To char or not to char?

Two different additives companies exhibited two different (but potentially complementary) approaches to non-halogenated fire retardants for PU foams at last month's K-2022, writes James Snodgrass

Swiss charred: ancient Japanese and Swiss charring techniques preserve wood from weather, insects and fire

MidJourney

As reported elsewhere in this special issue, fire retardants represent – by quite some margin – the biggest sector within PU additives. And with good reason: fire is fundamental (if not elemental, in our post alchemical era), one of the biggest threats to human life outside natural death, disease, homicide and drug overdose. Every year some 150,000 people are killed by fire (and seven million receive serious injuries from burns).

One of the most successful flame retardants comes from fire itself: char. The Japanese technique of Yakisugi (sometimes known as 'shou sugi ban') has been used for over 300 years to protect wood from weather, insect infestation, and fire. Similar processes have also been used for generations in other cultures: as evident in the timber chalets seen in the Swiss Alps.

Charring is the chemical process of incomplete combustion of materials exposed to high heat. The heat removes oxygen and hydrogen (plus water vapour and VOCs) from the material, leaving a char principally composed of carbon. The char is evident from its black colour, literally 'carbon black'. Whereas ash that results from complete combustion presents a grey or whitish colour.

The charred wood becomes more impervious to fire (and the weather), which is why Alpine chalets, often inaccessible to quick-response fire crews, will largely be constructed from charred wood.

The other common way to prevent flaming is to retard the flame in its gas phase, starving it from its supply of oxygen.

At K-2022 *Urethanes Technology International* spoke with two companies who are marketing non-halogenated flame-retardant additives – Clariant and Repi – to compare their different approaches. Clariant's additives are – largely – designed to extinguish flame in the gas phase (with some char), while Repi's Antifiamma (styled antiFIAMMA) product is a liquid dispersion designed to complement primary flame retardants by exhibiting a 'significant impact on char formation'.

APP as an alternative to TCPP

In general, Clariant's flame retardant additive portfolio for PUs come in two kinds: reactive and additive. Dr Florian Clausen, product manager, phosphorous chemicals, at Clariant explained: 'The reactive ones are more specialised, they are liquid. They have OH groups, so they're going to react into the polymer matrix. Then we have additive ones, which are based on either ammonium polyphosphate (APP) or red phosphorus'.

The reactive additives, branded as the Exolit OP series, are tailored specifically for flexible foams in automotive interiors.

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Let's cook: Christian Battenberg (L) and Florian Clausen (R) discuss red phosphorous
Plastics News/ Caroline Seidel

Tight lipped: Paolo Banfi holds foam containing Repi's secret natural ingredient
Plastics News/ Marco Stepniak

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They could potentially be used in slabstock foam for furniture but there's the pesky Crib problem.

'We have, of course, the issue in the UK with this Crib 5 test [see p. 8],' said Clausen, 'which is so very specific to the UK. Our customers are mainly in automotive. But for furniture foams, this could also be a nice TCPP [Tris(chloropropyl) phosphate] replacement for viscoelastic foams and the like.'

Clausen said reactive additives incorporate better into the matrix. As a result, the chemical bonds prevent leaching and migration, thus bringing down VOC emissions. Clausen said: 'Nowadays OEMs require these be very low. You don't want to have a high VOC level because the OEM won't buy your foam. So for headlining foams, for instance, our Exolit OP 560 is coming best in class in these tests.

'TCPP has high VOC because it's a small molecule. And if you are incorporating small molecules – it could also be other phosphate esters – if they're not reactive, then when you do the [German automotive association tests] VDA 278 or 277, there may be phenolic residues in your foam. This is all going to show up on those VDA tests'

Dr Christian Battenberg, Clariant's global sector manager for thermoset flame retardants, said: 'These tests are so stringent today that if you leave an apple inside your car, over time it will emit ethylene and acetaldehyde, and these emissions will give you VOC levels above the target.'

Two Clariant products for automotive interior applications are Exolit OP 550 and OP 560. Both are phosphorus-based but with different OH values. Clausen explained: 'Hydroxyl numbers are the biggest differentiation the foaming plant has to take into consideration.'

A disadvantage is that phosphorus-based products are prone to hydrolysis in their pure form. Clausen admits this makes it hard to pre-batch for water blown systems: 'We are working in the lab to get a product that is not prone to hydrolysis, so it can be pre-blended.'

TCPP has been widely used as a fire retardant in the PU industry, particularly for PIR foam, and foamers like it because it's a liquid. But it's a halogenated phosphate and therefore under increased scrutiny from regulators. Battenberg said: 'The European Council wants to limit its use, regulate it, or even prohibit all chlorinated phosphate ethers.

'It's still used, so the industry clearly needs an alternative for PIR foam, and we see APP, ammonia polyphosphate, as a nearly-as-good, highly efficient alternative. But it's a powder.'

The PU foaming industry, by and large, prefers liquid additives. TCPP fitted the bill because it was liquid and also lowered the viscosity of the blend. 'It's such a nice product,' said Clausen, 'but the industry needs to have something in the draw if the [European] Commission decides to ban TCPP, or ban chlorinated esters.'

'APP, with low loadings, can be as efficient as TCPP. You don't have drawbacks in terms of isolating performance, you don't have drawbacks in terms of panel rigidity. It's a good flame retardant. It's non-toxic – you can take APP and use it in your garden as fertiliser.'

Clariant is working on a new APP-based additive called AP 8421, a liquid alternative to TCPP. Clausen said: 'It's not 100% "drop in", because its viscosity is not as good as TCPP. But we see it as an intermediate until our customers say, "Okay,

Wooden inspiration: a close up of traditional Yakisugi
Getty Images/iStockphoto

maybe we should alter our plans to also be able to handle powders in the future".'

The flagship product in the Exolit range, OP 1230, is a gas-phase flame retardant for high density foams, suited to e-mobility applications, such as battery insulation. It is based on diethylphosphinic acid aluminum salt. Battenberg said: 'You might think, "It's a salt, will it somehow dilute?", but it's super hydrophobic, and gives a lot of phosphorus in its molecular structure.'

Clausen added: 'Because it's phosphinic, its main mechanism is in the gas phase. So it's not going to make a huge char. Though you might think about using it in combination with other products, if you do want a char.'

The Walter White conundrum

The production of red phosphorous [RP] is highly regulated because it is a precursor used in the production of methamphetamine, a drug of misuse. But it has properties that are highly useful for fire retardants. '[Crystal meth] has become very popular since *Breaking Bad*. And this is why, of course, RP has to be regulated,' said Clausen.

Clariant, fortunately, has the appropriate permissions to make RP, and does so at its Knapsack facility near Cologne, Germany. 'Because it's neat phosphorus, the phosphorus content is as high as it can get,' said Clausen, 'with minimal introduction into your material, you get a really high phosphorus content. And that way it achieves flame retardant performance you simply cannot achieve with any other materials.'

Clariant offers RP 6520, a dispersion of RP in castor oil, which, Clausen suggested, makes it something most PU manufacturers can handle: 'It has a phosphorus content of almost 50%. So you can really get a lot of phosphorus in there if you need it.'

Despite its superior properties, RP can react with moisture in the air. Clausen said: 'When I say *react*, it's very, very, very slow, but it will generate phosphene that you can smell. In our RP grade it's encapsulated and also chemically stabilised, so phosphine emission is cut to a minimum.

'But because phosphine is detectable in the PPM or even PPB ranges, you would probably be able to smell it in an interior application with a lot of heat and no exchange of air. But if you have it inside a rigid foam, with a closed cell, there's no problem. Or if you have cast resins then it's inside the rigid matrix.'

A natural route to charring

Switzerland-based additives company Repi introduced its Antifiamma non-halogenated flame retardants at the K-2022 fair. The range is intended to complement primary fire retardants within the polyol blend and is suitable for flexible and rigid PU foams.

'We are getting a very good result not only in terms of flame resistance, but – of interest to rigid panel producers – we notice an increase in the thermal insulation,' said Paolo Banfi, manager, polyurethanes technical group, Repi: 'This means we are able to reduce the lambda value. And these are the typical targets for the final producer: increasing the flame resistance and improving the thermal insulation.'

Antifiamma is a liquid dispersion containing an active, 'natural' ingredient (which remains unidentified, despite persistent prodding of Signor Banfi by your correspondent). The addition rate of the additive to the polyol is, Banfi claims, 'very low', typically around two to three parts per 100 parts of polyol.

The natural ingredient works particularly well, Banfi insists, because of the way it is processed: 'It's because of the way we are mixing and the way we are grinding into the polyol. We are reducing the particle size so that it is really fine, and we are doing a sort of exfoliation of the molecule.'

Development of the product began 'a couple of years ago' and has been trialled with several systems houses and also with Repi's partner producer. But its public debut was at the K-2022 fair in Düsseldorf in October.

Banfi explained how the additive works: 'The additive is creating a char layer. So it's protecting against the passage of the oxygen, it is reducing the dripping, it is reducing the smoke – and [reducing] the density of the smoke. So with these [characteristics] this technology is able to greatly improve the performance of the primary flame retardants.'

Banfi suggested that the addition of Antifiamma allows foamers to reduce the volume of primary flame retardants by 30% to 40%. The additive can be used to complement the flame retardation properties of traditional solutions like TCPP and also newer, non-halogenated alternatives.

'It's about future-proofing the products for international regulation,' said Banfi. As the active ingredient of Antifiamma is natural, Banfi believes it is immune from future regulation. When pressed to at least *hint* at the class of material used in the product, Banfi laughed and said: 'This is our proprietary know-how'.

One can only speculate at the type of 'natural' solid processed within the liquid dispersion. But, regardless of its composition, what Antifiamma does offer is the flexibility for foamers to migrate away from halogenated flame retardants at their own pace. Those foamers still using TCPP will be able to use less TCPP in their formulations. While those foamers that have already migrated to non-halogenated flame retardants will be able to complement their fire resistance with the charring potential of the new additive.