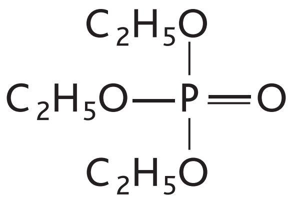
Eastman™ triethyl phosphate (TEP)



$$\begin{array}{rcl} & C_2H_5O & \\ & | & \\ C_2H_5O - & P & = O \\ & | & \\ & C_2H_5O & \end{array}$$

(CAS: 78-40-0)

Effective viscosity reduction in:

- Filled and unfilled unsaturated polyester resins for fiberglass-reinforced plastic (FRP)
- Aliphatic polyester polyols for flexible urethane foams
- Aromatic polyester polyols and sucrose-amine polyols for rigid urethane foams
- Acrylic resins and saturated polyester resins for high-solids protective coatings

Synergist for flame resistance with:

- Highly filled reinforced plastic (RP) systems
- Halogenated unsaturated polyesters for RP applications

Effective viscosity reduction in polymer systems

Liquid resins of relatively low molecular weight are polymerized or cross-linked to produce a variety of articles used in transportation, residential, and recreational applications. Frequently, fillers, pigments, or reinforcements are added to the resins to reduce cost, enhance appearance, or improve the physical properties of the final products. The additives usually increase resin viscosity, making more difficult the spraying or molding operations required to process resins into useful articles. Because of high viscosity, some resins are difficult to process even when unfilled and may be virtually unprocessable when filled.

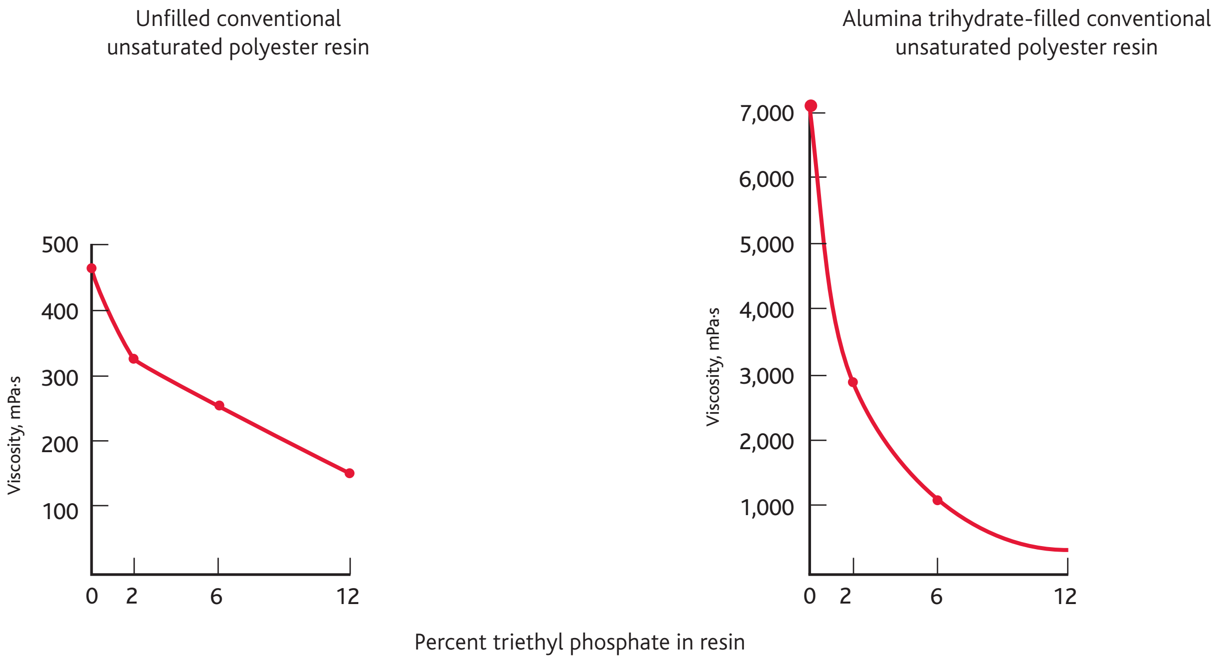
In laboratory studies of several resin systems, adding a small amount of Eastman™ triethyl phosphate (TEP) significantly reduced resin viscosity, thereby improving processability and/or providing higher filler- or additive-loading capability.

These commercially available resin systems were used in the study: (1) filled and unfilled unsaturated polyester resins used to fabricate fiberglass-reinforced plastics, (2) aliphatic polyester polyols used to manufacture flexible urethane foams, (3) aromatic polyester polyols and sucrose-amine polyols used to produce rigid urethane foams, and (4) acrylic resins and saturated polyester resins used to formulate high-solids protective coatings. Viscosities were determined at 26°C (78°F) using a Model LVF Brookfield™ viscometer. The viscosity was investigated at 0, 2, 6, and 12 weight % concentrations of TEP.

Fiberglass-reinforced plastics

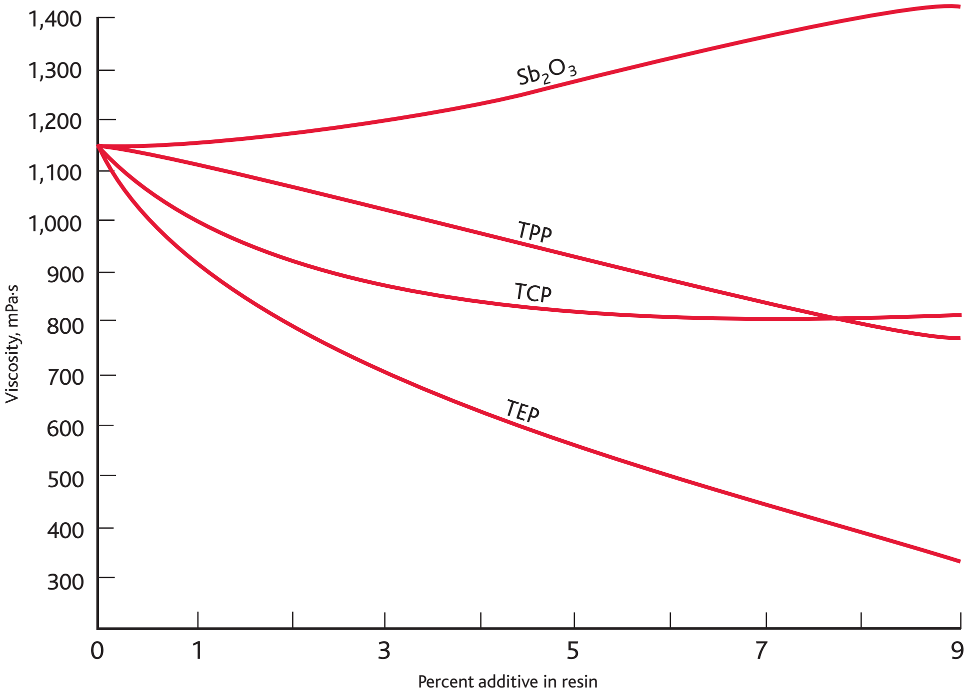
Many fiberglass-reinforced plastics are used in applications that require some degree of flame resistance. One commonly used approach for achieving flame resistance is incorporating a halogenated intermediate in the polyester polymer structure. Another approach is offered by the use of alumina trihydrate as a filler in low-cost, general-purpose resins, but this can result in objectionably high viscosity. Eastman™ TEP has been found to be an effective additive in both types of flame-resistant resin systems. Figure 1 shows how TEP can reduce the viscosity of unfilled and filled systems.

Figure 1
The effect on resin viscosity of adding Eastman™ TEP to filled and unfilled unsaturated polyester resins



Eastman™ TEP was found to be more effective than any of the other synergists in reducing viscosity of the polyester/styrene solution. Table 4 gives the viscosity of the resin samples; Figure 2 also shows the results graphically. Adding 3 weight % TEP was sufficient to lower the viscosity of the original polyester/styrene solution from 1,150 to 720 mPa•s.

Figure 2
Effect of additive on solution viscosity



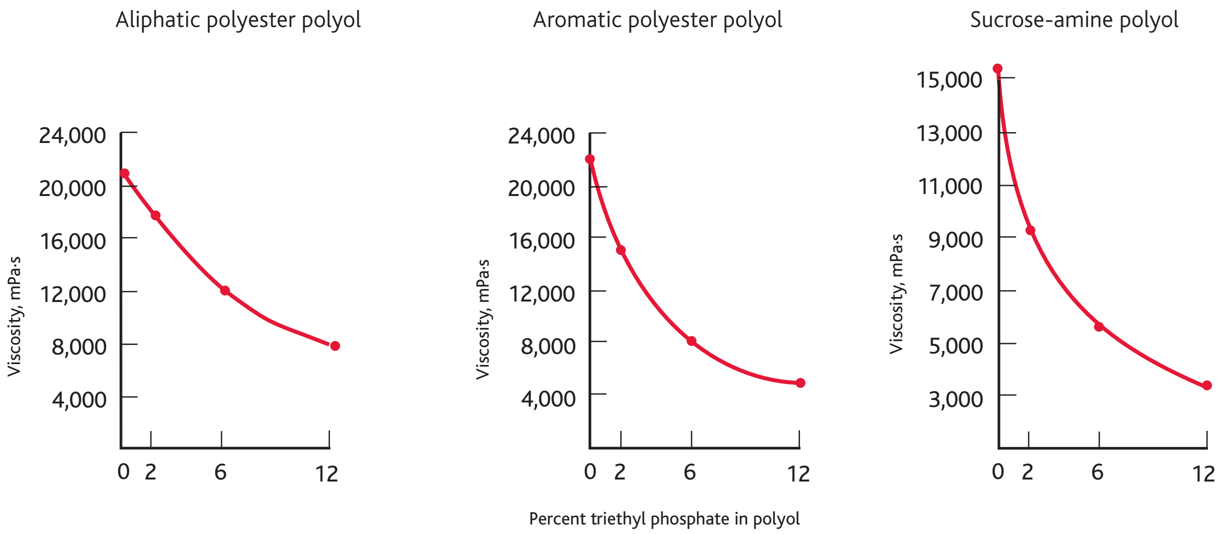
The effects of the synergists on cure characteristics are indicated by the SPI gel test data given in Table 4. Each synergist caused a progressive increase in gel time and lowering of peak exotherm, depending on concentration used. However, the effects of Eastman™ TEP on cure characteristics were considered acceptable when it was used at 1–5 weight % concentration.

Also, each of the three phosphorus-containing synergists imparted some plasticization effects to the cured polyester samples but the effects were insignificant at 1–5 weight % concentrations.

Urethane foams

As Figure 3 shows, adding 6 weight % Eastman™ TEP reduced the viscosity of a typical aliphatic polyester polyol used to manufacture flexible urethane foams by about 50%. Adding TEP caused an even greater reduction in viscosity of an aromatic polyester polyol and a sucrose-amine polyol, both of which are used to manufacture rigid urethane foams.

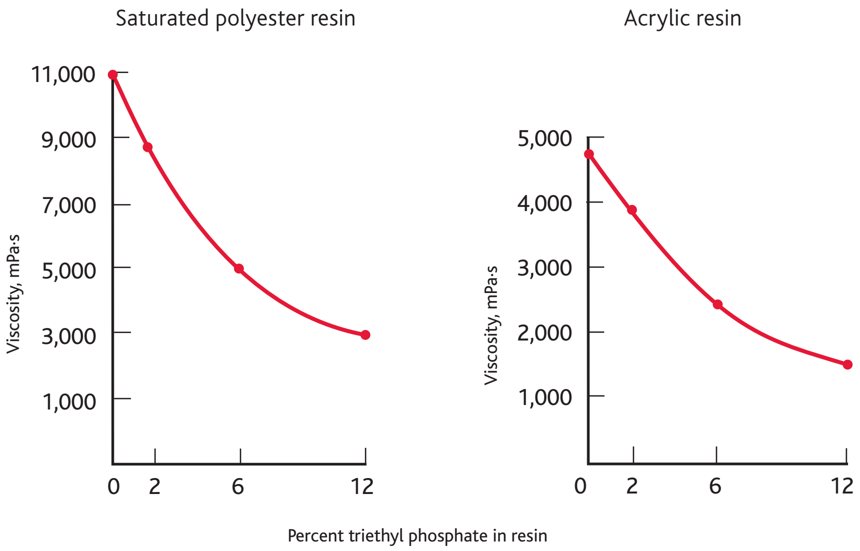
Figure 3
Effect of Eastman™ TEP on viscosity of urethane foam polyols



Protective coatings

One method of reducing the quantity of organic solvents emitted to the atmosphere from protective coatings is to use high-solids formulations. Figure 4 shows the effects of adding Eastman™ TEP to acrylic and saturated polyester coatings resins used in such formulations.

Figure 4
Effect of Eastman™ TEP on viscosity of coatings resins



Eastman™ TEP in alumina trihydrate-filled resins

Tests conducted in Eastman laboratories have shown that flame-resistant resins can be prepared with a low-cost, general-purpose polyester resin formulated with alumina trihydrate filler and Eastman™ TEP. If alumina trihydrate is used alone in a general-purpose resin, significant flame resistance can be obtained, but resin viscosity is considerably increased, which makes spray application difficult. TEP is being used in filled unsaturated polyester resins to reduce the solution viscosity of the filled resin, permitting better wet-out of fiberglass laminates and increasing their flame resistance.

The effect of TEP on viscosity reduction and increased flame resistance of castings prepared from a commercial general-purpose resin containing alumina trihydrate filler was determined. Table 1 gives the results. Formulation D, containing 50 parts by weight alumina trihydrate and 6 parts by weight Eastman™ TEP, gave a casting with the best level of flame resistance. Adding 6 parts per hundred by weight TEP lowered the heat deflection temperature (HDT) of the filled casting prepared with general-purpose resin from 74°C to 50°C (165°F to 122°F); however, high HDTs can be obtained by increasing the percentage of unsaturation in the resin formulation.

Table 1 **Effect of Eastman™ TEP on alumina trihydrate-filled commercial general-purpose resin castings (3.2-mm [0.125-in.] castings)**

	Formulation			
Composition	A	B	C	D
Commercial general-purpose resin, weight %	100	50	50	50
Alumina trihydrate filler, weight %	—	50	50	50
TEP, parts per hundred by weight (based on resin and filler)	—	0	4	6
	100	100	104	106
Properties				
Viscosity, mPa•s	400–500	3,840	1,480	900
Oxygen index[a,d,e]	18	25	28	29
Burn rate, in./min[a,b,e]	1.0	0.16	0.11	0.09
mm/min	25.4	4.06	2.79	2.29
Heat deflection temperature (HDT), °C (°F)[a,c]	68 (154)	74 (165)	57 (135)	50 (122)

[a] *Tests conducted on 0.125-in. castings cured with 1 weight % benzoyl peroxide and heated for 3 h @ 70°C, 1 h @ 100°C, and 1 h @ 150°C.*

[b] *ASTM D757 Globar™ test*

[c] *ASTM D468 combined with ASTM D116*

[d] *ASTM D2883*

[e] *The results of these tests have not been validated in actual fire situations. As a result, Eastman makes no representation that these data will be meaningful for end-use products in such situations.*

Table 2 shows additional test results obtained with FRP laminates containing 25% fiberglass. The results show that TEP permits laminates to be prepared with 50 parts per hundred by weight of alumina trihydrate, which increases the flame resistance with an acceptably small increase in resin viscosity. The use of TEP in alumina trihydrate-filled resins offers a potentially more economical alternative to halogenated resins for applications requiring flame resistance.

Table 2 **Effect of Eastman™ TEP on alumina trihydrate-filled laminates prepared from a commercial general-purpose resin (3-ply, 1.5-ounce, chopped-strand mat)**

	Formulation			
Composition	**A**	**B**	**C**	**D**
Commercial general-purpose resin, weight %	100	50	50	50
Alumina trihydrate, weight %	—	50	50	50
TEP, parts per hundred by weight (based on resin and filler)	—	0	4	6
	100	100	104	106
Properties				
Glass content, weight %	25	—	25	25
Viscosity, mPa•s	400–500	3,840[c]	1,440	900
Oxygen index[a,d,e]	19	—	29	29
Burn rate, in./min[a,b,e]	0.35	—	0.08	0.07
mm/min	8.89	—	2.03	1.78
Flexural strength,[a] Pa	2.48	—	2.44	2.20
psi	17,100	—	16,800	15,200
Flexural modulus, 10^{-5}[a]	9.70	—	8.00	7.00

[a] *Tests conducted on 3-ply, 1.5-ounce, chopped-strand mat laminate cured using the following:*
Gel time extender—150–250 ppm by weight hydroquinone
Promoters—0.2–0.4 weight % N,N-*dimethyl-p-toluidine and 0.3–0.6 weight % of 6 weight % cobalt solution*
Catalyst—1.0 weigh %–1.5 weight % methyl ethyl ketone peroxide (60 weight %)
All percentages are based on weight of resin on filler.

[b] *ASTM D757 Globar™ test*

[c] *Laminates could not be prepared because of high viscosity.*

[d] *ASTM D2883*

[e] *The results of these tests have not been validated in actual fire situations. As a result, Eastman makes no representation that these data will be meaningful for end-use products in such situations.*

The superior efficiency of Eastman™ TEP at lower concentrations may be due partly to the higher concentration of phosphorus in TEP, relative to the phosphorus concentrations of tricresyl phosphate (TCP) and triphenyl phosphate (TPP). TEP contains 17.0% phosphorus; TCP, 8.5% phosphorus; and TPP, 9.5% phosphorus by weight.

Figure 5 shows the effects of available phosphorus on burn rate, with respect to the variation in phosphorus content among the three phosphate esters. Allowing for the variation in phosphorus content among the additives, Figure 5 indicates that TEP is still more effective than TCP or TPP at phosphorus concentrations up to approximately 0.4 weight %.

Another laboratory method, the Oxygen Index Test (ASTM D2883), was used to evaluate flammability by measuring the minimum oxygen concentration by volume in a gaseous mixture required to support combustion of the samples. The smaller the oxygen index value, the more flammable the specimen.

The oxygen index ratings obtained with the resin samples (see Figure 7) indicate again that none of the phosphate esters are as effective as antimony trioxide (Sb_2O_3) in reducing flammability. In concentrations of 1–5 weight %, TEP imparts degrees of lower flammability that are intermediate between those of antimony trioxide and the other phosphate esters. At concentrations above 5 weight % synergist, TCP becomes more effective than TEP. As Table 4 shows, however, the use of these synergists at concentrations within the upper range becomes impractical.

Eastman™ TEP as a synergist in halogenated resins

The use of Eastman™ TEP and other compounds of phosphorus as additives to improve flame resistance in unsaturated resins is well known. TEP is commonly used in halogenated unsaturated polyesters because of the synergistic effects between phosphorus compounds and noncombustible halogenated gases, which retard combustion when such plastics are decomposed by ignition temperatures.

Although antimony trioxide is perhaps the most commonly used and the most effective additive for increasing flame resistance in halogenated plastics, the opacity it produces is sometimes undesirable; it may settle out of polyester/styrene solutions during storage. Phosphate esters such as TEP, TPP, or TCP are much more compatible with polyester/styrene solutions and are preferred for use in plastics that must be clear.

Experiments were conducted in Eastman laboratories to determine the relative effectiveness of TEP, TPP, TCP, and antimony trioxide in a general-purpose, flame-resistant unsaturated polyester resin. Among effects considered were flammability, viscosity, physical properties, and cure characteristics.

During the Eastman test program, TEP was found to be more effective than TCP or TPP on an equal-weight basis in reducing flammability of a chlorinated unsaturated polyester resin, especially when used at concentrations of 1–3 parts per hundred by weight synergist. TEP also gave lower resin solution viscosities than did TCP or TPP.

FRP laminates prepared from polyesters containing Eastman™ TEP had good clarity and should interest producers of products requiring flame resistance and clarity.

Preparation of polyester samples

The halogenated polyester resin used in the study was prepared by reacting propylene glycol with tetrachlorophthalic and maleic anhydrides. Table 3 gives the molar ratios used and the physical constants of this polyester. The molten polyester was diluted in styrene to a monomer concentration of 30% by weight. The polyester/styrene solution contained 20% chlorine by weight.

Table 3 Formulation and properties of flame-resistant unsaturated polyester resin

Reactants		Moles	Grams
Propylene gycol		6.66	507
Tetrachlorophthalic anhydride		3.06	876
Maleic anhydride		3.00	294
			1,677
		Theoretical H_2O	–108
		Yield	1,569
Styrene monomer		6.45	673

Physical constants	
Glycol excess, mole %	10
Acid number, mg KOH/g resin	40
Molecular weight, Mn	1,148
Monomer	Styrene
Resin/monomer ratio by weight	70/30
Chlorine content, weight %	20
Viscosity, mPa•s	1,150
Color, Gardner™	2–3

A series of polyester synergist solutions were prepared containing TEP, TPP, TCP, or antimony trioxide at concentrations of 1, 3, 5, 7, and 9% by weight.

Unfilled castings were prepared from each solution with 0.5 weight % benzoyl peroxide as the initiator; the castings were oven cured for 3 hours at 70°C (158°F), 1 hour at 100°C (212°F), and 1 hour at 150°C (302°F). The castings were used to determine flexural strength, heat deflection temperature, and Barcol hardness.

Two-ply fiberglass-reinforced laminates, 0.125-inch thick and containing 25% glass by weight, were prepared from each solution in accordance with ASTM D581. The laminates were cured at room temperature with MEK peroxide and cobalt naphthenate. Cure was achieved in 16 hours at room temperature, followed by 2 hours postcure at 100°C (212°F). Suitable test specimens were prepared from the cured laminates for use in flammability determination by two separate test methods: ASTM D757, the Globar™ test; and ASTM D2883, the Oxygen Index Flammability Test.

Effect of synergists on polyester performance

Table 4 summarizes the results of the flammability tests and other tests used in this study. Note that the concentration of phosphorus-containing synergist in each resin sample is expressed as both percent additive and as percent phosphorus by weight. Table 4 does not show performance properties of resin samples containing 9 weight % synergist because the use of any of these synergists at that concentration would be impractical.

Effect of synergists on flame resistance properties

The numerical results obtained with each of the two flammability test methods used are listed in Table 4 and are depicted in Figures 5, 6, and 7. None of the phosphate esters evaluated were as effective as antimony trioxide in reducing the burn rate of the chlorinated polyester, as determined by the Globar™ test. Of the phosphate esters, TEP was more effective than TCP or TPP in reducing the burn rate (see Figure 5), especially at concentrations of 1–5 weight % synergist.

Table 4 **Effects of additive on the physical properties of flame-resistant resin (3.2-mm [0.125-in.] castings)**

	Properties									
	Additive concn, %	Phosphorus concn, %	Viscosity, mPa•s	SPI gel time, min	Peak exotherm, °C (°F)	Barcol hardness	Heat deflection temp, °C (°F)	Flexural strength, MPa (psi)	Flexural modulus x 10^{-6}	Globar™ test ASTM D757 mm/min	Oxygen index, ASTM D2883
Resin, no synergist	0	0	1,150	3.6	187 (368)	50	91 (196)	94 (13,600)	0.75	6.7	21.1
Triethyl phosphate	1.0	0.170	900	3.4	182 (359)	50	86 (187)	88 (12,750)	0.75	3.3	22.7
Tricresyl phosphate	1.0	0.085	990	4.5	179 (355)	50	84 (183)	83 (12,100)	0.63	5.0	21.1
Triphenyl phosphate	1.0	0.095	1,120	5.6	147 (297)	47	84 (183)	88 (12,800)	0.66	6.0	21.1
Antimony trioxide	1.0	—	1,190	7.3	114 (237)	47	90 (194)	90 (13,100)	0.70	2.1	23.1
Triethyl phosphate	3.0	0.510	720	4.3	176 (348)	45	79 (174)	94 (13,650)	0.71	2.7	24.7
Tricresyl phosphate	3.0	0.255	910	4.2	182 (360)	49	79 (174)	91 (13,150)	0.70	4.2	21.9
Triphenyl phosphate	3.0	0.285	1,020	5.9	135 (275)	48	79 (174)	84 (12,200)	0.65	4.2	22.3
Antimony trioxide	3.0	—	1,210	4.5	196 (385)	47	92 (198)	97 (14,000)	0.76	2.0	27.2
Triethyl phosphate	5.0	0.850	540	4.3	182 (360)	41	71 (160)	88 (12,700)	0.65	2.3	24.6
Tricresyl phosphate	5.0	0.425	830	7.1	159 (318)	48	77 (171)	85 (12,400)	0.66	2.6	23.9
Triphenyl phosphate	5.0	0.475	920	6.2	128 (263)	47	76 (169)	81 (11,750)	0.64	3.0	23.1
Antimony trioxide	5.0	—	1,260	4.5	191 (376)	47	91 (196)	92 (13,400)	0.71	1.4	29.6
Triethyl phosphate	7.0	1.190	390	4.5	143 (290)	36	61 (142)	79 (11,500)	0.55	2.6	24.6
Tricresyl phosphate	7.0	0.595	910	6.2	155 (311)	47	71 (160)	88 (12,700)	0.66	2.3	26.5
Triphenyl phosphate	7.0	0.665	830	6.9	93 (200)	46	71 (160)	70 (10,150)	0.62	2.7	23.5
Antimony trioxide	7.0	—	1,360	4.8	189 (372)	46	91 (196)	95 (13,700)	0.75	1.5	30.6

Figure 5
Effect of additive on flame resistance ASTM D757—Globar™ test

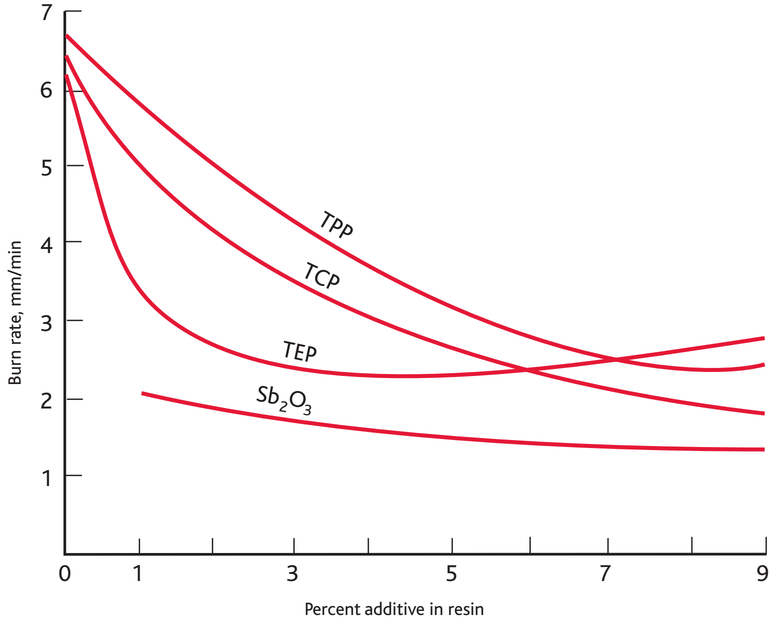


Figure 6
Effect of phosphorus content on flame resistance ASTM D757—Globar™ test

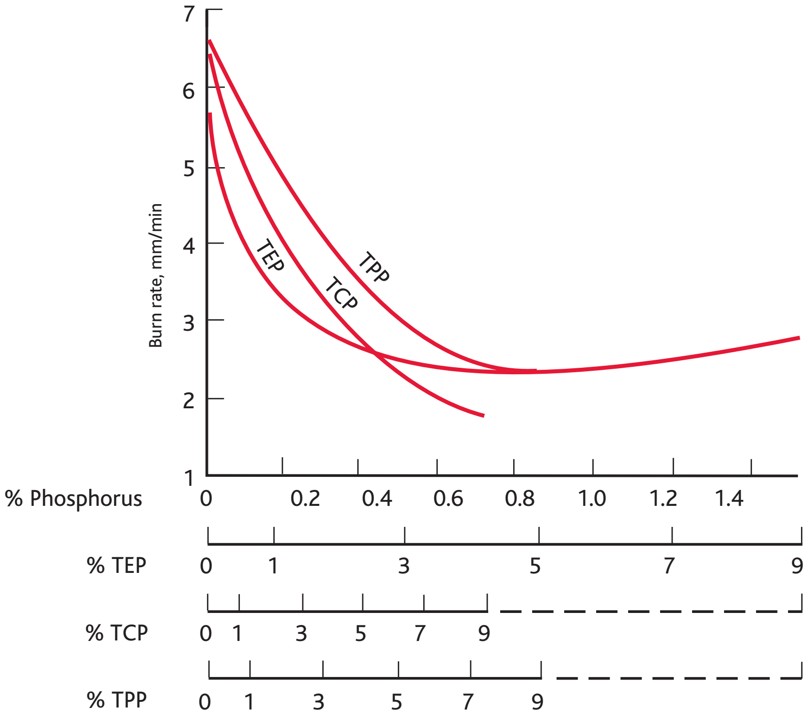
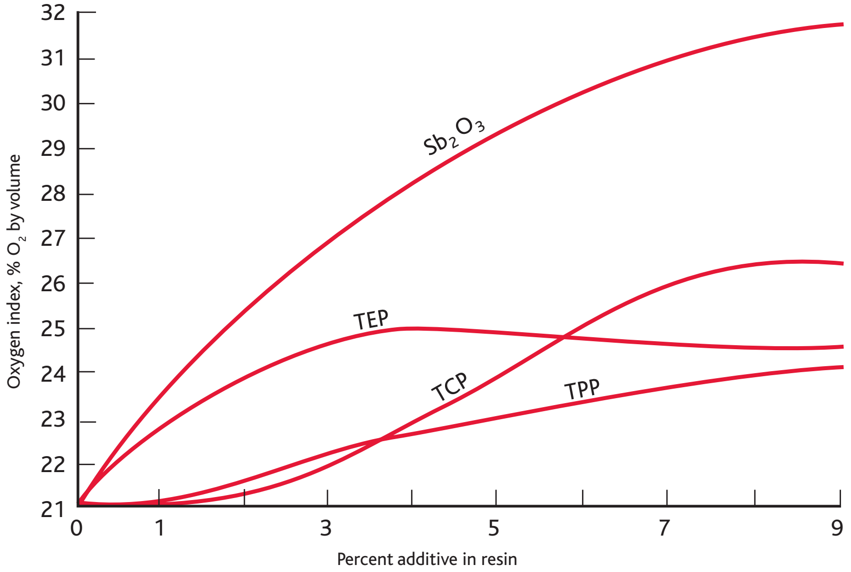


Figure 7
Effect of additive on flame resistance (oxygen index) ASTM D2883



Summary

In Eastman's studies, adding Eastman™ triethyl phosphate reduced the viscosity of filled and unfilled resins without adversely affecting the commonly tested properties of the finished products. Also, when added to resin systems, Eastman™ TEP may improve the flame resistance of articles made from such systems. It is suggested, however, that potential users fully evaluate the effect of TEP on the final performance properties in their specific systems before proceeding to production scale.

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