

# Flame Retardants

## Product Range



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Polymers



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- ▶ Several grades adjusted for your application
- ▶ Controlled quality

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## EFFECTIVE FIRE PROTECTION

Potential combustion sources lurk everywhere and can ignite upholstery, cars or electronic devices. Especially polymers are easily flammable and have to be fire retarded. To reduce flammability of polymer based products, flame retardants are used. These additives can influence the flammability, the propagation of the flame and/or the fire load. For each application the most suitable flame retardant solution should be used to assure a high fire retardant effect of the material and to prevent negative effects such as release of toxic gases, smoke or odors.

During the last years standards of modern flame retardants have changed. Besides effective fire retardancy also the environmental protection plays a more important role throughout the whole life time cycles of the products. As a consequence flame retardants should not be toxic for humans, animals or plants.

Generally, there are two main groups of flame retardants: halogen containing and halogen-free additives such as phosphorous or nitrogen based flame retardants. Depending on the type of flame retardant additive, they can act in the gas and/or condensed phase with a chemical and/or physical mode of action. The HARKE Coatings, Plastics & Polymers team offers you a broad range of flame retardants of both mentioned groups.



HARKE Chemicals GmbH stands for certified quality and constant engagement for a sustainable protection of the environment.

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## HALOGENATED FLAME RETARDANTS

**ANTIMONY TRIOXIDE (Sb<sub>2</sub>O<sub>3</sub>)****Chemical Characterization**

Antimony oxide is a very fine, crystalline white powder having a controlled particle size. At high temperatures it stores oxygen atoms and becomes antimony tetraoxide.

**Applications**

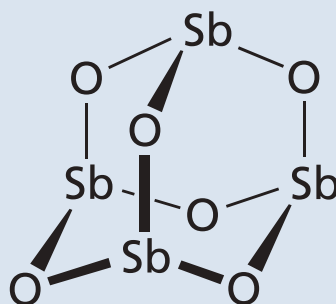
Besides the application in flame retardants antimony oxide is for instance used in plastics as a catalyst or for discoloration of glass. Moreover, it is used in enamel production and electroplating.

**Mode of Action**

Antimony trioxide is a chemical used in flame retardants as a synergist in order to, for instance, intensify the effect of chlorinated paraffins.

**Properties**

Antimony trioxide is insoluble in water and nitric acid. It is little soluble in sulfuric acid and hydrochloric acid, whereas it shows a better solubility in a concentrated solution.





## CHLORINATED PARAFFINS – CLOPARIN®



### Chemical Characterization

In the field of halogenated flame retardants we offer various types of chlorinated paraffins under the trade mark Cloparin® from our Italian partner Caffaro Industrie S.p.A. These products consist of chlorinated hydrocarbons having different chain lengths and chlorine content depending on their applications. It is distinguished between short-chain (C10 - C13), middle-chain (C14 - C17) and long-chain (> C18) chlorinated paraffins. The chlorine content lies between 20 and 73%. Depending on chain length and chlorine content, chlorinated paraffins are transparent to yellowish highly viscous liquids or paraffin like solids.

### Applications

Short-chain chlorinated paraffins are mainly used in cooling lubricants which are used for the industrial metal production. Medium- and long-chain chlorinated paraffins are suitable as flame retardants and plasticizers for rubber products and plastics. Cloparin® is mainly used in PVC-compounds. The different types can be used both as flame retardants and as plasticizers, and thus replace partly or even totally the conventional plasticizers. According to today's state of knowledge chlorinated paraffins, especially short-chain products, are considered as environmentally dangerous materials.

### Mode of Action

Similar to all halogen compounds the flame-retardant effect of chlorinated paraffins depends on their capacity as scavenger. The non-combustible hydrogen chloride is eliminated at high temperatures, and additionally chain break-up reactions disturb the combustion process and the flame expansion. In order to achieve the same flame-retardant properties as the bromine compounds, often twice the amount has to be formulated. Chlorinated paraffins decompose only at temperatures higher than 200 °C, and are chemically almost inert. This means that under normal conditions they react not at all or only to an evanescently little degree with potential reaction partners, like e.g. air.

### Types and Properties

Our chlorinated paraffins feature various viscosities and chlorine contents whereby the right compatibility and performance is ensured for any application. They are compatible with most resins and polymers, as for instance with natural and synthetic rubber, chlorinated polyethylene, polyester, polystyrol, polyacrylate, PVC, polyvinyl acetate and chlorinated copolymers. Furthermore, our Cloparin® types are also well mixable with other additives like phthalates, stearates and phosphates.

#### Advantages of Cloparin®

- Boiling point at > 200 °C
- Extremely resistant against acids and alkalis
- Soluble in most organic solvents
- Insoluble in water and short-chain alcohols

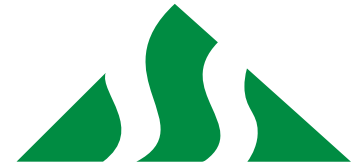
Cloparin® 50	Broad application spectrum
Cloparin® 44	Flow viscosity
Cloparin® 56	Broad application spectrum
Cloparin® 49 ST	Medium viscosity, high stability
Cloparin® 56 ST	High viscosity and stability



## TCPP



From our partner Jiangsu Yoke Technology Co., Ltd, we offer you two different organic triphosphates: tris(2-chlorisopropyl) phosphate (TCPP) and halogen-free triethyl phosphate (TEP) – see more on page 9.



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PhireGuard TCPP (CAS: 13674-81-5) is used in flexible and rigid polyurethane/polyisocyanurate foams to enhance flame retardant properties and to reduce viscosity of the systems.



### Physical Properties of TCPP

Appearance	Transparent liquid
Phosphorous content, % (w/w)	9.4
Chlorine content, % (w/w)	32.5
Specific gravity @ 20 °C	1.29
Viscosity @ 25 °C, cPs	65
Acid value, mg KOH/g	≤ 0.1
Water content, % (w/w)	≤ 0.1
Odor	Mild, characteristic

## ZINC BORATE ZINBOREL®



Zinc Borate will be obtained by the reaction of zinc oxide and boric acid. It is widely used as a flame retardant and smoke suppressant in the plastics industry. Zinc Borate is also used in adhesives, pigments and paints. In the wood industry it works as preserver and flame retarder. Furthermore, Zinc Borate acts as a synergist in plastics and rubber.

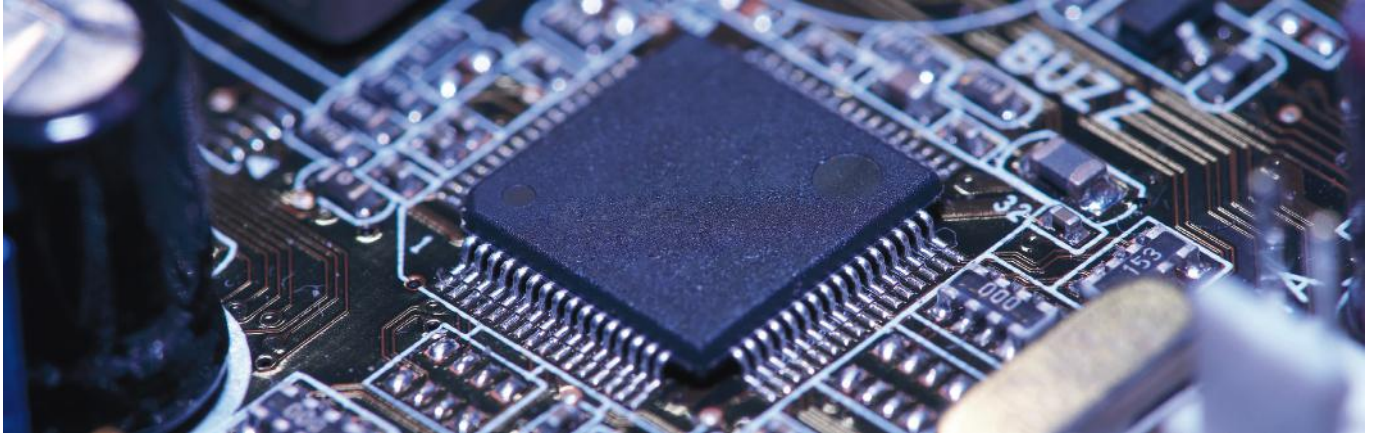
### Physical Properties of Zinc Borate Zinborel®

CAS	Characteristic	Unit	Typical Values	Description
12767-90-7	Volatile Loss (24 hrs. at 120 °C)		< 1.0%	• <b>Package:</b> 25 kg bag
	Weight Loss at 950 °C		< 15,5%	
	Approx. Dehydration Temperature	°C	290	
	Refractive Index		1.57	
	Crystal Density (at 20 °C)	g/cm <sup>3</sup>	2.8	
	Oil Absorption	w/w	24%	
	Water Solubility	w/w	< 0.1%	
	Crystallisation in water		min. 11.5 max. 16.5	
	Moisture	%	max. 1.0	
	Particle size distribution values	µm D10 µm D50 µm D99	0.7 ÷ 0.9 3.0 ÷ 3.8 10.2 ÷ 18.0	



## HALOGEN-FREE FLAME RETARDANTS

### DOPO

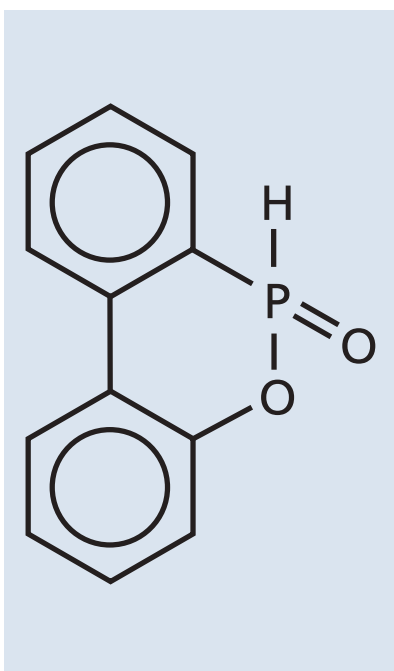


#### Chemical Characterization

DOPO (CAS: 35948-25-5) is a halogen-free flame retardant. DOPO stands for 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide. It shows properties similar to the often-used brominated epoxy resins, however, without evaporation. The reason for this is that it is chemically bound to the matrix. During processing it has to be kept in mind that DOPO has to be used together with multifunctional epoxy resins, due to the fact that one epoxy group reacts at a time with one molecule DOPO.

#### Applications

DOPO is mainly used in epoxy resins that are used in glues, electric casting resins, coatings and composites for the electrical and electronics industry as well as for the aerospace industry. More-over, DOPO is used in other applications requiring fire protection for example polyurethane products in mattresses, foam insulation, foamed materials or upholstered furniture.



#### Mode of Action

The flame retardant effect of DOPO is due to several processes: A protective carbon layer is formed at the sample surface to reduce transport of flammable gases and material fragments from the material to the heat source. Additionally, PO-radicals are formed during the decomposition of DOPO acting as scavenger in the combustion process.

#### Physical Properties of DOPO

P-content	min. 14%
Melting point	117 - 121 °C
Appearance	Powder or platelets



## TEP



From our partner Jiangsu Yoke Technology Co., Ltd, we offer you the halogen-free organic triphosphate triethyl phosphate (TEP).



PhireGuard TEP (CAS: 78-40-0) is mainly used in rigid foams and boards based on polyurethane/polyisocyanurate. The halogen-free TEP is used to improve the flame retardancy and to reduce the viscosity.



Additional organic triphosphates like e.g. Trioctyl Phosphate (TOP)/Tris (2-ethylhexyl) Phosphate (CAS 78-42-2) are available on your request.

### Physical Properties of TEP

Appearance	Transparent liquid
Phosphorous content, % (w/w)	17
Purity, % (w/w)	> 99.0
Acid value, mg KOH/g	< 0.05
Water content, % (w/w)	< 0.1

## AMMONIUM POLYPHOSPHATES



### Chemical Characterization

Ammonium phosphates are formed through reaction of ammonia and phosphoric acid, whereas several types of ammonium phosphates are formed: monoammonium phosphate, diammonium phosphate and ammonium polyphosphate. Often ammonium phosphates are coated to improve dispersion of the additive in the polymeric matrix on the one hand and to enhance flame retardant effect on the other hand. Ammonium polyphosphate can be coated using melamine or silicones for example.

### Mode of Action

Ammonium phosphates have a flame retardant effect in the gas and the condensed phase. Ammonium phosphates are decomposed thermally when submitted to an external heat source. In a first step water and ammonia are evolved. Ammonia then reacts in presence of oxygen to nitrogen monoxide and water. The presence of water in the gas phase reduces the concentration of flammable gases and thus provides a flame retardant effect. After the release of water and ammonia the phosphoric acid part of ammonium phosphate stays in the condensed phase. Due to the presence of oxygen phosphor oxides are formed at higher temperatures. During this reaction water is again released to the gas phase. At the same time it can be observed that the formed phosphor oxides react with organic fragments of the decomposition of the polymeric matrix. This leads to formation of a high-melting glass-like layer at the sample surface. This layer protects the underlying material and prevents migration of flammable gases from the material to the heat source and reduces the impact of the heat source to the material.

### Types and Properties – Ammonium Polyphosphates

Type	Characteristic	Unit	Typical Values	Description
<b>Exflam APP 201</b> <b>CAS: 68333-79-9</b>	Phosphorus	% (w/w)	≥ 31	<ul style="list-style-type: none"> <li>Exflam APP 201 is Ammonium Polyphosphate Phase II N &gt; 1000 Non-Coated. It is our standard grade</li> <li><b>Application:</b> Intumescent Paints and Coatings Sealants Thermoplastics PP/PE Thermoset (PU, Epoxy, UP)</li> <li>For Exflam APP 202, 203, 204 encapsulated</li> <li><b>Package:</b> 25 kg paper bag or 875 kg big bag</li> </ul>
	Nitrogen	% (w/w)	≥ 14	
	pH value	(10% suspension)	5.5 - 7.0	
	Water content	% (w/w)	≤ 0.25	
	Thermal decomposition	°C	≥ 275	
	Density at 250 C	kg/L	1.9	
	Apparent density	kg/L	0.7	
	Viscosity (250 C in 10% suspension)	mPa.s	≤ 100	
	Solubility in water (g/100 cm <sup>3</sup> )	% (w/w)	≤ 0.5	
	Average particle size	µm	≤ 15	

## Types and Properties – Ammonium Polyphosphates

Type	Characteristic	Unit	Typical Values	Description
<b>Exflam APP 202</b> CAS: 68333-79-9	Phosphorus	% (w/w)	≥ 28	<ul style="list-style-type: none"> <li>• Exflam APP 202 is Melamine Reacted Coated based on Exflam APP 201 standard grade</li> <li>• <b>Application:</b> Outdoor Paints and Coatings</li> <li>• <b>Advantage:</b> Low solubility: 0.05% Good weatherability</li> <li>• <b>Package:</b> 25 kg paper bag</li> </ul>
	Nitrogen	% (w/w)	≥ 15.5	
	pH value	(10% suspension)	6.5 - 7.5	
	Water content	% (w/w)	≤ 0.25	
	Thermal decomposition	°C	300	
	Density at 250 C	kg/L	1.9	
	Apparent density	kg/L	0.7	
	Viscosity (250 C in 10% suspension)	mPa.s	≤ 20	
	Solubility in water (g/100 cm <sup>3</sup> )	% (w/w)	0.05	
	Average particle size	µm	15	
<b>Exflam APP 203</b> CAS: 68333-79-9	Phosphorus	% (w/w)	≥ 28	<ul style="list-style-type: none"> <li>• Exflam APP 203 is Melamine Modify Coated based on Exflam APP 201 standard grade</li> <li>• <b>Application:</b> Thermoplastics (PP/PE) Flexible PU</li> <li>• <b>Advantage:</b> Low solubility: 0.3% Good flowability for process</li> <li>• <b>Package:</b> 25 kg paper bag</li> </ul>
	Nitrogen	% (w/w)	≥ 18	
	pH value	(10% suspension)	7.5- 8.5	
	Water content	% (w/w)	≤ 0.25	
	Thermal decomposition	°C	300	
	Density at 250 C	kg/L	1.9	
	Apparent density	kg/L	0.7	
	Viscosity (250 C in 10% suspension)	mPa.s	≤ 20	
	Solubility in water (g/100 cm <sup>3</sup> )	% (w/w)	0.3	
	Average particle size	µm	≤ 15	
<b>Exflam APP 204</b> CAS: 68333-79-9	Phosphorus	% (w/w)	≥ 28	<ul style="list-style-type: none"> <li>• Exflam APP 204 is Silicon Coated based on Exflam APP 201 standard grade</li> <li>• <b>Application:</b> Car inner textile coating, Electronic coating</li> <li>• <b>Advantage:</b> Low solubility: 0.1% Good weatherability Anti-Conductivity</li> <li>• <b>Package:</b> 25 kg paper bag</li> </ul>
	Nitrogen	% (w/w)	≥ 14	
	pH value	(10% suspension)	6.5 - 7.5	
	Water content	% (w/w)	≤ 0.25	
	Thermal decomposition	°C	≥ 300	
	Density at 250 C	kg/L	1.9	
	Apparent density	kg/L	0.7	
	Viscosity (250 C in 10% suspension)	mPa.s	≤ 20	
	Solubility in water (g/100 cm <sup>3</sup> )	% (w/w)	≤ 0.1	
	Average particle size	µm	≤ 15	
<b>Special Grade</b>				
<b>Exflam APP 201X</b> CAS: 68333-79-9	Phosphorus	% (w/w)	min. 31	<ul style="list-style-type: none"> <li>• Exflam APP 201X is a fine particle ammonium polyphosphate</li> <li>• <b>Application:</b> Intumescent Coatings, Adhesive and Sealants</li> <li>• <b>Advantage:</b> Largely insoluble in water and completely insoluble in organic solvent</li> <li>• <b>Package:</b> 25 kg paper bag or 875 kg big bag</li> </ul>
	Nitrogen	% (w/w)	min. 14	
	pH value	(10% suspension)	5.5 - 7.0	
	Thermal decomposition	°C	min. 275	
	Viscosity (250 C in 10% suspension)	mPa.s	max. 100	
	Solubility in water (g/100 cm <sup>3</sup> )	% (w/w)	max. 0.5	
	Average particle size	µm D50 µm D98	5 10	

More special grades can be provided based on your request.

## MELAMINE AND MELAMINE DERIVATIVES



### Chemical Characterization

Besides phosphorous containing additives also nitrogen based ones are used as flame retardants. The most popular nitrogen containing flame retardants are melamine and melamine derivatives. We provide you melamine, melamine polyphosphate (MPP) and melamine cyanurate (MCA).

### Applications

Melamine and its derivatives are used in a broad range of applications.

MPP is often used in epoxy and unsaturated polyester resins. MCA instead is mainly used in polyamide but also in polybutylene terephthalate (PBT), thermoplastic polyurethane (TPU) and epoxy resins.

### Mode of Action

As described for phosphorous containing flame retardants, melamine and melamine derivatives show a fire retardant effect in the gas and the condensed phase. Exposure to a heat source leads to sublimation of melamine. Moreover, it is possible that melamine condensates are formed.

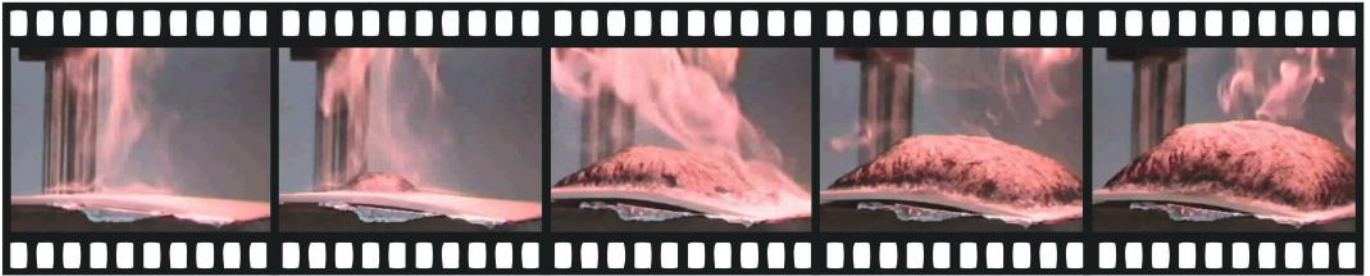


## Types and Properties – Melamine and Melamine Derivatives

Type	Physical and Chemical Properties				
<b>MELAMINE</b> <b>Exflam Melamine F40</b> Micro-Melamine CAS: 108-78-1  No REACH	Appearance	White powder			
	Purity %	99.8 min.			
	Moisture %	0.1 max.			
	pH	7.5 - 9.5			
	Formaldehyde dissolve test	All dissolved in 10 minutes			
	Ash content %	0.03 max.			
	Colority (platinum-cobalt color)	20 max.			
	Particle size $\mu\text{m}$	40 max.			
	Turbidity (Kaolin Turbidity)	20 max.			
	<b>MELAMINE DERIVATIVE MPP</b> Melamine Polyphosphate CAS: 218768-84-4	Nitrogen content	42 - 44%		
Phosphorus content		12 - 14%			
Water content		max. 0.2%			
Water solubility 20 °C		max. 0.01 g/100 ml			
pH value (saturated sol., 20 °C)		approx. 5			
Specific gravity		1.85 g/cm <sup>3</sup>			
Bulk density		approx. 500 kg/m <sup>3</sup>			
Particle size		D50 $\mu\text{m}$	5 max.		
		D98 $\mu\text{m}$	35 max.		
<b>MELAMINE DERIVATIVE MCA</b> Melamine Cyanurate CAS: 37640-57-6	Appearance	MCA 8	MCA 25	MCA 50	
		White powder	White powder	White powder	
	Melamine Cyanurat % (w/w)	≥ 99.5%	≥ 99.5%	≥ 99.5%	
	Excess Cyanuric acid % (w/w)	≤ 0.2%	≤ 0.2%	≤ 0.2%	
	Excess Melamine % (w/w)	≤ 0.3%	≤ 0.3%	≤ 0.3%	
	Water content % (w/w)	≤ 0.2%	≤ 0.2%	≤ 0.2%	
	pH	5 - 6	5 - 6	5 - 6	
	Particle size	D50 $\mu\text{m}$	≤ 2	≤ 4	≤ 10
D98 $\mu\text{m}$		≤ 8	≤ 25	≤ 50	



## INTUMESCENCE



Swelling of a material to a multiple of its original size due to exposure to an external heat source is called intumescence. During the process of swelling the volume of the material increases whereas its density decreases. In an intumescent system a barrier is formed at the sample surface that protects the underlying material thermally from the external heat source and prevents flammable decomposition gases to migrate to the surface.

To assure the formation of an intumescent system three components are required: a blowing agent, an acid source and a carbonizing agent. Ammonium polyphosphate is used as acid source, melamine as blowing agent and dipentaerythritol or pentaerythritol as carbonizing agent

### Types and Properties – Intumescence

Type	Physical and Chemical Properties		
<b>EXFLAM PENTA D40</b> Micro-Dipentaerythritol CAS: 126-58-9	Appearance	White powder	
	Di-PE % (w/w)	85	
	Mono-PE % (w/w)	3 max.	
	Tri-PE % (w/w)	8 max.	
	Ash content %	0.05 max.	
	Moisture %	1.0	
	Hydroxyl group content %	38 - 40	
	Particle size $\mu\text{m}$	40 max.	
	Phthalic color	2 max.	
	Melting Point $^{\circ}\text{C}$	215 min.	
<b>EXFLAM PENTA M40</b> Micro-Pentaerythritol CAS: 115-77-5		<i>Type A</i>	<i>Type B</i>
	Appearance	White powder	White powder
	Monopentaerythritol content %	95 min.	98 min.
	Hydroxyl group content %	47.5 min.	48.5 min.
	Water content %	0.5 max.	0.2 max.
	Ash content %	0.1 max.	0.05 max.
	Phthalic color	2 max.	2 max.
	Particle size $\mu\text{m}$	40 max.	40 max.
Melting Point $^{\circ}\text{C}$	240 min.	240 min.	

## TEXTILE FLAME RETARDANTS



The Cyclic Phosphate Esters (liquid) are efficient flame retardants for treatment of textile and fabric to apply fireproof properties for curtains, bed sheets, children's clothes, car interiors and nonwoven fabric.

### Types and Properties – Textile Flame Retardants

Type	Physical and Chemical Properties		
<b>CU</b> Cyclic Phosphate Ester CAS: 170836-68-7	Appearance	Colourless to light yellow	<ul style="list-style-type: none"> <li>• <b>Chemical Character:</b> CU is a efficient cyclic phosphonate flame retardant for treatment of textile</li> <li>• <b>Application:</b> Treatment of Polyester and T/C blends, Coating treatment of Polyester and PU fabric</li> <li>• <b>Package:</b> 125 kg drum or 1250 kg IBC</li> </ul>
	Active component	100%	
	Density (g/cc @ 25 °C)	1.20 - 1.30	
	Phosphorus	20% min.	
	pH (10% solution)	2.0 - 3.0	
	Acid number (mg KOH/g)	30 max.	
	Viscosity @ 20 °C (Cps)	60,000 - 100,000	
<b>CT93</b> Cyclic Phosphate Ester CAS: 170836-68-7	Appearance	Colourless to light yellow	<ul style="list-style-type: none"> <li>• <b>Chemical Character:</b> CU is a efficient cyclic phosphonate flame retardant for treatment of textile</li> <li>• <b>Application:</b> Polyester fabric and Nylon fabric (durable or non-durable) Automotive use like car seat fabric, ceilings, coatings with acrylic binder Adhesive (also pressure sensitive) &amp; Sealants</li> <li>• <b>Package:</b> 125 kg drum or 1250 kg IBC</li> </ul>
	Active component	93%	
	Density (g/cc @ 25 °C)	1.20 - 1.30	
	Phosphorus	20% min.	
	pH (10% solution)	2.0 - 3.0	
	Acid number (mg KOH/g)	30 max.	
	Viscosity @ 25 °C (Cps)	2,000 - 10,000	



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