Phosphorus Rich Polymers and Mixed Intumescent Polymeric Salts

Technical Briefing

(1) INTRODUCTION

Phosphorus Rich Polymers are the end product of a development programme that may traced back to 1987. The objective of the development programme is to provide an almost universal fire protection system applicable to most substrates and fire regimes. The flagship products from this technology are non-flammable polyurethanes foams.[1]

The underlying principle is the production of phosphorus rich oligomers which are subsequently reacted to polymeric materials. The oligomers appear as pale yellow liquids with a viscosity varying from low to high depending on the molecular structure of the oligomer. In all the products the components of a phosphate catalysed intumescent system are present in the polymer backbone, such that on thermal decomposition the majority of the polymer is pyrolised to condensed phosphorus oxy acids and carbon, and hence is non-flammable and produces very little smoke or toxic decomposition products.

The char produced from pyrolysis is non flammable and may form insulating layers that will protect the underlying polymer or substrate. Depending on the phosphorus content, the majority of the polymer forms char, rather than flammable fractions or smoke. Further, the system operates without the need for halogens or heavy metals.

The PRP project is a second generation technology that advances beyond that body of information encompassed by the Intrinsically Intumescent Polymer (IIP) materials which was the first attempt at the principle of molecular integration of intumescent functionalities.

The new work overcomes the limitations of both the ammonium polyphosphate and IIP technologies. It also avoids those elements of the preceding technology which are revealed in and the subject of preceding patents.

The procedure for the production of the oligomers depends on a novel previously unreported reaction sequence. The process only uses commodity raw materials in a simple batch process that produces the product at 100% solids with no by products .

The manufacturing sequence for PRP materials is neither complex nor difficult. However, while the process is novel and the plant is idiosyncratic it is readily obtainable by conversion of conventional batch process reactors.

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[1]This document is a non confidential briefing of Phosphorus Rich Polymer Technology. A detailed briefing is available under the usual confidentiality arrangements. A separate market survey is also available.

The title, Phosphorus Rich Polymers, is chosen not only to differentiate the new work from the Intrinsically Intumescent Polymers but to indicate that the polymers are not necessarily intumescent, although they are always non flammable.

(2) UNDERLYING THEORY.

While working on the IIP, it had become apparent that the mechanism which produces intumescent chars may be used to provide polymeric materials which, although not intumescent, are fire resistant. By extending the understanding of intumescent chemistry, it is known that to achieve the desired properties, with respect to fire response, heat release, insulation values and smoke emission, certain ratios of phosphorus, carbon and possibly nitrogen must be present. These elements must also be present in particular molecular structures and in particular arrangements.

When these structures are integrated into a polymeric form, then the polymer itself demonstrates these fire resistant properties, without the addition of further flame retarding agents. Variation of the structure and composition of the heteropolymer can provide a range of products from strong, flexible, fire stable resins for fire resistant composites through to flexible, intumescent coatings for the flame proofing of fabrics, paper and cardboard, including exposure tolerant, structural steel fire protection coatings.

Carbonaceous materials can exhibit low flammability when exposed to a fire situation which can be described as having an elevated heat flux and a continuous oxygen supply. To do so the carbon rich components must be caused to decompose to carbon rather than to volatile fragments of the original molecular structure. These volatile fragments, which appear as gases, ignite in the fire environment.

A combusting solid can be seen as a heterogeneous three phase reaction. Combustion is not a function of a solid or liquid phase. Combustion is gas phase reaction. Therefore, for a solid to combust, the reaction must either take place at the phase interface or components of the solid phase must volatilise into the gas phase.

If the solid polymeric material can be arranged such that it contains non flammable components and the carbon containing structures can be caused to reduce to solid carbon rather than volatile fractions, then the polymeric structure will demonstrate low flammability.

If the non flammable "inorganic" component of the polymer is itself non volatile, and the "organic" components reduce to carbon, then this flame resistant surface layer becomes persistent rather than labile and only this resistant source will be exposed to the fire regime, such that the underlying solid structure cannot be exposed to the reaction (fire) phase.

Further, if the carbonaceous char layer can be caused to expand (intumesce) then this persistent fire resisting layer exhibits a reduced thermal conductivity and, in consequence, insulates the underlying strata from the heat of the fire regime.

In the conventional products, generally used as intumescent coatings, the inorganic source is phosphorus, usually present as ammonium polyphosphate, and the carbon provider is present as a relatively insoluble polyhydric, such as pentaerythritol.

When these conventional formulations are exposed to fire the ammonium polyphosphate reduces to condensed phosphoric acid which dehydrates the polyol to carbon leaving a dispersion of elemental carbon in condensed phosphoric acid. The carbon particles are extremely finely divided at below colloidal particle sizes. Once this reaction has commenced the condensation-decondensation of the phosphorus oxy acids, together with the finely divided carbon can reduce other structures to carbon and water.

However, in conventional formulations the ammonium poly-phosphates must first decompose to phosphorus acids by loss of ammonia and then form esters with the carbonific polyols prior to the decomposition of the esters to carbon and water.

In the IIP and PRP systems the phosphorus is present in esters of carbonific polyols. Hence, decomposition to carbon and water takes place very rapidly as the intervening steps required in APP systems are already completed. The effect of this is that reduction to a non combustible carbon char and/or intumescence takes place far more rapidly and at substantially lower temperatures in the IIP and PRP systems when compared to the preceding APP technology.

A key element in the PRP theory is a new understanding of what comprises a carbonific polyol.

If the polymer can be arranged to include a proportion of aromatic carbon, preferably as a component of the polymer backbone rather than pendant to the backbone, this carbon can be caused to reduce to finely divided graphite, thus further enhancing the fire resistance of the char. Oxygenated and nitrogenous polymers (e.g. acrylics, PUs, epoxies) can also be reduced to carbon once the initial decomposition of the phosphate esters of carbonific carbon has occurred.

Nitrogen containing products are also usually present in conventional intumescent products, normally as melamine or one of its salts. The presence of such cyclic nitrogenous materials greatly enhances the quality of the char in terms of its structure and the particle size. The decomposition of the nitrogenous compounds causes the expansion where it is required in intumescent compounds. These components act only as assistants to intumescence, not for the formation of the carbon char. Indeed the PRP products are intumescent purely by virtue of the water vapour released on decomposition.

However, if the product is present in the resinous system in low concentrations below that where true intumescence appears, the nitrogenous material is still effective in enhancing fire reaction performance. It is particularly effective in reducing the amount of material that can be volatilised to the vapour phase where otherwise the combustion of the volatilised materials will increase both smoke emission and heat release.

The condensed phosphoric acid/carbon char is non flammable and persistent under fire regimes. The addition of a non reactive refractory (glass, titania) enhances char durability and, hence, the fire protection provided.

However, these conventional products that are added to materials like polyurethane foams, rubber, ABS and polyolefins are solids and, therefore, must be carried in a polymeric material which, as for an intumescent product, serves as a glue.

If the reaction mixture is present in the polymer purely to provide fire resistance, not as an intumescent, clearly the physical properties of the polymer are degraded by the materials which are present as soft fillers and contribute nothing to the physical properties of the polymer. Indeed laminating resins for structural composites are significantly weakened by the inclusion of flame retarding systems. If the flame retarding/intumescent system is part of the polymer or matrix then these disadvantages are overcome.

The theory underlying both the preceding IIP technology and the current PRP projects is that if these functionalities (phosphorus oxides, carbonific polyols, and nitrogen) are made to form the backbone of polymeric materials, then the polymer would be inherently non flammable or intrinsically intumescent. While the products must be essentially rich in phosphorus (> 4% for non flammability, > 9% for intumescence), the rest of the polymer structure must still contain the other two functional groups.

It should be appreciated that because the phosphorus is present as the orthophosphate, a P content of 9% represents a PO_4 content of 27% and the PO_4 is therefore a major constituent of the polymer backbone. Hence, the need to carefully design the polymer structure.

(3) PROJECT STATUS AND PROGRESS

The technology has evolved from the original IIP system of aqueous solutions of partial phosphate esters subsequently cross linked with aqueous solutions of simple urea and melamine formaldehyde resins licensed to Chemische Fabrik Budenheim in 1992

Subsequent developments of this technology include the use of the partial phosphate esters as cross linkers for phenolic resins. Commercialisation of end products derived from this technology was continued by various companies as fire protection coatings using new amino/phenolic resin systems (1992 onwards.)

While significant advances in the cross linker have been made, it had become apparent that improved partial phosphate esters to replace the CFB product were required. New synthesis routes were devised and investigated and it became clear that further major advances in the technology were possible. The new synthesis routes have lead to the new structures for the partial phosphate esters and wider applications through to the formation of non-flammable PU foams.

The PRP project has been running for 10 years with aid from EU and UK government development grants. Significant progress has been made in understanding the synthesis routes, the structures produced, the behaviour and structure of the intermediates, the development of novel control techniques, the design of process plant and the establishment of reaction conditions. IPR protection has been secured under world wide patent applications with a priority date of 10/2/97.

In view of the available markets we define the forms of PRP according to their usage and cross linking mechanism. It should however be noted that all the products are amber liquids in which the viscosity varies upwards with chain length and acid value

4) PRP and MIPS Forms

Form 1 Intumescent products with combinations of amino and phenolic resins.

Form 1 and variants are designed as alternatives to the IIP partial phosphate ester, and intended to be cross-linked with amino resins to produce low cost intumescent coatings. Form 1 has a lower acid value than IIP partial phosphate ester and a higher phosphorus content. It will be supplied at 100% solids. It has no other function than to compete in the market that has been opened up by the IIP system. In particular it will be offered to be cross linked with UF resins to provide flame resistant particle boards.

The PRP synthesis procedure provides methods of total control of the free acidity with no orthophosphoric acid produced as a by product. This means that less of the methalol functional cross linking agent is required, producing higher phosphorus content polymers and, hence, stronger more fire resistant chars and better intumescence. This also means lower film thicknesses and, hence, more economic products. As this also indicates more flexible films, these products will have greater utility particularly in paper and cloth coating.

PD can demonstrate a number of effective formulations using form 1 PRP, including paper coatings, clear varnishes and paints for wood, structural steel fire protection products as well as an intriguing formulation for the internal fire protection of aircraft engines.

Form 2 Cold curing of Phenolic resins

It has been demonstrated that form 2 PRP gives cold cures of resole phenolic resins. The PRP based phenolics are hard, resilient and aesthetically pleasing. The most useful emergent property is that the product allows the rapid cold curing of resol phenolic resin laminates without the need for subsequent thermal cycling. This has significant import to the development of large composite marine structures.

Form 3 Advanced intumescent coatings.

Form 3 products are a series of low acid value partial phosphate esters designed to produce intumescent films, glues and coatings. Unlike, the IIP partial phosphate ester they are cross linked without the use of methalol resins and, therefore, do not emit formaldehyde on curing. This drawback has been one of the properties that has prevented the IIP technology taking a greater market share.

Form 3 products are cross-linked using other reactions of the organic acid orthophosphate. which behave very much like carboxylic acids. Hence, any system used for cross-linking carboxylic acid functional resins may be used with low acidity polymeric orthophosphate esters. Thus, cycloaliphatic epoxides, polyfunctional aziridines, poly carbomides, and zinc and zirconium ammonia complexes will cross link either at room or elevated temperature depending on the cross linker and the acid value.

The PRP theory indicates that it is possible to reduce the residual acidity of the ester so low that other fully stable, formaldehyde free cross linking agents may be used for products that appear entirely different to the IIP films, with greater can stability, and greater toxicological acceptability of the finished intumescent paints and varnishes.

Form 4 PRP products are a series of neutral and hydroxyl functional short chain oligomeric phosphate esters. As such they react with isocyanates to give polyurethanes, thus giving non flammable polyurethane products.

Sampling the product to foam blowers has indicated that there are some formulation problems to be resolved. However, the latest products provide a good solution to the current requirement for combustion modified PU foam to meet UK and Eire standards, without the use of halogens. In this case the Form 4 PRP is blended off with other polyols.

Foams made with MDI using PRP form 4 as the only polyol are entirely non-flammable. While they have adequate flexibility, development work is required on foam structure and stabilisation. In this form the product is entirely suitable for use in automobile and aerospace applications.

Good non-flammable PU elastomers and rigid foams may also be made with PRP form 4 products. Current work is concentrating on the use of the PRP oligomers in aliphatic isocyanate coatings to produce fire resistant coatings that retain all the properties of aliphatic PUs.

Variants of form 4 will also act as a flame retardant for other polymer species with which cross linking is not possible. In such applications it will promote anaerobic pyrolysis and, thus, raise the char forming properties of the polymer under fire regimes.

MIPS (Mixed Intumescent Polymeric Salts)

MIPS are a precipitated form of PRP form 1. They will be available as either a very high solids water dispersion or as a dried powder. The product can take many forms and can be varied in terms of TG, but all provide a new single component intumescent additive

MIPS are compatible with most polymeric materials. They can be alloyed with poly olefins to render them inflammable. It was for this purpose they were originally designed. However MIPS may be dispersed in latex resins to produce intumescent paints and sealants, with no other addition than pigment, thus making formulation extremely easy.
MIPS may also be dispersed in epoxy resins. In fact the MIPS aqueous dispersion will further disperse into epoxy resins without further modification. Using this technology water based off shore intumescent coatings and fire resistant fillers and patches are under development.

5) Development and Exploitation.

With support from the DTI and our exploitation partner production of all PRP forms is being run up to pilot (250 kg) scale in preparation for full scale production.

As with all new technologies significant experience is required in understanding how to formulate with these new products. Potential users are warned against assuming a simple addition to existing formulations will achieve the required result. While it may be assumed that MIPS are approximately 4 times more efficient than ATH on a weight for weight basis, this will depend entirely on the application and final fire test requirements.