DION® FR
Fire Retardant Systems

REICHHOLD

Introduction

The **DION® FR** polyester, vinyl ester and gelcoat product range covers all market segments and includes products for all major application methods and end uses. The **DION® FR** range makes full use of both halogenated and non-halogenated technology.

Over the next few pages this guide will explain why fire occurs, what happens once a fire starts and how product design can render a product more resistant to ignition.

Fire retardant materials are designed to minimise the chance of fire occurring when the end product is in contact with a small heat source (matches, cigarettes, candles etc.) or to slow down the combustion process, should a fire start.

Product and Application Considerations

The following are the key points to consider when discussing fire retardants with the end user. All are critical to understanding the product requirements and will help in making the correct recommendation.

1. End use of the composite part and where it will be used
2. Application method/ process
3. Halogenated or non-halogenated
4. Clear or filled
5. Fire standard required and classification to that standard
6. Laminate construction and thickness
7. Gelcoat required (yes or no)

The answers to these points will in some cases limit your options but are critical in guiding your final product selection.


FR Product Line

Product data is available on Technical Data Sheets and MSDS's from your local Reichhold Technical Service or Sales Representative. Typical examples of the DION® FR product range, with the results of tests carried out on panels at independent test houses are listed in the tables at the end of the brochure.

Please remember that the final FR performance is dependent on the construction produced by the end user. It is possible that this final part should have its own certification. As a manufacturer we can supply example certification based on panels prepared in our laboratories, but these can only give the end user an idea of anticipated product behaviour.

Filled systems have a tendency to settle during storage, and as such it is advised that the volume in the container is properly **stirred thoroughly before use**, to ensure that the end product is made with a resin system with the fire retardant qualities as anticipated and required.

FR Gelcoats

Within the NORPOL range of gelcoats there are three series with FR properties, all of these products are based on non-halogenated technology.

1. NORPOL SVG X2 – Hand or Spray
2. NORPOL SVG X3 – Hand
3. NORPOL GX1 – Hand or Spray

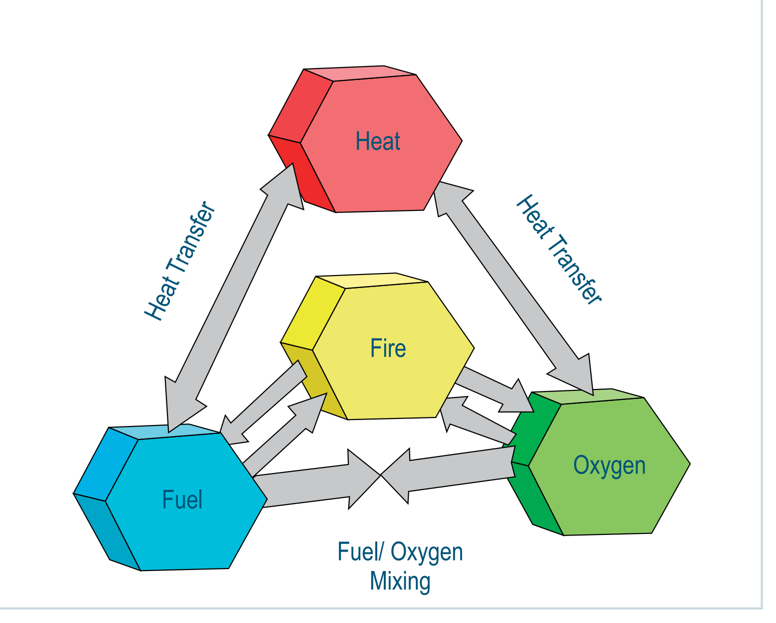
SVG gelcoats are all based on Low VOC, Premium ISO/NPG technology with excellent application properties.

Reaction of Composites to Fire

Fire results when three key elements are present, Heat, Fuel and Oxygen. The resulting chemical reaction (fire) can be influenced (retarded) by removing any one of these three components.

Heating

The GRP laminate is heated by an external heat source and in addition by thermal feedback once combustion has started. When heating provides sufficient energy, endothermic decomposition occurs.



Decomposition

Decomposition occurs once the high binding energies between the individual atoms in the polymer are overcome. In general, decomposition occurs via free radical chain reactions initiated by oxygen or oxidising impurities which are trapped in all plastics during manufacture. These free radicals are responsible for the flame spread in the combustion process.

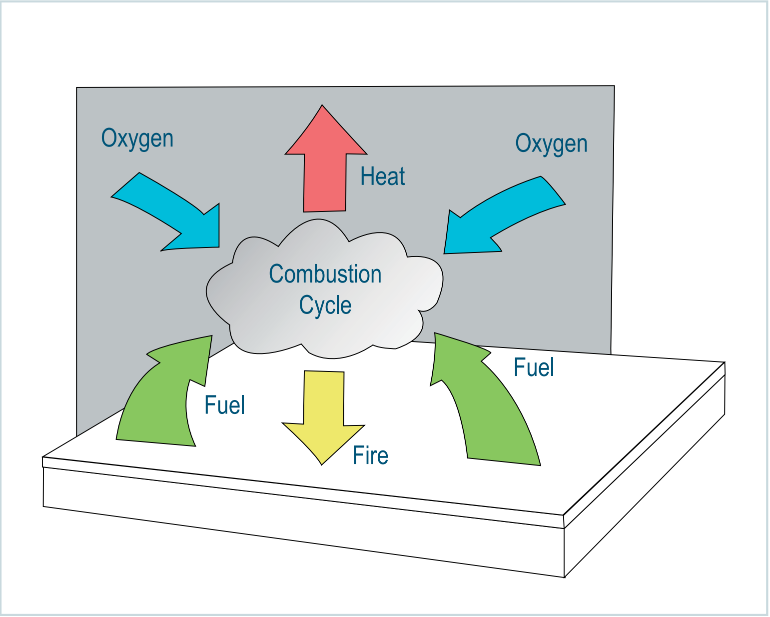
Ignition

The flammable gases that are formed by the decomposition process are mixed with atmospheric oxygen and ignited by an external flame, or alternatively by self-ignition if the temperature is sufficiently high compared to the oxygen to flammable gases ratio. When ignition occurs there will be thermal feedback due to the exothermic nature of the combustion process.

Flame spread

Thermal feedback from the combustion process provides more energy to the decomposition process during which new flammable gases are produced, thus feeding the combustion process.

During flame spread the temperature of the polymer is typically 500°C while the temperature of the flame where the reaction with oxygen takes place is approximately 1200°C.



Smoke development

Smoke is a result of incomplete combustion and is a dispersion of solid/ liquid particles in a carrier gas consisting of combustion gases and air. The liquid particles are tar-like droplets or mist composed of liquid products from pyrolysis; their partially oxidised derivatives, and water. The solid particles contain soot, ash, sublimed pyrolysis products and oxides of inorganic compounds.

Combustion products

The composition of gases during combustion of solid plastics is mainly dependent on the combustion temperature as well as the availability of oxygen. The supply of oxygen and the temperature will vary constantly during the fire; as a result of this the composition of the combustion gases will also vary. It is, therefore, too complex to measure the composition of the gases throughout the fire's duration.

During combustion of a halogenated fire retardant polyester laminate, formation of gaseous Hydrogen Chloride and/or Hydrogen Bromide will result; in addition to the above mentioned combustion products.


Mechanisms of Flame Retardation

The DION® FR range makes use of both halogenated and non-halogenated technology to interfere or retard the chemical reaction caused by fire. This is achieved by using one or more of following **four modes of action**.

1. Cooling
2. Dilution
3. Termination by free radical acceptors
4. Formation of intumescent layers (carbonization)

The temperature of a fire can be lowered below the temperature at which it can be sustained, thus putting the fire out or slowing down its flamespread. **Cooling** may be achieved by introducing additives such as Alumina Tri-Hydrate (ATH), which releases water at temperatures above 200°C, into the solid laminate. The decomposition of ATH and the evaporation of the released water is an endothermic process, resulting in overall cooling effect. Other side products from this reaction influence the **carbonization** of the laminate surface isolating it against the effect of further heat and gases.

Addition of inert fillers into a laminate reduces (**dilutes**) the fuel available in the solid phase as well as introducing inert gases into the gaseous phase. The total amount of combustible material is cut and the lower ignition temperature limit shifted upwards.

Termination by free radical acceptors is achieved by the introduction of halogens such as Chlorine and/or Bromine. Incorporation of these elements is often by reaction into the polymer backbone, but it is also possible by use of an additive. The decomposition of the solid plastic will then produce free radical acceptors which will stop the exothermic process in the gaseous phase, suppressing the flammable gases.


An **intumescent** layer is a physical hindrance between the solid phase and the gaseous phase. This layer is formed by the combustion process and consists of inert gases and/or a solid crust that cools the solid phase by reducing heat transfer as well as shielding it from oxygen, breaking one side of the fire triangle. An **intumescent** layer may be formed by the introduction of phosphorous additives into the product.

Combination of these modes of action by use of different base resins and additives often results in a greater benefit (**synergy**) than if they were used individually. A common synergist with halogenated products is Antimony Trioxide (ATO).

Consequently it is possible to design composites with different degrees of smoke and flame spread performance to meet the various standards required by the end user.

Laminate Construction and Resin Usage

When designing and producing a laminate using a fire retardant resin the user should select a resin based on the required fire test criteria and end application. Once this is done the following points which influence the performance of the end product should be taken into consideration.

1. Content of glass
2. Air voids, surface smoothness and geometry
3. Thickness of laminate
4. Post curing

The **content of glass** in products requiring fire retardancy is important not only by acting as reinforcement, but also due to its inertness to fire. Thus, one should generally try to maximise the content of glass in the finished laminate.

Air voids, surface smoothness and geometry of the end product are the other factors that may impact the total performance of a fire retardant laminate. In general, one should aim to reduce air voids as well as having a surface that is smooth as possible since these factors may contribute positively in preventing the propagation of flames.

Selecting the **optimal laminate thickness** is a balance between opposing factors; total amount of combustible material available, time to ignition and speed of fire propagation. By keeping the laminate thickness low one ensures that the total amount of combustible material is low. On the other hand, a thin laminate will be heated up to the temperature at which decomposition occurs much sooner than a thick laminate.

Due to the low thermal conductivity of GRP laminates it will take a longer time to reach the decomposition temperature in a laminate of 4-8 mm, thus delaying both time to ignition and the propagation of fire. Once ignition has started the total heat release in a fire will be higher for a laminate of 4-8 mm compared to a laminate of 3 mm or less. Generally we can say that thick laminate (>7 mm) perform better in a fire test compared to a thin laminate (<3 mm).

To get optimal fire retardancy out of a laminate it is important to **post cure** at elevated temperature. The process of post curing reduces the amount of residual styrene in a laminate. Since styrene is highly flammable, as well as volatile, post curing will contribute positively with respect to the fire retardant properties of a laminate.

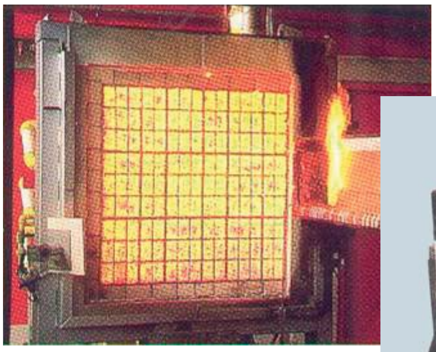
Many of the **DION® FR** range of products contain fillers of different types. Fillers have a tendency to settle during storage, and as such it is advised that the volume in the container is properly **stirred thoroughly before use**, to ensure that the end product is made with a resin system with the fire retardant qualities as anticipated and required.

Fire Tests and Classifications

A wide selection of fire standards currently exist, which vary depending on end use, market segment and country of origin. Some are more common than others; however, they all make use of one or more of a combination of the following parameters:

1. Ignitability
2. Flame spread
3. Smoke development
4. Smoke density and toxicity
5. Rate of heat release
6. Total heat release

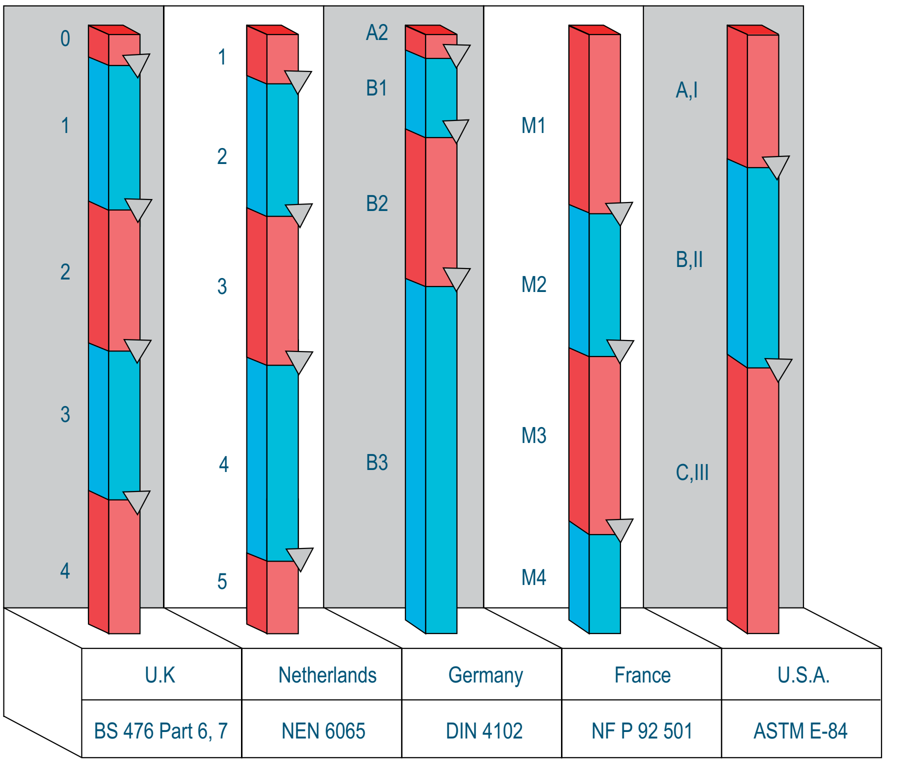
Standard	Description
ASTM E 84	**ASTM E 84** or the Steiner Tunnel Test from the USA measures surface burning characteristics, such as flame spread and smoke emissions. Values of Flame Spread Index (FSI) range from 0 to 200, with ratings of **Class I to III.** Under NFPA rules these are Class A to C.
ASTM E 162	**ASTM E 162** is a Radiant Panel Test and measures flame spread and rate of energy release under varying radiant flux, the higher the calculated flammability index the more flammable the material.
BS 476	**BS 476, Part 3** is used by the UK corrugated roof industry; the test is a combination of surface flame spread and fire penetration. Typical ratings are **SAA** and **SAB**.
BS 476	**BS 476, Part 7** is the main UK standard and measures surface spread of flame, **Class 1 to 3** are possible.
BS 476	**BS 476, Part 6** measures fire propagation, compliant materials must also reach Class 1 under Part 7 to be awarded **Class 0**.
DIN 4102	**DIN 4102 Part 1** from Germany measures Reaction to Fire, FRP materials/ constructions typically achieve either **B1** (low flammability) or **B2** (moderate flammable). The test is a combination of the Brand Schacht and/or a small burner test.
NF P 92 501	**NF P 92 501** or "Epiradiateur" is used in France to measure reaction to fire; FRP materials typically achieve **M1 to M3** ratings.
NF F 16 101	**NF F 16 101** is the French standard for the evaluation of smoke parameters, it is a combination of smoke emission (density) by **NF X 10 702** and toxicity index **NF X 70 100**. The most typical values are **F1 to F3** for composite materials.
UL 94	**UL 94** from the Underwriters Laboratory in the USA determines the relative flammability and the dripping behaviour of plastics used in electrical applications. Typical ratings are **V0 to V2**.
ISO 5660-1	**ISO 5660-1** (cone calorimeter) will play an increasing role in the modelling of a product's fire performance, as it allows the determination of key fire parameters such as ignition time and heat release rate.



BS 476, Part 6

BS 476, Part 7

Comparison of Regional FR Standards



This comparison should only be used as an initial guide to evaluating test classifications, users should note that each countries standards measure different aspects of fire behaviour so an absolute correlation is possible.

Final classification would also depend in actual laminate construction and resin to glass ratios.

ISO 5660-1

Transportation

Probably some of the most complex and toughest regulations cover passenger transit vehicles.

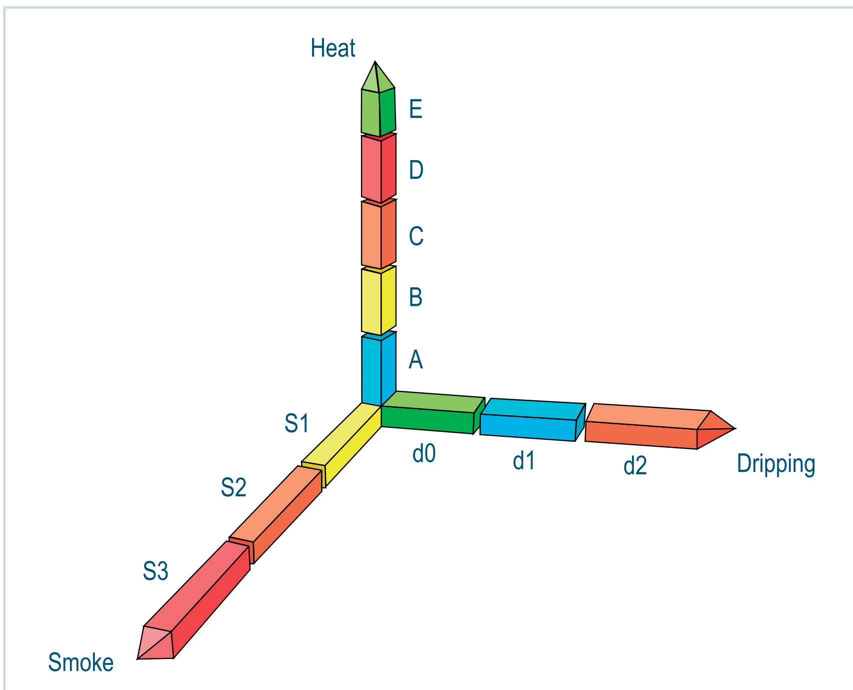
Standard	Parameter	Description
BS 6853		**BS 6853** in the UK is a General Code of Practise which defines the requirements for the material, and is dependent on whether the vehicle is used underground or on the surface; whether the part is external or internal; whether the part is installed horizontal or vertical. Three or four key parameters are measured.
	Fire	Evaluation by **BS 476 Part 6/7**.
	Smoke	Smoke density evaluated by the **$27m^3$ Smoke Chamber**.
	Toxicity	Smoke toxicity profile is measured by either **ISO 5659-2** or **NF X 70 100**.
DIN 5510 Part 2		DIN 5510 Part 2 from Germany measures a combination of combustibility **(S2 to S5)**, smoke development **(SR1 or SR2)** and dripping **(ST1 or ST2)**.
EN 45545 Part 2		The proposed replacement **EN 45545** will also focus on smoke and toxicity. Three classes are expected **HL1** to **HL3**, class is dependent on part type and its location in the vehicle. The adoption of **EN 45545** as a full standard is unlikely before 2012, until this time local standards will continue to be required. Three parameters are required for the evaluation of the final class.
	Fire	**ISO 5658-2** to measure flame spread.
	Heat	**ISO 5660-1** to measure ignition time and heat release rate.
	Smoke	**ISO 5659-2** to measure smoke density and toxicity profile.

Marine

Within the marine and offshore market, Lloyd's Register, Det Norske Veritas and the US Coast Guard all have their own test programmes for FR systems. The International Maritime Organization (IMO) also has a variety of resolutions regulating the materials used at sea, many of which are relevant to the composites industry, including SOLAS.

Building and Construction

The development of European standard **EN 13501-1** will replace all national standards by “Euro classes”. Products will be rated from **A to F**, though composite materials are most likely to be classified as **B, C or D**. This measurement of reaction to fire is a new test known as the Single Burning Item (SBI). Additional criteria measured will be dripping (**Class d0 to d2**) and smoke (**Class S1 to S3**). Composite materials expected classification under the SBI can be modelled using a cone calorimeter study.



Industrial

Industrial applications use a combination of the tests already discussed, but it should be noted that halogenated based products such as the vinyl ester DION® FR 9300-00 also offers chemical resistance benefits in addition to its fire retardancy. Further details can be found in the **Reichhold Chemical Resistance Guide**. Alternate application methods such as Pultrusion are also used in this market segment.

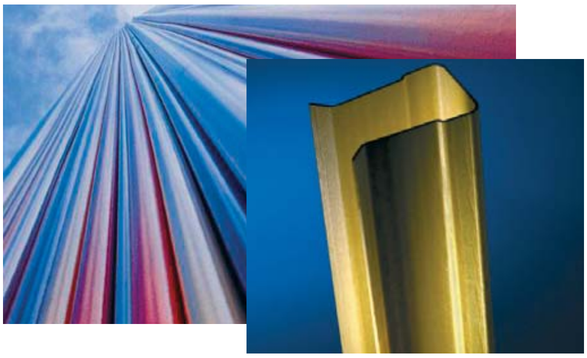
FR Pultrusion Systems

Non-halogenated additives such as Aluminium Tri-Hydrate (ATH) or Ammonium Polyphosphate (APP) can be used in Pultrusion to achieve high fire retardant performance combined with a low smoke density. The most important property for a resin when these fillers are used is the ability to add large amounts without a too high viscosity increase.

POLYLITE® 680-191 is a specially designed resin that can be filled with up to 200 parts ATH (where the resin = 100 parts) whilst having a viscosity below 2000 mPas. The glass content should be around 35 wt%. Higher amounts of filler will result in poor mechanical properties as the volume fraction of resin should be at least 45%. For applications with smaller amounts of filler, POLYLITE® 510-010 can be used. It should be noted that POLYLITE® 510-010 is more reactive than POLYLITE® 680-191.

Halogenated systems offer some benefits over non-halogenated systems, due to the fact that the glass content and therefore the mechanical properties can be higher. Halogens are traditionally used together with Antimony Trioxide (ATO), in order to obtain synergistic effect. An example would be DION® FR 9300, a brominated vinyl ester. Additional data is listed in the Product Tables and further information can be obtained from our Application Specialists.

Standard	Expected	Halogenated	Formulation	Viscosity	Thickness
DIN 5510	S4/SR2/ST2	No	100 parts POLYLITE® 680-191; 180-200 parts ATH	1000-1200	
DIN 5510	S4/SR2/ST2	No	100 parts DION® FR 7721		
DIN 5510	S4/SR2/ST2	No	100 parts POLYLITE® 510-010; 80 parts APP	3700	>4 mm
DIN 5510	S3/SR2/ST2	No	100 parts POLYLITE® 680-191; 130 parts ATH	300	
UL 94	V0	No	100 parts POLYLITE® 680-191; 150 parts ATH	500-600	3.2 mm
UL 94	V0	No	100 parts POLYLITE® 510-010; 80 parts APP	3700	>4 mm
UL 94	V0	No	100 parts POLYLITE® 510-010; 80 parts APP	3700	>4 mm
DIN 4102	B1	No	100 parts POLYLITE® 510-010; 80 parts APP	3700	>4 mm
DIN 4102	B2	No	100 parts POLYLITE® 680-191; 140 parts ATH	350	3 mm
BS 476 part 7	Class 2	No	100 parts POLYLITE® 680-191; 60-80 parts ATH	150	
BS 476 part 6	Class 0	Yes	100 parts DION® FR 9300; 5 parts ATO		4 mm
NFF 92-501 NFP 16-101	M2/F1	No	100 parts POLYLITE® 680-191; 150 parts ATH	350	
NFF 92-501 NFP 16-101	M2/F2	No	100 parts POLYLITE® 510-010; 80 parts APP	3700	>4 mm
NFF 92-501	V0	No	100 parts POLYLITE® 510-010; 80 parts APP	3700	>4 mm
NFP 16-101	M2/F2	No	100 parts POLYLITE® 510-010; 80 parts APP	3700	>4 mm



FR Products Test Results

Product	Filled	Halogens	Test	Result
American				
DION® FR 800-200	Yes	Yes	UL 94 5V	Pass
DION® FR 800-200 (+ variants)	Yes	Yes	ASTM 635-81	AEB - 10 mm, ATB - 25 secs
DION® FR 800-577	Yes	Yes	UL 94 Vertical	V-0 at 3 mm
DION® FR 820-034	No	Yes	UL94 HB	94HB at 3 mm
DION® FR 820-M723	No	Yes	FMV SS No 302	Pass
DION® FR 820-M878	Yes	Yes	MIL-R-21607 or MIL-R-7575	Grade A
DION® FR 840-820	Yes	Yes	ASTM 162-83	F = 3.1, Q = 10.2, I = 32
DION® FR 840-850	Yes	Yes	UL 94 Vertical	V-0 at 3 mm
DION® FR 850-Series	Yes	No	MIL-R-21607 or MIL-R-7575	Grade A
DION® FR 9300-00	No	Yes	MIL-R-24779	Approved for use
DION® FR 9300-00	No	Yes	ASTM E-84	FSI = 30 mm (Class II or B)
DION® FR 9300-00 + 3% ATO	Yes	Yes	ASTM E-84	FSI = 15 mm (Class I or A)
DION® FR 9325-00	No	Yes	ASTM E-84	Class I or A
Danish				
Product	Filled	Halogens	Test	Result
DION® FR 840-850	Yes	Yes	UIC Kodex 564-2 App 4	Class A
DION® FR 850-864	Yes	No	UIC Kodex 564-2 App 4	Class A
French				
Product	Filled	Halogens	Test	Result
DION® FR 7721-00	Yes	No	NF P 92 501	M2
DION® FR 7721-00	Yes	No	NF F 16-101	F1
DION® FR 840-744	No	Yes	NF P 92 501	M2
DION® FR 840-820	Yes	Yes	NF P 92 501	M1
DION® FR 840-820	Yes	Yes	NF F 16-101	F2
DION® FR 840-820 + NORPOL NGA HX3	Yes	Yes	NF P 92 501	M1
German				
Product	Filled	Halogens	Test	Result
DION® FR 7721-00	Yes	No	DIN 5510 Part 2	S4, SR2, ST2
DION® FR 800-577	Yes	Yes	DIN 5510 Part 2	S4, SR1, ST2
DION® FR 840-850 + NORPOL GX1-H	Yes	Yes	DIN 4102	B2
DION® FR 850-700 (4 mm)	Yes	No	DIN 5510 Part 2	S4, SR2, ST2
DION® FR 850-700 (3 mm)	Yes	No	DIN 5510 Part 2	S3, SR2, ST2
DION® FR 850-864	Yes	No	DIN 5510 Part 2	S4, SR2, ST2

FR Products Test Results

International Marine Organization				
Product	Filled	Halogens	Test	Result
DION® FR 820-606	No	Yes	IMO MSC Circ 1006	Ignition at 50 kW/m^2 - 42.3 secs
DION® FR 820-606	No	Yes	IMO MSC Circ 1006	Extinguish Time = 10 secs
DION® FR 820-M878	Yes	Yes	IMO MSC 81(70) Part 1	SOLAS
DION® FR 820-M878	Yes	Yes	IMO MSC Circ 1006	Ignition at 50 kW/m^2 - 46 secs
DION® FR 820-M878	Yes	Yes	IMO MSC Circ 1006	Extinguish Time = 7 secs
DION® FR 840-850 + NORPOL NGA X3	Yes	Yes	IMO FTPC Part 5	Pass

Italian				
Product	Filled	Halogens	Test	Result
DION® FR 800-200	Yes	Yes	CSE RF 3/77	Class 2

Russian				
Product	Filled	Halogens	Test	Result
DION® FR 840-810 + NGA X2	Yes	Yes	GOST	Approved for use

British				
Product	Filled	Halogens	Test	Result
DION® FR 800-M750	Yes	Yes	BS 476 Part 7	Class 2
DION® FR 820-080	No	Yes	BS 476 Part 7	Class 3
DION® FR 820-600	No	Yes	BS 476 Part 7	Class 2
DION® FR 820-M723	No	Yes	BS 476 Part 7	Class 2
DION® FR 821-M760/M800	No	Yes	BS 476 Part 7	Class 2
DION® FR 840-810	Yes	Yes	BS 476 Part 7	Class 1
DION® FR 840-820 + NORPOL NGA HX3	Yes	Yes	BS 476 Part 6/7	Class 1/0
DION® FR 840-850	Yes	Yes	BS 6401 (NBS Smoke)	Dmc/g = 42.6
DION® FR 840-850 + NORPOL GX1-H	Yes	Yes	BS 476 Part 6/7	Class 1/0
DION® FR 844-030	No	Yes	BS 476 Part 7	Class 1
DION® FR 844-M778	No	Yes	BS 476 Part 7	Class 1
DION® FR 850-700 + NORPOL NGA HX3	Yes	No	BS 476 Part 7	Class 2
DION® FR 850-M850	Yes	No	BS 476 Part 7	Class 2
DION® FR 9300-00	No	Yes	BS 476 Part 7	Class 2
DION® FR 9300-00 + 3% ATO	Yes	Yes	BS 476 Part 7	Class 1