Zinflam®

Zinc hydroxystannate
Zinc stannate

Flame retardants
and smoke
suppressants

Larderello Group

Italian tradition, global horizons. Since 1818.

INDEX

Summary

ZINFLAM® zinc hydroxystannate (ZHS) and zinc stannate (ZS) are fine white powders, which can act as multifunctional flame-retardants and smoke-suppressants in a variety of different polymeric and polymer-based systems.

The products are non-toxic, and are REACH registered (registration number 01-0000015398-62-000).

ZINFLAM® ZHS	
Composition	Zinc hydroxystannate ZnSn (OH)6
Molecular weight	286.12
C.A.S. number	12027-96-2
Specification	
Appearance	Free flowing white powder
Sn content	41.0% typical
Zn content	22.0% typical
Volatile loss 1 hour at 105°C	1.5% max
Sieve analysys (200 Mesh)	0.1% max
Mean particle size	1-2 microns
Decomposition temperature	~200°C-

ZINFLAM® ZS	
Composition	Zinc stannate ZnSnO
Molecular weight	232.07
C.A.S. number	12036-37-2
Specification	
Appearance	White powder
Sn content	51.0% typical
Zn content	28.0% typical
Volatile loss 1 hour at 105°C	1.0% max
Sieve analysys (200 Mesh)	0.1% max
Mean particle size	1-2 microns
Decomposition temperature	>570°C

Benefits

The following benefits have been observed in various formulations containing ZINFLAM® ZHS and ZS.

- Greatly improved smoke suppression
- Reduced **rate** of heat release and **total** heat release
- Improvement in LOI
- Reduction of burning drips
- Increased time to ignition
- Achievement of Ul V0 in PVC, Pa and unsaturated polyester
- Low toxicity - **NO RISK PHRASES** with ZINFLAM® ZHS / ZS
- Can completely replace antimony trioxide (Sb_2O_3) in formulations
- Lower overall FR filler-loading with ZHS/ZS incorporation achieved
- Can be effective in halogenated and halogen-free systems
- Fine particle size ~1-2 microns average

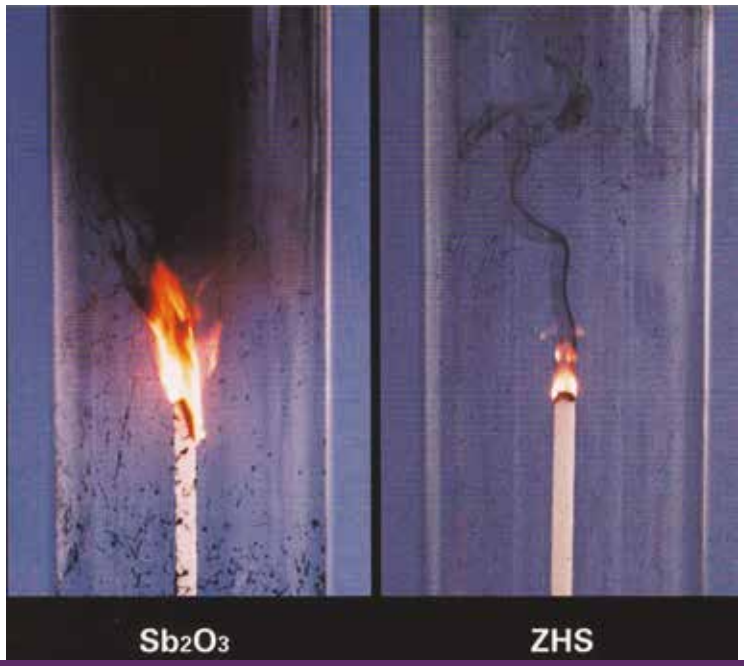
Mechanism

In the case of zinc hydroxystannate, the product's mode of action as a flame retardant is firstly as a result of endothermic dehydration, resulting in the loss of ~19% by weight of water from the ZHS. This water loss cools a potential fire and dilutes the oxygen available to sustain a fire.
In addition to this action, the tin component has been shown to catalyse the formation of a carbonaceous char in which tin-carbon bonds have been observed. This char acts as a barrier between a fire-retarded system containing ZHS and a potential fire, thereby reducing the smoke produced as a result.
In the presence of halogens, there is strong evidence of gas-phase flame retardant behaviour, which further hinders fire propagation.

The mode of action of zinc stannate, which is used for higher temperature applications, is essentially the same as the above, but without the dehydration step.

ZINFLAM® zinc hydroxystannate and zinc stannate are effective in a variety of polymer and polymer-based systems and are at least compatible with and their action complimentary to a variety of other flame-retardants.
In many cases, synergies have been reported, i.e. the fire-retardant action of a multicomponent system containing ZINFLAM® zinc hydroxystannate (ZHS) and zinc stannate (ZS) is greater than the combined effect observed by the addition of each component in isolation.

ZINFLAM® zinc hydroxystannate and zinc stannate are non-toxic alternatives, which can be used to completely replace antimony trioxide (Sb_2O_3) in formulations, whilst maintaining or improving most fire-retardant properties. In addition, the incorporation of zinc hydroxystannate and zinc stannate leads to significant and substantial smoke reduction, whilst ATO often generates additional smoke.



Advantage of replacing antimony trioxide (ATO) with ZINFLAM® products

Why replace antimony troxide?

Price volatility - expensive formulations
H&S handling issues - toxicity
Cost saving of ~25% of ATO spend
End-users deselectingmulations

Why use ZINFLAM® ZB to partially replace antimony trioxide?

Boron char formation
Water of hydration released
Reduces arcing and tracking in polymers
Used in low smoke zero halogen systems
Improved smoke suppression
Afterglow/burning drip suppression
Lower toxicity than ATO
Translucent formulation = Pigment savings

Why use ZINFLAM® ZHS to completely replace antimony trioxide?

Tin char formation
Water of hydration released
Used in low smoke zero halogen systems
Better smoke suppression
No toxic
Translucent formulation = Pigment savings

What are optimum addition level?

ZINFLAM® ZB
ZINFLAM® ZHS
33 -66% ATO replacement
Typically 2 - 3%

What are potential cost savings?

When antimony trioxide is twice the zinc borate price, a 50% substitution by zinc borate would give a ~25% cost saving on antimony trioxide spend, along with the technical benefits outlined above.
Even though zinc hydroxystannate is double the antimony trioxide price, total replacement with zhs at 2-3% could lead to cost savings in systems where >4% antimony trioxide is used.
In some PVC systems, as much as 7.5% antimony trioxide may be used to give a specified level of fire performance. Just 2.5% of ZHS could be used to replace this and achieve the same level of fire performance, a ~33% cost saving on annual antimony trioxide would result, with the technical benefits described above.

ZINFLAM® ZHS in PVC applications

Application data

1. PVC cable

Formulation evaluated	(A)	(B)
Alumina trihydrate, martinal OL 104	60	--
Calcium carbonate, winnofil	--	60
PVC, EVC S71/102	100	100
Plasticiser	45	45
Stabiliser	5	5
Calcium stearate	1	1

	Results	LOI% DMC/g*	Smoke	% Smoke reduction
(A)	9 phr antimony trioxide	38.5	37.9	--
	9 phr ZINFLAM® ZHS	38.2	27.0	29%
	6 phr ZINFLAM® ZHS	36.0	23.3	39%
(B)	9 phr antimony trioxide	29.0	43.3	--
	9 phr ZINFLAM® ZHS	30.0	28.2	35%
	6 phr ZINFLAM® ZHS	30.5	27.8	36%

**NBS Smoke Box (Flaming Mode)*

	FR additive	LOI (%)	VO
PVC+phosphate ester			
Control sample	-	21.8	V
1	5 phr ZHS	33.1	V
2	10 phr ZHS	33.1	V
3	5 phr ATO	31.1	V
4	10 phr ATO	31.3	V
PVC+phthalate plasticiser			
Control sample	-	22.8	V
5	5 phr ZHS	25.6	V
6	10 phr ZHS	26.8	V
7	5 phr ATO	26.8	V
8	10 phr ATO	27.8	V

	FR additive	Smoke factor (MW/m^2)	Total smoke (I)	TTP (s)	PHR (kW/m2)
PVC+phosphate ester					
Control sample	-	1017	638	122	320
1	10 phr ZHS	401	614	209	126
2	10 phr ATO	455	705	103	160
PVC+phthalate plasticiser					
Control sample	-	993	901	70	360
3	10 phr ZHS	420	754	278	172
4	10 phr ATO	507	1102	363	168

2. Expanded PVC sheet

Product	Addition rate	Oxygen index
No flame retardant	-	43.5
ZINFLAM® ZHS	1% 2%	49.5 53.5
Antimony trioxide	2% 3%	49.5 51.5
Alumina trihydrate	4% 3%	45.5 46.5

NBS Smoke box tests showed ZINFLAM® ZHS reduced smoke emission by 30 to 40%, whilst Sb_2O_3 produced an increase in smoke emission.

3. Rigid PVC

Sample 1
Control - contains no FR additive

Sample 2
Contains 3 parts zinc hydroxystannate

Sample 3
Contains 3 parts zinc borate grade ZB2335

Sample 4
Contains 3 parts 50:50 blend ZB:ATO

Sample 5
Contains 3 parts antimony trioxide

	1 Control	2 ZHS	3 ZB 2335	4 50:50 blend ZB:ATO	5 Sb_2O_3
Time to ignition (sec's)	55.5	73.00	42.5	99.50	90.00
Peak rate of heat release (kWm^{-2})	270.5	139.50	137.50	138.50	165.00
Total rate released (mJm^{-2})	13.03	13.47	11.77	9.70	7.11
Fire performance index ($m2skW^{-1}$)	0.21	0.52	0.31	0.72	0.55
Smoke parameter index ($MWkg^{-1}$)	267.25	98.14	99.21	128.74	217.74

4. PVC Plastisols

Highly plasticized PVC suspension usually in liquid form.

Applications

Moulding or coating, e.g. glass-fibre filament coating, which can be woven to produce sun screens.

Benefits

Incorporation allows the exacting french m1 flame-retardant standard to be met.

5. Flexible PVC

Plasticized PVC can be moulded, extruded, calendered and used to formulate PVC compounds.

Applications

Wire and cable insulation, conveyor belting.

Benefits

Reduced heat release, improved FPI and lower smoke.

ZINFLAM® ZHS in Halogen-free application

Application data

1. Halogen-free polyolefin cables

a) Effect on LOI in a 50:50 PE/EVA cable compound with 170 phr ATH

Zinc borate	ZINFLAM® ZHS	LOI (%)	Increase in LOI
---	---	34.5	---
---	3%	38.0	3.5
---	5%	41.5	7.0
5%	---	41.5	7.0
5%	3%	43.5	9.0

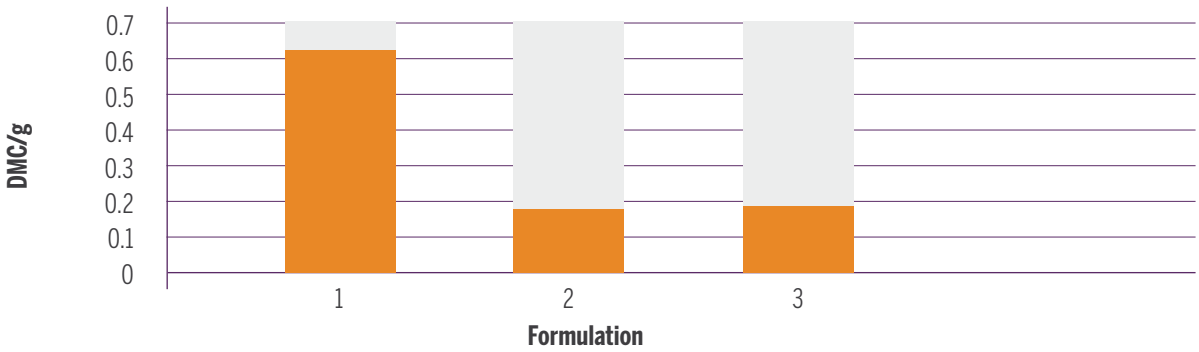
For each 1% addition, both zinc borate and ZINFLAM® ZHS improve the oxygen Index by between 1.2% and 1.4%. They therefore appear effective at improving the flame retardancy at relatively low addition levels.

b) ZINFLAM® ZS has been added to magnesium hydroxide filled polypropylene to determine whether filler loading can be reduced

Magnesium hydroxide grade
Magnifin H10/B (Martinswerk)
Polypropylene grade
Vestolen P G002 (Huls)
LOI of blank polypropylene
18

Formulation	LOI (%)*	Smoke DMC/g**	Smoke reduction
65% Mg(OH)2 35% Polypropylene	28.5	0.61	---
50% Mg(OH)2 47% Polypropylene 3% ZINFLAM® ZS	25.5	0.17	72%
65% Mg(OH)2 44% Polypropylene 6% ZINFLAM® ZS	26.0	0.18	70%

* Quoted LOI value subject to erroof 0.5 unit
** NBS Smoke Box (Flaming Mode) Average of 3 independent determinations



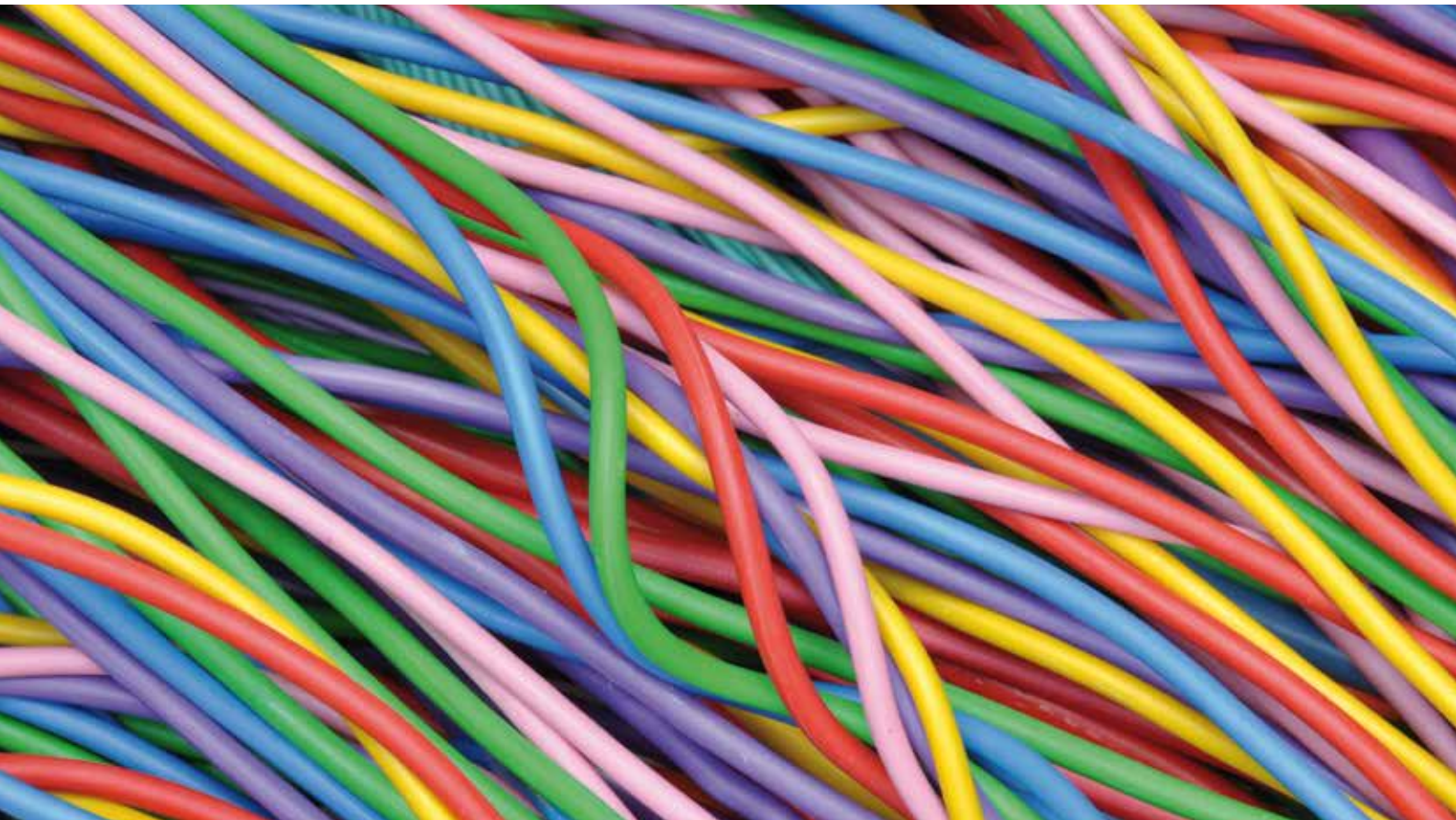
With reduced loadings from 65% to 50% of magnesium hydroxide and a corresponding increase in PP content, ZINFLAM® ZS has a significant positive effect on the smoke suppression. The oxygen index level, however, is slightly reduced.

c) Ethylene - acrylic rubber (Vamac G ex Du Pont)

A 60% loading of alumina trihydrate has been generally found necessary to raise the LOI of ethylene - crylic rubber to 33 and meet the UK MOD naval specification NES 518.
The tests show a reduction of ATH loading to 50% gives a lower lol of 27.5.
2.5% addition of ZINFLAM® ZHS to 50% ATH loading improves the lol to the original figure of 33.

The polymer composition containing ZINFLAM® ZHS has a temperature index of at least 250°C and above that of the rubber containing ATH alone, which is about 200°C.
A significant reduction in ATH content is possible and this means that better physical and mechanical properties could be achieved with ZINFLAM® ZHS in Vamac formulations.
The inherent low smoke level of Vamac meant that no smoke performance differences were measurable. However in most cases the use of ZINFLAM® ZHS leads to smoke improvement.

	Formulation	LOI (%)	Temperature index
1	**60% A.T.H**	33.0	---
2	**50% A.T.H**	27.5	200°C
3	**50% A.T.H + 2.5% ZINFLAM® ZS**	33.0	>250°C

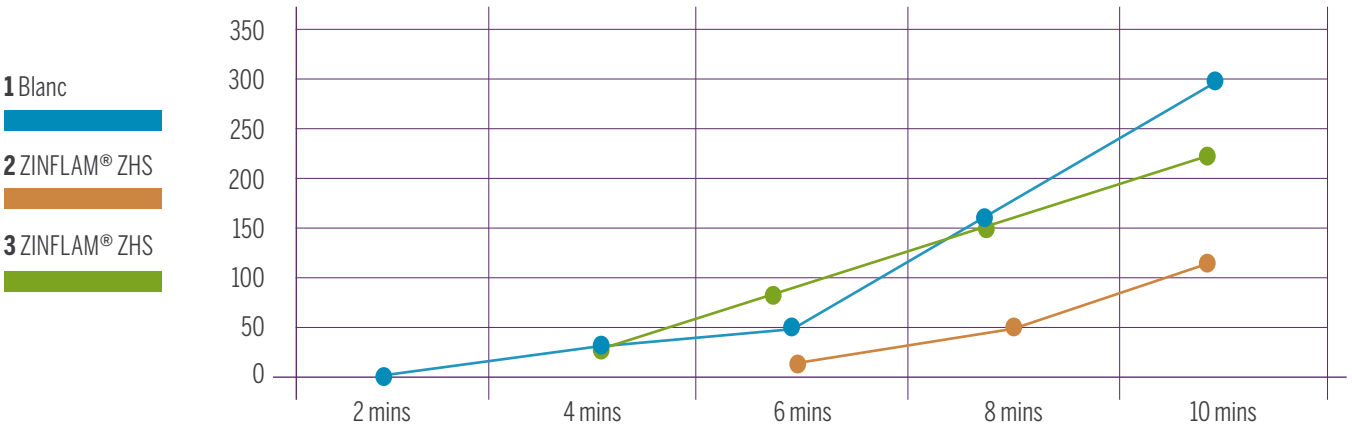


2. Halogen-free epoxy resins

a) Smoke tests - NBS smoke box (Flaming Mode) Ds

	Formulation	2 mins	4 mins	6 mins	8 mins	10 mins (Dmax)
1	**60% A.T.H**	5	30	40	160	304
2	**50% A.T.H**	---	---	10	50	113
3	**50% A.T.H**	---	30	80	150	222

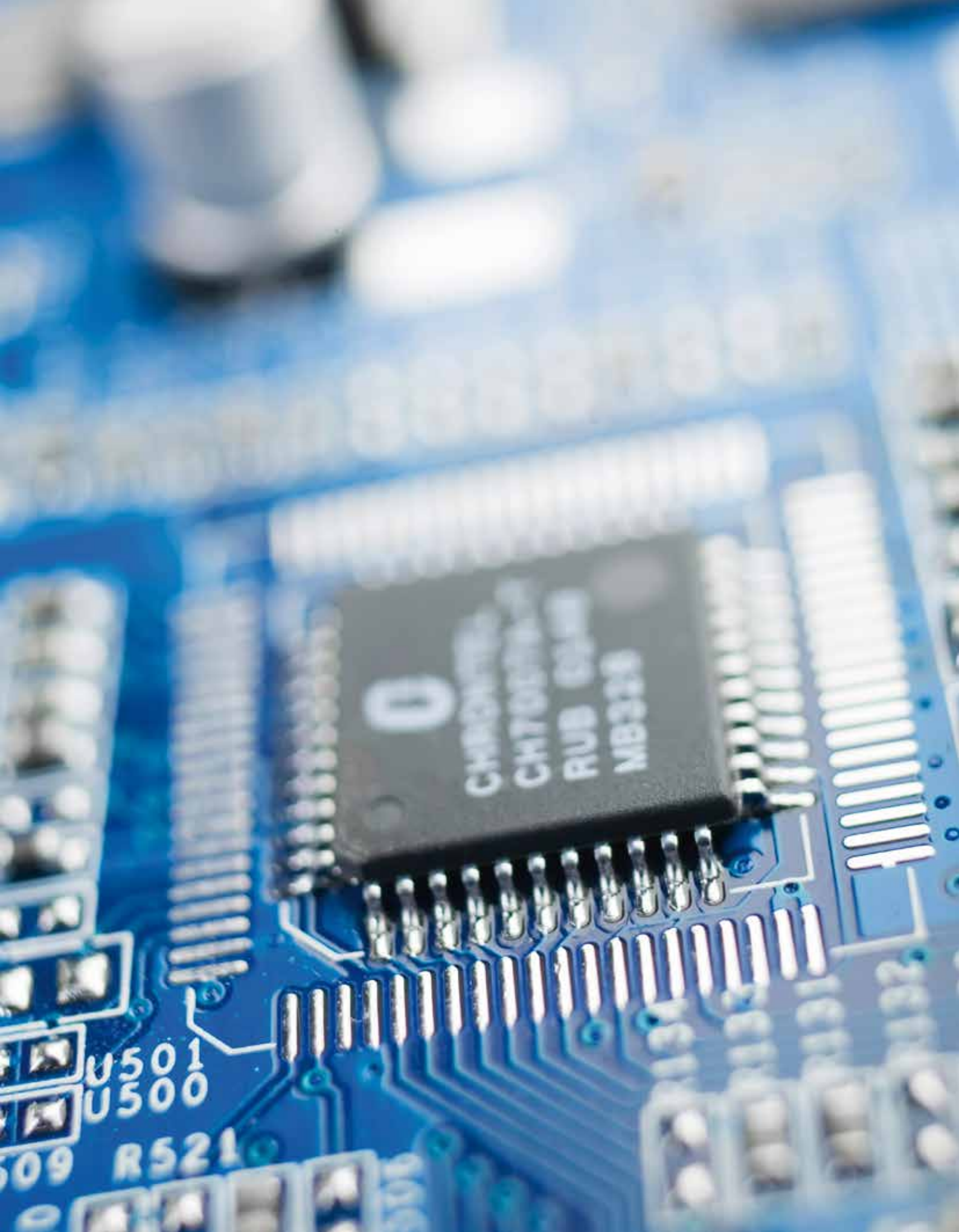
b) Oxygen Index (%)



	Formulation	LOI (%)
1	**Blank**	22.0
2	**3% ZINFLAM® ZHS**	26.5
3	**3% ZINFLAM® ZHS**	24.5

NB Formulations 2 and 3 containing ZINFLAM® ZHS had further modifications carried out

The addition of 3% ZINFLAM® ZHS can assist in improving the smoke emission and flammability of epoxy resins protected by it.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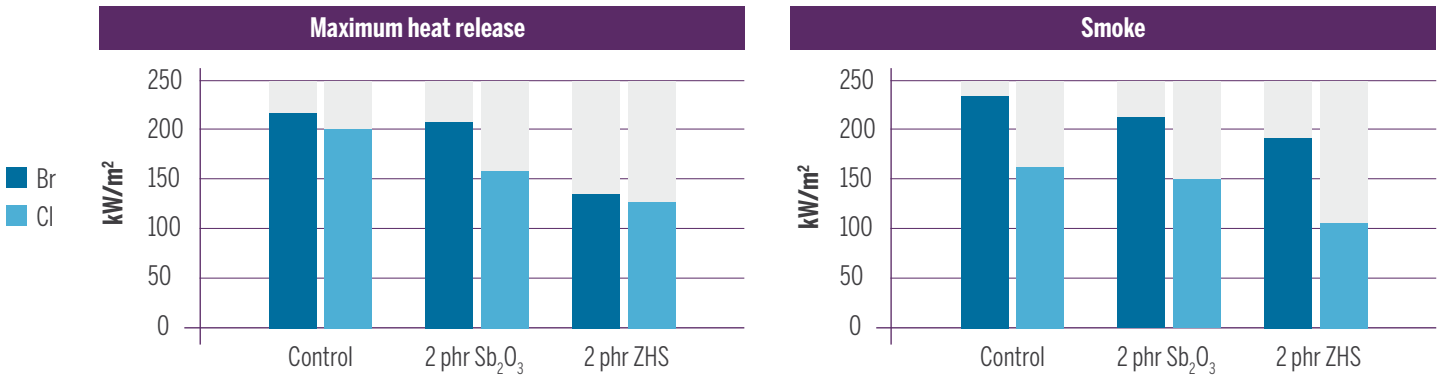
ZINFLAM® ZHS in Unsaturated Polyester Resins application

Application data

1. Halogenated polyester resins

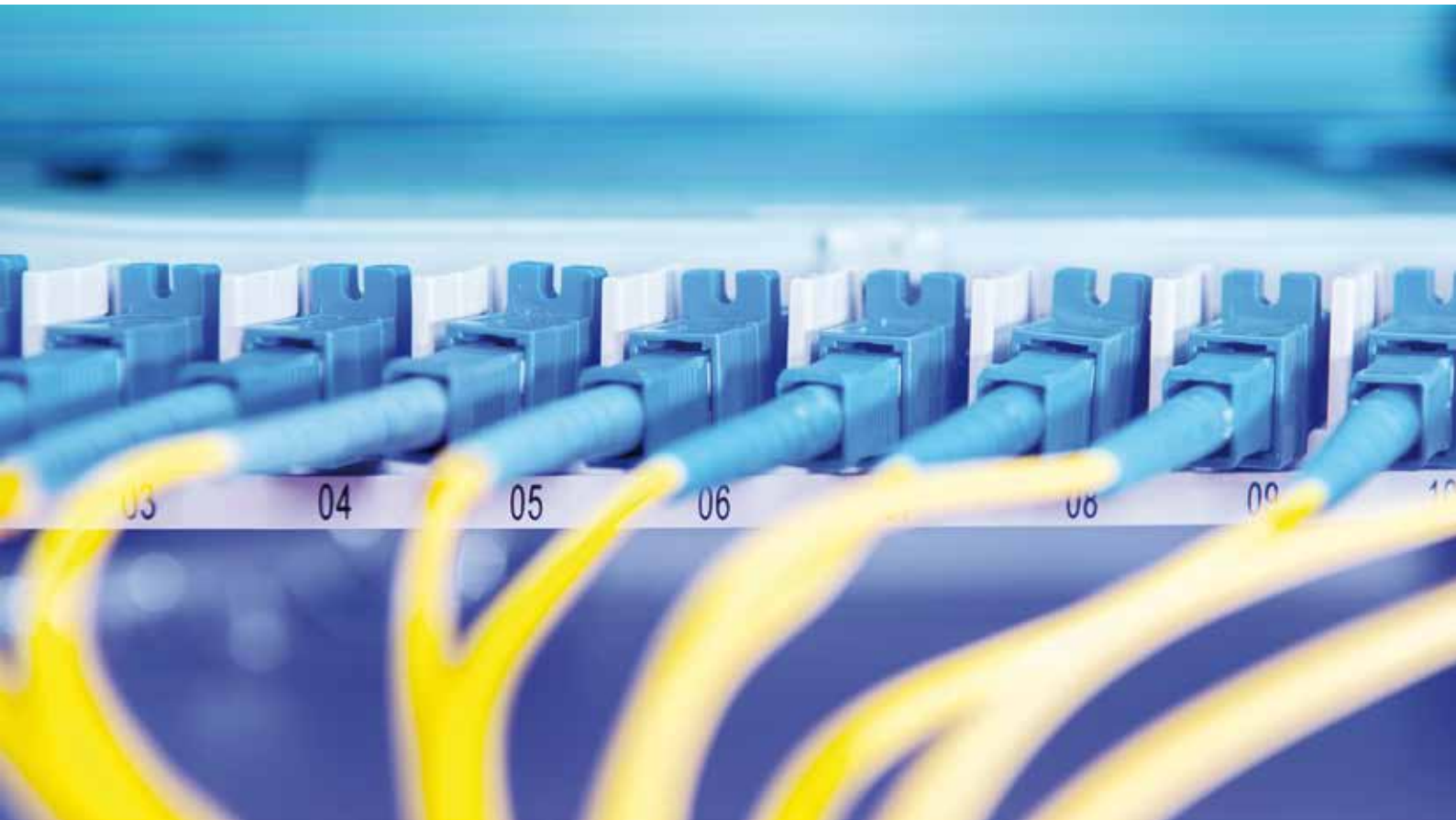
		Tests results		Effects	
	Rate of heat release	**Br**	**Cl**	**Br**	**Cl**
1	**Control**	128 kW/m²	115 kW/m²		
2	**Sb_2O_3**	88 kW/m²	87 kW/m²	31%	24%
3	**ZINFLAM® ZHS**	95 kW/m²	68 kW/m²	26%	41%
	Maximum heat release reduction	**Br**	**Cl**	**Br**	**Cl**
1	**Control**	221 kW/m²	202 kW/m²		
2	**Sb_2O_3**	210 kW/m²	156 kW/m²	5%	23%
3	**ZINFLAM® ZHS**	135 kW/m²	126 kW/m²	39%	37%
	Smoke reduction	**Br**	**Cl**	**Br**	**Cl**
1	**Control**	1141 m²/kg	825 m²/kg		
2	**Sb_2O_3**	1059 m²/kg	589 m²/kg	7%	28%
3	**ZINFLAM® ZHS**	972 m²/kg	415 m²/kg	15%	50%

Cone calorimeter comparison of ZINFLAM® ZHS and antimony trioxide in halogenated polyester resins (50 kW/m2 heat flux, 2 phr addition of each).



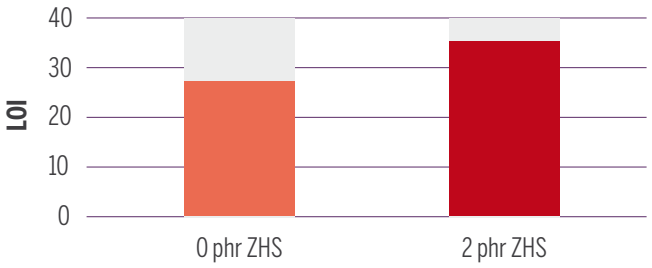
Cl is 28% Cl - Hetron 92, Br is 28% Br - Stypol R1264 (ex DSM Resins UK)
Results are by kind permission of ITRI where copies of the full technical paper can be obtained.

Heat release measurements show ZINFLAM® ZHS to be an effective alternative at 2 phr addition to antimony trioxide with the added advantage of an improvement in smoke emission.



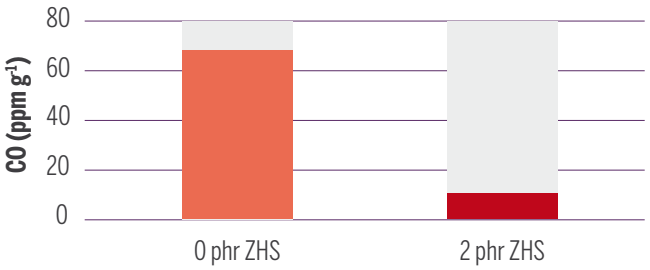
2. Chlorinated systems

a) Effect on Limiting Oxygen Index



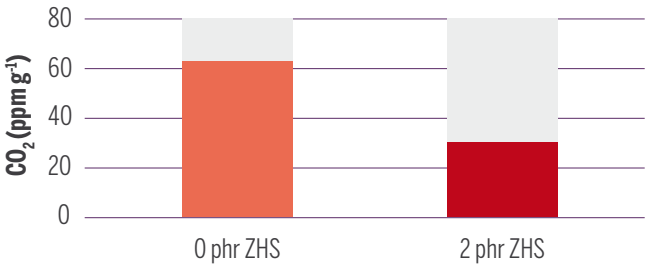
	LOI (%)
0 phr ZHS	26.8
2 phr ZHS	35.0

b) Effect on Carbon Monoxide Emission



	CO (ppm g-1)
0 phr ZHS	66.5
2 phr ZHS	11.8

c) Effect on Carbon Dioxide Emission



	CO_2 (ppm g^{-1})
0 phr ZHS	810.5
2 phr ZHS	379.7

d) Smoke Density

	Max Optical Density (g-1)
0 phr ZHS	810.5
2 phr ZHS	379.7

Smoke and gas emissions were measured using an NBS smoke box.
The advantages of including 2phr ZHS include an 8.2 unit increase in LOI, an 82% reduction in carbon monoxide emission, a 53% reduction in carbon dioxide emission and a 51% reduction in smoke emission. Without ZHS, the formulation would fail the UL 94 (3.2mm thickness), but the addition of 2phr ZHS gives it a V0 rating.

3. Brominated systems

Resin
10% bromine
as dibromoneopentylglycol

*Smoke and gas emissions were measured using NBS smoke box

	Effect of 2 phr ZINFLAM® ZHS	2 phr ZINFLAM® ZHS	No Additive
Oxygen Index	7.2 units increase	32.8	25.6
Max Optical density (g^{-1})*	19% reduction	56.8	69.2
Carbon Monoxide (ppm g^{-1})*	25% reduction	106.8	141.7
Carbon dioxide (ppm g^{-1})*	45% reduction	997	1800
UL 94 (3.2 mm thickness)*		V0	fail

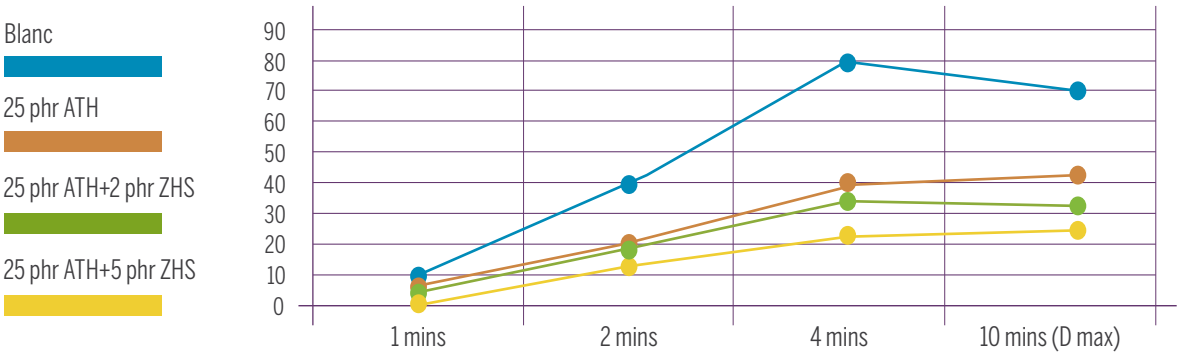
Limiting oxygen index is improved and V0 rating can be obtained with 2phr ZINFLAM® ZHS, whilst smoke and toxic gas emissions can be reduced.

4. Halogen-free systems

a) **Smoke tests** - NBS smoke box (Flaming Mode)

Resin
Crystic 471 PA LV - Scott Bader

	1 mins	2 mins	4 mins	10 mins (Dmax)	Reduction
Blank	10	42	78	72	
25 phr ATH	5	20	38	41	43%
25 phr ATH + 2 phr ZHS	3	15	32	31	57%
25 phr ATH + 5 phr ZHS	2	12	22	24	67%



25phr alumina trihydrate reduces maximum smoke emission by 43%. The further addition of 2phr and 5phr ZHS improves this reduction to 57% and 67% respectively.

b) Oxygen index

LOI (%)	
Blank	18,9
25 phr ATH	20,4
25 phr ATH + 2 phr ZHS	20,5
25 phr ATH + 5 phr ZHS	20,8

ZINFLAM® ZS in Polyamide application

Application data

1. Nylon 6 and 6,6 unfilled

Formulation
A: Nylon 6 - 79 parts
Chlorinated FR - 15 parts
Synergists - 6 parts
B: Nylon 6,6 - 77.5 parts
Chlorinated FR - 15 parts
Synergist - 7.5 parts

Formulation	Synergist (s)	UL 94 (3.2 mm)	UL 94 (1.6 mm)	UL 94 (0.8 mm)
A	6% Sb_2O_3	Fail	Fail	Fail
A	6% ZB	Fail	Fail	Fail
A	4% ZS + 2% ZB	V0	V0	V1
B	7.5% Sb_2O_3	V2	V2	V2
B	7.5% ZS	V0	V0	V0

V0 can be achieved with reduced smoke by replacing Sb_2O_3 with ZINFLAM® ZS.

2. Nylon 6 and 6,6 unfilled and unfilled

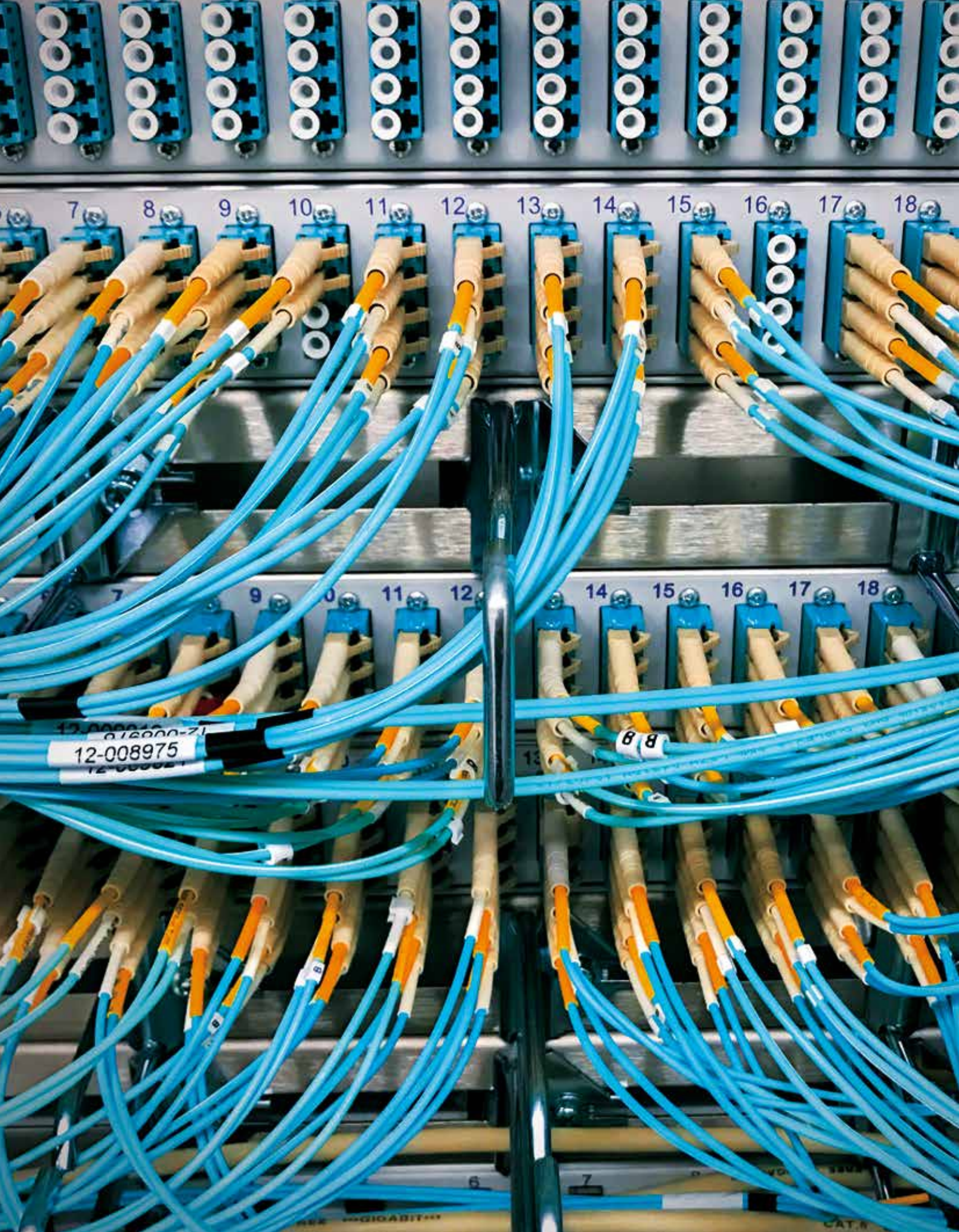
Formulation
C: Nylon 6,6 - 78 parts
Chlorinated FR - 15 parts
Synergists - 6 parts
D: Nylon 6 - 51 parts
Fiberglass - 25 parts
Chlorinated FR - 16 parts
Synergists - 8 parts
E: Nylon 6,6 - 51 parts
Fiberglass - 25 parts
Chlorinated FR - 14 parts
Synergists - 4 parts

Formulation	Synergist (s)	UL 94 (3.2 mm)	UL 94 (1.6 mm)	CTI (Kc) volts
C	2% Sb_2O_3 + 4% ZB	V0	V0	450
C	2% ZS + 4% ZB	V0	V0	600
D	6% Sb_2O_3 + 2% ZB	V0	V0	325
D	6% ZS + 2% ZB	V0	V0	350
E	2% Sb_2O_3 + 2% ZB	V0	V0	350
E	1% ZS + 1% ZnO + 2% ZB	V0	V0	425

V0 can be achieved with reduced smoke and lower CTI values when replacing Sb_2O_3 with ZINFLAM® ZS.

3. Halogen-free systems

Incorporation of ZINFLAM® ZS in non-halogen, flame retardant PA6 formulations can enhance fire-resistance properties by increasing char formation in these systems. ZINFLAM® ZS can act synergistically in combination with aromatic phosphates, melamine salts and metal phosphinates to improve the overall flame retardant behaviour of the nylon. Furthermore, addition of ZINFLAM® ZS shouldn't adversely affect the thermal stability of FR formulations of PA6 in which it is incorporated and can lead to improvement of the tensile properties that would otherwise be compromised by addition of phosphorus-based flame retardants.
Formulating non-halogen FR systems in PA6 with ZINFLAM® ZS should be possible to achieve good levels of flame retardant behaviour, optimised tensile performance coupled with reduced smoke generation.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