TECHNICAL BULLETIN

Firebrake® ZB

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RioTinto

An alternative to antimony oxide

The use of antimony oxide (also referred as antimony trioxide or ATO) as a synergistic additive to enhance fire retardancy is very well known in the plastics industry. It is mainly used in halogenated polymers such as polyvinyl chloride (PVC) and with halogenated-based flame retardants (bromine, chlorine).

The largest producer of antimony is China with almost half of the global production. However, production has declined and demand in another growing market (photovoltaic) has created supply constraints and price increases[1]. Price doubled or tripled during summer 2024, and export limitations of antimony from China is likely to create even more of a supply shortage as well as continued price increases[2].

In addition, ATO has raised many toxicity concerns as it is suspected to be a human carcinogen[3].

Much effort has been made in the past to find partial or complete substitutes for ATO. Depending on the polymeric system, *Firebrake*® ZB has shown to be an effective complete or partial substitute. In most polymers, the combination of both products displays synergistic effects. Moreover, in contrast to ATO which promotes smoke formation, *Firebrake* ZB reduces smoke emission and acts as a strong char promoter.

This Technical Bulletin reviews the work that has been done to partially or completely substitute ATO with *Firebrake* ZB in various polymeric systems.

Polyvinyl chloride (PVC)

Firebrake ZB is well-established in PVC as a partial replacement for ATO with the distinct advantage of smoke and afterglow suppression[4].

As can be seen in the oxygen index test in Figure 1, ATO alone is effective but starts to level off at a dosage of 8-10 phr. *Firebrake* ZB displays strong synergistic effect with ATO at a 1:1 ratio and outperforms ATO alone at a total loading of more than 10 phr.

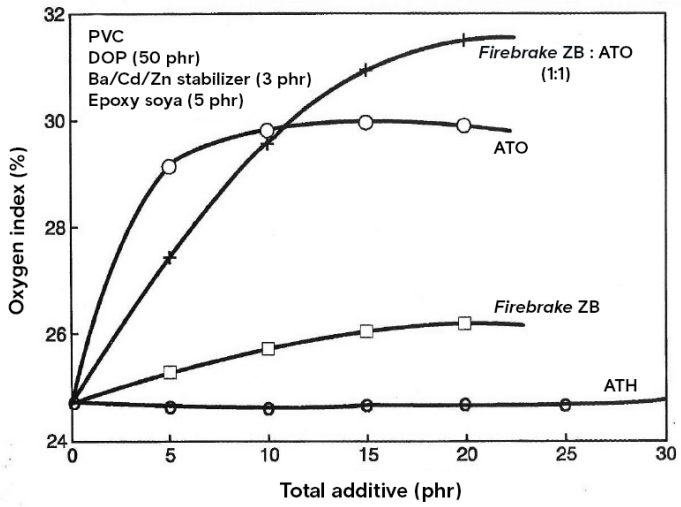

Figure 1: Oxygen index test of flexible PVC (DOP: Dioctyl Phthalate)[5]

Similar effects have been found when alumina trihydrate (ATH) is used in a flexible PVC formulation. The cone calorimeter test (Figure 2) shows that 50 wt% replacement of ATO with *Firebrake* ZB results in a drastic reduction in the rate of heat release.

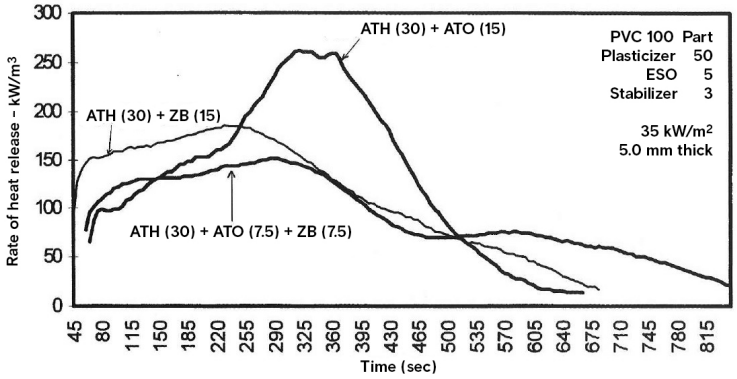

Figure 2: Cone calorimeter test of flexible PVC (ZB: Firebrake *ZB)[6]*

Although ATO prerforms well as a flame retardant for PVC, its use can drastically increase the production of smoke during combustion. *Firebrake* ZB, on the other hand, is an effective smoke suppressant with ATH (Figure 3) or without ATH (Figure 4).

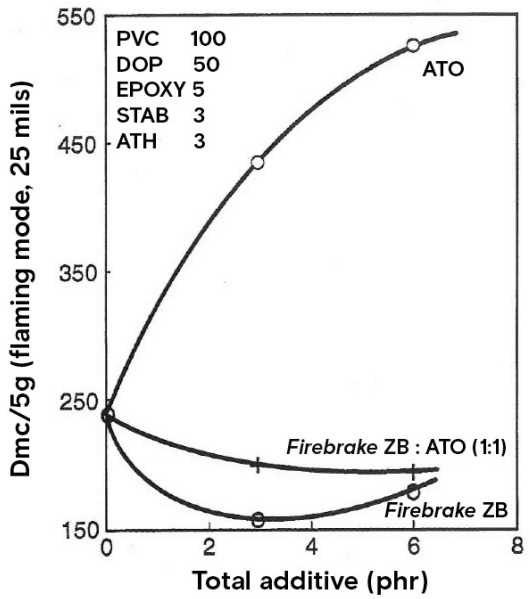

Figure 3: NBS smoke test of flexible PVC

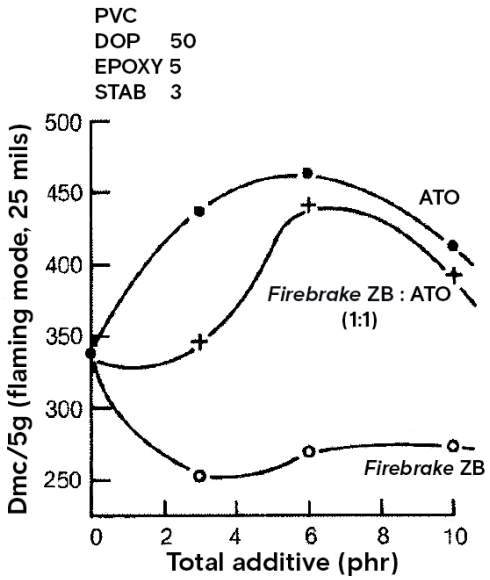

Figure 4: ASTM E662 smoke test of flexible PVC (without ATH)

This improvement is particularly seen when using less plasticizer. In this study (Table 1), a 50 wt% replacement of the ATO with *Firebrake* ZB resulted in higher Limited Oxygen Index (LOI) and a significant reduction of the smoke. The use of *Firebrake* ZB Fine further improves those properties. Total replacement of the ATO with *Firebrake* ZB results in further decreases in smoke but with decreased LOI compared to ATO alone.

Components (phr)	#1	#2	#3	#4	#5
Geon 30	100	100	100	100	100
DOP	40	40	40	40	40
ATH	30	30	30	30	30
Plaschek 775	5	5	5	5	5
Themchek 120	3	3	3	3	3
ATO	6	3	0	3	0
Firebrake ZB	0	3	6	0	0
Firebrake ZB Fine	0	0	0	3	6
Properties					
LOI (%O_2)	32.4	34.2	29.8	35.4	29.8
NBS smoke chamber (Dmax)	513	386	167	305	153
Ave % char	15.8	13.8	14.2	13.2	15.8

Table 1: LOI and NBS smoke chamber test of flexible PVC[7]

Tables 2 and 3 show that ATO replacement with *Firebrake* ZB in a PVC cable formulation still maintains the same firetest performance. More importantly, the replacement results in drastic smoke reduction.

NBS smoke test[a]

Fire retardant additive	D_{mc}	D_5 (4 minutes)	O.I. %[b]	UL94[b]
None			27.4	V-O
ATO	371	371	31.2	V-O
Firebrake ZB (3 phr) (extruded sample)			30.3	V-O
Firebrake ZB (3 phr)			29.6	V-O
Firebrake ZB (1.5 phr) / ATO (1.5 phr)	284	289	31.1	V-O
Firebrake ZB (2 phr) / ATO (1 phr)	276	276	30.9	V-O

Formulation: Geon 103EP (100phr), 7,9,11 mixed alkyl phthalate (40phr), ATH (15phr), coated tribasic lead sulfate (5phr), petroleum wax (0.5phr), plus additives, prepared in Brabender mixer.
a Sample thickness 20 mils, flaming mode. Dmc is corrected maximum specific optical density and D5 (4 minutes) is specific optical density at 4 minutes.
b Oxygen index and UL94, sample thickness 1/8 inch
Table 2: Tests on flexible PVC jacket formulation[5]

Components (%wt)	#1	#2	#3	#4
PVC	100	100	100	100
Dioctyl phthalate	50			
Polyester-W2310			55	45
Octyl trimillitate		50		
ATO		10	10	10
Firebrake ZB		5	10	10
ATH		20	40	50
$Mg(OH)_2$		5		
Disbasic lead sulate	1	1	1	1
Ba / Zn			5	
Expoxy oil		1	2	2
Tribasic lead sulfate	5	4		4
Properties				
LOI (%)	27.6	32.0	42.1	47.4
Smoke (C_5 max)[a]	5.2	1.58	0.39	0.33

Note: Japan, Kokai Tokkyo Koho 83 37 (1983, Dainichi Nippon Cables)
a C5max = (2.303/L)log(100/T), L= 0.5m
Table 3: Tests on flexible PVC wire and cable formulation[5]

Epoxy

The effectiveness of *Firebrake* ZB as a flame retardant in epoxies depends strongly on the type of halogen source used (aromatic vs aliphatic or alicyclic).

When an alicyclic compound is used, *Firebrake* ZB alone outperforms ATO up to a loading of 6 phr in both LOI and UL94 tests (Figure 5). The combination of *Firebrake* ZB with ATO at 1:1 ratio provides the best performance between 3 – 10 phr total loading showing the synergistic effect of the two additives.

With aromatic halogen source, *Firebrake* ZB alone is not as effective as ATO but partial replacement with *Firebrake* ZB (50 wt%) provides similar or better results than ATO alone (Figure 6).

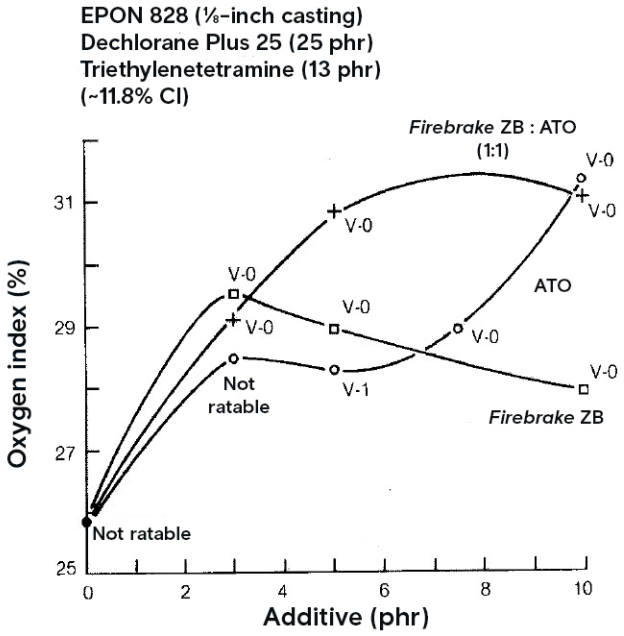

Figure 5: LOI and UL94 tests with an aliphatic compound

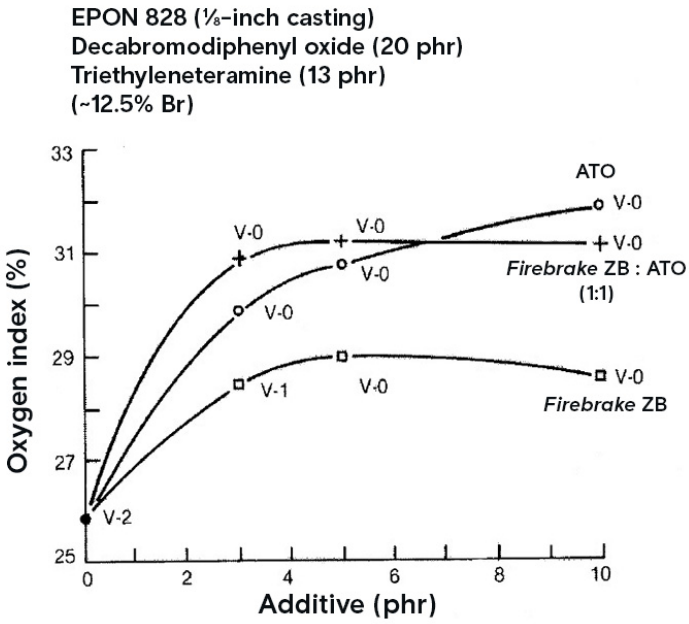

Figure 6: LOI and UL94 tests with an aromatic compound

Firebrake ZB is also a strong smoke suppressant in epoxy depending on the halogen source. With an aliphatic source, *Firebrake* ZB provides a 40% decrease in smoke in the NBS smoke chamber test compared to ATO (Table 4). However, such decrease is not observed with an aromatic source.

Additives	D_{mc} [a]
Dechlorane Plus® 25 (25 phr)	737
Dechlorane Plus® 25 (25 phr) / *Firebrake* ZB (5 phr)	587
Dechlorane Plus® 25 (25 phr) / ATO (5 phr)	833
DBDPO[b] (20 phr) / *Firebrake* ZB (5 phr)	855
DBDPO[b] (20 phr) / ATO (5 phr)	798

Note: Cured with TETA, 1/16–inch thick, flaming mode
a Corrected maximum specific optical density
b Decabromodiphenyl oxide
Table 4: NBS smoke chamber test in epoxy

Polyolefins

Firebrake ZB has been successfully used as a partial replacement for ATO in halogenated polyethylene formulations.

A UL94 rating of V-0 was obtained when 50 wt% of the ATO was replaced with *Firebrake* ZB when used with an aliphatic source and when 33 wt% of the ATO is replaced with *Firebrake* ZB in an aromatic source as seen in Tables 5 and 6.

Components (%wt)	#1	#2	#3
LDPE[a]	100	100	100
Dechlorane Plus® 25	60	60	60
ATO	20	15	10
Firebrake ZB		5	10
Properties			
UL94 (1/4 inch)	V-1 (1, 14)[b]	V-1 (0, 7)	V-0 (1, 4)
LOI (%)	29.4	27.5	28.3

a Exxon LD400 (MI 2.7), Santonox R (0.5), and Dicup (2)
b Burn times in seconds after first and second ignition
Table 5: UL94 and LOI tests on low-density polyethylene with aliphatic compound

Components (%wt)	#1	#2	#3	#4	#5	#6
LDPE	100	100	100	100	100	100
DBDPOa	30	30	30	30	30	30
ATO	15	15	15	10	10	10
Firebrake ZB				5	5	5
Talc		25			25	
ATH			30			30
Properties						
UL94 (1/8 inch)	V-2 (0,1)[b]	V-2 (0,10)	V-2 (0,2)	V-2 (0,21)	V-0 (0,0)	V-2 (2,20)
LOI (%)	27.1	27.0	28.6	24.7	28.3	26.5

a Decabromodiphenyl oxide
b Burn times in seconds after first and second ignition
Table 6: UL94 and LOI tests on low-density polyethylene with aromatic compound

Polyamides (nylon)

The combination of *Firebrake* ZB and ATO at 1:1 ratio has been successfully used in polyamide formulations such as Nylon 6/6 to meet UL94 V-0 rating (Table 7).

A high level of ATO can decrease electrical properties as shown in Table 8. For high-quality electrical parts, the preferred composition contains high levels of *Firebrake* ZB with a low level of ATO in a halogenated formulation.

Components (%wt)	1a	2b
Nylon 6/6	52	75
Dechlorane Plus® 25	17	19
ATO	3	3
Firebrake ZB	3	3
Glass fiber	25	
Properties		
UL94	V-0	V-0

a Cerny J, Troney BR, inventors; Rhone-Poulenc, assignee. 1978. Flameproofed plastic compositions. Patent 1,512,300.
b ibid, Ger. Offen. 2,656,883
Table 7: UL94 test on Nylon 6/6 formulation

Additives	UL94		Tensile strength	CTRc
	50% RH[a]	**70C[b]**	**(MN/m²)**	
Firebrake ZB (15 wt%)	Fail	Fail	141	>600
Dechlorane 515 (10 wt%)	Fail	Fail	147	300
Dechlorane 515 (10 wt%) / ATO (5 wt%)	V-0	V-0	140	200
Dechlorane 515 (10 wt%) / *Firebrake* ZB (15 wt%) / ATO (0.1 wt%)	V-1	V-1	138	500
Dechlorane 515 (10 wt%) / *Firebrake* ZB (15 wt%) / ATO (1 wt%)	V-0	V-1	137	475
Dechlorane 515 (10 wt%) / *Firebrake* ZB (15 wt%) / ATO (2 wt%)	V-0	V-0		<350

Note: Maslen AJ, Taylor WH, inventors; ICI, assignee. 1978. Nylon 6/6 with 28% glass fiber. United States patent 4,105,621.
a Measured on a sample of 1.6 mm thick after conditioning at 50% RH and 23°C for 48 hours
b Measured on a sample of 1.6 mm thick after conditioning at 70°C for one week
c Comparative Tracking Resistance
Table 8: Tests on Nylon 6/6 / glass fiber formulation

In Nylon 6/6 containing brominated polystyrene, *Firebrake* ZB can almost replace ATO completely and still maintain the same UL94 rating[8] (Table 8).

In addition to improving electrical properties as seen with the CTI (Comparative Tracking Index), *Firebrake* ZB was also found to improve thermal stability, color stability, melt viscosity stability, and corrosion resistance of the processing equipment in polyamides.

Components (%wt)	#1	#2	#3	#4
Polyamide 6,6	47	47	44	44
Fiberglass	25	25	25	25
Brominated polystyrene	21	21	24	24
ATO	7			
Firebrake ZB		7	7	
Firebrake ZB-XF (extra fine)				7
Properties				
UL94 1.6 mm		V-2	V-0	V-0
0.8 mm	V-0	V-2	V-0	V-0
CTI (V) (dry as molded)	225	475	450	475
IZOD (kJ/m^2)		11.8	13.1	13.9

Table 9: Tests on glass-reinforced Nylon 6/6

Acrylonitrile butadiene styrene (ABS)

The combination of aromatic bromine flame retardant and ATO has proven to be very efficient in ABS. ATO can be replaced with zinc borate at up to 75 wt% and sustain flame properties while suppressing smoke.

Table 10 shows the results of an injection molding grade ABS (Terluran® GP-22 from BASF) with an aromatic brominated compound (ethane-1,2-bis pentabromophenyl, Saytex™ 8010 from Albemarle) and various ratio of ATO and ZB (3:1, 1:1, 1:3).

The results show that when ATO was replaced with ZB, UL94 rating of V-0 was maintained in all ratios. LOI was slightly reduced when increasing the *Firebrake* ZB ratio but was still maintained at the 3:1 (ATO:ZB) ratio.

Additives	UL94 rating[a]	LOI (%)
ABS	Fail	19
ABS / 6% ATO	V-0	30
ABS / 4.5% ATO / 1.5% ZB	V-0	30
ABS / 3% ATO / 3% ZB	V-0	29
ABS / 1.5% ATO / 4.5% ZB	V-0	27
ABS / 6% ZB	Fail	23

a 1/8in thickness

Table 10: UL94 and LOI flammability tests in ABS9

The mass loss calorimeter test shows improvement with the substitution of ATO with *Firebrake* ZB (Table 11). The compound with 50 wt% replacement resulted in the best performances with the highest suppression in the peak heat release rate and total heat evolved values.

This study also shows that tensile mechanical properties are maintained or even increased with the replacement of ATO with ZB.

Additives	Peak heat release rate (kW/m^2)	Total heat evolved (MJ/m^2)	Time to peak heat released rate (s)	Time to ignition (s)
ABS	900	134	192	83
ABS / 6% ATO	239	44	188	64
ABS / 4.5% ATO / 1.5% ZB	257	40	197	67
ABS / 3% ATO / 3% ZB	203	31	246	65
ABS / 1.5% ATO / 4.5% ZB	265	35	192	60
ABS / 6% ZB	360	57	199	72

Table 11: Mass loss cone calorimter test

In another study[9] using an aromatic bromine (Ethyl Saytex™ BT-93), a 50 wt% or 75 wt% of ATO replacement with *Firebrake* ZB provided V0 rating (Table 12).

With a brominated polystyrene (Pyrocheck™ 68-PB), a 50 wt% replacement of the ATO with *Firebrake* ZB was achieving similar V0 rating. At higher *Firebrake* ZB loading, the rating went down to V1.

Components (phr)			UL94 rating[a]
Bromine	**ATO**	***Firebrake* ZB**	
20	10		V-0
20		10	V-1
20	5	5	V-0
20	2.5	7.5	V-0
20	1	9	V-1
Bromine (68-PB)	**ATO**	***Firebrake* ZB**	
20	10		Fail
20		10	Fail
24	6	6	V-0
24	3	9	V-1

a 1/8in thickness
Table 12: UL94 test on ABS with Saytex™ BT-93 and Pyrocheck™ 68-PB

Polystyrene

The same study above was done on high impact polystyrene (HIPS) and a similar trend was seen when the Ethyl Saytex™ BT-93 was used as bromine flame retardant. A 75 wt% replacement provide same UL94 rating of V-0 (Table 13).

However, with the brominated polystyrene (Pyrocheck™ 68-PB), the replacement of ATO with *Firebrake* ZB resulted in a decrease of the rating to V-1. This replacement offered some benefits by reducing the afterglow which was very high with ATO alone.

Components (phr)			UL94 rating[a]
Bromine (BT-93)	**ATO**	***Firebrake* ZB**	
20	10		V-0
20		10	V-1
20	5	5	V-0
20	2.5	7.5	V-0
Bromine (68-PB)	**ATO**	***Firebrake* ZB**	
20	10		V-0
20		10	Fail
20	5	5	V-1

a 1/8in thickness
Table 13: UL94 test on HIPS with Saytex™ BT-93 and Pyrocheck™ 68-PB

Unsaturated polyester resin

Firebrake ZB can be used to replace ATO either completely or partially and unlike ATO, *Firebrake* ZB allows the resins to retain their translucency.

Firebrake ZB has shown to improve fire-test performance in halogenated unsaturated polyester (UP) resins with either aliphatic or alicyclic halogen sources (such as dibromoneopentyl glycol) as shown by the Oxygen Index test (Figure 7).

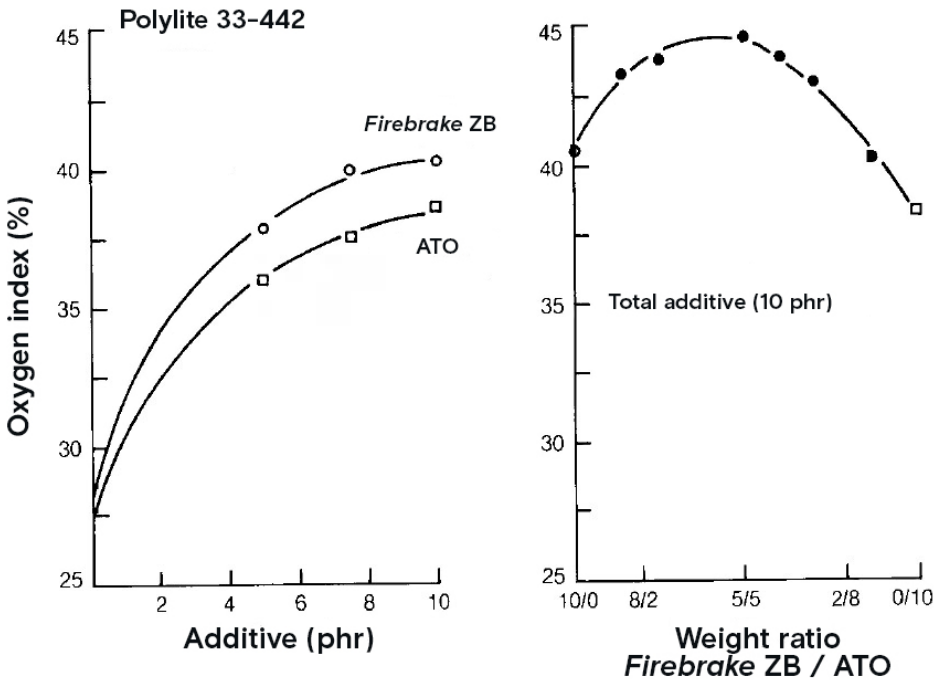

Figure 7: Oxygen index of UP with dibromoneopentyl glycol[10]

However, Oxygen Index tests have shown that *Firebrake* ZB is much less effective in polyesters with aromatic halogen sources.

Elastomer

In halogen-containing elastomers, such as styrene-butadiene rubber (SBR), ethylene propylene diene monomer (EPDM), or neoprene, a good starting point is the replacement of 30-50 wt% of ATO with *Firebrake* ZB. If equal or improved fire performance is achieved, a complete replacement can be targeted.

Urethane

A patent for a carpet backed with polyurethane shows that the addition of *Firebrake* ZB to the ATO allow to pass the Federal Aviation Regulation test.[12]

Componentsa (%wt)	#1	#2	#3
ATO		85	60
Firebrake ZB			20
ATH	170		30
Vinyl chloride / vinylidene chloride (1:9)		85	60
Viscosity-reducing agent (KR-46B)		1	1
Flammability testsb			
Temp, deg C	1204	1204	1204
Afterflame, sec	>60	>60	None
Afterglow, sec	5	None	None
Char length, cm	30.5	16	5.6
Pass or fail	Fail	Fail	Pass

Note: McKinney LD, Jenkines RC, inventors; Dow Chemical Co, assignee. 1984. Woven carpet substrate manufactured by Bigelow Sanford with a greige weight of 35 oz/yd^2 and a stitch rate of 72 tufts / in^2. United States patent 4,435,459.
a Urethane consisted of polyol (100 parts), polyisocyanate (60), and catalyst (0.2).
b Federal Test Method Standard 191, Method 5903.2

Table 14: Federal Aviation test on carpet backed with polyurethane

Antimony oxide vs *Firebrake* ZB: Advantages and disadvantages

ATO	*Firebrake* ZB
Unsteady price	Stable price
Tends to promote smoke	Good smoke suppressant
Tends to promote afterglow	Inhibits afterglow
Effective flame retardant in most halogen-containing systems	Used either as a complete or partial replacement of ATO; can display synergistic effects with ATO
Generally not a synergist of other fillers	Synergist of ATH and other fillers
Generally poor for anti-tracking	Good anti-tracking agent
Does not have any biocidal effects	Has biocidal properties
Water insoluble / Has good wet electrical properties	Vert slightly souble in water / Has poor wet electrical properties
Considered toxic	Not on substance of Very High Concern (SVHC) list
Tends to stabalize PVC slightly	Tends to destabilize PVC or aliphatic halogen source
High hiding power	Does not induce opacity
High specific gravity / Tends to settle in solvents	Lower specific ravity / Less tendency to settle in solvents
Usually not used in halogen free systems	Can be used in halogen-free systems

References

[1] Du X. Supply constraints push antimony prices to record high. 4 July 2024. MMTA; [accessed date]. https://mmta.co.uk/supply-constraintspush-antimony-prices-torecord-high/.

[2] China to limit antimony exports in latest critical mineral curbs. 15 Aug, 2024. Reuters, [accessed date]. https://www.reuters.com/world/china/china-limit-antimonyexports-latest-critical-mineral-curbs-2024-08-15/

[3] Antimony Trioxide. 2021. Report on Carcinogens, 15th ed. National Toxicology Program, U.S. Department of Health and Human Services.

[4] Weil ED, Levchik S, Moy P. 2006. Flame and Smoke Retardants in Vinyl Chloride Polymers – Commercial Usage and Current Developments. J Fire Sci. 24(3):211-236.

[5] Shen KK. 1985. Firebrake ZB: The Unique Multifunctional Additive. Plastics Compounding.

[6] Shen KK. 2006. Overview of Flame Retardancy and Smoke Suppression of Flexible PVC. Paper presented at: SPE Vinyltech Conference; Atlanta, GA, USA.

[7] Ferm, DJ. 2000. Low-Smoke, Antimony-Free PVC: Fire Retardancy and Smoke Tests. U.S. Borax Internal Report TEC-2000-03.

[8] Shen KK, Kochesfahani S, Jouffret F. 2008. Zinc borates as multifunctional polymer additives. Polym Adv Technol. 19:469-474.

[9] Kaynak C, Ozkaraca, A. 2011. Use of Zinc Borate as the third component of a traditional Brominated flame retardant system in ABS. FMATDV. 11:0091.

[10] Zinc Borate with Various Halogen Compounds in Styrenic Polymers 1991. U.S. Borax Internal Report TR-91-3.

[11] Shen KK, Sprague RW. 1981. On the Use of a Unique Form of Zinc Borate as Flame Retardant in Fiberglass Reinforced Unsaturated Polyesters and Vinyl Esters. Paper presented at: 36th Annual Conference, Reinforced Plastics/Composites Institute, the Society of the Plastics Industry, Inc. Session 13B.

[12] McKinney LD, Jenkines RC, inventors. The Dow Chemical Co., assignee. 1983 Mar 18. Carpet backed with fire suppressant polyurethane composition. United States patent US 4,435,459.

About U.S. Borax

U.S. Borax, part of Rio Tinto, is a global leader in the supply and science of borates—naturally-occurring minerals containing boron and other elements. We are 1,000 people serving 650 customers with more than 1,800 delivery locations globally. We supply around 30% of the world's need for refined borates from our world-class mine in Boron, California, about 100 miles northeast of Los Angeles.

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U.S. Borax produces the *20 Mule Team*® borates family of products from naturally occurring minerals and have an excellent reputation for purity and safety when used as directed. Borates are key ingredients in a number of industrial applications including fiberglass, glass, ceramics, batteries and capacitors, wood preservatives, and flame retardants.

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