

High Performance N-P Flame Retardants for Polypropylene

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Introduction

Flame retarded polypropylene compounds are mainly used in the electrical and electronic market sector where the key flammability test specification is the internationally recognised UL94-V0 rating. The majority of the flame retarded polypropylene compounds produced today are flame retarded using traditional brominated flame retardants, in particular decabrominated diphenyl oxide (DECA) in combination with antimony trioxide. The main technical disadvantages of these systems are surface bloom of the flame retardant, poor impact strength and increased density. The aromatic bromine used in these systems also interferes with the Hindered Amine Light Stabilisers (HALS) predominantly used in polypropylene resulting in limited light stability performance. These factors have in some cases limited the growth of flame retarded polypropylene into applications where they would have to compete with flame retardant ABS or HIPS which both provide products with superior surface qualities. Although there is no legislation to ban the use of these brominated flame retardants, there are several voluntary codes, especially in the electrical and automotive sectors, that aim to eliminate or reduce their use. Additionally there is extreme pressure from consumers, influenced by environmental groups, to move towards halogen-free flame retardant solutions. The increased need for product recycling also drives the producers to seek alternative solutions whilst hopefully not compromising on consumer safety by reducing the flammability requirements.

Halogen-free solutions for polypropylene, based on intumescent technologies, have been available commercially for many years but their use and acceptance has been somewhat restricted due to current product limitations, especially as regards processing, water extraction, cost performance, and the high load levels required which cause degraded mechanical properties. It would be difficult for any new halogen-free systems to be cost competitive with the existing brominated solutions, but improved performance in certain aspects should provide greater opportunities for growth of these halogen-free flame retarded polypropylene compounds.

Many of the existing halogen-free solutions are based on ammonium polyphosphate combined with different nitrogen sources and other co-additives to provide the three essential components for an intumescent flame retardant system¹:-

- Acid source (catalyst/initiator such as ammonium polyphosphate)
- Char promoter (carbonific additive/cross-linker such as pentaerythritol)
- Blowing agent (spumific additive such as melamine)

As the polypropylene polymer itself has no char forming ability, the additive system must be sufficiently effective to quickly provide a strong and stable layer to protect the polymer from further degradation during combustion. Since polypropylene degrades predominantly by surface oxidation the intumescent systems are more suited to this polymer than for example a styrenic polymer such as ABS or HIPS. Most of the commercial intumescent systems need to be used at load levels of 30-40% in order to meet the UL94-V0

performance in polypropylene homopolymer at a thickness of 1.6mm which makes dispersion of the additive during processing somewhat difficult and can result in reduced physical properties.

Great Lakes has developed a new nitrogen-phosphorus based flame retardant specifically designed for UL94-V0 polypropylene applications which is melt blendable and is effective at reduced load levels. The new product, designated CN-2616, offers a unique combination of efficient halogen-free flame retardant performance with no bloom and low water absorption. The product can be melt-blended with polypropylene under processing conditions, leading to improved retention of the base resin's mechanical properties; low density being just one of these properties. Surprisingly, the use of CN-2616 allows both reduced melt viscosity during processing and at the same time, increased heat distortion temperature in the final parts.

Product Profile

CN-2616 is a nitrogen-phosphorus proprietary flame retardant system for polyolefins. It is targeted primarily at the UL94-V0 polypropylene applications but its performance benefits could also make it suitable for other polyolefin applications such as the wire and cable or building industries.

It is a white powder additive, which melts at 190-200°C allowing for ease of processing due to its melt blendability in polypropylene. Table 1 gives the typical properties for the product showing the low density of the product.

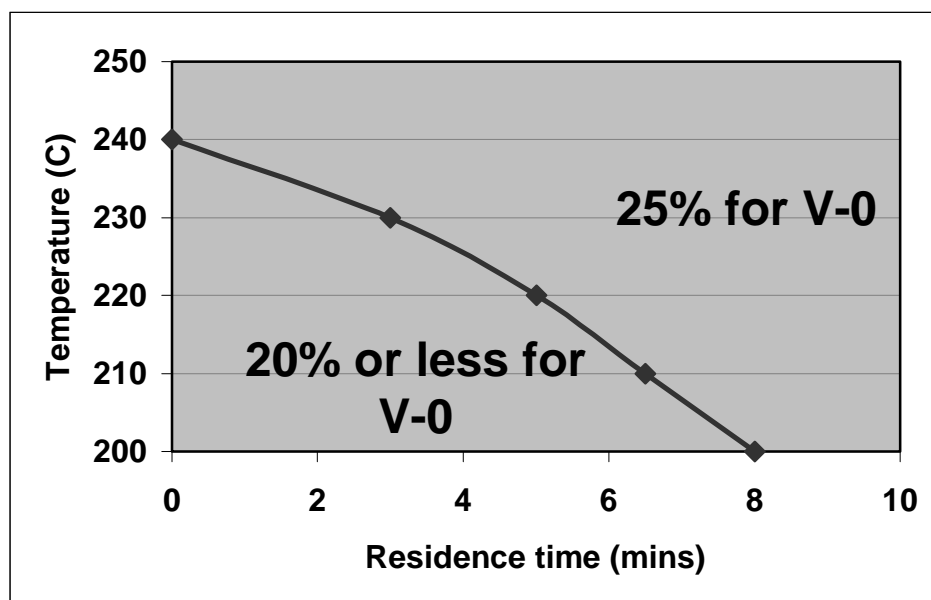
Table 1

Typical Properties			
Appearance	White Powder		
Melt Range, °C	190 - 200		
Bulk Loose Density @ 25°C, g/ml	0.6		
Bulk Packed Density @ 25°C, g/ml	0.8		
Thermogravimetric Analysis (10mg @ 10°C/minute under N ₂)			
Weight Loss, %	5	10	25
Temperature, °C	274	310	390
Solubility (g/100g solvent @ 20°C)			
Water	1	Toluene	Insoluble
Methylene Chloride	Insoluble	Methyl Ethyl Ketone	1
Methanol	2	Acetone	2
Hexane	<0.5		

As with most intumescent flame retardant systems it is important that the processing temperatures during extrusion and subsequent moulding are not above 220°C as at higher temperatures the beginnings of the intumescent reaction can be initiated prematurely causing a reduction in the mechanical properties and possibly the flammability performance. If the processing temperatures are too high then a higher amount of the flame retardant will be required to maintain the desired flammability performance. For injection moulding of large parts where the residence times are increased it is even more

important that the processing temperature is kept between 200 and 220°C. This ensures good dispersion of the additive by melt blending and eliminates the risk of any degradation of the additive. The graph in figure 1 shows how with increasing temperature or residence time the load level required for UL94-V0 will need to be increased from 20% to 25%.

Figure 1 – Additive level for temperature/exposure profile



Performance Data

As with other intumescent systems, there is a minimum loading at which a UL94-V0 can be met. If this is not used, then the flammability performance will be reduced to either a UL94-V2, or more commonly, unclassified, depending on whether the failure mode is by igniting drips or extended burn timesⁱⁱ. For CN-2616 a good robust UL94-V0 performance is consistently met with a 20% loading of the additive in a polypropylene homopolymer, even with different grades of polymer such as melt flow 0.4 to 12. Since the loading for a borderline UL94-V2/unclassified performance would only be 2-3% less than for the UL94-V0 rating, these intumescent systems are unlikely to compete in UL94-V2 type applications where very low loadings of brominated flame retardants are currently used.

The main technical advantages of CN-2616 over the other commercial halogen-free system is its superior water resistance, heat distortion temperature and impact performance. Compared with the brominated compounds it offers bloom resistance, non-dripping UL94 V-0 and reduced compound specific gravity which results in less polymer required to fill a given mould cavity. The superior heat distortion temperature, without the need for a talc reinforcing filler, will allow polypropylene compounds flame retarded with CN-2616 to be considered for applications where previously only filled grades could be considered. The additional benefit of maintaining the living hinge capability of the polypropylene whilst meeting the UL94-V0 rating using CN-2616 will allow its use in areas such as complex housings/chassis with snap fit fastenings.

Table 2 gives comparative flammability and physical property data for CN-2616 versus other commercial flame retardant systems.

Table 2 – Comparative performance data

Formulation	Control	CN-2616	P-Based Control	Halogen Control A	Halogen Control B
Polypropylene Profax 6524	100	80	70	87	59
Flame Retardant Level, %	-	20	30	10	20
Sb ₂ O ₃ , TMS HP, %	-	-	-	3	7
Talc Filler	-	-	-	-	14
Flammability Performance					
UL94 @ 1.6mm	Fail	V0	V0	V0 (Drips)	V0
Physical Properties					
Specific Gravity	0.89	0.99	1.06	0.97	1.28
Bloom, 168hrs @ 70°C	None	None	None	Severe Bloom	Mod. Bloom
Water Absorption, %	<0.1	<0.1	0.4	<0.1	<0.1
Izod Impact, unnotched, J/m	>1000	595	425	>1000	390
Izod Impact, notched, J/m	48	37	27	32	27
Tensile Strength, Mpa	33	30	30	33	28
Elongation @ Break, %	450	110	100	300	88
Flexural Strength, Mpa		48	48	39	50
Flexural Modulus, GPa	1.4	1.9	1.9	1.2	2.3
HDT @ 0.46MPa, °C	84	110	93	91	120

Polymer Grade: Profax® 6524, MFI=4, homopolymer

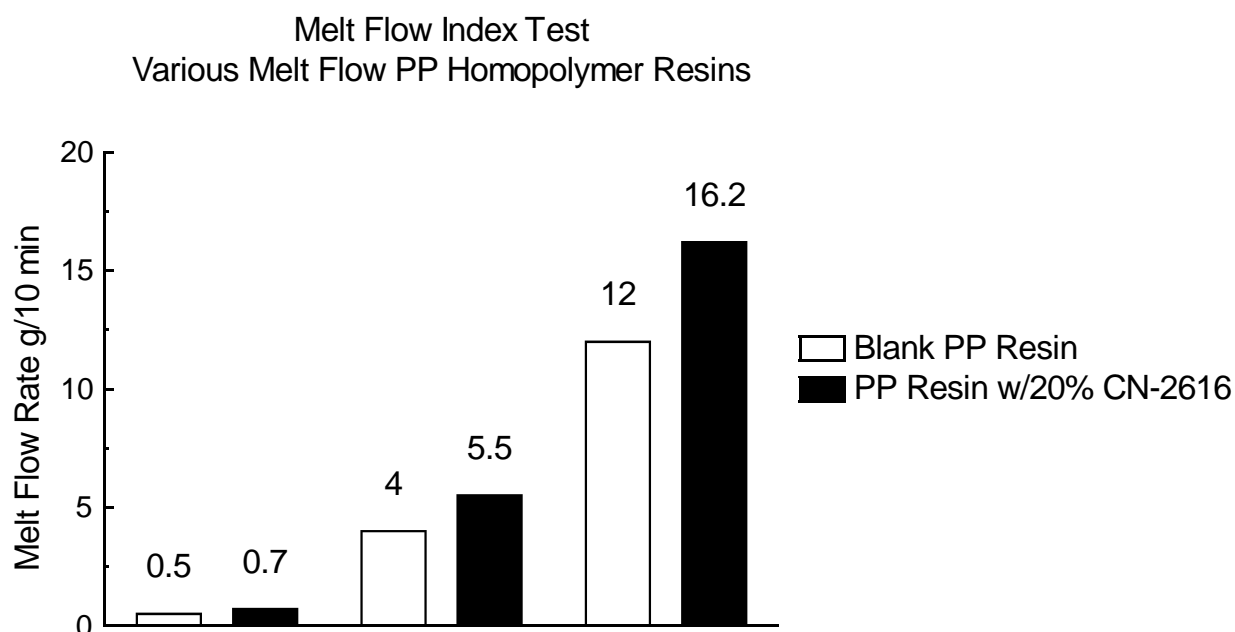
P-Based Control: Exolit® AP-750

Halogen Control A: PE-68

Halogen Control B: DE-83R

As CN-2616 is a melt blendable flame retardant, it increases the melt flow of the polymer compound allowing for a maintenance of processing speeds even at the recommended lower processing temperatures. When tested in a range of different polypropylene grades the addition of 20% CN-2616 would give approximately a 35% increase in the melt flow rate of the base polymer as shown in Figure 2 below.

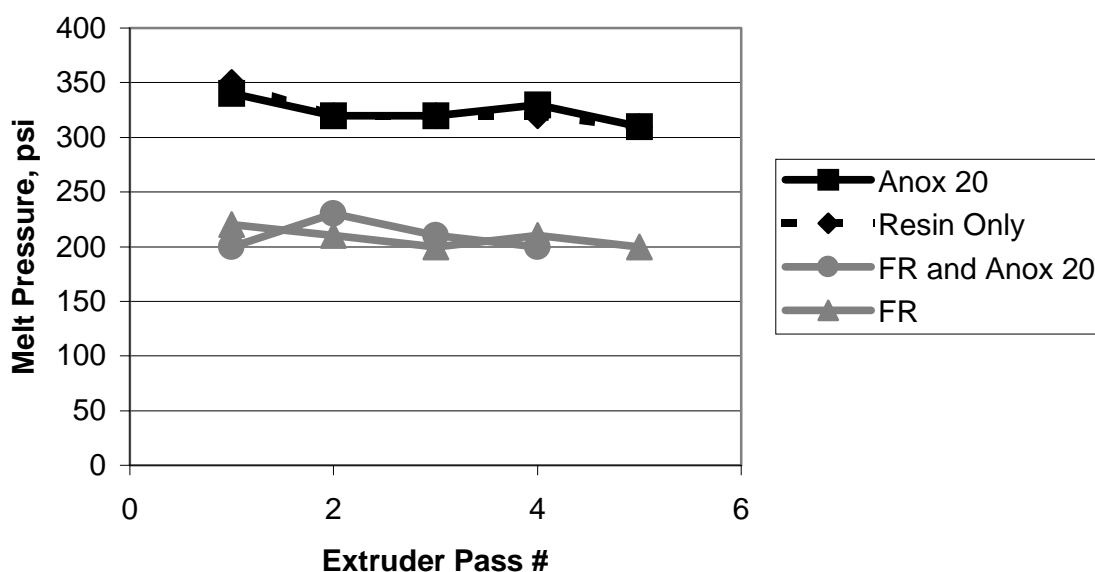
Figure 2 – Melt Flow Rate Data for 20% CN-2616



Melt Flow Rate Increases 35-40% w/addition of 20% CN-2616

Additionally it has been found during our studies on this additive that the addition of CN-2616 to a polypropylene homopolymer (MFI=4) resulted in a significant drop in the melt pressure during extrusion which was maintained over 5 multipass extrusions as shown in Figure 3. These were run at an extruder temperature within the recommended processing guidelines demonstrating that even at processing temperatures considered to be low by normal polypropylene compounding standards, there is no increase in the melt pressure in the extruder.

Figure 3 – Melt pressure data (22% CN-2616 and/or 0.25% Anox® 20)



Since polypropylene is increasingly used in areas where there is a greater demand for recyclability of the products it is important that any new flame retardant systems can withstand reprocessing whilst still maintaining their original flammability performance. Studies made on polypropylene compound flame retarded with CN-2616 have shown that the UL94-V0 performance is maintained even after these 5 multipass extrusion runs. The yellowness and whiteness of the compounds also show minimal change over the 5 extrusion passes.

Influence of Impact Modifiers

The notched impact performance of polypropylene is important for many of its application areas and unfortunately the addition of most flame retardant additives tend to cause some reduction in this performance property. Several different classes of impact modifiers have been studied in combinations with CN-2616 to determine their effect on the flammability and impact performance of the resultant compounds. Certain classes of impact modifier were found to be more suited to this application. Nordel® IP (an EPDM impact modifier) and Engage® 8180 (a metallocene PP modifier), both maintained the flammability performance of the system whilst improving the impact strength back to at least that of the base resin. The addition level of these impact modifiers was varied from 3 to 10 and a loading of approximately 5% impact modifier improved the impact strength back to that of the base resin whilst still maintaining the UL94-V0 flammability performance. A styrene-butadiene multiblock copolymer modifier and an LDPE based modifier did give some improvement in the impact performance but unfortunately these two impact modifiers reduced the flammability performance to an unclassified rating on the UL94 test. Our recommendation, then, is that an impact modifier should be chosen from the families of EPDM and metallocene polypropylene products after screening to verify achieving the desired performance enhancement.

Copolymer Systems

As the degradation mechanism of polyethylene is less reliant on surface oxidation of the polymer it is less suited to intumescent flame retardant systems than polypropylene. Copolymers traditionally require higher loadings of flame retardants to meet a given flammability specification compared with homopolymer systems, even with the traditional brominated flame retardants. This is not different for the halogen-free systems as these generally require the loading of CN-2616 to be increased from 20% for a UL94-V0 in a homopolymer to around 25-30% of CN-2616 to meet the UL94-V0 in copolymer systems.

Since one of the main reasons for using a copolymer grade is to improve the impact performance, it can in fact be a more cost effective solution to use a homopolymer with one of the preferred impact modifiers and still be able to use the normal load level of 20% CN-2616 flame retardant.

Effect of Fillers

Due to interference with the mechanism of the intumescent flame retardants like CN-2616, cost reducing fillers such as calcium carbonate are not suited to these types of flame retardant compounds. The addition of only small amounts of calcium carbonate prevent the UL94-V0 rating being achieved even at increased loadings of CN-2616. Talc fillers can be used but only at loadings of up to 10% and again the CN-2616 loading needs to be

increased to about 30% to maintain the UL94-V0 rating, presumably due to interference with the intumescent reaction and char stability. Glass fillers are more suited to these types of flame retardant systems and can be used at loadings of 10-30% whilst only having to increase the CN-2616 loading to 30% to maintain the UL94 flammability performance. Since the CN-2616 flame retardant by itself gives some improvement in the heat distortion performance of the polypropylene resin it may not actually be necessary to use the reinforcing fillers whilst still maintaining adequate performance.

MVSS 302 Applications

Automotive applications are an important growth area for polypropylene. As auto manufacturers move to comply with plastic recycling initiatives, they increasingly push for halogen-free polyolefin solutions. CN-2616 has been evaluated in both polypropylene and high-density polyethylene for performance in the MVSS 302 test with positive results. As shown in Table 3, at 3.2mm thickness CN-2616 allows polypropylene to meet the standard at 12% load level with no burn length. CN-2616 in HDPE readily passed the test at 18% loading. Clearly, there is opportunity to optimise the flame retardant load level to meet the MVSS 302 standard.

Table 3 – MVSS 302 Test Data – 3.2mm thickness

Resin System	PP			HDPE		
% CN-2616	12	15	18	12	15	18
MVSS 302 Data	NB means flame spread did not consume any length of the plaque					
Trial 1	NB	NB	NB	> 60 sec	NB	NB
Trial 2	NB	NB	NB	> 60 sec	NB	NB
Trial 3	NB	NB	NB		NB	NB
Trial 4	NB	NB	NB		> 60 sec	NB
Trial 5	NB	NB	NB		> 60 sec	NB
Pass (Y / N)	Y	Y	Y	N	N	Y

NBS Smoke Chamber

CN-2616 gives the expected low-smoke performance in the standard smoke chamber test. Smoke density is comparable to the other phosphorus-based flame retardants, much lower than a typical halogen flame retardant's performance.

Table 4 – NBS (ASTM E662) Test Data

Flame Retardant	CN-2616	DE-83R	AP-750	EDAP*
Wt. % FR	20	20	30	37
Max. Smoke Density	246	576	257	226

* Antiblaze® NK

The importance of low smoke generation from flame retarded plastics is being increasingly recognised. Public gathering facilities such as sports arenas, schools, museums and shopping centers, as well as mass transit systems share the need to prevent smoke from obscuring the vision of people as they exit in the event of a fire.

Heat Release and Smoke Production

Since the development of the cone calorimeter in the early 1990s and larger scale calorimeter based equipment the use of heat release and smoke production measurements of flame retarded compounds have increased. The heat release and ignitability data can be used in modeling to predict the performance in a real fire situation, which is considered to be more meaningful for fire safety than the traditional small scale tests. Although there are only a limited number of application areas, predominantly in the maritime and aircraft organisations, that specify specific heat release values for materials, there is an increased use of heat release and smoke measurement techniques being applied to existing flammability test rigs. One example of this is in the area of cable fire testing such as the UL910 test for smoke production of cable used in plenum areas and more recently in the proposed changes to the IEC332:Part 3 test for cables in Europe where heat release and smoke data will be measured together with the existing flame spread data. The Single Burning Item (SBI) test will include heat release data as specifying data for more products when it eventually becomes accepted as a standard for construction products in Europe.

Existing halogen-free polyolefin cable formulations based on magnesium hydroxide as a flame retardant system do give delayed ignition and reduced heat release on the cone calorimeter, mainly as a function of the reduced flammable polymer concentration in the final compounds. Figure 4 and figure 5 give comparative heat release and smoke optical density values respectively for polypropylene compound with CN-2616 versus a commercial Magnesium Hydroxide filled polypropylene cable compound and a PVC plenum cable compound.

Figure 4 - Heat Release Data - Cone Calorimeter at 50kW/m²

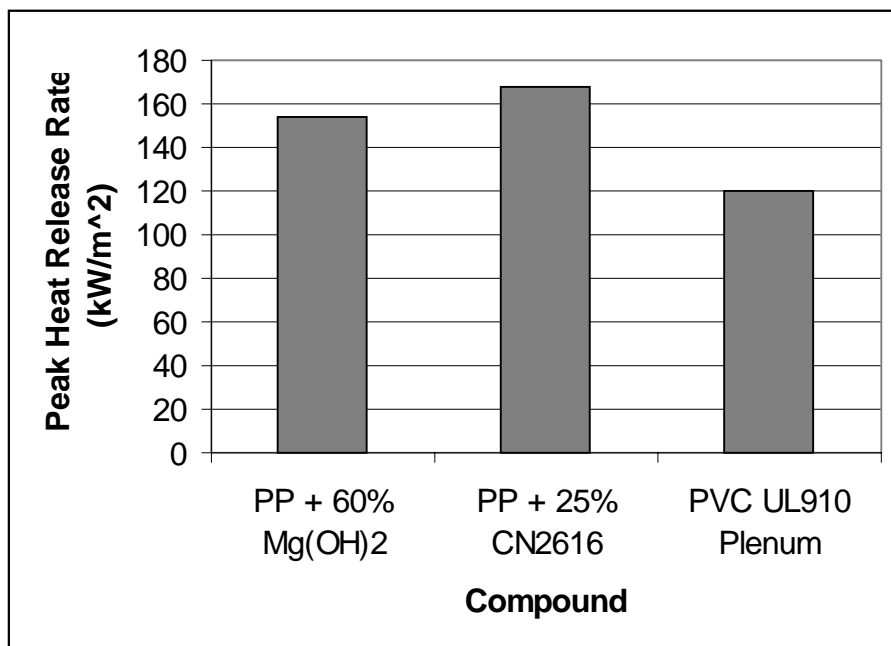
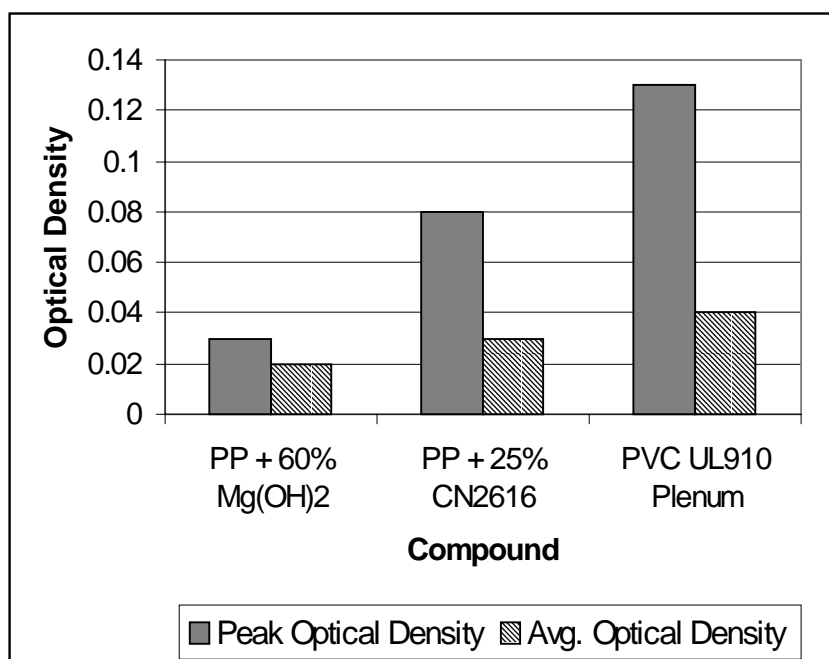


Figure 5 - Smoke Production Data - Cone Calorimeter at 50kW/m²



In order to have sufficiently low heat release, large amounts of magnesium hydroxide have to be used, up to 60%, which also results in very low smoke production as it is mainly only the reduced concentration of polypropylene that contributes to the smoke generation. PVC plenum formulations that are able to meet the stringent smoke production requirements of the UL910 test are still more smokey than the magnesium hydroxide based polyolefin compounds. Polypropylene compounds flame retarded with CN-2616 at about a 25% loading can give similar heat release performance to a magnesium hydroxide filled polypropylene compound at a much lower density, and achieve a UL94 V-0 rating as opposed to a V-2. The system using CN-2616 can at least match the smoke production on the cone calorimeter of a UL910 PVC based plenum cable compound.

Electrical Properties

CN-2616 presents an exciting opportunity for electrical applications such as wire and cable. The existing bromine-based flame retardants are very efficient and allow good dielectric properties, but as already mentioned, there is a strong drive in many regions to use non-halogen flame retardants. The existing non-halogen products have inferior dielectric properties in polyolefins compared to the typical halogenated systems. CN-2616 is unique in that it is a non-halogen flame retardant that gives dielectric properties comparable to halogenated flame retardants. As illustrated in Figures 6 and 7, CN-2616 does not significantly alter the dielectric constant of the base resin, allowing much better performance than the Mg(OH)₂ filled system and a step-change better than conventional phosphorus-based flame retardants.

Figure 6 – Dielectric Constant at 1MHz of CN-2616 in PP Copolymer

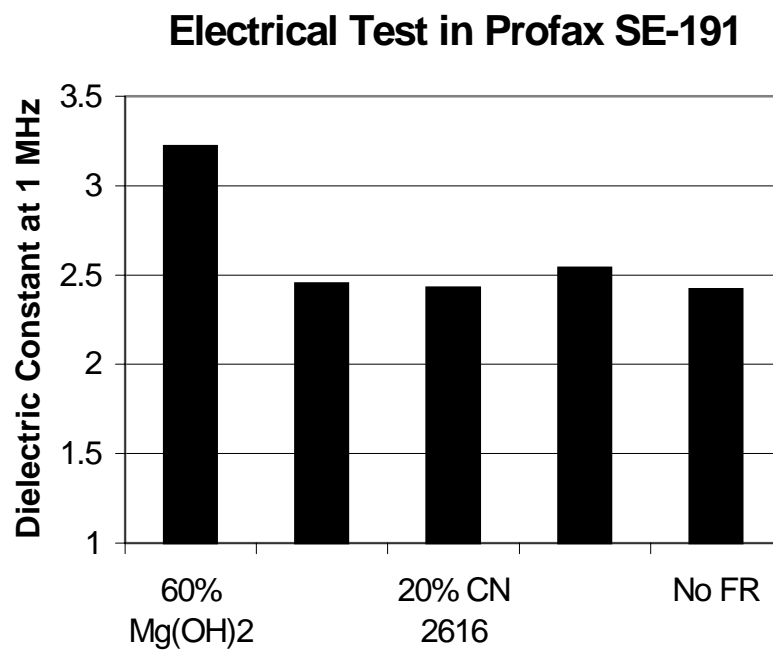
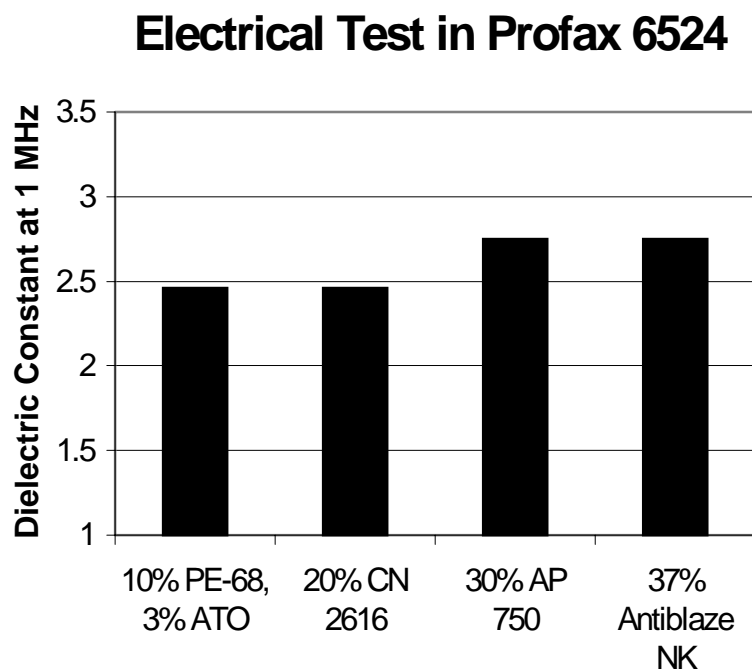


Figure 7: Dielectric Constant at 1MHz in PP Homopolymer



Cost-Performance

With a high-performance plastic additive, the cost of the additive per kilo can give an incomplete comparison between options. With CN-2616, for example, the overall system cost should be considered as a more accurate comparison. In a number of cases this analysis can reveal that CN-2616 is a more attractive choice than a “low cost” flame retardant solution.

The low density allowed by CN-2616 translates directly to less plastic per part, hence savings can be realised in resin, flame retardant, stabilisers and other additives. In addition, CN-2616 allows formulators options to use less expensive homopolymers with impact modifying additives.

The reduced viscosity allows processing temperatures to be lowered (as recommended for the flame retardant), leading to energy savings. The combination of reduced melt viscosity and increased heat distortion temperature could allow easier and faster processing.

The retention of mechanical properties and compatibility of CN-2616 with polypropylene could also allow polyolefins to be used in place of higher-cost resins in certain applications. One important area where this may occur is in automotive plastics, as this sector have long expressed a desire to expand the use of polyolefins, and at the same time reduce consumption of vinyl compounds. The automotive industry is also a highly visible sector making a voluntary shift to halogen-free flame retardants.

Conclusions

Although there already exist several commercial halogen-free flame retardants for polypropylene in the marketplace these tend to be confined to certain niche markets where the properties and cost performance of the systems are acceptable.

CN-2616 steps beyond the performance limitations of existing flame retardant solutions for polyolefins with a unique set of properties. It is versatile enough to meet MVSS 302, UL-94 V0 and 5V requirements, and initial results following European test protocols have also been positive. The reduced load levels required compared to existing non-halogen flame retardants, along with its melt-blending behaviour allow CN 2616 to retain more of the desirable properties of the base resin. Electrical properties of polypropylene with CN-2616 are comparable to brominated flame retardant systems, while the low smoke generation is representative of halogen-free systems. The unusual coupling of reduced plastic melt viscosity and increased heat distortion temperature are expected to allow compounders and moulders easier and possibly faster processing.

The performance profile of CN-2616 should allow greater formulating flexibility to compounders and moulders to produce articles using flame retardant halogen-free polypropylene that were previously difficult or impossible with the existing solutions. This could potentially open up the opportunities for increased interpolymer competition between polypropylene and the more expensive styrenic polymers. We believe that the reduced loading of CN-2616 required to meet the UL94-V0 test requirements and the superior performance in terms of water resistance, electrical and physical properties will lead to increased use of halogen-free polyolefin compounds.

ⁱ International Plastics Flammability Handbook, Jurgen Troitzsch

ⁱⁱ New developments with phosphorus-based flame retardants for the plastics industry, Sebastian Hoerold, Recent advances in flame retarded polymeric materials, 1999, 10, pg278-302