ENRICO J. TERMINE*
KEVIN G. TAYLOR*

A New Low Smoke Intumescent Flame Retardant for Thermoset Composites

ABSTRACT

The use of a new low smoke intumescent flame retardant for thermoset composites is described. This material, CN-1197 flame retardant, is a phosphorous-based compound which is very effective in promoting an intumescent char on the polymer surface during flammability tests.

CN-1197 flame retardant allows fabrication of composites with excellent physical property retention. The utility of CN-1197 is broad, especially in unsaturated polyesters, vinyl esters, and epoxies.

Composites formulated with CN-1197 received very low smoke values. For example, Class I reinforced polyester systems with smoke development values less than 100 are achieved with a 10–20 weight percent loading.

This paper reports recent studies to broaden the utility of CN-1197 in thermoset applications. Specifically, formulation information is presented, covering flammability and physical property performance, and processing considerations.

INTRODUCTION

Public awareness about risk and hazard assessment during fire situations, and technical limitations of flame retardant additives warrant a need for new flame retardant products. In particular, the thermoset composite industry needs a flame retardant that passes flammability standards with low smoke and combustion by-product formation, and does not detract from overall polymer performance.

Several approaches are used to reduce the flammability of plastic materials. One method involves reactive or additive halogenated organic agents. Other methods employ either inorganic fillers or special formulations based on phosphorous and ammonium salts. Although these approaches work well in reducing the flammability of plastics, each misses the goal of producing a plastic composition with a satisfactory balance of physical properties and low smoke generation.

Inorganic additives, such as alumina trihydrate, zinc borate and magnesium hydroxide, are useful in producing low smoke thermoset composites. However, these additives are used at very high load levels (as much as 50–80 percent in some cases) to achieve moderate flame retardant performance.

Not surprisingly, the high load level of inorganic fillers necessary for effective flame retardant performance has a profoundly negative impact on polymer processing. End users of this technology complain about poor polymer performance.

Recently, a novel flame retardant additive for thermoset composites was introduced by Great Lakes Chemical Corporation [1]. This material, CN-1197 flame retardant, is a phosphorous-based compound which is very effective in promoting an intumescent char on the polymer surface during flammability tests. Composites formulated with CN-1197 received very low smoke values, and had excellent physical properties.

This paper describes new studies to broaden the utility of CN-1197 in thermoset applications. Specifically, formulation information for meeting low smoke ASTM E-84 Class 1 flammability requirements is presented for orthophthalic and isophthalic unsaturated polyesters, vinyl esters and epoxy resin systems.

*Great Lakes Chemical Corporation, West Lafayette, Indiana 47906.

EXPERIMENTAL

Preparation of Unsaturated Polyesters and Vinyl Ester Systems

Unsaturated polyesters (USPE) and vinyl ester (VE) thermosets were prepared by standard hand lay-up procedures. Uncured resin was promoted with cobalt napthanate, blended with fillers, additives, and chopped strand fiberglass reinforcement. The mixture was degassed in a vacuum oven, treated with methyl ethyl ketone peroxide catalyst, and cured at room temperature for 12 hours followed by 1 hour at 100°C.

USPE Formulations

Component	PBW
Koppers Dion 8101 (Isophthalic Resin)	varied
Flame Retardant	varied
Chopped Strand Glass	20
TiO_2	1
MEK Peroxide	1
Cobalt Naphthanate	0.5
Alpha Altek 7-750 (Orthophthalic Resin)	varied
Flame Retardant	varied
Chopped Strand Glass	20
TiO_2	1
MEK Peroxide	1
Cobalt Naphthanate	0.5

VE Formulation

Component	PBW
Dow Derakane 411-45 (VE Resin)	varied
Flame Retardant	varied
Chopped Strand Glass	25
TiO_2	1
MEK Peroxide	1
Cobalt Naphthanate	0.5

Preparation of Epoxy Resin Systems

Epoxy thermosets were prepared with a bisphenol A based resin, using procedures similar to those of the USPE composites, except that triethylene tetramine was incorporated as the catalyst.

Epoxy Formulation

Component	PBW
Ciba Geigy Araldite (6010 Resin)	varied
Flame Retardant	varied
Triethylene Tetramine	10

Flammability Test Procedures

Flammability and physical property testing were performed on each resin system. Relevant test protocols were selected based on the particular resin under study. The following methods were used throughout the study.

Test Method	Description
Four Foot Tunnel Test	Apparatus to measure flame spread and smoke development in accordance with ASTM-E-84 test procedures. Low values indicate better flame retardancy.
ASTM D-2863 Limiting Oxygen Index	Measurement of the minimum oxygen necessary to sustain burning of a vertically supported sample for three minutes. High values indicate improved resistance to burning.
HLT-15 Vertical Flame Test	A test method which ranks specimen based on time to extinguish a flame after ignition. The highest rating (best flame retardant) is 100.

RESULTS AND DISCUSSION

Description of CN-1197

The flame retardant used in this study is a new developmental product from Great Lakes Chemical Corporation. This product, CN-1197, is a white crystalline material, characterized as having 17 percent phosphorous, a specific gravity of 1.6, and a melting range of 210–212°C. A thermogravimetric analysis of CN-1197 shows a five percent weight loss at 290°C.

Performance in Isophthalic Unsaturated Polyesters

CN-1197 was evaluated in an isophthalic unsaturated polyester resin. Table 1 shows a comparison of CN-1197 with ammonium polyphosphate, alumina trihydrate, magnesium hydroxide, zinc borate, and decabromodiphenyl ether.

Flammability test results on the CN-1197 composite revealed excellent fire retardant properties. In four foot tunnel testing the CN-1197 formulation displayed Class I flame spread ratings with very low smoke evolution.

Incorporating CN-1197 in the isophthalic polyester had a minimal effect on physical properties. Formulations containing CN-1197 displayed significant physical property improvements over the composites containing inorganic additives.

Table 2 shows the performance highlights of blends of CN-1197 and inorganic flame retardant in isophthalic polyester. Generally, ten percent substitution of these inorganic additives equates to a 5% loading of CN-1197.

Indoor light stability testing was conducted in a xenon arc weatherometer for 1000 hours. The CN 1197 composite exhibited the lowest E-color value and change in Yellowness Index (Y.I.) of the formulations tested.

Performance in Orthophthalic Unsaturated Polyesters

Table 3 shows the effect of CN-1197 load level on flammability and physical property performance in an orthophthalic unsaturated polyester resin. As little as 15 percent CN-1197 is sufficient to achieve a Class I rating in these composites.

Catalyst Selection and Effect on Gelation Time

The effect of CN-1197 on gelation time in unsaturated polyester systems is shown in Table 4. CN-1197 has little effect on the gelation time of benzoyl peroxide systems promoted with dimethyl aniline. In systems promoted with cobalt naphthanate, prolonged gelation times were observed. Gelation times in cobalt naphthanate promoted resins may be decreased by raising the level of promoting agent.

Performance in Vinyl Ester Resin

CN-1197 was evaluated in a vinyl ester resin composite. Table 5 shows a comparison of CN-1197 with ammonium polyphosphate, alumina trihydrate, magnesium hydroxide, zinc borate, and decabromodiphenyl ether.

Vinyl ester composites are extremely difficult to get low smoke, flame retardant performance. Of the flame retardants tested, only CN-1197 gave Class I performance in the four foot tunnel test.

Tensile and flexural strength properties were preserved with CN-1197 formulations. CN-1197 showed comparable physical performance to decabromodiphenyloxide and ammonium polyphosphate.

Performance in Epoxy Resin

CN-1197 was evaluated in an epoxy resin composite. Table 6 shows a comparison of CN-1197 with ammonium polyphosphate, alumina trihydrate, magnesium hydroxide, zinc borate, and decabromodiphenyl ether.

As in the unsaturated polyesters and vinyl ester resin systems, CN-1197 showed the best low smoke flame retardant performance in epoxy resin.

CONCLUSIONS

Great Lakes CN-1197 flame retardant is a very effective intumescent flame retardant for thermoset composites. A thermally stable phosphate ester, CN-1197 flame retardant allows fabrication of low smoke composites with excellent physical property retention. The utility of CN-1197 is broad, especially in unsaturated polyesters, vinyl esters, and epoxies.

A summary of performance highlights of CN-1197 flame retardant is given below:

- In isophthalic unsaturated polyester resin, a 20 percent load level gives Class I flammability performance with smoke development values under 100.
- In orthophthalic unsaturated polyester resin, a 25 percent load level gives Class I flammability performance under 50.
- CN-1197 is compatible with conventional inorganic flame retardants, such as alumina trihydrate, magnesium hydroxide and zinc borate. When CN-1197 is used with these additives, intumescent behavior is maintained without detracting from overall polymer performance.
- In vinyl ester and epoxy resin systems, a 20 percent load level yields Class I flammability performance with smoke development values under 200.

REFERENCES

1. Termine, E. J. and K. G. Taylor. The Society of Plastics Engineers, *Proceedings of the RETEC meeting, Toronto (September 1989).*

TABLE 1. Comparison of CN-1197 with Other Non-Halogenated and Halogenated Flame Retardant Additives in Isophthalic Unsaturated Polyester Resin.

	CN-1197	APP[1]	ATH[2]	MH[3]	ZB[4]	DECA[5]
FR LEVEL, wt %	20	20	38	38	38	14
FOUR FOOT TUNNEL						
Flame Spread	13	27	25	29	57	25
Smoke Development	90	210	600	640	945	690
OXYGEN INDEX	48	30	27	26	25	37
MLT-15 BURN TEST	100	60	36	24	24	100
TENSILE YIELD, psi	11100	10400	7500	7200	7720	11020
TENS. MOD., 10^5 psi	2.0	2.5	0.8	0.6	0.9	2.0
ELONGATION, %	1.9	1.7	0.8	0.8	0.9	2.0
FLEXURAL YIELD, psi	21700	20800	11260	11040	12190	18000
FLEX. MOD., 10^5 psi	5.1	6.9	2.9	3.0	3.8	4.6
BARCOL HARDNESS	58	55	48	47	48	56
E-COLOR[6]	4.2	10.2	14.6	15.2	15.5	24.9
Y.I. BASE	10.7	20.6	23.3	17.9	21.3	12.5
DELTA Y.I.	4.2	10.2	14.6	15.2	15.2	24.8

[1]Ammonium Polyphosphate
[2]Alumina Trihydrate
[3]Magnesium Hydroxide
[4]Zinc Borate
[5]Decabromodiphenyl ether; formulation contains 3.5% Sb_2O_3

BIOGRAPHIES

Enrico J. Termine

Dr. Termine manages the Polymer Additives Application Group at Great Lakes Chemical Corporation in West Lafayette, Indiana.

He was granted a Ph.D. degree in Synthetic Organic Chemistry from the University of Miami, in Coral Gables, Florida.

Dr. Termine has been involved with new product development of plastic additives for eight years. His work has resulted in numerous patents and commercial products.

Kevin G. Taylor

Mr. Taylor is an Applications Chemist in the Polymer Additives Application Group at Great Lakes Chemical Corporation in West Lafayette, Indiana.

He was granted a B.S. degree in Polymer Science and Engineering from The Pennsylvania State University, in University Park, Pennsylvania.

During the last four years, Mr. Taylor has been involved in new product research and technical service development for thermoset and thermoplastic resin systems.

TABLE 2. Interaction of CN-1197 with Conventional Inorganic Flame Retardants in Isophthalic Unsaturated Polyester.

	CN-1197	CN-1197 ATH[1]	CN-1197 MH[2]	CN-1197 ZN[3]
FR LEVEL, wt %				
CN-1197	20	15	15	15
Other Additive	--	10	10	10
FOUR FOOT TUNNEL				
Flame Spread	15	18	18	24
Smoke Development	90	120	130	190
OXYGEN INDEX	47	42	41	36
MLT-15 BURN TEST	92	92	92	88
TENSILE YIELD, psi	13030	10280	10550	11770
TENSILE MOD., 10^5 psi	1.4	0.9	1.1	1.1
ELONGATION, %	2.2	1.6	1.6	1.7
FLEXURAL YIELD, psi	27790	22620	22830	21590
FLEXURAL MOD., 10^5 psi	7.5	6.0	6.0	6.2
BARCOL HARDNESS	54	51	52	52

[1]Alumina Trihydrate
[2]Magnesium Hydroxide
[3]Zinc Borate

TABLE 3. The Effect of CN-1197 Load Level on Flammability and Physical Property Performance in Orthophthalic Unsaturated Polyester.

CN-1197 LEVEL, wt %	0	10	15	20	25
FOUR FOOT TUNNEL					
Flame Spread	BURN	26	16	14	12
Smoke Development	>1000	290	150	100	<50
OXYGEN INDEX	19	27	33	45	56
MLT-15 BURN TEST	0	44	52	100	100
TENSILE YIELD, psi	11900	10520	10370	10550	10270
TENSILE MOD., 10^5 psi	3.5	3.2	3.2	3.0	2.8
ELONGATION, %	1.5	1.9	1.4	1.9	1.4
FLEXURAL YIELD, psi	19890	20100	20780	21950	22120
FLEXURAL MOD., 10^5 psi	4.5	4.7	4.7	5.0	5.2
BARCOL HARDNESS	66	65	64	61	58

TABLE 4. The Effect of Peroxide Catalyst and Promoting Agents on Gel Times for Unsaturated Polyesters [1].

CN-1197 LOADING	CATALYST TYPE	CATALYST LOADING	PROMOTING AGENT TYPE	PROMOTING AGENT LOADING	CURE TEMP °C	GEL TIMES (MINUTES)
0	MEK[4]	1.5	CoN[2]	0.5	25	8.5
20	MEK	1.5	CoN	0.5	25	18.2
20	MEK	1.5	CoN	0.9	25	7.9
0	BzOOH[5]	2.5	DMA[3]	0.2	25	6.0
20	BzOOH	2.5	DMA[3]	0.2	25	6.0
20	BzOOH	2.5	DMA[3]	0.4	25	3.2
0	t-BCP[6]	1.5	CoN	0.5	140	13.6
20	t-BCP	1.5	CoN	0.5	140	19.1
20	t-BCP	1.5	CoN	0.9	140	14.1
0	BuOOH[7]	1.5	CoN	0.5	75	16.5
20	BuOOH	1.5	CoN	0.5	75	18.2
20	BuOOH	1.5	CoN	0.9	75	14.2

[1]Alpha Aitek 52-2H-6 resin.
[2]Cobalt Napthenate.
[3]Dimethyl aniline.
[4]Methyl ethyl ketone.
[5]Benzoyl peroxide (40% emulsion)
[6]t-Butyl cumyl peroxide.
[7]t-Butyl hydroperoxide.

TABLE 5. Comparison of CN-1197 with Other Halogenated and Non-Halogenated Flame Retardant Additives in Vinyl Ester.

	CN 1197	APP[1]	ATH[2]	MH[3]	ZB[4]	DECA[5]
FR LEVEL, wt %	20	30	35	35	35	14
FOUR FOOT TUNNEL						
Flame Spread	17	68	40	45	51	24
Smoke Development	180	810	670	710	840	900
OXYGEN INDEX	42	30	27	26	24	33
MLT-15 BURN TEST	84	20	40	32	20	100
TENSILE YIELD, psi	12300	11700	8900	7980	8330	12970
TENS. MOD., 10^5 psi	1.8	1.4	1.1	1.2	1.1	2.0
ELONGATION, %	1.5	1.4	0.9	0.8	0.8	1.3
FLEXURAL YIELD, psi	19000	20100	11600	11060	10570	22000
FLEX. MOD., 10^5 psi	8.7	8.7	6.6	6.5	6.3	10.8
BARCOL HARDNESS	62	58	54	54	53	66

[1]Ammonium Polyphosphate
[2]Alumina Trihydrate
[3]Magnesium Hydroxide
[4]Zinc Borate
[5]Decabromodiphenyl ether: formulation contains 3.5% Sb_2O_3

TABLE 6. Comparison of CN-1197 with Other Non-Halogenated and Halogenated Flame Retardant Additives in Epoxy.

	CN-1197	APP[1]	ATH[2]	MH[3]	ZB[4]	DECA[5]
FR LEVEL, WT %	20	20	40	40	40	28
FOUR FOOT TUNNEL						
Flame Spread	18	22	37	41	49	25
Smoke Development	130	175	510	590	620	500
OXYGEN INDEX	39	33	27	27	25	35
MLT-15 BURN TEST	80	76	36	38	24	84
TENSILE YIELD, psi	8410	4970	4550	4690	4830	7380
TENS. MOD., 10^5 psi	3.8	2.4	1.8	1.9	2.0	3.2
ELONGATION, %	2.8	3.2	1.3	1.2	1.3	2.3
FLEXURAL YIELD, psi	13450	9590	10410	10000	10550	11520
FLEX. MOD., 10^5 psi	5.7	4.9	4.5	4.3	4.5	5.3
BARCOL HARDNESS	23	22	20	20	20	23

[1]Ammonium Polyphosphate
[2]Alumina Trihydrate
[3]Magnesium Hydroxide
[4]Zinc Borate
[5]Decabromodiphenyl ether: formulation contains 3.5% Sb_2O_3