The Synthesis and Evaluation of Inherently Fire

Retardant/Low Smoke Unsaturated Polyester Resins

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A thesis submitted in partial fulfilment of the requirements of Kingston University for the Degree of Doctor of Philosophy

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July 1997

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One and All, I thank you

<u>Abstract</u>

A study has been undertaken to attempt to overcome three major problems associated with common unsaturated polyester resins. These problems are the emissions of free styrene, high flammability and the emission of thick black smoke during combustion. A novel cross-linking monomer, containing two allyloxy substituents and one diethylamino substituent, has been synthesised and purified in a two stage reaction using cyanuric chloride as the starting material. This new monomer contains five nitrogen atoms in an attempt to reduce smoke evolution and has a low volatility to reduce volatile organic emissions.

It was found that this monomer was totally miscible with all resin types, based on both aromatic and aliphatic alkyds, and produced a degree of cross-linking in excess of 95% when cured with dicumyl peroxide at 90°C for 16 hrs and then 140°C for 3 hours.

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Combustion tests showed that the new resins produced considerably less smoke than the styrenated resins, show higher LOI values, i.e. require a higher percentage of oxygen to sustain combustion, and a lower surface spread of flame. These improved combustion properties are a direct result of the improved charring characteristics of the resins caused by the incorporation of the triazine monomer. It has been shown, however, that normal fire retardant phosphorus additives used in unsaturated polyester resins (UPRs) have little or no effect in the triazine resins and do not show any synergism with the nitrogen atoms in the new monomer. As a result of this, at high additive loading levels, the combustion behaviour improvements shown by the triazine resins over the styrenated resins are drastically reduced. It has also been shown that the triazine resins have a very high burning rate.

The lack of phosphorus activity in the triazine resins has been shown to be caused by these resins thermally decomposing at low temperatures where the phosphorus is not active. This low decomposition temperature also leads to rapid decomposition and thus a high burning rate. The lack of synergism might be caused by the tertiary amine substituent being too stable towards interaction with the phosphorus additives; a primary amine might be more suitable.

Mechanical studies have shown the new resin to be brittle in comparison to the styrenated resins but that it has increased Barcol hardness values, heat distortion temperature and flexural modulus.

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1.0 Introduction

The second states of the second se 1.1 Introduction to Polymers

The word polymer comes from the Greek *poly* and *meros* meaning many and parts, respectively. Polymers are also often referred to as macromolecules which simply means large molecule. Polymers can occur naturally in nature in forms such as proteins, wool or cellulose. They can also be made synthetically in the laboratory. One of the first artificial polymers produced was a thermoplastic - celluloid - which was synthesised in the 1860s by Parkes and Hyatt(1). Thermoplastics consist of two-dimensional molecules which may be softened and melted by heat and then cooled to return to their original state. They are also soluble in various organic solvents. Examples of these include poly(vinyl chloride) (PVC) and poly(ethylene terephthalate) (PET).

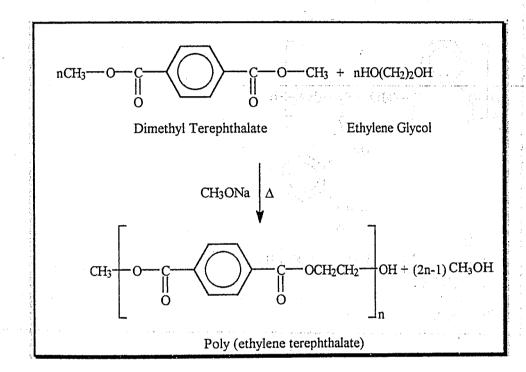
The other class of polymers is the thermosets. These are three dimensional network polymers which do not melt under heating and are virtually insoluble in any solvents. Examples of these types of polymers include unsaturated polyesters and epoxy resins.

1.2 Introduction to Polyesters

Polyesters are formed via a condensation reaction between a diacid and a diol to leave a polymeric chain containing ester linkages. There are three main types of polyesters. These are thermoplastic polyesters, glyptals and alkyds.

1.2.1 Thermoplastic Polyesters

Thermoplastic polyesters are used in the formation of fibres and food packaging materials. The most commonly produced thermoplastic polyester is poly(ethylene terephthalate) (Fig. 1). In 1992 the annual production of PET in the United States alone was 1.5 million tonnes (1).



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Fig. 1: Synthesis and structure of PET.

1.2.2 Glyptal Polyesters

These polyesters come under the thermosetting class of polymers and were first synthesised in 1901 by heating glycerol with phthalic anhydride. As the secondary hydroxyl group in glycerol is less reactive than both of the terminal primary hydroxyl groups, the first product formed from this reaction is a linear polymer (Fig. 2). Further heating then activates the secondary hydroxyl group which reacts further with the phthalic anhydride to form a cross-linked polymer (Fig. 2).

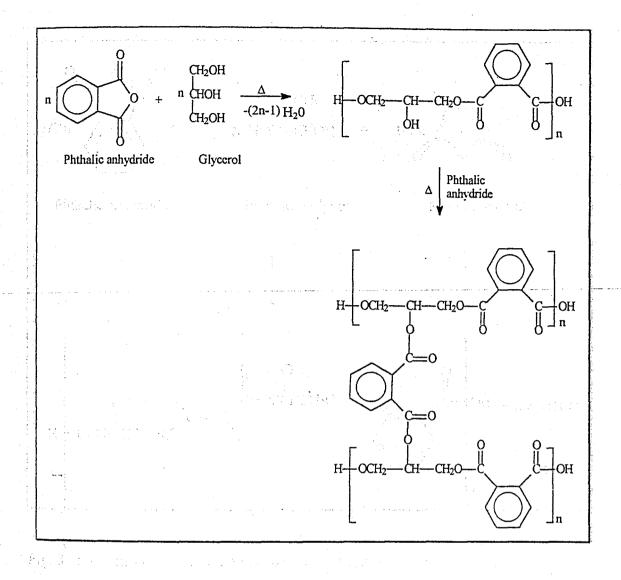
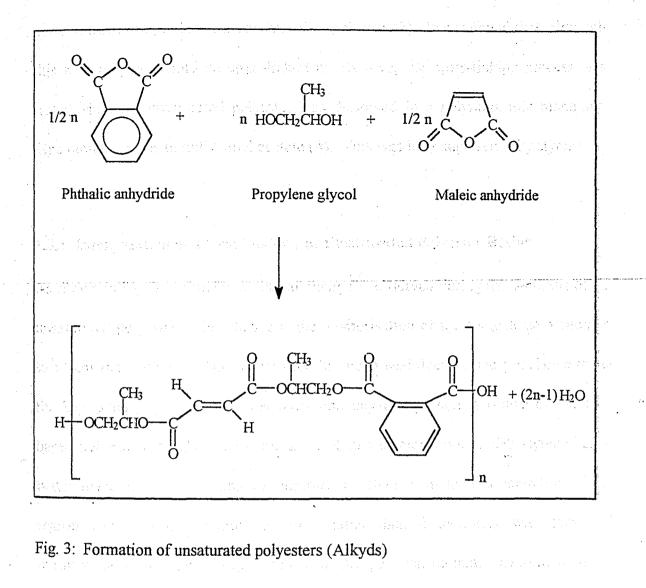


Fig. 2: Formation of crosslinked glyptal polyesters.

1.2.3 Alkyd Polyesters

This sub-group of polyesters is often referred to as unsaturated polyesters. This is because of the unsaturation in the backbone of the polymer. This polyester is formed via a condensation reaction between a diol, a saturated or an aromatic dibasic acid/anhydride and an unsaturated dibasic acid/anhydride (Fig. 3). The polymer formed from the condensation reaction is a glassy solid at room temperature and is dissolved in a cross-linking monomer, typically styrene, to form an unsaturated polyester resin, which is a viscous liquid at room temperature.



It is these unsaturated polyesters that are of importance in this project and so they will be discussed in more detail.

1.3 Unsaturated Polyesters - Production and uses

The first unsaturated polyester was produced by Vorlander in 1894 (2). This was a condensation product from a glycol and maleic anhydride. A well defined and reproducible method for the production of unsaturated polyesters was not available until Carothers established a synthetic method whereby the reagents were reacted

under nitrogen to produce the condensation polymer (3). It was found that, although this new polymer could be cross-linked on its own, the cross-linking process was faster when the unsaturated polyester was dissolved in a polymerisable monomer. This monomer was initially vinyl acetate (4). This was later superseded by styrene.

1.3.1 Isomerisation and Cross-linking in Unsaturated Polyester Resins

As shown in Fig. 3 one major structural change is observed during the synthesis of an unsaturated polyester. This change is the isomerisation of the cis maleate monomer to a trans fumarate unit. This observation has been well documented and shown to be the key factor in the excellent reactivity and physical properties shown by maleate based polyesters (5 - 8). The importance of this isomerisation is that styrene has a better reactivity ratio to fumarate unsaturation than to maleate unsaturation. The reason why maleic anhydride is used rather than a monomer with fumarate unsaturation is that it does isomerise and is cheaper than fumarate based monomers. Obviously then, the extent of isomerisation is important in determining the physical properties of the cured resin. If less isomerisation occurs then fewer reactive sites of unsaturation will be available for cross-linking with styrene. If this is the case then there will be fewer cross-link bridges in the cured resin which will, consequently, be less rigid. Many methods have been employed to study the isomerisation process (5, 8, 9) and these have shown that the trend is that the more sterically hindered the glycol, the more isomerisation to fumarate that occurs (Table 1).

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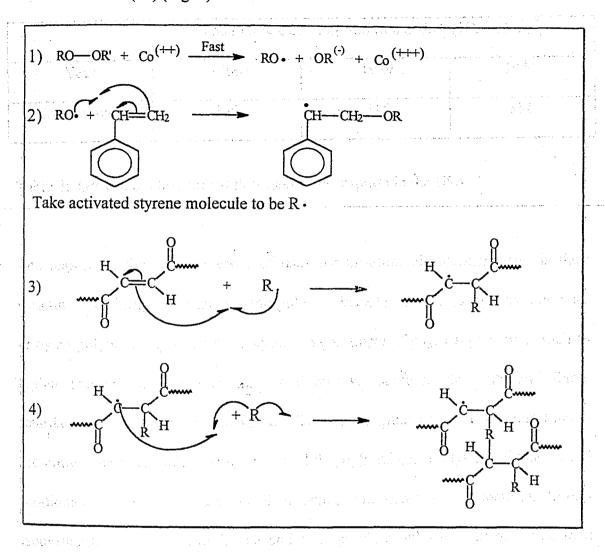
Monomers				Res	sin C	omp	ositic	on (m	ionor	ners	prese	ent)			
Cullaborational		X	-							X					X
Cyclohexanedimethanol Diethylene glycol		х			X		• • ·	an an t	X					X	
Neopentyl glycol				X		$a^{(i)}$		X					X		
Ethylene glycol			X				Χ					X			
1,2-Propylene glycol	X					X					X				
2,2,4-Trimethyl-1,3- pentanediol		· · · ·			a an	aa Ag	17 Jac 1				X				
Maleic anhydride	X	X	Χ	X	X	X	·X	X	X	Χ	X	X	X	X	X
Isophthalic acid	X	X	Χ	X	X									- -	
Phthalic anhydride				2	4	X	Х	X	X	X					
% Fumarate	95	96	71	72	65	94	84	85	82	52	93	75	50	50	33

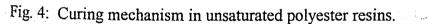
 Table 1: Isomerisation of maleate to fumarate for different resin compositions (6).

Once the monomers have been polymerised to give the unsaturated polyester alkyd with fumarate unsaturation, the polymer is dissolved in the crosslinking monomer, this is typically styrene. The resin is now ready to be cured. Curing of a polyester resin is an addition co-polymerisation between the styrene and the alkyd. The curing process and the resultant three dimensional matrix have been extensively studied (10 - 21). This co-polymerisation requires a free-radical initiator to provide reactive free radicals which initiate the free radical cross-linking process. Typical initiators are organic peroxides or hydroperoxides, such as methyl ethyl ketone peroxide, although other materials such as azonitriles may be used (22).

The initiation process can occur in two different ways. The first of these is the thermal degradation of the initiator to produce the free radicals. This process, however, is sometimes slow so a catalyst is often used to speed up the process. In the case of the styrene based systems the catalyst is a cobalt salt (often cobalt naphthenate

or cobalt octanoate). The co-polymerisation occurs according to the following reaction scheme (10) (Fig. 4).





Once cured the polyester resin has extremely good physical and chemical properties, which facilitate its use in many various areas of life. Use of polyesters, commercially, has grown rapidly since their first use in making aircraft radomes in the second world war (23). Table 2 shows the growth of unsaturated polyester consumption in the USA (24 - 26). Polyesters are used in a diverse number of areas from boat hulls, car

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frames, ornamental baths, insulation for electrical wires to armament applications or high durability coatings (27 - 36).

yan di mananan a	Total UPR Consumption in the USA (1000 tonnes)							
Year	1966	1979. active at 1979.						
Consumption	205							
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Table 2: Growth of Unsaturated Polyester consumption in the USA

The reason for this large diversity of uses for unsaturated polyester resins is their structural flexibility. By changing the polymer backbone, the cross-linking monomer or by co-polymerising with other polymers a great deal of physical properties, such as higher, thermal stability, electrical conductivity, increased flexibility and flame retardance (37 - 48) can be achieved. This has included the use of cross-linking monomers such as diallyl phthalate, diallyl isophthalate, triallyl trimellitate, vinyl propionate, triallyl cyanurate, vinyl toluene, chlorostyrene, acrylonitrile, triallyl isocyanurate, N-vinyl pyrrolidinone and zinc acrylate (49 - 63), all of which lend differing physical and mechanical properties to the final cured resins.

Despite being so versatile and so widely used, unsaturated polyester resins are far from perfect. They suffer from two major disadvantages. The first of these is the presence of styrene in the vast majority of the resins. Total exposure to styrene in the workplace has been a problem for many years and recent legislation throughout the world has drastically reduced the legal total exposure to styrene in the workplace. In Germany, for example, the total exposure has been reduced from 100ppm to 20ppm (64). In the UK the maximum exposure limit is 100ppm with a self imposed

restriction of 50ppm in place. As a result of this there has been a large increase in research into unsaturated polyester resins with low styrene emissions. The second problem, and perhaps the most important, is the ease of flammability of unsaturated polyesters and the excessively large amounts of thick, black, toxic smoke evolved on burning. This is a major problem when one considers that practically all of a polyester is consumed during a large scale fire (65) and that the greatest factor leading to deaths in a fire is not the flames but the smoke (66 - 68).

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1.4 Unsaturated Polyester Resins with Low Styrene Emissions As has been previously mentioned the emission of styrene from unsaturated polyester resins in the work place is an area of concern. There has, therefore, been a large amount of research into the reduction of styrene emissions. This research has taken the form of two distinctly different approaches. The first, and arguably the quickest and most cost-effective method, is the use of additives to suppress the emission of styrene. The second method has centred around actually reducing the amount of styrene used in the unsaturated polyester resin. This method relies on the chemical modification of either the polymer backbone or the cross-linking monomer itself.

1.4.1 Suppression of styrene emissions using additives

One major area of interest in this field has been the addition of paraffin type waxes, in quantities ranging from 0.001 - 7 phr (parts per hundred parts of resin), to the styrene-containing polyester (69 - 74). The paraffin waxes possess a lower density than the

polyester resin so they have the tendency, on curing, to rise to the surface of the polymer and form a thin, impenetrable film. This film prevents volatilisation of the styrene from the unsaturated polyester. Another advantage of this film is that it prevents oxygen inhibition of the free radical curing process. On their own, however, the paraffin waxes were not entirely of much effective use because they tended to reduce the adhesion properties of the polymer. To remedy this adhesion promoters (0.5 - 10 phr) were added to the resins to increase the adhesion of the polymers. These promoters usually took the form of low molecular weight polymers such as poly(butyl acrylate) (69) or the co-polymerisation products obtained from the reaction between alcohols and dicarboxylic

acids, and epoxy compounds (72). Other promoters were synthesised from C16 fatty alcohols, maleic anhydride and epoxy resins (71) or C5 - 30 fatty acids and mono- or diepoxides (70).

Poly(butyl acrylate) was not totally miscible with styrene and so separation occurred lessening the effectiveness of the promoter (69). In this case non-ionic surfactants or further additives based on polyethylene glycol maleate - styrene copolymers were added. The use of a copper salt cure catalyst and alpha - methylstyrene was also investigated in these systems (70). It was found that these reduced the maximum cure exotherm. The effect of this is to produce less heat during the curing process and so reduce heat induced styrene evaporation.

Another additive method of reducing styrene emissions, not relying on the use of paraffin waxes, was patented by the Standard Oil Co., USA (74). In this case the additives were based on m-isopropenyl dimethylbenzyl isocyanate-terminated ethylene oxide-propylene oxide block copolymers (0.5 - 5.0 phr). This additive

worked in much the same way as the paraffin waxes in that it formed a thin, impenetrable layer on the surface of the polymer. This invention, though, did not suffer from the drawbacks of reduced adhesive properties.

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This method of reducing styrene emissions is regarded as being more difficult to achieve than the use of additives, because when a polymer is changed structurally, its mechanical and physical properties are altered in an unpredictable way. This alteration, when compared to the excellent physical and mechanical properties of styrene-based polyesters, is almost always detrimental. A greater amount of research and development is, therefore, needed to produce a novel structure with sound properties.

One obvious solution to the reduction of styrene emissions was to reduce the amount of styrene present in the resins themselves. The difficulty with this was the subsequent drastic increase in resin viscosity leading to processing difficulties. BASF AG (75) patented an invention based on dihydrodicyclopentadiene terminated polyester resin having low molecular weights. As the resin was of a lower molecular weight it was a viscous liquid. Added to this, there were fewer cross-link sites on the polymer backbone facilitating the use of less styrene (1 - 30% compared to >35% for ordinary resins) to give an excellent degree of cure without the resultant reduction in the ease of processability. One problem with this solution, however, was the loss of good mechanical properties of the new resin. This was remedied by adding the

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reaction products obtained by reacting hydroxyalkyle (meth)acrylates with diisocyanates.

Other developments have revolved around the removal of styrene totally from the resins. These have mainly centred on the use of modified polyester backbones and derivatives of acrylates as the cross-linking monomer (76 - 79). Aristech Chemical Corp., USA (76, 77) patented a modified polyester, comprised of maleic anhydride, phthalic anhydride, various glycols and dicyclopentadiene, a diacrylate or dimethacrylate of alkoxylated bisphenol A (as the cross-linking monomer) (Fig. 5) and ethylene glycol dimethacrylate, as a low styrene emitting resin.

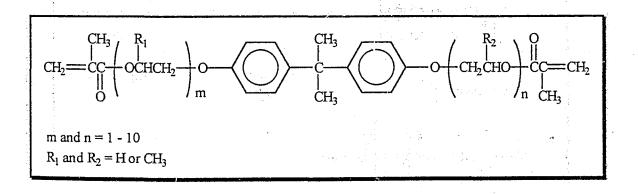
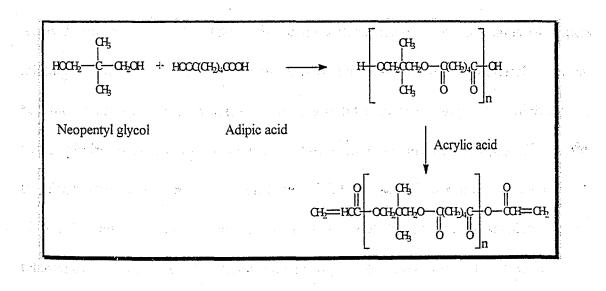


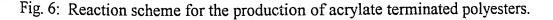
Fig. 5: Novel cross-linking monomer used in low styrene emission polyester resin.

This resin, containing no styrene and having a cross-linking monomer with a very low volatility showed extremely low organic emissions.

A German invention (78) details the production of a low molecular weight polyester (typical weight 500 - 1500) with acrylate or methacrylate end-groups. This was achieved by reacting a saturated diacid with a glycol and then endcapping the resultant polymer with methacrylic or acrylic acid to give unsaturation in the polymer backbone (Fig. 6.). The acrylate end-groups were used rather than maleic acid endgroups to facilitate the replacement of styrene with methacrylate cross-linking monomers such as 2-ethylhexylmethacrylate or N,N-dimethylaminomethylmethacrylate. As before, this invention contained no styrene. The cross-linking monomer was again a compound of low volatility which showed little tendency to evaporate during storage or cure. One patent describes the use of novel cross-linking monomers without any structural changes to the polyester backbone (79). In this case the cross-linking monomer was a member of the acetoacetoxyalkyl (meth)acrylates (Fig. 7).



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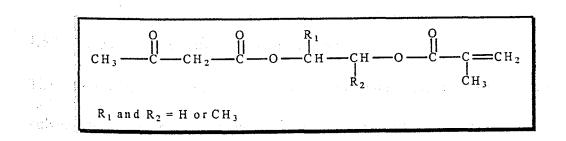


Fig. 7: Structure of acetoacetoxyalkyl (meth)acrylates

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These inventions all claim to reduce the styrene emissions from unsaturated polyester resins but they do not alleviate the problem of combustion and smoke production. This is a completely separate area of research and as such will be discussed separately.

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1.5 Fire Retardation and Smoke suppression

1.5.1 Introduction to Fire retardation

Fire retardation dates back many years with the first reference to fire retardants for wood dating back to 1905 (80). Since then there have been thousands of papers relating to fire retardation in polymers and naturally occurring materials. It has become clear that fire retardation centres around a core of elements which appear frequently in fire retardant formulations. These elements are P, N, Sb, Al, Cl, Br and B. There are other elements which have useful fire retardant properties such as Sn, Fe, Zn, Mo and Mg but they are not so widely used. Before the mechanisms of fire retardancy for individual elements can be discussed, however, it is vital that the fundamentals of fire and combustion are fully understood.

1.5.2 Fire and Combustion - The principles

The combustion of polymers is a very complicated process which varies from polymer to polymer and depends entirely on the structure of the polymer and the combustion conditions. This process, however, can be discussed in general terms. In general the combustion of a polymer can be considered on three distinct scales: micro, macro and mass (81). Micro scale combustion considers only a single polymer

molecule, macro scale relates to 1 gram of material and mass scale discusses the combustion of a fully furnished room. It is obviously not economically feasible to constantly carry out combustion research on an entire room full of polymeric materials, conversely it is also not always a simple matter to study the combustion behaviour of a single molecule. Most research is, therefore, carried out on the macro scale.

1.5.2.1 The Burning Cycle

For any material to burn three components are always essential. These are the fuel, a heat source and oxygen (Fig. 8). This is called the 'Fire Triangle'

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Fig. 8: The Fire Triangle

If any one of these three components is deficient to any extent then no combustion will take place. The process of combustion itself is essentially a four stage, self-accelerating process (82 - 84). The stages are as follows:

- 1) Transfer of heat to the polymer surface.
- 2) Thermal degradation and decomposition of the polymer to give volatile and reactive species (fuel production).

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- 3) Exothermic oxidation of the decomposition products (combustion) resulting in the production of light and heat as by-products.
- 4) Transfer of the resultant heat back to the polymer surface.

As has been stated, when a polymeric material is subjected to an external heat source it begins to thermally degrade. This results in the elimination of gaseous products. This loss of gaseous products is, of course, not an instantaneous occurrence and occurs in several stages, which are temperature dependent. At lower temperatures of around 100 - 250°C only very low energy reactions will occur. This includes the loss of functional groups, condensation and dehydro-halogenation. This renders the carbon skeleton of the polymer increasingly more unsaturated and conjugated but essentially still intact (85).

At the higher end of this temperature range there is enough energy for individual bonds to be broken. The order of this bond scission is dependent on the respective bond energies. Some bond energies of typical components found in polymers are given in Table 3 (86).

Bond	Energy (kJmol ⁻¹)	Bond	Energy (kJmol ⁻¹)
C-I	192	N-H	385
C - Br	226	C-H	410
C - N	247	H-H	431
C - C1	326	О-Н	460
C-C	335	0=0	494
<u>C-O</u>	335	C = C	607

 Table 3: Mean bond energies of typical components found in polymers

At temperatures between 250 - 500°C the polymer decomposes further to produce tar, gas and char. This is essentially a disproportionation reaction which yields hydrogen-rich and hydrogen-poor fragments, the char being poor in hydrogen and containing mainly an unsaturated carbon chain. At these temperatures even the strongest bonds are broken, resulting in three possible outcomes:

1) Unzipping of the polymer chain itself yielding flammable monomers,

e.g. PMMA

CH3 CH3 CH3 CH₃ ·CH2 CH, CH CH₁C CH₃O ĊO₂CH₃ CO₂CH₂ ö ö Гн.

2) Random elimination of small chemical fragments

e.g. poly (ethylene)

CH2CH2 CH3 CH3 $CH_2=CH_2 + CH_3CH_3 + CH_3CH = CH_2$

3) Combination of both 1 and 2

The products from all three of these combinations can sustain the combustion reactions. Above 500°C the char becomes increasingly more condensed. The resultant secondary char is extremely insulating and acts as a barrier protecting the polymer surface from the flame.

As the polymer sequentially degrades the gaseous products are exothermically oxidised by atmospheric oxygen. This is a very complex series of reactions. The complexity of this can be highlighted by the number of reactions which take place in a simple methane flame (Fig. 9)(82,87).

$$CH_4 + OH \cdot \longrightarrow CH_3 \cdot + H_2O$$

$$CH_4 + H \cdot \longrightarrow CH_3 \cdot + H_2$$

$$CH_4 + O \cdot \longrightarrow CH_3 \cdot + OH \cdot$$

$$CH_3 \cdot + O_2 \longrightarrow HCHO + OH \cdot$$

$$HCHO + OH \cdot \longrightarrow HCO \cdot + H_2O$$

$$HCO \cdot + OH \cdot \longrightarrow CO + H_2O$$

$$CO + OH \cdot \longrightarrow CO_2 + H \cdot$$

$$H \cdot + O_2 \longrightarrow OH \cdot + O \cdot$$

$$O \cdot \cdot + H_2 \longrightarrow OH \cdot + O \cdot$$

Fig. 9: Some of the reactions taking place in a methane - oxygen flame

It must, however, be stressed that this series of reactions by no means represent the reactions that occur when a polymeric system burns. These reactions were obtained from a pre-mixed flame with an excess of oxygen. The combustion of polymers, on the other hand, proceeds with an oxygen deficient flame. It has been suggested that, in polymeric systems, important oxidation reactions actually occur at the polymer surface (88,89) which contribute to the overall flammability of the polymer.

Given a schematic representation of the combustion process (Fig. 10), it can be seen that for a combustion process to be cyclic and self-sustaining the heat feed-back from the combustion must be enough to decompose the polymer further, i.e. Q_2 must be equal to if not more than Q_1 .

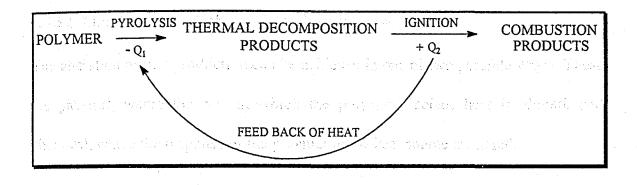


Fig. 10: Schematic representation of the burning cycle

As can be seen from the diagram Q_1 is endothermic, i.e. it requires and takes in heat and Q_2 is exothermic, i.e. it emits heat. For a polymer to be flame resistant it would need to have a high Q_1 value and a low Q_2 value. In this case the heat being returned to the polymer surface from the combustion would not be enough to degrade the polymer. If, on the other hand, the polymer has a low Q_1 value and a high Q_2 value it will be extremely flammable. For a polymer to be rendered fire retardant this burning cycle must be modified in such a way that combustion cannot take place.

1.5.3 Modification of the Burning Cycle

The incorporation of flame retardancy into a polymer can be achieved in many ways. All of these methods have one thing in common, however, in that they all modify the magnitude of Q_1 and Q_2 , as described above, i.e. modification of the fuel production or interference with the flaming combustion process.

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1.5.3.1 Interference with the Fuel Production Stage of the state of th

The alteration of fuel production can be achieved in one of two possible ways. These are physical, where the rate at which the polymer receives heat is altered, and chemical, where the response of the polymer to the heat source is altered.

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1.5.3.1.1 Physical Mechanisms

The rate at which the polymer receives heat from the external fuel source can be reduced by additives which change the thermal conductivity of the polymer formulation. This is achieved by more effective heat dissipation throughout the bulk of the polymer. The effect of this is to drastically increase the amount of time taken to reach a temperature at which the polymer decomposes. Additives that absorb and remove heat by melting or evaporation are known as transpirational coolants.

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1.5.3.1.2 Chemical interference

A fire retardant which chemically affects the fuel production in a polymer can act in one of two ways. The first way is to promote the formation of a non-flammable char and to reduce the amount of flammable gases that are produced during the degradation process. The production of the char barrier is useful in several ways. Firstly, a char reduces the amount of fuel that it available for decomposition. Secondly, it acts as a thermal barrier for the polymer and so prevents further degradation and finally it can act as a heat sink by radiating excess heat away from the polymer surface. In this case then the value of Q_1 , as described earlier, is increased and the value of Q_2 is decreased. The second way in which a chemical modification can occur is to increase the rate of fuel production. In this case the fuel is produced at lower temperatures where a flammable fuel/air mixture is never reached.

1.5.3.2 Modification of the Combustion Stage

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Flaming combustion is essentially an oxidation reaction between atmospheric oxygen and reactive free radicals produced from the degrading polymer. Interference with this process should, then, be a case of producing free radical traps which inhibit this reaction. An additive that breaks down during the decomposition process to produce free radicals that compete with reactive free radicals to produce less energetic radicals than the existing H', OH', and O', would act as a flame inhibitor. This process, called "poisoning", reduces the amount of heat radiated back to the surface of the polymer by reducing the number of exothermic reactions taking place in the flame.

It has been reported, that in hydrocarbon flames, some ionisation reactions occur (90,91). These have been theorised to be:

 $CH_3 \cdot + O \cdot \longrightarrow CH_3 O^+ + e^-$

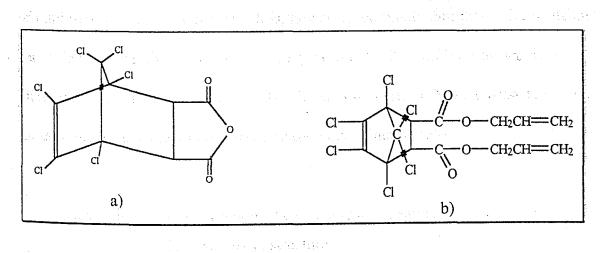
These only occur in very small quantities, however, and any fire retardant designed to specifically inhibit these ionisation reactions would be of little practical use.

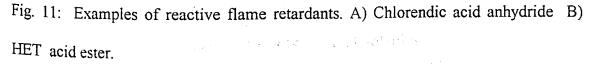
1.5.4 Fire Retardants - Types and Mode of Action

There are several words related to how fire retardants are incorporated into a polymer system, where they affect the burning cycle and how they operate. These words are additive and reactive for how they are incorporated, condensed phase action or vapour phase action, for where they act and finally additively, synergistically and antagonistically, for how they act.

1.5.4.1 Additive vs Reactive Flame Retardants

An additive flame retardant is a compound which is merely blended into the polymer itself (92). Such a flame retardant would be something like hydrated aluminium (III) oxide $(Al_2O_3.3H_2O)$ or triethyl phosphate (($CH_3CH_2O)_3P(O)$). When a flame retardant is reactive it has been chemically incorporated into the actual structure of the polymer. This can be achieved by backbone modification or cross-linking monomer modification. Examples of this are shown in Fig. 11.





Structure a) is used in place of phthalic anhydride and b) is used rather than styrene. As can be expected both types of flame retardants have drawbacks. In the case of additive flame retardants they have the tendency, over a period of time, to leach from the polymer resulting in a reduction of the fire retardant effect. Reactive flame retardants do not leach from the polymer as they are an integral part of the network. They are, unfortunately, expensive to synthesise and also a great deal more research is needed to ensure that there is no resultant loss of physical and mechanical properties.

1.5.4.2 Vapour Phase vs Condensed Phase action

Fire retardants act in the condensed phase by altering the thermal decomposition of the polymer to promote char formation or increase the decomposition rate at lower temperatures. This has the effect of reducing the amount of fuel available for combustion. In the vapour phase the fire retardants act by trapping the reactive free radicals that are produced by the thermal decomposition process. This has the effect of inhibiting flaming combustion. It is, however, extremely rare that a fire retardant acts solely in one phase without affecting the other. It is difficult to decide which phase the retardant actually acts in. Hastie has summarised the macroscopic criteria for defining a gas phase or condensed phase mode of action (93).

Gas Phase:

Loss of retardant element from substrate Insensitivity to structure Sensitivity to oxidant No change in composition of volatiles

Condensed Phase: Enhanced char formation Retention of retardant element in substrate Retardant element ineffective in gas phase Sensitivity to structure of polymer Insensitive to oxidant Change in volatile pyrolysis products

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Despite these definitions deciding where a fire retardant element operates is not a simple matter. The difficulties associated with this will be discussed in section 1.5.5 along with the individual elements used as fire retardants.

1.5.4.3 Additivity, Synergism and Antagonism

These three phenomena only occur when two or more fire retardant elements are used in conjunction. An additive fire retardant effect is the sum of the individual effects of the elements when taken independently. A synergistic effect is when the two elements combine together to give a fire retardant effect which is greater than the additive effect, assuming the same amounts of fire retardant elements are present. An antagonistic effect is when the effect produced is less than the additive effect.

Obviously the most desirable effect is synergism. In a synergistic system less of the respective elements can be used to confer a specific fire retardant effect on the polymer. The actions of individual elements will be discussed later but synergism in general will be discussed in more detail here.

In determining whether or not two fire retardant elements are synergistic, it is necessary to study the effects of the individual elements. First a concentration -

response curve is drawn for each element. This can be achieved by taking the oxygen index (O.I.) value for each element at various concentration levels and drawing a graph. The O.I. value of a burning polymer is obtained by burning the polymer in a known mixture of nitrogen and oxygen. The O.I. value is taken to be the percentage of oxygen at which the polymer is self-extinguishing after 3 minutes, as the fraction of the total amount of nitrogen and oxygen present (Equation 1)

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 $O.I. = \frac{[O_2]}{[O_2][N_2]}$ en el possibilitza este comb

Equation 1: Calculation of O.I. value and antibased provider and the construction

From the concentration - response curve an algebraic function describing the fire retardant effect of the element is derived. The algebraic functions are then summed to give the effect as described by an additive system. This is then compared to the actual experimental effect obtained when the two elements are used in conjunction with each other.

Take, for example, two fire retardant elements A and B. When taken individually the concentration - response curves show the flame retardant effects of the elements X_A and X_B to be the functions F(A) and F(B). The additive flame retardant effect $X_{A,B}$ is then calculated as:

$X_{A,B} = F(A) + F(B)$

If the theoretical response, as calculated by the above equation, does not match the response as shown experimentally by the action of the two elements together then a third term is needed to compensate for this discrepancy:

$X_{A,B} = F(A) + F(B) \pm S_{A,B}$

If this third term is positive then the effect is greater than the additive effect and the elements can be considered as synergistic. If, on the other hand, the third term is negative then the elements are antagonistic. Unfortunately this concept is not as straight forward as it seems. A phenomenon called pseudo-synergism has been described (94). When this occurs it is possible to demonstrate a synergistic interaction between two elements when no such effect occurs.

Lyons (95) reported a synergistic effect between phosphorus and bromine. In his review he took literature values given for the fire retardant effect of bromine and phosphorus when used individually. He then assumed that the concentration - response relationship was linear. From this he calculated the additive effect of the two elements when used together, assuming no synergistic interaction. This theoretical additive effect was then compared to the actual amounts needed as derived experimentally.

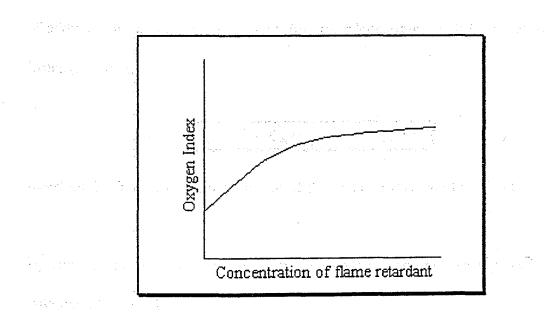
From his work with acrylic polymers he found that 5% phosphorus or 16% bromine was needed to impart fire retardant properties to the polymer, when used individually. Assuming a purely additive effect he used the following formula to calculate the amount of Br, when used with 1% phosphorus, needed to impart the same level of fire retardation as 5% P or 16% Br, when used alone:

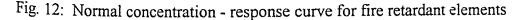
$$T_{P+X} = T_X - (M_{P+X})\frac{T_X}{M_P} = \frac{M_P - M_{P+X}}{M_P}T_X$$

Here the own the part of the transmission of the provider of the providence of the p Where: $M_P = Level of P$ alone for fire retardant properties $M_P = Level of P$ alone for fire retardant properties of the encoded T_x = Level of Br alone for fire retardant properties

> M_{P+X} = Level of P in mixed system needed for fire retardant properties T_{P+X} = Level of Br in mixed system needed for fire retardant properties

Using this equation he calculated that 12% Br would be needed, in an additive system, with 1% P present. The actual amount, found experimentally, was determined to be 3%. Lyons, therefore, deduced that synergism was taking place. Weil criticised this deduction because it was based on the assumption that the concentration - curve was linear. In most cases the response is actually a diminishing slope (Fig. 12) S. Cher





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From his own studies on the bromine - phosphorus interactions in acrylates, Weil found that the best algebraic function to describe the individual fire retardant effects of the elements was in fact a half power relationship:

$$O.I._{(Observed)} = K_{P} x C_{P}^{0.5} + (O.I.)_{o}$$
$$O.I._{(observed)} = K_{Br} x C_{Br}^{0.5} + (O.I.)_{o}$$

Where: K = A constant C = Concentration of the element $(O.I)_o = O.I.$ value for untreated polymer

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Using these equations, Weil postulated that if an additive effect were in operation and 1% phosphorus were used then the effect of this 1% P together with a certain amount of additive Br should have the same fire retardant effect as 16% Br, as stated by Lyons (Equation 2)

$$K_P(1)^{0.5} + K_{Br}(C_{Br})^{0.5} = K_{Br}(16)^{0.5}$$

Equation 2: Calculation of the amount of Br needed for an additive effect

By dividing this equation through by the constant K_{Br} and rearranging Weil came up with the following formula:

$$\frac{K_P}{K_{Br}} + (C_{Br})^{0.5} = 4$$

From the following equation Weil calculated K_P/K_{Br} to be 1.78. In this equation he assumes that 5% P has the same fire retardant effect as 16% Br.

$$\left(K_{P}(5)^{0.5} = K_{Br}(16)^{0.5}\right) \cong \left(\frac{K_{P}}{K_{Br}} = \frac{4}{2.24}\right)$$

smedeux ll'y d'he place de the campseule aufortations i protoches cano. Therefore $C_{Br} = (4 - 1.78)^2 = 4.9$. Weil's results, then, also indicated that there was some synergism because in practice

only 3% Br was needed rather than the calculated 4.9%. The extent of the synergism however, was not as great as Lyons reported.

Having now discussed the fundamentals of combustion and the ways in which it can be prevented, it is perhaps prudent to talk about the elements which confer flame retardancy onto a polymer and their modes of action.

Flame Retardant Elements and their Modes of Action 1.5.5

As has been previously mentioned there are seven elements that are frequently named in fire retardant formulations. These are Cl, Br, Al, B, N, P and Sb. Fire retardant formulations are not, however, limited to just these seven elements. There has also been a large amount of research into transition metal elements and their synergistic effects with other elements.

1.5.5.1 Chlorine and Bromine

These two elements are banded together as they impart flame retardancy in exactly the same way. In unsaturated polyesters alone there has been huge interest in halogenated fire retardants (96 - 114) of both the reactive and additive type. The

types of compounds that have been used are extremely diverse, ranging from modified cross-linking monomers (Fig. 13), modified glycols (Fig. 14) or modified anhydrides (Fig. 15) to purely additive compounds such as chlorinated paraffin waxes.

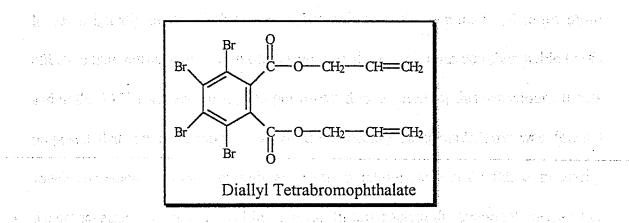


Fig. 13: Brominated cross-linking monomer (96) to allowed the trans

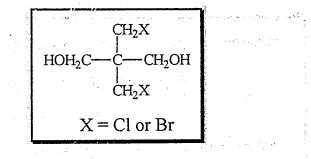


Fig. 14: Halogenated glycol: Dichloro- or Dibromoneopentyl glycol (97)

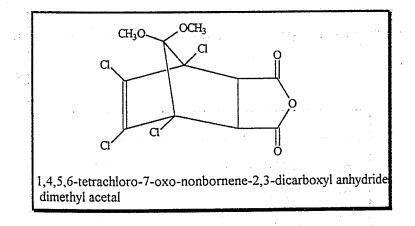


Fig. 15: Chemically modified anhydride (106)

A detailed review on the halogenated compounds that are used for flame retardation and their respective advantages and disadvantages could be carried out here. However, in the context of this thesis it is, perhaps, more important to discuss the modus operandi of halogenated fire retardants rather than to catalogue the ones that exist, as there is some controversy as to how they operate.

It was originally observed that certain bromohydrocarbons were 5 - 8 times more effective than nitrogen or CO_2 in rendering volatile gas mixtures non-flammable (115) and in the 1950's a mechanism was put forward to account for this behaviour. It was proposed that, upon decomposition of these bromo compounds, HBr was formed which competed with the free radical reactions taking place in the flame, primarily the propagation and chain branching stages. In this context the important reactions in the combustion of methane, as discussed earlier, are shown below:

propagation $CH_4 + OH \cdot - CH_3 \cdot + H_2O$ $CH_3 \cdot + O_2 \longrightarrow HCHO + OH \cdot$ $CO + OH \cdot \longrightarrow CO_2 + H \cdot$ $H \cdot + O_2 \longrightarrow OH \cdot + O \cdot cH$ chain branching

HBr, when present in the combustion zone, competes with these reactions in the following way:

All of these competitive reactions are less exothermic than the normal combustion reactions and so the amount of heat available, in the presence of HBr, to radiate back

to the polymer surface is reduced. This leads to a reduction in the decomposition rate of the polymer, a subsequent reduction in the burning rate and finally the extinction of the flame.

It was concluded by Butlin and Simmons (116) that the main HBr inhibiting stage is the removal of H radicals in the chain branching step, from the reaction zone. They went on to study the relative efficiencies of HBr, HI and HCl in this inhibition stage. This was carried out by comparing the rate of removal of the H radicals compared to the reverse reaction where the halide radical reacts with H_2 to form a hydrogen radical:

In the case of HBr and HI the probability of this reverse reaction taking place is extremely small. The effect of these halogens, then, is to inhibit the flame by removing H radicals from the reaction zone. In the case of HCl however it was found that there was an equal chance of either reaction occurring. The net effect is that HCl does not effectively remove H radicals from the reaction zone. It was, therefore, concluded that HCl acts as a diluent to the flame. These findings were confirmed by Petrella (117) who found that the bromine reacts with H₂ to form HBr and a H radical. This radical could then react either further with Br₂ or with O₂. Petrella found that significant amounts of HBr were formed and that the combustion of H₂ was delayed. The combustion reaction only took place after almost all of the Br₂ was consumed.

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Although this free radical trap mechanism is generally accepted as being the mechanism by which halogens operate, there is some evidence to show that they act in a purely physical way.

It has been found that the minimum weight of halogen required in the combustion zone, to prevent flame propagation, was 75 - 80% by weight of the sum of the weights of fuel and agent.

Larsen and Ludwig (118) argue that most halogen-containing polymers only contain 1 - 30% halogen. If all of the polymer was vaporised then there would not be enough halogen present to extinguish the flame. The authors go on to compare the Spalding Mass Transfer Number for various halogenated fuels (Table 4). The Spalding Mass Transfer Number, when applied to liquids, can be simplified to be the ratio of the heat of combustion per gram, ΔH_o J/g, to the heat of vaporisation per gram, ΔH_v J/g. This is essentially the ratio of the amount of heat given off on combustion per gram of fuel to the amount of heat needed for further vaporisation for 1 gram of fuel. The higher the figure the more flammable the fuel and vice versa.

Fuel	Halogen (% Wt)	Flash Pt. (°C)	Fire Pt. (°C)	ΔH _c J/g	ΔH _v J/g	$\Delta H_o/\Delta H_v$
C ₆ H ₆	0	13	~14	40 000	376	106
C ₆ H ₅ Cl	32	40	51	26 000	312	83
$C_6H_4Cl_2$	48	68	403	18 400	260	70
C ₆ H ₅ Br	51	52	154	~18 400	232	~80
C ₆ H ₃ Cl ₃	58.6	99	-	16 000	212	75

Table 4: Spalding Mass transfer Number for halogenated fuels.

It can be seen that as the halogen content of the fuels increase the ΔH_{e} value decreases markedly whereas the ΔH_{v} value is altered to a lesser extent. This has the effect of reducing the Spalding Mass Transfer Number dramatically showing that there is less energy available from the flames to facilitate further vaporisation from the surface of the fuel. Consequently more of the material needs to pyrolyse to sustain combustion or alternatively a further, external, heat source is needed. This work has some valid points but one major failure in the work is its assumption that all of the polymer vaporises to provide the halogen to the vapour phase. It is not necessarily true that the release of the halogen into the vapour phase coincides with total degradation of the polymer. It can be said that, in the early stages of pyrolysis, only dehydro-halogenation occurs which provides a total weight % of halogen in the vapour phase of around 75 - 80%.

Further studies into the mode of action of brominated fire retardants (119, 120) have shown that the introduction of HBr into the oxygen free zone surrounding polyethylene causes a significant reduction in the weight loss of the polymer. The reverse is true for polypropylene, where the rate of degradation was increased. Both of these will result in flame retardancy. The reduction in weight loss results in less flammable fuel being available in the vapour phase. The increase results in the flammable fuel being available at temperatures where no flammable mixture is present. All of this work into the action of halogens in flame retardancy has shown that there is no definite mode of action, with some flame retardant effects being seen in both the condensed and vapour phase. Chamberlain (121) tried to explain how this phenomenon could come about. He stated that "The bromine acts in the condensed phase to alter the fuel production by acting as a catalyst for condensed phase

degradation. The organic bromide decomposes at such a temperature and rate that the concentration of HBr in the vapour phase is very high just at the time when a flammable mixture of fuel and air is formed."

Iodo-compounds are effective free radical trapping agents in polymers (116) but their cost is prohibitive in their use as fire-retardant additives. Fluorine compounds have very stable C-F bonds which are resistant to oxidation. In this case, then, there would be no free radical trapping agents present in the vapour phase. The pyrolysis of fluoro - polymers has, however, been studied by Madorsky et al (122 - 123). The conclusion of these studies was that the degradation mechanism of fluoro - polymers was dominated by the loss of HF. This leads, depending on factors such as amount of fluorine and its position in the backbone, to chain-scission, the production of unsaturation and cross-linking. HF has no activity in the gas-phase.

Whatever the action of halogens in polymers, it is safe to say that the fire retardant effect of the halogen will only be effective as long as the hydrogen halide is formed along with the pyrolysis products.

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1.5.5.2 Phosphorus as a Flame Retardant.

As with halogenated fire-retardants there has been a great deal of research carried out into the action of phosphorus compounds as well as the formulation of new phosphorus based fire retardant compounds. Phosphorus compounds have been used to impart flame retardancy into unsaturated polyesters (124 - 129), polyurethane foams (130 - 132), phenolic resins (133), poly(methyl methacrylate) (134) and cellulosic materials (95, 135, 136). Again a full review of phosphorus containing compounds used as fire retardants could be undertaken but again this is of lesser importance than a full understanding of the mode of action of phosphoruscompounds, which is very reliant on the structure of the polymer. Unlike halogens, the generally accepted mechanism for phosphorus compounds is a condensed phase action. Phosphorus may be incorporated into the polymer either as an additive or as a reactive co-monomer. Reactive species have the effect of altering the pyrolytic fuel production stage. In all cases the presence of phosphorus in the polymer increases the char formation of the polymer on combustion.

In cellulosic materials the pyrolysis stage starts with the unzipping of the polymeric chain (137) to produce monomer units. These can then degrade in two ways, 1) via an epoxide to form levoglucosan and then to tar and volatile products or, 2) by dehydration and dehydrogenation to form a char. It is known that phosphorus compounds can form acidic compounds on combustion which accelerate the dehydration route to form char in cellulose (93). This occurs via esterification, thermal decomposition and the formation of an unsaturated backbone (115, 116) which leads to char formation.

Phosphorus fire retardants in polyurethane foams will be discussed in the phosphorusnitrogen synergism section as the phosphorus does not directly cause the fire retardant effect, rather it catalyses a degradation reaction which leads to char formation. In unsaturated polyester resins the fire retardant effect of the phosphorus compounds is the same as in cellulose with phosphorus acids or polyphosphates leading to an

increase in char formation.

Additive phosphorus compounds need to be matched to the decomposition temperature of the polymer. This has been referred to as the "right place at the right

time" theory (138). Fire retardants are often assessed by using thermogravimetry. This procedure compares the thermal degradation profile of the polymer to those of the fire retardants (Fig. 16). In this case fire retardants 1 and 2 are too volatile and they would vaporise from the polymer before a flammable mixture of fuel and air could be formed. Retardant 5, on the other hand, would only be effective at temperatures higher than the thermal degradation temperature of the polymer, by which time the polymer has already degraded and started combustion. Retardant 4 would be the most suitable fire retardant with 3 also being of limited use.

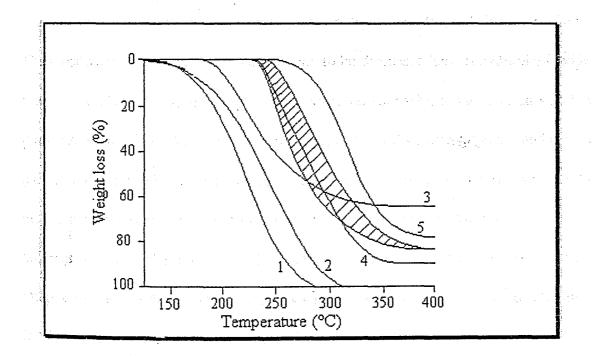


Fig. 16: Thermogravimetric curves for polymer (shaded area) and five potential fire retardants.

It has been further suggested that the use of two additives, with different volatilities, would be more effective. The use of one additive which decomposes at about 60 -

75°C before the polymer would ensure a high concentration of fire retardant in the vapour phase at the same time as a flammable fuel/air mixture was produced. A second additive could, then, be used which did not decompose until a large amount of the polymer had degraded. Using this method there would be effective fire retardancy over the complete thermal degradation range of the polymer.

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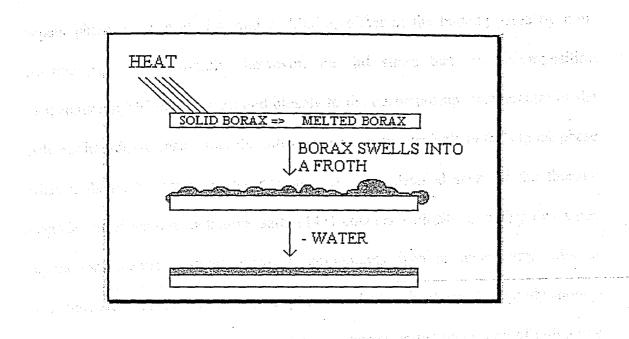
1.5.5.3 Aluminium Flame Retardants

Aluminium flame retardants are actually the most commonly used flame retardants. The most common of these, and the only one to be discussed here, is aluminium oxide trihydrate (ATH) (Al₂O₃,3H₂O). This is a white powder which is used as an additive flame retardant. It operates in two main ways, one in the condensed phase and one in the vapour phase (82). In the condensed phase it acts primarily as a heat sink. This means that it absorbs heat and conducts it away from a concentrated area on the polymer surface. There is, then, less heat to cause degradation of the polymer. Despite this action there comes a stage where the ATH reaches its thermal saturation level and no more heat can be removed from the polymer surface. This is when thermal degradation of the polymer starts. At temperatures of around 200 - 250°C, however, the ATH releases its water into the vapour phase. As ATH is often used in quantities as high as 100phr or more and its water content is 35%, a large amount of water is released into the vapour phase. This has the effect of diluting the flame and also reducing the amount of heat radiating back to the surface of the polymer thus inhibiting further degradation. This causes flame extinction.

1.5.5.4 Boron Flame Retardants

Although boron is used as a flame retardant additive in polymers, it has never really enjoyed the same amount of use and study as elements such as phosphorus or the halogens. Due to this the mode of action of boron will only be discussed briefly. Boron usually operates in one of three ways depending on the boron compound used. When borate esters are used in a polymer, such as cellulose, they produce acidic compounds which accelerate the dehydration process in the polymer leading to char formation. This is similar to the mode of action that is seen with phosphorus compounds in these polymers.

The use of borax $(Na_2B_4O_7.10H_2O)$ highlights the other two modes of action seen with boron compounds (82). The solid borax additive in the polymer melts when heat is applied to the polymer surface. This molten borax then rapidly swells to form a froth on the surface of the polymer. Subsequent dehydration of this froth causes a thermally stable glassy layer to be formed on the polymer surface (Fig. 17). This glassy layer prevents oxygen from reaching the polymer and so prevents the combustion process from taking place. This layer is also heat resistant so less heat can reach the polymer surface. This leads to a reduction in the degradation rate of the polymer and so less fuel is available for combustion. The water lost from the borax is released into the vapour phase where it has the same effect as the water released from ATH, as described earlier.



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Fig. 17: Fire retardant activity of borax.

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1.5.5.5 Nitrogen Flame Retardants

Fire retardants that are based on nitrogen alone are relatively rare but are gaining in popularity. The reason for this increase in popularity of nitrogen fire retardants is that considerations such as smoke and the evolution of toxic and corrosive materials is now being considered along with the fire retardant properties of the element. Usually nitrogen is used in conjunction with phosphorus to produce a synergistic effect. Most nitrogen fire retardants are based around triazines and melamine and its derivatives (139 - 147). The mode of action of fire retardant nitrogen compounds varies greatly depending on the type of compound used and the structure of the polymer matrix. Stern (142) reported that melamine cyanurate (MC) degrades at temperatures of around 410°C to produce non-flammable and non-toxic gases such as nitrogen. He postulated that the effect of this was very much the same as having water in the

vapour phase, i.e. a heat sink and a diluting effect of the burning gases by nonreactive gases. Importantly, however, he did stress that the decomposition temperature of MC must correspond closely to the decomposition temperature of the polymer in order to ensure that the nitrogen gases were available in the vapour phase when a flammable mixture was present. A more detailed study of the thermal degradation of various melamine salts (143) concurs with Stern, in that this study agrees that thermally stable nitrogen compounds such as ammonium salts or melamine are released into the vapour phase to blanket the flame. This study showed that the condensed phase action of melamine centres on the production of polymeric products named "melam", "melem" and "melon" (Fig. 18). It was found that melamine mostly evaporated above 250°C but did leave a small amount of residue (ca. 7%). This residue was analysed at various temperatures and was found to consist of melam to about 300°C, melem to about 450°C and melon to 600°C. The evaporated melamine has a blanketing effect on the flame in the vapour phase.

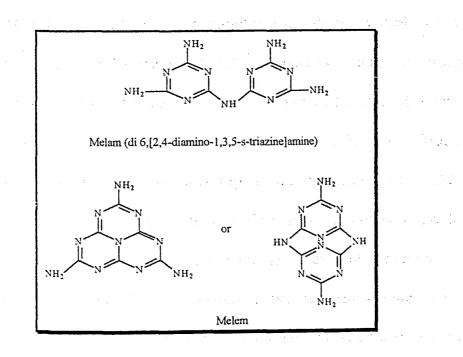


Fig. 18: Structures of Melam and Melem.

When melamine is used in polymers as a salt its decomposition process is changed. Essentially, however, the release of non-volatile melamine into the vapour phase and the formation of the melon char at high temperatures stays the same. It is, merely, the route by which this is achieved that changes.

It has been shown with dimelamine cyanurate that between 250 and 350°C one molecule of melamine is lost leaving melamine cyanurate. Above 360°C (its melting point) 90% of this was volatilised to form free melamine and eventually, via dissociation, cyanuric acid. The cyanuric acid later decomposed to cyanic acid which acts in the vapour phase. At 450°C it was found that the residual char was similar to melon, which normally only occurs with melamine at temperatures above 500°C. It was proposed that the cyanuric acid catalysed the condensation of melamine to form melon. The efficiency of this is limited by the decomposition of cyanuric acid to cyanic acid. Upon heating to 650°C the char totally decomposed to form volatile products such as HCN, $(CN)_2$ and NH₂CN.

If, on the other hand, an additive were required that was thermally stable to very high temperatures, it was found that the use of melamine borates would be of considerably advantage. It was found that melamine borate decomposed in three distinct stages. Firstly at around 130 - 270°C the borate dehydrates to form boric anhydride (B_2O_3) and melamine, with the release of water vapour into the vapour phase. At higher temperatures (270 - 350°) the melamine itself decomposes as normal to produce the melam condensate and boric anhydride, with the release of melamine into the combustion zone. The degradation procedure above these temperatures is not fully understood but it is thought that melamine is further condensed and lost from the

residue. It is also thought that extremely stable polyamino-borazines may be produced. These are stable to temperatures of about 1100°C.

As has been shown, by understanding the thermal degradation mechanism of various salts, it is possible to tailor the fire retardant to the polymer.

Now that the fire retardant elements have been discussed individually it is time to consider the synergistic interactions displayed by these elements when used together.

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1.5.5.6 Antimony - Halogen synergism

Antimony is used in the trioxide form (Sb_2O_3) but has no fire retardant effects when used alone. Pitts (148) found that when antimony trioxide is added to halogenated polymers the fire retardant properties are greatly improved.

War-time research found that the optimum mole ratio of Sb:Cl to impart the most effective fire retardant effect was 1:1. The explanation for this was that the HCl evolved reacted with the antimony oxide to produce SbOCl (149). The presence of this oxychloride was later concurred by other authors (150 - 152). Fenimore and Jones were the first to study where antimony - halogen systems operated (153). They found that antimony - halogen systems were only effective in oxygen-containing flames. They then concluded that this system must act as a flame poisoner which was specific to reactions with oxygen. They also found that 75% of the antimony was lost from the polymer. As antimony trioxide is thermally stable they concluded that a volatile antimony - halogen compound was formed. Several authors have noted the efficiency of a Sb:Cl ratio of 1:3 as opposed to the previously noted 1:1 (154 - 156). This was suggested to be SbCl₃. It was found that the amount of chlorine volatilised

from the polymer compared to the amount of antimony was 1 mole of Sb_2O_3 to 6 moles HCl. The reaction of Sb_2O_3 with HCl is very complex but can be summarised as shown below.

$$Sb_2O_3 + 6HCl \rightarrow 2SbCl_3 + 3H_2O$$

Despite the fact that the antimony - halogen species that imparts flame retardancy into the polymers had been elucidated, the actual mechanism by which they poison the flame has not. Several theories have been put forward (148):

- 1. Trivalent antimony facilitates the generation of halogen radicals which
 - interfere with the normal free radical reactions in flame propagation.
- 2. SbOCl and SbCl₃ delay the rate of escape of halogen free radicals from the flame, thus increasing the chance of a reactant free radical reacting with the halogen.
- 3. Volatile SbCl₃ blankets the flame.
- 4. SbCl₃ and SbOCl act as dehydrating agents to promote char formation.

Pitts (148) found that the following reactions took place when a polymer containing antimony and chlorine degraded:

$$\begin{array}{c}
\begin{array}{c}
245^{\circ}\text{C} - 280^{\circ}\text{C} \\
5 \text{ SbOCl}_{(\text{S})} & & \text{Sb}_{4}\text{O}_{5}\text{Cl}_{(\text{S})} + \text{ SbCl}_{3} \\
4 \text{ Sb}_{4}\text{O}_{5}\text{Cl}_{(\text{S})} & & \frac{410 - 475^{\circ}\text{C}}{5} \\
5 \text{ Sb}_{3}\text{O}_{4}\text{Cl}_{(\text{S})} & & \frac{410 - 475^{\circ}\text{C}}{5} \\
3 \text{ Sb}_{3}\text{O}_{4}\text{Cl}_{(\text{S})} & & \frac{475 - 565^{\circ}\text{C}}{5} \\
4 \text{ Sb}_{2}\text{O}_{3}_{(\text{S})} & & \frac{475 - 565^{\circ}\text{C}}{5} \\
8 \text{ Sb}_{2}\text{O}_{3}_{(\text{S})} & & \frac{658^{\circ}\text{C}}{5} \\
\end{array}$$

: 44

He concluded that the formation of SbCl₃ resulted from the thermal degradation of SbOCl. Hastie (157) went on to study the reaction that took place between SbCl₃ and the reactive free radicals in the combustion zone. Some of these reactions are shown below to highlight the number of interactions that take place, in this system, to inhibit the flame (Fig. 19). These studies concluded that the antimony halides did indeed inhibit the free radical combustion reactions that took place in the combustion zone. Hastie also found that the HX species was dominant at cooler temperatures where no flammable fuel/air mixture was present and that the SbO species was prevalent in the reaction zone. He therefore stated that the fire retardant action of antimony halides occurred in two stages. Firstly the HX species reacts with reactive free radicals before combustion takes place and then the more stable SbO species takes over to catalyse hydrogen recombination in the reaction zone.

	· · · ·				1.11		
SbX	3 + H•	>	ΗХ	+	SbX_2		
SbX	3	→	Х•	+	SbX ₂	-	
SbX3	+ CH3•	>	CH₃X	+	SbX_2		
SbX ₂	+ H•	>	HX	+	SbX		•
SbX ₂	+ CH3•	>	CH3X	+	SbX		
SbX	+ H•.	>	HX	÷	Sb		1
SbX	+ CH3•	>	CH3X	÷	Sb		
$Sb + O^{**}$	+ M	>	SbO	+	М		
Sb + OH•	+ M	>	SbOH	+	М	ŀ	
SbOH	+ H•		SbO	+	H ₂		, ,
SbO	+ H•	>	SbOH*	•		Į,	
	+ H ₂ O	>	SbO	+	H ₂		
X• + X•	+ M	>	X_2	+	М		
X2	+ CH3•	>	CH ₃ X	+	X• .		÷.
M + X•	+ CH3•	>	CH3X	+	M		i.
	+ CH3*	· · · · · · · · · · · · · · · · · · ·	CH4	+	X•	. * Marya"	• •
	+ H•	>	H ₂				
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Fig. 19: Flame inhibiting reactions involving SbCl₃

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1.5.5.7 Phosphorus - Halogen Synergism

The use of phosphorus and halogens together is a very popular method of incorporating fire retardancy into a polymer because, even if no synergism occurred, there would be the condensed phase action of the phosphorus being used in conjunction with the vapour phase action of the halogens. This system has, therefore, been extensively used in polymers (158 - 160). The presence of a synergistic interaction between these two elements, however, is an area of dispute with some authors proposing a synergistic interaction and some opposing this interaction. Hindersinn (161) carried out research into the effect of phosphorus and halogens in unsaturated polyesters. He determined the burning times for %C1 vs P content of the resin and vice versa. He then combined the results from these two studies to derive a graph showing the %C1 and %P required for a given burning rate assuming additivity of the two elements (Fig. 20)

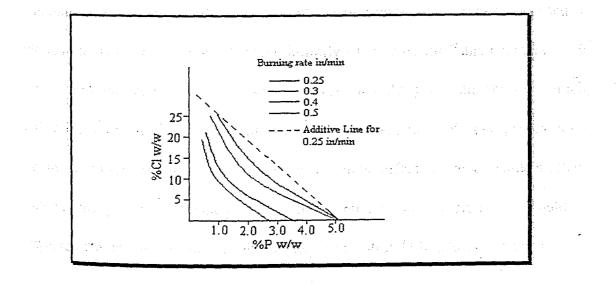


Fig. 20: Amounts of Cl and P needed to give a specified burning rate compared to additive amounts needed.

Hindersinn concluded that, as the deviations from the additive line were negative, some synergism was taking place in this system.

Weil criticised these results on several grounds. Firstly, he stated no intercept values were given for the amount of Cl needed at 0% P. From the graph it appeared that, for each burning rate, the amount of Cl needed at 0% P was around 26 - 27%. Weil concluded that this would mean that the burning rate was not a function of the amount of chlorine which was not true. Hindersinn also stated that the burning rate for the polymer containing 26.3% Cl and no P was 0.19 in/min. If this were true then for a longer burning time with no P, considerably less Cl would be needed, pushing the intercept at 0% P below the shown 26 - 27%.

A study by Piechota (131) on rigid polyurethane foams containing phosphorus and chlorine or bromine showed no synergism. In this study Piechota observed a peak flame retardant effect, for phosphorus, at 1.5% weight of phosphorus. He also found that, for the halogens alone, there was a decrease in fire retardant effect as the amounts of the halogens increased. The interesting part of the study came when he plotted the optimum amounts of P and, initially, Br needed for flame retardancy. He found that the graph obtained was an exceptionally good straight line graph, indicating an additive fire retardant effect. In this case the 1.5% phosphorus is the optimum amount of phosphorus needed for the most effective flame retardant effect, without the presence of halogens. If the elements were synergistic it would be expected that the graph would deviate away from a straight line to a concave line

bending towards the axes. It was concluded that, as the graph was a straight line, the two elements acted additively rather than synergistically. Despite these arguments against synergism there have still been theories put forward to explain how a synergistic phenomenon occurs.

One theory put forward is that phosphorus halides and oxychlorides are produced which are free radical scavengers. These were thought to be more effective than hydrogen halides because of their increased vapour densities which cause these halides to stay in the combustion zone longer than the less dense hydrogen halides (162). This theory gains credence when one considers that phosphorus oxychlorides have been shown to exert a flame quenching effect when introduced directly into a flame (163, 164). However, there has been no evidence that such reactions actually take place in phosphorus - halogen systems.

1.5.5.8 Phosphorus - Nitrogen Synergism

The use of phosphorus - nitrogen containing additives for flame retardancy has been extensively reported in the literature (165 - 176). Mechanistic studies of P-N interactions have shown that a condensed phase mode of action is predominant in most polymers. The mode of action, however, is different depending on the polymer matrix. It was discovered by Patil et al (177) that the presence of monohydrazinium phosphate caused cellulose to degrade at below 300°C. At these low temperatures very little levoglucosan is produced and so less fuel would be available for combustion. This additive also had the effect of reducing depolymerisation and promoting dehydration resulting in the formation of char and water. It was found in

most polymers that more char was formed when phosphorus and nitrogen were used in conjunction.

The mechanism for nitrogen-phosphorus synergism in cellulose has been documented (178). It was proposed that compounds such as phosphoramides containing 2° amine groups (Fig. 21) cause the synergistic effect to take place.

 $\sum_{i=1}^{n} \frac{\sum_{i=1}^{n} \sum_{j=1}^{n} \sum_{i=1}^{n} \sum_{j=1}^{n} \sum_{j=1}^{n} \sum_{j=1}^{n} \sum_{i=1}^{n} \sum_$

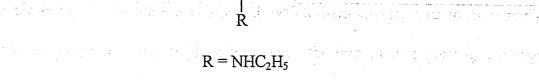


Fig. 21: General structure of phosphoramides used for N-P synergism in cellulose

The 2° amine containing compounds can easily lose an amine group upon pyrolysis leaving a reactive P=N bond which can then attack the hydroxyl group on the cellulose molecule to bond the phosphorus to the cellulose itself. Repetition of this results in the phosphorus being chemically bound onto the cellulose backbone (Fig. 22). Less phosphorus is then lost during the burning process due to volatilisation. The effect of this is that less phosphorus additive is needed to produce the same fire retardant effect as when the phosphorus is not bound to the cellulose chain.

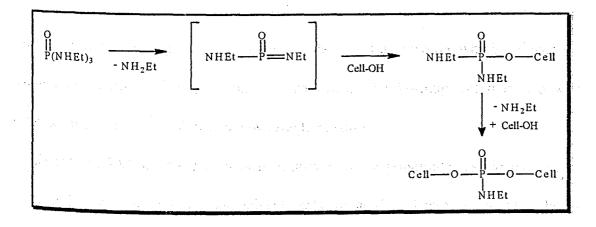
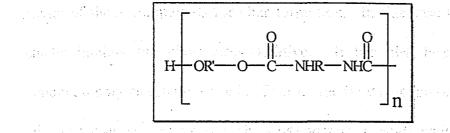


Fig. 22: Schematic representation of proposed P-N synergism in cellulose.

The synergistic effect in polyurethanes, however, is different from that postulated in cellulose (82). Polyurethanes are nitrogen containing polymers of general formula:



Upon thermal degradation of this polymer isocyanate (RNCO) groups are produced. In the presence of a phosphorus compound, which thermally degrades to form acidic phosphorus compounds such as phosphoric acid, the formation of isocyanurate rings from the isocyanate groups is catalysed (Fig. 23).

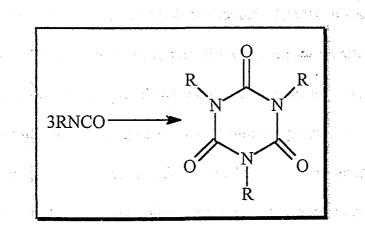


Fig. 23: Formation of isocyanurate rings from isocyanate groups catalysed by acidic phosphorus compounds.

These isocyanurate rings cause charring of the burning polymer which reduces the amount of volatile decomposition products from the burning polymer and also insulates the rest of the polymer against the heat source.

In the case of PMMA the phosphorus additives, as in polyurethanes, decompose to give acidic compounds such as poly(phosphoric acid). These acidic phosphorus compounds cause char and CO_2 formation in the burning polymer which leads to

flame extinction (134). In most cases the presence of relatively basic nitrogen compounds reduces the acidity of the phosphorus compounds and so lessens the activity of these compounds for char formation. In this case the nitrogen additive actually inhibits the phosphorus additive. It has also been shown that when ammonium polyphosphate is used in PMMA the only reaction of the organic polymer under pyrolysis conditions is with poly(phosphoric acid) which is the breakdown product of the ammonium salt. The nitrogen plays no part.

In the case of polyacrylamide (PAM), a nitrogen-containing polymer, it has been found that there is a large amount of synergism in the presence of phosphorus compounds (179). In this study diethyl vinyl phosphonate was copolymersised into several polymers including PMMA and polyacrylonitrile (PAN). It was found that the incorporation of 5.6% w/w phosphorus into PAN caused an increase in O.I. value from 0.18 to 0.275. In the case of PAM, however, this increase was much greater with slightly less phosphorus being incorporated into the polymer (5.3% phosphorus gave an increase in O.I. from 0.273 to 0.579). It was proposed that the copolymerisation reaction taking place between the amide groups and the phosphonate groups (Fig. 24) led to a high degree of crosslinking between the polymer chains. This leads to a higher degree of thermal stability during the earlier stages of combustion and so a lower rate of degradation.

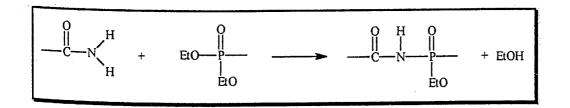


Fig. 24: Reaction between amide groups and phosphonate groups.

1.5.5.9 Other Elements

The majority of elements that have been used in addition to the above mentioned elements are metals in the form of compounds with valency states such as Cr(III), Fe(III), Co(II), Ni(II), Cu(II), Zn(II), Mo(III), Mg and Sn(IV). These metals have been used to impart flame retardancy as well as reduce smoke in burning polymers and have been shown to work in numerous different ways. It is, however, well known that these metals are not effective fire retardants in their own right and rely on the presence of halogens.

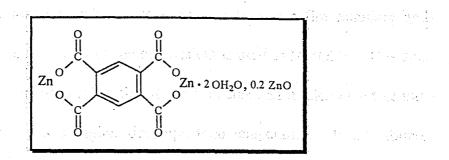
It has been shown (180 - 183) that the oxides of metals such as Mo, Cu and Fe act as fire retardants in halogen-containing polymers. Besides giving fire retardation, they give more efficient smoke suppression than the antimony oxide - halogen system. The mechanism by which these additives operated was assumed to be the same as the antimony system, although some evidence does suggest that these metals actually act in the condensed phase rather than the vapour phase.

Brauman carried out work on the use of zinc pyromellitates (Fig. 25) and their use as fire retardants in halogenated polymers (184, 185). She found that, in PVC and poly(bromostyrene), the zinc pyromellitate promoted the formation of char at the expense of flammable fuel production. In PVC she postulated that the zinc formed $ZnCl_2$ which promoted dehydrochlorination of the PVC and cross-linking of the resultant unsaturated polymer chain.

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Fig. 25: Zinc Pyromellitate flame retardant additive

In poly(bromostyrene), however, she found that the metal portion of the additive retarded the polymer degradation rate by possibly complexing with the bromine substituent on the polymer. The organic portion of the additive promoted crosslinking and fragmentation of the degrading polymer. It was thought that the cross-linking process was brought about by the organic portion degrading to form phenyl and acyl radicals.

The use of anhydrous and hydrous tin (IV) oxide has been studied by Cusack(186). He found that the hydrous form was a much more effective flame retardant and smoke suppressant than the anhydrous form. He did, however, concede that neither additive worked in the absence of halogens. The reason, he stated, for the improved effectiveness of the hydrated oxide was that it released water into the vapour phase which the anhydrous form could not. He suggested that the mechanism for the flame retardant action of anhydrous tin(IV) oxide with halogens was a two-phase system, with the tin oxide reducing smoke production by promoting cross-linking in the condensed phase with the halogen working in the vapour phase. It has, however, been suggested that, when the hydrated form of tin oxide with bromine is used and the ratio of Br:Sn is above stoichiometric, large amounts of tin(IV) bromide are volatilised into the vapour phase to act as a free radical scavenger.

Magnesium is another metal which has received attention as a fire retardant and smoke suppressant (187). In this case the magnesium is used as $Mg(OH)_2$. This acts in very much the same way as ATH in that it is a heat sink and it releases water into the vapour phase, but it has a higher decomposition temperature. It was found, however, that this additive was not as effective as ATH. The reason given for this was the large amount of research into optimising ATH for use in polymers whereas very little work has been carried out on magnesium hydroxide.

Having taken into account all of the main elements and modes of action used for imparting fire retardant properties into polymers, it was decided to undertake an investigation into the uses of substituted triazine rings as potential reactive fire retardants and smoke suppressants.

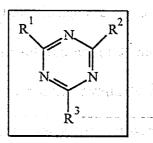
1.6 1,3,5 - s - Triazines

1.6.1 Synthesis of s-Triazines

The 1,3,5 - triazines are amongst the oldest known organic compounds. Originally they were called symmetrical triazines or s-triazines. As these compounds have been around for so long there is still a tendency to use non-standard names for some of the most common s-triazines. These include melamine, cyanuric chloride, cyanuric acid, ammeline, ammelide and acetoguanamine (Fig. 26).

The first 1,3,5-triazine was synthesised in 1895 by Nef (188) by treating hydrogen cyanide with ethanol in an ether solution saturated with hydrogen chloride. The resultant salt was treated with base to yield an imidate which formed 1,3,5-triazine on distillation (Fig. 27). Today the 1,3,5-triazines are very important synthetic

intermediates because they are very reactive. Of their derivatives cyanuric chloride is, perhaps, the most important as it is the major starting material for other 1,3,5triazine derivatives. In fact the majority of 1,3,5-triazine based herbicides are synthesised from cyanuric chloride.



Common Name	$\mathbb{R}^{\mathbf{I}_{A} + \cdots + \mathbf{I}_{A}}$	\mathbb{R}^2	\mathbb{R}^3	
Cyanuric chloride	nd Clar and Clark	Cl · · · ·	Cl	
Cyanuric acid	OH	OH	OH	
Melamine	NH ₂	NH ₂	NH ₂	
Ammeline	OH	NH ₂	NH ₂	
Ammelide	OH	ОН	NH ₂	
Acetoguanamine	Me	NH ₂	NH ₂	

Fig. 26: Structures and names of common s-triazines

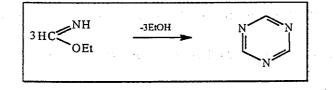


Fig. 27: First synthetic route to 1,3,5-triazine

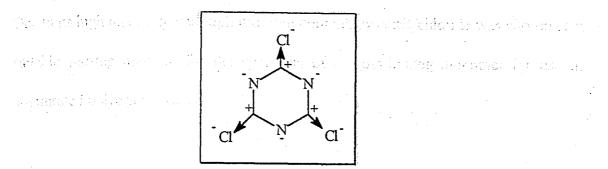
s-Triazines have also been extensively used in modifying polymers. These modifications have centred around three major areas of use: imparting inherent

thermal stability into polyurethanes, epoxides and poly(olefins) (189 - 192); antioxidants in electronic insulators (193 - 196) and finally as dyes and bleaching agents in poly(acrylonitrile) fibres (197 - 199).

Although s-triazines have been extensively used in polymers it appears that very little use has been made of their high nitrogen content and potential char promoting properties, to impart reactive fire retardancy and smoke suppression into polymeric systems. As cyanuric chloride is readily available and known to be an important intermediate for many 1,3,5-triazine derivatives, it was decided to use it as the starting material for the synthesis of a potential reactive, fire-retardant, reduced volatility monomer for use as a cross-linking monomer for unsaturated polyester resins.

1.6.2 Cyanuric chloride

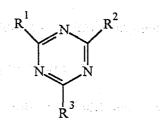
Cyanuric chloride is extremely sensitive to nucleophilic attack and the chlorine atoms can be sequentially replaced by a nucleophile. The reason for this openness to nucleophilic attack lies with the lack of electron delocalisation in this system (200). In an un-substituted 1,3,5-triazine the delocalised electron cloud, which is normally seen in aromatic systems, is substantially localised onto the nitrogen atoms. This reduces the delocalised electron cloud to about one tenth of that found in benzene. Obviously the presence of strongly electron withdrawing groups reduces the electron delocalisation more. This results in polarisation of the molecule so that the carbon atoms are electron deficient making them extremely susceptible to nucleophilic attack. (Fig. 28). Obviously, then, if an electron-donating group were used as a substituent the π -electron cloud is extended making the positive character of the carbon atom less pronounced and so reducing its susceptibility to nucleophilic attack.



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Fig. 28: Charge delocalisation in cyanuric chloride

The high reactivity of cyanuric chloride to nucleophilic attack is demostrated by the reactions and conditions for the displacement of chlorine in cyanuric chloride as shown in table 5. It is observed that sequential removal of the chlorine atoms can be achieved by a relatively small change in the severity of the reaction conditions.



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	Triazine Product			
R ¹	R ²	R ³	Conditions	Temperature (°C)
RO	Cl	Cl	ROH, NaHCO ₃	30
RO	RO	Cl	ROH, NaHCO ₃	65
RO	RO	RO	ROH, NaOH	25-30
R ₂ N	Cl	Cl	R ₂ NH, H ₂ O	0
R ₂ N	R ₂ N	C1	R ₂ NH, H ₂ O	30-50
R_2N	R ₂ N	R_2N	R ₂ NH, H ₂ O	90-100
$(RO)_2P=O$	$(RO)_2P=O$	(RO) ₂ P=O	P(OR) ₃	60

Table 5: Some typical reactions of cyanuric chloride

Due to its high reactivity and high nitrogen content, cyanuric chloride was chosen as a suitable starting material for the synthesis of a cross-linking monomer for use in unsaturated polyester resins.

1.7 Aim of project

The aim of this project was to synthesise a reactive cross-linking monomer for use in unsaturated polyesters using cyanuric chloride as a starting material. The prerequisites for this monomer were that it:

- 1) Had a high nitrogen content to try and suppress smoke evolution from
- to define the burning polymer. The trade base of beyond the set as a sign of
- 2) Contained no halogens as these cause corrosive and toxic gases to be released from the burning polymer.
- 3) Had a low volatility to reduce the volatile organic content of the polyester and so reduce emissions of organic vapours.
- 4) Had sites of reactive unsaturation to facilitate cross-linking with the polyester.
- 5) Reacted sufficiently well with the unsaturation in the polyester back-bone to give good mechanical and physical properties to the cured resin.

2.0 Experimental

2.1 Terms of Reference

MEKP = Methyl ethyl ketone peroxide free radical initiator (33% w/w) phthalate plasticiser

BPO = Benzoyl peroxide free radical initiator (50% w/w) in phthalate paste

DCPO = Dicumyl peroxide free radical initiator (99% w/w)

AZBN = 2,2'-Azobisisobutyronitrile free radical initiator (99% w/w)

CN = Cobalt naphthenate cure catalyst (1% w/w) in styrene

DMA = Dimethyl aniline tertiary amine cure catalyst (99% w/w)

DMMP or D (in tables) = Dimethylmethyl phosphonate fire retardant additive

TEP or T' (in tables) = Triethyl phosphate fire retardant additive

ATH or A' (in tables) = Aluminium trihydrate fire retardant additive

TCEP or C (in tables) = Trichloroethyl phosphate fire retardant additive

T*PP (in tables) = Triphenyl phosphate fire retardant additive

M (in tables) = Melamine fire retardant additive

S (in tables) = Styrene monomer used for cross-linking

- A (in tables) = Aliphatic alkyd (adipic acid, maleic anhydride and diethylene glycol) used
- N (in tables) = Aromatic/normal alkyd (maleic anhydride, phthalic anhydride and propylene glycol) used

T (in tables) = Triazine monomer used for cross-linking

F (in tables) = Fire testing carried out

phr = parts per hundred parts

2.2 Synthesis program Several synthetic routes were considered to try and produce a thermosetting polymer with a high s-triazine content. The entire synthesis scheme can be seen in Appendix A as Figures A1 and A2.

2.2.1 Synthesis of 2,4-dichloro-6-diethylamino-s-triazine (Fig. 2.1)

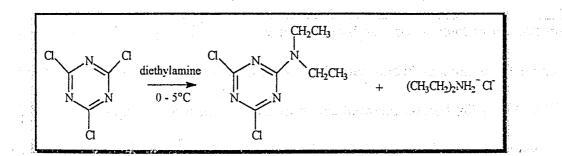
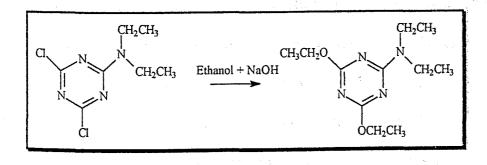


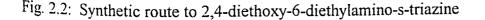
Fig.2.1: Synthetic route to 2,4-dichloro-6-diethylamino-s-triazine

This synthesis was previously documented in the literature (201) and proven to be successful.

A round bottomed flask (21) was placed into an ice bath and fitted with a stirrer, stirrer motor and thermometer. Water (600ml) was added to the flask, the stirrer started and the water was cooled to below 5°C. During this cooling period cyanuric chloride (183g, 1 mole) was dissolved in acetone (400ml). This hot acetone/cyanuric chloride mixture was rapidly poured into the cold water. The reason for this was to create a very fine suspension of the cyanuric chloride in the water in order to increase the effectiveness of the reaction. The solution was then again cooled to below 5°C. Diethylamine (146g, 2 moles) was added dropwise to the cyanuric chloride solution. It was vital that the reaction temperature never exceeded 5°C during this process to prevent di- or tri-substitution of the triazine ring. As the reaction is very exothermic this addition process was very time consuming. After the addition of the diethylamine to the solution, the reaction was allowed to proceed for another hour at $0 - 5^{\circ}$ C before being stopped. At the end of the reaction the contents of the flask were filtered using a Buchner funnel. The solid residue was then thoroughly washed with distilled water until these washings were clear. This washing process removed the water soluble (CH₃CH₂)₂NH₂⁺Cl⁻ that was produced as a by-product in the reaction. The solid was re-crystallised from toluene and dried under vacuum for 2 hours at 65°C. The average % yield for the reaction was between 80 and 90%. ¹H and ¹³C NMR and Mass spectra were taken of the product. The spectra for these are shown in Appendix B as Figures B1 (¹³C NMR), B2 (¹H NMR) and B3 (Mass Spectrum). ¹³C chemical shifts: 170ppm (aromatic C-Cl); 163ppm (aromatic C-amine), 42ppm (CH₂), 12ppm (CH₃). ¹H chemical shifts: 3.8ppm (CH₂), 1.2ppm (CH₃).

2.2.2 Synthesis of 2,4-diethoxy-6-diethylamino-s-triazine (Fig 2.2)





This reaction was also documented in the literature (202).

A round bottomed flask (21) was placed into an electric heating mantle and fitted with a stirrer, stirrer motor and a thermometer. Ethanol (99%, 900ml) was poured into the flask and to this crushed sodium hydroxide pellets (80g, 2 mole) were added. The sodium hydroxide was allowed to dissolve in the ethanol under stirring. The temperature of this solution was then raised to 32°C. Upon reaching this temperature the 2.4-dichloro-6-diethylamino-s-triazine (221g, 1 mole) was slowly added to the solution. Care was taken to prevent the temperature of the reaction from exceeding 40°C during the addition process. Again due to the exothermic nature of this reaction the addition of the reagents took a long period of time. After the s-triazine has been added the reaction was kept at between 30 and 40°C for half an hour after which the temperature was raised to between 60 and 75°C. This temperature was maintained for a further 3 hours. At the end of the reaction the contents of the flask were filtered - A. S. through a hot Buchner funnel to remove the NaCl by-product. The filtrate was then placed into a rotary evaporator where the excess ethanol was removed. After the ethanol had been evaporated off the warm contents of the flask were poured into a beaker. This was because the product was a solid at room temperature and as such would be difficult to remove from the evaporation flask. The product was recrystallised from toluene and dried under vacuum for several hours at room temperature. The average yield for this reaction was 85 - 90%. ¹H, ¹³C NMR and mass spectra were taken of the product. These can be seen in Appendix B as Figures B4 (¹³C NMR), B5 (¹H NMR) and B6 (Mass spectrum) ¹³C chemical shifts: 169ppm (aromatic C-O), 163ppm (aromatic C-amine), 65ppm (O-CH₂), 45ppm (N-CH₂), ¹⁶ppm (alkoxy CH₃), ¹⁴ppm (amine CH₃). ¹H chemical shifts: ⁴.1ppm (alkoxy CH_2), 3.3 (amine CH_2), 1.1ppm (alkoxy CH_3), 0.9ppm (amine CH_3).

2.2.3 Transesterification of 2,4-dimethoxy-6-diethylamino-s-triazine with a glycol (Fig. 2:3)

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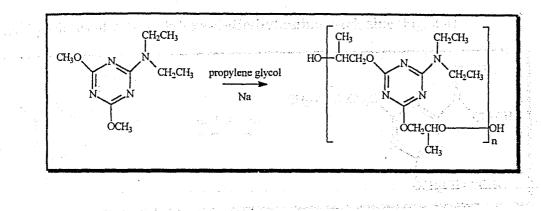
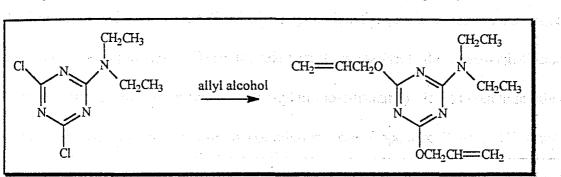


Fig. 2.3: Transesterification reaction to produce s-triazine oligomer.

This general synthetic procedure was detailed in literature to be viable (203).

A three necked round bottomed flask (250ml) was set up with a thermometer and a distillation head. A condenser was connected to the distillation head. A side arm was then connected to the condenser, to which another round bottomed flask (100ml) was connected. Diethylene or propylene glycol (0.062 mole) was poured into the 250ml round bottomed flask and Na metal (2.1 x 10^{-3} mole) was dissolved in the glycol. After the Na had dissolved the triazine (10g, 0.042 mole) was added. The reaction mixture was then heated to 140 - 155°C. The reaction proceeded for 1.5 hours with diethylene glycol and 4.5 hours with propylene glycol. The endpoint was judged to be when no more ethanol distilled off from the reaction. The two oligomers obtained were very different in appearance: a dark brown tacky gum from diethylene glycol and a clear viscous syrup from propylene glycol. ¹³C NMR was carried out on the product from diethylene glycol. This spectrum can be seen in Appendix B (Fig. B7).

Most important ¹³C chemical shifts: 174ppm (aromatic C-O (methoxy group), 172ppm (aromatic C-O (glycol) 168ppm (aromatic C-amine).



2.2.4 Synthesis of 2,4-diallyloxy-6-diethylamino-s-triazine (Fig. 2.4)

Fig. 2.4: Synthesis of 2,4-diallyloxy-6-diethylamino-s-triazine

The reaction was also documented in the literature (202).

A round bottomed flask (21) was placed into an electric heating mantle and fitted with a stirrer, stirrer motor and a thermometer. Allyl alcohol (99%, 900ml) was poured into the flask and to this crushed sodium hydroxide pellets (80g, 2 mole) were added. The sodium hydroxide was allowed to dissolve in the allyl alcohol under stirring. The temperature of this solution was then raised to 32°C. Upon reaching this temperature the 2,4-dichloro-6-diethylamino-s-triazine (221g, 1 mole) was slowly added to the solution. Care was taken to prevent the temperature of the reaction from exceeding 40°C during the addition process. Again due to the exothermic nature of this reaction the addition of the reagents took a long period of time. After the s-triazine has been added the reaction was kept at between 30 and 40°C for half an hour after which the temperature was raised to between 60 and 75°C. This temperature was maintained for a further 3 hours. At the end of the reaction the contents of the flask were filtered through a hot Buchner funnel to remove the NaCl by-product. The filtrate was then placed into a rotary evaporator where the excess allyl alcohol was removed. After the allyl alcohol had been evaporated off the warm contents of the flask were poured into a beaker. It was found from GC - MS analysis that the product was contaminated with up to 8% impurities. These included starting material, the mono-substituted alkoxy triazine (2-chloro-4-allyloxy-6-diethylamino-s-triazine). It was concluded that the reaction was not proceeding to completion (see Appendix C Figs. C1 (mass spectrum of starting material), C2 (mass spectrum of mono-substituted product) and C3 (mass spectrum of desired product)

2.2.4.1 Modification of synthesis of 2,4-diallyloxy-6-diethylamino-s-triazine

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The reaction was set up as previously documented and allowed to proceed, the difference being that the reaction temperature was raised to 96°C, close to the boiling point of the alcohol. The reaction was allowed to proceed for 10 hours and samples were removed at half hourly intervals. Each of these samples was analysed using GC-MS analysis. After this testing the reaction was modified to be carried out at 96°C for 7 hours to ensure complete reaction. The now complete reaction product was purified by repeat washings with distilled water. This was to remove any allyl alcohol which was present after the rotary evaporation of the excess alcohol. The final product from this purification process was a waxy solid which was dried in a vacuum oven at 100°C for several hours. ¹H, ¹³C and mass spectra were taken of the product. These can be seen in Appendix B as Figures B8 (¹³C NMR) B9 (¹H NMR) and B10 (mass spectrum). ¹³C chemical shifts: 173ppm (aromatic C-O (alkoxy)), 168ppm (aromatic

C-N (amine)), 135ppm (CH=), 118ppm (=CH₂), 58ppm (O-CH2 alkoxy), 42ppm (N-CH₂), 17ppm (CH₃ amine). ¹H chemical shifts: 6.1ppm (CH=), 5.5ppm (=CH₂), 4.9ppm (OCH₂), 3.6ppm (N-CH₂), 1.1ppm (CH₃ amine).

2.2.5 Determination of monomer melting point

This was carried out using a hot-stage microscope fitted with calibrated thermometer. A small sample of the solid monomer was placed between two thin cover slips, this reduced the thermal lag incurred when using the thicker, normal microscope slides. The sample was then placed into position on the microscope. After focusing on three individual crystals, of varying sizes the sample was heated from a temperature of 25°C. This heating was continued until the crystals had melted. The temperature at which discernible melting began was noted as well as the temperature at which all the crystals had melted.

2.3 Curing Unsaturated Polyesters with novel-Monomer

Before curing could take place it was necessary to determine whether the new monomer was miscible with the alkyds that had been supplied. This was simply a process of melting the monomer into a liquid form and mixing it with the alkyds as supplied. The composition of these resins is given in Table 2.1.

	Co	Composition of alkyd (molar ratios of components)			
Alkyd type	Maleic anhydride	Phthalic anhydride	1,2- Propylene glycol	Diethylene glycol	Adipic acid
8134	1	-	-	2	1
8123	1	1	2	- -	-
815	5	1	6		-
8633	1	2	3		-

Table 2.1: Types and compositions of alkyds used

For the curing process several different initiators were used with various accelerators. Cure was attempted at both room temperature and elevated temperatures.

The alkyds were mixed with the monomer in a 2:1 monomer:unsaturation mole ratio. To small samples of these resins (~20g), the initiator and catalyst were added (see Table 2.2 for details of cold cure and Table 2.3 for details of hot cure). This mixture was thoroughly mixed to produce a homogenous mixture of resin, initiator and catalyst. The cold cure was carried out at room temperature in all cases and the samples were post-cured where appropriate at 80°C for three hours. In the following list MEKP = methyl ethyl ketone peroxide (33% w/w in phthalate paste), BPO = benzoyl peroxide (50% w/w in phthalate paste), DCPO = dicumyl peroxide (99% powder), CN = cobalt naphthenate (1% w/w in styrene) and DMA = N,N-dimethylaniline. Cold curing samples were allowed to cure overnight at room temperature.

Sample	% w/w MEKP	% w/w DCPO	% w/w BPO	% w/w CN	% w/w DMA
A	2	nter jed O Andru (A	sur com O Screbast	1.5	0.6
В	2			1.5	0.5
C	2	0	0	1.5	0.4
D	2	0	0	1.5	0.3
E	1.5	0	0	1.5	0
F	2	0	0	1.5	0
G	5	0	0	3	0
H	10	0	0	5	0
I	5	0	0	5	0
J	10	0	0	7.5	0
K	0	0	3	0	0.3
L	0	0	4	0	0.9
n M	0	0	3	0	0.5
N	0	0	3	0	0.5
0	0	0	10	0	1
Р	0	0	7.5	0	1
Q	0	0	7.5	0	1.5
R	0	2	0	0	0.1
S	0	2	0	0	0.15
Т	0	2	0	0	0.2
U	0	3	0	0	0.1
V	0	3	0	0	0.15
W	0	3	0	0	0.2

Table 2.2: Initiator systems used for cold curing tests.

Preparation of the samples for hot curing was carried out in exactly the same way as

the preparation for cold-cure samples. However, these samples were cured and postcured in an oven. The samples which were cured using a hot-cure process are as follows:

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Cure Time % w/w Post-Cure Initiator Cure Post-Cure Temp (°C) (Hrs) Temp (°C) Time (Hrs) 2% + 3% 16 Benzoyl Peroxide 80 120 5 Benzoyl Peroxide 2% + 3% 80 16 135 3 5 Benzoyl Peroxide 2% + 3% 80 16 135 5 Benzoyl Peroxide 2% + 3% 90 16 135 3 Benzoyl Peroxide 2% + 3% 90 16 120 5 **Benzoyl** Peroxide 2% + 3%140 100 16 **Dicumyl** Peroxide 2% + 3%120 5 80 16 3 Dicumyl Peroxide 2% + 3%80 16 135 135 5 Dicumyl Peroxide 2% + 3% 80 16 135 Dicumyl Peroxide 5 2% + 3% 90 16 3 **Dicumyl** Peroxide 90 2% + 3% 16 120 **Dicumyl** Peroxide 140 5 16 2% + 3% 100 5 AZBN 120 2% + 3% 80 16 3 135 AZBN 2% + 3% 80 16 5 AZBN 2% + 3% 80 16 135 5 AZBN 2% + 3% 90 16 135 AZBN 2% + 3% 120 3 90 16 100 5 AZBN 2% + 3% 16 140

Table 2.3: Composition of samples and conditions of cure for hot-cure trials with new monomer

2.4 Sol-Gel Analysis of Resins Cured with New Monomer

The samples were hot-cured according to the following specifications: The resins were mixed with the s-triazine monomer in a 1:2 unsaturation in polymer backbone:monomer molar ratio. Only resins 8123 and 8134, as specified in Table 2.1

were used. To the resins benzoyl peroxide (93% water damped, 2% w/w and 3% w/w) or dicumyl peroxide (99%, 2% w/w and 3% w/w) or AZBN (99%, 2% w/w and 3% w/w) was added. These resins were then cured under the conditions as shown in Table 2.3. The resultant cured polymers were then ground into very fine powders using a coffee grinder. Samples of between 7 and 10g were accurately weighed into large boiling tubes fitted with quickfit stoppers. Dichloromethane (DCM,100ml) was added to each sample and the stopper was replaced to seal the tube. Each sample was then left in the DCM for ten days. The samples were shaken vigorously twice a day on each day of the test. At the end of this time period the samples were quantitatively filtered through accurately pre-weighed filter paper. The filter paper and the solid residue were then completely dried for 2 hours in a vacuum oven at 50°C. Once completely dry the samples were allowed to cool to room temperature under vacuum before being accurately weighed again. This determined the amount of the cured polymer which was insoluble (Gel portion). The filtrate was also collected and 10cm³ portions were pipetted into a dry and accurately pre-weighed evaporating basin. The basin and filtrate were then placed into a vacuum oven at 50°C. These samples were left in the oven until all the DCM had evaporated off. This left the soluble portion of the polymers. The basin was then accurately re-weighed to determine the amount of soluble material. This procedure was then repeated but the samples were left for 20 days as opposed to ten.

2.5 Smoke Testing an era the first the spectrum of the fill dest access to make Architer

Smoke testing was carried out on 24 samples (each in triplicate). The samples that were prepared consisted of one of two alkyds: 8134 and 8123 (8134 = 1:1:2 molar ratio adipic acid:maleic anhydride:diethylene glycol; 8123 = 1:1:2 molar ratio phthalic anhydride:maleic anhydride:propylene glycol) cross-linked with either styrene or the novel monomer. The samples were treated with various amounts of dimethyl methylphosphonate, DMMP (0 - 10% w/w), triethyl phosphate (0 - 10%) and aluminium oxide trihydrate (50 - 100phr). See Tables 2.4 (DMMP), 2.5 (TEP) and 2.6 (ATH) for compositions of samples tested. Curing of the styrenated resins was carried out at room temperature overnight with post-cure at 80° C for 3 hours using 2% w/w MEKP (33% in phthalate plasticiser) and 1.5% cobalt naphthenate (1% w/w in styrene). Curing of the resins containing the new monomer was carried out at 90°C overnight with post-cure at 140°C for 3 hours using 3% w/w dicumyl peroxide, (DCPO). Sample dimensions were 60mm x 60mm x 3mm. Smoke testing was carried out using a smoke chamber supplied by BIP according to ASTM D 2843.

2.5.1 Testing Apparatus

The smoke testing was carried out according to ASTM 2843. Samples of dimensions 60mm x 60mm x 3mm were burnt under standard conditions in an enclosed chamber as shown in Appendix D (Fig. D1). The chamber was a metal box of dimensions 300mm x 300mm x 790mm with a heat resistant hinged door containing a glass viewing panel. The chamber was totally enclosed apart from four 25mm x 230mm holes at the bottom of the chamber. Inside the chamber was a specimen holder and

the burner. The holder consisted of two pieces:- firstly the actual sample holder which was a metal frame made to the same dimensions as the sample and secondly another metal frame, the same size as the first, suspended directly under the sample holder containing a metal mesh to catch any drips from the specimen. The burner was made to prescribed specifications (for details of this see ASTM 2843) and was positioned under the specimen diagonally across the chamber and at an angle of 45° to the plane of the specimen. The burner was fuelled by propane gas at a pressure of 40 psi.

The means of smoke detection and quantification was a photoelectric cell. A light source was positioned on one side of the chamber so that it shone directly across the width of the chamber into a photometer which detected and quantified the amount of light passing through the chamber. This photometer was connected to a YT recorder which plotted a graph of light absorption vs time (See Appendix D for diagram of chamber).

2.5.2 Testing Method

The specimens were weighed before the test. The photometer was calibrated before each test at 0 and 100% obscuration. The sample was placed onto the sample holder and the flame was ignited at the correct pressure. The door was totally closed and sealed around the edges with tape to prevent any smoke loss through the cracks in the door. The exhaust vent was closed and the fume cupboard turned off. The flame was positioned under the sample and the recorder was turned on. The flame was left under the sample for the entire duration of the test which was 4 minutes. At the end

of the testing period the chamber was cleared of smoke through the exhaust vent and					
the b	urnt sample was re-weighed to determ	ine the amount of specim	nen consumed in		
the te	est. During the test several observation	s need to be taken:			
1)	Time until maximum light obscurati	on is reached	1. Solution of the second s		
2)	Time until flame extinction				
3)	Maximum light obscuration	n en ser en en ser en			
4)	Appearance of smoke evolved.	t da	a An an		
5)	Weight of sample hurnt during test				

After each test the front viewing panel was cleaned as well as the light source and the photometer. Before commencing any subsequent tests 15 minutes was allowed to cool the chamber back to room temperature so that the starting temperature of every test was constant.

Specimen	% DMMP (w/w)	% P (w/w)	% N (w/w)
SAD01	0	0.0	· · · · · · · · · · · · · · · · · · ·
SAD02	a an	0.2	·····
SAD03	· · · · · · · · · · · · · · · · · · ·	0.75	
SAD04	5	1.25 states	n an
SAD05	<u> </u>	1.74	0
SAD06	10	2.50	<u> </u>
SND01	0	,	<u> </u>
SND02	<u> </u>	0.2	· · · · · · · · · · · · · · · · · · ·
SND03	3	0.75	· · · · · · · · · · · · · · · · · · ·
SND04	5	1:25	
SND05	7	<u> </u>	••••••••••••••••••••••••••••••••••••••
SND06	10	2.50	0
TAD01	0	0	12
TAD02	1	0.2	12
TAD03	3	0.75	12
TAD04	5	1.25	12
TAD05	7	<u> </u>	12
TAD06	10	2.50	12
TND01	0	0	12.4
TND02	1	0.2	12.4
TND03	3	0.75	12.4
TND04	5	1.25	12.4
TND05	7	1.74	12.4
TND06	10	2.50	12.4

Table 2.4: Details of specimens tested in the smoke chamber, see below for key to samples

S = Styrene monomer, T = Triazine monomer

A = Aliphatic alkyd (adipic acid, maleic anhydride, diethylene glycol)

N = Standard alkyd (maleic anhydride, phthalic anhydride, propylene glycol)

D = Dimethylmethyl phosphonate

Specimen	% TEP (w/w)	% P (w/w)	% N (w/w)
SAT'01	0	0.0	0
SAT'02		0.17	and the second of the second
SAT'03	3	0.51	
SAT'04	5	0.85	0
SAT'05		1.19	0
SAT'06	10 <u>10</u>	1.70	0
SNT'01	0	0.0	0
SNT'02	1	0.17	0
SNT'03	3	0.51	ана (1) ала (1) ала (1) ала (1)
SNT'04	5	0.85	0
SNT'05		1.19	0
SNT'06	10		0 · · · ·
TAT'01	0	0.0	12
TAT'02	<u></u>	0.17	12
TAT'03	3 , 1	0.51	12
TAT'04	5	0.85	12
	7	1.19	12
TAT'06	10	1.70	12
TNT'01	0	0.0	12.4
TNT'02	1	0.17	12.4
TNT'03	3	0.51	12.4
TNT'04	5	0.85	12.4
TNT'05	7	1.19	12.4
TNT'06	10	1.70	12.4

Table 2.5: Details of specimens tested in the smoke chamber, see below for key to samples

S = Styrene monomer, T = Triazine monomer

A = Aliphatic alkyd (adipic acid, maleic anhydride, diethylene glycol)

N = Standard alkyd (maleic anhydride, phthalic anhydride, propylene glycol)

T' = Triethyl phosphate

SPECIMEN	ATH (PPH)	966 (% W/W)	980 (% W/W)
SNA'/SAA'01	50	0.5	-
SNA'/SAA'02	75	0.5	-
SNA'/SAA'03	100	0.5	-
SNA'/SAA'04	50	0.75	u prigo 1496 <u>–</u> tradicio e sub-
SNA'/SAA'05	- 75	0.75	1. 小白盒 一 彩彩的小小小
SNA'/SAA'06	100	0.75	-
SNA'/SAA'07	50	-	0.5
SNA'/SAA'08	75		0.5
SNA'/SAA'09	-100 setting to date	e lidro e t a braca en	0.5
SNA'/SAA'10	50	ta an ta an <mark>a</mark> ta an ing ta ang	0.75
SNA'/SAA'11	75		0.75
SNA'/SAA'12	100	n en sej <u>e</u> tenske pro	0.75
TNA'/TAA'01	50	0.5	na an a
TNA'/TAA'02	75	0.5	.
TNA'/TAA'03	100	0.5	-
TNA'/TAA'04	50	0.75	an tha <u>an a</u> n tha an ta
TNA'/TAA'05	75	0.75	a anti-arms 🗖 the states and
TNA'/TAA'06	100	0.75	-
TNA'/TAA'07	50	-	0.5
TNA'/TAA'08	75	* -	0.5
TNA'/TAA'09	100		0.5
TNA'/TAA'10	50	-	0.75
TNA'/TAA'11	75	-	0.75
TNA'/TAA'12	100	.	0.75

Table 2.6: Details of specimens tested in the smoke chamber, see below for key to samples

S = Styrene monomer, T = Triazine monomer

A = Aliphatic alkyd (adipic acid, maleic anhydride, diethylene glycol)

N = Standard alkyd (maleic anhydride, phthalic anhydride, propylene glycol)

A' = ATH containing sample

966 = Viscosity additive 966 (supplied by BIP), 988 = Viscosity additive 988 (supplied by BIP)

n.B. SNA'/SAA' etc refers to two separate specimens with the same composition

2.6 Flammability Testing of the state party party of the stream barran a party of the first stream of the stream of the

2.6.1 LOI Testing

The samples prepared consisted of one of two alkyds: 8134 and 8123 (8134 = 1:1:2 molar ratio adipic acid:maleic anhydride:diethylene glycol; 8123 = 1:1:2 molar ratio phthalic anhydride:maleic anhydride:propylene glycol) cross-linked with either styrene or the novel monomer. The samples were treated with various amounts of dimethyl methylphosphonate, DMMP (0 - 20% w/w), triethyl phosphate (0 - 20% w/w), trichloroethyl phosphate (0 - 20% w/w), triphenyl phosphate (0 - 20% w/w) and melamine (1.875 - 18.75% w/w). Curing of the styrenated resins was carried out at room temperature overnight with post-cure at 80°C for 3 hours using 2% w/w MEKP (33% w/w in phthalate plasticiser) and 1.5% w/w cobalt naphthenate (1% w/w in styrene). Curing of the resins containing the new monomer was carried out at 90°C overnight with post-cure at 140°C for 3 hours using 3% w/w dicumyl peroxide, (DCPO). Compositions of the tested samples can be seen in Tables 2.7, 2.8, 2.9, 2.10 and 2.11. For the calculation of %N in the samples containing melamine the proportion of N as contributed by the triazine monomer was ignored.

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This test is designed to meet ASTM D 2863-70 entitled "Standard method for test for flammability of plastics using the oxygen index method".

The oxygen and nitrogen lines were attached to the equipment in the specified way and the analyser and digital display voltmeter were turned on. The equipment was adjusted so that the displays were working within specified limits according to the instructions in the manual. The gas cylinders were turned on to a pressure of 29 p.s.i.. The 100% oxygen level was calibrated at an oxygen flow rate of 18 litres/min and 100% oxygen flowing through the chimney. 0% oxygen was calibrated with 100% nitrogen flowing through the chimney at a flow rate of 18 litres/min.

The samples were prepared in the normal manner and cured in moulds of dimension: 150mm x 6mm x 3mm. 10 specimens of each sample composition were tested.

The sample was placed into the sample holder and placed into the glass chimney. The combined gas flow rate was put at 18 litres/min and set to the desired oxygen percentage. If the sample was an unknown then this was normally 25% oxygen. The chimney was purged at this oxygen concentration for 30 seconds. The sample was then ignited with a high heat butane gas burner. The desired oxygen percentage for the purpose of this test was deemed to be where the sample burnt for a period of three minutes or a length of 5 cm and then extinguished itself. This percentage of oxygen was then recorded to be the minimum percentage of oxygen required to sustain combustion of the sample.

	·		
Specimen	% P Additive (w/w)	% P (w/w)	% N (w/w)
SAFD01	0		0
SAFD02	· · · · · · · · · · · · · · · · · · ·	0.25	
SAFD03	5	1.25	0
SAFD04	10	2.50	
SAFD05	20	5.00	0
SAFT'01	0	0 ¹	0 0 0
SAFT'02		0.25	0
SAFT'03		1.25	0
SAFT'04	10	2.50	0
SAFT'05	20	5.00	
SNFD01		0	0
SNFD02	11	0.25	0
SNFD03	5	1.25	0
SNFD04	10	2.50	0
SNFD05	20	5.00	0
SNFT'01	0	0	0
SNFT'02	1	0.25	· . , 0
SNFT'03	5	1.25	0
SNFT'04	10	2.50	0
SNFT'05	20	5.00	00

Table 2.7: Details of styrene based samples tested for LOI

S = Styrene monomer, F = Fire test

A = Aliphatic alkyd (adipic acid, maleic anhydride, diethylene glycol)

N = Standard alkyd (maleic anhydride, phthalic anhydride, propylene glycol)

T' = Triethyl phosphate, D = Dimethylmethyl phosphonate

Specimen	% P Additive (w/w)	% P (w/w)	% N (w/w)
TAFD01	0	0	12.0
TAFD02	1	0.17	12.0
TAFD03	5	0.85	12.0
TAFD04	10	1.70	12.0
TAFD05	20	3.40	12.0
TAFT'01	0	<u>6 0 1 6 6 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 </u>	12.0
	1 · · · · · · · · · · · · · · · · · · ·	0.17	12.0
	5	0.85	12.0
TAFT'04	10	1.70	12.0
	20	3.40	12.0
TNFD01	0	0	12.4
TNFD02	1	0.17	12.4
TNFD03	5	0.85	12.4
TNFD04	10	1.70	12.4
TNFD05	20	3.40	12.4
	0	0	12.4
TNFT'02	11	0.17	12.4
TNFT'03	5	0.85	12.4
TNFT'04	10	1.70	12.4
TNFT'05	20	3.40	12.4

Table 2.8: Details of triazinated specimens tested for LOI, see below for key to samples.

T = Triazine monomer, F = Fire test

A = Aliphatic alkyd (adipic acid, maleic anhydride, diethylene glycol)

N = Standard alkyd (maleic anhydride, phthalic anhydride, propylene glycol)

D = Dimethylmethyl phosphonate

T' = Triethyl phosphate

Sample	% TCEP	% P w/w	% Cl w/w	% N w/w
SAFC01	0	0	0	0
SAFC02	1	0.11	0.37	· · · · · · · · · · · · · · · · · · ·
SAFC03	5	0.55	1.85	0
SAFC04	10	1.11	3.70	0
SNFC01	0	0		- 70 °
SNFC02	1	0.11	0.37	0
SNFC03	5	0.55	1.85	0
SNFC04	10	1.11	3.70	
TAFC01	0	0	0	12.0
TAFC02	1	0.11	0.37	12.0
TAFC03	5	0.55	1.85	12.0
TAFC04	10	1.11	3.70	12.0
TNFC01	0	0		12.4
TNFC02	1	0.11	0.37	12.4
TNFC03	5	0.55	1.85	12.4
TNFC04	10	1.11	3.70	12.4

Table 2.9: Compositions of samples tested for LOI with TCEP as the additive

S = Styrene, T = Triazine monomer, F = Fire test

A = Aliphatic alkyd (adipic acid, maleic anhydride, diethylene glycol)

N = Standard alkyd (maleic anhydride, phthalic anhydride, propylene glycol)

C = Trichloroethyl phosphate

SERIES	% P ADDITIVE (%W/W)	% P W/W	% N W/W
TAFT*PP01		0	12
02	1,	0.0949	
03	5 ja	0.4745	12
04	10	0.949	12
05	20	1.898	12
TNFT*PP01			12.4
02		0.0949	12.4
03	5	0.4745	12.4 ·····
04	10	0.949	12.4
05	20	1.898	12.4
SAFT*PP01	0 0		.
02	1	0.0949	· · · · · · · · · · · · · · · · · · ·
03	5	0.4745	0
04	10	0.949	0
05	20	1.898	
SNFT*PP01	0	0	0
02	1	0.0949	0
03	5	0.4745	0
04	10	0.949	0
05	20	1.898	0

Table 2.10: Compositions of samples tested for LOI.

T = Triazine, S = Styrene, N = Normal resin, A = Aliphatic resin,

T*PP = triphenyl phosphate, F = Fire testing

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Specimen	% P additive	% P w/w	% N additive	% N w/w*
SAFMD01	a a O a anna at	<u> 0 </u>	1.875	1.25
SAFMD02	0	00	18.75	12.5
SAFMD03	<u> </u>	0.25	1.875	1.25
SAFMD04	1	0.25	18.75	12.5
SAFMD05	10	2.5	1.875	1.25
SAFMD06	<u>- 10 - 10 - 10 - 10 - 10 - 10 - 10 - 10</u>	ant 2.5 1	18.75	12.5 ····
SAFMT'01	00	00	1.875	1.25
SAFMT'02	00		18.75	12.5
SAFMT'03	1	0:25	1,875	<u> </u>
SAFMT'04	1	0.25	18.75	12.5
SAFMT'05	10	2.5	1.875	1.25
SAFMT'06	10	2.5	18.75	12.5
	0	0	1.875	1.25
	0	0	18:75	12.5
	1	0.25	1.875	1.25
TAFMD04	1	0.25	18.75	12.5
	10	2.5	1.875	1:25
	10	2.5	18.75	12.5
	0	0	1.875	1.25
	0	0	18.75	12.5
	1	0.25	1.875	1.25
	1	0.25	18.75	12.5
	10	2.5	1.875	1.25
TAFMT'06	10	2.5	18.75	12,5

* This value excludes N present in the triazine monomer.

Table 2.11: Sample compositions of LOI specimens containing melamine, see below for key

S = Styrene monomer, T = Triazine monomer

A = Aliphatic resin (adipic acid, maleic anhydride, diethylene glycol)

F = Fire test specimen

M = Melamine containing

D = DMMP, T' = TEP

2.62 Surface Spread of Flame Testing

Samples were 2-ply laminates made up from a 2:1 resin:glass ratio. Styrenated resins were cured with 2% w/w 50% MEKP and 1.5% w/w 1% CN overnight at room temperature and post-cured at 80°C for 3 hours. New resins were cured with 3% w/w DCPO at 90°C overnight and post-cured at 140°C for 3 hours. These laminates were machined into 100mm x 225mm x 2 ply specimens. These specimens were marked with a line exactly down the centre from top to bottom and with two further lines at 50mm and 80mm from the top edge. These two latter lines represent the cut off points for class 1 and class 2 fire performance respectively (Fig. 2.5).

Problems were encountered with the impregnation of the new triazine system into the emulsion bound chopped strand matting (CSM). It was found that the triazine resin would not impregnate into the fibres of the CSM at all, leaving the fibres totally unwetted. This problem was solved by using a powder bound CSM which was compatible with the new resin system.

Flame spread testing was carried out on the apparatus at BIP, Oldbury. This consisted of a heating filament rated to 1100 ± 50 watts, a sample support and a safety grid. Surrounding this equipment was a metal guard to prevent draughts.

The apparatus was turned on and allowed to heat up for 4.5 mins. After this the guard was put into place and the element was left for a further 30 seconds. The sample was then placed into the sample holder and slid into place so that it lightly touched the heating element. The stop watch was started as soon as flames were observed and stopped immediately upon extinction of the flame. The time of burning and the distance burnt were recorded. Each sample was tested in triplicate.

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Fig. 2.5: Diagram of sample and markings at 50 and 80mm

2.7 Thermogravimetric analysis

TGA was used to determine whether there was any interaction between the phosphorus additive and the triazine resin and to determine the decomposition stages of the resins.

The resins were treated with DMMP (20% w/w), TEP (20% w/w) and TCEP (20% w/w) and cured in the normal manner, as described earlier. The monomer itself was also homopolymerised by hot curing with 3% w/w DCPO at 90°C for 16 hrs and postcuring at 140°C for 3 hrs. The homopolymer was also treated with each of the additives (20% w/w). The resin samples were then ground up into a powder and weighed out into the sample holder of the TGA apparatus (~ 5 -10mg). This was then heated, in air, at a constant heating rate of 20°C/min to 650°C. The progressive weight loss of each sample was automatically recorded by the TGA.

2.8 FT-IR Analysis of Charred Residues

Samples of polyesters based on both styrene and the new triazine monomer were mixed with the appropriate quantities of TEP, DMMP and TCEP (20% w/w). These were then cured in the normal manner as detailed in previous sections. Upon complete post-curing the samples were ground up into fine powders of particle sizes of 250µm or less. These samples were then weighed out accurately and placed into a muffle furnace and heated from 20°C to 600°C at a rate of about 15°C/min. Samples were taken out of the oven at 50°C intervals starting at 150°C. The residues were then made up into KBr discs using ~ 5mg residue in 500mg KBr. Using these discs the IR spectra of the samples were taken on an FT-IR spectrophotometer. IR spectra were taken of each of the additives as well as the resins incorporating the additive before combustion. This procedure was repeated using chars from samples that had been completely combusted using a Bunsen Burner on its hottest flame. Complete combustion was deemed to be when no more combustion could be spontaneously supported upon removal of the flame.

2.9 Determination of Initial Char Temperature and Stability

Samples of polyesters based on both styrene and the new triazine monomer were cured in the normal manner as detailed in previous sections. Upon complete postcuring the samples were ground up into fine powders of particle sizes of 250µm or less. These samples were then weighed out accurately and placed into a muffle furnace and heated from 20°C to 600°C at a rate of about 15°C/min. Samples were

checked at 50°C intervals starting at 150°C. The temperature at which the first signs of char appeared was noted as was the temperature at which the char totally degraded.

2.10 Phosphorus Content Analysis of Char and % Char Determination

The samples were prepared incorporating 20% w/w of the respective additives (TEP, DMMP and TCEP) and cured and post-cured in the normal manner. After post-cure the samples were cut into 60 x 60 x 3mm squares. These squares were accurately weighed before burning and then subjected to a Bunsen Burner flame on the highest setting until complete combustion of the square had taken place. The residual char was then weighed and the % char formation was calculated.

Samples of the uncharred resins and the charred residues were digested in a Kjeldahl flask by heating vigorously in 98% sulphuric acid (50ml) containing 1 titanium Kjeldahl digestion tablet. The digestion was carried out until the initially brown solution had turned yellow. The digestion solution was then diluted to 250ml with distilled water and analysed for total phosphorus content on an ICP-AES. Calibration of the ICP was with a phosphorus standard. The amount of phosphorus remaining in the char was calculated from the concentration found in the char solution.

2.11 Mechanical Testing

2.11.1 Flexural Testing

Samples of both styrene based and triazine based resins were cured and post-cured as previously described. It was vital to ensure that no voids were present in the samples

as voids adversely affect the results. No additives were added to the resins for the purposes of this testing. The samples were then machined into the following sizes:

length:Any length can be used as long as it is longer than 16 x
thickness of sampleWidth:10 - 12 mmThickness:4 - 7 mm

After the samples were machined to size the edges of the specimens were sand papered for a period of five minutes to ensure that there were no imperfections on the edges of the specimens. The testing was carried on an Instron 1414 using the following parameters:

Span of bottom sample supports:16 x thickness of sample (mm)Cross Head Speed:2mm/minChart Paper Speed:2cm/minFull Scale Deflection:100kgf

The sample was placed into the sample holder as shown in Fig. 2.6.

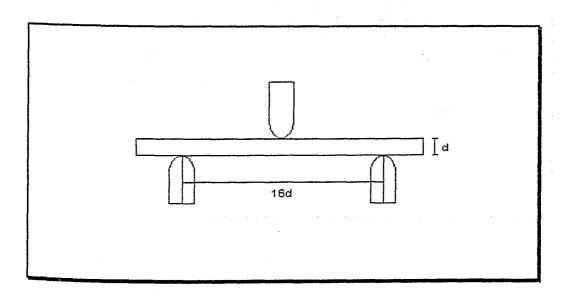


Fig. 2.6: Diagram showing sample in place in sample holder.

Once the sample was placed into position and the instrument had been calibrated at 0 and 100% full scale deflection the test was started. At the end of the test, when the sample had failed, the jaws were returned to the starting position and the next sample was tested.

2.11.2 Heat Distortion Temperature (Method 102G)

The apparatus used for this testing is shown in Fig. 2.7.

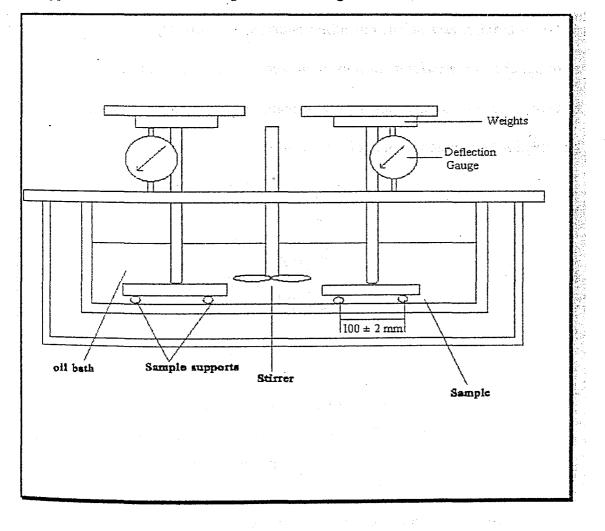


Fig. 2.7: Schematic diagram of HDT apparatus

The specimens were cured and post-cured in the normal manner for the individual resins. The samples were then machined into sample sizes within the following ranges:

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Length:	> 110mm
Width:	9.8 - 12.8mm
Thickness:	3 - 7mm

The samples were measured for their thickness and width before being placed into the oil bath. The samples were placed, on their side, symmetrically across the supports in the oil bath. In this position the previous width dimension was referred to as the thickness of the sample and the previous dimension for thickness was referred to as the width of the specimen. The specimen was then subjected to a bending stress of 1.81 MN/m^2 (18.5 kgf/mm²). The total mass in kilograms (consisting of weights and the rod) to be used is calculated by:

$$M = \frac{Sbd^2}{150L}$$

Where: $S = 18.5 (kgmm^{-2})$

b = width of specimen as defined above (3 - 7mm)

d = thickness of specimen as defined above (9.8 - 12.8mm)

L = distance between supports in mm

The samples were then allowed to condition in the bath for 5 mins before the deflection gauge was set to zero. The temperature of the bath was then raised at a rate of 2° C/min and the temperature at which the deflection of the specimen reaches the

value given in Table 2.12 was recorded. The mean result of the two specimens was then taken to be the temperature of deflection under load at 1.81 MN/m^2 .

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Depth of test bar (mm)	Standard deflection (mm)
9.8-9.9	0.33
10.0 - 10.3	0.32
10.4 - 10.6	Proceeding work there the 0.31 hereight a fact when the
10.7 - 10.9	0.30
11.0 - 11.4	o til solverska stry skal sjeldaret i sen terninen i i solet i 0,29
<u>11.5 - 11.9</u>	en des methodes : 0.28 hand self har and
12.0 - 12.3	0.27
12.4 - 12.7	0.26
12.8	0.25

Table 2.12: Standard deflection needed for defined depth of test bar

2.11.3 Barcol Hardness

The Barcol Hardness rating is used to determine the hardness of a sheet of resin. This is an indication of the degree of cross-linking in the cured polymer. The higher the hardness value the higher the degree of cross-linking.

Cast sheets of untreated samples were used for this testing. The sheets were prepared, cured and post-cured in the normal manner for the individual resins. A Barber-Colman Impressor type 934-1 was used for the testing. The impressor was calibrated at 43-45 and 85-87 hardness units on standard discs supplied by the manufacturer.

2.12 Scanning Electron Microscopy of the Charred Residues

The charred residues left over from the phosphorus analysis of the char determination were blasted with compressed air to remove any loose fragments that may come loose in the spin coating chamber of the SEM. The chars were then stuck on the specimen holder with a conductive glue. Once secure the samples were coated with twelve coats of gold. The reason for using so many coats was that the surfaces of the chars were very uneven and only with so many coats could an adequate coverage of gold be achieved. The samples were then placed into the microscope and pictures of relevant structural details were taken. Relevant structural details included voids in the surface of the char (including the structures within the voids) as well as the general surface of the charred residues.

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Results and Discussion

3.1 The Synthesis Program

3.1.1 Introduction to Synthesis Program

The rationale behind this synthesis program was that a new cross-linking monomer or polymer backbone was required to reduce the flammability and smoke evolution of a conventional unsaturated polyester resin. In addition to this it was hoped to reduce styrene and volatile organic emissions from the resin. Previous attempts to alleviate these problems, although successful, have not achieved these goals using only one additive/monomer. Usually a mixture of additives or alternative monomers were used. It is well known that 1,3,5-triazine derivatives are capable of imparting fire retardancy into a polymer (melamine polymers are known to be flame retardant and polyurethanes form isocyanurates upon combustion to promote char formation). It was also thought that the removal of three carbon atoms from the aromatic ring would reduce smoke evolution. The use of triazine chemistry seemed to be perfectly suited to provide both fire retardancy and smoke suppression in a polyester.

The choice of starting material was relatively simple. It has been extremely well documented that cyanuric chloride is very reactive towards nucleophilic substitution and that substituents such as amines and alkoxides can easily be placed onto the triazine ring. It was also known that alkoxy substituents could be transesterified with glycols to produce oligomeric triazine chains. A simple end-capping process with an unsaturated acid could result in a cross-linkable triazine oligomer. As the project revolved around the synthesis of either a novel monomer or a new oligomer, with large amounts of nitrogen, cyanuric chloride was an ideal starting material. One

major restriction to the synthesis was that all of the chlorine had to be substituted from the ring. The production of a monomer or an oligomer required only two chlorines to be substituted. To this end a blocking group was needed to remove the chlorine but not allow tri-substitution of alkoxy groups onto the ring. An amine seemed suitable for this blocking group as it de-activated the α -carbon to further nucleophilic attack and also imparted more nitrogen into the systems for smoke suppression. The entire, envisaged, synthesis program is shown in Appendix A as Figures A1 and A2.

3.1.2 Synthesis of 2,4-dichloro-6-diethylamino-s-triazine

The product from the reaction as described in Section 2.1.1 was analysed using ¹³C and ¹H NMR as well as mass spectrometry. Figure 3.1 shows the expected product with distinct carbons and protons labelled.

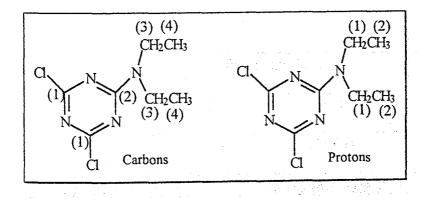


Fig. 3.1: 2,4-Dichloro-6-diethylamino-s-triazine with distinct carbons and protons marked.

The relevant spectra for this product are shown in Appendix B (Figures B1-3). Tabulated results for the spectra are shown in Tables 3.1, 3.2 and 3.3.

	Carbon Atom Identification				
	=C-Cl	C-N (aromatic)	N-CH ₂ (amine)	CH ₃ (amine)	
Chemical Shift	170 ppm	163 ppm	42 ppm	13 ppm	

Table 3.1: Chemical shift values and carbon atom identification for peaks shown on ¹³C NMR spectrum for 2,4-dichloro-6-diethylamino-s-triazine.

	Peak Characteristics				
Identified Proton	Chemical Shift	Splitting Pattern	Integral Value		
CH ₂	3.7 ppm	Quartet	68		
CH3	1.1 ppm	Triplet	107		

Table 3.2: Peak characteristics and peak identification for ¹H NMR spectra obtained from 2, 4-dichloro-6-diethylamino-s-triazine.

	Fragment Peak				
M/z Value	221	206	191	176	
Fragment lost	Parent Ion	CH ₃	CH ₃ CH ₂	NCH ₂ CH ₃	

Table 3.3: Fragmentation peak identification for the mass spectrum obtained from 2,4-dichloro-6-diethylamino-s-triazine

Looking first at the ¹³C NMR it can be immediately seen that the four expected distinct carbons are indeed present in the trace. From the chemical shifts it can be seen that the carbon atoms that are present in the triazine ring fall in the general region for aromatic carbons. More importantly the larger carbon peak is further downfield (170 ppm) than the smaller carbon peak (163 ppm). This gives two pieces of information, firstly the peak which is further downfield is more de-shielded than the one which is upfield from it. This indicates bonding to a more electronegative atom which is "pulling" electrons away from the carbon thus facilitating resonance at a lower field intensity. Out of Cl and N the chlorine is the more electronegative. This coupled with the fact that there are two carbons bonded to chlorine and only one bonded to nitrogen shows that the peak further downfield is the C-Cl carbon and the peak just upfield from this is the C-amine peak. Using the same principles on the remaining peaks it can be seen that the two remaining, equally sized peaks have differing chemical shifts. The one which is downfield (42 ppm) is, then, more deshielded than the upfield peak (13 ppm). This must correspond to the CH₂ attached directly to the nitrogen on the amine group as nitrogen is more electron withdrawing than CH₂. The remaining peak is, therefore, the terminal methyl group on the amine substituent.

The proton NMR shows that there are two distinct protons present in the compound, this is in keeping with the structure of the expected compound. Looking at the spectrum in more detail it is apparent that one of the proton types (3.7 ppm) is being de-shielded to a greater extent than the other proton (1.1 ppm). The structure indicates that this must relate to the CH_2 protons attached directly to the nitrogen of the amine group. The quartet splitting pattern of this peak indicates coupling to a group containing 3 protons (from the n-1 rule for splitting patterns). The peak at 1.1 ppm is, because of its upfield placement, less deshielded than the other proton indicating coupling to a less electronegative group. The triplet splitting pattern shows coupling to a group with two protons. The integral values are also of importance in determining the identification of a peak. In the case of this proton NMR it can be seen that the ratio of peak integrals is 68:107. This, allowing for slight errors in the automated integration system, is a very good match to the 2:3 proton ratio as expected from the compound.

From the mass spectrum only the four largest peaks have been assigned. The main reason for this is that the NMR spectra have already shown the product to be the desired product. The mass spectrum was only taken to reinforce this deduction by giving an indication of the fragments that are present. The parent ion is shown to be at 221 mass units. This is the expected R.M.M. of the product which has an empirical formula of $C_7H_{10}N_4Cl_2$. The first fragment peak at 206 is equal to a loss of 15 mass units which is equivalent to the loss of CH₃. The second peak at 191 is equal to a mass loss of 30. This is actually one mass unit more than the expected 29 for the loss of CH₂CH₃. It can be assumed, however, that this peak does correspond to the loss of an ethyl group as there are no other substituent groups or derivatives of groups that could give a peak corresponding to this weight loss. It could be that some sort of rearrangement has taken place during fragmentation. The peak at 176 mass units shows a loss, from the parent ion, of 45 mass units. This corresponds to the loss of NH₂CH₂CH₃ which could be a bi-product of NCH₂CH₃ loss followed by protonation by two hydrogen atoms. Also of note in the mass spectrum is the presence of an M+2 peak at 176, 191, 105 and 221. This indicates the presence of Cl groups in the

compound. In summary the three spectra taken of the product prove unequivocally that 2,4-dichloro-6-diethylamino-s-triazine was the product of the reaction.

3.1.3 Synthesis of 2,4-diethoxy-6-diethylamino-s-triazine

The product from the reaction as described in Section 2.1.2 was analysed using ¹³C and ¹H NMR as well as mass spectrometry. Figure 3.2 shows the expected product with distinct carbons and protons labelled.

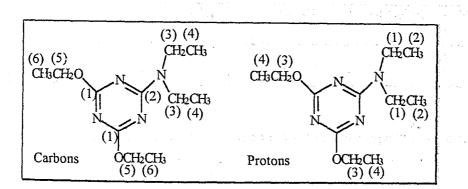


Fig. 3.2: 2,4-Diethoxy-6-diethylamino-s-triazine with distinct carbons and protons marked.

The relevant spectra for this product are shown in Appendix B (Figures B4-6). Tabulated results for the spectra are shown in Tables 3.4, 3.5 and 3.6.

	Peak Identification					
	Aromatic	Aromatic	Alkoxy	Amine	Alkoxy	Amine
	C-O	C-N	CH_2	CH_2	CH3	CH3
Chemical Shift	173 ppm	163 ppm	64 ppm	43 ppm	16 ppm	14 ppm

Table 3.4: Chemical shift values and carbon atom identification for peaks shown on ¹³C NMR spectrum for 2,4-diethoxy-6-diethylamino-s-triazine.

		Peak Characteristics	un ann 21 1949 ann agus a
Identification	Chemical Shift	Splitting pattern	Integral Value
Alkoxy CH ₂	4.3 ppm	Quartet	0.98 [°] - 100° -
Amine CH ₂	3.6 ppm	Quartet	1.06
Alkoxy CH ₃	1.4 ppm	Triplet	1.52
Amine CH ₃	1.1 ppm	Triplet	1.66

Table 3.5: Chemical shift values and proton identification for peaks shown on ¹H NMR spectrum for 2,4-diethoxy-6-diethylamino-s-triazine.

		Pe	ak Identificatio	on	
	Parent ion	CH3	CH ₃ CH ₂	OCH ₂ CH ₃	N(CH ₂ CH ₃) ₂
Fragment Peak	240	225	211	195	169

Table 3.6: Fragmentation peak identification for the mass spectrum obtained from 2,4-diethoxy-6-diethylamino-s-triazine.

Looking, initially, at the ¹³C NMR spectrum, it can be seen that the 6 expected distinct carbon atoms are indeed present. The peak seen at about 80 ppm comes from the solvent and can be ignored. The two peaks at 173 and 163 ppm give two pieces of information. Secondly these two peaks fall in the aromatic carbon region. It can be concluded that these two peaks relate to the C-O and C-N carbons in the triazine ring. Looking at the chemical shifts it can be seen that the larger of the two peaks is downfield. Using the principles of de-shielding, as described in Section 3.1.2, the peak at 173 ppm is the C-alkoxy carbon in the triazine ring and the peak at 163 ppm is the C-amine carbon in the ring. The presence of four distinct carbons, in the 10 - 70

ppm region, is be expected. Using the principles as explained earlier it can be seen that the peak at 64 ppm is the O-CH₂ carbon atom and the peak at 43 ppm comes from the N-CH₂ carbon atom. There is very little resolution between the last two peaks at 16 and 14 ppm. The reason for this is that the electron withdrawing groups are one carbon atom removed from these groups and so the de-shielding effect exerted on these otherwise identical carbon atoms is greatly reduced. The observed difference in chemical shift comes from the fact that, although the de-shielding effect is greatly reduced, some de-shielding does occur and the extent of this is different between oxygen and nitrogen. The peak at 16 ppm corresponds to the alkoxy CH₃ group and the peak at 14 ppm is the amine methyl group.

Four factors must be considered when analysing the ¹H NMR spectrum. These are the number of peaks, their chemical shift, their splitting pattern and finally their integral value. Firstly there are four proton peaks which would be expected from the structure of the compound. From this chemical shifts, splitting patterns and integral values of the peaks it can be concluded that the two peaks at 4.3 ppm and 3.6 ppm were caused by the hydrogen atoms on the CH_2 groups of the alkoxy and amine substituents respectively. The final two peaks at 1.4 and 1.1 ppm come from the terminal methyl protons on the ethoxy group and the protons on the terminal amine methyl group respectively.

Only a few peaks from the mass spectrum have been allocated to fragments. A full interpretation of the mass spectrum is not necessary as the NMR spectra give adequate proof as to the nature of the compound. The parent ion peak at 240 mass units is in keeping with a compound with empirical formula $C_{11}H_{20}N_4O_2$. The first fragment loss equates to 15 mass units indicating the loss of CH₃. The second peak, a

loss of 29, is caused by the loss of an ethyl group. The loss of OCH_2CH_3 is indicated by the peak at 195. Finally the removal of the diethylamino group is indicated by the fragment peak at 169 mass units. In this case, the mass spectrum also gives some indication as to the purity of the product. It can be seen from the fragment peaks that there are no M+2 peaks. This clearly shows that there is no chlorine present in the compound. This means that there is no starting material or mono-substituted triazine present. All the spectra prove beyond doubt that the product obtained from the reaction is 2,4-diethoxy-6-diethylamino-triazine.

3.1.4 Transesterification of 2,4-dimethoxy-6-diethylamino-s-triazine with a glycol

The idea behind this reaction was to obtain a triazine oligomer which had reactive hydroxyl groups at each end of the chain. These hydroxyl groups would then be available for further reaction with an unsaturated acid such as acrylic or methacrylic acid to give an oligomeric chain with reactive unsaturation at the end of the chain to use as cross-linking sites. It was deemed vital that the addition of the unsaturated acids had to take place at both ends of the chain. If this did not occur then it would only be possible to get a straight chain copolymer with the cross-linking agent. It was assumed that there was a possibility that the reaction would not proceed as expected and that the glycol group would only displace the alkoxy group at one end of the chain, leaving only one reactive site for end-capping. The two possible products from this reaction are shown in Figure 3.3. Only ¹³C NMR analysis was carried out on this product initially, this was to save resources and time if the undesired product had

been synthesised. The reason for only using ¹³C NMR as opposed to proton NMR or mass spectrometry will become clear. Tabulated results of the ¹³C NMR are shown in Table 3.7. The spectrum itself is shown in Appendix B (Figure B7). As can be seen only three peaks have been assigned from the ¹³C NMR. This is because these peaks are the most vital in determining the exact nature of the product.

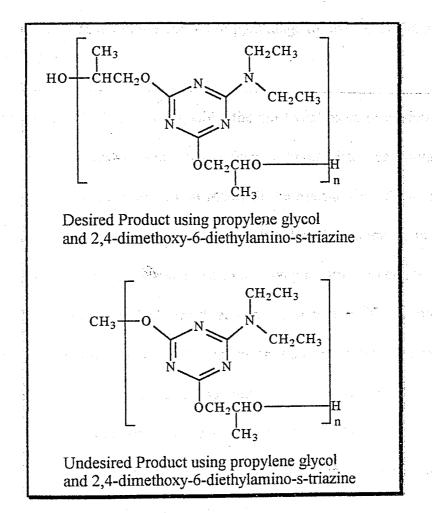


Fig. 3.3: Chemical structures of the two possible transesterification products.

	Identity of Carbon						
	C-O(methoxy gp)	C-O(glycol bridge)	C-N (amine)				
Chemical Shift	173 ppm	172.5 ppm	167 ppm				
Integral Value	2.5	17.1	9.75				

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Table 3.7: Identification of peaks in the 166 - 174 ppm range for the ¹³C NMR of the transesterification product.

The presence of the peak at 173 ppm is, arguably, the most vital piece of evidence in determining the structure of the product. If the desired product had been obtained then there would only be two distinct carbon atoms in the triazine ring, these being the carbon atom attached to the amine and the two, identical, carbon atoms connected to the glycol. These would also be seen in a two to one integral ratio. As can be seen from the blown up NMR spectrum there are three carbons present in this region and these are in a 1:7:4 integral value ratio. If it is taken for granted that the peak at 167 ppm corresponds to the C-amine carbon in the ring, then it can be seen, from the integral value, that there are four of these relative to the C-methoxy carbon in the ring. This leads to the assumption that the oligomer must be four repeat units long, or a multiple thereof. The structure of this is shown in Figure 3.4.

The structure of the repeat unit, assuming the undesired product is present and that it contains four repeat units, shows that there are indeed three distinct carbons in the triazine ring and that these would be present in a 1:7:4 ratio. From these results it is clear that the undesired product has been produced rather than the expected product. Reasons for this could include factors such as the reaction not being allowed to

proceed for long enough or that an insufficient glycol excess was used for complete

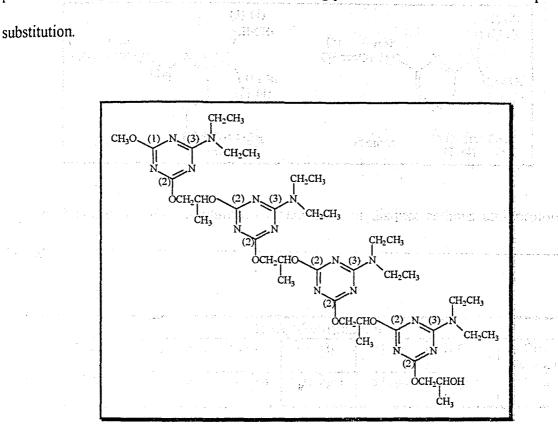


Fig. 3.4: Structure of undesired oligomer with four repeat units (distinct carbons are labelled)

3.1.5 Synthesis of 2,4-diallyloxy-6-diethylamino-s-triazine

The product from the reaction as described in Section 2.1.4 was analysed using ¹³C and ¹H NMR as well as mass spectrometry. Figure 3.5 shows the expected product with distinct carbons and protons labelled. The relevant spectra are shown in Appendix B (Figs B8 - B10). Tabulated results of the spectra are shown in Tables 3.8, 3.9 and 3.10.

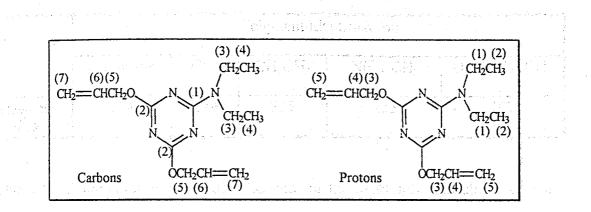


Fig. 3.6: 2,4-Diallyoxy-6-diethylamino-s-triazine with distinct carbons and protons marked.

	Peak Identification								
	Ring C-O	Ring C-N	CH=	=CH ₂	OCH ₂	N-CH ₂	CH ₃ (amine)		
Chemical Shift	173 ppm	168 ppm	134 ppm	118 ppm	67 ppm	43 ppm	13 ppm		

Table 3.8: Chemical shift values and carbon atom identification for peaks shown on ¹³C NMR spectrum for 2,4-diallyloxy-6-diethylamino-s-triazine.

		Peak Identification							
	=CH	$CH_2 =$	OCH ₂	N-CH ₂	CH ₃				
Chemical Shift	6.1 ppm	5.4 ppm	4.8 ppm	3.6 ppm	1.2 ppm				
Splitting pattern	quintet	doublet	doublet	quartet	triplet				
Integral Value	28	60	58	677	108				

Table 3.9: Peak characteristics and peak identification for ¹H NMR spectra obtained from 2, 4-diallyloxy-6-diethylamino-s-triazine.

	Fragment Identification						
	Parent Ion	CH ₃	CH ₂ CH ₃	NCH ₂ CH ₃	OCH ₂ CH=CH ₃		
Fragment peak	264	249	235	223 (Alto)	207		

Table 3.10: Fragmentation peak identification for the mass spectrum obtained from2,4-diallyloxy-6-diethylamino-s-triazine.

Keeping to the same principles of de-shielding by electronegative groups and the resultant downfield shift of the peak it is safe to say that the peaks at 173 ppm and 168 ppm on the carbon NMR spectrum relate to the carbon atoms in the ring attached to the allyloxy group and the amine group respectively. In the same vein, from the other spectra that have been obtained, it can be easily concluded that the peaks at 43 and 13 ppm relate to the amine substituent CH_2 and CH_3 groups respectively. Unsaturated groups such as alkene groups tend to fall further downfield than alkoxy carbons, in the 100 - 145ppm range. It is clear, then, that the peaks at 134 and 118ppm relate to the carbons either side of the double bond. The sole remaining peak must be the OCH_2 carbon, such carbons tending to fall in the 40 - 80 ppm range.

Looking at the proton NMR trace it can be assumed that the chemical shifts for the protons on the amine substituent are the same as for the other compounds previously described. Therefore, the peaks at 3.6 and 1.2 ppm must relate to the amine CH_2 and amine CH_3 respectively. The integral values and splitting patterns are also in keeping with this deduction. Alkene protons tend to fall in the 4.6 to 6.4 ppm range so the peaks at 5.4 and 6.1 ppm must be from the alkene group. The splitting pattern and the

integral value of the peak at 6.1 ppm show that this peak is the =CH peak (coupling to four protons gives quintet splitting and only one proton has half the integral value of two). The peak at 4.8 ppm is from the OCH_2 group and this is in keeping with the range within which these protons fall (3.6 - 5.2 ppm).

As far as the mass spectrum is concerned the first thing to see is the parent ion at 264 mass units. This would be expected from a compound with an empirical formula of $C_{13}H_{20}N_4O_2$. The important fragment peaks for the purposes of identification are at 221 and 207. These correspond to a fragment loss of 43 and 57 mass units respectively. The loss of 43 mass units is equal to the loss of an NCH₂CH₃ fragment. The loss of 57 is the same as losing an OCH₂CH=CH₂ fragment. There is no indication of any M+2 peaks in the mass spectrum. This indicates that the compound is free from chlorine containing impurities such as starting material or monosubstituted intermediates.

3.1.6 Modification of Monomer Synthesis

During the analysis of the new monomer for purity it was found that the reaction was not consistently proceeding to completion, with starting material and the monosubstituted product being present in relatively large amounts in the product. This was discovered using GC-MS analysis of the product. The GC-MS traces of the impure monomer can be seen in Appendix C (Figs C1-3). The results are, however, tabulated in Table 3.11. The peak appearing with a retention time of 13.77 minutes has been identified as being due to the starting material from its mass spectrum. The peak appearing at 15.95 minutes is from the mono-substituted monomer containing one chlorine group and one allyl group. The peak at 17.68 minutes is due to the desired product (see Table 3.11 for interpretation of MS traces).

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	Possible Fragment Identification					
MS peak label	Peak at 13.77 min	Peak at 15.96 min	Peak at 17.66 min			
А	Starting material	Mono-substituted	Desired monomer			
В	CH3 loss	CH ₃ loss	CH ₃ loss			
С	CH ₃ CH ₂ loss	CH ₃ CH ₂ loss	CH ₃ CH ₂ loss			
D	CH ₃ CH ₂ N loss	Cl loss	CH ₂ CH=CH ₂ loss			
Е	₩₩.₩₩₩₩₩₩₩₩₩₩₩₩₩₩₩₩₩₩₩₩₩₩₩₩₩₩₩₩₩₩₩₩₩₩	CH ₂ CH=CH ₂ loss	CH ₃ CH ₂ N loss			
F		OCH ₂ CHCH ₂ loss*	OCH ₂ CH=CH ₂ loss			
G	(CH ₃ CH ₂) ₂ N loss*	(CH ₃ CH ₂) ₂ N loss	(CH ₃ CH ₂) ₂ N loss*			

Table 3.11: Interpretation of MS traces. Refer to GC-MS traces in Appendix C.

* These assignments are not exact, possibly because of proton loss from the fragment or some sort of rearrangement reaction.

In trying to improve the synthesis of the monomer the reaction was carried out using essentially the same procedure as before. Sodium hydroxide pellets (2 moles) were dissolved in allyl alcohol (900 ml) used and then the triazine (1 mole) was added so that the temperature never rose above 40°C. It was at this stage that the reaction was modified. At first it was thought that the reaction had not been allowed to react long enough for complete conversion to occur. Here the temperature was allowed to rise

to 68°C and held for 7 hours. The result was that complete reaction had still not been obtained. It was then assumed that the temperature must be critical for complete reaction to occur. The reaction was, therefore, carried out at 94°C overnight. The reaction did go to completion using these conditions. The reaction time needed for completion was still unknown so during the next synthesis the reaction was "mapped" to determine the ideal reaction time for complete conversion to occur at 94°C. The first sample was taken from the reaction pot after 2 3/4 hours reaction time. Samples were then taken periodically over a period of 4 hours giving a total reaction time of about 6 1/2 hours. The analysis was carried out by GC-MS. The results can be see in Table 3.12

Reaction time	% Impurities	% Desired Product
2.75 hrs	49.1%	50.9%
3.25 hrs	22.7%	77.3%
4.5 hrs	14.8%	85.2%
5.25 hrs	7.7%	92.3%
6.5 hrs	0.0%	100%

Table 3.12: Results from synthesis mapping at 94°C

As can be seen, from the table 100% conversion was reached by 6.5 hrs reaction time. The GC-MS trace for the complete reaction can be seen in Appendix C (Fig. C4). It was, therefore, decided to use a reaction time of 7 hours and a temperature of 94 - 96° C for all future synthesis. It was also discovered that batch size affects the synthesis. On a 2L scale, typically 1.5 moles of starting material, the synthesis went to completion when reacted at 94°C for 7 hours and gave a product which was free from impurities. When this was scaled up to 3L, typically 2.5 moles of starting material, the product tended to be susceptible to discolouration and decomposition when reacted under the same conditions as the smaller scale reaction. The synthesis was, therefore, only carried out on a 2L scale. Final purification of the product involved distilling off the excess alcohol and then repeated by washing the product with distilled water until a cream coloured, waxy solid was obtained. This was then dried in an oven at 100°C for several hours. The melting point of this solid was determined, using a hot stage microscope, to be $28 - 29.5^{\circ}$ C.

3.2 Cure analysis

3.2.1 Cold Cure Analysis

Discussion of the cold cure of the resins will be carried out for each initiator system individually. In the following sections:

MEKP = Methyl ethyl ketone peroxide (33% w/w in phthalate plasticiser), BPO = Benzoyl peroxide (50% w/w in phthalate paste), DCPO = Dicumyl peroxide (99% powder), CN = Cobalt naphthenate (1% w/w Co in styrene), DMA = Dimethyl aniline (100%)

3.2.1.1 Methyl Ethyl Ketone Peroxide (MEKP) Initiator System

This initiator system relates to samples A-J as described in Section 2.3 of the experimental section. Results are shown in Table 3.13.

		an a stinartin attint A	Degree of Cure*	1
Sample	Composition	24 hrs @ Room Temp	3 hrs @ 80°C	3 hrs @ 100°C
· · · · · · · · · · · · · · · · · · ·	2% w/w MEKP, 1.5% w/w C.N., 0.6% w/w DMA	Slight gelation evident	no change in gelation state observed	no change
B B	2% w/w MEKP, 1.5% w/w C.N., 0.5% w/w DMA	no cure evident at all	no cure evident at all	slight gelation evident
C	2% w/w MEKP, 1.5% w/w C.N., 0.4% w/w DMA	no cure evident at all	no cure evident at all	slight gelation evident
D	2% w/w MEKP, 1.5% w/w C.N., 0.3% w/w DMA	no cure evident at all	no cure evident at all	slight gelation evident
:: E s	1.5% w/w MEKP, 1.5% w/w C.N.	Slight gelation evident	considerable hardening, very tacky	no change observed
F	2% w/w MEKP, 1.5% w/w C.N.	Slight gelation evident	considerable hardening, very tacky	no change observed
G	5% w/w MEKP, 3% w/w C.N.	Slight gelation evident	no change	no change
Н	10% w/w MEKP, 5% w/w C.N.	Slight gelation evident	no change	no change
Ι	5% w/w MEKP, 5% w/w C.N.	Slight gelation evident	no change	no change
J	10% w/w MEKP, 7.5% w/w C.N.	Slight gelation evident	no change	no change

 * Cure conditions were run subsequently, i.e. room temp. followed by 80°C followed by 100°C

Table 3.13: Results of cold curing of new monomer with MEKP initiator systems

These results show, categorically, that room temperature cure of the new triazine based resin with MEKP is not possible to a satisfactory degree.

3.2.1.2 Benzoyl Peroxide Initiator System

Results for the cold cure tests with benzoyl peroxide and dimethyl aniline are shown

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in Table 3.14.

		Degree of Cure*				
Sample	Composition	24hrs @ Room Temp.	3hrs @ 80°C	3hrs @ 100°C		
K	3% w/w BPO 0.3% w/w DMA	Reasonable cure but tacky and soft	No change	No change		
L	4% w/w BPO 0.9% w/w DMA	Reasonable cure but tacky and soft	No change	No change		
М	3% w/w BPO 0.4% w/w DMA	Reasonable cure but tacky and soft	No change	No change		
N	3% w/w BPO 0.5% w/w DMA	Reasonable cure but tacky and soft	No changè	No change		
0	10% w/w BPO 1% w/w DMA	Reasonable cure but tacky and soft	No change	No change		
Р	7.5% w/w BPO 1% w/w DMA	Reasonable cure, hard but tacky	No change	No change		
Q	7.5% w/w BPO 1.5% w/w DMA	Reasonable cure, hard but tacky	No change	No change		

* Cure conditions were run subsequently, i.e. room temp followed by 80°C followed by 100° C

Table 3.14: Results of cold curing of new monomer with BPO initiator systems.

Again it was concluded that this initiator system was not suitable for cold curing of

the new monomer

3.1.2.3 Dicumyl Peroxide (DCPO) Initiator System

None of the samples treated with DCPO gelled under any of the conditions of cure. It is thought that the reason MEKP and BPO did not produce adequate curing was that they are not sufficiently compatible with allyl unsaturation, i.e. the free radicals formed from MEKP and BPO are not reactive towards the allyl unsaturation present in the new monomer. Normally these initiators are used with vinyl unsaturation where they are exceptionally effective but they have been shown, here, to be ineffective with allyl unsaturation. The reason why DCPO did not produce any curing at all is that its critical temperature, i.e. the temperature at which it starts to rapidly produce reactive free radicals, is 100°C and this cannot be reduced by adding a catalyst or promoter (204). In other words DCPO only works at temperatures of around 100°C and is totally ineffective for cold curing. It is evident from this that at present cold curing of this resin is not a viable option.

3.2.2 Hot Cure Analysis

The idea behind Sol-Gel analysis is that fully cured thermosetting resins are totally insoluble in solvents. If, however, some monomer is not up used in the cross-linking process then this would be soluble.

The solvent is left to penetrate into the resin matrix and extract this soluble portion. The results from the Sol-Gel analysis are shown in Tables 3.15 (soluble portion of resins) and 3.16 (insoluble portion).

	Benzoyl Peroxide		Dicumyl	Peroxide		
	2% w/w	3% w/w	2% w/w	3% w/w	2% w/w	3% w/w
80°C 16hrs/120°C 5 hrs	28.48%	24.27%	4.95%	4.60%	17.00%	15.98%
80°C 16 hrs/135°C 3 hrs	18.06%	17.26%	3.25%	3.17%	15.95%	15.05%
80°C 16 hrs/135°C 5 hrs	17.52%	15.53%	3.65%	3.04%	14.65%	13.56%
90°C 16 hrs/135°C 5 hrs	16.25%	16.21%	2.95%	3.21%	15.34%	15.32%
90°C 16 hrs/ 120°C 3 hrs	27.45%	25.52%	5.77%	3.96%	18.94%	17.56%
100°C 16 hrs/140°C 5 hrs	16.10%	14.23%	3.00%	5.00%	13.26%	13.54%

 Table 3.15: Percentage soluble material determined by Sol-Gel analysis

	Benzoyl Peroxide		Dicumyl Peroxide		AZBN	
	2% w/w	3% w/w	2% w/w	3% w/w	2% w/w	3% w/w
80°C 16hrs/120°C 5 hrs	72.35%	79.00%	95.02%	96.32%	83.52%	85.21%
80°C 16 hrs/135°C 3 hrs	82.75%	81.99%	96.52%	95.98%	85.00%	85.29%
80°C 16 hrs/135°C 5 hrs	84.23%	86.87%	97.45%	96.50%	86.54%	82.96%
90°C 16 hrs/135°C 5 hrs	85.31%	85.62%	93.56%	95.25%	86.23%	86.43%
90°C 16 hrs/ 120°C 3 hrs	71.65%	74.63%	95.87%	97.67%	81.96%	82.85%
100°C 16 hrs/140°C 5 hrs	85.64%	87.59%	96.34%	94.67%	87.36%	86.48%

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Table 3.16: Percentage insoluble material determined by Sol-Gel analysis

The first thing to notice from these results is that the combined totals for the soluble and insoluble portion do not add up to 100% exactly. There are several reasons for this which mainly lie with the crudity of the experiment. Firstly, the cured polyester is less dense than the dichloromethane so it floats on the surface of the liquid. When the solution was agitated the resin had the tendency to remain stuck on the sides of

the tube. The results of this was that not all of the weighed resin was used 100% of the time in the test. This meant that not all of the soluble portion was extracted from the resins in all cases. In an attempt to compensate for this the samples were left in solution longer and shaken less frequently. This gave roughly the same results as before. The ideal method for this extraction would be to use a Soxhlet extraction system. In this case the samples could be heated to expedite the extraction of the soluble portion. Another advantage would be that the samples would not need to be shaken as the dichloromethane would be continuously dripped down onto the samples. The reason why the soxhlet was not used was because of the sheer number of samples involved. There were essentially too many samples and too few soxhlet extractors available for use. Despite this the results can be regarded as a good representation of the extent of cross-linking in the resins. The results clearly show that BPO and AZBN do not produce an adequate degree of cure in the resins. Acceptable degrees of cure are when there is 5% or less soluble material left in the resins. Dicumyl peroxide, on the other hand, shows an excellent degree of cure, especially when cured at 80°C for 16 hrs and then post cured for 5 hours at 135°C. The conclusion drawn from this testing was that this initiator with these cure conditions should be adopted as the standard method for curing the new resin.

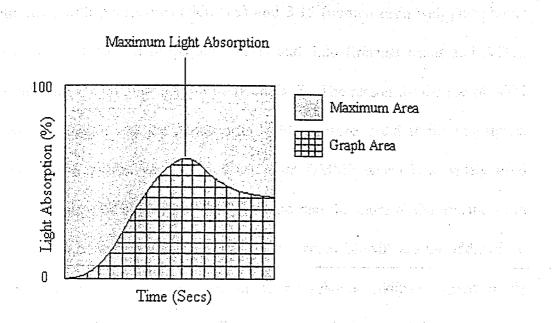
3.3 Smoke Testing Results

The smoke testing was carried on separate occasions during the project. Initially only resins treated with DMMP were studied and then at a later stage resins with TEP were studied. It was found that the results differed quite markedly. These results are

shown in Appendix E (Table E1 and Figs. E1 - E4 refer to results from testing with DMMP and Table E2 and Figs. E5 - E8 refer to testing with TEP). This was assumed to be because of a fault with the light bulb for the photometer which resulted in a new bulb being inserted into the apparatus. This bulb was unfortunately not exactly of the same type as the old bulb which could no longer be obtained. In addition to this, there seemed to be some problems in achieving a satisfactory flame at times during the testing. To try and compensate for these discrepancies in testing, the samples were prepared, cured and post-cured at the same time under exactly the same conditions. The samples were then tested as quickly as was possible. The results are shown in Appendix F.

3.3.1 Treatment of Data

As well as recording the time to flame extinction and the maximum light absorption (this is taken to be the highest point on the graph), the smoke density rating and the amount of smoke evolved per gram of sample burnt were also calculated. The smoke density rating is calculated by dividing the total area under the graph by the maximum possible graph area, i.e. the area given by a maximum 100% light absorption for the entire four minutes of the test and multiplying this figure by 100 to get a results in percent, see Fig. 3.7. The smoke per gram of sample is calculated by dividing the area under the graph by the number of grams of sample consumed during the test.



Smoke Index Rating = (Maximum Area ÷ Graph Area) x 100

Fig 3.7: Typical YT plot for smoke evolution showing maximum light obscuration point and calculation for Smoke Index Rating.

It may appear, at first glance, that the units for the total smoke evolved and the smoke evolved per gram or resin burnt are rather peculiar, being in seconds and seconds/g respectively. The reason for this is that units for the area under the graph and the total maximum area are a function of both the Y-axis and X-axis units. As the Y-axis is given as % it has no real units to use. The graph area can, then, only be expressed as a function of the X-axis units which is seconds. It must be stressed that this does not refer to a time or a definite quantitative amount of smoke. Rather, it gives a point of reference in comparing values from different samples. In this case the maximum graph area is taken to be 24000 seconds. This is calculated from 60 seconds x 4 (the length of the test is 4 minutes) x 100 (maximum % value - this has no units). The results obtained when the samples were tested together are shown in Tables 3.17 (aliphatic resin with phosphorus additives) and 3.18 (normal resin with phosphorus additives), 3.19 (styrenated resins and ATH) and 3.20 (triazine resins and ATH). These results are shown graphically in Appendix F. The reason for the use of ATH ties in with the reason why the phosphorus additives were tested at differing times. The initial smoke studies were carried out with DMMP which is a widely used additive for unsaturated polyesters. It was found that the more of the triazine resin was consumed in the test than the styrenated resin when DMMP was the additive. It was, therefore, decided to use a different phosphorus additive, which might conceivably reduce flammability as well as trying an additive which has been shown to reduce both flammability and smoke, in this case ATH. The results are shown graphically in Appendix F (graphs F1 - F18).

The smoke testing results, initially, show two things about the production of smoke as a result of the constituents of the resins. These are the contributions to the total smoke caused by styrene and phthalic anhydride. In the aliphatic resins the phthalic anhydride was replaced by adipic acid which has no benzene ring. In the triazine resins the styrene is replaced. Graphs F2 and F7, in Appendix F, show the amount of smoke per gram of resin burnt for the normal resins and the aliphatic resins respectively. These results are also shown in Table 3.17 and 3.18. It can be seen that on average the normal resins with styrene and no additives produces 3602 sec per gram of smoke. The equivalent aliphatic resins produce, on average, 2353 sec per gram smoke. This is a reduction of about 35%. It can, then, be said that 35% of smoke produced in the normal resin is caused by phthalic anhydride. It must be stressed, at this stage, that this figure for the amount of smoke produced by the phthalic anhydride is not an exact figure.

	T	i	1			
Sample	Tmax (sec)	ODmax (%)	Total smoke	Sample	Smoke/g	Smoke
			(sec)	Consumed	(sec/g)	Density
			· · · · · · · · · · · · · · · · · · ·	(g)		Rating (%)
SAD01	144	76.3	10110	3.88	2605	42.12
SAD02	160	86.3	11125	3.14	3543	46.35
SAD03	188	86.0	10110	3.27	3092	42.12
SAD04	172	76.3	10125	2.95	3432	42.18
SAD05	140	38.3	5365	2.80	1916	22.35
SAD06	140	40.0	5845	2.60	2248	24.35
TAD01	190	27.3	3440	2.98	1154	14.33
TAD02	176	30.0	3670	3.31	1109	15.29
TAD03	200	26.3	3210	2.95	1088	13.38
TAD04	196	36.7	3785	3.86	981	15.77
TAD05	187	32.4	3231	3.52	919	13.46
TAD06	195	30.2	3000	2.94	1020	12.50
SAT01	160	79.0	10140	3.84	2641	42.25
SAT02	156	85.3	10765	3.25	3312	44.80
SÁT03	156	290.3	12730	3.05	4174	53.04
SAT04	168	88.3	11745	3.23	3636	48.90
SAT05	152	59.3	7855	2.76	2846	32.73
SAT06	180	43.0	5950	2.31	2576	24.79
TAT01	186	30.5	3630	2.75	1320	15.12
TAT02	184	28.7	3240	3.40	953	13.50
TAT03	196	30.0	3590	4.23	849	14.96
TAT04	168	32.7	4210	3.09	1363	17.54
TAT05	162	29.1	4231	2.85	1485	17.63
TAT06	164	28.1	4031	2.91	1385	16.79

Table 3.17: Results from direct comparisons between aliphatic resin with either triazine monomer or styrene monomer and treated with either TEP or DMMP.

Sample	T _{max} (sec)	OD _{max} (%)	Total Smoke (sec)	Sample Consumed	Smoke/g (sec/g)	Smoke Density
				(g)		Rating (%)
SND01	128	98.0	15250	4.31	3583	63.54
SND02	136	97.0	14955	3.24	4616	62.31
SND03	148	94.0	13775	3.77	3652	57.38
SND04	168	89.0	11685	3.56	3283	48.69
SND05	124	93.3	13820	3.28	4214	57.58
SND06	112	91.3	13670	2.74	4989	56.96
TND01	152	46.7	6575	4.16	1581	27.39
TND02	138	52.0	7512	3.38	2223	31.30
TND03	156	53.7	8505	4.00	2126	35.44
TND04	120	59.7	8370	3.06	2735	34.88
TND05	135	60.3	8420	3.26	2583	35:08
	129	58.7	8129	3.54	2296	33.87
SNT01	2148	98.3	14560	-4.02	3621	60.66
SNT02	136	97.7	14550	3.44	4248	60.62
SNT03	152	96.0	13830	3.06	4520	57.62
SNT04	112	91.0	13255	2.66	4983	55.23
SNT05	128	78.7	11365	2.73	4163	47.35
SNT06	132	75.5	11175	2.86	3908	46.56
TNT01	132	53.0	8175	4.39	1863	34.06
TNT02	140	47.7	7055	4.36	1618	29.39
TNT03	96	58.0	8875	4.03	2202	36.98
TNT04	132	48.0	7508	4.25	1766	- 31.28
TNT05	. 120	49.2	7259	3.97	1828	30.25
	132	50.3	7356	4.01	1834	30.65

Table 3.18:Results from direct comparisons between normal resin with eithertriazine monomer or styrene monomer and treated with either TEP or DMMP.

Sample	T _{max} (sec)	OD _{max} (%)	Total smoke (sec)	Sample Consumed	Smoke/g (sec/g)	Smoke Density
	14			(g)	<u>.</u>	Rating (%)
SNA01	240	61.3	5155	4.77	1081	21.48
SNA02	240	38.6	3245	4.48	724	13.52
SNA03	240	47.0	3525	1.42	2482	14.69
SNA04	240	54.6	5300	5.18	1023	22.10
SNA05	240	32.0	2880	4.62	623	12.00
SNA06	240	47.5	3323	1.05	3164	13.84
SNA07	240	48.7	4075	5.36	760	16.98
SNA08	240	33.3	2665	4.66	573	11.52
SNA09	240	30.0	1680	1.42	1289	7.00
SNA10	240	51.0	4610	5.26	876	i9.20
SNA11	240	34.0	2875	4.33	664	11.98
SNA12	240	40.2	2363	1.53	1544	9.85
SAA01	228	20.1	3785	4.53	836	15.77
SAA02	240	19.3	1660	3.28	506	6.91
SAA03	234	28.6	2210	2.04	1083	9.21
SAA04	216	23.0	1898	4.42	429	7.91
SAA05	240	23.7	2335	3.54	660	9.73
SAA06	240	20.0	1320	2.78	475	5.50
SAA07	240	18.3	1375	4.46	308	5.73
SAA08	240	20.0	1595	2.78	573	6.64
SAA09	240	31.5	2055	2.80	734	8.56
SAA10	240	21.3	1455	4.51	323	6.06
SAA11	228	22.7	1784	2.94	607	7.43
SAA12	240	25.0	1780	2.87	620	7.42

Table 3.19: Results of smoke testing from styrenated resin samples with ATH and viscosity additives

Sample	T _{max} (sec)	OD _{max} (%)	Total smoke	Sample	Smoke/g	Smoke
	a de la ser ser	Nard Congr	(sec)	Consumed	(sec/g)	Density
				(g)		Rating (%)
TNA01	240	38.6 (1997)	6401 6 (199	3 .98 (2011)	100 <u>9</u> , 1009, 1983, 1	16.73
TNA02	240	29.5	2932	4.12	712 1997 - 1997 - 1997	12.21
TNA03	240	30.1	2982	2.01	1484	12.42
TNA04	240	25.0	3652	4.23	863	15.21
TNA05	240	22.1	2596	3.56	729 · · · ·	16.60
TNA06	240	28.6	2365	0.99	965	9.85
TNA07	240	27.3	3521	3.65	965	21.34
TNA08	240	24.7	2410	3.25	741	10.04
TNA09	240	22.9	1420	1.62	876	5.92
TNA10	240	27.4	19950 and 19950 and 1995	1	788	19.09
TNA11	240	21.9	2356	3.25	728	9.82
TNA12	240	21.8	1562	1.36	1148	6.51
TAA01	240	14.6	2987	5.23	571	12.44
TAA02	240	14.2	1420	4.32	- 328	5.92
TAA03	240	12.8	1565	2.51	623	6,52
TAA04	240	16.1	1253	3.41	367	5.22
TAA05	240	14.8	1352	1.65	819	5.63
TAA06	240	13.2	943	1.98	476	3.93
TAA07	240	20.6	1032	ti 3.89	265	4.3
TAA08	240	17.4	1348	2.65	508	5.62
TAA09	240	17.8	1432	1.98	723	5.97
TAA10	240	11.8	923	2.97	310	3.84
TAA11	240	14.7	1241	1.98	626	5.17
TAA12	240	19.4	631	1.02	618	2.63

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Table 3.20: Results of smoke testing from triazine resin samples with ATH and viscosity additives

The reason for the discrepancy lies with the fact it has been assumed that each component produces an exactly proportionate amount of smoke during combustion. This is not necessarily the case as the benzene rings might somehow interact within the network to produce more smoke than would otherwise be produced. The use of the smoke per gram resin burnt in this comparison is to compensate for discrepancies in the burning behaviour of the resins caused by slightly varying conditions within the smoke chamber which result in differing amounts of the resins being burnt. This leads to anomalous amounts of smoke being produced. As about the activity of the Looking at the effect of styrene on the overall smoke production of the resins it must be stated that the same principle applies to the effect caused by styrene as for phthalic anhydride. It must also be said that the triazine ring will also produce a certain amount of smoke. In the case of the normal resins (Graph F2 and Table 3.18) the styrenated resins produce, on average, 3602 sec per gram of smoke compared to 1722 sec per gram for the triazine resins. This is a reduction of about 52%. In the case of the aliphatic resins (Graph F7 and Table 3.17) this reduction is in the order of 53%. Again this appears to be disproportionate as the styrene only contributes 35% to the styrenated resins. The reason why such a large reduction is seen could lie with the fact that the triazine ring accounts for between 55 - 60% of the resins as opposed to 35%. This could lead to a larger reduction than would be expected because less of the other carbon rich components are present in these resins.

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It is now important to discuss the effects of phosphorus and resin flammability on the smoke production of the resins. Looking at the normal resins first (relating to Graphs F1 - F5 and Table 3.18) the first item to consider is the total amount of smoke produced from the burning polymer as this is more indicative of the true smoke

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behaviour of the resin. For this analysis the data as shown on graphs F1 and F3 are needed. Initially, with no phosphorus additives present, the triazine resins give a smoke reduction over the styrenated resins of about 52%. This is reduced to an average of 38% at 10% loading levels of phosphorus additives. The reason for this is that at these higher phosphorus loading levels the flammability of the styrenated resin is reduced considerably. On average 33% less of the sample is consumed at 10% additive level than when no phosphorus is present. In the case of the triazine resins the effect of the phosphorus on the flammability is negligible. On average only 12% less sample is consumed at 10% additive loading level than at 0% additive loadings. This shows that the amount of smoke produced is heavily dependent on the amount of resin burnt. When a sample chars due to the presence of a flame retardant additive less flammable material is available for smoke production. These results also show that the phosphorus is having very little flame retardant effect on the triazine resins. In general it can be seen that the presence of TEP or DMMP causes no major increase in the amount of smoke produced. TEP does, however, seem to reduce the amount of smoke produced in both types of resin, very slightly, over the DMMP. Graph F2 takes into account the amount of resin actually burnt. The untreated triazine resins produce an average of 52% less smoke than the untreated styrenated resins. At the higher loading levels of phosphorus the smoke reduction caused by the triazine ring is around 53%. This is constant with the untreated resins. Once again, it appears that at higher additive loading levels the TEP treated resins produce less smoke than the DMMP treated resins.

Graph F4 shows that the maximum light obscuration caused by the smoke produced from burning the untreated triazine resin is about 49% less than that from the

untreated styrenated resin. The importance of this is that in a real fire situation one major obstacle to escape is the blackness of the smoke. If, then, smoke produced from a burning resin does not obscure vision the escape would be easier. At the higher end of the additive scale this reduction falls to 35%. This change in reduction of light obscuration can be caused by one of two effects. The first of these is that at the higher loading levels of phosphorus less smoke is produced from the burning resins which leads to a subsequent reduction in light obscuration. The second possible cause for this phenomenon is that, in a system like this one, light obscuration is a function of particle size. Smaller particles scatter light more than larger particles and so would show a higher light obscuration. It is conceivable, then, that a system which produces less smoke of smaller particle size would show a higher light obscuration value than a system which produces large smoke particles.

The final graph (Graph F5) relating to the normal resins shows that, in most cases, the time taken for the untreated triazine resins to reach maximum light absorption is longer than the equivalent styrenated resins. When phosphorus is present in the resins, however, this is not the case and the styrenated resins take longer to reach maximum light absorption. The importance of this only becomes clear when this fact is considered along with the fact that, in all cases, the triazine resins took longer to start producing smoke during the test. It is clear, then, that once these resins start burning they do so very quickly, producing an initial rush of smoke evolution. The culmination of the results from the smoke testing of the normal resins is that the triazine resins reduce smoke production by up to 53% over the styrenated resins. The problem is that at higher additive loading levels the styrenated resins burn less and so produce less smoke. This effect, however, is not seen in the triazine resins which

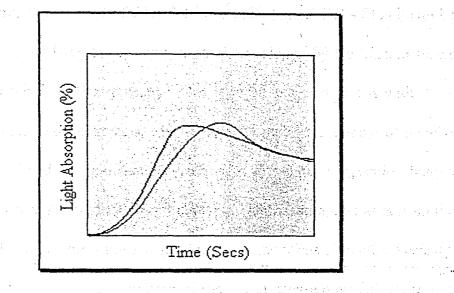
burn to roughly the same extent irrespective of the amount of phosphorus present and therefore do not show an appreciable reduction in smoke evolution over the additive content range. This combined with the fact that the triazine resins appear to produce smoke at a considerably quicker rate than the styrenated resins means that the advantages gained by incorporating the triazine ring into the normal resin are reduced by the rapid smoke production when phosphorus is added to the resins.

In considering the effect of the triazine ring and the addition of the phosphorus to the aliphatic resins, the same consideration are going to be taken into account as for the normal resins (Graphs F6 - F10 and Table 3.17). Again looking initially at the total smoke evolution from the resins (Graph F6) it is clear that the triazine resins show considerable advantages over the styrenated resins when no phosphorus is present. This is shown by a reduction in smoke evolution by the triazine resins of 65% over the styrenated resins. This advantage is increased, in the case of the triazine resins treated with TEP, up to 5% loading levels. In the case of the DMMP additive the overall reduction stays fairly constant. At 7% phosphorus additive levels there is a marked difference in the smoke production of the styrenated aliphatic resins. The smoke evolution is reduced from an average of about 10935 sec to as low as 6610 sec. This reduces the difference in smoke evolution between the two resins to about 40%. This can be attributed to the fact that at these higher loading levels the flame retardant effects of the additives is increased to such an extent that much more char is produced and so a subsequent reduction in smoke evolution occurs. This is shown by the fact that less of the samples containing the higher additive levels are consumed during the test. Saying this, however, the difference in sample consumption is much less marked from loading levels of 3% onwards. This, then, would seem to negate the theory that the reason for low smoke production comes predominantly from the reduction of sample consumption. It must be considered, in this argument, that the char in these resins does not contribute a great deal of weight to the remaining sample but do retain the carbon rich backbone in the sample so preventing smoke production. Allowing for this it is safe to say that a large reduction in smoke could be achieved whilst only reducing the sample consumption by about 0.5g.

Graph F7 shows the amount of smoke evolved from the resins whilst taking into account the amount of sample consumed. With no phosphorus additive present the triazine resins reduce the smoke evolved per gram or resin by about 53% over the styrenated resins. Again this reduction is constant up to loading levels of 3% additive. At loading levels greater than this the styrenated resins produce much less smoke per gram of resin burnt. This reduction in the smoke, at these levels for the styrenated resins, is much greater for resins treated with DMMP. This can also be said for the triazine resins which show a reduction in smoke evolution with increasing DMMP content. At additive levels of 7% and above the reduction of smoke evolved caused by the introduction of the triazine ring is 52% for the triazine resin with 7% DMMP, 48% for triazine resin with 7% TEP, 55% for the triazine resin treated with 10% DMMP and 46% for the triazine resins treated with 10% TEP. This shows that, although there is a reduction in the advantage gained by using the triazine monomer rather than styrene when phosphorus is present, the triazine resins still perform considerably better in terms of smoke production.

In terms of maximum light obscuration (Graph F9) it appears that the triazine resins cause considerably less light to be obscured than the styrenated resins at additive levels of 0 - 5%. This manifests itself by the triazine resins only obscuring 36% light

whereas the styrenated resins obscure a maximum of 88% light. At loading levels of 7% and above the styrenated resins obscure much less light. In the case of the resins treated with DMMP the difference in light obscuration between the two resins types drops to 6% at 7% DMMP and 10% at 10% DMMP. In the case of TEP, however, the light obscuration difference is 30% at 7% TEP and only 15% at 10% TEP. It could be assumed that this reduction in light obscuration is a direct result of the drastic reduction in total smoke evolved from the styrenated resins. This phenomenon of reduced smoke evolution is not seen in the triazine resins so the overall differences in light obscuration would be reduced. If this were the case, however, one would expect this difference to be in line with the change in total smoke evolved. As has been discussed, there is a 46 - 55% reduction in smoke evolution from the triazine resins over the styrenated resins at these higher phosphorus levels. Another anomalous effect is that the triazine resins treated with TEP show improved performance in terms of maximum light obscured but poorer performance in term of total smoke evolved than the DMMP treated resins. These effects can be explained when one considers the data shown in Graph F10 which shows the time to maximum light obscuration. At additive levels of 3% and above, the triazine resins treated with DMMP take much longer to reach maximum light absorption than those treated with TEP. The resins treated with TEP could, then, have a lower maximum but still produce more total smoke. This principle can also be applied to the comparison between the triazine resins and the styrenated resins. In general the styrenated resins reach maximum light absorption more quickly than their triazine equivalents. It is possible that the total smoke evolved could be very different even though the light obscuration values are relatively close together (Fig. 3.8).



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Fig. 3.8: Schematic representation of area differences caused by varying maximum values and the respective times to reach the maximum.

It can be clearly seen that the area mapped under the red line is larger than the area mapped under the black line even though the black graph has a higher maximum point.

The use of ATH was deemed useful as it was thought that this would give an indication as to how the triazine resins would behave in terms of smoke evolution when effectively fire retarded. It must be stressed here that these results can in no way be directly compared to the results obtained from the smoke testing with phosphorus. This is because, in all cases where ATH is added, the amount of resin actually available for burning is anywhere from 33% to 50% less than was available in the testing with phosphorus as the additive. The results are shown in Tables 3.19 and 3.20 as well as graphically in Appendix F as Figures F11 - F18. Taking this into account it is obvious that the resins containing ATH will produce less smoke than the resins not containing ATH.

Looking at the normal resins first (Tables 3.19 and 3.20, Figures F11 - F15) it can be seen that in general the largest reduction in smoke evolution by the triazine resins occurs when only 50phr ATH is present. This is to be expected as it is with these samples that the most resin is present. In the other samples the amount of resin is sequentially reduced and so the effective differences in sample composition have a smaller effect on the smoke production of the resin. The first surprise comes from the fact that at 100 phr ATH more smoke is produced, for the resins containing viscosity additive 966, than for the samples containing 75phr. The reverse is actually expected. This suggests that this additive acts to produce more smoke. Again, surprisingly, the amount of smoke evolved per gram of resin for all samples containing 100 phr ATH is more than that for samples containing 75 phr. This is particularly curious when one considers that in excess of 66% less of these samples are consumed during the test than samples containing 75 phr. This seems to indicate that at higher loading levels the ATH actually gives rise to more smoke being produced. This could be a result of the ATH causing more heat to be radiated away from the resin and so causing more incomplete degradation of the resin and so leading to more smoke. Once again samples containing the 966 viscosity additive produce more smoke than those with the 980 additive. Surprisingly some of the triazine resins produce more smoke per gram of sample than the styrenated equivalents. One reason for this could be a lack of complete sample homogeneity. If, for example, there were areas of the samples which, due to inadequate mixing or sedimentation of the ATH, had a lower concentration of ATH then these areas would be relatively resin rich. If these areas were exposed to the flame then more smoke would be produced. This is entirely

possible as some sedimentation of the ATH did occur with the triazine resins due to their prolonged cure time and reduced viscosity at high temperatures.

As is expected the maximum light obscuration (Graph F14) obtained from the triazine resins is less than that from the styrenated resins, with the largest reduction being observed at 50 phr ATH. Overall the amount of smoke produced from all the resins treated with ATH is less than the untreated resins. In the case of the 50 phr samples this reduction would be expected to lie in the region of 33% because the amount of resins present has been reduced by 33%. The actual value, using smoke per gram sample consumed data, is 70% for the normal styrenated resins and 43% for the normal triazine resins. In both sets of testing the amount of sample consumed is roughly equal so the reason for this cannot lie with the fact that less sample was consumed. Rather this indicates that ATH is being consumed during the test whilst not contributing to overall smoke evolution. It is perhaps more accurate to say that the ATH is decomposing to release its water content.

Very much the same smoke behaviour is seen with the aliphatic resins treated with ATH (Table 3.19 and 3.20, Figures F15 - F18). There appears to be no readily discernible pattern to total smoke evolution of the various resins (Graph F15) apart from the fact that the triazine samples produce less smoke than the equivalent styrenated samples. The amount of smoke per gram of resin burnt (Graph F16) also appears to have no real pattern save to say that in general there is little reduction, if any at all, in smoke evolved per gram of the triazine samples burnt over that produced per gram of the styrenated resins burnt.

In terms of maximum light obscuration it can be seen from Graph F17 that in all cases, except one, the maximum light obscured by the styrenated resins is greater than

that obscured by the triazine samples. From a detailed knowledge of the sample preparation it must be assumed that the discrepancies observed in the behaviour of the triazine resins lies solely with the sedimentation of the ATH and the subsequent lack of homogeneity in the triazine samples. As the use of ATH in the triazine samples is so problematic it is clear that this fire retardant additive may be of little practical use in this system. On top of this lack of compatibility comes the fact that the triazine resin on its own delivers a far greater improvement over the styrenated resins when no ATH is present. In general then, if ATH were to be used there is no great benefit in using the triazine monomer in the resin rather than styrene regarding smoke production.

Summarising the results it is clear that the triazine resin considerably reduces the amount of smoke produced during combustion in comparison to the styrenated resins. This reduction, however, is on a smaller scale when phosphorus is added to the resins because of the fire retardant effect of the phosphorus on the styrenated resins. This causes charring in the resins which retains the carbon rich, smoke producing components in the char. This fire retardant effect is not observed in the triazine resins.

Another problem observed with the smoke testing is that the test itself is inherently unreliable as far as giving exact quantitative amounts of smoke. There are several reasons for this. Such reasons include the deposition of soot on the light source and photometer which prevents light from passing through to the photometer and so would give a higher total smoke value. Secondly the chamber was not completely air tight and so small quantities of smoke were occasionally lost during the tests. Unfortunately this loss cannot be assumed to be a constant which could also lead to

misleading smoke results. Thirdly, the total smoke reading in a system like this is entirely dependent on the amount of light passing through the chamber from the light source to the photometer. This in turn depends on the smoke particle size. It is known that smaller particles scatter light more than larger particles, so a certain amount of small particles will scatter light more than the same amount of large particles. In this situation the smaller particles will show a larger smoke production than the large particles even though this is not the case.

The final major problem with this test is the fact that it only subjects the samples to a single heat flux. It has been identified that smoke production changes dramatically with varying heat fluxes (205). This test, then, does not allow the researcher to discover how the resins will behave with varying heat fluxes. A more useful test would include measures to combat all these problems. This would include a dynamic style test where the smoke is swept along in a stream of air. This would prevent the deposition of soot on the optical system. Secondly, if the soot was then carried through a pre-weighed filter then the total mass of smoke could be measured. This would give a much more quantitative measurement of the total amount of smoke produced. Such a system would have little or no smoke loss due to leaks and holes in the system. Finally, the sample could be placed in a tube through a tube furnace which was capable of placing the sample under varying temperature conditions and so varying the heat flux to the sample. A very similar system has been invented by Whitely (206) with only the filter excluded from the test (Fig. 3.9).

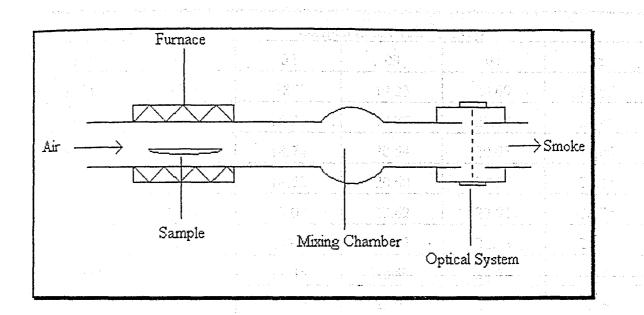


Fig. 3.9: Schematic representation of improved smoke testing chamber.

Despite the criticisms of the smoke chamber used it must be clarified that the smoke chamber conforms to an accepted standard test for smoke production and that it gives reasonable qualitative comparisons between samples.

3.4 Fire Testing Results

3.4.1 LOI Testing

The results from the limiting oxygen indexing testing are shown in Tables 3.21 (resins with TEP or DMMP), 3.22 (resins with TPP), 3.23 (resins with melamine) and 3.24 (resins with TCEP). These are represented graphically in the Appendix as Graphs G1 - G8.

	Oxygen Index Value (% O ₂)						
Sample	01	02	03	04	05		
SAFD	23.9	18.7	19.23	20.09	21.65		
SAFT'	18.23	18.26	19.27	20.18	21.88		
SNFD	18.17	18.74	20.54	20.93	23.65		
SNFT'	18.04	18.52	20.60	21.20	23.15		
TAFD	23.34	23.09	22.62	- 22.91	22.75		
TAFT'	22.99	23.01	22.63	22.53	23.20		
TNFD	21.01	21.35	22.56	22.74	23.75		
TNFT'	22.51	21.40	22.65	22.77	23.60		

Table 3.21: LOI Results from fire testing with TEP and DMMP

Oxygen Index Value (% O ₂)						
01	02	03	04	05		
18.21	18.83	19.62	20.25	22.42		
18.15	18.52	19.51	20.30	22.00		
22.51	22.76	22.65	22.81	23.64		
22.67	22.83	22.91	23.29	23.72		
	18.21 18.15 22.51	01 02 18.21 18.83 18.15 18.52 22.51 22.76	01 02 03 18.21 18.83 19.62 18.15 18.52 19.51 22.51 22.76 22.65	0102030418.2118.8319.6220.2518.1518.5219.5120.3022.5122.7622.6522.81		

 Table 3.22: LOI Results from fire testing with TPP

	Oxygen Index Value (% O ₂)						
Sample	01	02	03	.04	05	e tak 06 - K	
SAFMD	19.3	21.4	19.9	23.3	24.8	26.9	
SAFMT'	19.5	21.7	20.6	23.5	24.9	26.5	
TAFMD	23.6	25.6	23.5	25.9	24.5	26.6	
TAFMT'	22.9	25.3	23.9	25.8	24.2	26.7	

Table 3.23: LOI Results of fire testing with varying amounts of melamine and phosphorus additives.

	on and a state of Oxygen Index Value (% O ₂) and taken state data					
Sample Series	01 ⁻¹⁰ -10	executiona 02 disease a		1944 - 1944 - 1949 -		
SAFC	18.3		1999 20.9 - 1997	22.8		
SNFC	18.4	18:9	1995 (199 21.4 88 - 1997)	22.7		
TAFC	22.6	24.9 (1993) 24.9	25.1	24.5		
TNFC	21.6	21.75	24.8	26.1		

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Table 3.24: LOI Results for fire testing with TCEP additive.

The first thing to notice from these tests is that there is very little difference in flammability between the aliphatic and normal resins. In general some testing shows the untreated normal resins to be more flammable and some show the untreated aliphatic resins to be more flammable. The reasons for this probably lie with slight temperature fluctuations within the LOI chamber. If the temperature is not kept constant for each test then varying results will be obtained. This is because resins become more flammable at higher temperatures. This stems from the fact that degradation of the resins is more rapid at higher temperatures and so combustion becomes easier. It can be assumed that there is little or no difference in the flammability between the normal and aliphatic resins.

The second obvious deduction from these results is that the untreated triazine resins show on average a 4-5% increase over the equivalent styrenated resins as far as LOI value is concerned. Technically, from these results, the triazine resins should be selfextinguishing under normal atmospheric conditions. This is shown by the fact that

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the triazine resins have an LOI values greater than 22%. As the atmosphere only contains 21% oxygen, which is a lower value than is required for the triazine resins to sustain combustion, the triazine resins will self-extinguish. This does not mean that these resins will not ignite and it does not imply that the self-extinction of the flame is nearly instantaneous, rather it means that these resins will self-extinguish eventually although the time scale of this cannot be determined from this test. A standard of house the Table 3.21 and Graphs G1 and G2 show the testing of the normal and aliphatic resins respectively treated with either TEP or DMMP. There appears to be very little difference in the relative fire retardant effects of DMMP and TEP when used in the normal resins. Each seems to improve the LOI value by an equivalent amount. The most important observation is that the presence of the phosphorus has very little effect on the flammability of the triazine resin. The increase in LOI value from 0% additive to 20% additive is on average only 1.9%. For the styrenated resins this increase amounts to 5.3% giving an LOI value for these resins which is roughly equal to the triazine resins. It is conceivable that at higher loading levels of the phosphorus additives the LOI value for the styrenated resins would exceed that of the triazine resins. This gave an early indication that the phosphorus has no real fire retardant effect in the triazine resins and that there is no synergism between the phosphorus and the amine group as might have been expected. Indeed there is no effective additive effect between the triazine ring and the phosphorus either. This latter observation is also shown by the fact that the graph of LOI vs additive content for the triazine resins is a straight line (Graphs G1 and 2, yellow and light blue lines). If synergism were present then this line would curve away from the X-axis with a tailing effect at higher phosphorus levels. The line for styrenated resins is also, within experimental error

limits, a straight line (Graphs G1 and 2, dark blue and red lines). This is to be expected as the fire retardant effect is dependent on the phosphorus content concentration and gives a linear response. It would be expected that, at higher additive loading levels, the line would tail off as the maximum fire retardant effect is achieved.

These observations are also seen in the aliphatic resins. It must be stressed here that the first point on the SAFD series line is an anomaly and can be discounted as being inaccurate. Again it is observed that the styrenated resins have a higher LOI value at high additive loading levels than at low loading levels. This is again not observed with the triazine resins. One slightly encouraging observation is that at 20% additive levels the triazine resins still have a 1 - 1.5% advantage in limiting oxygen index values over the styrenated resins. Again no additive effect is seen in the triazine resins. This, as explained earlier, means that the phosphorus additive is somehow being swamped in the triazine system.

It was initially thought that, because the DMMP and TEP had such relatively low boiling points, they were evaporating from the triazine resins during the high temperature cure. To test this theory an additive with a high boiling point was used. This was triphenyl phosphate. It was thought that, as this additive had such a high boiling point, it would not evaporate during cure and would then give improved LOI results. The results in Table 3.22 and on Graph G3 show that this does not occur. Instead of the expected effect of increased LOI values for the triazine resins there is no real increase in LOI values as was seen with the other phosphorus additives. This indicates that evaporation of the additive from the resin is not the reason for the lack of fire retardant effects.

The testing with melamine was carried out to test the theory that the basicity of the amine group attached to the triazine ring was inhibiting the acidic fire retardant effect of the phosphorus additives. If this were the case then the incorporation of the melamine, which has three basic amine substituents, into the styrenated resins with phosphorus would inhibit the fire retardant effect of the phosphorus and so reduce the LOI values at higher phosphorus additive levels.

The first factor for comment is the fire retardant effect imparted by only incorporating the melamine. Table 3.23 and Graph G4 shows the results from adding melamine so that 1.87% nitrogen is added to the systems. Graph G6 shows these results compared to the results obtained from testing the same resins without melamine. The first thing to notice from this graph is the increase in LOI values, for the two resins, caused solely by melamine. This is shown by the increase at 0% P additive level. For the styrenated resins the melamine causes an increase of just over 1% in the LOI value compared to the resins with no melamine. For the triazine resins this increase is much less pronounced and is on average 0.1%. At 1% loading levels of the phosphorus additives the increase in LOI for the styrenated resins treated with melamine, compared to those with no melamine, rises to an average of 1.8%. This increase is slightly more than would be expected if only an additive effect were in action between the melamine and the phosphorus additives. If the additives were acting additively it would be expected that the rise is LOI value at the 1% phosphorus additive level, for the resins with melamine, would only be just over 1%. This is exactly the same as the increase caused by melamine alone. The extra increase in LOI value could, however, be caused by slight experimental error and is by itself inconclusive proof for any mild form of synergism.

At 10% phosphorus additive levels the melamine-containing resins show a very large increase in LOI value over the resins with no melamine. This increase is 3%. This is a 2% increase over the expected value, assuming additivity. The triazine resins show the same sort of behaviour with the LOI value increasing disproportionately to the expected additive increase. This increase is 1% at 1% phosphorus additive and 1.4% at 10% phosphorus additive levels. These results lead to two important observations, the first of which comes from relatively poor LOI increase for the triazine resins with melamine. In the case of Graph G4 the melamine is present at 1.87% w/w of the total resin. The structure of melamine is very similar to that of the triazine monomer and so can be assumed to act in much the same way in terms of fire retardant effect within the resin. This small increase in the triazine type fire retardant (as melamine) when compared to the fact that the triazine monomer already makes up about 55% of the total resin is relatively insignificant and such a large increase in LOI value would not be expected.

The second observation of importance to arise from these results is the disproportionate increase in LOI value seen in the melamine-treated resins. This indicates that there is indeed some synergism occurring between the melamine and the phosphorus additives. This synergism is more than likely between the amino substituents on the melamine and the phosphorus additive. It is possible that the methoxy or ethoxy groups on the phosphorus additives are becoming bonded to the amino groups on the melamine. This is very similar to the mode of synergy as seen in poly(acrylamides) with phosphonate-type additives. If this is the case then it proves that the basic nature of the triazine monomer is not the reason for the phosphorus additive having no effect in the triazine resins. In fact the graph shows that in the

triazine resins with melamine the phosphorus is having an increased effect on the LOI value of the resins. The results of the melamine testing with 1.9% melamine are repeated when 18.75% w/w melamine is used in the resins, except that this occurs on a slightly larger scale. The presence of the melamine alone in the styrenated resins leads to an increase in LOI of 3%. In the triazine resins this increase is 2%. At 1% phosphorus additive levels the increase for the styrenated resins is 5% and 3% for the triazine resins. At 10% phosphorus additive loading levels the styrenated resins with melamine show an increase over the styrenated resins with no melamine of 5% and for the triazine resins this is 4%. Again these results are showing some signs of slight synergism. There are, however, not enough results to categorically prove this theory of synergism and so this must be classed as a tentative thought. What is obvious, though, is that it is not the basic nature of the triazine that is preventing the phosphorus additive from behaving normally as a fire retardant. The reason must, then, lie elsewhere.

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Table 3.24 and Graph G8 show the results of the LOI testing carried out with TCEP. This was carried out because it was thought that if the chlorinated additive only operated in the vapour phase, as had been previously suggested, then the triazine ring would not be able to inhibit its mode of action and so LOI values greater than those obtained using TEP or DMMP would be achieved. If, on the other hand, the two elements only act additively, as has also been suggested, then again a greater LOI value would be achieved from the effect of the chlorine in the vapour phase. The graph shows that there is a reduction in LOI value for the normal styrenated resins treated with 10% TCEP compared to those treated with DMMP or TEP. This is surprising as at 5% TCEP loading levels the LOI value is slightly higher than for the

equivalent resins with TEP or DMMP. The aliphatic resins, on the other hand, show an increased LOI value, throughout the TCEP loading level range, when compared to when they are treated with TEP or DMMP. This leads to the conclusion that the value for the LOI at 10% TCEP for the normal resin is anomalous and caused by experimental error. More testing would be needed to give conclusive results as to the true effect of the TCEP in the styrenated resins. The triazine resins, however, show quite marked increases in LOI, when treated with TCEP, when compared to the resins treated with TEP or DMMP. This shows that the triazine ring is not interfering with the mode of action of TCEP as it does with TEP or DMMP. Whether this is because the TCEP acts in solely in the vapour phase or whether this is an additive interaction is not clear from these test results.

In summary, the important observations arising from the LOI testing are that untreated triazine resins are more inherently fire retardant than untreated styrenated resins but that phosphorus additives do not have any great fire retardant effect in the triazine-based resins. This inhibition of the fire retardant effect is not because of the basic nature of the triazine ring. Indeed, with primary amine substituents, such a ring type shows some synergy with the phosphorus additives. The use of TCEP in the triazine resins give much better fire retardance than the use of non-halogenated additives. The mode of action of this is not readily detectable from this testing. It may be necessary to modify the triazine monomer so that it contains primary amine substituents rather than the tertiary amine substituent that is currently present on the ring to see if phosphorus-nitrogen synergy is possible in this type of system. In order to determine the mode of action of the TCEP it will be necessary to carry out phosphorus analysis of the chars to see if any phosphorus is left in the char of resins

treated with this additive. If phosphorus is retained in the char to a large extent then this is proof that no phosphorus-chlorine synergy is taking place.

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3.4.2 Surface Spread of Flame Testing

The results for this testing are shown in tables 3.25 (normal resins) and 3.26 (aliphatic resins). These are shown graphically in Appendix H as graphs H1 - H9.

Sample	Burn time (sec)	Burn length (mm)	Burn length/sec (mm/sec)
SNFSD01	328	195	0.59
SNFSD02	229	159	0.69
SNFSD03	203	78	0.38
SNFSD04	179	89	0.49
SNFST'01	299	169	0.56
SNFST'02	230	127	0.55
SNEST'03	229	125	0.55
SNFST'04	216	120	0.56
TNFSD01	156	129	0.83
TNFSD02	150	137	0.91
TNFSD03	78	46	0.59
TNESD04	144	<u></u>	0.52
TNSFT'01	165	136	0.82
TNFST'02	178	109	0.61
TNFST'03	138	98	0.71
TNEST'04	144	83	0.58

Table 3.25: Results from surface spread of flame tests on normal resin containing either styrene or triazine with either TEP or DMMP.

Sample	Burn time (sec)	Burn length (mm)	Burn length/sec (mm/sec)
SAFSD01	255	121	0.47
SAFSD02	193	80	0.41
SAFSD03	217	72	0.32
SAFSD04	201	74	0.36
SAFST'01	262	115	0.44
SAFST'02	341	150	0.44
SAFST'03	206	80	0.39
SAFST'04	214		0.39
TAFSD01	160	94	<u> </u>
TAFSD02	175	<u> </u>	0.63
TAFSD03	151	95	0.63
TAFSD04	155	68	0.44
TASFT'01	180	90	0.50
	154	92	0.60
	144	86	0.60
TAEST'04	147	65 and 65	0.44

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Table 3.26: Results from Surface spread of flame testing with aliphatic resin

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Graph H1 shows the amount of time that each sample burnt before extinction of the flame. The triazine resins do not burn for as long as the styrenated resins at all of the phosphorus additive levels. This backs up the results of the LOI testing which show that the triazine resins are less flammable than the styrenated resins. These results indicate that DMMP is better at retarding fire in both systems. This is shown by the fact that the resins treated with DMMP burn for a shorter period of time than those treated with TEP. Graph H2 shows the flame spread of each sample. The first most noticeable observation is that the triazine resins show a smaller surface spread of flame at all additive levels. Secondly it appears, again, that DMMP is giving the best performance in both resin types. Only three samples, however, pass the test. These samples are the triazine resin with 5 and 10% DMMP and the styrenated resin with

5% DMMP. Only one of these shows class one performance, this one being the triazine resin with 5% DMMP. None of the resins with TEP give acceptable performance in this test. It has been shown, however, that additives such as TEP and DMMP may actually contribute to the flame spread of resins (158) because of their low boiling and flash points. It was found, in this study, that the optimum levels for % phosphorus was 0.2% for TEP and 0.6 - 0.8% for DMMP. This is not the case in our study where the optimum levels are slightly higher at 1.7% for TEP and 0.85% for DMMP. Also our study showed that for both types of resin the surface spread of flame was actually reduced by the presence of the phosphorus additives.

Graph H3 shows the surface spread of flame per second for the samples. In the case of the resins treated with TEP it appears that for all loading levels of TEP the triazine resins burn faster than the styrenated resins. At 10% of the TEP, however, the triazine resin burns at very close to the same rate as the equivalent styrenated resins. For the resins treated with DMIMP it is only at 10% loading levels that the styrenated resin actually has a slower burning rate than the styrenated resins. It is obvious then that although the DMIMP and TEP may have been implicated in adding slightly to the surface spread of flame they are, in this case, actually aiding in reducing the surface spread of flame as well as the burning rate. It is clear that the normal resins require a better additive to give them acceptable surface spread of flame performance.

For the aliphatic resins Graph H4 shows the amount of time each sample burnt before flame extinction. As for the normal resins the triazine resins achieve flame extinction much more quickly than the styrenated resins. This occurs at all loading levels of the phosphorus additives. On average this reduction in burn time is about 77 seconds. In terms of actual surface spread of flame it can be seen that, on average, the triazine

resins treated with TEP have a lower surface spread of flame than the styrenated resins treated with TEP (Graph H5). The only case where this does not occur is at 5% loading levels of the additive. Surprisingly the resins treated with DMMP do not follow the expected trend, with the triazine resins having a smaller surface spread of flame. The triazine resins treated with DMMP only show better performance at 0% and 10% loading levels of DMMP. It is only at 10% loading levels of the phosphorus additives that acceptable fire performance is achieved in the aliphatic triazine resins. For the styrenated resins treated with DMMP, class 2 fire performance is achieved at loading levels of DMMP of 5% and over. TEP in the styrenated resins does not give acceptable fire performance at any loading levels. Importantly, it can be seen from Graph H6 that in all cases the styrenated resins burn more slowly than the triazine resins, the major differences in burn coming at 1 and 5% of the additive loading levels.

Comparing the behaviour of the aliphatic resins to the normal resins (Graphs H7 - H9) it is clear from Graph H7 that the untreated aliphatic styrenated resins have a lower burn time than the equivalent normal resins. The triazine resins, on the other hand, do not show such a clear cut difference, and allowing for experimental fluctuations, it can be said that the triazine resins have roughly the same burn time. When the resins are treated with phosphorus additives it is clear that the aliphatic resins treated with DMMP actually have a longer burn time than the normal equivalents, at the additive levels where these resins show better flame spread performance. It is, then, prudent to look at the burning rate of the polymers (Graph H9). The aliphatic styrenated resin with DMMP has a slower burn rate than the normal equivalent. In fact, in just about all cases for all the resins, the aliphatic resins show slower burning rates than the

normal resins. Given that the difference in burning times at phosphorus loading levels of 1% and above, for all resin types, is small and the fact that the aliphatic resins have a slower burning rate explains why the aliphatic resins have better flame spread performance. The reason for the slower burning rates for the aliphatic resins must lie with the change in structure which is somehow causing these resins to degrade more slowly than the normal resins. In summary, the surface spread of flame testing has shown that overall the triazine resins do perform better than the styrenated resins. Unfortunately, however, none of the resins show acceptable fire performance. The major disadvantage of the triazine resins is their fast burning rate which means that they burn along a longer distance in a short time. For the triazine resins to be improved it is necessary to find out why they have such a fast burn rate. One area to look at, initially, would be the difference that the use of the powder bound CSM makes on the flame spread compared to the emulsion bound CSM.

3.5 Thermogravimetric Analysis (TGA)

Thermal gravimetric analysis is used to determine the thermal decomposition characteristics of a sample. It measures the weight loss from the sample at various temperatures. This way the thermal decomposition stages of the sample can be determined. The main reason for this testing was to see if the triazine resins degraded more quickly than the styrenated resins at lower temperatures. If this proved to be the case then this would provide the explanation for the higher surface spread of flame of the triazine resins. The TG traces for the resins can be seen in Appendix I as Figures I1 and I2 for the normal styrenated resins with no phosphorus and 20% TEP respectively; I3 - 16 for the aliphatic styrenated resin with no phosphorus, 20% TEP, 20% DMMP and 20% TCEP respectively, I7 - I10 for the normal triazine resins with no phosphorus, 20% TEP, 20% DMMP and 20% TCEP respectively and I11 - I14 for the aliphatic triazine resins with no phosphorus, 20% TEP, 20% DMMP and 20% TCEP respectively. Each figure has two traces on it, the first being the thermal decomposition profile of the sample. This shows how much of the sample remains at any given temperature during the test. The second trace, called the first derivative, shows the individual decomposition stages of the sample and the amount of weight loss each stage represents. The first derivative also shows the temperature of each decomposition stage at which the maximum rate of weight loss occurs. The most important aspect of this testing, for the purposes of this project, was the direct comparison of the thermal behaviour of the triazine and styrenated resins.

Looking, initially, at the normal, untreated resins (Figs. I1 and I7) it can be seen that the triazine resin decomposes more quickly than the styrenated resin at lower temperatures. Indeed the triazine resin begins its first major decomposition stage at around 234°C peaking at a loss of about 21 %/min at 360°C. The styrenated resin begins its first major decomposition stage at around 280°C peaking at a weight loss rate of 24 % per minute at 398°C. The total weight loss of the first decomposition stage for the triazine resin is considerably less than that for the styrenated resin. By around 600°C virtually all of the styrenated resin has been lost. At the same temperature around 14% of the triazine resin still remained. In fact at all

temperatures above about 390°C the triazine resin retains more of its original weight than the styrenated resin.

From this information an explanation for the increased surface spread of flame rate for the triazine resins can be postulated. It is obvious, from the design of the surface spread of flame equipment that there is a temperature gradient along the length of the sample. At the hotter areas of the sample the triazine resin will readily decompose to release flammable products. This process will happen more quickly than with the styrenated resin because the triazine resin begins to decompose at lower temperatures than the styrenated resin. The reason why the styrenated resin burns longer than the triazine resin is that it is inherently more flammable than the triazine resin. Unfortunately no analysis of the thermal decomposition products from the first decomposition stages was carried out. This would have given a good indication as to the nature of these products and from that their relative flammabilities.

The incorporation of phosphorus additives into the resins has the effect of increasing the temperature at which thermal decomposition starts. In the case of TEP (Fig. I2) in the styrenated resins this increase amounts to about 42°C with the peak weight loss rate occurring at 425°C. In the case of the triazine resin with TEP (Fig. I8) the onset of decomposition occurs at 280°C with the peak weight loss rate occurring at around 360°C. With DMMP (Fig. I9) the triazine resin initially decomposes at 319°C with the peak weight loss rate occurring at 382°C. Finally for the triazine resin with TCEP (Fig. I10) the initial decomposition stage begins at 303°C with the peak weight loss rate occurring at 402°C. By raising the temperature at which thermal decomposition starts the surface spread of flame rate will be reduced. This is because the samples

are more thermally stable and less prone to rapid decomposition at lower temperatures.

Again, with the aliphatic resins, there are differences between the styrenated and triazine resins as far as thermal decomposition is concerned. Most importantly in terms of explaining the fast surface spread of flame is the temperature of the first thermal decomposition stage. The aliphatic styrenated resin (Fig. I3) has its first thermal decomposition stage at around 320°C which peaks at 426°C. For the untreated aliphatic triazine resin (Fig. 111) this stage is at 280°C and peaks at 385°C. So once again the triazine resin is more prone to rapid thermal decomposition and so would have a quicker surface spread of flame. A second builder de assection and a second The introduction of phosphorus into the aliphatic resins (Figs. 14 - 16, styrenated resins, I11 - I14, triazine resins) has the same effect as in the normal resins. This is to retard the initial decomposition stage to a higher temperature. The subsequent effect of this is to reduce the decomposition rate and so reduce the surface spread of flame rate. Another important fact arising from this testing is the appearance of peaks relating to the loss of the phosphorus additive from the styrenated samples. In all cases where phosphorus is present in the styrenated resins there is an early weight loss peak relating to the loss of the phosphorus additive. In the case of the triazine resins this peak is only significant when TCEP is the additive (Fig. 114). This indicates that the triazine resins actually help retain the phosphorus additive in the polymer matrix whereas the styrenated resins do not. This observation obviously needs to be checked more accurately but does go some way to indicating an incompatibility problem between the triazine resins and the phosphorus additive. It was stated in the introduction that for an additive to be effective as a flame retardant in a sample then it

must be functional within the main thermal decomposition range of the sample. Additives such as TEP and DMMP are used in styrenated polyesters exactly because they do function in the thermal degradation range of these polymers. It has been shown, however, that the triazine resins actually decompose at entirely different temperatures to the styrenated resins. This means that the polymer has already undergone decomposition before the TEP and DMMP become effective as flame retardants. These results gives rise to several items which need investigating in more detail in order to prove the theory. These include the analysis of the phosphorus content of the char, the temperature at which charring occurs, an IR investigation into what happens to the phosphorus additive during combustion and finally the general structures of the chars formed.

3.6 Char Analysis

This testing was carried out to see if the phosphorus actually remained in the resins as was indicated by the TGA testing. If the phosphorus is actually retained in the resins then this would prove that the loss of the additives from the resin is not to blame for the lack of synergistic interaction. It would also go further to show that the phosphorus additives and the triazine resins are incompatible as far as flame retardance goes. At the same time the amount of char produced from each resin sample was determined. The results of this testing are shown in Table 3.27. In each case the phosphorus additive was used at 20% w/w loading levels. The respective amount of phosphorus expected for each additive is then 5% for DMIMP, 3% for TEP and 2% for TCEP.

	1			<u> </u>		% P	found				· · · · · · · · · · · · · · · · · · ·	
	TN Series			TA series		SN Series		SA Series				
P Additive	No Char	% Char	Charred	No Char	% Char	Charred	No char	% Char	Charred	No Char	% Char	Charred
TEP	3.3	26.50	5.98	3.25	21.59	6.21	3:15	13.29	5.99	3.45	12.85	4.5
DMMP	4.75	20.24	0.64	4.85	19.42	0.99	5.1	4.68	1.31	4.67	0.00	0.00
ТСЕР	2.1	43.06	3.24	2.02	41.97	2.4	2.11	11.28	2.8	1.99	9.98	3.1
No Additive		17.06	-	-	16.98	-		-	1. .			

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3.27: Tabulated results for phosphorus analysis of chars.

Within experimental error, the values obtained for the amount of phosphorus present before combustion are in keeping with the expected values. In all cases, assuming no phosphorus was lost during combustion, it would be expected that the phosphorus would make up a larger percentage of the char than the un-combusted resin. Table 3.28 shows the amount of phosphorus expected for each char based on the amount of char left at the end of the combustion process.

	% P I	EXPECTED IN C	CHARRED SAME	PLES
	TN RESIN	TA RESIN	SN RESIN	SA RESIN
TEP	12.45	15.05	23.70	26.85
DMMP	23.47	24.97	108.97	ing official factor factor
TCEP	4.88	4.81	18.71	19.93

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Table 3.28: Expected amount of phosphorus in charred samples

These results are significant in that they categorically show that phosphorus is indeed lost from the resins as they burn. This would be more significant if this only occurred from the triazine resins. This is not the case and phosphorus is lost from both resins but remains in the styrenated resins in quantities sufficient to cause charring. This then proves that although the triazine resins do lose phosphorus this is not the cause of the inactivity of the phosphorus in the triazine resins. This is especially true as it appears that more phosphorus is lost from the styrenated resins than from the triazine resins.

It appears that nearly all of the DMMP additive is lost from the resins during combustion and that it is relatively poor at causing charring compared to the TEP and TCEP additives. It is, also, of note that the untreated triazine resin produces more char than the styrenated resins with any of the additives at 20% loading levels. It is also important to notice that the incorporation of the phosphorus additives into the normal triazine resins gives rise to a 3% increase in char formation for DMMP, a 9.5% increase for TEP and a 26% increase for TCEP. These rises in char formation are very similar in the aliphatic resins treated with the phosphorus additives. It is these rises in the char production that leads to the slight increases in LOI value of the triazine resins treated with the phosphorus additives compared to the untreated resins. This increase in char formation contradicts the theory previously put forward that the phosphorus and the triazine resins are thermally incompatible, i.e. the triazine resin has a decomposition range that is not the same as the temperature range within which the phosphorus additives become active char producers. It could also be stated that, as the untreated triazine resin produces more char without phosphorus than the styrenated resins with high phosphorus loading levels, the phosphorus could not cause excessive charring in the triazine resins. If, however, the results obtained from the charring temperature are considered (Table 3.29) along with the information gleaned from the TGA work then another theory can be put forward as to the observed low activity of the phosphorus additives.

	TN RESIN	TA RESIN	SN RESIN	SA RESIN
Temp. Initial Char (°C)	260°C	270°C	310°C	315°C
Temp. 100% Char loss	650°C	635°C	600°C	580°C

Table 3.29: Initial char temperatures and temperatures for total char loss for each untreated resin.

As has been discussed, and has been proved with the results above, the triazine resins decompose to form an initial char at temperatures that are much lower than for the styrenated resins. The TGA results, however, show the phosphorus additives raise the initial decomposition temperatures of these to give lower burn rates. This would have no real effect on the flame retardance of these resins. As it has been shown, the phosphorus remains in the condensed phase so it is possible that the phosphorus is actually working as it normally would. The reason why the phosphorus is only showing very small effects comes from the fact that, when it is present at 10% loading levels in the triazine resins, it is only making up about 16% of the total fire retardant content of the resins. In the triazine resins the triazine monomer itself is a char promoting fire retardant and it makes up approximately 60% of the total resin. The 10% phosphorus additive, then, which is also a char promoter only makes up a small portion of the fire retardant content of the resin and can only contribute a small amount to the overall charring of the combusting resin. In order to test this theory it is important to show that the phosphorus additives are acting in the same way, during combustion, in both the styrenated and triazine resins. This can be shown by FT-IR analysis of the chars obtained from the burnt polymers.

3.7 FT-IR Analysis of Resins

The analysis of each individual portion of the resins is shown in Tables 3.30 - 3.34. These were carried out from the pure compounds and also from the resins treated with the additives. The spectra for the treated resins are shown in Appendix J as Figures J1

- J17.

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Wavelength (cm ⁻¹)	Peak assignment		
2985	CH ₃ asymmetric stretch		
1480	O-CH ₂ deformation		
1445	CH ₃ asymmetric deformation		
1394	O-CH ₂ wag		
1370	CH ₃ symmetric deformation		
1274	P=O stretch		
1167	CH3 rock system to the CH3 rock		
1100	Out Of Plane CH ₃ rock		
1031/976	asymmetric P-O-C deformation		
822/801/744	symmetric P-O-C deformation		

Table 3.30: Peak assignments for TEP additive (207)

Wavelength (cm ⁻¹)	Peak assignment		
1732	C=O stretch		
1600	Ring deformation		
1582	Ring deformation		
1280	C-O stretch		
1120	O-CH ₂ deformation		
745	Ring		

Table 3.31: Peaks in IR spectrum from phthalate ester portion of the unsaturated polyester resin (UPR) (208)

Wavelength (cm ⁻¹)	Peak assignment		
1732 ····································	C=O stretch		
1265 - 1265 - Statistic (JC. 1988)	C-C(O)-O stretch		
1050	O-CH ₂ -C asymmetric stretch		
979	trans CH₃ wag		

Table 3.32: IR peaks caused by fumarate ester portion of UPR (208)

	化合成 化乙酸盐 医黄疸性 医结合的 化化合物 化合物		
Wavelength (cm ⁻¹)	Peak assignment		
2959	-CH ₃ asymmetric stretch		
2855	-CH ₃ symmetric stretch		
1464	-CH ₃ asymmetric deformation		
1315	P-CH ₃ symmetric deformation		
1233	P=0		
1186	CH ₃ -O-P rock		
1033	P-O-CH ₃		
916	$P-CH_3$ on $(OR)_2P(O)Me$		
825	P-O-C symmetric stretch		

Table 3.33: Peak assignments for IR spectrum of DMMP (207)

Wavelength (cm ⁻¹)	Peak assignment
2963	CH ₃ asymmetric stretch
2889	CH ₃ symmetric stretch
1457	CH ₃ asymmetric deformation
1280	P=O and CH ₂ -Cl
1028	P-O-Et asymmetric deformation
972	P-O-Et asymmetric deformation

Table 3.34: Peak assignments for IR spectrum from TCEP. n.B. shouldering on peak at 1280 cm-1 is due to the presence of the P=O and the CH_2 -Cl group which cause peaks in the same region. (207)

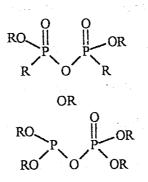
The major problem observed in the interpretation of these spectra is that, one of the most identifiable groups in the TEP (Fig J3) i.e. the P=O group gives rise to a peak in exactly the same region as the C-C(O)-O group of the fumarate ester and the C-O group of the phthalate ester. This could cause problems in determining the existence of the P compound in the UPR. To overcome this the most obvious solution is to look at the P-O-C group peaks at 1031 and 976cm⁻¹. As can be seen in the non-combusted samples the TEP is indeed present as indicated by the peaks at 1031 and 976 cm^{-1} . The reason for combustion without the phosphorus additive was to determine the IR spectrum of the charred resin without phosphorus (Figs. J6 - normal styrenated, J10 normal triazine and J14 - aliphatic triazine). No detailed analysis of these spectra was carried out and their only use was for comparison with the charred resins with phosphorus. The first samples that were analysed were the SN and TN resins with TEP additive (Figs J7 and J11 respectively). There were several peaks which occurred on the resin with phosphorus additive spectra which were not readily visible on the spectra from the resins charred with no phosphorus additive. These peaks were at 1320, 1260, 1082 and 980 cm⁻¹. The peak at 1260 cm⁻¹ could cause problems with the interpretation if it came from any C-O group from the ester parts of the resin. In the interpretation it was therefore important to eliminate the presence of ester groups and their subsequent peaks on the spectra. It was seen from the spectra that there were no peaks at 1730 cm⁻¹ (indicative of C=O) 1120cm⁻¹ (indicative of O-CH₂ in phthalate portion) or 1050cm⁻¹ (indicative of O-CH₂-C asymmetric stretch from fumarate). This evidence shows that the ester linkages are not present in the charred samples. It can, therefore, be said that the peak at 1260cm⁻¹ comes from a P=O group and not a C-O group. The presence of phosphorus was confirmed from the ICP-AES

work. The presence of the above peaks can, then, be interpreted as follows (Table 3.35)

Wavelength (cm ⁻¹)	van dere geneer in Peak assignment chinaeser gewende.
1320	relations sécult for the second states to
1260	P=O
1082	P-O-CH ₃
the second s	an and a star and the second second second second second second
980	P-O-P
	· · · ·

Table 3.35: Peak assignments for extra peaks on charred resin + TEP Spectra

These peaks occur in both the TN resins and the SN resins treated with TEP. It is clear from the spectra that a P-O-P bond has been formed during the combustion process. The presence of P-O-CH₃ is also clear as is the presence of P=O. The frequencies of these peaks also gives away a great deal of information as to the nature of the formed compound. From these frequencies there are two possibilities (204):



Obviously such detailed identification is not possible with a great deal of accuracy using only IR analysis. It is, however, safe to say that some sort of polyphosphate/phosphonate has been produced by the combustion process. There are no signs of any P-N interaction.

The presence of the triazine ring, then, does not actually inhibit the change which occurs in the phosphorus additive upon combustion. Much the same sort of changes are seen when DMMP and TCEP are used. These changes are also observed with the aliphatic resins. It has now been proved that phosphorus is present in the chars of the resins and that the same types of phosphorus compounds are formed in both the triazine and styrenated resins during the combustion process. This, used in conjunction with the fact that the phosphorus does cause some charring, would seem to concur with the theory that the phosphorus is acting in its normal manner but that, as it only constitutes a small portion of the total fire retardant compliment in the resin, it can only have a very limited effect in char promotion.

It has been shown that the triazine resins do have better burning behaviour than the styrenated resins in terms of smoke production, LOI values and surface spread of flame and that they actually burn faster than the styrenated resins. It has also been shown that there is no phosphorus-nitrogen synergism in this system although this may be feasible if a primary amine substituent were used rather than the tertiary amine that is currently being used. Finally, it has been suggested that the phosphorus only has a small effect as it only makes up a small portion of the char-promoting compounds in the resin. It is now time to consider the relative mechanical properties of the two resins.

3.8 Mechanical Testing

3.8.1 Flexural Testing of the Untreated Resins

The graph shape obtained from the testing is shown in Fig. 3.10:

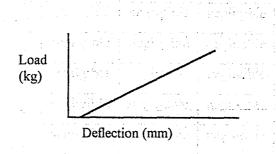


Fig. 3.10: Diagram showing approximate graph shape obtained from flexural testing (some tailing of the graph may occur towards the apex)

The following equations were used to calculate flexural strength and modulus:

 $F \max$ x 1.5 x span x 9.81 = flexural strength BD^2 10045*dF* = Flexural Modulus Bδ Fmax =Full Scale Deflection (kg) Max. Load (kg) dF В Deflection (mm) Width (mm) δ D Thickness (mm)

dF and δ in the Flexural Modulus calculation were calculated by extrapolating the graph line along the steepest part of the graph to a pre-determined point along the Y-axis. At this point a vertical line was dropped to the X-axis. dF was the full scale deflection value at the end of the extrapolated line to the X-axis and δ was the deflection from the intersection point of the extrapolated line with the X-axis to the

point where the downline meets the X-axis. The results are shown in Table 3.36.

				1			
Sample	Width B	Depth	Fmax (kg)	dF (kg)	δ (mm)	Flex.	Flex. Mod.
	(mm)	D	ang	kingin Marina	and a second	Strength	MPa
		(mm)				MPa	
SA01	10.9	6.35	negligible	negligible	negligible	negligible	negligible
SA02	10.9	6.35	negligible	negligible	negligible	negligible	negligible
SA03	10.8	6.30	negligible	negligible	negligible	negligible	negligible
SA04	10.85	6.30	negligible	negligible	negligible	negligible	negligible
SA05	10.75	6.25	negligible	negligible	negligible	negligible	negligible
SA06	10.75	6.25	negligible	negligible	negligible	negligible	negligible
SA07	10.73	6.20	negligible	negligible	negligible	negligible	negligible
SN03	11.91	4.15	17.75	40	13.4	84.55	2517.6
SN04	11.50	4.76	27.8	40	9.9	119.57	3529.2
SN05	11.35	4.60	17.5	40	10.5	78.92	3371.5
SN06	11.10	4.40	25.0	40	12.5	120.52	2895.9
SN07	11.09	4.30	16.5	40	13.3	81.46	2742.1
TA01	11.5	6.75	7.8	20	21.05	23.65	738.67
TA02	11.1	6.80	11.0	20	20.1	34.31	900.45
TA03	11.5	6.80	10.0	20	22.2	30.11	786.92
TA04	11.5	6.75	8.5	20	22.2	25.78	786.92
TA05	11.3	6.75	10.25	20	16.4	31.64	1084.07
TN01	11.1	4.5	3.1	20	4.9	14.61	3693.7
TN02	11.6	4.78	7.5	20	5.2	31.85	3330.6
TN03	11.6	4.70	8.5	20	4.9	36.71	3534.5
TN04	11.5	4.40	3.5	20	5.4	16.29	3235.1
TN05	11.8	4.35	2.5	20	6.1	11.47	2791.1
TN06	11.6	4.35	3.1	20	5.5	14.46	3148.9

Table 3.36: Results from flexural strength testing

Averaged out these results give the following values:

Specimen	Flexural strength (Mpa)	Flexural Modulus (Mpa)
SA	negligible seasons and	n han berginegligible and the
SN	91.49 (1996) (19	teline electronic 3090 Criticarelle line
TA	29.10 · · · · · · · · · · · · · · · · · · ·	859.41
TN	20.90 (14.21)	3289.0

and a second second stand and a second of

 Table 3.37: Averaged values for Flexural strength and modulus. (Figures in brackets are those obtained when exceptionally high or low results are ignored)

The results show that the styrenated aliphatic resins have no resistance to bending (shown by the flexural modulus value) and that they require very little force at all to produce excessive flexing. In contrast to this the SN resins require the largest amount of force to break (shown by the highest flexural strength value) and they also have a high resistance to bending. The results seem to indicate that the TN resins have the highest resistance to bending, shown by the high flexural modulus value, but they unfortunately have a very low flexural strength. The TA resins have a higher flexural strength than both the SA and TN resins but, compared to the SN and TN resins have a relatively low resistance to flexing. This resistance is much greater than the SA resins. This loss of flexibility in the TA resins and the very low flexural strength in the TN resins could be due to the cross-linking monomer having two reactive sites which may lead to a higher cross-link density in these resins than the styrenated resins. If this is the case then there would be less "space" for the force to be distributed in the triazine resins

leading to an increase in brittleness and so a reduction in flexural strength. This can be disadvantageous as in some application a high flexural strength is needed. Initially this problem can be solved by the use of glass reinforcements which will greatly improve the performance of the triazine resins. In a longer term approach the use of a mono-functional monomer may be more advantageous in increasing the flexural strength of the triazine resin. One other factor to look at in altering the flexural strength of this resin is the reactivity ratio of the allyl unsaturation to the maleate unsaturation in the polymer backbone. It is known that with styrene the cross-link bridges can vary from two styrene units to seven. It is thought that with allyl groups there is close to an alternating structure, with the allyl groups showing little tendency to homopolymerise. We have shown that the triazine monomer will homopolymerise but it may be that it preferentially polymerises with the maleate unsaturation. If this is the case then the same theory applies that the chains are tightly bound together and so there is no room for the flexural force to be distributed through the polymer matrix.

3.8.2 Heat Distortion Temperature

The results from the heat distortion temperature testing are shown in Table 3.38. These results support the theory that the triazine resins have a higher crosslink density than the styrenated resins. This is shown by the increase in heat distortion temperature (effectively the glass transition temperature) of the triazine resins over the styrenated resins. When a polymer has a high cross-link density then the chains are tightly bound together. The effect of this is that more energy is needed to soften the polymer. This gives rise to a higher heat distortion temperature (or glass transition temperature). The differences in heat distortion temperatures between the styrenated and triazine resins is quite large indicating a large difference in cross-link densities.

			· · · · · · · · · · · · · · · · · · ·		af a stran stran	
Sample	Width	Thickness	Length	Load (kg)	Deflection	Deflection
	(mm)	(mm)	(mm)		(mm)	Temp (°C)
SN01	4.28	11.75	101	.722	.30	72.3
SN02	4.53	11.60	101	.744	.31	72.6
SA01	-	-	101	-	-	-
SA02	-		101	-	-	
TN01	4.5	11.4	101	.714	.29	106
TN02	4.5	11.2	101	.689	.29	110
TA01	6.53	10.38	101	.859	.31	56.0
TA02	6.60	10.60	101	.906	.31	58.0

Table 3.38: Table showing results from HDT testing on all resins. n.B. No testing was carried out for the SA series as these resins deflected fully upon application of the load at temperatures below room temp.

3.8.3 Barcol Hardness Testing

This testing is carried out to find out how hard the polymer is. This is also an indication of the crosslink density of the polymer matrix. Basically the resistance to penetration by a sharp needle is being measured. When a polymer matrix has a large crosslink density then needle penetration is obstructed giving a high hardness value. It is often advantageous to have a good hardness as this means that the surface of the polymer is less prone to abrasion and erosion. The results are shown in Table 3.38.

These results are averaged from ten individual readings taken over the entire surface of the polymer sample.

or the polymer			la colore da color de como tres de
	Sample		Barcol Hardness
t de Maria	SA resin	a - Lawang	0
	SN resin		en netterele saatje ti 32-36 gul estastanas aad ty
	TA resin		e de la terra des 18-21 los deserveix de la la s
	TN resin		51-56 Store - State - Stat

Table 3.39: Results from Barcol Hardness Testing

The results show that the triazine resins are much harder than the corresponding styrenated resins. This again could be due to a higher cross-link density in the triazine resins. Factors affecting the Barcol Hardness value include poor curing at the polymer surface caused by oxygen inhibition of the curing process. It is important, then, to ensure that complete curing takes place.

4.0 Summary of Results

The main aim of this section is not only to review the results obtained from the project but, perhaps more importantly, to consider how this project can be modified to give a more acceptable novel resin system.

化氯化乙酸乙酸乙酯 激化性的 计分子通知分词 The synthesis of the new monomer is a relatively easy two stage reaction using cyanuric chloride as the starting material to give the intermediate product, 2,4dichloro-6-diethylaminotriazine. This reaction gave conversions of in excess of 85%. From this product two synthetic routes were thought to be of interest. The first was to produce a dialkyloxy derivative of this which could then be transesterified to produce a triazine - glycol oligomer. The synthetic route to the dialkyloxy intermediate was a simple reaction involving the reaction of an alcohol, in this case ethanol, with the 2,4dichloro-6-diethylaminotriazine. The product was 2,4-diethoxy-6-diethylamino triazine, with a conversion of over 90%. The transesterification of this product with a glycol, in this case diethylene glycol proved possible but did not give the exact product desired. The glycol was "activated" with sodium metal and then reacted with the diethoxytriazine derivative. It was hoped that the product would have hydroxyl end groups at both ends of the oligomeric chain. These end groups would then have been end-capped with and unsaturated acid to produce a potentially cross-linkable high nitrogen containing oligomer. It was found, however, that only one hydroxyl group was present at the end of the chain, the other end being an unconverted ethoxy group. The most probable reason for the failure of this experiment was that there was not sufficient excess of the glycol to achieve the removal of both ethoxy groups from the chain. If this synthesis were to be carried out at a future date then a 10:1

glycol:triazine ratio may give more desirable results. The reason for not trying this was that the synthesis of a potential cross-linking monomer was successful. This synthesis involved the reaction of the 2,4-dichloro-6-diethylaminotriazine with allyl alcohol to give a liquid product, which after removal of the excess allyl alcohol using a rotary evaporator and then washing with water, gave a waxy solid with a melting point of $28 - 29.5^{\circ}$ C.

This difunctional monomer, 2,4-diallyloxy-6-diethylaminotriazine gave a degree of cure of 97%. This, however only occurred with dicumyl peroxide at high temperatures. No cold cure was achieved using various initiator systems. It is probable that no other peroxides produce free radicals with a high enough affinity to the diallyloxy unsaturation to produce adequate curing in this novel system. The main disadvantages of this curing mechanism are that it can only be carried out at elevated temperatures and that it is slow. This is because the dicumyl peroxide has a high critical temperature (100°) and will not produce free radicals below this point. At this temperature it also has a relatively long half life of around 1.5 hours (204) so the release of free radicals is slow, leading to a slow cure time.

Smoke testing of the new resins gave varying results when carried out at different times. The main reason for this was the simplicity of the testing procedure. The fact that a constant flame could not be maintained throughout the testing period caused some adverse effects on the results and also the fact that the light bulb for the photocell had to be changed during the testing for a bulb which was not exactly the same caused some variations in the results.

Taking the results at face value, however, it has been shown that the triazine resins, containing no additives, reduce the amount of smoke released during combustion by

52 - 65% over the styrenated resins with no additives. This reduction is caused by two main factors. The first is that the triazine ring has a much higher nitrogen content than styrene. It is well-known that nitrogen containing compounds produce little smoke during combustion. The second reason is that the triazine resins actually contain up to 60% w/w of the triazine monomer. This drastically reduces the amount of non-nitrogen-containing components in the resins and so producing even less smoke. It is possible that if the amount of triazine in the resins were reduced to a 1:1 ratio of monomer: fumaric unsaturation then the smoke production of the resins would increase.

It has been found that the phthalic anhydride in the UPRs accounts for approximately 35% of the total smoke produced during combustion. The aniount of smoke caused by styrene could not really be determined because of the disproportionate amount of triazine monomer present in the novel resins compared to the amount of styrene in the old resins. The effect of phosphorus on the smoke production of the triazine resins is negligible but in the case of the styrenated resins the amount of smoke is reduced to quite a large extent. At 10% loading levels of the phosphorus additives the reduction in total smoke caused by the triazine is only 38 - 40% over the styrenated resins are much less flammable at these loading levels, whereas the flammability of the triazine resins is hardly affected by the phosphorus additives. When one takes into account the amount of resin burnt during the test it can be seen that at the highest phosphorus additive loading levels the triazine resins cause a 53 - 55% reduction in smoke evolution compared to the equivalent styrenated resin. This shows that on an

equivalent scale the triazine resins produce much less smoke than the styrenated resins.

It appeared that TEP treated resins gave slightly better smoke performance than ones treated with DMMP. One major problem in fires is the loss of visibility which severely hampers escape. When the triazine resins are used they cause much less light obscuration than the styrenated resins and so visibility is greater. From these results it can be clearly seen that the triazine resins have greatly improved smoke production compared to the styrenated resins. In fact these resins seem to give the best comparative performance when they are not treated with any additives at all. It must be stressed here that the NBS smoke chamber used in this study is far from perfect in terms of giving totally representative results. An improved smoke test would incorporate a gravimetric analysis of the smoke evolved as well as a facility for varying the heat of the degradation temperature. This would take into account the inaccuracies caused by soot deposition on the photocell as well as the differences in smoke evolution caused by varying heat fluxes.

The use of ATH in the resins as a flame retardant additive which was likely to be more effective than the phosphorus additives showed again that the triazine resins tended to produce less smoke than the equivalent styrenated resins. In general the resins treated with ATH evolved much less smoke than the resins without ATH, the reason being that the ATH accounts for 33 - 50% of the total sample and so much less smoke would be expected.

LOI testing has shown that the triazine resins have better flame retardant properties than the styrenated resins when no phosphorus is present. At these loading levels the styrenated resins achieve LOI values which are very much in line with those of the

triazine resins. This occurs for TEP, DMMP and TPP showing that these additives have very little effect on the flame retardant properties of the triazine resins. This also shows that there is no N-P synergism between the phosphorus additives and the amine group on the triazine ring, as might be expected.

The use of melamine in the resins with the phosphorus additive gave rise to some interesting results. It appeared that the combined effects of the phosphorus additives and the melamine was greater than the expected additive effects, indicating the presence of a synergistic interaction between the two. This synergism most probably comes from the interaction between the primary amine substituent on the melamine ring and the phosphorus additives. When they interact the phosphorus becomes an inherent part of the melamine ring and so is not lost from the condensed phase as the combustion process proceeds. In this way the phosphorus has a greater effect than when it is used alone and can be lost from the burning sample. In fact studies of the char have shown that in the styrenated resins a large amount of the phosphorus is lost from the sample during combustion. It is conceivable then that if the triazine ring had a primary amine substituent rather than the current tertiary amine then phosphorus nitrogen synergism may occur. This possibility should certainly be tested in any future work on this project.

The use of the chlorinated additive also gave rise to a greater increase in LOI value of the resins than the use of un-chlorinated additives. This was shown, by the char analysis, to be an additive effect from the phosphorus in the condensed phase and the chlorine in the vapour phase. Again, as for the smoke testing, it seems that, although the best LOI value is gained at 10% loading levels of the phosphorus additives, the

best comparative improvement is seen when the resins contain no phosphorus additives at all.

In terms of the surface spread of flame testing it is again seen that the triazine resins do perform better than the styrenated resins. Unfortunately this improvement in performance is not as great as expected. The reason for this is that the rate of flame spread in the untreated triazine resins is much greater than in the untreated styrenated resins. The effect of this is to cause the flame to spread much more before the natural fire retardance of the resins can extinguish the flame. It is, then, advantageous that the triazine resins have a much shorter burn time than the styrenated resins.

It has been proved, from TGA studies, that the reason for this accelerated burn rate lies with the fact that the triazine resins show a first decomposition stage at lower temperatures than the first decomposition stage in the styrenated resins. The effect of this is to accelerate decomposition at higher temperatures which leads to faster burning. The presence of the phosphorus additives in the resins, both styrenated and triazine, leads to a reduction in burn rate and so the surface spread of flame. Despite this, however, none of the resins show acceptable surface spread of flame performance. The TGA studies showed that the reason for the lower burning rates in the presence of the phosphorus additives is caused by an increase in the temperature at which the first decomposition stage occurs. The effect of this is to lower the decomposition rate at higher temperatures and so reduce the burning rate of the resin. Studies on the charring temperature of the resins has shown that the triazine resins produce a primary char at much lower temperatures than the styrenated resins. This occurs at the first decomposition stage as shown by the TGA studies. It has also been seen that the triazine resins produce much more char without phosphorus than do the

styrenated resins with 20% additives loading levels. Along with this a small additive effect has been seen between the phosphorus and the triazine. This comes from the fact that an increase in percent char produced is seen in the triazine resins with 20% phosphorus along with a small increase in the LOI value of the treated triazine resins. From the fact that the phosphorus additives actually do increase the charring of the triazine resins it can be deduced that the triazine ring itself does not produce the maximum amount of charring that could possibly occur in this resin.

From the studies carried out on the chars it has been seen that the phosphorus additives behave in exactly the same way in both types of resins, during combustion. It can be assumed, with confidence, that the phosphorus behaves normally as a fire retardant in the triazine resins. The reason why only very a very small effect is seen in the triazine resins is that both the triazine monomer and the phosphorus additives are char promoters, i.e. they work in the same way. The phosphorus additive, however, only makes up about 16% of the total fire retardant components of the triazine resin and as such can only exert a very small fire retardant effect compared to the triazine monomer.

A further test that should be carried out to prove this theory more is to reduce the amount of triazine monomer in the triazine resins. In this case there should be a small decrease in the LOI value of the untreated resins. The phosphorus would then make up a larger proportion of the fire retardants in the resins and so should show a larger fire retardant effect than in the resins with more monomer.

It is very interesting to see that the TCEP additive produces such a large amount of charring in the triazine resins. If it assumed that the halogen actually acts in the vapour phase then this extra charring can only be caused by the phosphorus portion of

the additive. There must, then, be some sort of obscure interaction between the remnants of the TCEP additive, after the chlorine has been released to the vapour phase and the triazine ring. A detailed study of this phenomenon would be extremely interesting.

Mechanically the triazine resins do not possess all of the advantages of the styrenated resins. In terms of the flexural testing it is clear that although the normal triazine resins possess a larger resistance to flexing (flexural modulus) they have a considerably lower flexural strength. That means that these resins resist flexing to a greater extent but will break under a flexural strain that is much lower than the strain needed to break the styrenated resins. In the case of the aliphatic resins the triazine resin has a greater modulus and strength than the equivalent styrenated resin. The presence of as high flexural modulus and low flexural strength is indeed indicative of a very highly cross-linked brittle resin. This observation is backed up by the high Barcol hardness of the triazine resins compared to the styrenated resins and the higher heat distortion temperature of these resins compared to the equivalent styrenated resins. High values for both of these tests indicate a high cross-link density. For some applications this is advantageous as a resin which does not distort under high heat conditions and is hard wearing has some useful applications in industry. Obviously the brittleness of the triazine resins is not desirable and needs further investigation. There are two possible reasons for this brittleness. The first, and perhaps least likely, is the fact that the triazine monomer is difunctional. In this scenario much more crosslinking can occur because there is a 4:1 monomer unsaturation:polymer unsaturation in this system. This leads to the chains being more tightly bound together and so energy dissipation within the system is more difficult

leading to a greater ease of fracture. The reason that this is less likely is that in this system there is only a certain amount of cross-linking that can occur and there are far more sites of unsaturation on the monomer than the polymer. With the fact that styrene uses up just about all of the double bonds when it cross-links the UPRs it becomes clear that a large amount of the unsaturation on the monomer will not be used.

Of course it is possible that the monomer unsaturation will homo-polymerise to form an even more interwoven cross-link matrix but the argument against this is the second explanation for the observed brittleness of the resin. It is known that in a polyester system allyl-containing monomers have a low tendency to homo-polymerise. In fact it is thought that they produce a nearly alternating matrix with the polymer backbone. If this is the case, then, the polymer backbone chains will be more tightly bound together than in the styrenated resins where the styrene cross-links are between 2 and 7 styrene links long. It is known, from the project, that the triazine monomer will homo-polymerise but this is a very slow process and it is likely that the allyl unsaturation has a higher reactivity ratio to the fumarate unsaturation than to itself. In future studies to address this problem this must be investigated. If this proves to be the case then the monomer could be modified by using a vinyl amine substituent as the source of the monomeric unsaturation and the other two sites could be substituted with primary amine substituents (See Fig 4.1)

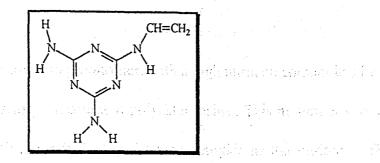


Fig 4.1: Structure of modified monomer with vinyl unsaturation and primary amine groups

A monomer such as this one could show a synergistic interaction with phosphorus additives such as TEP and DMMP via the primary amine groups and may well show better cross-link characteristics in terms of brittleness due to the presence of only one site of reactive unsaturation which, being a vinyl group, could show a better affinity to itself and so give longer cross-link chains, thus reducing the brittleness of the resin. In all the new triazine resin shows the best improvement in terms of fire behaviour over the styrenated resins when it is not treated with phosphorus additives. It does, however, show better performance when treated with phosphorus, although this improvement is not as great as would be hoped for.

In terms of mechanical performance the triazine resins have some advantages but there is scope for improvement. Future work on this project must concentrate on determining whether synergism with primary amines is possible; finding a suitable phosphorus additive, which is active when the triazine resin decomposes, if synergism is not possible; determining the cross-link structure of the resin to see why the resin is so brittle and then modifying the monomer accordingly. There is a lot of scope for this project and the future of the monomer or a modified version could be long and prosperous.

- 5.0 Conclusions
- ⇒ A new, di-functional cross-linking monomer, with a high nitrogen content has been synthesised for use in various unsaturated polyester resins. This monomer gives a high degree of cure in these resins using dicumyl peroxide as the initiator. The main drawback in cross-linking with this new monomer is that it is only possible at high temperatures. Room temperature cure is the accepted "norm".

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- ⇒ Comparative smoke testing of resins containing the new monomer compared to resins containing styrene has shown that the resins with the new triazinic monomer emit much less smoke during combustion than the equivalent styrene based resins.
 On average, 50 60% less smoke is produced from the triazine based resins.
 The use of phosphorus flame retardants had no real effect in terms of reducing smoke production in the triazine based resins. A much larger reduction was noticeable in the styrene based resins.
- ⇒ The limiting oxygen index of the triazinic resins was considerably higher than the equivalent styrenated resins, indicating a reduced tendency to burn.

The use of phosphorus flame retardants in the triazine based resins resulted in no significant increase in the limiting oxygen index. In the styrenated resin, however, a large increase in LOI value was seen with increasing amounts of the phosphorus flame retardant.

The incorporation of both melamine and phosphorus flame retardants into the resins, both triazine and styrene based, showed a small synergistic interaction between the phosphorus and the melamine. Ostensibly this is from the interaction

of the phosphate/phosphonate groups with the primary amine groups on the melamine.

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- ⇒ Resins containing the triazine monomer have a tendency to burn more quickly than resins containing styrene. The positive side of this is that they extinguish much more rapidly. Consequently the triazinic resins have a lower surface spread of flame compared to the styrenated resins. The scale of this, however, is not as large as might be wished for.
- \Rightarrow Again the use of phosphorus flame retardants has a greater effect in the styrenated resins than the triazinic resins, in terms of reducing the surface spread of flame.
- ⇒ TGA studies have shown that the triazine resins thermally decompose at lower temperatures than the styrenated resins. This is the reason for the faster burn rate shown by the triazinic resins.
- ⇒ The reason why phosphorus has a greatly reduced fire retardant effect in the triazine resins compare to the styrenated resins has been shown to lie with the fact that in all cases where phosphorus was present in the triazine resins it only made up about 16% of the total fire retardant components of the resin. The rest was made up by the triazine monomer. Under these circumstances the phosphorus was acting as it normally would but its effect was being completely masked by the effect of the triazine monomer.

- ⇒ Mechanically, the triazine based resins are much stiffer, harder and brittle, in the cured state, than the styrenated resins. This has been attributed to the nearly alternating copolymerisation seen with allyl groups in unsaturated polyester resins. This gives rise to a very high cross-link density which leads to brittleness.
- ⇒ In general the new monomer imparts many favourable characteristics into an unsaturated polyester resin. These include reduced smoke emission, improved flame retardancy and surface spread of flame, greater hardness and stiffness. On the negative side the resin is too brittle to be of use as a casting resin and it cannot be cured at room temperature.
- ⇒ The monomer could be improved by using vinyl substituents rather than allyl ones, to reduce brittleness and give room temperature cure. Also the use of phosphorus substituents may be of interest in terms of reducing flammability even more.

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APPENDIX A

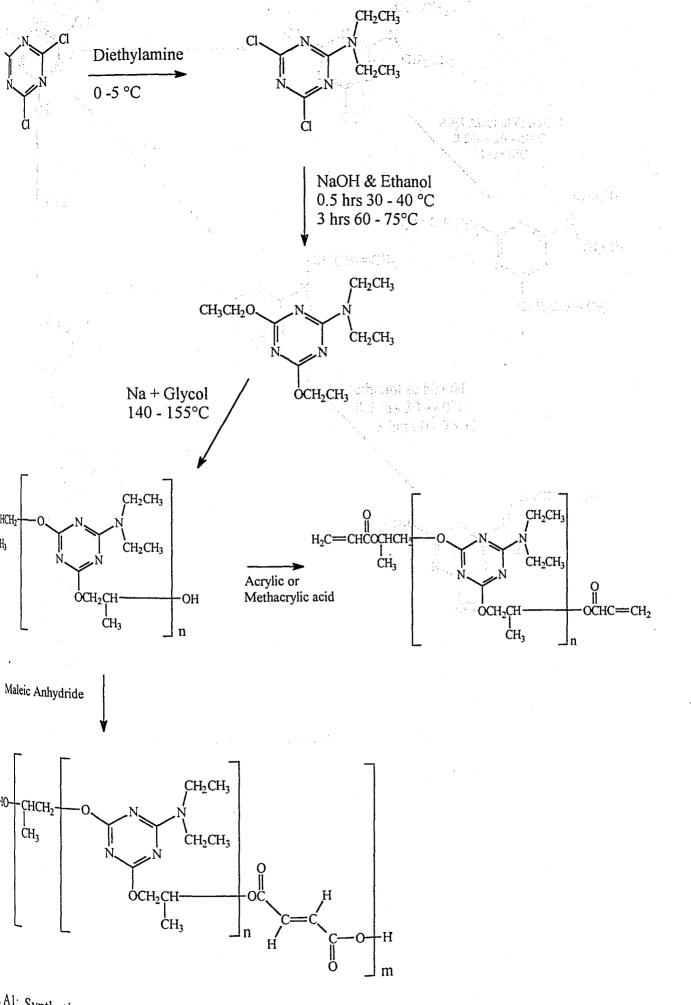
SYNTHETIC ROUTES



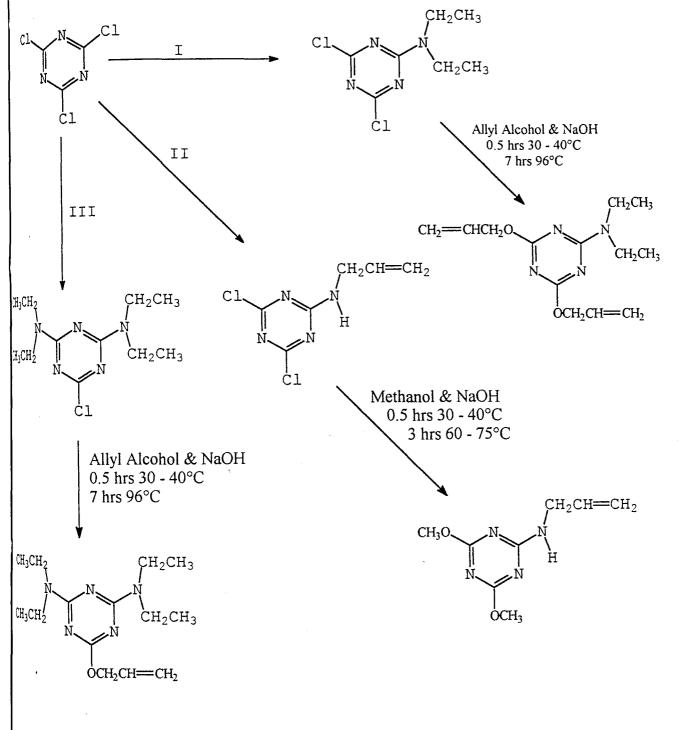
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Al: Synthetic routes to oligomeric triazine backbone



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Fig A2: Synthetic routes to alternative novel monomers

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APPENDIX B

SPECTRA OF SYNTHESISED COMPOUNDS

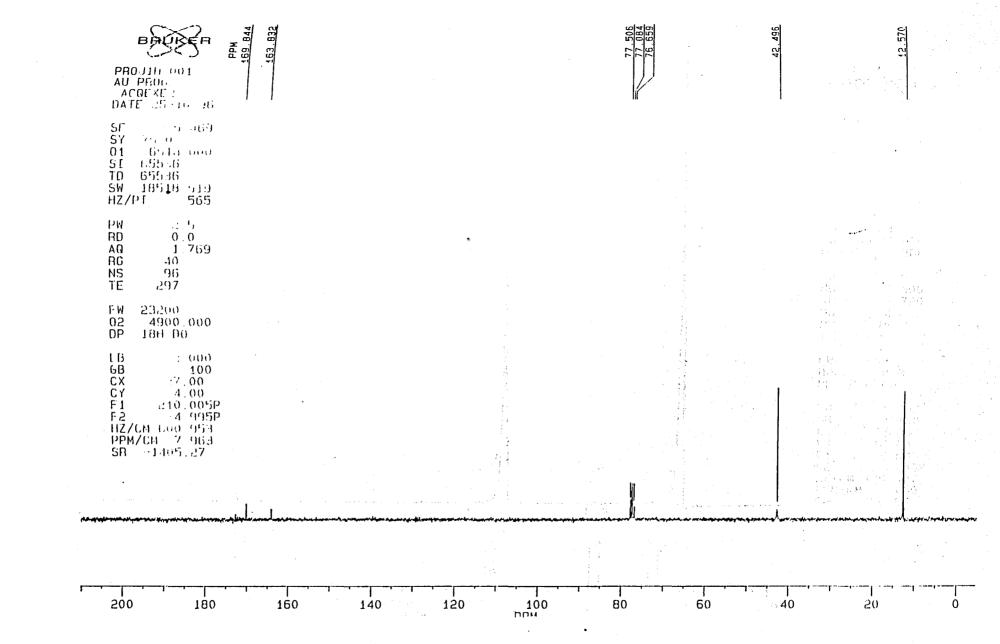


Figure B1: ¹³C NMR of 2,4-Dichloro-6-diethylamino triazine

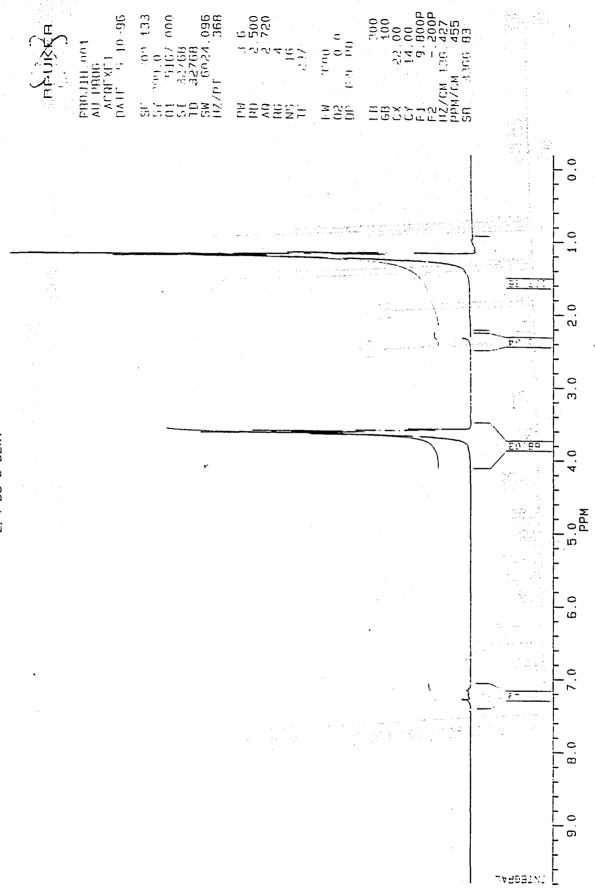


Figure B2: ¹H NMR of 2,4-Dichloro-6-diethylamino triazine

2.4-DC-6-DEAT

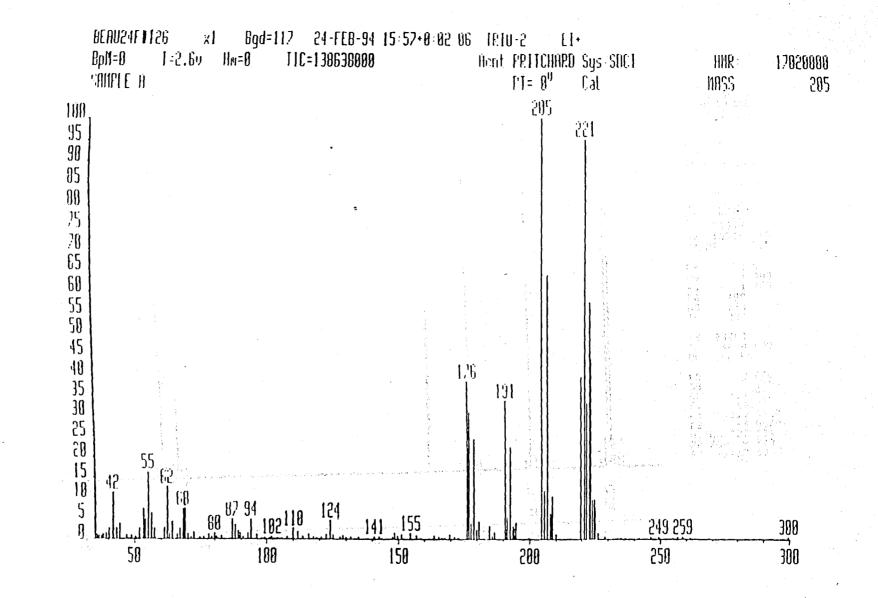
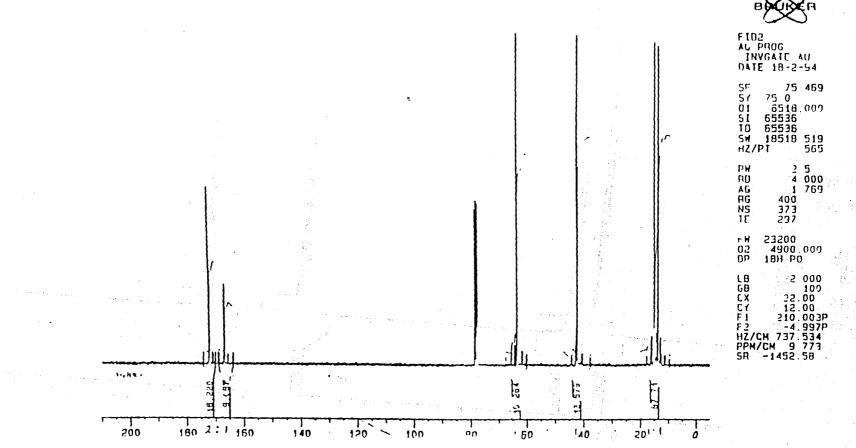
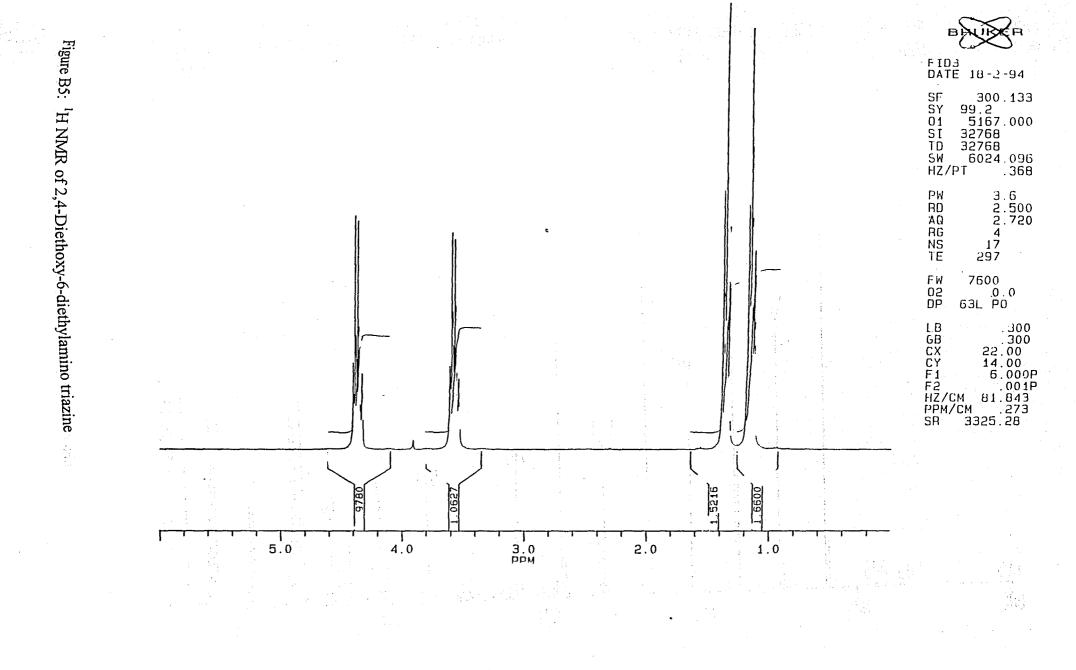


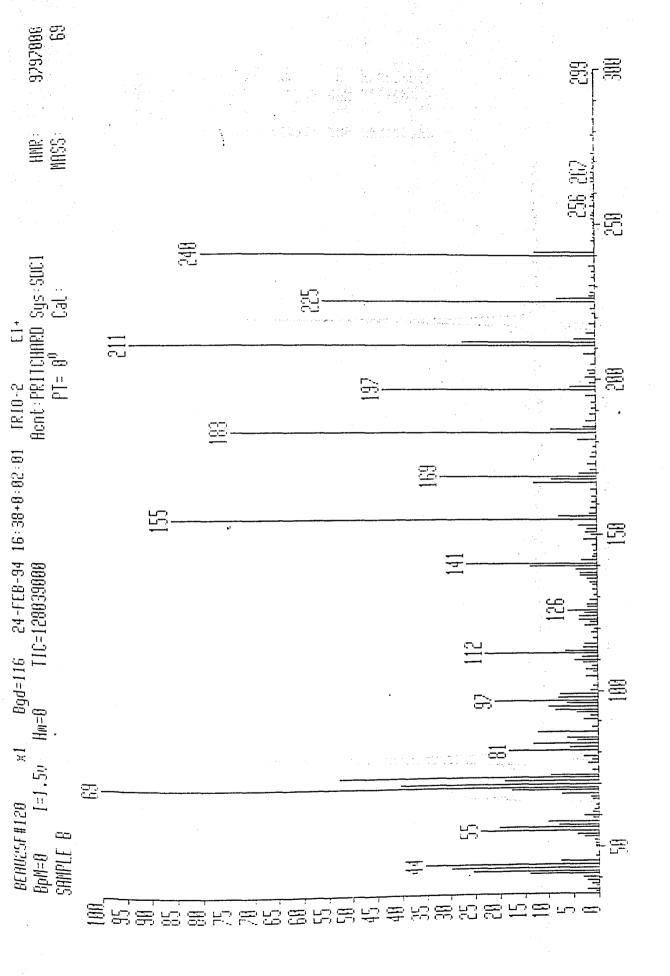
Figure B3: Mass spectrum of 2,4-Dichloro-6-diethylamino triazine

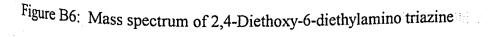
Figure B4: ¹³C NMR of 2,4-Diethoxy-6-diethylamino triazine

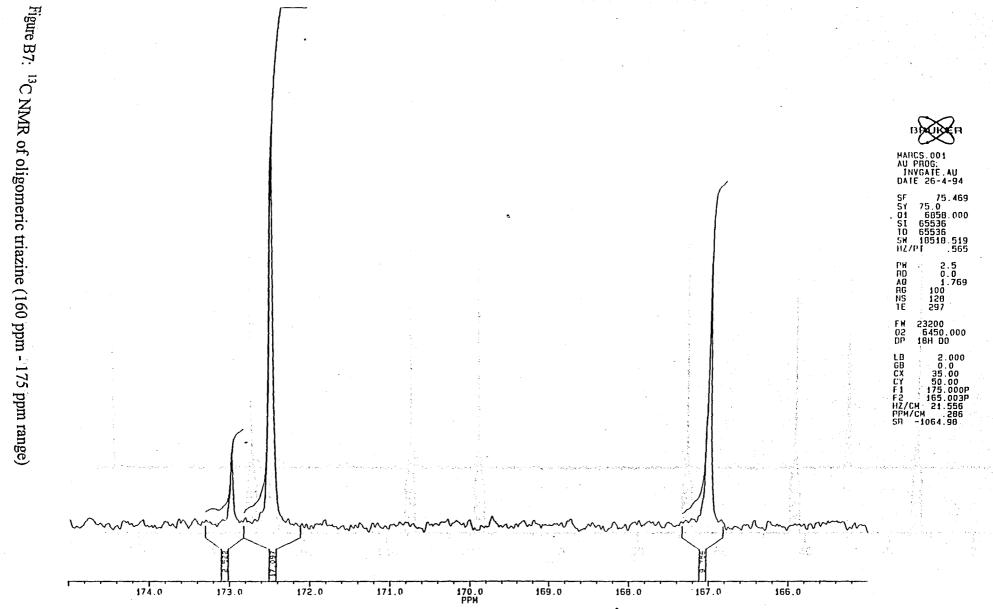


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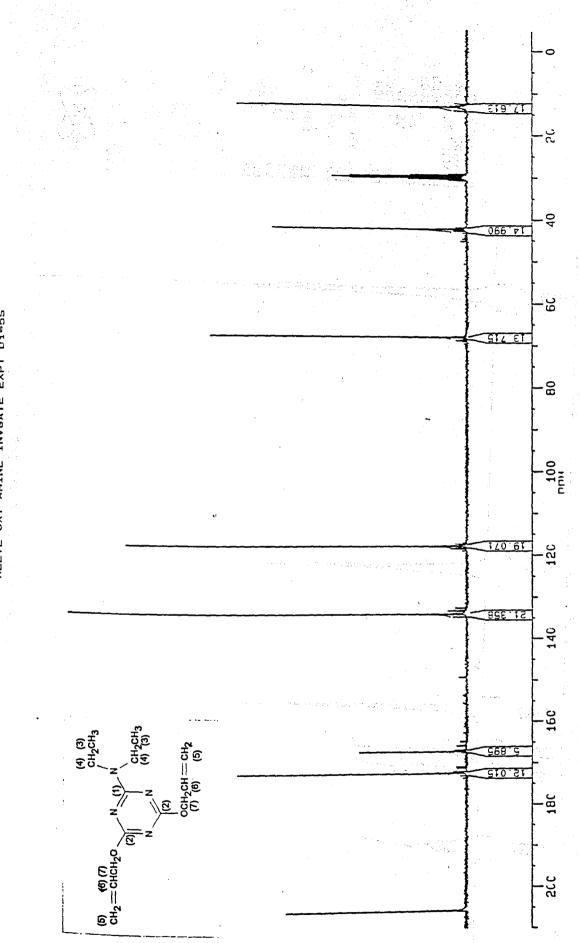


Figure B8: ¹³C NMR of 2,4-diallyoxy-6-diethylamino triazine

ALLYL OXY AMINE INVGATE EXPT D1=55

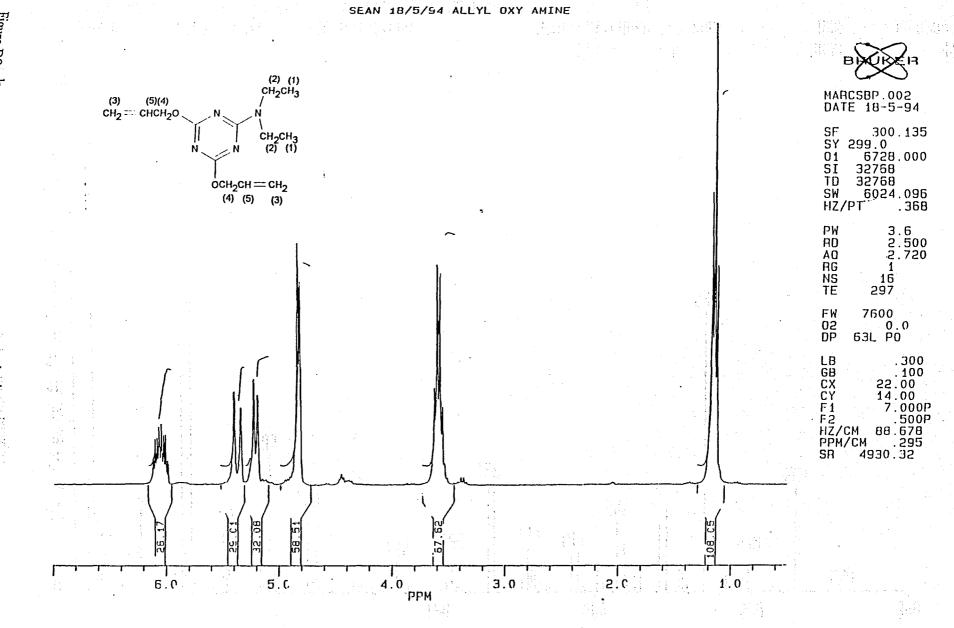


Figure B9: ¹H NMR of 2,4-diallyoxy-6-diethylamino triazine a tradition

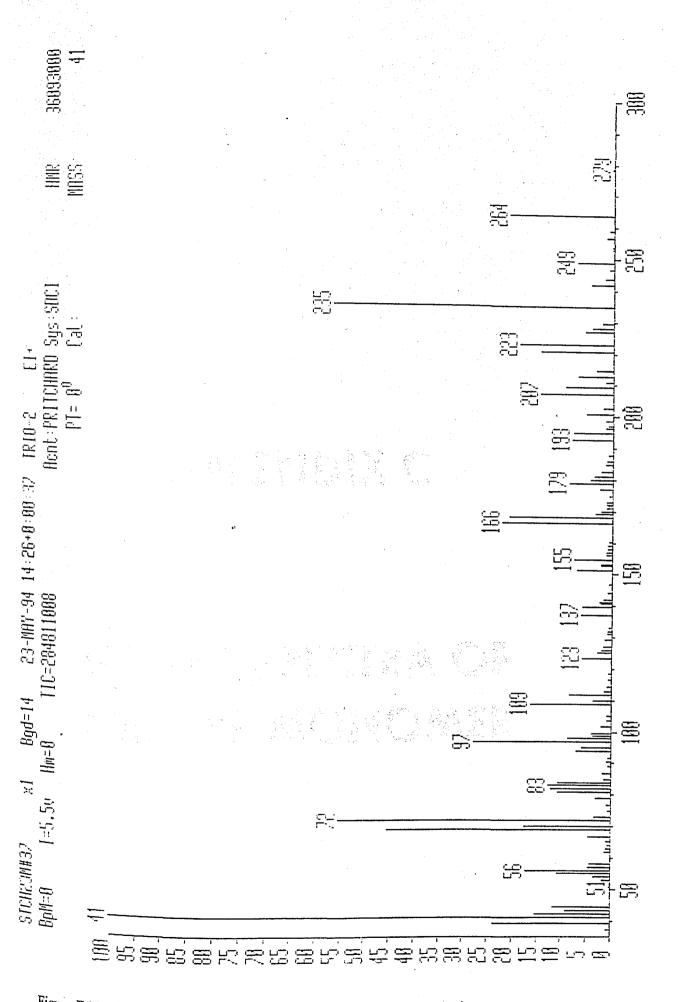
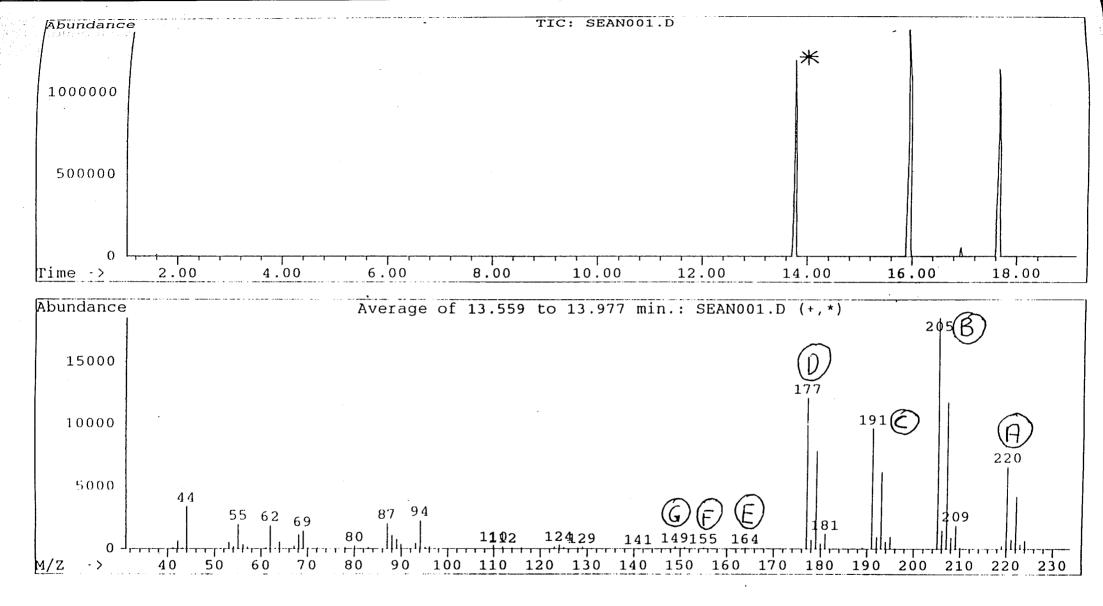
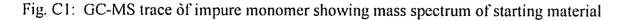


Figure B10: Mass spectrum of 2,4-diallyoxy-6-diethylamino triazine

GC-MS SPECTRA OF IMPURE MONOMER

APPENDIX C





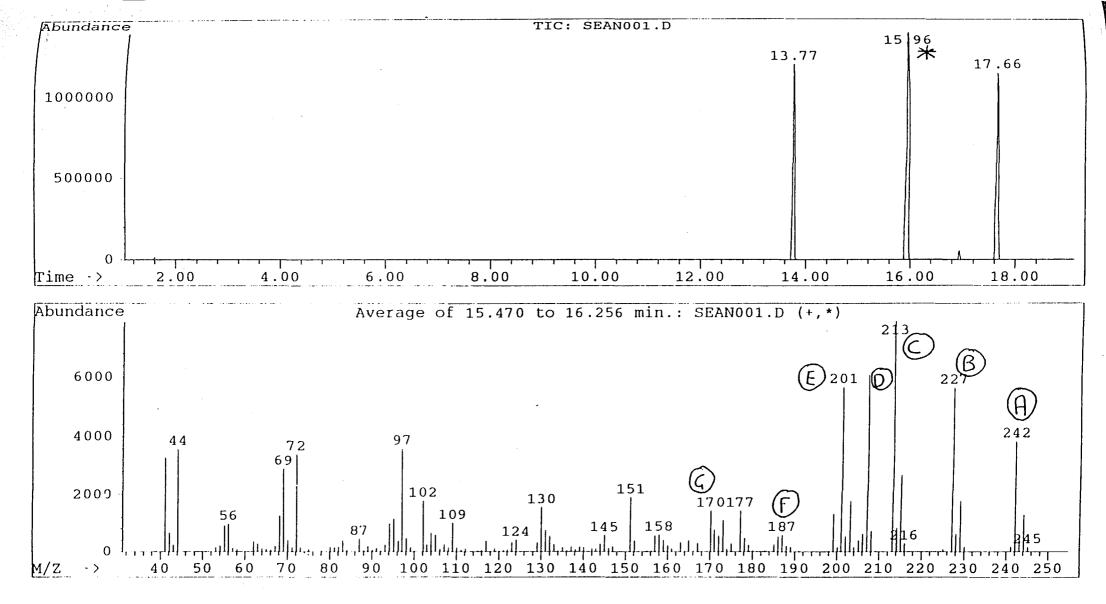


Fig. C2: GC-MS trace of impure monomer showing mass spectrum of mono-substituted monomer

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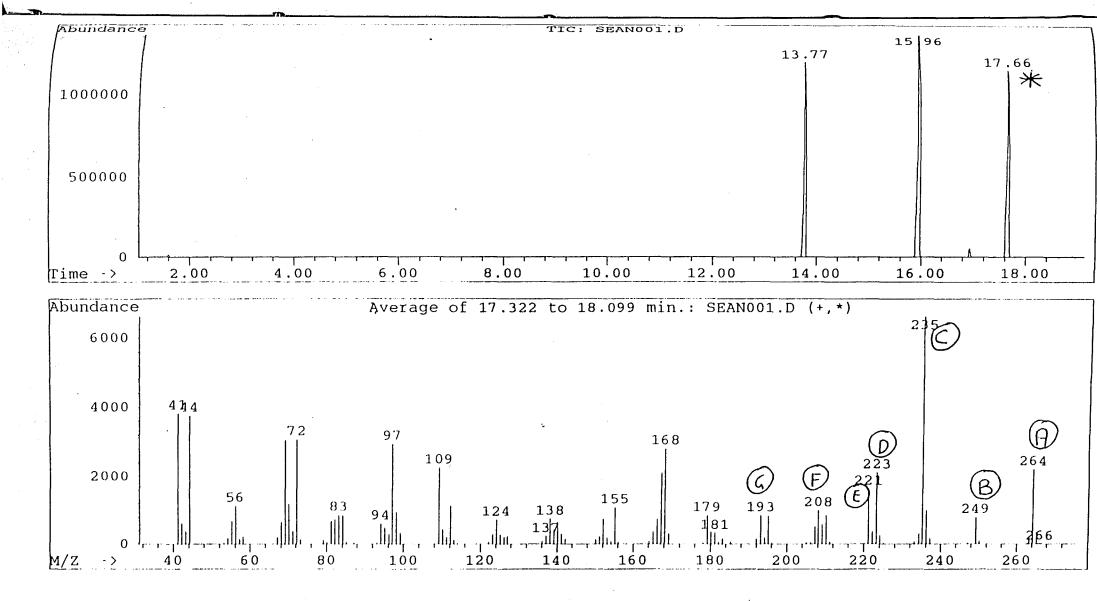


Fig. C3: GC-MS trace of impure monomer showing mass spectrum of desired monomer

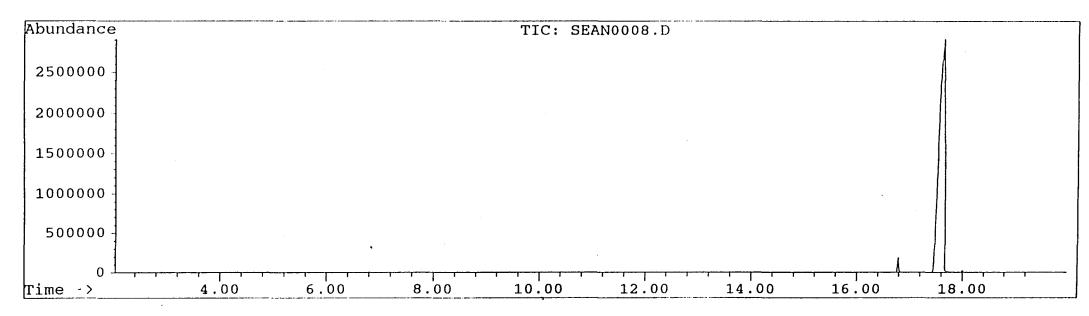


Fig. C4: GC trace of pure monomer

SMOKE TESTING APPARATUS

APPENDIX D

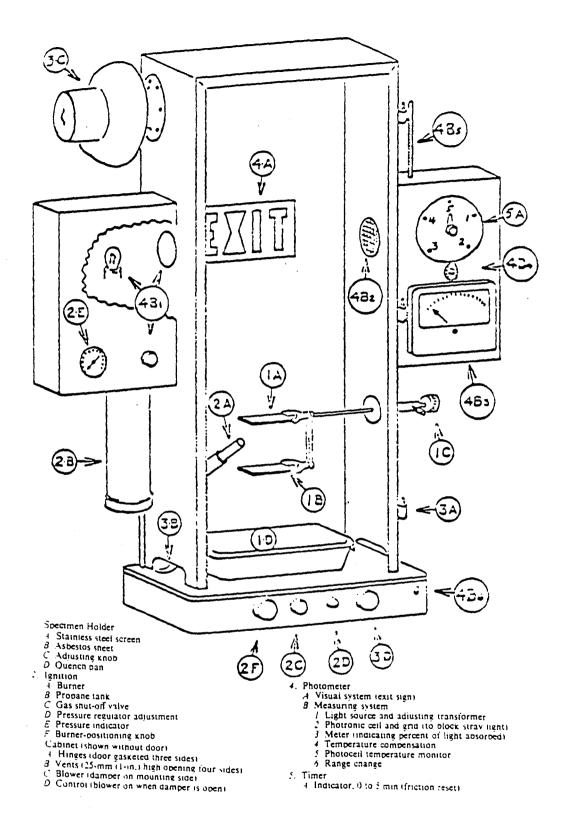


Figure D1: Schematic diagram of Smoke Chamber

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APPENDIX E

INITIAL SMOKE TESTING RESULTS

Sample	Tmax (sec)	ODmax (%)	Total Smoke (sec)	Sample Consumed (g)	Smoke/g (sec/g)	Smoke Density Rating (%)	Text (sec)
SAD01	99	49.3	6995	3.9	1793	29.18	140
SAD02	104	43.0	6290	3.2	1965	26.21	124
SAD03	144	38.0	5154	3.2	1610	21.47	135
SAD04	142	43.7	5988	2.8	2138	24.95	135
SAD05	148	54.3	7265	3.6	2018	30.27	136
SAD06	134	58.5	7972	3.3	2415	33.22	128
TAD 01	180	39.5	4449	5.7	780	18.54	158
TAD02	180	26.0	2872	4.8	598	11.95	138
TAD03	198	34.5	3825	5.3	721	15.94	162
TAD04	200	58.3	5955	5.6	1063	24.81	170
TAD05	192	67.0	7895	5.2	1518	32.90	160
TAD06	195	74.0	8310	5.0	1662	34.63	152
SND01	129	72.7	11825	4.1	· 2884	49.27	150
SND02	101	91.0	14048	4.5	3121	58.53	151
SND03	113	88.3	13465	3.7	3639	56.11	123
SND04	101	96.0	15234	3.5	4352	63.48	120
SND05	94	97.0	15995	4.0	3998	66.64	101
SND06	72	98.3	17095	3.8	4498	71.23	131
TND01	162	83.0	9053	6.1	1484	37.72	140
TND02	146	50.5	6592	5.1	1292	27.47	136
TND03	142	55.5	11797	5.8	2033	49,15	148
TND04	139	62.1	11077	5.6	1977	46.15	143
TND05	135	58.3	9228	5.8	1591	38.45	151
TND06	146	60.3	10118	6.2	1631	42.16	126

Table E1: Results from initial Smoke testing with DMMP

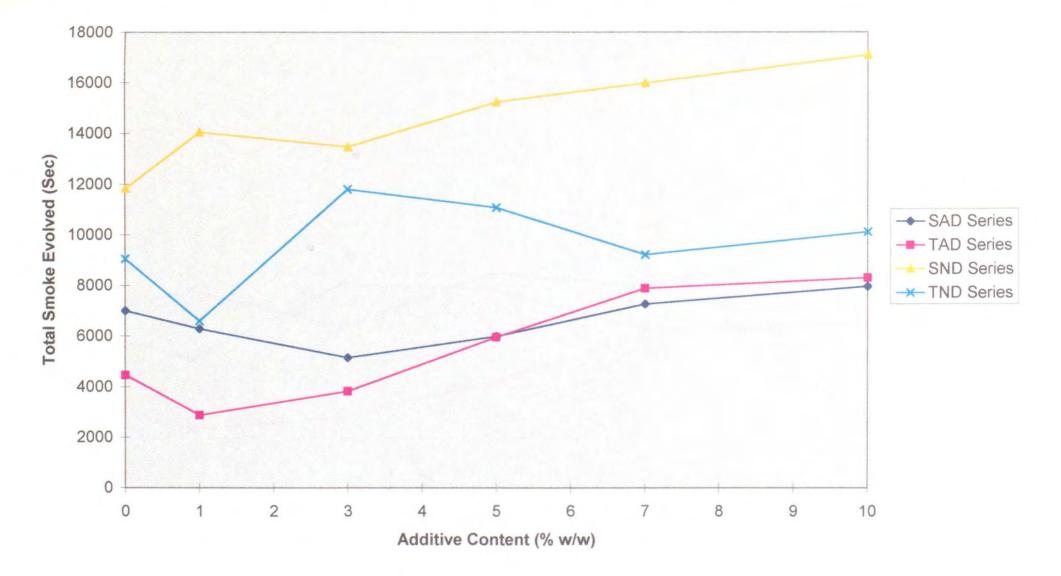


Fig. E1: Total Smoke Evolved vs DMMP Content of Resin

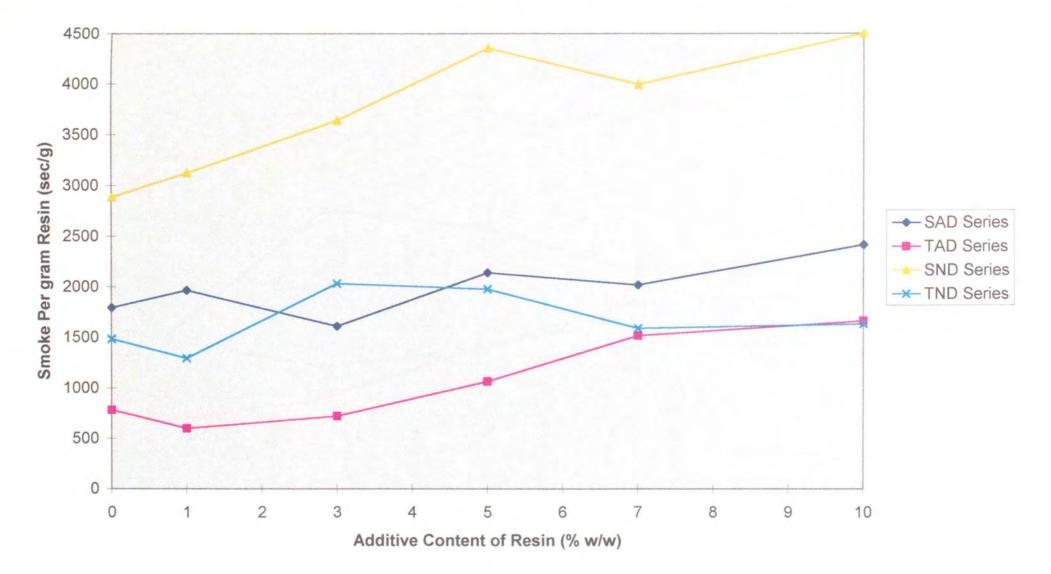


Fig. E2: Smoke per Gram Resin Burnt vs DMMP Content of Resin

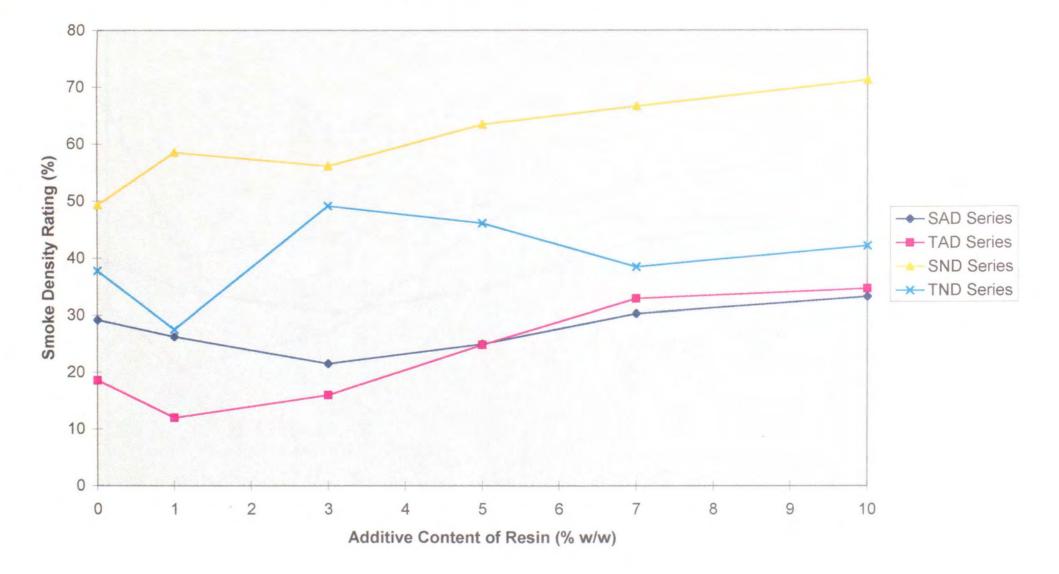


Fig. E3 :Smoke Density Rating vs DMMP Content of Resin

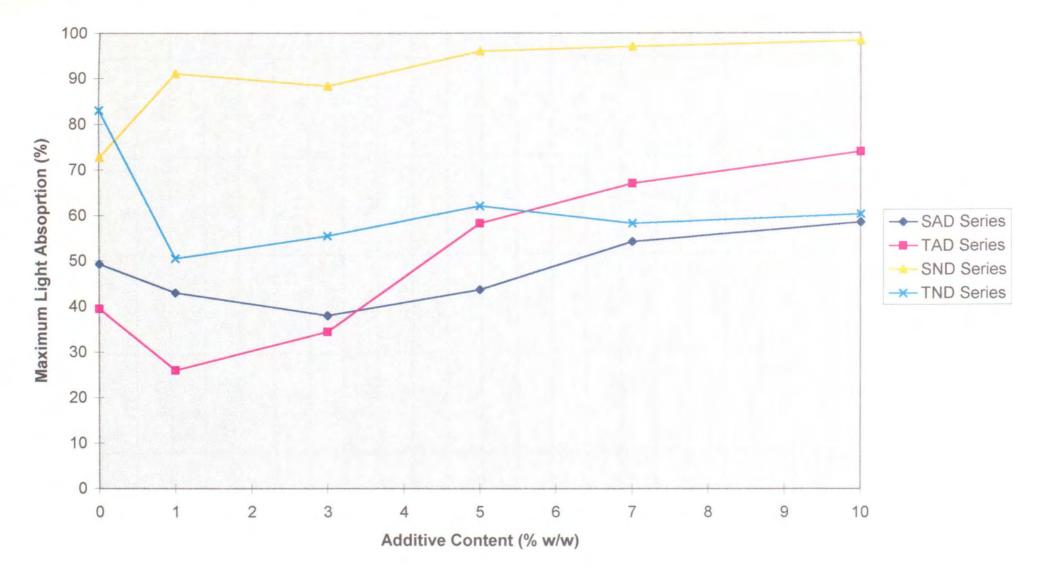


Fig. E4: Maximum Light Absorption vs DMMP Content of Resin

Sample	ODmax (%)	Sample	Total	Smoke/g	Smoke
Sample		Consumed	Smoke (sec)	(sec/g)	Density
			Sinoke (See)	(300/g)	
		(g)			Rating (%)
SAT'01	86.0	4.28	13315	3111	55.48
SAT'02	76.3	3.44	10430	3031	43.36
SAT'03	72.7	3.14	10535	3355	43.89
SAT'04	64.3	3.06	90825	3969	37.95
SAT'05	79.0	3.60	10995	3054	45.81
SAT'06	59.0	3.33	8085	2428	34.81
TAT'01	37.3	4.62	3440	745	14.33
TAT'02	44.5	4.25	3938	927	16.41
TAT'03	41.5	4.94	3938	797	16.41
TAT'04	42.6	4.34	3625	835	15.10
TAT'05	24.0	3.77	2820	748	11.75
TAT'06	30.0	3.55	2737	771	11.41
SNT'01	84.0	4.15	13125 *	3162	54.69
SNT'02	97.0	4.81	15615	3246	65.05
SNT'03	95.7	4.25	15890	3739	66.21
SNT'04	95.0	3.29	13225	4020	55.10
SNT'05	97.7	4.86	14925	3071	62.19
SNT'06	98.0	5.17	16820	3149	67.83
TNT'01	52.0	4.21	9965	2367	37.85
TNT'02	59.0	3.69	10045	2722	41.85
TNT'03	57.7	4.00	9255	2313	38.56
TNT'04	68.7	4.00	11230	2808	46.79
TNT'05	59.3	3.86	13260	3435	55.25
TNT'06	62.3	3.56	12985	3647	54.10

Table E2: Results from Initial Smoke Testing with TEP

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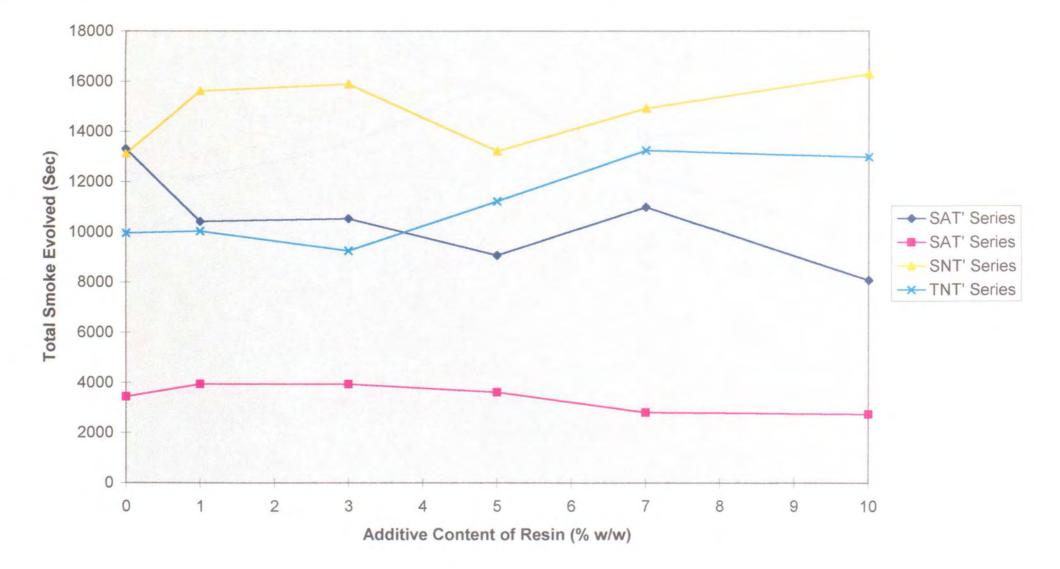


Fig. E5: Total smoke evolved vs TEP content of resin

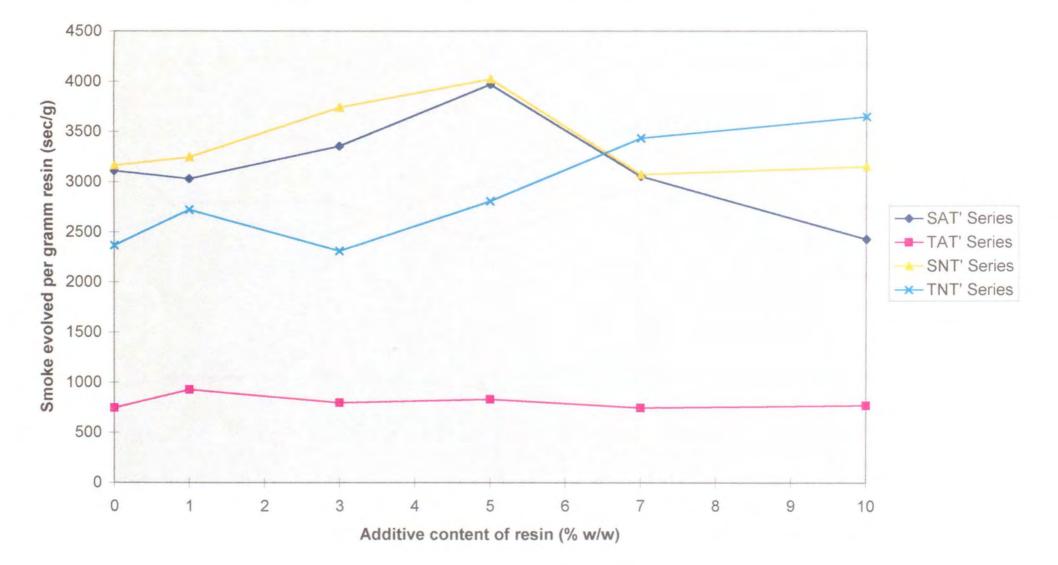


Fig. E6: Smoke per gram resin burnt vs TEP content of resin

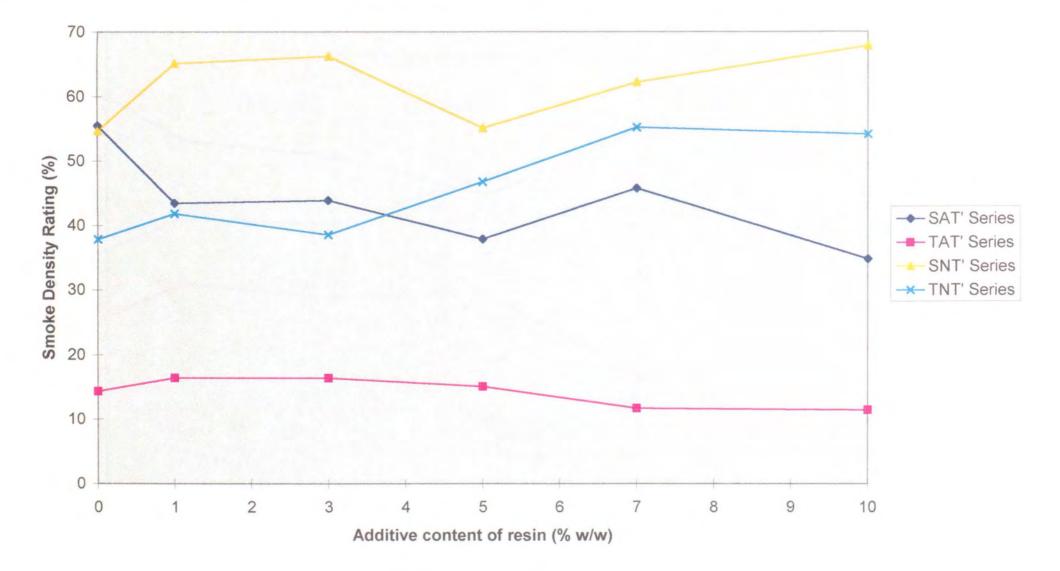


Fig. E7: Smoke Density Rating vs TEP Content of Resin

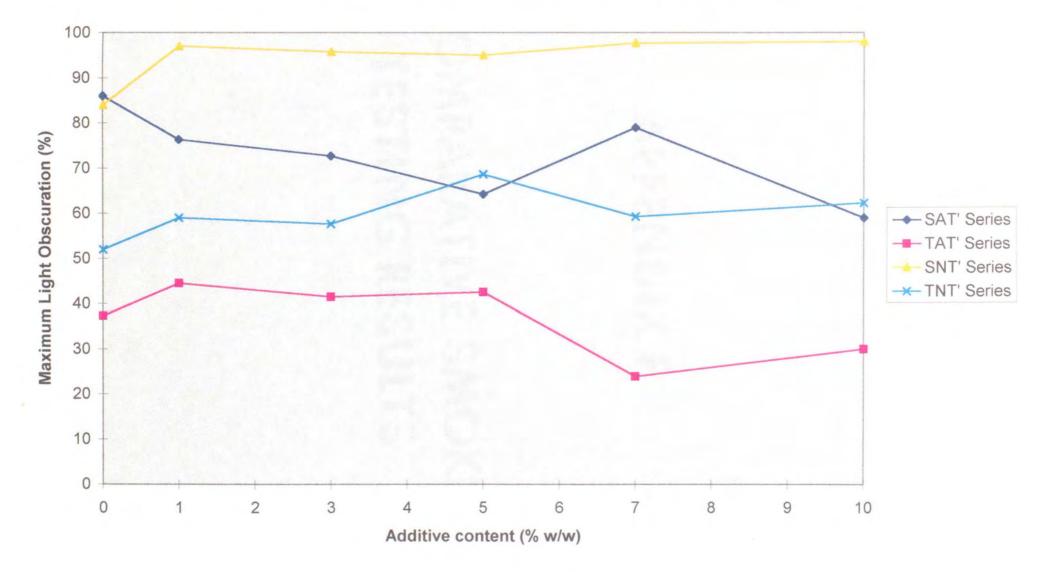


Fig. E8: Maximum light obscuration vs TEP content of resins

COMPARATIVE SMOKE TESTING RESULTS

APPENDIX F

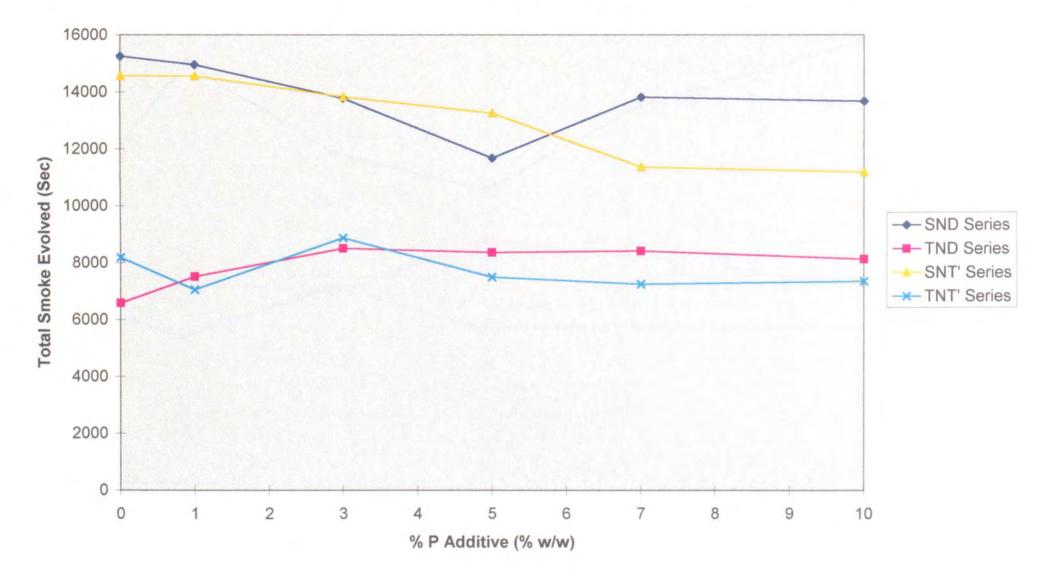


Fig. F1: Total smoke Emission vs Additive Content of Normal Resins

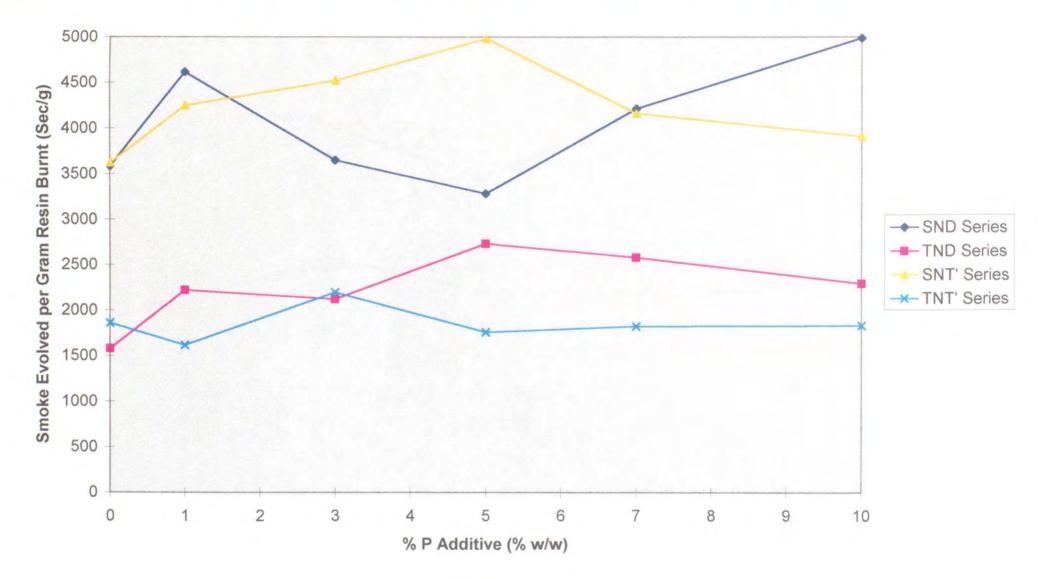


Fig. F2: Smoke evolved per gram resin burnt vs Additive content of normal Resins

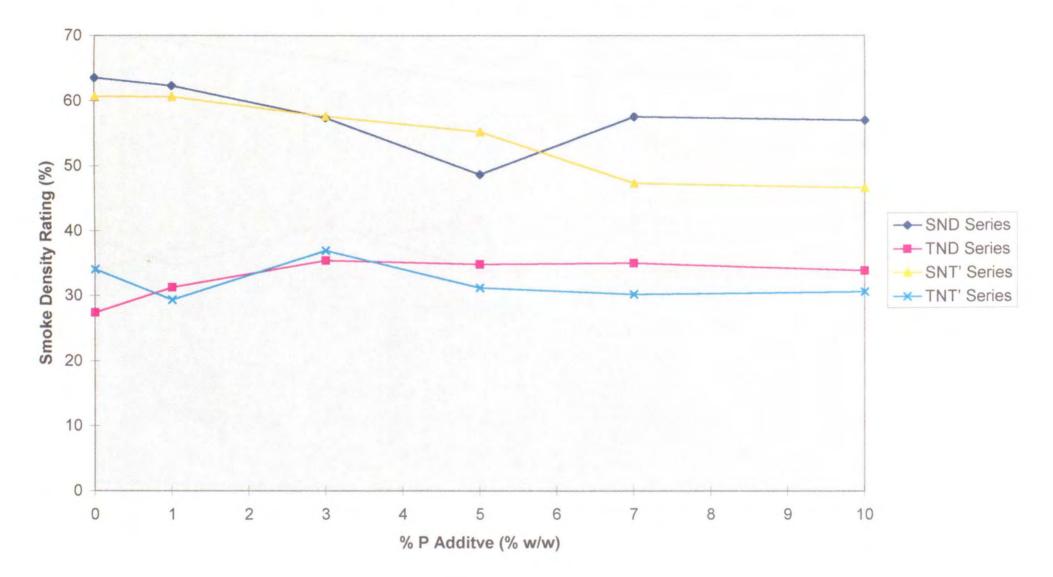


Fig. F3: Smoke Density Rating vs Additive Content of Normal Resins

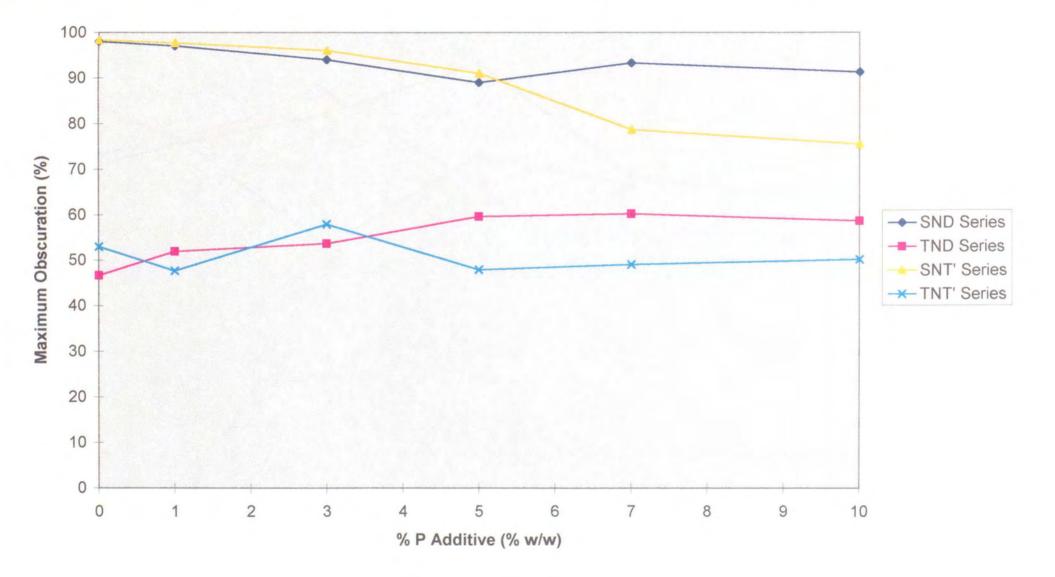


Fig. F4: Maximum Light Obscuration vs Additive Content of normal Resins

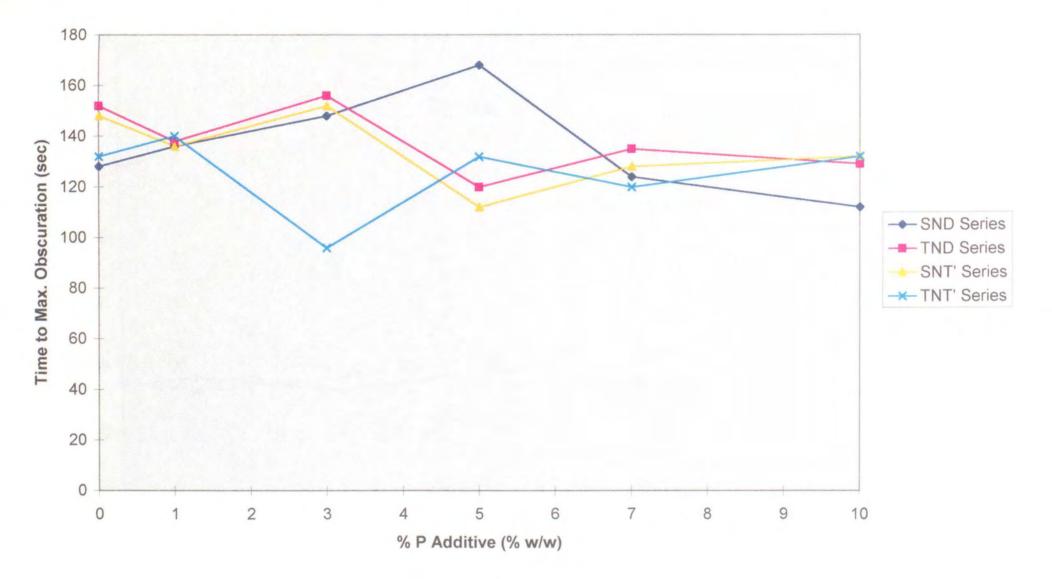


Fig. F5: Time to Maximum Light Absorption vs Additive Content of Normal Resins

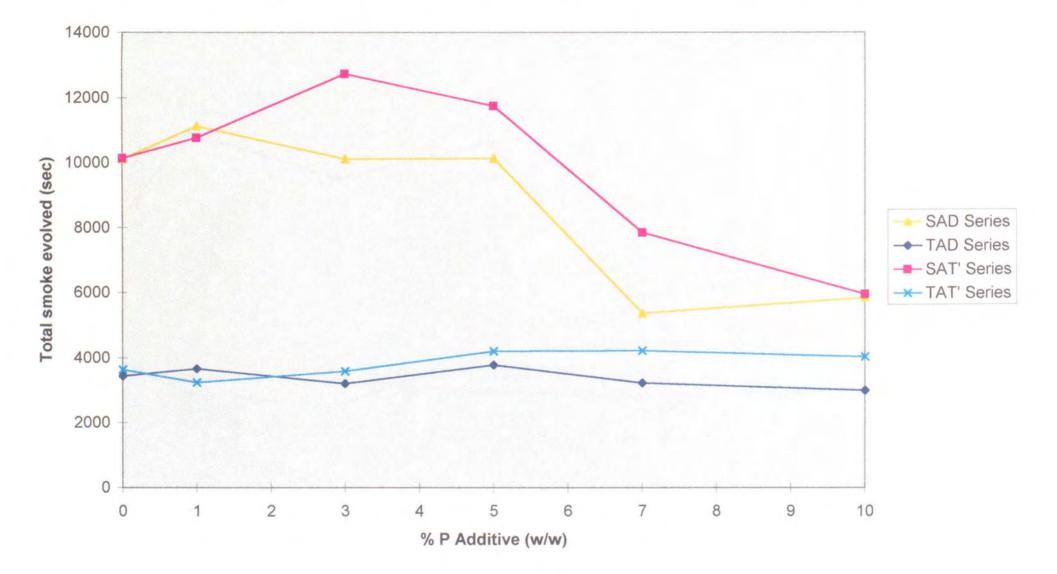


Fig. F6: Total Smoke Emission vs Additive Content of Aliphatic Resins

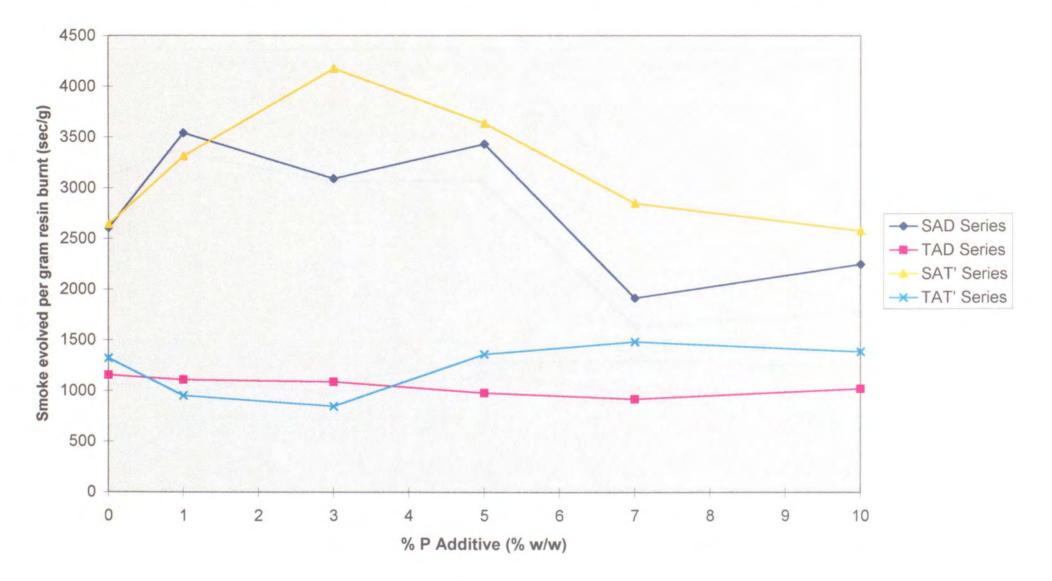


Fig. F7: Smoke Evolved per Gram Resin Burnt vs Additive Content of Aliphatic resins

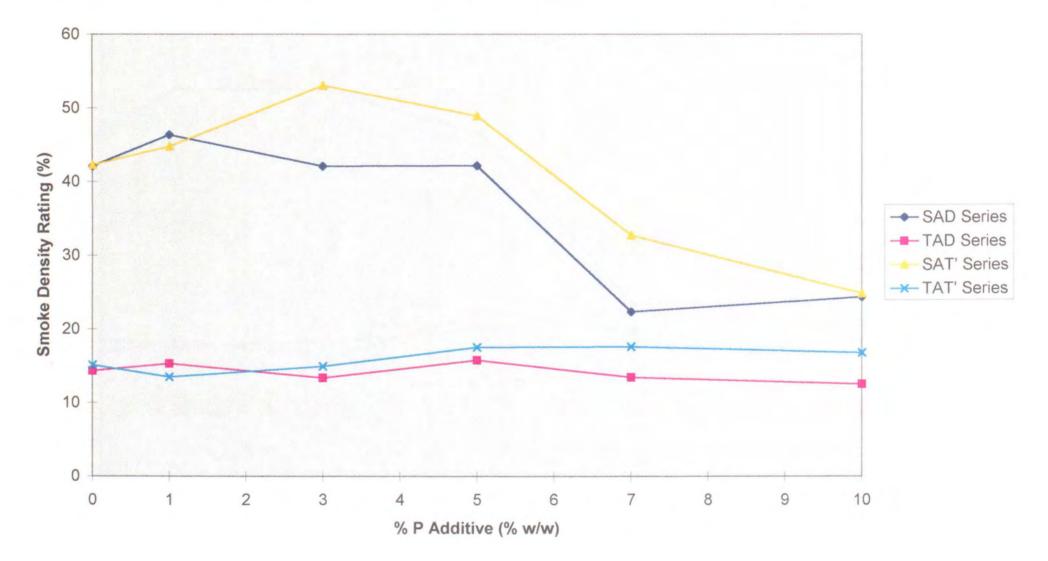


Fig. F8: Smoke Density Rating vs Additive Content of Aliphatic Resins

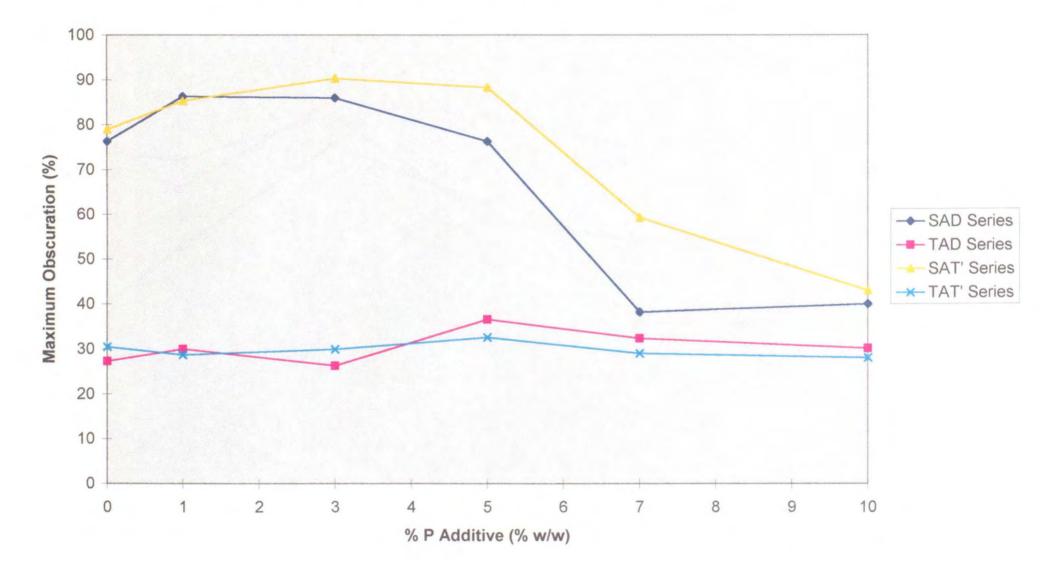


Fig. F9: Maximum Light Absorption vs Additive Content of Aliphatic resins

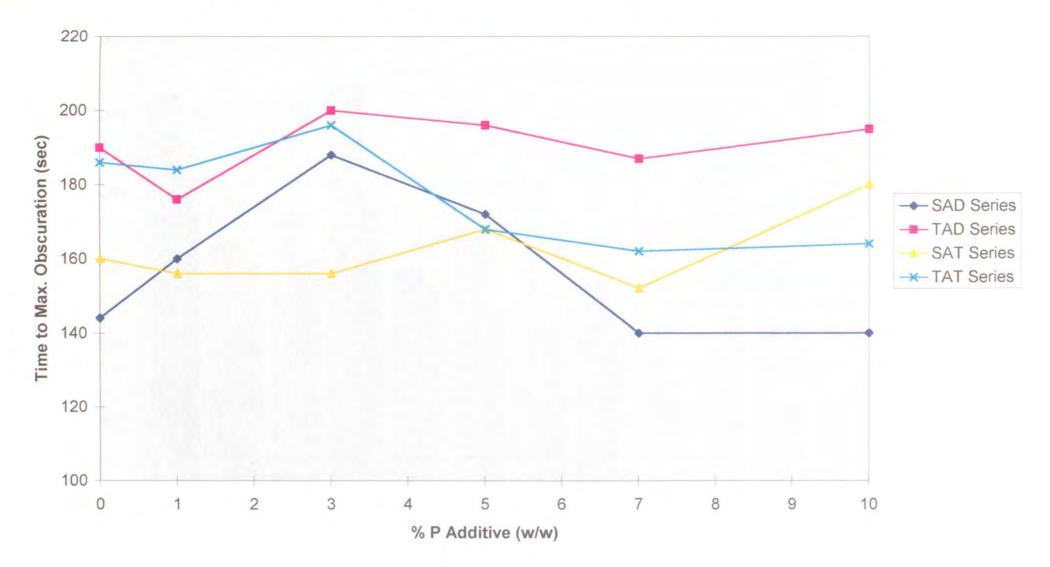


Fig. F10: Time to Maximum Light Obscuration vs Additive Content of Aliphatic Resins

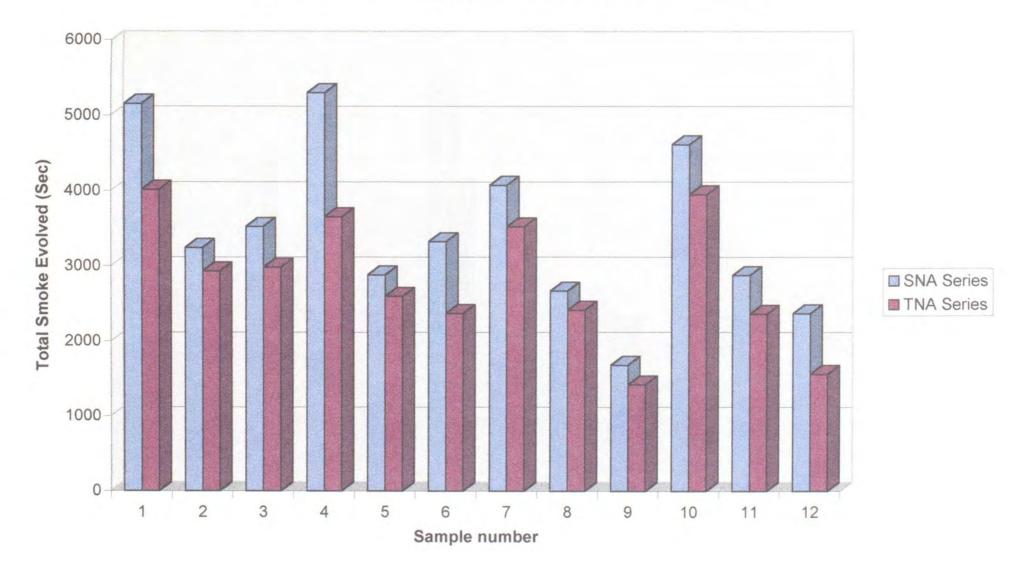


Fig. F11: Total Smoke evolved for Normal Resins Treated with ATH

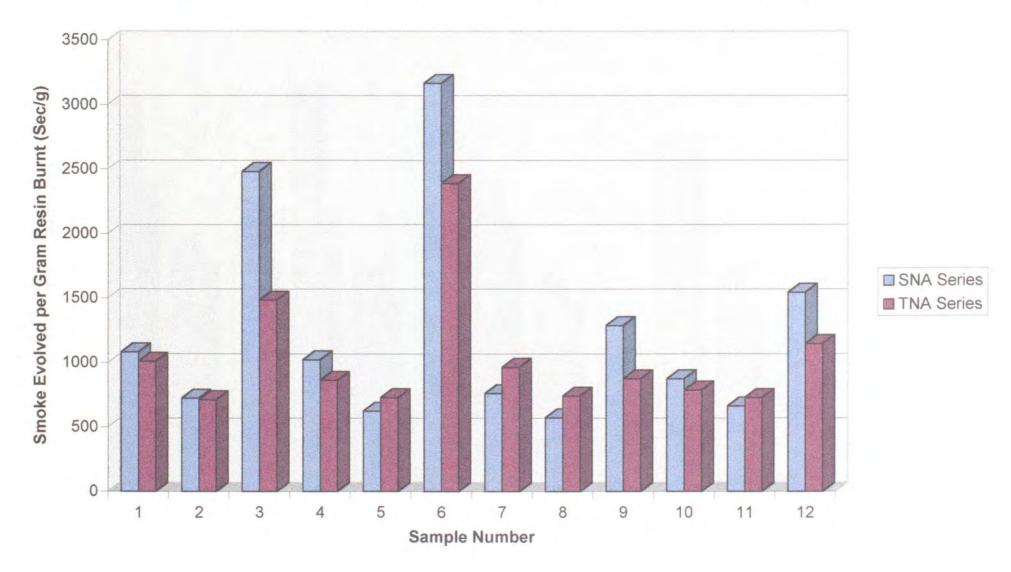


Fig. F12: Smoke Evolved per Gram Resin Burnt for Normal Resins Treated with ATH

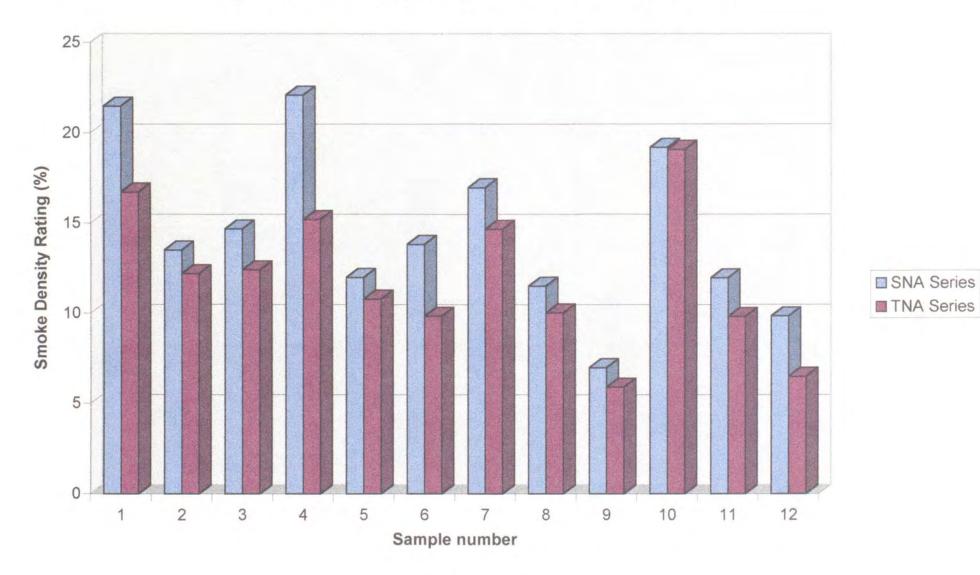


Fig. F13: Smoke Density Rating for Normal Resins Treated with ATH

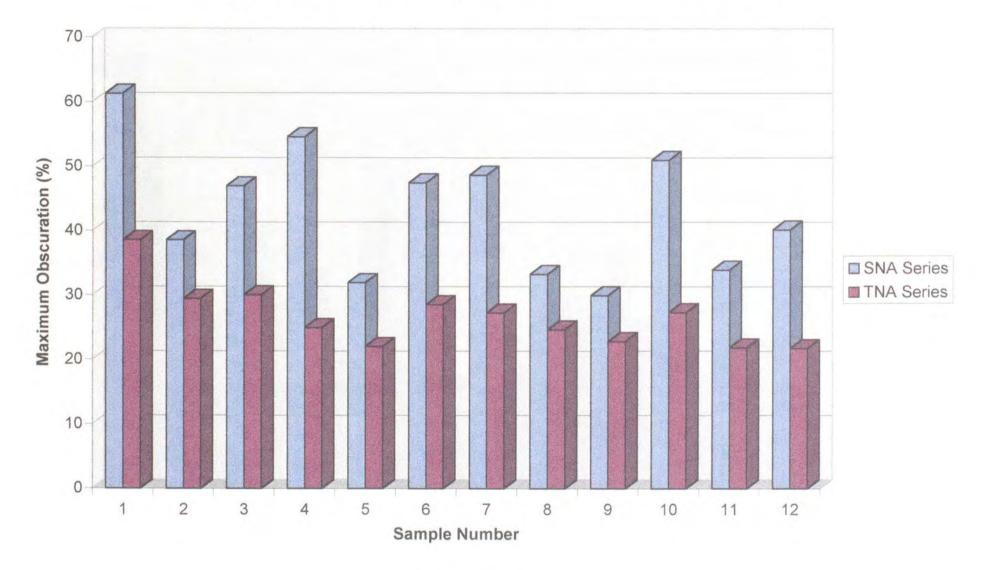


Fig. F14: Maximum Light Absorption for Normal Resins treated with ATH

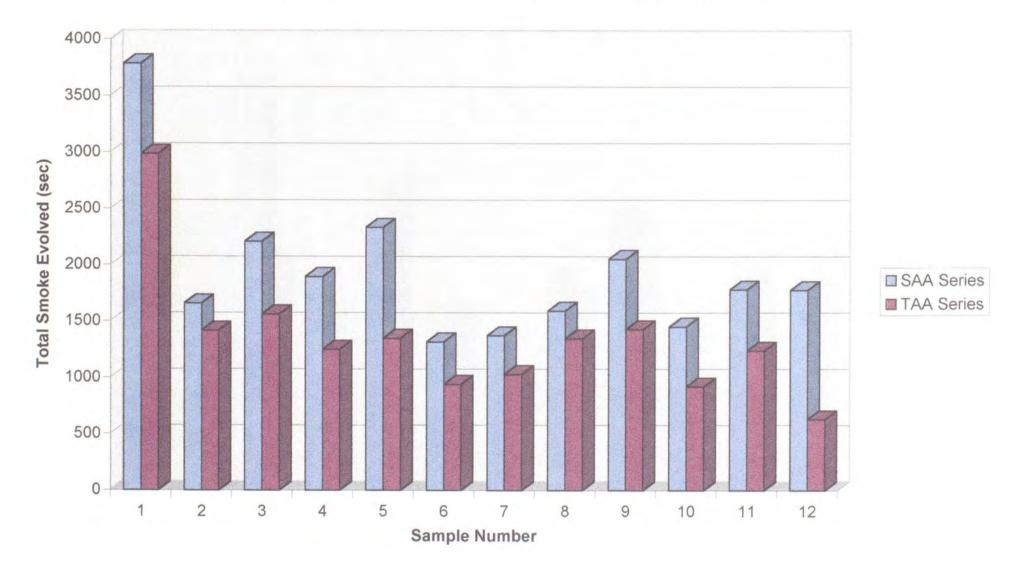


Fig. F15: Total Smoke Evolved for Aliphatic Resins treated with ATH

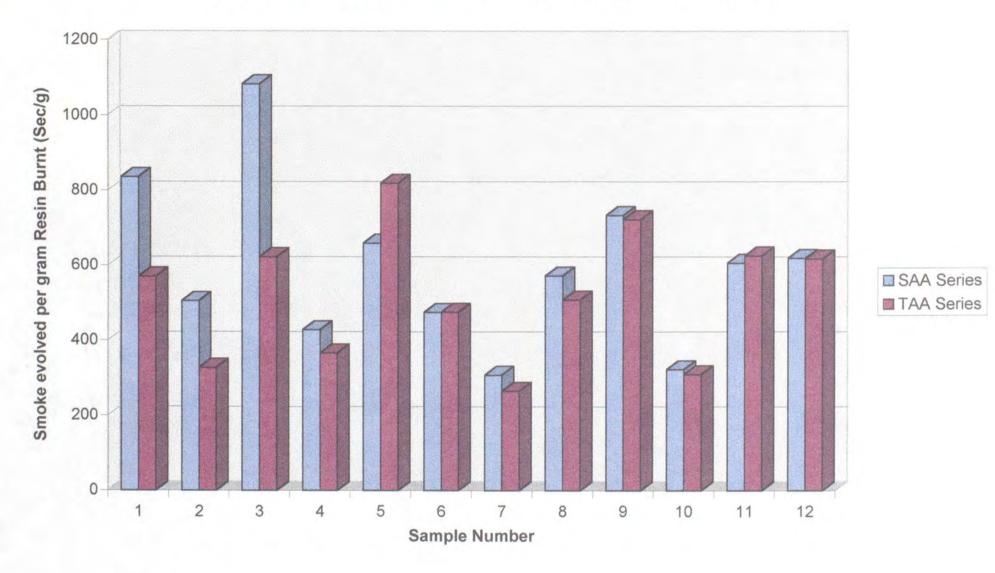
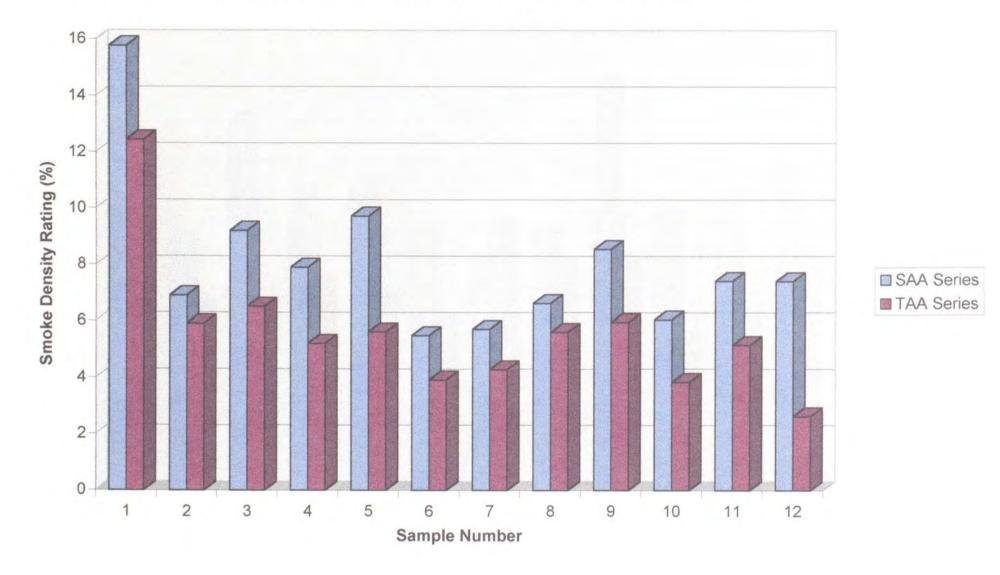


Fig. F16: Smoke Evolved per gram aliphatic Resin, Treated with ATH, Burnt



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Fig. F17: Smoke Density Rating for Aliphatic Resins Treated with ATH

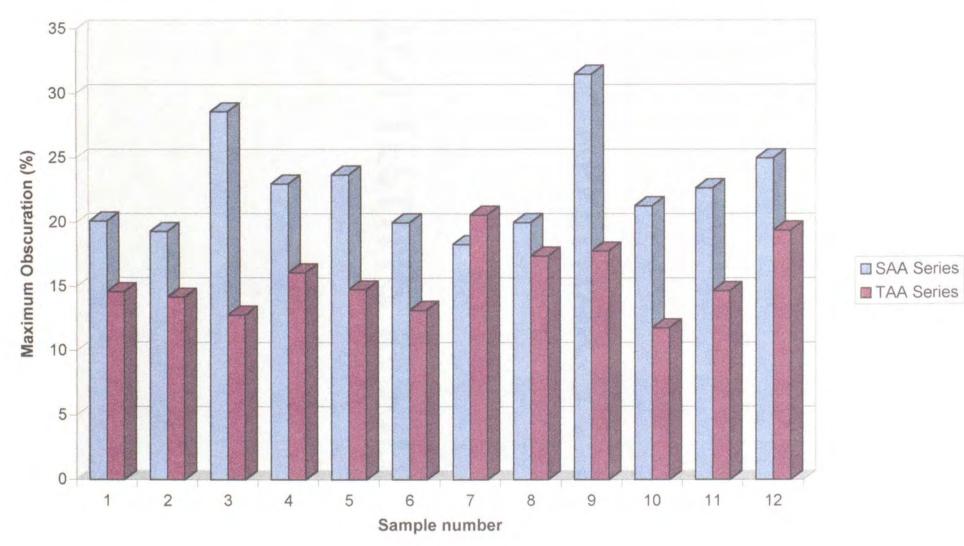


Fig. F18: Maximum Light Obscuration for Aliphatic Resins Treated with ATH

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APPENDIX G

LOI TESTING RESULTS

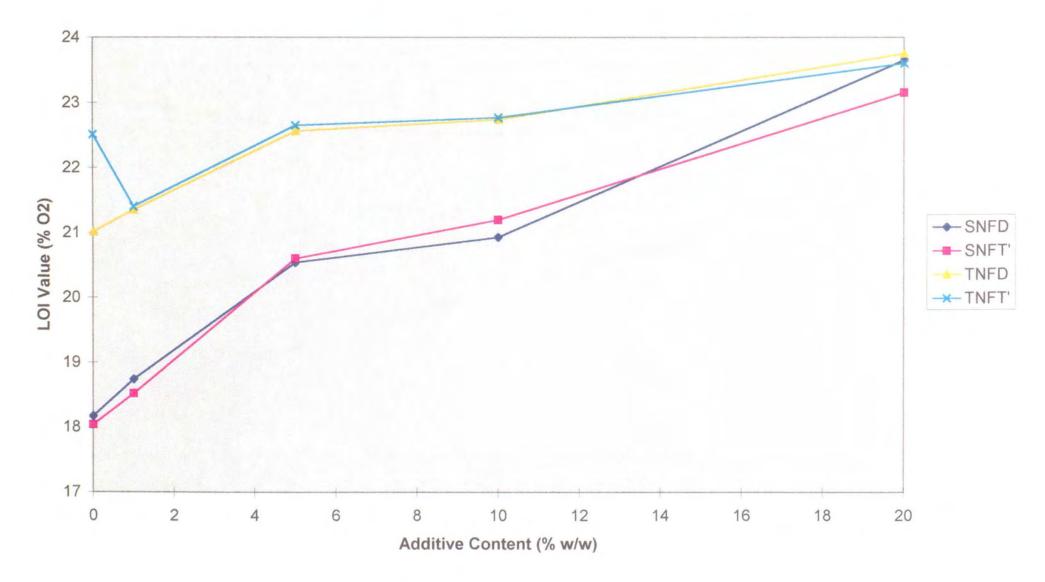


Fig. G1: LOI Value vs Additive Content of Normal Resins

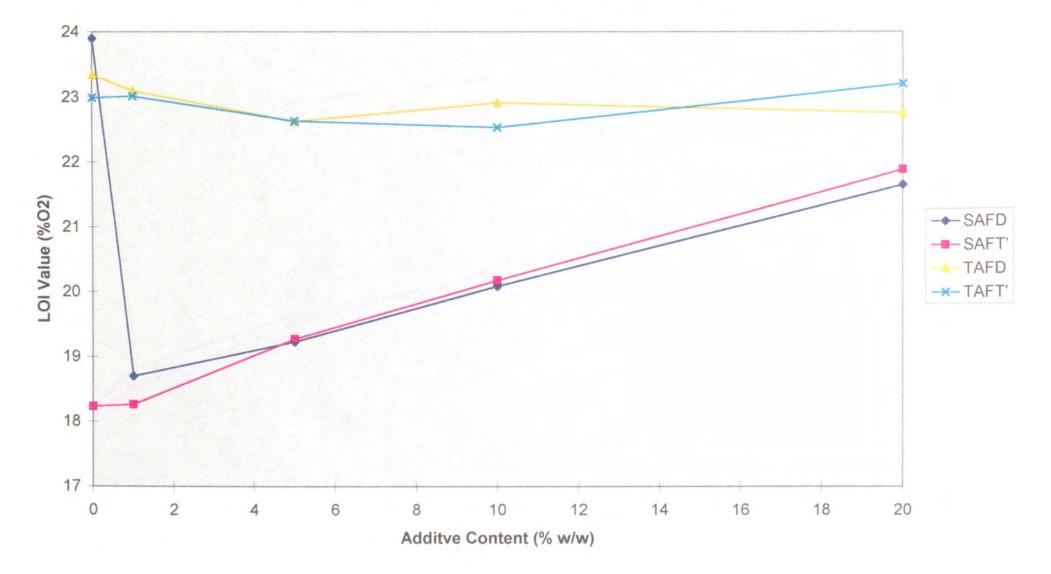
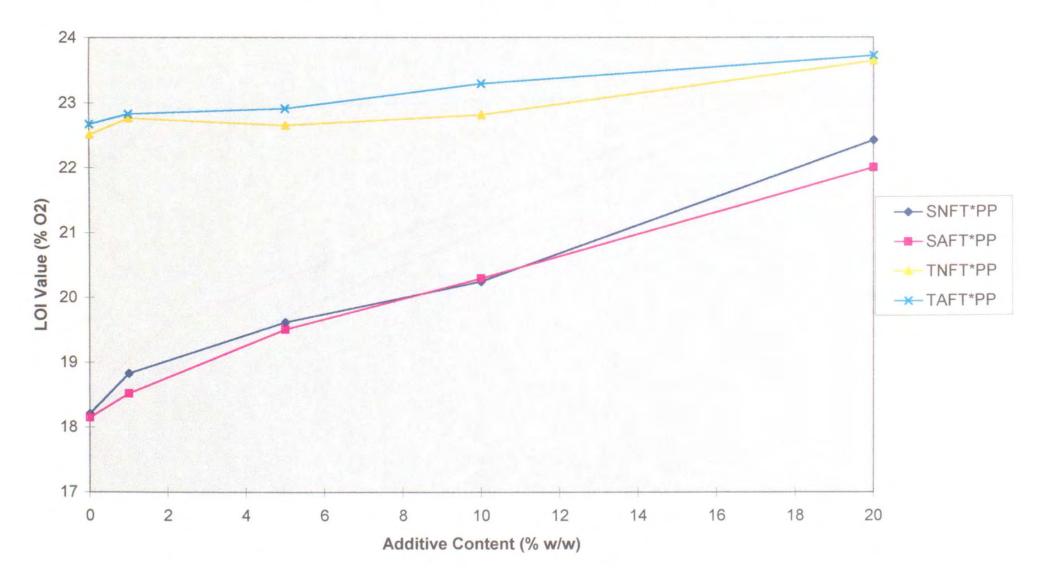


Fig. G2: LOI Value vs Additive Content of Aliphatic Resins





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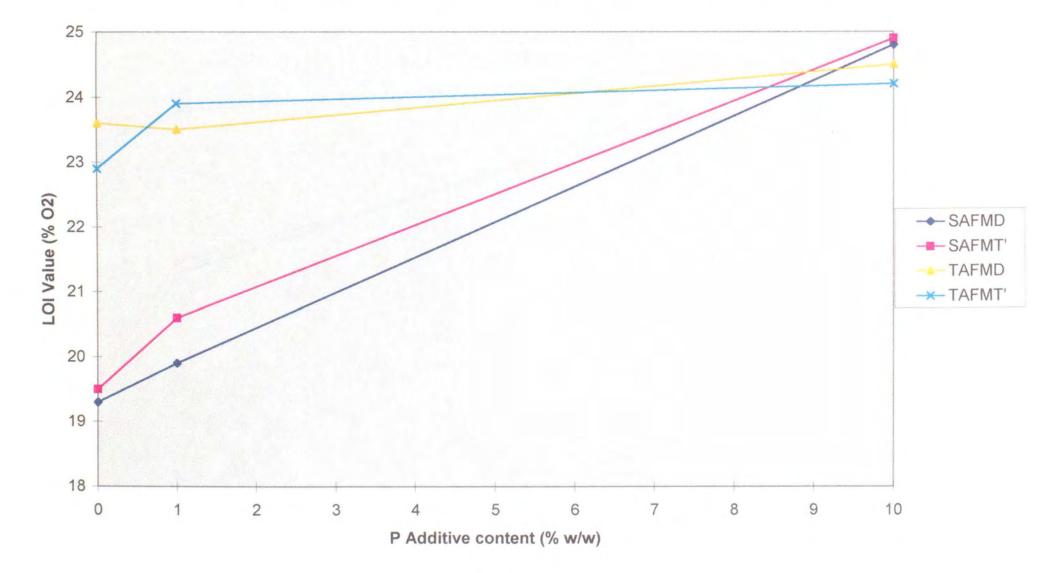


Fig. G4: LOI Value vs Additive Content for Aliphatic Resins treated with 1.875% Melamine

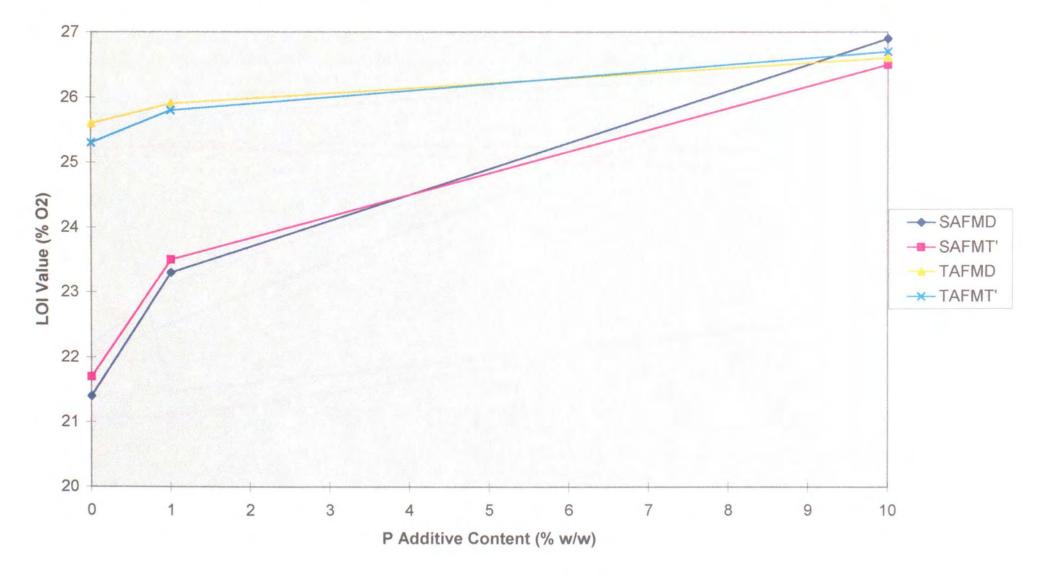


Fig. G5: LOI Value vs Additive Content of Aliphatic Resisn Treated with 18.75% Melamine

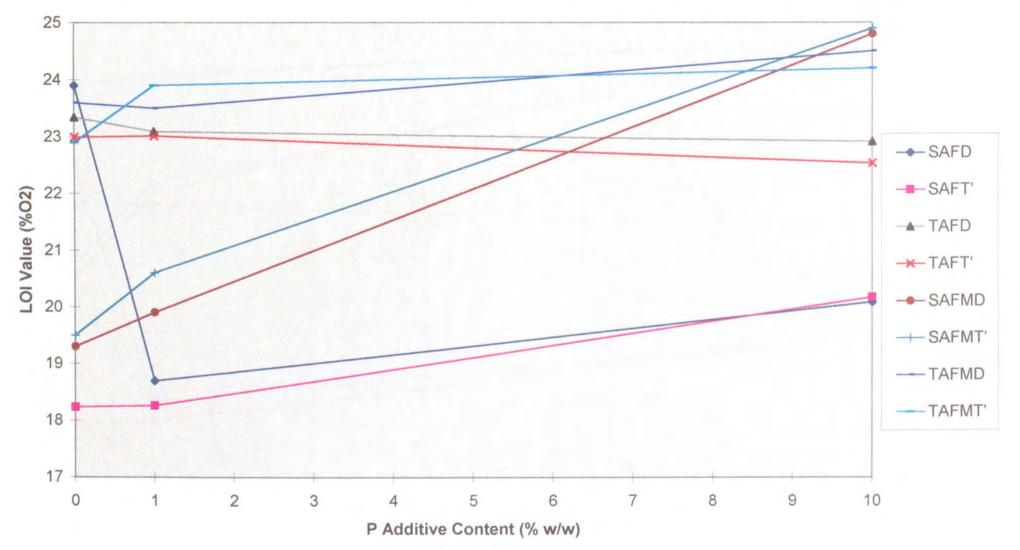


Fig. G6: Comparison of Aliphatic Resins Treated with Phosphorus Alone and with Phosphorus and 1.875% Melamine

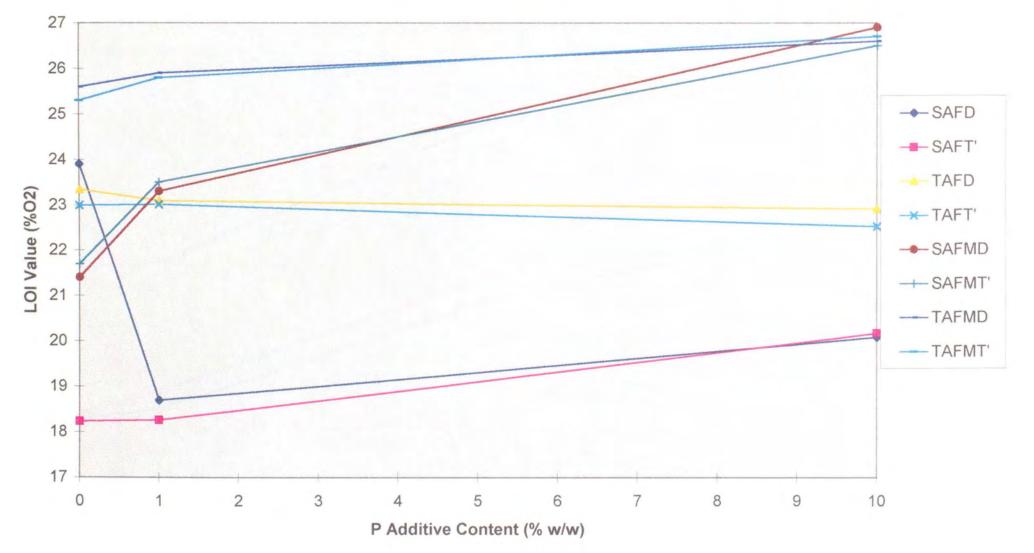
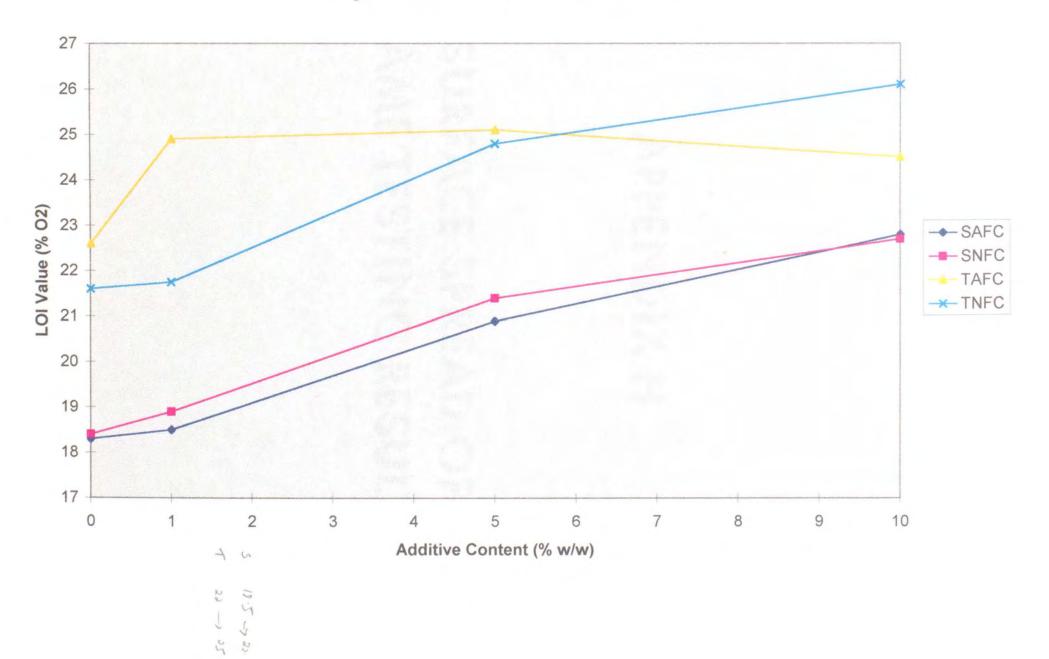


Fig. G7: Comparison of Aliphatic Resins Treated with Phosphorus alone and Phosphorus and 18.75% Melamine

Fig. G8: LOI Value vs TCEP Content of Resins



SURFACE SPREAD OF FLAME TESTING RESULTS

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APPENDIX H

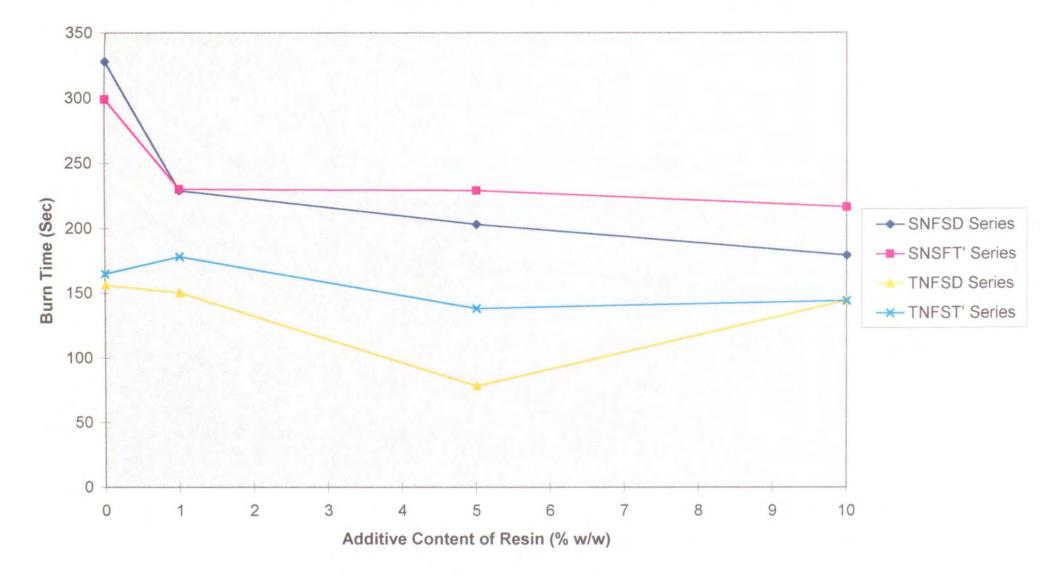


Fig. H1: Burn Time vs Additive Content of Normal Resins

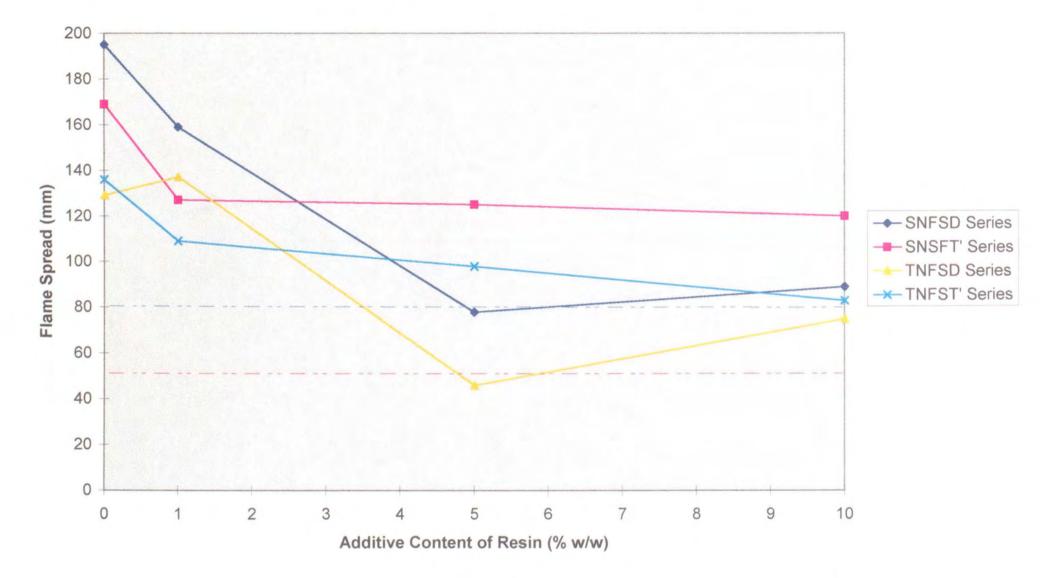


Fig. H2: Flame Spread vs Additive Content of Normal Resins

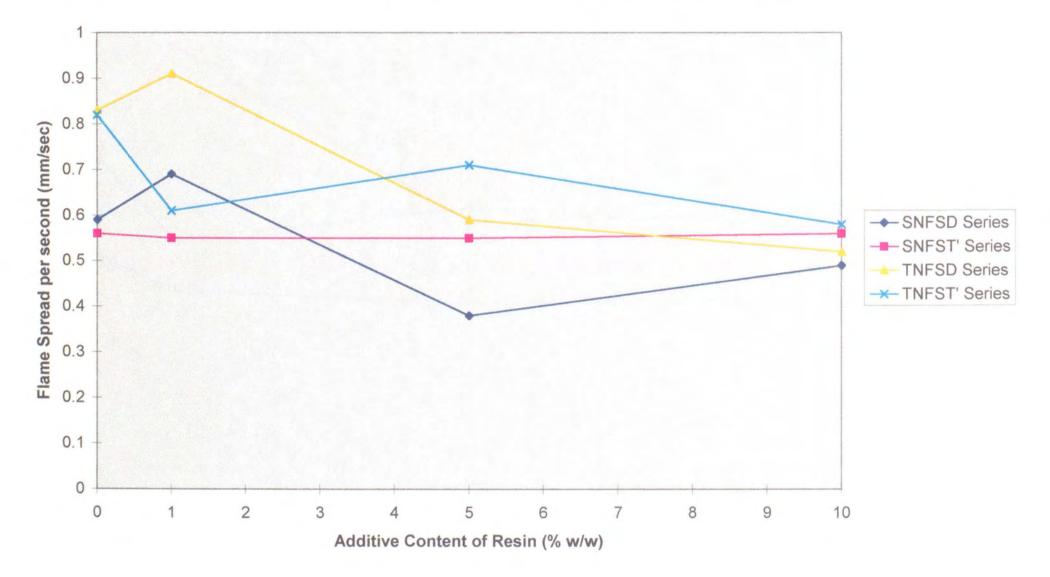


Fig. H3: Flame Spread per Second vs Additive Content of normal Resins

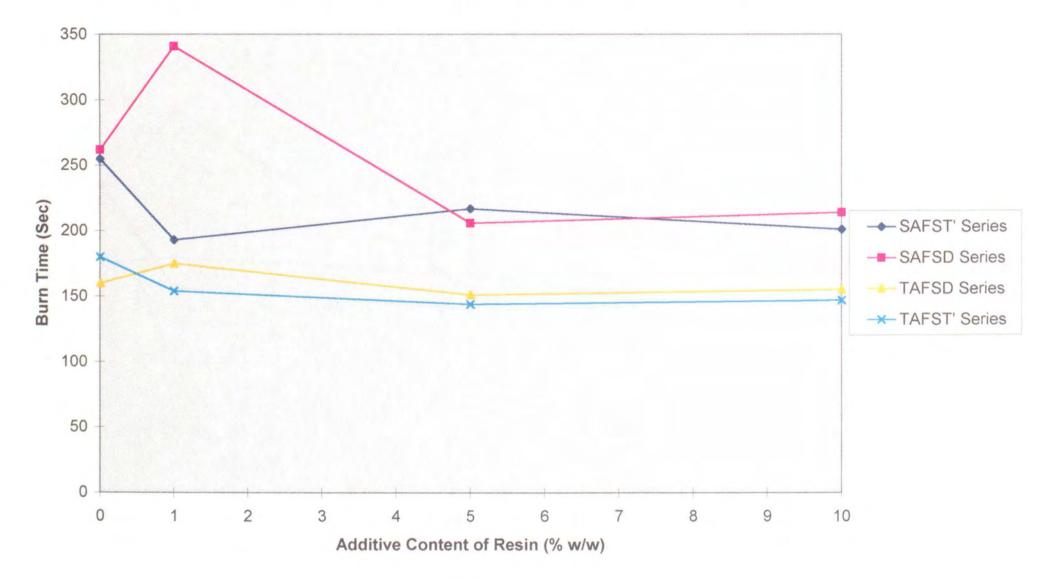


Fig. H4: Burn Time vs Additive Content of Aliphatic Resin

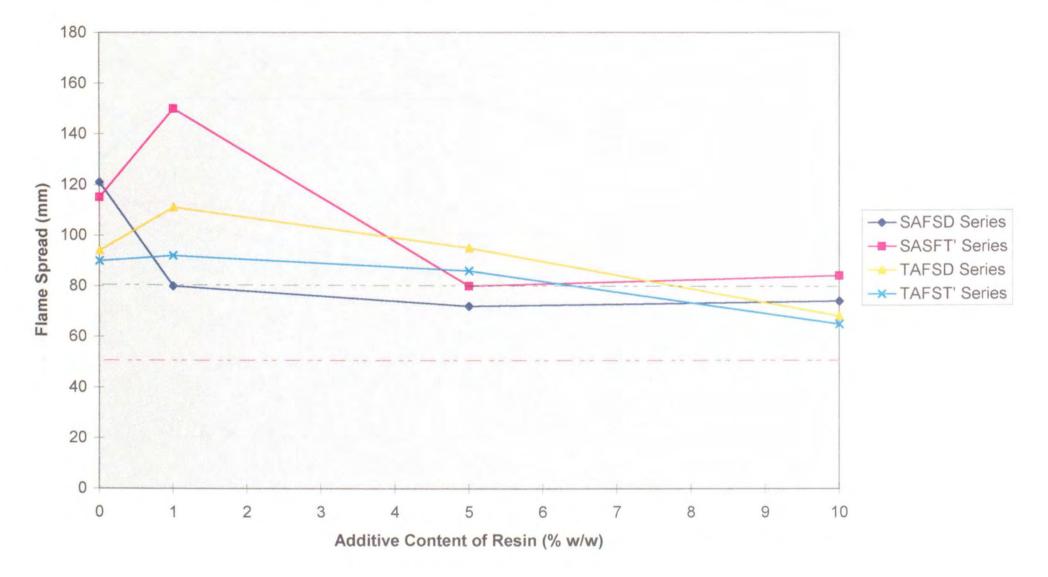


Fig. H5: Flame Spread vs Additive Content of Aliphatic Resin

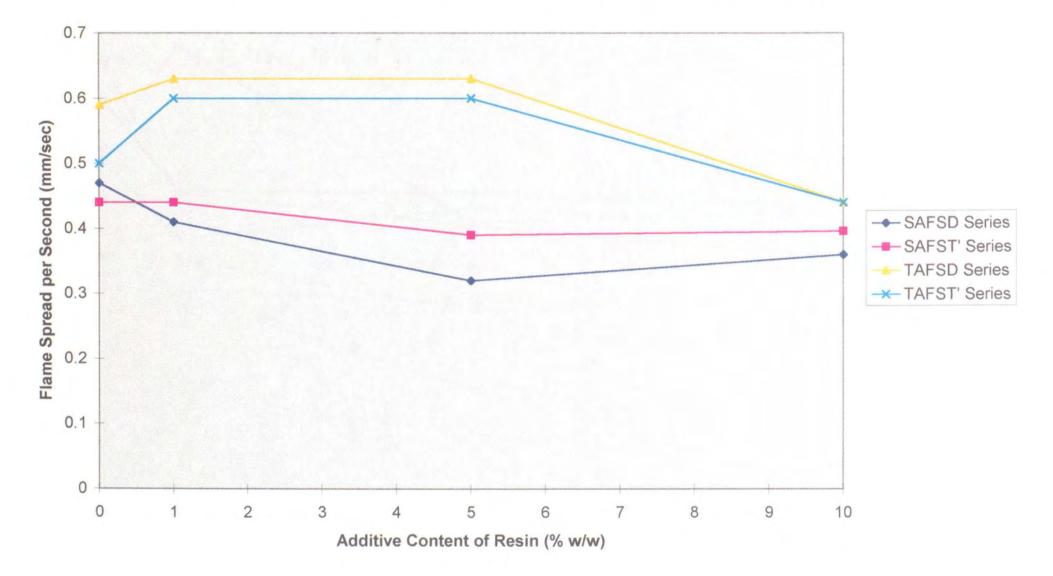


Fig. H6: Flame Spread per Second vs Additive Content of Aliphatic Resins

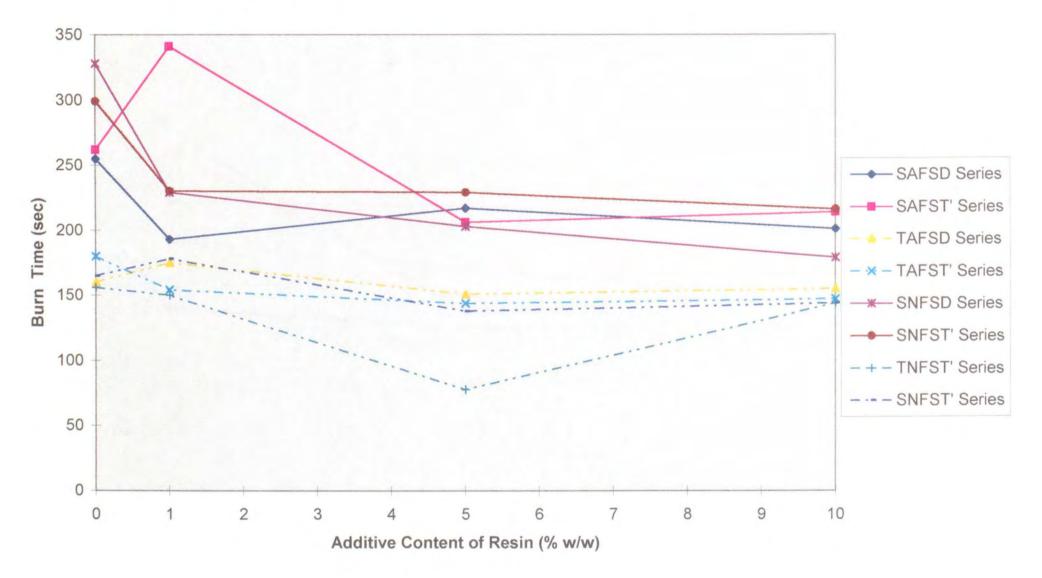


Fig. H7: Comparison of Burn Time for Aliphatic and Normal Resins

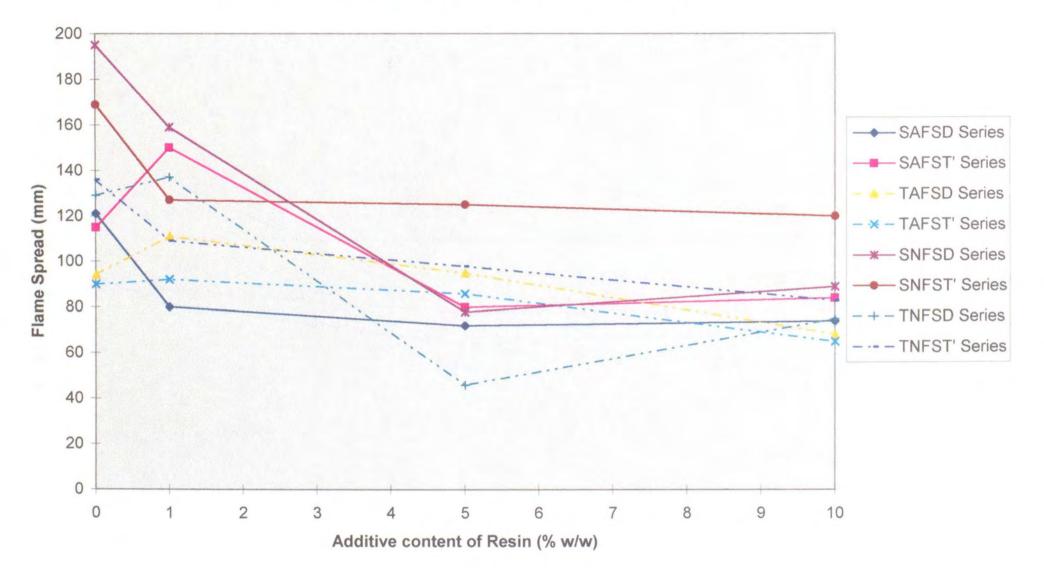


Fig. H8: Comparison of Flame Spread for Aliphatic and Normal Resins

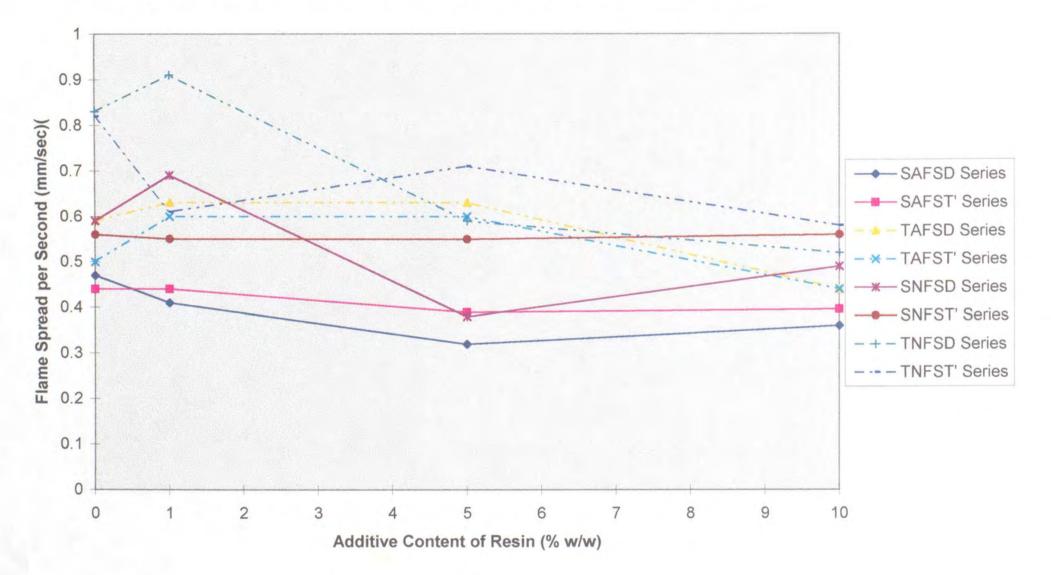


Fig. H9: Comparison of Flame Spread per Second for Aliphatic and Normal Resins

APPENDIX 1

TGA GRAPHS

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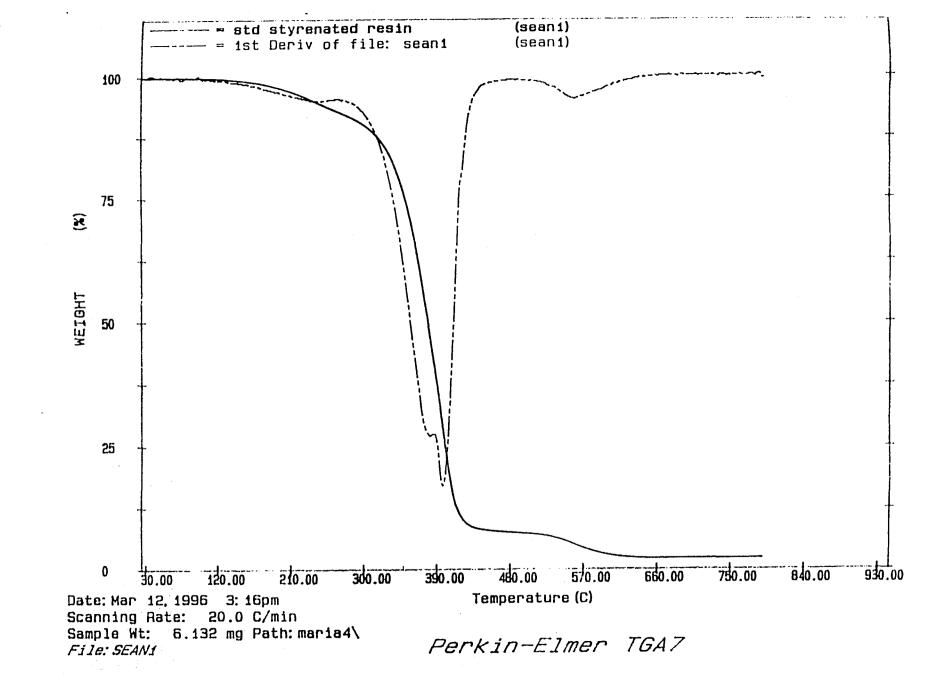


Fig. II: TGA trace for a normal styrenated resin with no additives.

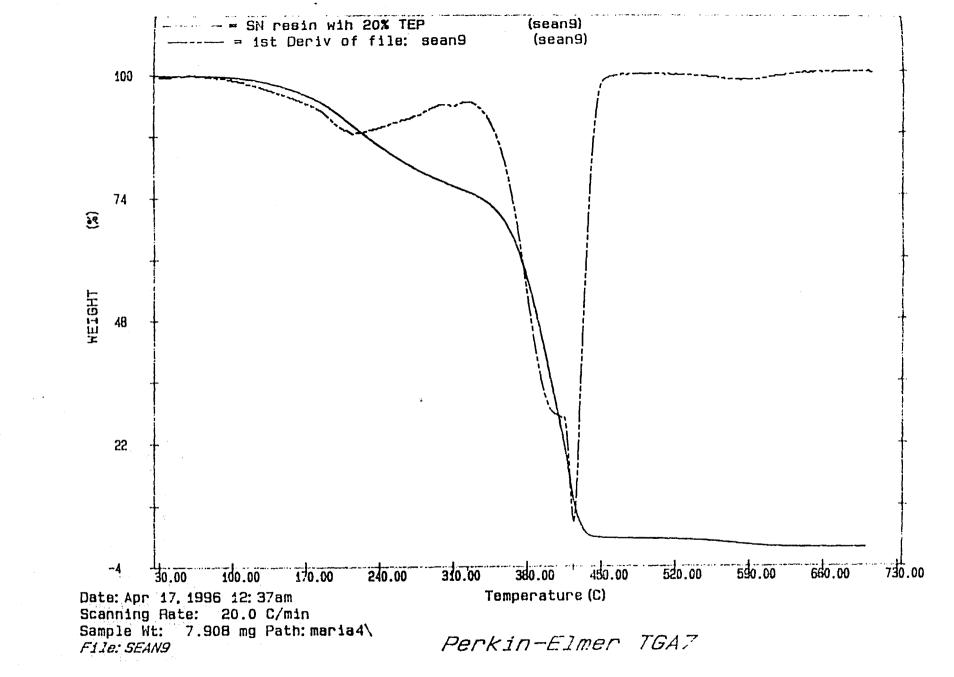


Fig 12: TGA trace for a normal styrenated resin treated with 20% w/w TEP

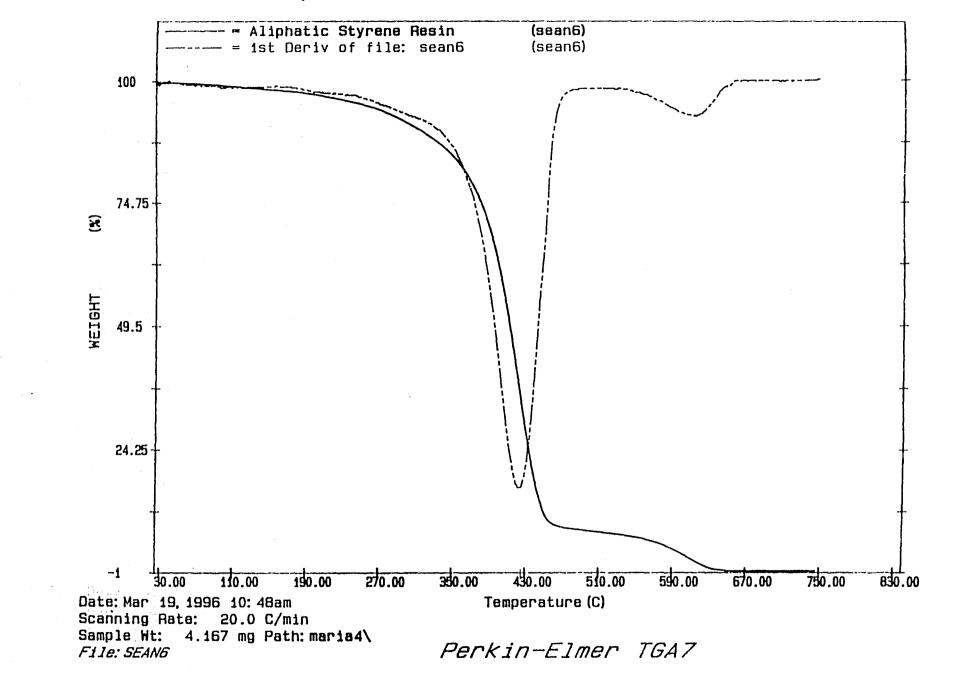


Fig ដ TGA trace for an aliphatic styrenated resin treated with no additives.

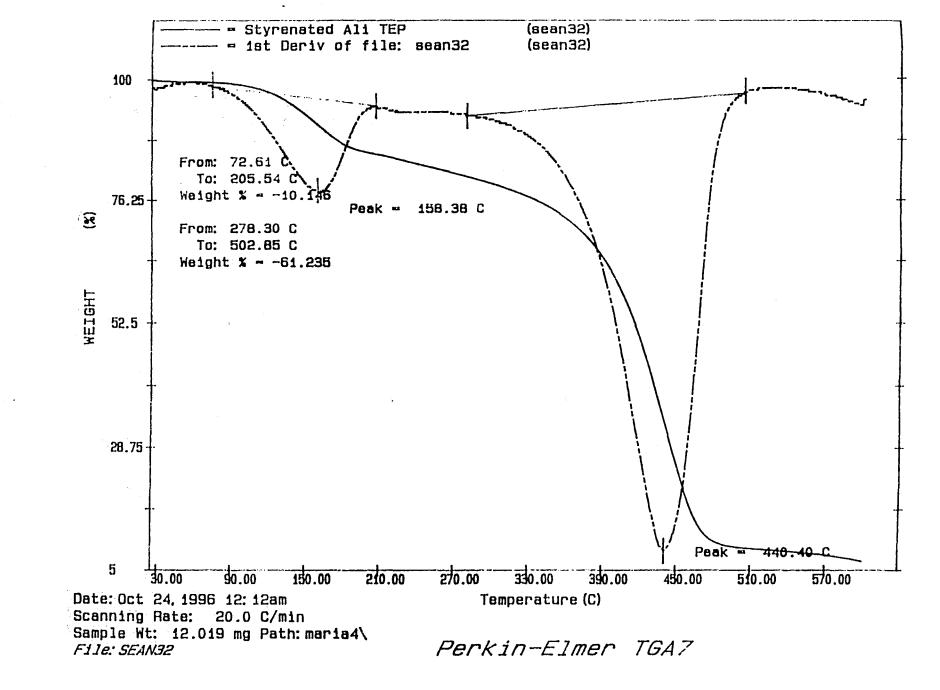


Fig. I4: TGA trace for an aliphatic styrenated resin treated with 20% w/w TEP $^{\circ}$

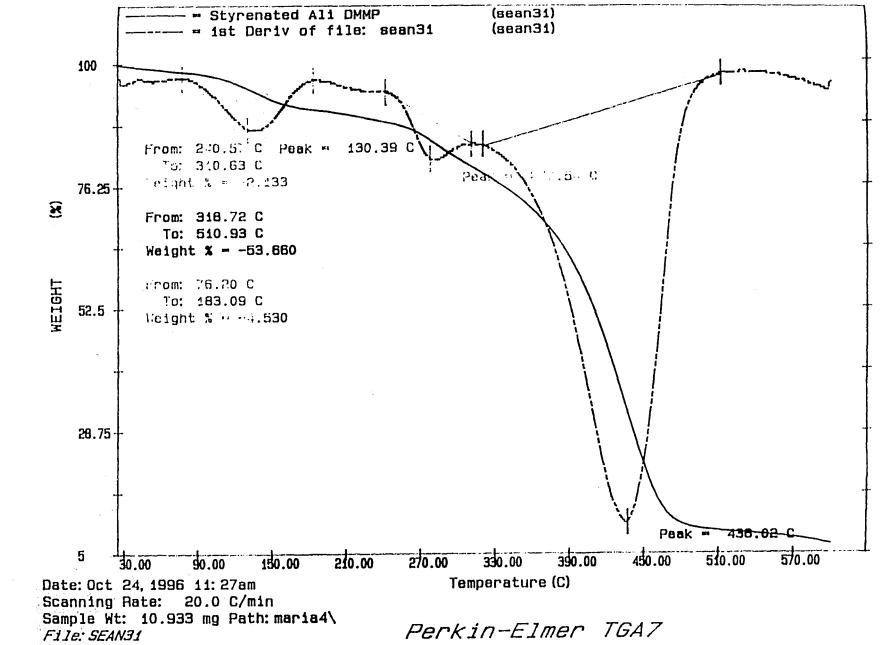


Fig. 15: TGA trace for an aliphatic styrenated resin treated with 20% w/w DMMP.

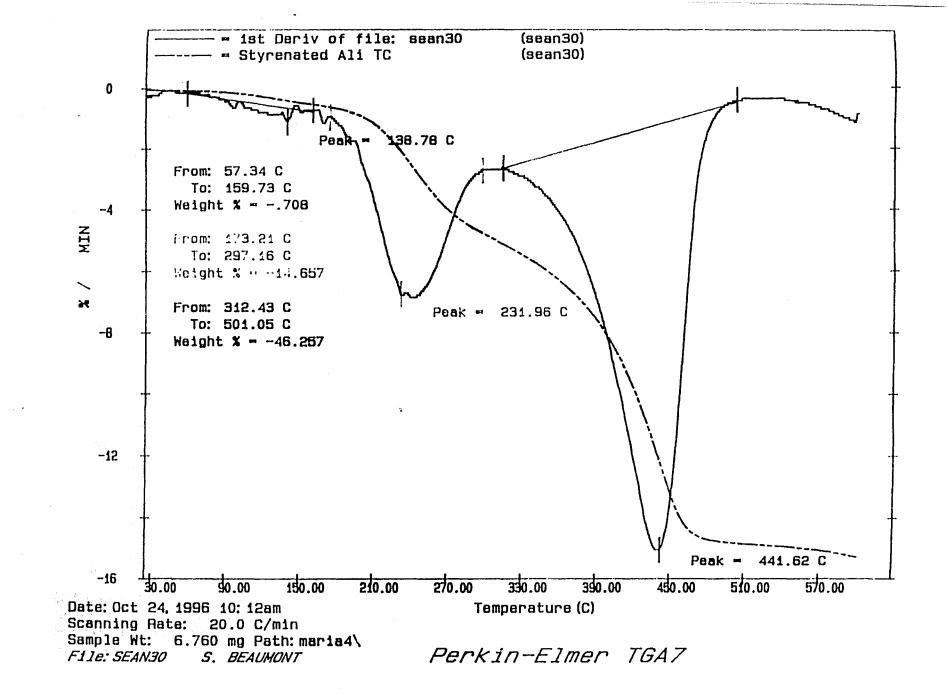


Fig. I6: TGA trace for an aliphatic styrenated resin treated with 20% w/w TCEP

1% w/w TCEP.

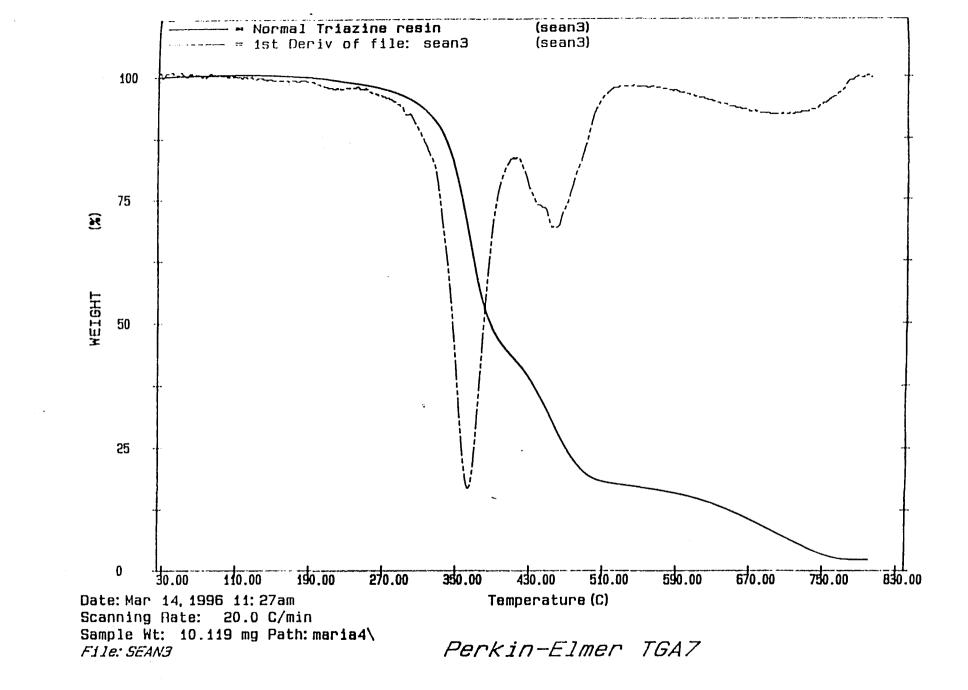


Fig. 17: TGA trace for a normal triazine based resin treated with no additives.

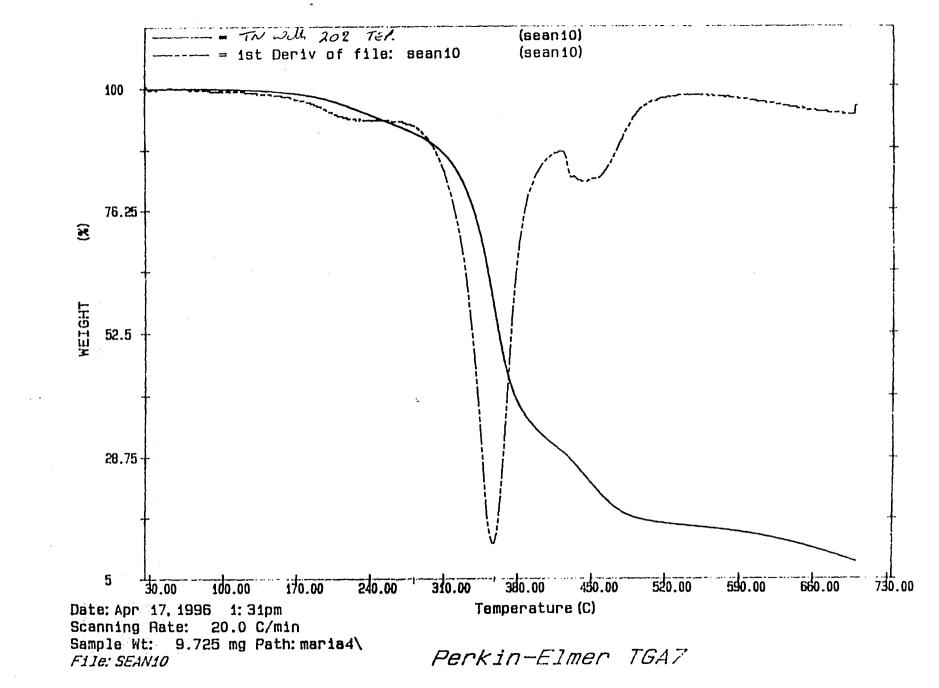


Fig. 18: TGA trace for a normal triazine based resin treated with 20% w/w TEP.

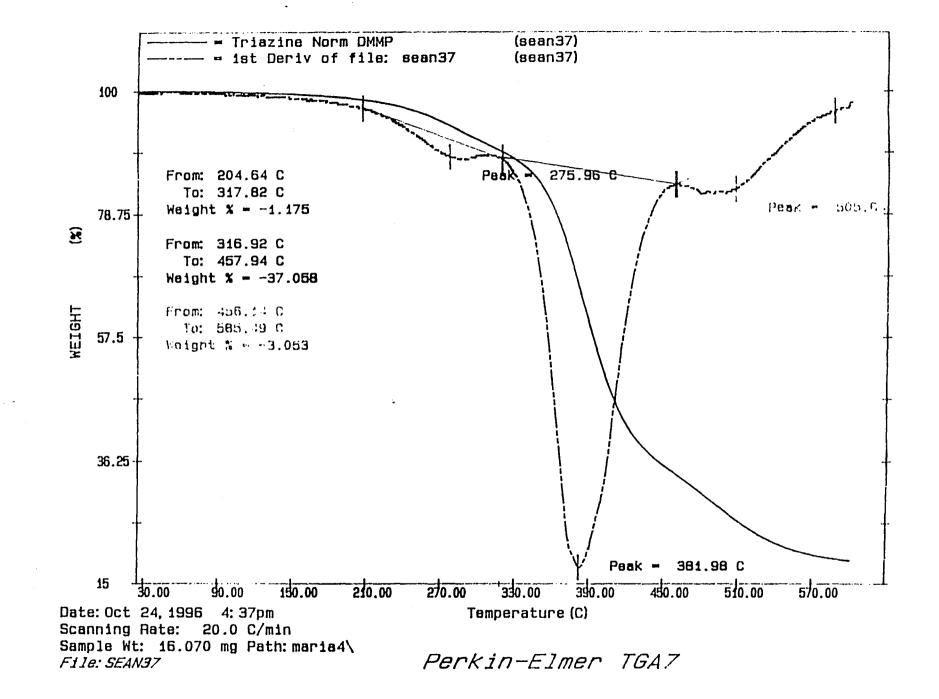


Fig. 19: TGA trace for a normal triazine based resin treated with 20% w/w DMMP.

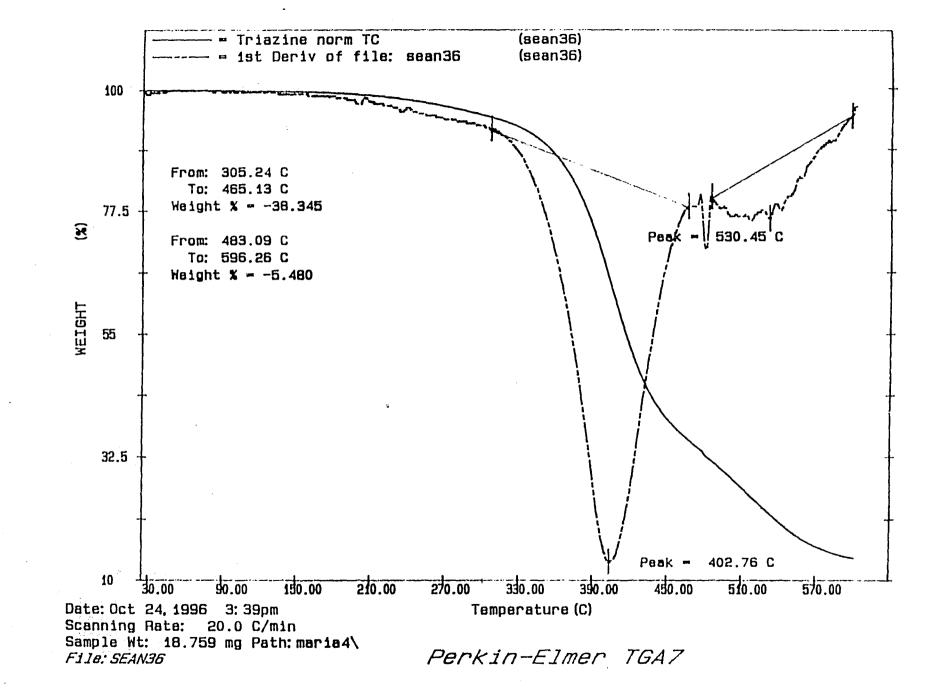
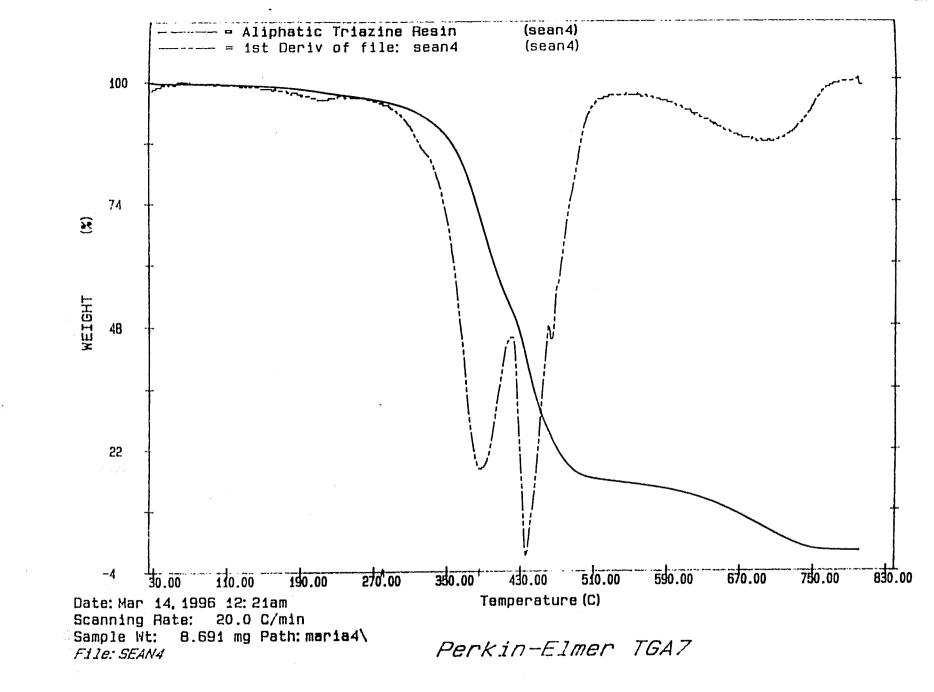


Fig. 110: TGA trace for a normal triazine based resin treated with 20% w/w TCEP.

0% w/w TCEP.



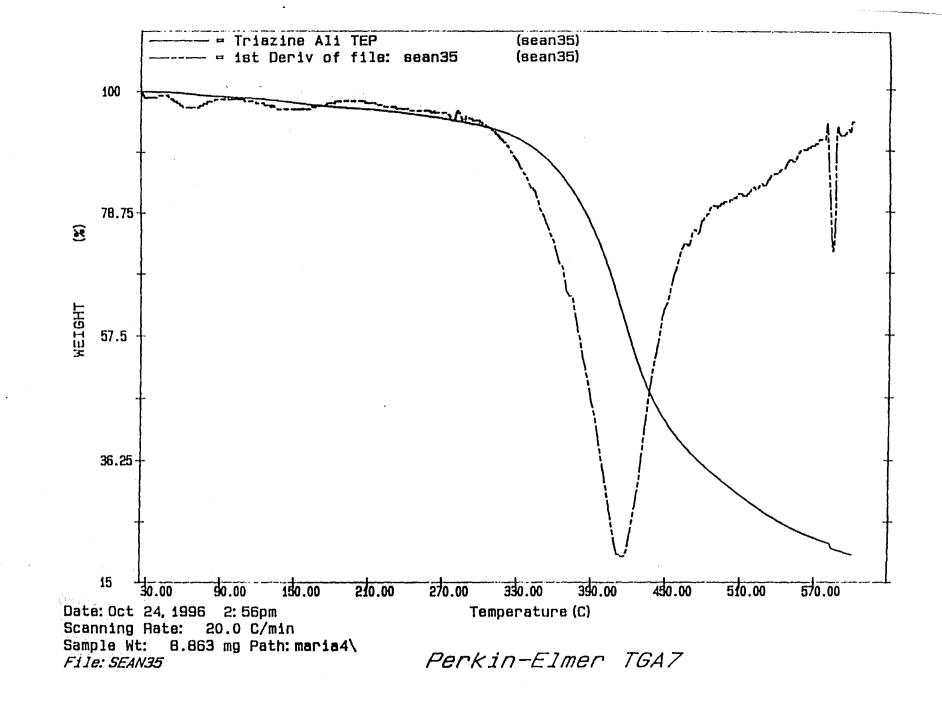
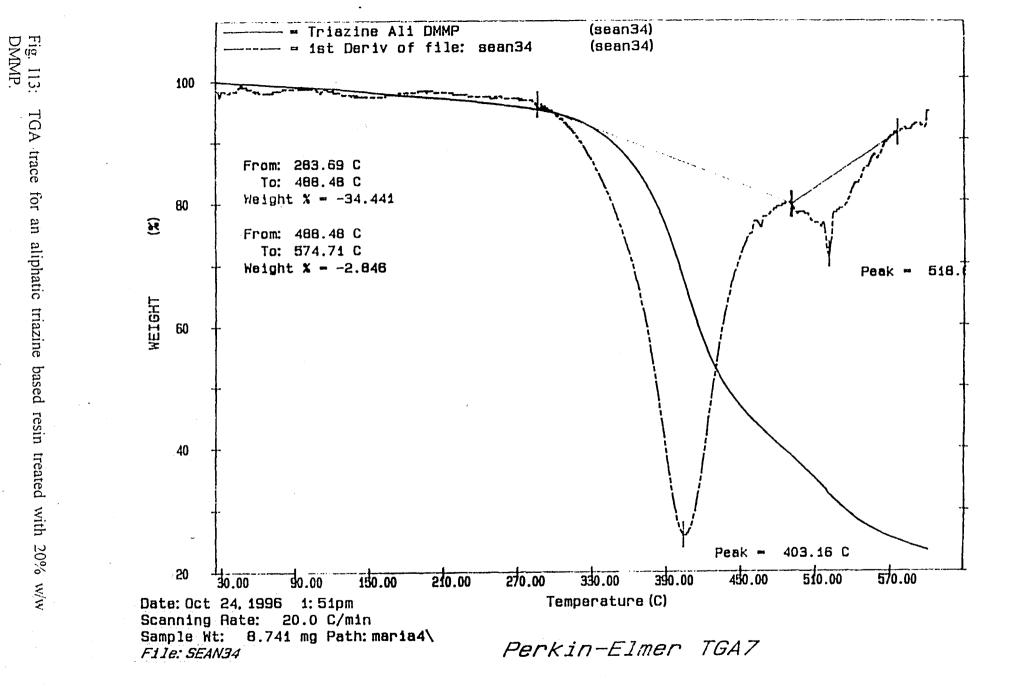


Fig. I12: TGA trace for an aliphatic triazine based resin treated with 20% w/w TEP.

20% w/w TEP.



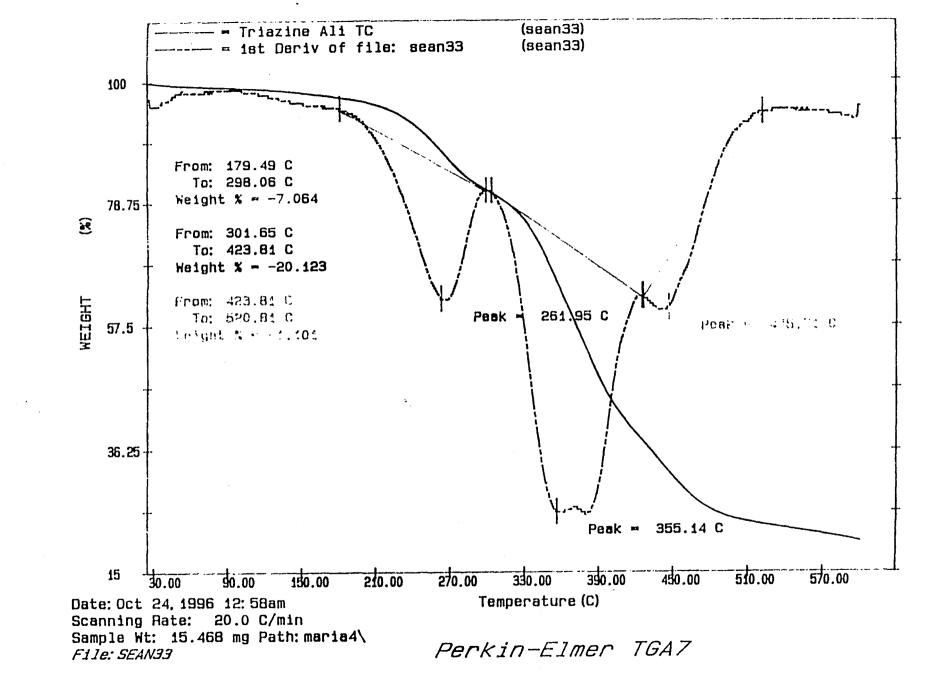
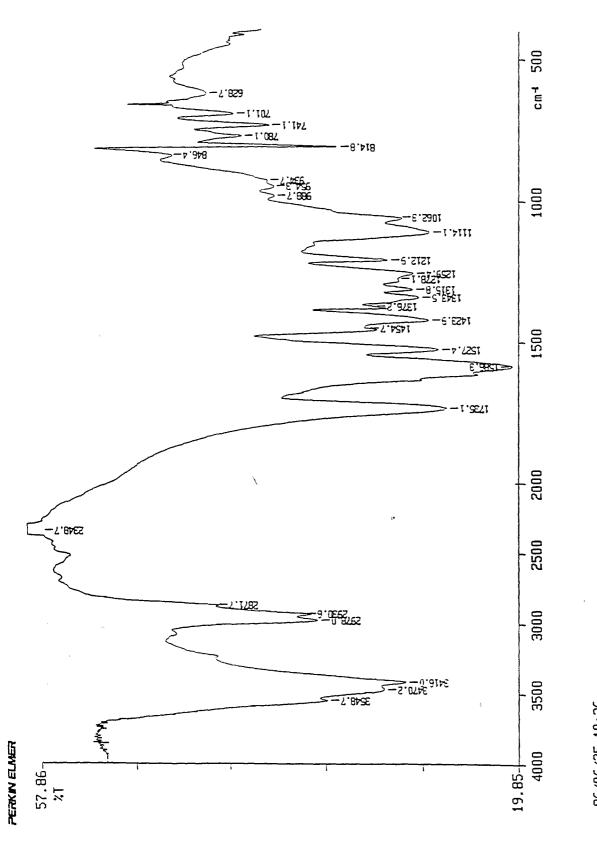


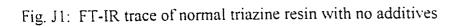
Fig. 114: TGA trace for an aliphatic triazine based resin treated with 20% w/w TCEP

CEP.

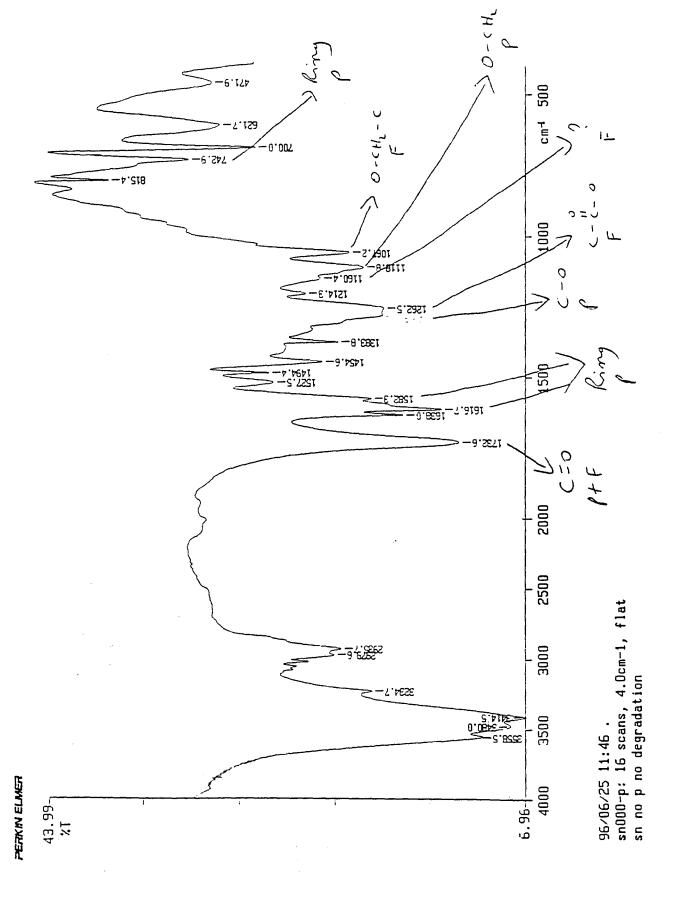
APPENDIX J

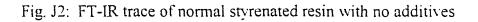
FT-IR TRACES

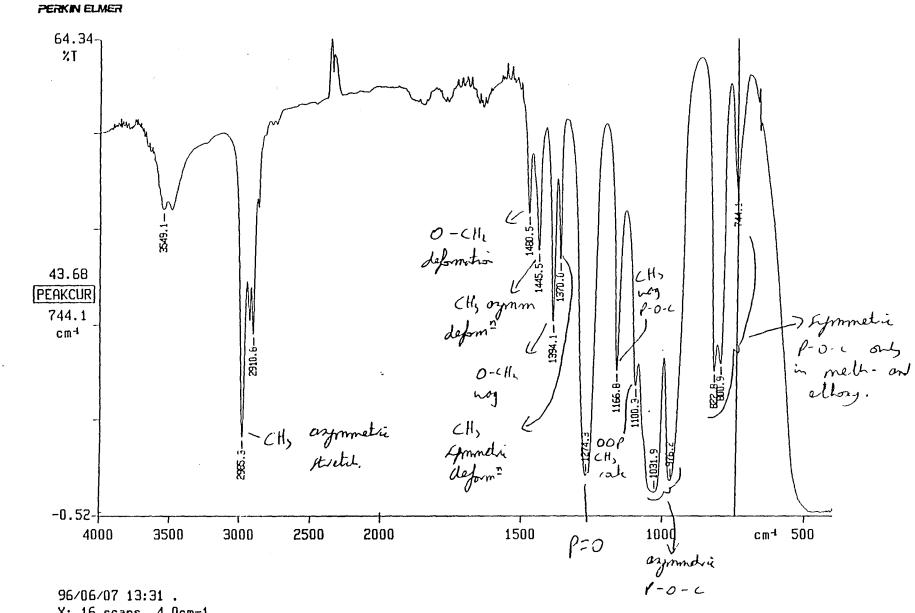




96/06/25 10:36 . tnooo-p: 16 scans, 4.0cm-1 tn no p with no degradation

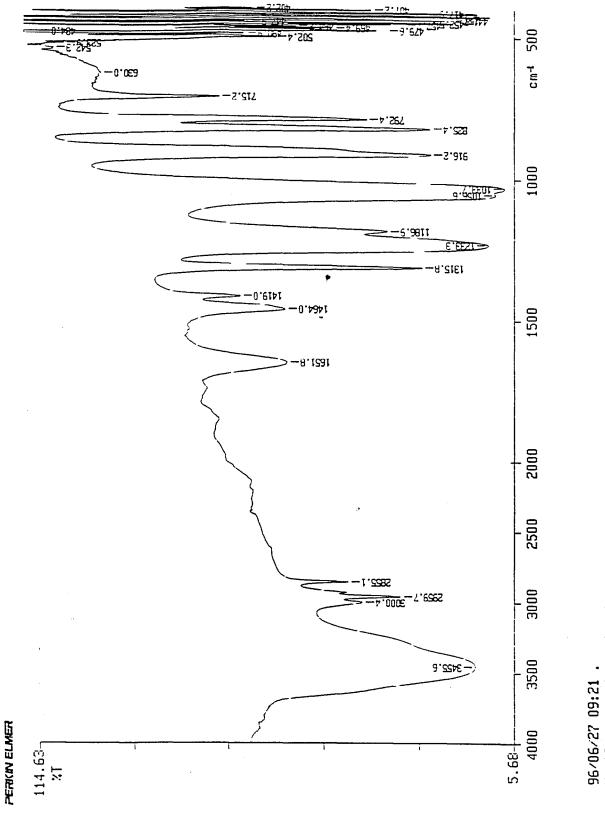


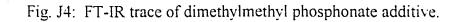




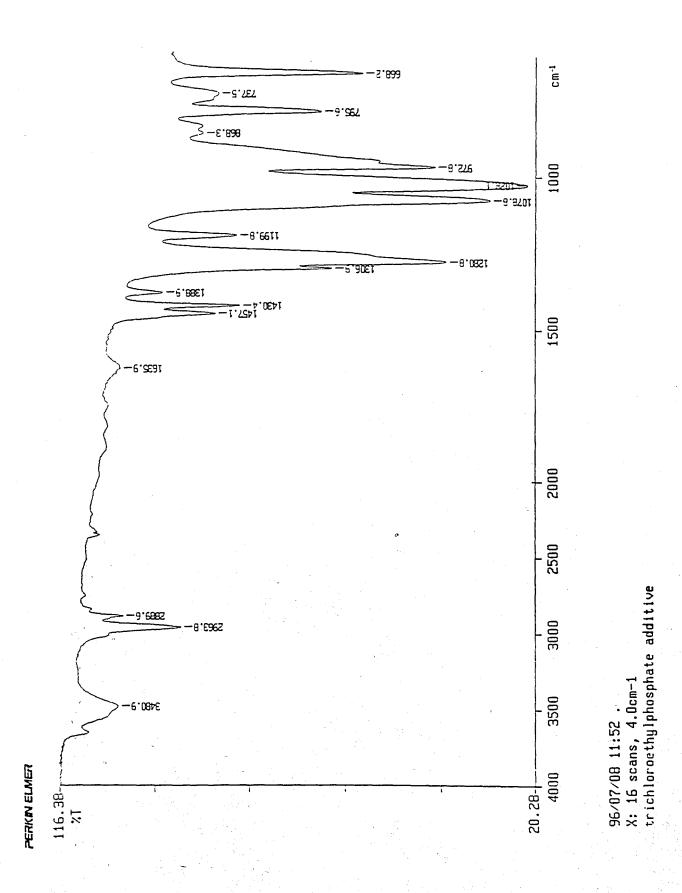
96/06/07 13:31 . X: 16 scans, 4.0cm-1 tep additive

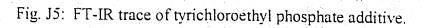
Fig. J3: FT-IR trace of triethyl phosphate additive.

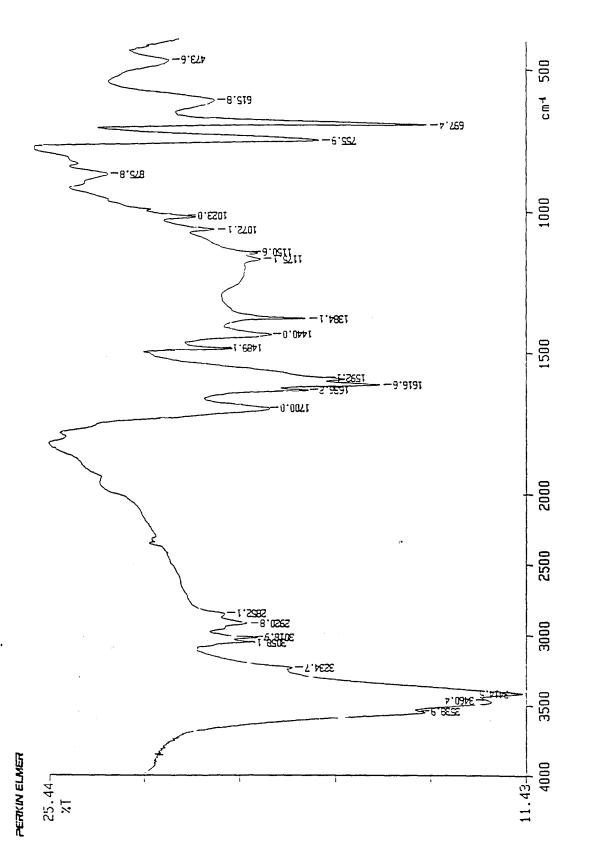


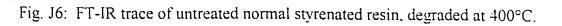


96/06/27 09:21 . X: 16 scans, 4.0cm-1, flat dmmp additive









96/06/25 12:40 . sn400-p: 16 scans, 4.0cm-1, flat sn no p degraded at 400c

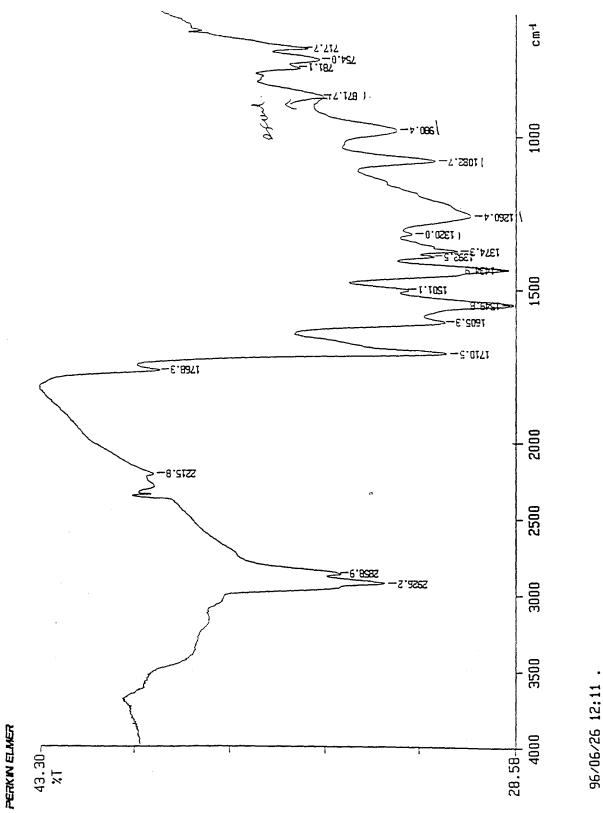
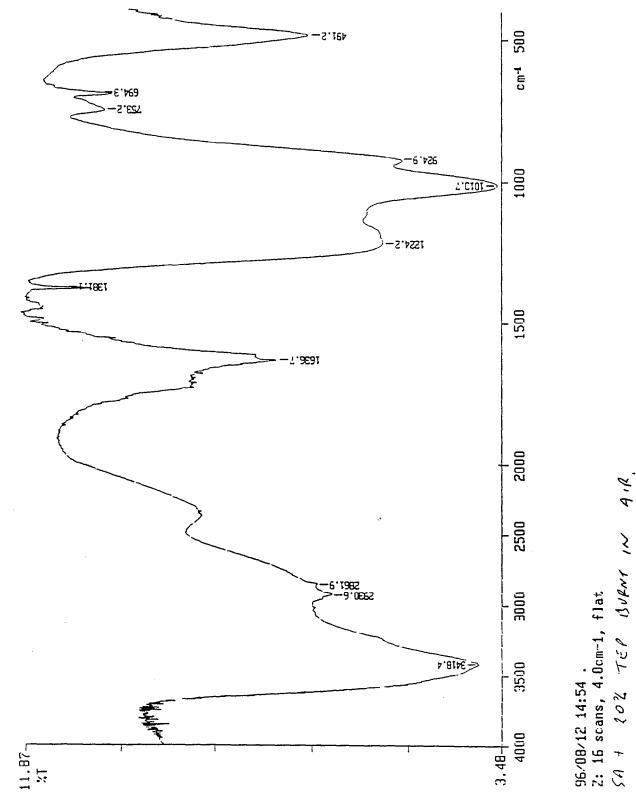
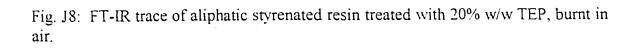


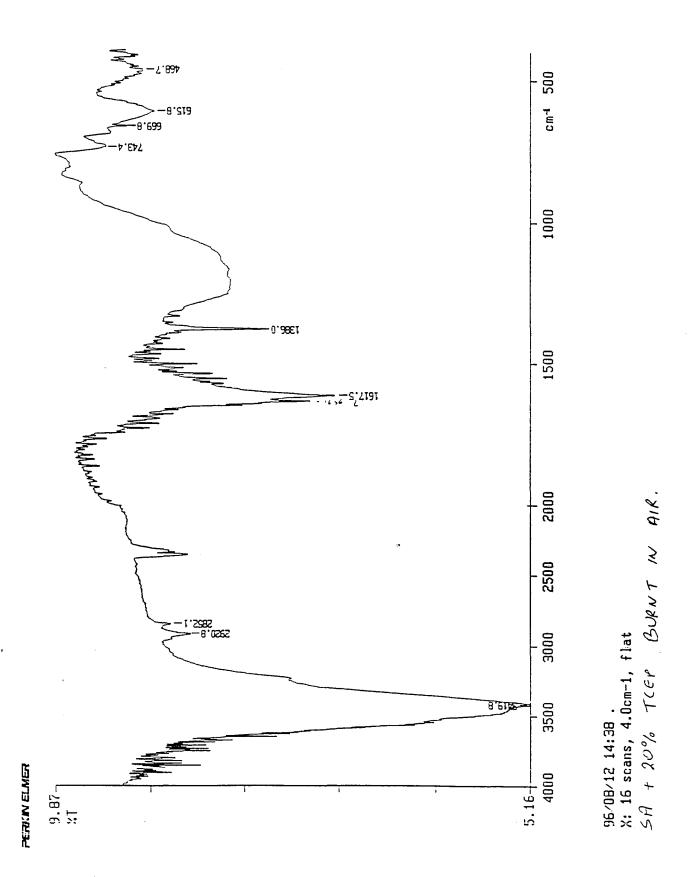
Fig. J7: FT-IR trace of normal styrenated resin treated with 20% w/w TEP, burnt in air.

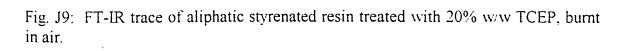
96/U6/26 12:11 . suburn: 16 scans, 4.0cm-1, flat sn burnt in air + 2.02 TEP.

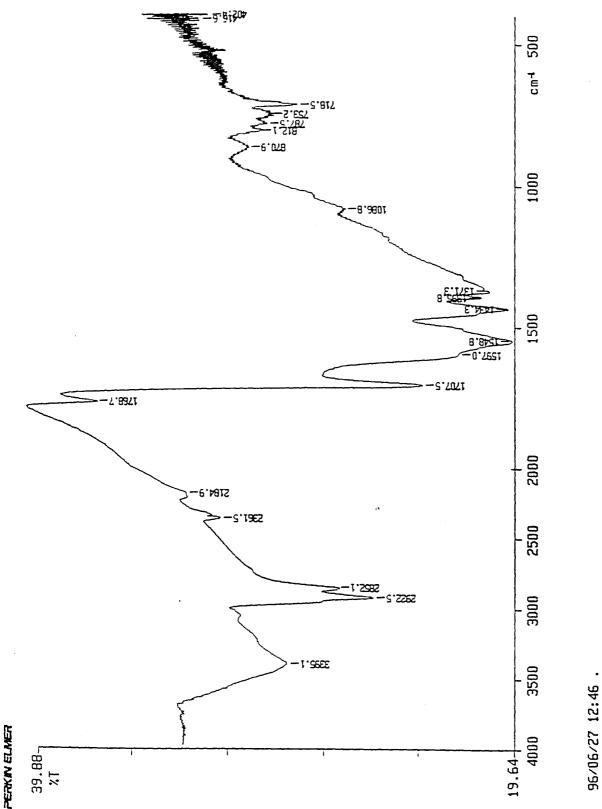


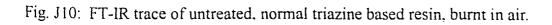


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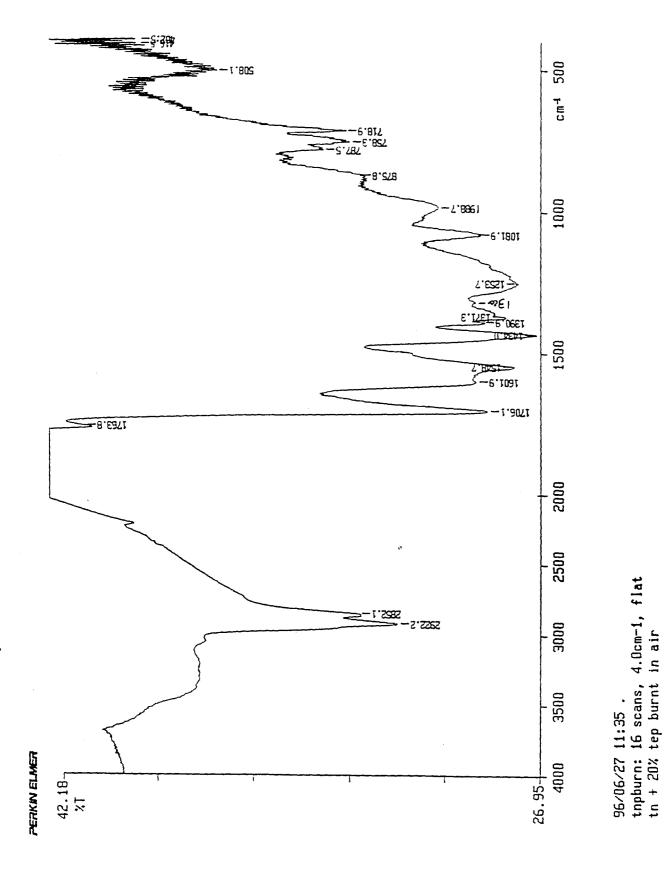


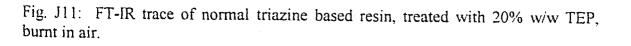


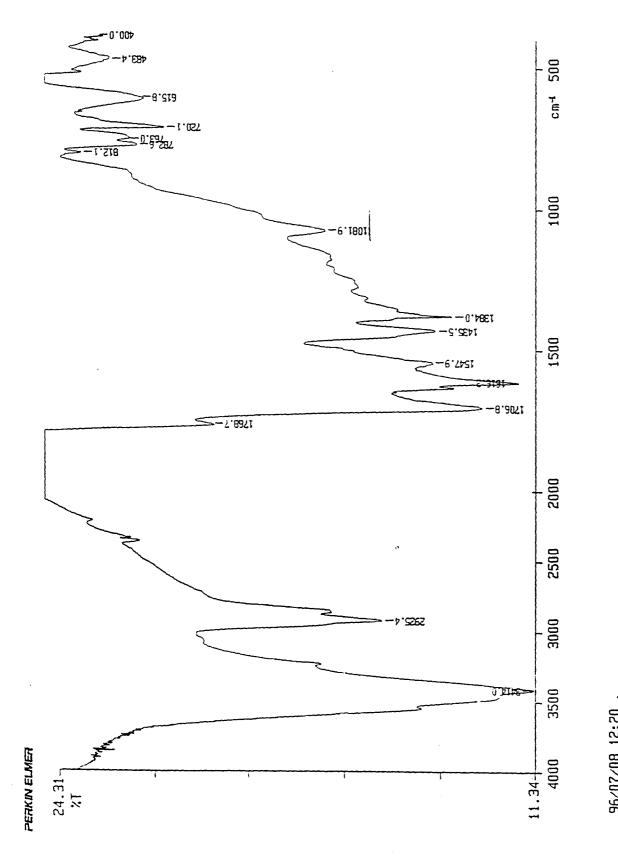


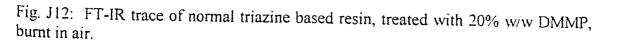


96/06/27 12:46 . X: 16 scans, 4.0cm-1, flat tn no p burnt in air

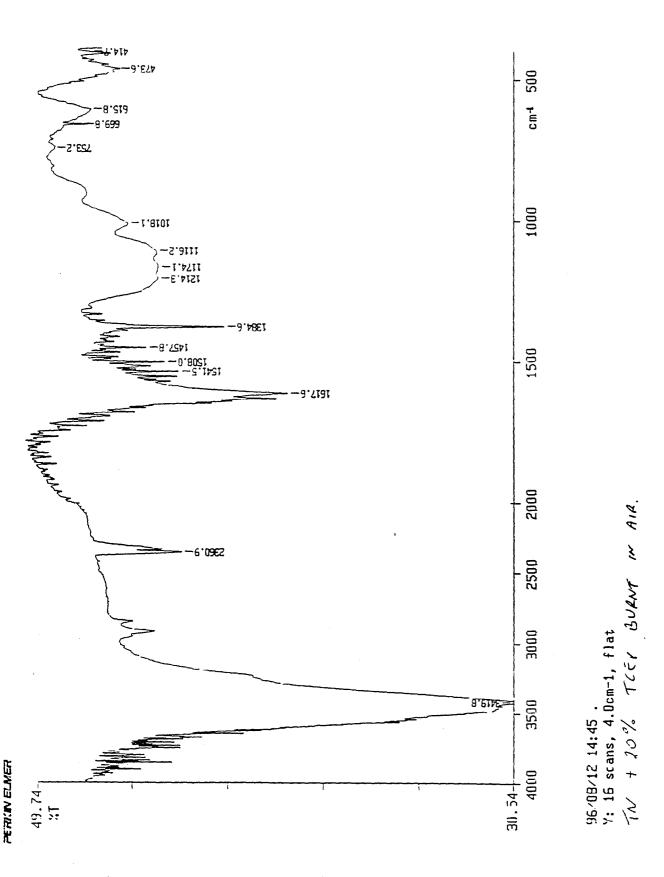


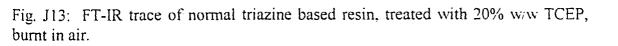


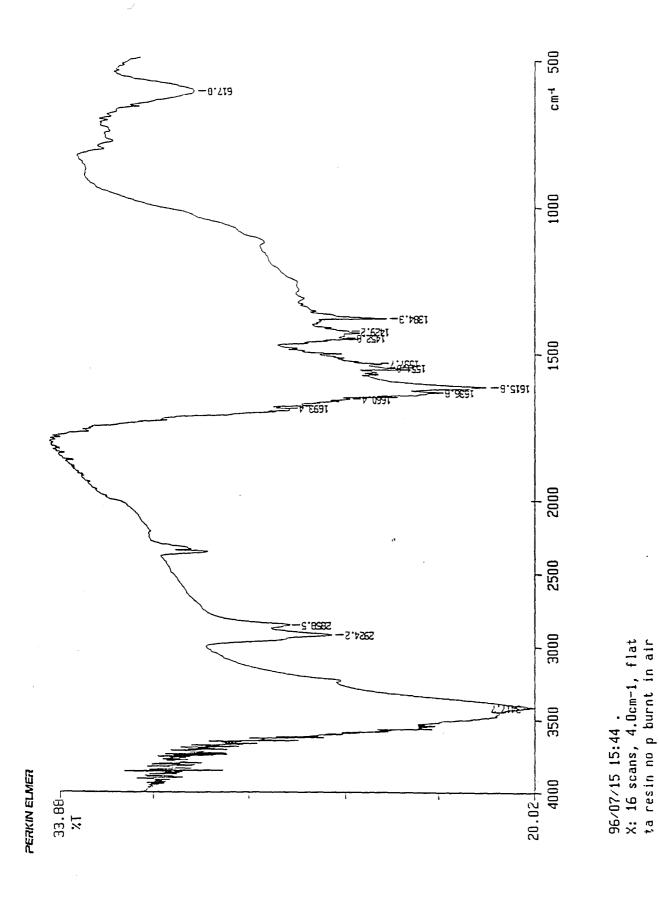


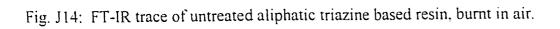


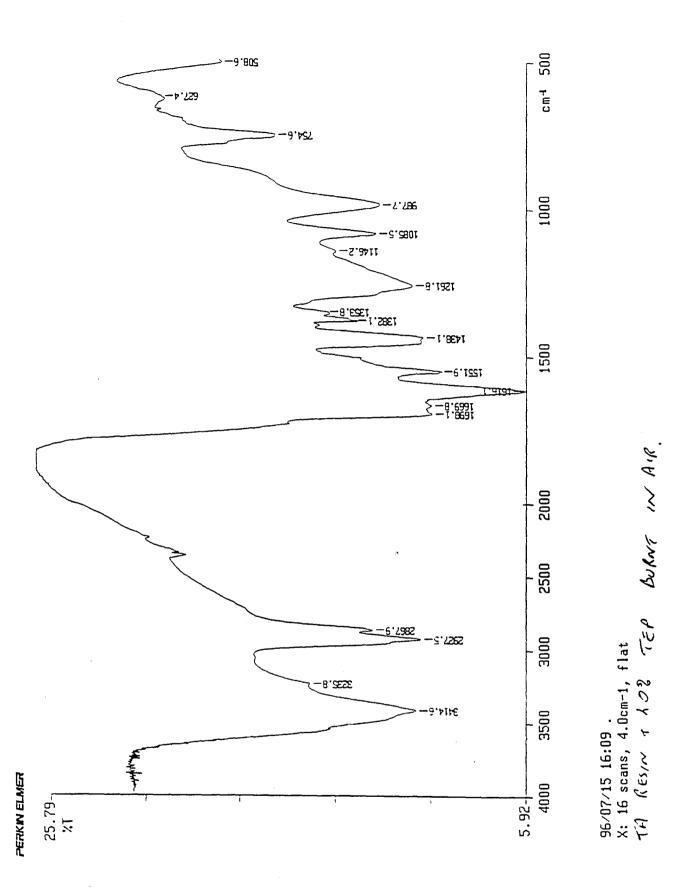
96/07/08 12:20 . Z: 16 scans, 4.0cm-1, flat tn 4 dmmp burnt in air

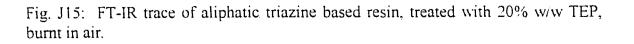


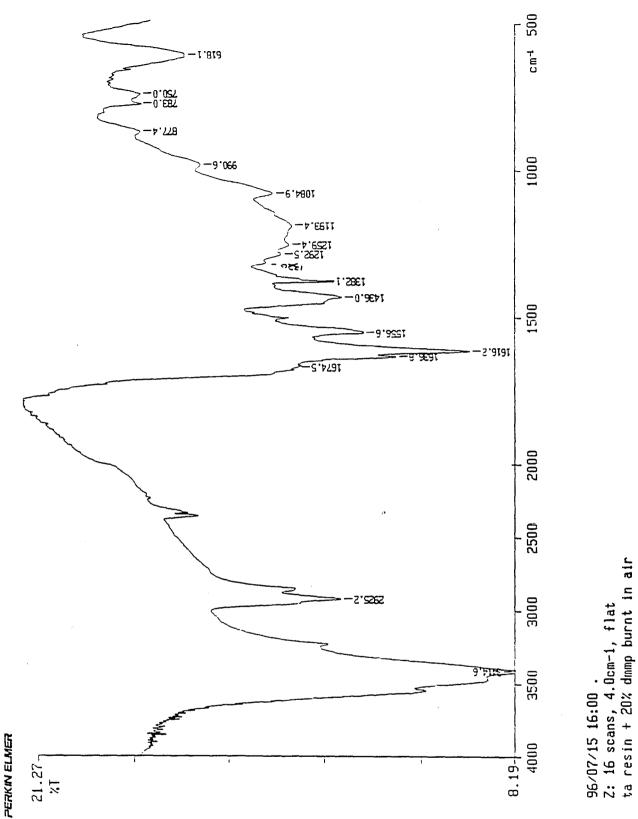


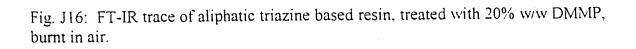












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