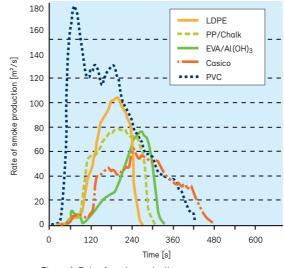


Figure 4: Rate of smoke production

The material that begins to burn first is PVC. It has, however, the lowest Total Heat Release (THR) of the materials investigated (Figure 3). Non-flame retardant low density polyethylene (LDPE) has a longer ignition time but a very short and intensive peak heat release (PHR). By adding filler, the PHR is reduced, especially for the hydrate filled ethylene (vinyl acetate) copolymer. The ignition times are the same as for unfilled LDPE. The Casico compound has the longest ignition time and a similar THR and PHR to the hydrate filled compound. Light obscuration is presented in Figure 5. As expected, PVC gives off much more dense smoke than the polyolefin based compounds.

Fire growth rate (FIGRA) is plotted against specific extinction area (SEA) as an indication of overall product hazard (Figure 5). FIGRA is defined as the maximum heat release divided by the time to maximum heat release. Thus, a fire which generates a high heat release in a short time is defined as hazardous. SEA is the measure of smoke density. The preferred products are therefore those combining low FIGRA with low SEA.

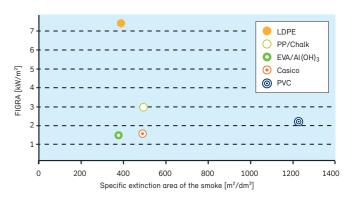


Figure 5: Product hazard vs smoke generation

In addition to the density of smoke, toxicity and corrosiveness are also important factors. The majority of fatalities are due to the inhalation of poisonous gases and not directly to contact with fire. Carbon monoxide (CO) is the component in most fire gases that causes the greatest immediate threat to life. During combustion, a PVC cable compound can generate significantly more CO than an equivalent volume of polyolefin (Figure 6).

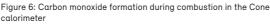
The pH and the conductivity of different flame retardant systems have been measured according to IEC 60 754-2 (Figures 7 & 8). The pH of the combustion fumes from polyolefin compounds is about 6 and the conductivity about 10 μ S/cm. The smoke from PVC results in a pH of about 2 and a conductivity of 2890 μ S/cm.

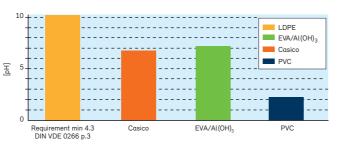
These results are expected. The degradation products from polyolefins and its additives are not normally corrosive. A typical PVC compound intended for cable applications will generate about 250 g/kg hydrogen chloride (HCl) when heated or burnt. This fits well with the measured pH. HCl is a strong acid and powerful irritant, which increases the toxicity of the fire gases.

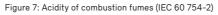
Due to its severe effects on the eyes and lungs, HCl gas adversely affects the ability to escape from a fire situation. The gas is corrosive, destroying metal surfaces, electronic apparatus and in the worst cases diminishing the strength of reinforced concrete. Often, the cost of damage due to corrosion far exceeds the cost of damage directly attributed to the fire.

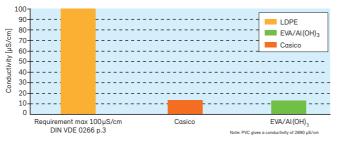
The smoke density of different materials has also been investigated using the NBS smoke chamber (Figure 9). In the flame phase PVC reaches the maximum smoke density of 350 almost immediately – within approximately 6 seconds. The results correspond with the smoke data from the cone calorimeter i.e. the polyolefin based compounds show much lower smoke densities.



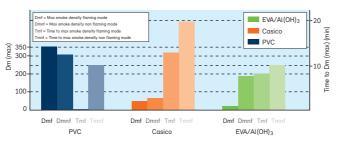








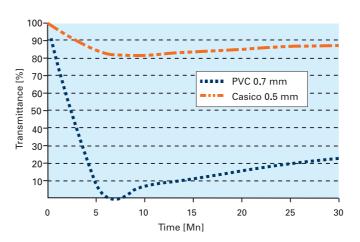






Similar performance is found in respect of cables (Figure 10). The measurement is conducted in a 3 m³ test according to IEC 61 034-1 and 2. Test pieces consist of straight 1 m samples of cables – the number of test pieces depends on the outer diameter of the cable. The samples are laid horizontally and centred above a tray containing one litre of alcohol, which is then ignited. The test is ended when there is no decrease in light transmittance in a 5-minute period after the fire source has been extinguished, or when the test duration has reached 40 minutes. Light transmittance is recorded as a function of time.

The requirement for this test is a minimum 50% optical transmittance value. The cable in this case is a three core building wire corresponding to German building wire standards. In Germany all building wires are of jacketed construction and consist of a number of cores twisted together, a bedding compound and an outer jacket. The PVC reference cable conformed to VDE 0250 Part 204, type NYM. The non-halogen flame retardant (NHFR) developments conform to VDE 0250 Part 215, Type NHMH. The various materials used in the cable construction are described in Figure 10.



VDE 0250 Part 215 is a specification aimed at defining a NHFR cable which matches the overall performance of PVC but with superior low smoke and fume (LSF) properties. In comparison with traditional LSF cables the cost premium is modest.

- This is achieved through a number of factors:
- 1. The use of Casico type compounds as jacket
- 2. By moving from PVC to thermoplastic polypropylene as insulation, improved electrical properties make it possible to reduce insulation wall thickness from 0.7 to 0.5 mm

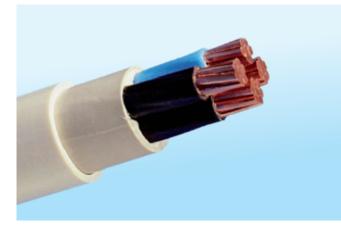
In comparison with traditional LSF cable, the vertical flame test requirement is relaxed from a bunch cable flame test (IEC 60 332-3) to the standard single wire burning test (IEC 60 332-1).

Description of cables tested in 3 m³ test			
Insulation	Thickness [mm]	Jacket	
PVC 1 (YI1)	0.7	PVC (YM1)	
Casico PP/PP4821	0.5	Casico (FR4803)	

Figure 10: 3 m^3 test building wires (3 x 1.5 mm^2). Cable 2, 3 and 4 produced according to VDE 0250 pt 215 (NHMH), cable 1 produced according to VDE 0250 pt 204 (NYM)

The application of NHFR materials

The main application of hydrate filled materials is as jacketing for 90°C-rated power (1 kV) cables (BS6724, VDE 0250 Part 214) and various communication cables. In both applications, the same bunch cable tests must be fulfilled e.g. IEC 60 332-3. The corresponding PVC cable (BS 6346, VDE 0250 Part 204) has a lower temperature rating (70°C) and has a more relaxed specification in terms of flame retardancy, IEC 60 332-1. With improved properties and a cost structure closer to that of PVC cables, Casico-based materials offer a realistic alternative to PVC for these standard cable applications.



Main applications are:

- Building wire jacket (VDE 0250 Part 215 'NHMH') SS 424 02 19-5 and SS 242 02 19-6
- Alternative to PVC in all 1 kV cables
- Data cable jacket (EN50290)
- Jacket and insulation flexible wires
- Insulation appliances and conduit wires
- Exchange wire jacket
- Telecom cable jacket
- · Jacket over XLPE/mica tape in safety cables

As yet no specification exists for NHFR cables in most of these applications. They are therefore specified according to existing PVC cable criteria.

Sources for further information

- 1) Low cost building wire in a large scale fire, Plastics in Telecommunication VIII, London, September 1998.
- 2) Internal telephone:

The development of a cost effective internal telephone cable having good flame retardancy and the lowest possible halogen content, Plastics in Tele communication VII, London, September 1998.

3) Casico technology:

Novel halogen free flame retardant polyolefins intended for internal wiring - Properties and flame retardant mechanism, IWCS, Philadelphia (November 1998). The cost effective replacement of halogenated materials for the wiring of buildings, Eurocable 1997, Manchester, UK, June 1997.

4) Euroclassification and legislation The Euroclassification of cables. Eurocable 1999, Delft, June 1999,



- 5) The flame retardant mechanism of polyolefins modified with chalk and silicone elastomer, Fire and Materials 2003, 27:51-70 (DOI:10.1002/fam.817), A. Hermansson, T. Hjertberg and B.Å. Sultan.
- 6) Extrusion:

High speed extrusion of non halogenated flame retardant compounds based on silicon elastomer modified polyolefin, Eurocable, Antwerp, 1998.

7) Toxicity:

Combustion atmosphere toxicity of polymeric materials intended for internal cables, FROCC Symposium, Cologne, March 2002. The toxicity of combustion gases, International Wire & Cable Symposium (IWCS), Providence, USA, November 2005.

Borealis – Dedicated to Wire & Cable Solutions

Borealis and Borouge are the world's leading providers of innovative, value creating plastics solutions for the wire and cable industry. Our solutions are customer-driven and designed to satisfy the industry's continuously evolving demands for higher technical performance. Consequently, they can be found in the most challenging EHV and HV cable applications, as well as MV and LV energy transmission and distribution cables, building wires, and communications cables.

In answer to the need for production, installation and cable-system lifetime enhancements, we create the innovation links that secure world-class, step-change solutions and benefit the whole wire and cable value chain. Through the introduction of unique polymer technologies, which include Borlink[™], Visico[™]/Ambicat[™], Borstar®, and Casico[™], we continue to pioneer the development of advanced insulation and jacketing systems for both energy and communication cables.

Built on more than 50 years experience, Borealis and Borouge have a well-established track record in serving customers' needs with the consistently high quality products expected of global leaders. We are committed to extending that leadership position and our role as reliable partners for the long-term – a commitment not only supported by our forward thinking in innovative solutions, but also confirmed by ongoing investments for our customers' continued success.

Putting customers' needs at the centre of our planning is reflected in Borealis' largest investment in Europe to date, the new 350,000 t/y high-pressure, low-density PE plant in Stenungsund, Sweden, was inaugurated in June 2010, further strengthening Borealis' capabilities to meet the needs of the growing wire and cable markets. Furthermore, Borouge's expansion of Borstar® and Borlink™ capacity in Abu Dhabi, UAE, allows us to satisfy growing customer demand for wire and cable products in the Middle East and Asia Pacific markets and other emerging markets.

Through ongoing research and development, investment in the future and a dedicated team with solid industry knowledge, we aim to remain fully responsive to our customers' needs throughout the world.

Bringing energy all around | Date of issue: March 2014

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