Citation: Madden, R. G. (1987). Phosphorus compounds as flame retardants for cotton cloth. (Unpublished Masters thesis, The City University, London)

A thesis

entitled

Phosphorus Compounds as Flame Retardants for Cotton Cloth

Submitted by:

Raymond Gabriel Madden

for the Degree of Doctor of Philosophy

at The City University, London

June 1987

Department of Chemistry

Chapter 1 - Introduction

Chapter 2 - Experimental

Chapter 3 - Results

Chapter 4 - Discussion

Lists of Tables

List of Figures

Page

Page

Acknowledgements

I would like to take this opportunity to offer my sincerest thanks to those who have helped me during my doctoral research programme.

I am grateful to Professor C.F. Cullis for his supervision and the task of reading the thesis from draft to completion, providing continuous critical analysis and encouragement. I am also indebted to [redacted] [redacted] [redacted] of the Combustion and Oxidation Research Unit for his useful suggestions and stimulating discussions regarding the present work. I also thank [redacted] [redacted] [redacted] of B.F. Goodrich Ltd. for help in the early stages of the research.

I would like to thank Dr. [redacted] [redacted] of Montedison, Italy, who whilst on secondment to The City University prepared two novel flame retardant compounds and [redacted] [redacted] [redacted] of Frost + Sullivan Ltd. for the donation of market research forecasts dealing with flame retardant consumption.

I am also grateful for the technical support provided by the Chemistry Department staff, particularly the late [redacted] [redacted] [redacted], [redacted] [redacted], Laboratory Superintendent, [redacted] [redacted] for his skilful glass-blowing and [redacted] in the Stores.

Finally, my deepest thanks go to my friends here and abroad who have made this work worthwhile. Firstly, [redacted]

Erbach for her skillful wordprocessing. Without her this task would have never been completed; [redacted] [redacted], [redacted] [redacted] [redacted] [redacted] [redacted] [redacted] [redacted] [redacted] [redacted] [redacted] [redacted] and family who all have helped in their own way.

Abstract

This thesis describes studies of the behaviour of a number of phosphorus compounds as flame-retardant additives for cellulose cotton cloth. Particular attention is paid to the effect of their structure and composition and of the effects of nitrogen compounds as co-additives.

In the Introduction, a survey of recent fire disasters and fire statistics is first presented. There follows a general description of the combustion process with special emphasis on the reactions involved in the decomposition and burning of organic polymers. A detailed account is given of the combustion of cellulose and possible mechanisms of its inhibition. An examination is also made of the modes of action of flame retardants for organic polymers with particular reference to phosphorus-based compounds used with cellulose.

The Experimental Section describes techniques used to prepare the cotton samples and modified forms of cellulose for flammability determination by the limiting oxygen index (LOI) method. A description is given of the computer program used to fit the polynomial functions to the flammability data and to present these functions in the form of triangular diagrams. The model used has been extended to deal with ternary additive systems where the data are represented by a tetrahedron. Thermal analysis of the various systems was carried out to complement the flammability measurements. Gas-phase infrared spectroscopy has also been used to identify species produced when cellulose flame-retardant systems decompose.

In the Results Section, the flammability and thermoanalytical measurements are presented for all the cotton - phosphorus systems in both the absence and presence of co-additives. Red phosphorus causes a significant increase in the LOI of cotton cloth and nitrogen compounds (especially melamine) have a useful synergistic effect. The flammability data show however that, on a percentage weight of phosphorus basis, tritolyl phosphate, triphenyl phosphite and triphenyl phosphine are the most effective phosphorus compounds. Thermal analysis shows little correlation between flammability and extent of char production. The infrared results show evidence that gas phase species including phosphorus pentoxide and ammonia are produced on decomposition of some of the systems.

In the Discussion, mechanisms are proposed to account for the flame-retardant effectiveness of the various phosphorus additives. Some of these appear to act essentially as dehydrating agents for cellulose to form char, whereas others bring about their effect in the gas phase by production of radical scavengers or by "blanketing" the flame. Suggestions are made about the synergism found between some of the phosphorus and nitrogen compounds.

Abbreviations used in text

CBO	Carbon burn off
DBB	Decabromobiphenyl
DTA	Differential thermal analysis
DTG	Differential thermogravimetric analysis
LOI	Limited oxygen index
Mel	Melamine
RP	Red phosphorus
TG	Thermogram
TTP	Tritolyl phosphate
wt	Weight

Chapter 1 - Introduction

"Everything that happens is due to the flow and transformation of energy ... Control fire and you control everything. The discovery of fire ... lifted man from the level of the beast and gave him dominion over the earth".

Morton Mott-Smith in his Introduction to Heat and its Workings. D. Appleton & Co. (1933)

1.1 Fire Statistics

1.1.1 Survey of Fire Disasters

One of the most important discoveries made by prehistoric man was fire. However this phenomenon was seen at first as a deadly, uncontrollable natural force against which man could be helpless. Fire, however, enabled prehistoric man to reduce his dependence on a hostile environment. It allowed him to cook food, extract and mould metal and produce clay objects. Man's civilization process caused him to build settlements which developed into villages and then towns. This urbanization process was however extremely susceptible to fire catastrophes, as history has shown.

Some notable examples are:

In AD 64, Rome was burnt to the ground in eight days.

In 1666 the Great Fire of London destroyed 13,200 houses, 94 churches and many other buildings in just three days.

In 1812 the Russians set fire to Moscow to repel Napoleon's army. The conflagration raged for five days and destroyed 90 percent of the city.

In 1842, 4,200 buildings were destroyed in Hamburg by a fire killing one hundred people and making 20 percent of the town's population homeless.

In 1906, as a result of an earthquake in San Francisco and the resulting fires, 1,000 people died.

In 1923 Tokyo and Yokohama were almost completely destroyed by fires following earthquakes.

Fires caused by enemy action during the Second World War accounted for numerous deaths and injuries and immense physical damage which added a new dimension to the problems associated with fire.

The devastation of fire has also been evident during recent times in the British Isles. In 1972 fire broke out in the Coldharbour Hospital, Sherborne, Dorset resulting in 30 deaths. During 1973, 50 people died on the Isle of Man at the "Summerland" entertainment centre. In July 1978 a sleeping car caught fire on a train travelling near Taunton, Somerset. Deaths occurred as a result of the rapid release and spread of combustion products due to the use of modern synthetic polymers. (Anon 1978). In Dublin, during February 1981 the "Stardust" discotheque disaster cost 40 lives (Anon 1981). The most recent event, which had considerable press coverage, was the fire at Bradford Association Football Club which killed more than 50 people and injured over 200.

The previous-mentioned fire catastrophe shows clearly the problem of large numbers of people congregating in entertainment venues and the lessons learnt are applicable to town centre developments, enclosed shopping malls and sports centres. The main problem with such buildings is the way in which fire can take hold of a building in a very short space of time. This, along with panic, often results in deaths and serious injuries which could, with hindsight, have been prevented.

In the Bradford Association Football Club fire the overall mechanism of the fire was complex and involved a number of intermediate steps of fire development. Conditions appear to have existed by way of building construction, materials and design such that fire development at each stage was very rapid. Design played an important role throughout. In the initial stages of the fire the design of the seating permitted a fire to grow rapidly beneath the timbers, and then spread to the upper surfaces. In the developing stages the roof provided an effective means to contain the hot gases and subsequently the flames, and to encourage their lateral spread along the grandstand. The intense downward heat radiation both accelerated the fire and caused severe escape difficulties to persons in the stand. These features, coupled with the reluctance of people present to evacuate quickly, the design of escape routes (leading people upwards to a corridor incapable of dealing with the necessary flow under emergency conditions), the rapid deterioration in visibility and increase in toxic products in the corridor, and the rapid spread of flame beneath the roof (with very high levels of downward radiation) had tragic consequences. This only reiterates the need for the use of flame-retardant materials and treatments in venues where large numbers of people congregate for entertainment.

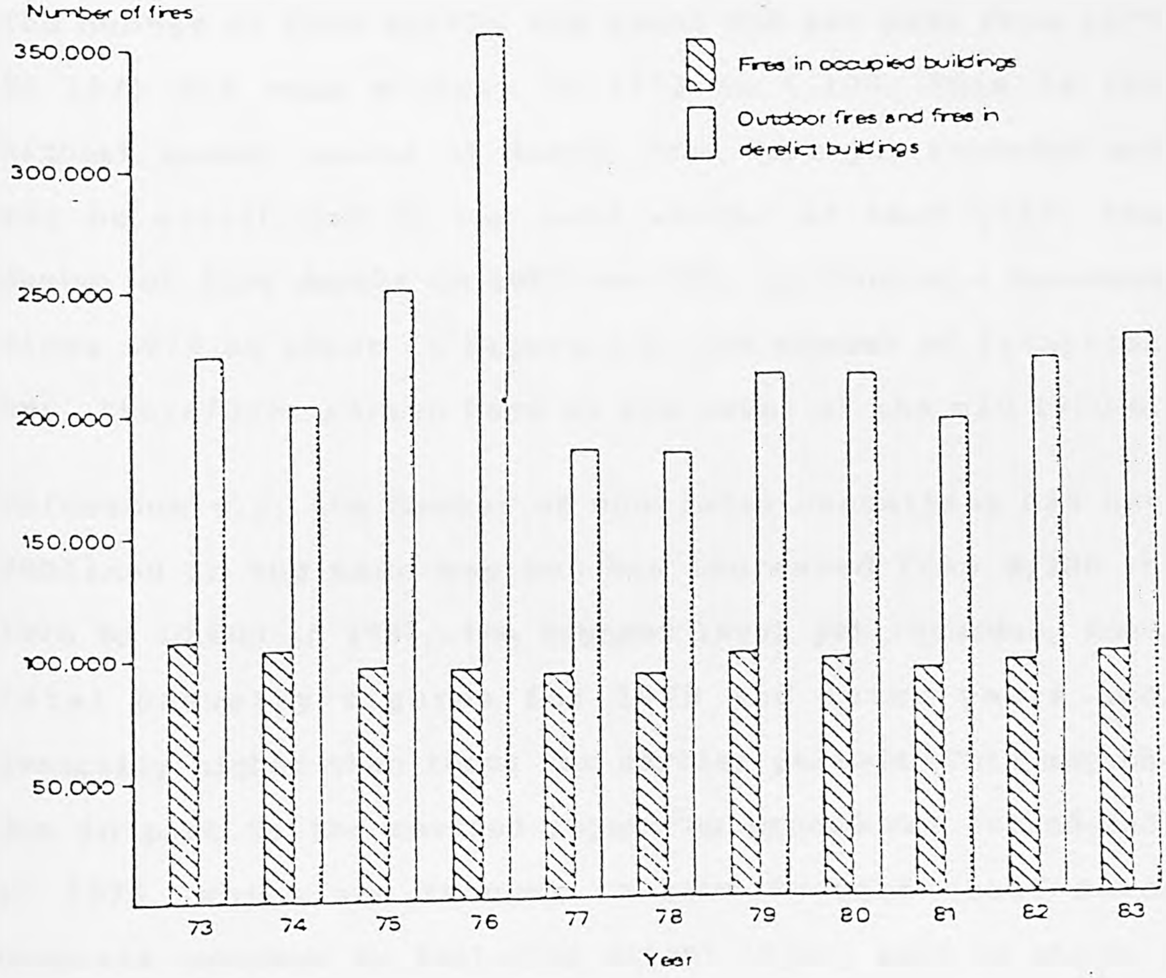
In the main the threat of fire tends to grow annually as society calls for advances in technology, for exploitation of new constructional materials and methods and for new concepts for the environment of buildings and transport. Buildings are becoming much more complex with moves for example towards very large enclosures (atrium buildings) for people's work, accommodation and leisure pursuits etc. In all walks of life there has been a demand for greater opulence of furniture, furnishings and general concepts of buildings and transport.

1.1.2 Statistical Fire Data

Recent fire statistics show that about 372,000 total fires were reported in 1983, an increase of about 4 percent on the 1982 figures. The increase from 1981 to 1982 was a substantially larger one, namely 9 percent. From these 372,000 fires of which 97,000 were in occupied buildings, 11,000 were in derelict buildings and 47,000 were confined to chimneys, the number of deaths was about 900 and there were about 10,000 non-fatal casualties.

Statistical data for fires in the UK between 1973 and 1983 are shown in Figure 1.1. The number of fires in occupied buildings i.e. those in use, although not necessarily having occupants in them at the time of the fire, has remained relatively constant at around 100,000 p.a. since 1973. A larger number of fires (of the order of 200,000) occur in derelict buildings or are outdoor fires. The number of fires in this class depends on external circumstances. For example, the particularly large number (over 350,000) of outdoor fires in 1976 was due to the unusually long, hot summer. Over the period 1973 - 83 as a whole, fires in occupied buildings in total have fallen by 8 percent from the peak of 105,000 in 1973. Within this same period, however, fires in dwellings have increased slightly from 55,000 in 1973 to the highest recorded figure (59,000) in 1979. This latter figure partly reflected the previous cold winter. Since then the number of fires has fallen to around

Figure 1.1 Fires by location group, United Kingdom, 1973-83



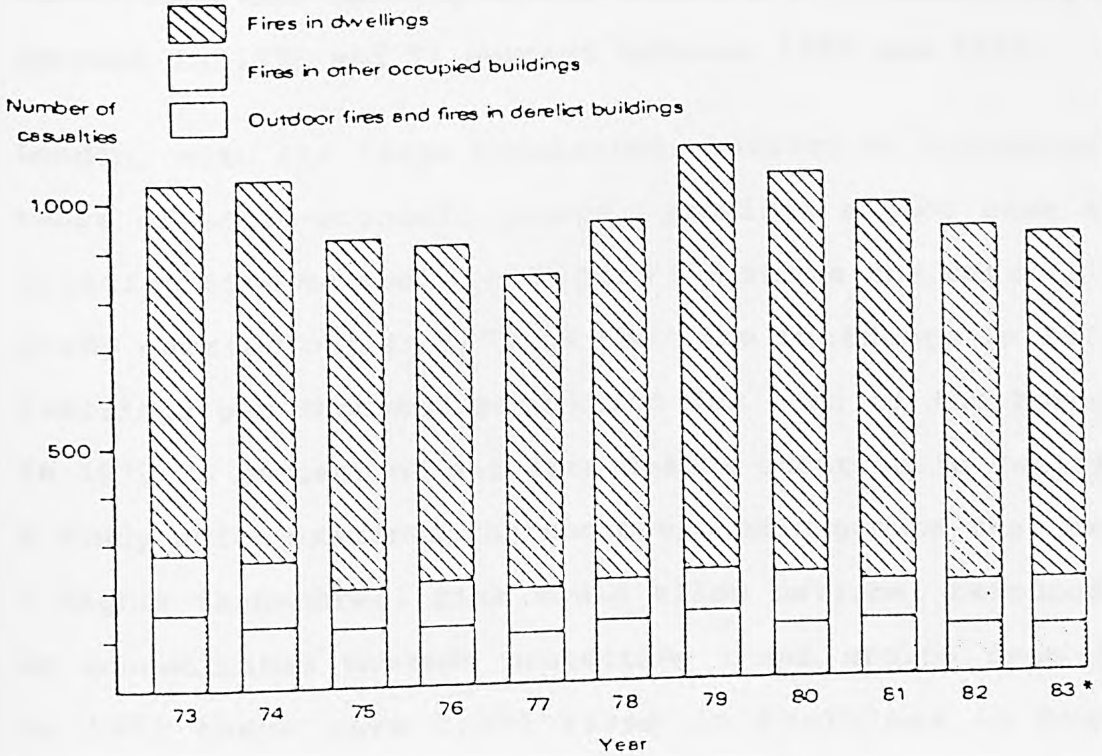
56,000 per year, which is nevertheless above the figure of ca. 52,000 recorded between 1975 and 1978. Thus between 1973 and 1983 the total number of fires in occupied buildings fell by 8 percent from the peak of 105,000 in 1973 to 97,000, two years later. Of the 97,000 fires in occupied buildings in 1983, 57,000 (59%) were in dwellings and 40,000 (41%) were in other occupied buildings.

The number of fire deaths was about 900 per year from 1975 to 1978 and rose sharply in 1979 to 1,100. This is the highest annual number of deaths from fire yet recorded and may be attributed to the cold winter of that year. The number of fire deaths in 1983 was 903, continuing a decrease since 1979 as shown in Figure 1.2. The number of fataltiės has, therefore, fallen back to the level of the mid 1970's.

Unfortunately, the number of non-fatal casualties has not declined in the same way but has increased from 8,200 in 1978 to 10,000 in 1983, the highest level yet recorded. Non-fatal casualty figures for 1978 and later years are generally higher than those for earlier periods. This may be due in part to the revised reporting procedures introduced in 1978, which are thought to have brought about more complete coverage by including slight injury such as shock.

The large majority of deaths and non-fatal casualties in fires occur in dwellings rather than in other occupied buildings, although overall only about 15 percent of fires happen in dwellings. The proportion of deaths from fires in

Figure 1.2 Fatal casualties by location group, United Kingdom 1973-83



* This figure includes casualties resulting from terrorist activity (10 fatal and 118 non-fatal in 1983) which are not included in pre-1982 figures.

happen in dwellings. The proportion of deaths from fires in dwellings to total fire deaths rose from 73 percent in 1973 to 80 percent between 1980 and 1985, while for non-fatal to 80 percent between 1980 and 1985, while for non-fatal casualties the corresponding figures were lower, viz. 62 to 80 percent between 1980 and 1985, while for non-fatal casualties the corresponding figures were lower, viz. 62 percent in 1973 and 71 percent between 1980 and 1985.

London, with its large population, variety of buildings and range of socio-economic groups, provides a good case study relating fire to society. Figure 1.3 shows the results of a study carried out in 1979 of the fire incidence in 1972 in dwellings per thousand population for each of the boroughs. In 1979 75 percent of all fire deaths occurred in dwellings. A study which examines the socio-economic groups that are at a higher-than-normal risk would allow national resources to be concentrated towards protecting these groups from fire. In 1972 there were 8,284 fires in dwellings in Greater London. The average domestic fire incidence in the Greater London Council area was 1.13 fires per thousand of the population, the average figures for Inner and Outer London being 1.42 and 0.88 per thousand respectively. The domestic fire frequency for the whole of the United Kingdom in 1972 was 0.95 fires per thousand of the population.

Table 1.1 shows the socio-economic factors affecting each borough. The boroughs are listed in order of fires per thousand people. It has been claimed (Chandler 1979) that

Figure 1.3 Fires per thousand population in Greater London boroughs (1972) (Inner London Boroughs shown by dotted line)

For reasons of clarity, borough names are omitted

Table 1.1 Socio-economic Study of Fire Incidents in London Boroughs in 1972

Borough	Nos of fires per thousand people	Highest level of non owner occupied housing(%)[a]	Lack of basic household amenities[b]	Density of population in residential areas[c]
Hackney	1.91	88	39	-
Camden	1.88	-	-	-
Tower Hamlets	1.86	98	na	332
Kensington and Chelsea	1.79	-	-	368
Islington	1.62	87	49	307
Westminster	1.60	89	-	441
Lambeth	1.60	-	-	-
Hammersmith	1.47	-	45	319
Southwark	1.37	87	-	-

na = not available

(a) average level of non-owner occupation in Greater London was 60%, Inner London proportion was 82% and that for Outer London was 46%

(b) The measure used was the number of households in 1971 that lacked the exclusive use of hot water, fixed bath or inside W.C. In the whole of Greater London, 24% of households lacked exclusive use of one or more basic amenities in 1971.

(c) The residential population density is classified by "persons per residential hectare" (260 hectares - 1 sq. mile) there is a significant relationship between the number of fires and the percentage of non-owner-occupied accommodation, as is seen for the boroughs of Hackney and Tower Hamlets. Although these boroughs appear high in the table relating the number of fires per thousand people, the table relating the number of fires per thousand people, the statistical data are rather limited and only cover half of the boroughs mentioned. The statistical difference between Hackney and Southwark, which occupy the highest and lowest positions respectively in Table 1.1 is only 1 percent and is not therefore appreciable. The suggestion that there is a significant relation between owner-occupation and fire incidence is not well substantiated. However it would not be unexpected in view of the fact that carelessness is a major cause of fire and people who own their homes could well be more careful than those who live in rented accommodation. The improvement of household amenities is seen not to have a major effect on the number of fires. The figure for the borough of Tower Hamlets, for which data are not available due to the fact that a major redevelopment programme has been carried out, still appears to be high (Table 1.1). This suggests that the provision of amenities will not by itself reduce the incidence of fire.

There also seems to be little correlation between density of population and fire incidence. A relationship between number of fires in overcrowded housing conditions may exist, as one might expect, but this was not analysed in this particular study. From the limited data available, there seems to be little correlation between fire incidence and the social factors mentioned. This would suggest the desirability of an extension of the above study over a longer period of time and of a more detailed analysis of the data.

1.2 The Combustion of Organic Polymers

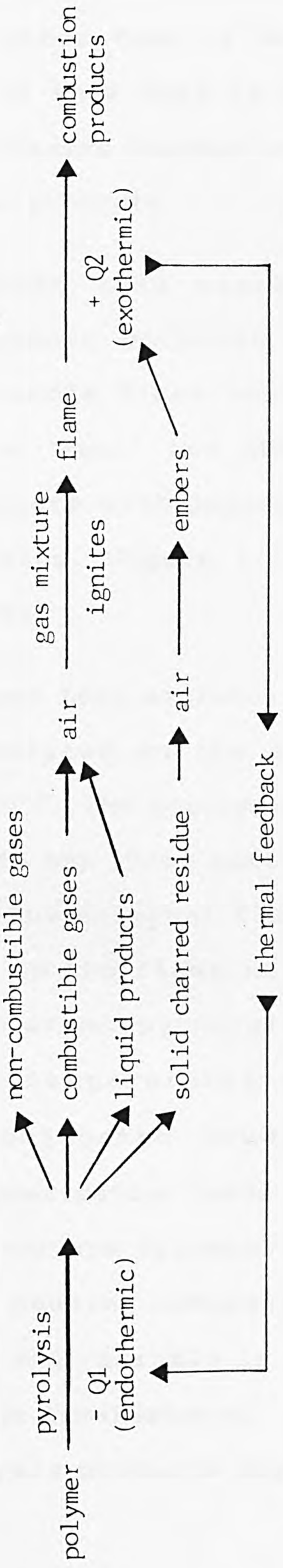
1.2.1 General Characteristics of Flaming and Smouldering Combustion

Combustion is sometimes defined as the reaction of a substance with oxygen or other gaseous oxidant with release of substantial amounts of heat and the accompaniment of flames and the emission of smoke. Various types of combustion behaviour can however be observed. Sometimes the materials undergoing combustion simply react smoothly and isothermally with the oxidant; this is termed "slow combustion". Under more severe conditions, however, there may be rapid and substantial changes in temperature in different parts of the system.

Essentially, two types of combustion may be observed during the burning of organic polymers. With most thermoplastics, relatively large amounts of combustible volatile products are formed from the polymer; these subsequently mix with the air or other oxidant and then burn in the gas phase above the polymer.

The process is termed "flaming combustion". Sustained flaming combustion can be considered as taking place in several distinct stages as shown in Figure 1.4. The polymer first reacts in the condensed phase to yield combustible gaseous products. These then burn in the flame zone above

Figure 1.4 The Combustion Process



Source: Troitzsch, J., Chapter 4, p. 17

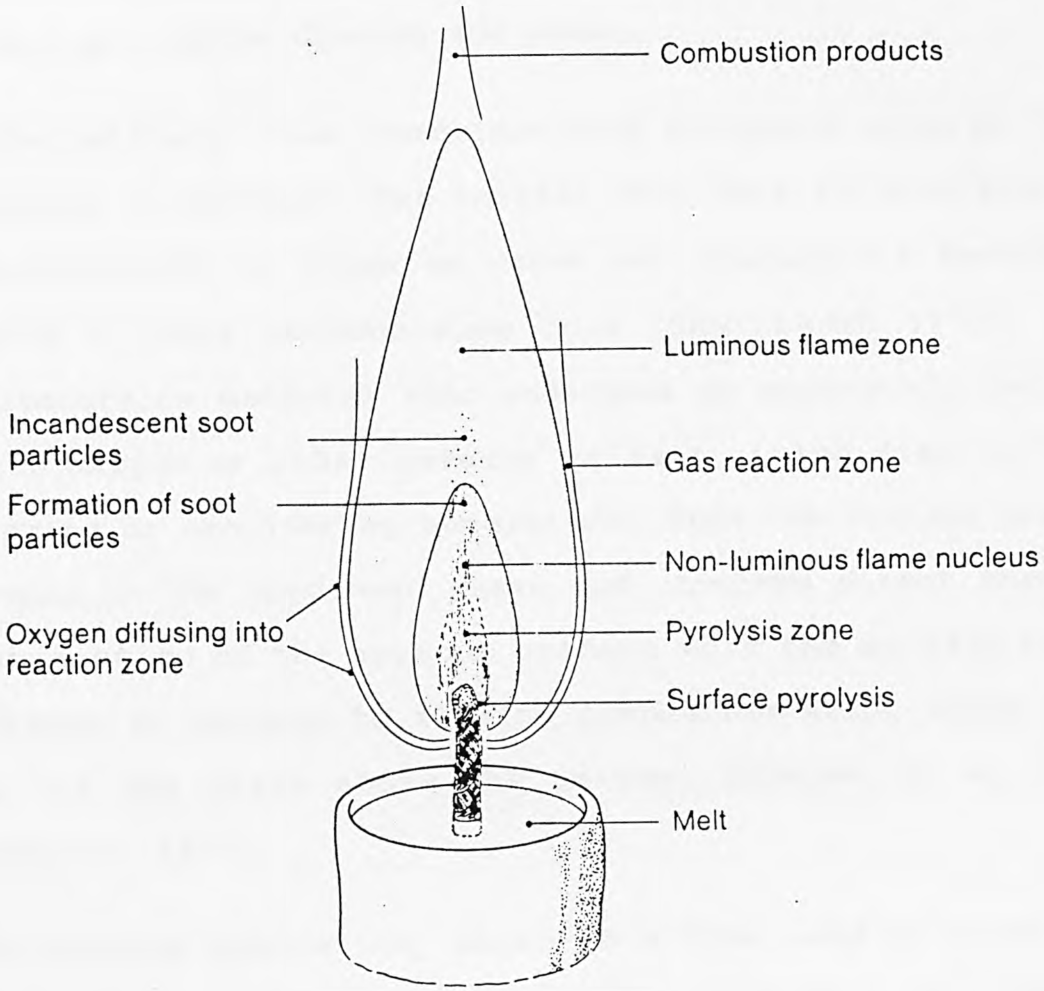
the polymer, leading to the formation of final combustion products and the liberation of heat. Under steady state conditions, some of this heat is transferred back to the polymer, where it causes further reactions and gives more combustible gaseous products.

The processes which take place during the "flaming combustion" of organic polymers can, in principle, be illustrated by a candle flame which involves essentially decomposition of a "fuel" and subsequent mixing of its decomposition products with oxygen, the resulting mixture subsequently igniting. Figure 1.5 shows an ordinary wax candle (Walker 1978).

Wax melted by radiant heat migrates up the wick by capillary action and is pyrolysed on its surface at temperatures between 600 and 800°C. The pyrolysis gases migrate further and either remain in the inner part of the flame, i.e. the nucleus, or reach the external flame mantle. A reducing atmosphere exists in the flame nucleus owing to lack of oxygen. The hydrocarbon pyrolysis fragments migrate to regions in which temperatures may reach 1000°C and generation of conjugated double bonds followed by cyclisation and aromatisation leads to the formation of soot particles. The latter are transported further up the flame and start to glow, causing luminescence. The production of excited molecules and radicals in the combustion reaction further enhances the luminescence.

Some of the pyrolysis products are however carried to the

Figure 1.5 Candle Flame



edge of the flame and encounter oxygen diffusing inwards. In this reaction zone, high energy, oxygen-containing radicals are generated at temperatures around 1400°C and these maintain the combustion reaction. If the process is uninterrupted and an adequate supply of oxygen is maintained, the end products of combustion of the candle flame are carbon dioxide and water.

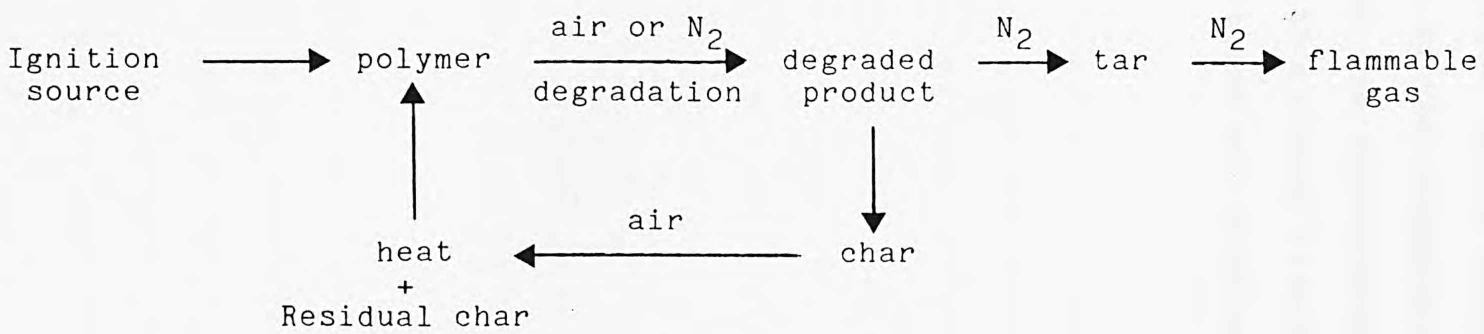
Alternatively some thermosetting polymers undergo "non-flaming combustion". The initial step here is generally the splitting-off of water or other non combustible species to leave a loose carbonaceous char (Shafizadeh 1975). This carbonaceous material then undergoes an exothermic reaction with oxygen or other gaseous oxidant giving rise to "non-flaming or smouldering combustion". Thus the burning process occurs in the condensed phase and involves direct chemical interaction of the gaseous oxidant with the surface of the polymer as opposed to flaming combustion which takes place in the gas phase above the polymer (Moussa et al. 1977; McCarter 1977).

Non-flaming combustion, which is a term used to cover both smouldering and glowing combustion, propagates by a "front" or "wave" involving the gaseous oxidation of the pyrolysis products of the polymer material. This has been demonstrated experimentally by Kashiwagi et al. (1971), who showed by high speed photography that, when a polymer was placed in a stream of high temperature air, ignition occurred only downstream of the solid. Glowing combustion is generally accompanied by pale flames due to the burning of carbon to form carbon oxides. However smouldering combustion is generally self-sustaining, although it may require assistance from an energy source if the thermal conductivity of the material is very low (Einhorn 1971). Smouldering combustion usually occurs when solid materials with high surface to weight ratios are either isolated from an appropriate heat sink or, if in contact with it, are of a certain minimum thickness (Friedman 1977). As expected, it is typified by combustion of a solid without flame, often evidenced by visible smoke. Smouldering can be initiated by small sources of ignition, especially in dust, and can persist for an extended period of time after which flames may appear.

Smouldering generally causes incomplete oxidation of the fuel, with the result that the gaseous products formed are toxic and include significant amounts of carbon monoxide. The high toxicity of this latter compound, coupled with the possibility of transition to flaming combustion, makes smouldering combustion potentially very hazardous. Smouldering combustion tends to be a less rapid process than flaming combustion and occurs at lower temperatures e.g. 180°C - 370°C depending on the system. Materials which smoulder have a tendency to form char when they are in the presence of oxygen (Bauer 1978). A general model for smouldering combustion was suggested by Rogers et al. (1978), and is shown in Figure 1.6.

Figure 1.6 General scheme for smouldering combustion

General scheme for smouldering combustion



SOURCE: Rogers et al (1978). J. Fire Flammability, 9, 5

Both flaming and non flaming combustion can be regarded as processes involving several distinct stages. In both cases the first step involves the decomposition of the polymer, the following section gives therefore an account of the essential features of the combustion of organic polymers. In flaming combustion the decomposition products and oxidant ignite and burn with a steady flame and therefore in a later section flame reactions are examined in further detail.

1.2.2 Mechanisms of Polymer Decomposition

As mentioned in the previous section polymer decomposition is the first important stage of the combustion process. The mechanisms of thermal decomposition of organic polymers being of primary importance will therefore be considered in this section.

When an organic polymer is heated, it eventually reaches a temperature at which the weakest bonds start to rupture. The breaking of only relatively few bonds is generally referred to as polymer degradation and results in only minor changes in structure and properties. However at higher temperatures more extensive breakdown of the polymer structure starts to take place and this breaking of a significant proportion of the total number of constituent chemical bonds is sometimes called polymer decomposition. Although the distinction between the two processes is not always well-defined, it is as a rule only the latter more extensive process of decomposition which is directly relevant to the combustion of polymers.

In the thermal decomposition of organic polymers, four general mechanisms can be identified (Wall 1972). These are (Table 1.2): end-chain scission which produces almost entirely monomer as the product, random-chain scission which produces variable chain length products and little if any monomer, chain-stripping which involves the splitting-off of the substituent groups and therefore produces molecules of

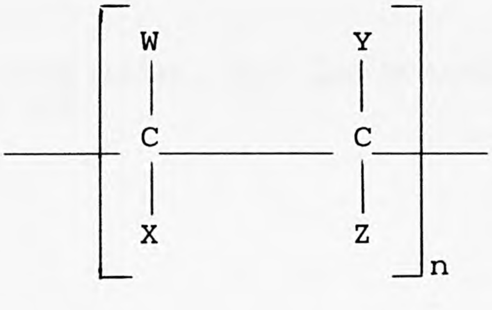
Table 1.2 General mechanisms of thermal decomposition of organic polymers

Mechanism	Polymer (examples)	Products
Random-chain scission	Polyethylene, polypropylene	Alkanes, alkenes very little monomer
	Polystyrene[a]	Styrene monomer, dimer, and trimer
	General	monomers and oligomers
End-chain scission	Poly(methyl methacrylate) Polymethacrylonitrile Poly(.-methyl styrene) Polytetrafluoroethylene Polyformaldehyde	90-100% monomer
	General	Monomer
Chain-stripping	Poly(vinyl chloride)	Hydrogen chloride aromatic hydrocarbons and char
	Poly(vinylidene chloride)	Hydrogen chloride and char
	Poly(vinyl alcohol)	Water and char
	General	Small molecules and char
Cross-linking	Polyacrylonitrile	Char
	Poly(oxy-m-xylene)	Char
	General	Much char, few volatile products

a = Decomposes by a mechanism involving both random- and end-chain scission

SOURCE: Wall, Cameron 1972 in: Cullis, C. F. and Hirschler, M. M., The Combustion of Organic Polymers, p. 117

relatively low molecular weight, and cross-linking which produces char as its only product. While some polymers undergo reactions which fall almost exclusively into one of these four classes, others exhibit mixed behaviour. For example, polystyrene, which yields up to 50 percent of monomer together with some oligomeric fragments, decomposes by a mixture of random-chain and end-chain scission. Similarly, poly(methyl acrylate), which gives a wide variety of oligomeric fragments as well as carbon dioxide and methanol but hardly any monomer, breaks down by a combination of random-chain scission and chain-stripping. With organic polymers containing exclusively carbon chains, certain generalizations can be made regarding the relation between polymer structure and mechanism of decomposition. All these polymers, except polydienes, have the general formula:



$$-\left[\overset{W}{\underset{X}{\overset{|}{\underset{|}{C}}}} - \overset{Y}{\underset{Z}{\overset{|}{\underset{|}{C}}}} \right]_n-$$

Yields of monomer obtained when some vinyl polymers decompose are given in Table 1.3. When neither W nor X are hydrogen atoms but Y and Z are, yields of monomer are very high. When X is replaced by hydrogen, the monomer yield falls significantly (compare polystyrene with poly(α-

Table 1.3 Yields of monomer from the thermal decomposition of polymers of general formula $[CWX\text{-}CYZ]_n$

Polymer	W	X	Y	Z	Monomer Yield (wt. %)	Decomposition mechanism[a]
Polystyrene	H	H	H	C_6H_5	42-45	EC/RC
Poly(α-methylstyrene)	H	H	CH_3	C_6H_5	95	EC
Poly(α-deuterostyrene)	H	H	D	C_6H_5	70	EC
Poly(β-deuterostyrene)	H	D	H	C_6H_5	42	EC/RC
Polyethylene	H	H	H	H	<1	RC
Polypropylene	H	H	H	CH_3	<1	RC
Poly(methyl methacrylate)	H	H	H	CO_2CH_3	<1	RC
Polyisobutylene	H	H	CH_3	CH_3	18-25	EC/RC

[a] RC, random-chain scission
EC, end-chain scission
CS, chain-stripping
CL, cross-linking

SOURCE: Modified from Cullis, C.F. and Hirschler, M. M. in The Combustion of Organic Polymers, p. 119

methylstyrene)). If X is deuterium, the yield of monomer still decreases but less markedly (compare poly(α-deuterostyrene)). This emphasises the key role played by α-hydrogen atoms in the decomposition mechanism (compare poly(β-deuterostyrene) with polystyrene). Polymer molecules are frequently oriented in such a way that the nearest radical centre within the chain is at a distance of 1-4 monomeric units. Thus the new radical may, after abstracting a hydrogen atom from another chain, volatilize as a relatively low molecular weight fragment. This random-chain scission process does not, however, normally yield monomer, because intramolecular transfer is unlikely to involve such a near carbon atom.

When there are no hydrogen atoms in the polymer, transfer reactions are less favoured and one of the other mechanisms takes over. Probably the most closely related process is end-chain scission or depolymerization (often also called "unzipping") which can be represented by the general equation:

$$M_i \longrightarrow M_{i-1} + M$$

This leads to the formation of monomer as the principal, if not the exclusive, product. The presence or otherwise of hydrogen in the β-position (Y or Z) has a considerably smaller effect than in the α-position, as shown by the relative yields of monomer formed from poly(α-

methylstyrene) and poly(β-methylstyrene) (Table 1.3). If the availability of hydrogen atoms were the only important factor governing the decomposition behaviour of this polymer, monomer yields would be expected to be either very small, as with polyethylene and polypropylene, or very large as with poly(methyl methacrylate) but not moderately large as with polystyrene and polyisobutylene.

If the polymer radical has a very low transfer rate constant, random-chain scission will be less likely than end-chain scission and the yield of monomer will be correspondingly higher. This occurs with the polystyryl radical, where the benzene ring clearly has a stabilizing effect. The stability of this radical may be significantly affected by substituents in the ring, the effect depending both on the nature of the substituent and on the polymerization mechanism. Although there are no reactive α-hydrogen atoms in polyisobutylene, the stabilizing influence and steric hindrance of the two methyl groups is not large enough to counterbalance the high reactivity of the polyisobutyl radical, so that β-hydrogen transfer leads to the formation of some oligomeric products and hence less monomer.

Chain stripping involves interaction of the substituents W, X, Y and Z. When the substituents are halogen atoms (other than fluorine) or hydroxy or acetate groups, decomposition tends to involve the loss of small molecules, such as water, hydrogen chloride, or acetic acid, provided that at least one of the four positions contains a hydrogen atom. (Madorsky 1964). Here free radicals are not normally involved, although processes such as the concurrent formation of aromatic compounds from poly(vinyl chloride) (O'Mara 1977) may occur by a free-radical mechanism. Decomposition continues until the polymer chain has been stripped entirely of its substituent groups. The loss of volatile side groups takes place almost quantitatively and indeed this type of decomposition provides a method for the production of highly pure stereoregular graphitisable carbon (Brooks and Taylor 1968; Fitzer, Mueller and Schaefer 1971). The presence of chain branching frequently increases the thermal stability of polymers which undergo chain-stripping by interfering with the normal chain mechanism. When fluorine is a substituent, the C-F bond (495 kJ mol^{-1}) is so strong and the highly electronegative fluorine atoms have such a high shielding effect that no chain-stripping at all occurs with perfluorinated polymers. These latter materials yield virtually only monomer as a result of end-chain scission which takes place at much higher temperatures than with the non-fluorinated analogues (Grassie 1972). Even if only one fluorine atom is replaced by chlorine, the monomer yield decreases dramatically. However, when one or more fluorine atoms are replaced by hydrogen, no monomer is formed, only partial chain-stripping occurs and the thermal stability is significantly reduced.

The position with respect to cellulose is more complicated and its behaviour cannot easily be described in terms of the four general mechanisms mentioned in Table 1.2. Cellulose breaks down via a combination of end-chain scission to form laevoglucosan and cross-linking to form char.

1.2.3 Flame Reactions

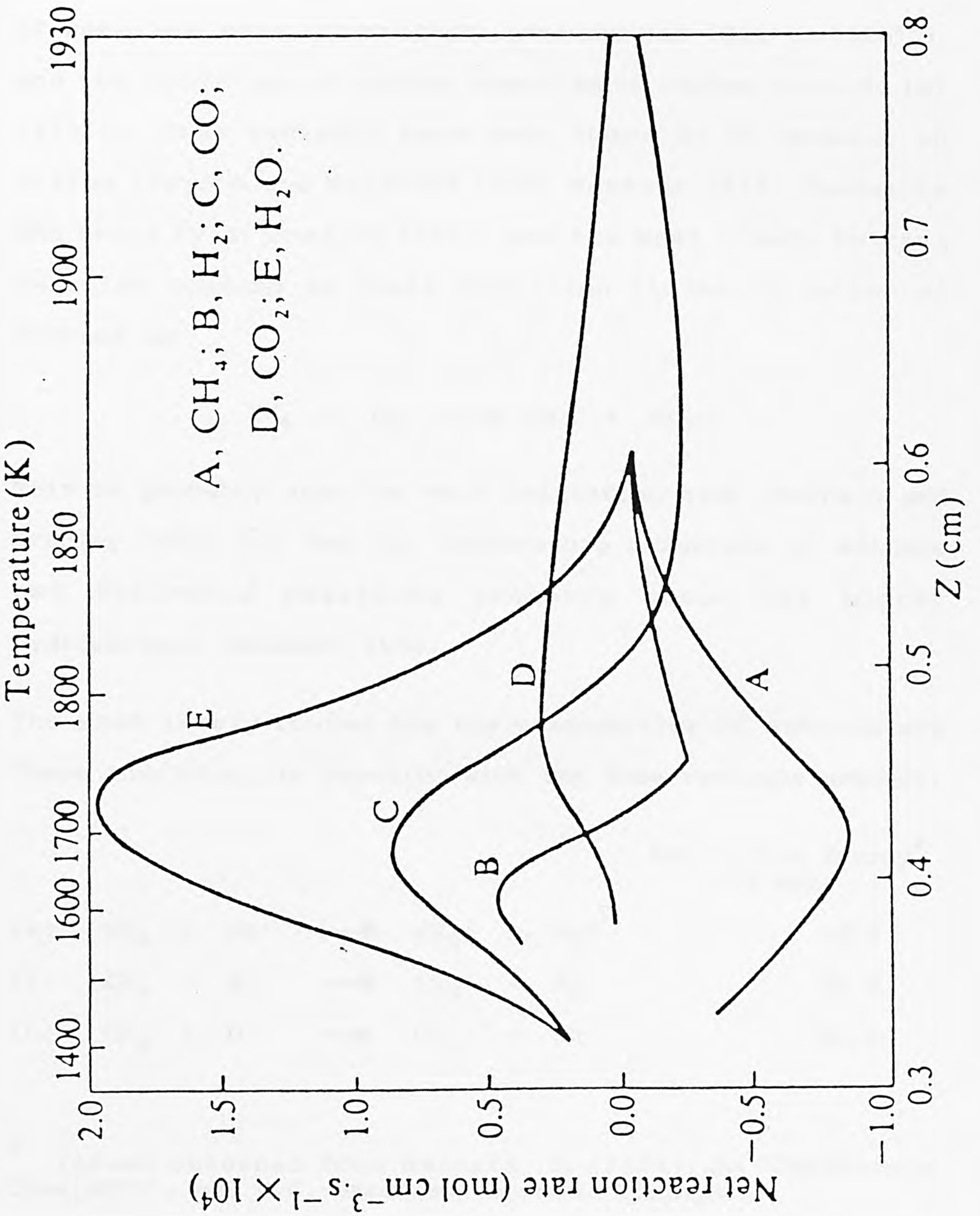
When the gaseous products of the decomposition of a polymer mix with oxygen or other oxidants, the resulting mixture may ignite to give a flame. Flame reactions constitute another important stage in the overall process of the combustion of organic polymers. Two main classes of flame exist, propogating and stationary flames. The former can be best described by considering a gaseous mixture of fuel and oxidant in a sealed container. Below a certain temperature the heat produced by the reaction is effectively dissipated by the walls of the container. Since the rate of heat generation equals the rate of heat loss, isothermal conditions are maintained and reaction proceeds smoothly to completion by what is referred to as slow combustion. However, above a certain temperature, which depends on the physical properties of both the reactants and the container, the rate of heat release will exceed the rate of heat loss, in which case the temperature will rise. Under these conditions the rate of reaction will steadily increase, resulting eventually in a violent increase in pressure and temperature and the production of a propagating or exploding flame. An important application of propagating flames is in the internal combustion engine.

The second class of flame is the stationary flame of which there are two extreme types, diffusion flames and premixed flames. In diffusion flames the fuel burns as it is brought into contact with the oxidant. Thus the combustion processes are mainly determined by the rates of mixing of the oxidant and the fuel. A burning candle discussed in Section 1.2.1 is an example of a diffusion flame. Premixed flames are kinetically controlled, and have the fuel and the oxidant uniformly distributed in the gas phase. A Bunsen burner with the air-port fully open is an example of a premixed flame. Under these conditions the premixed gases flow up the burner tube at a rate which equals the normal burning velocity of the mixture, producing a steady flame.

Premixed flames have been the subject of much greater scientific investigation than diffusion flames, because they can be used to give information about a number of fundamental properties of a gas mixture, such as its burning velocity. With diffusion flames there is a steady change in chemical composition on passing through the flame, and there are few physical constants which can be measured. In order to understand the chemical reactions occurring in stationary flames, measurements can be made of the concentration profiles of the various species throughout the flame zone.

As far as stable species are concerned, this has been carried out for a number of hydrocarbon flames. The net reaction profiles for the five principal molecular species in a lean methane-oxygen flame are shown in Figure 1.7. No appreciable chemical reaction takes place until a temperature of about 1025°C is reached. At this point the methane starts to disappear and much of the water, hydrogen

Figure 1.7 Net rates of formation and consumption of molecular species in a premixed lean methane-oxygen flame at a pressure of about 5kPa



and carbon monoxide are formed. At about 1475°C carbon monoxide is converted to carbon dioxide. The observed variation of reactant and product concentrations involves the consumption of methane (at about 1025°C) the formation of water and some intermediate products (at 1325 to 1425°C), and the oxidation of carbon monoxide to carbon dioxide (at 1475°C). Free radicals have been shown to be present in flames (Gaydon and Wolfhard 1979; Hawkins 1978; Chedaille and Brand 1972; Bradley 1969), and the most likely initial reaction leading to their formation in the oxidation of methane is:

$$CH_4 + O_2 \longrightarrow CH_3^{\cdot} + HO_2^{\cdot}$$

This is probably also the main initiation step (Barnard and Bradley 1985) for the low temperature oxidation of methane and analogous reactions probably occur for higher hydrocarbons (Semenov 1958).

The most likely routes for the consumption of methane are those involving its reaction with the free radicals present:

		Activation Energy* ($kJ\ mol^{-1}$)
(a)	$CH_4 + OH^{\cdot} \longrightarrow CH_3^{\cdot} + H_2O$	10.3
(b)	$CH_4 + H^{\cdot} \longrightarrow CH_3^{\cdot} + H_2$	36.6
(C)	$CH_4 + O^{\cdot\cdot} \longrightarrow CH_3^{\cdot} + OH^{\cdot}$	31.9

---

* Values obtained from Warnatz, J. (1984). In "Combustion Chemistry", ed. W.C. Gardiner, London, Springer.

These reactions have been discussed in more detail in the following reviews: CH_4 + OH (Ernst et al. 1978), $CH_4 + H^{\cdot}$ (Clark and Dove 1973; Roth and Just 1975) and $CH_4 + O^{\cdot\cdot}$ (Roth and Just 1977, Klemm et al. 1981).

All these reactions have rather low activation energies. At normal flame temperatures, reaction (c) is slower than reactions (a) and (b) and accounts for only a small part of the methane consumed (Wong and Potter 1963). Under fuel-lean conditions reaction (b) can be neglected in comparison with raction (a), but in a fuel-rich methane flame the situation is reversed (Fenimore and Jones 1961). The only reasonably stable intermediate molecular products are carbon monoxide, hydrogen and formaldehyde. The two latter compounds are, however, present only in small amounts. It is likely that the carbon monoxide is derived from the methyl radicals generated in reactions (a) - (c), which react further with oxygen:

(d) $$CH_3^{\cdot} + O_2 \longrightarrow HCHO + OH^{\cdot}$$

However, since little formaldehyde is actually present at any stage (Fenimore and Jones 1961), its formation is probably followed by its rapid removal, viz

(e) $$HCHO + OH^{\cdot} \longrightarrow HCO^{\cdot} + H_2O$$

(f) $$HCO^{\cdot} + OH^{\cdot} \longrightarrow CO + H_2O$$

Thus, for every $CH_3^{\cdot}$ radical reacting by (d), one molecule of carbon monoxide would eventually be produced.

A scheme illustrating the complete oxidation of methane and the products of the reactions involved is shown as a flow diagram in Figure 1.8. The rate of formation of carbon monoxide should approximately equal the rate of reaction of methyl radicals with oxygen, which in turn approximates to the rate of consumption of methane as long as no appreciable recombination of methyl radicals occurs. This will only be true however before the secondary oxidation of carbon monoxide starts to take place. The most probable reaction by which carbon monoxide disappears both in the later stages of a methane flame and in a flame of carbon monoxide itself is:

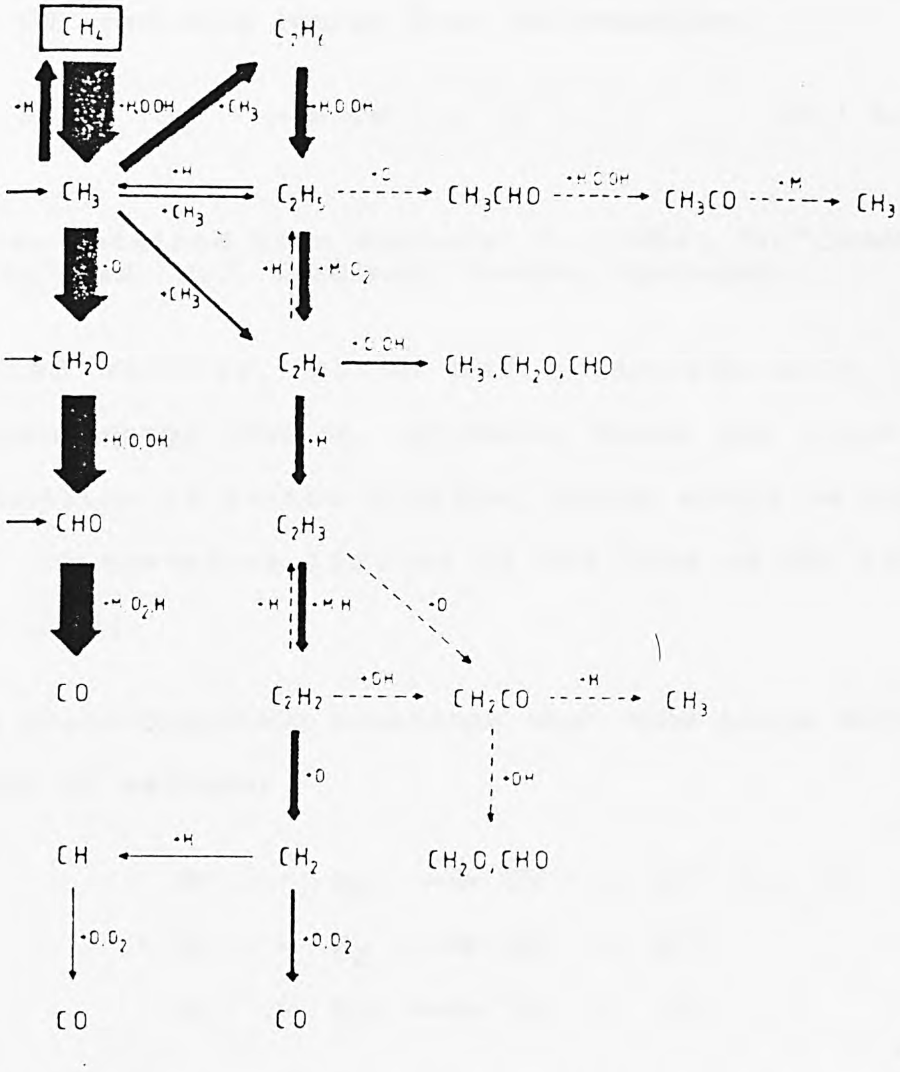
$$CO + OH^{\cdot} \longrightarrow CO_2 + H^{\cdot}$$

The competitive reaction of carbon monoxide with molecular oxygen

$$CO + O_2 \longrightarrow CO_2 + O^{\cdot}$$

is unlikely to occur, since dry, hydrogen-free mixtures of carbon monoxide and oxygen burn only with difficulty (Wines, Watermeier and Strehlow 1959). Sawyer (1971) pointed out the anomaly that carbon monoxide can remain unchanged in hydrocarbon flames even when there is an excess of oxygen. The reason for this is that most of the carbon monoxide is formed when the burnt flame gases are cooled very rapidly to below 725°C. The incompleteness of the conversion of methane to carbon dioxide can be explained kinetically because, although the activation energy for the reaction:

Figure 1.8 Flow diagram for the oxidation of methane in stoichiometric methane-air flames at P = 1 bar, T = 25°C



The thickness of the arrows is proportional to the reaction rates integrated over the whole flame front.

Source: J. Warnatz (1984). In Combustion chemistry, ed. W.C. Gardiner, Jr., p. 203

Activation Energy[*]

$$CO + OH^{\cdot} \longrightarrow CO_2 + H^{\cdot} \qquad 33.0\ \text{kJ mol}^{-1}$$

is low, $OH^{\cdot}$ radicals result from the reaction:

$$H^{\cdot} + O_2 \longrightarrow OH^{\cdot} + O^{\cdot\cdot} \qquad 69.1\ \text{kJ mol}^{-1}$$

mentioned earlier, which has a considerably higher activation energy (Baulch, Drysdale, Horne and Lloyd 1972). The formation of carbon dioxide, which would be rapid at 1225°C, is therefore limited by the lack of $OH^{\cdot}$ radicals (Palmer 1974).

Various chain-branching reactions also take place during the oxidation of methane:

$$\begin{aligned} H^{\cdot} + O_2 &\longrightarrow OH^{\cdot} + O^{\cdot\cdot} \\ O^{\cdot\cdot} + H_2 &\longrightarrow OH^{\cdot} + H^{\cdot} \\ O^{\cdot\cdot} + H_2O &\longrightarrow OH^{\cdot} + OH^{\cdot} \end{aligned}$$

Chain-termination reactions generally require the presence of a third body (M) and include:

$$\begin{aligned} H^{\cdot} + H^{\cdot} + M &\rightleftharpoons H_2 + M \\ O^{\cdot\cdot} + O^{\cdot\cdot} + M &\rightleftharpoons O_2 + M \\ H^{\cdot} + OH^{\cdot} + M &\rightleftharpoons H_2O + M \\ CH_3^{\cdot} + CH_3^{\cdot} + M &\rightleftharpoons C_2H_6 + M \end{aligned}$$

The complete analysis of such flame systems is however very

---

[*] Values obtained from Warnatz, J. (1984). In "Combustion Chemistry", ed. W.C. Gardiner, London, Springer.

complicated and has been achieved only for relatively few simple hydrocarbon-oxygen systems.

Since the majority of common polymeric materials are hydrocarbon-based, the flames above such polymers are essentially hydrocarbon flames and contain large radical species which break down to give smaller radicals. The latter species tend to be involved in all hydrocarbon flames and the chemistry of such flames is effectively the high temperature chemistry of a small number of quite simple free radicals. In the same way, oxygen-containing polymers such as cellulose tend also to produce oxygenated hydrocarbons and the associated free radicals.

It is worth considering briefly the type of radical reaction that might take place with a simple oxygenated hydrocarbon such as methanol, as this may provide information relevant to cellulose, which under combustion conditions yields oxygen-containing volatile products.

The most likely initial reaction for the oxidation of methanol is:

$$CH_3OH \;+\; O_2 \longrightarrow CH_2OH^{\cdot} \;+\; HO_2^{\cdot}$$

The majority of the reactions in a methanol flame involve $OH^{\cdot}$, $O^{\cdot\cdot}$ or $H^{\cdot}$ radicals, but although $CH_3O^{\cdot}$ has also been detected (Warnatz 1985), $CH_2OH^{\cdot}$ is a more likely primary product since it has a lower enthalpy of formation than $CH_3O^{\cdot}$ (Vandooren 1981).

Rate constants have been determined for the following reactions: (Reactions i, ii Vandooren and Van Tiggelen 1981; reactions iii, iv Spindler and Wagner 1982)

i $CH_3OH + H^{\cdot} \longrightarrow CH_2OH^{\cdot} + H_2$

ii $CH_3OH + OH^{\cdot} \longrightarrow CH_2OH^{\cdot} + H_2O$

iii $CH_3OH + CH_3^{\cdot} \longrightarrow CH_2OH^{\cdot} + CH_4$

iv $CH_3OH + M \longrightarrow CH_3^{\cdot} + OH^{\cdot} + M$

(M = Argon)

The flames involved in polymer combustion are invariably of the stationary type and in general have a greater similarity to gaseous diffusion flames than to premixed flames. Nevertheless, with certain polymers, air may be in contact with the polymer surface so that the flame is at least partly premixed. Although these flames are extremely complicated, reactions in simple hydrocarbon flames give information on the type of reactive species that may be present.

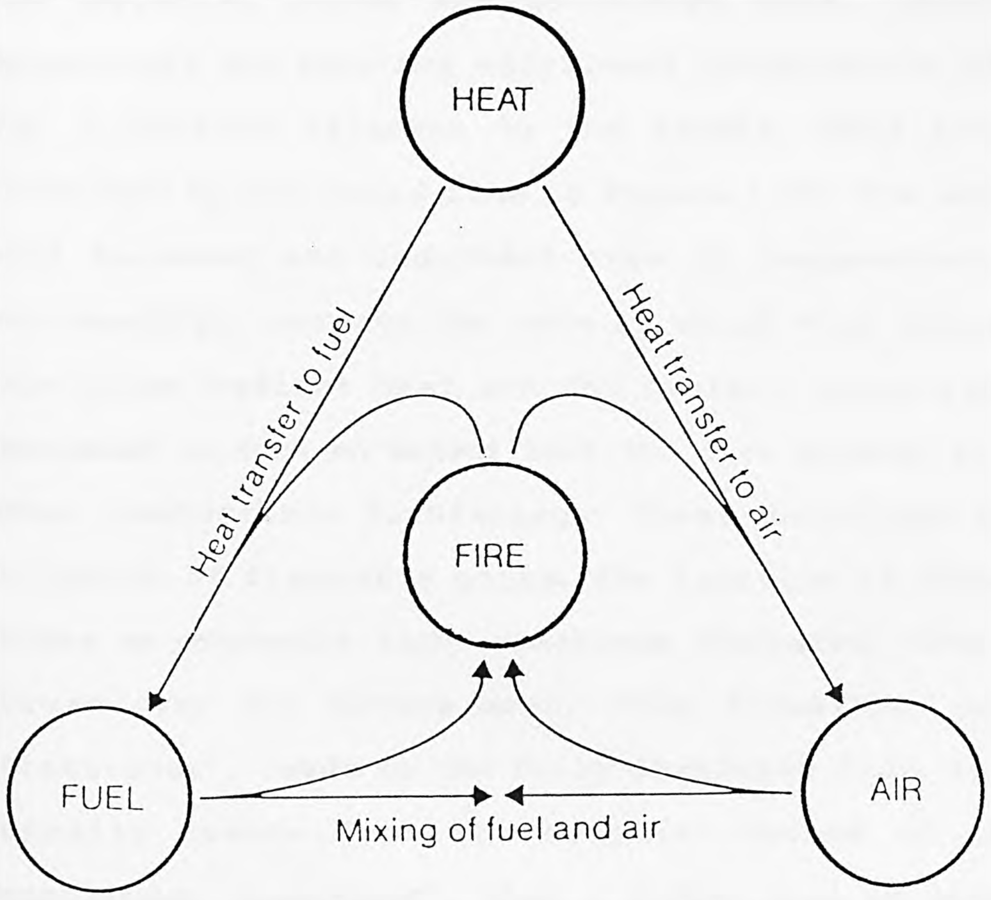
1.2.4 Fire as a combustion process

Following an examination of reactions which take place in flames, which can be considered as a microscopic description of the combustion process, it is useful to consider combustion as a macroscopic process.

In order for a fire to start, three components are necessary, fuel, oxygen and energy. Emmons (1973) illustrated this clearly by means of the fire triangle shown in Figure 1.9. The three factors which affect fire are themselves effected by a multitude of variables. It is therefore difficult to describe a fire quantitatively or to predict its course exhaustively. Some progress has been made in this direction however with the aid of detailed computer modelling which inevitably makes certain assumptions regarding the nature of fire.

Some of the factors which influence the components of fire will now be considered. Firstly, energy can be transferred to the fuel by radiation or from a flame. An important criterion for the continuation of the fire is the intensity of the energy source and the duration of the source ignition. Secondly, oxygen is essential for the burning process, i.e., for combustion of the fuel and must be present in sufficient quantities, i.e. via ventilation at the site of the fire. Finally, the fuel itself influences the fire situation significantly depending on its physical and chemical characteristics, e.g. flash point, specific

Figure 1.9 Fire triangle (according to Emmons 1973)



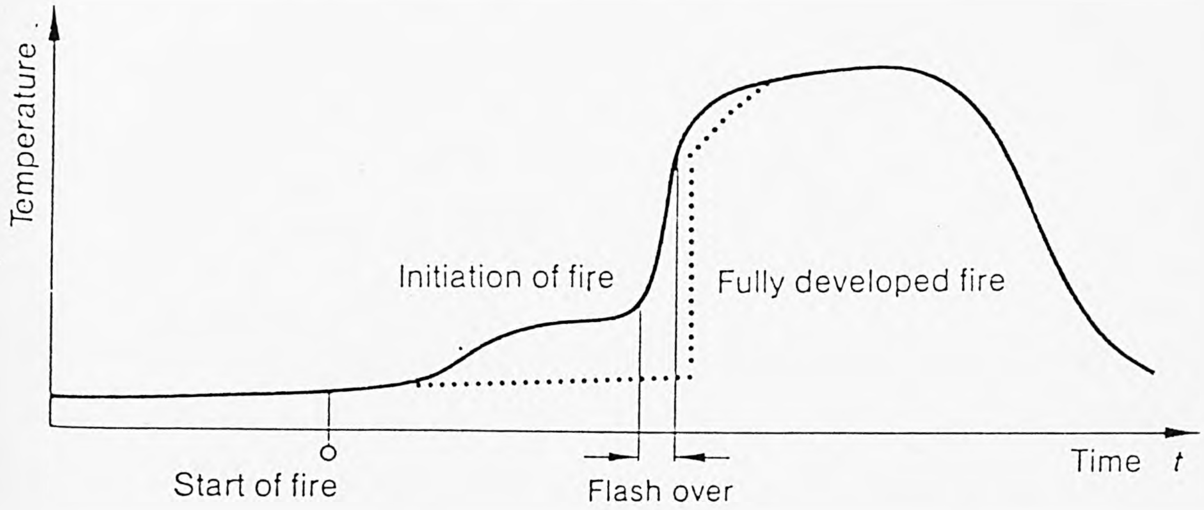
heat of combustion and thermal conductivity.

The course of a fire can be split into several phases as shown by Becker (1975) in Figure 1.10, which relates to a fire in a building.

An ignition source, e.g. a burning cigarette, ignites a combustible material, e.g. paper in a waste paper basket. The material burns and generates heat, raising the temperature and igniting additional combustible material, e.g. a curtain adjacent to the basket. This process is indicated by the solid line in Figure 1.10. The additional heat released and resultant rise in temperature of the surroundings increase the rate at which fire develops. At this stage radiant heat and the overall temperature have increased to such an extent that the fire extends to include other combustible furnishings. These decompose with the evolution of flammable gases. The ignition of these gases causes an extremely high, sometimes explosive, rate of fire spread over the entire area. This situation, known as "flash-over", leads to the fully developed fire. If a point formally remote from the original source of the fire experiences "flash-over", then a sudden rise in temperature occurs indicated by the dotted line in the figure.

Once the fire has developed it penetrates doors, walls, ceilings and spreads to neighbouring rooms until the whole building is ablaze. At this point the fire has reached an optimum point. Depending on the size of the fire and the

Figure 1.10 The course of a fire - variation of temperature with time



_____ Temperature variation at point near centre of fire

..... Temperature variation at point remote from fire

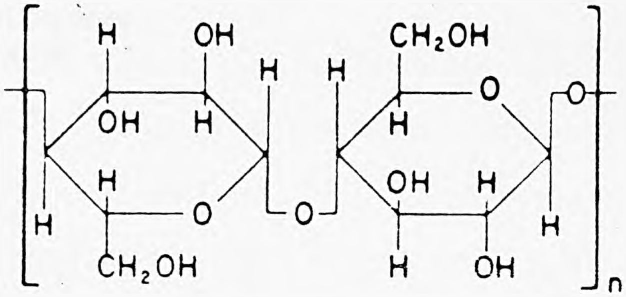
Modified after Becker (1975)

supply of oxygen to support the fire, the fire passes through its climax and begins to decrease.

1.3 The Decomposition of Cellulose

1.3.1 Decomposition mechanisms

The basic building block of cellulose is the β -glucose unit shown below:



$-\!(C_6H_{10}O_5)\!-_n$

The value of n ranges from 20,000 to 500,000 depending on the type or source of this important natural polymer. Cellulose is a solid with no appreciable vapour pressure which does not itself burn, but rather decomposes to give volatile flammable products which react with oxygen generating heat. Some of the heat evolved is transferred back to the cellulose, causing further decomposition and thus continuing the combustion cycle.

The thermal degradation of cellulose, which will be the primary consideration in this Section, occurs through a complex series of consecutive and concurrent chemical reactions forming up to eighty volatile products, the most important of which are laevoglucosan (1, 6 - anhydro - β - D - glucopyranose) and water. Table 1.4 lists the products

Table 1.4 Products Identified from the Pyrolysis of Cellulose

Laevoglucosan (1,6-anhydro-β-D-glucopyranose)*
1,6-Anhydro-β-D-glucofuranose
Glyoxal (mono)
Glyoxal (bis)
Hydrogen
Acetone
Water
Methyl ethyl ketone
Carbon Monoxide
Diacetyl
Carbon dioxide
Furan
Methane
2-Methylfuran
Acetylene
Furfural
Ethylene
5-(Hydroxymethyl)furfural
Ethane
Formic acid
Methanol
Acetic acid
Ethanol
Lactic acid
Formaldehyde
Pyruvaldehyde (mono)
Pyruvaldehyde (bis)
Acetaldehyde
Propionaldehyde
Hydroxypyruvaldehyde
Acrolein
Mesoxaldehyde (1,2-bis)
Mesoxaldehyde (tris)
Laevalinic acid
n-Butyraldehyde
Glycolaldehyde
Crotonaldehyde
Glyceraldehyde
Dihydroxyacetone
Hydroxymethyl 2-furyl ketone
Glyoxylic acid
Pyruvic acid

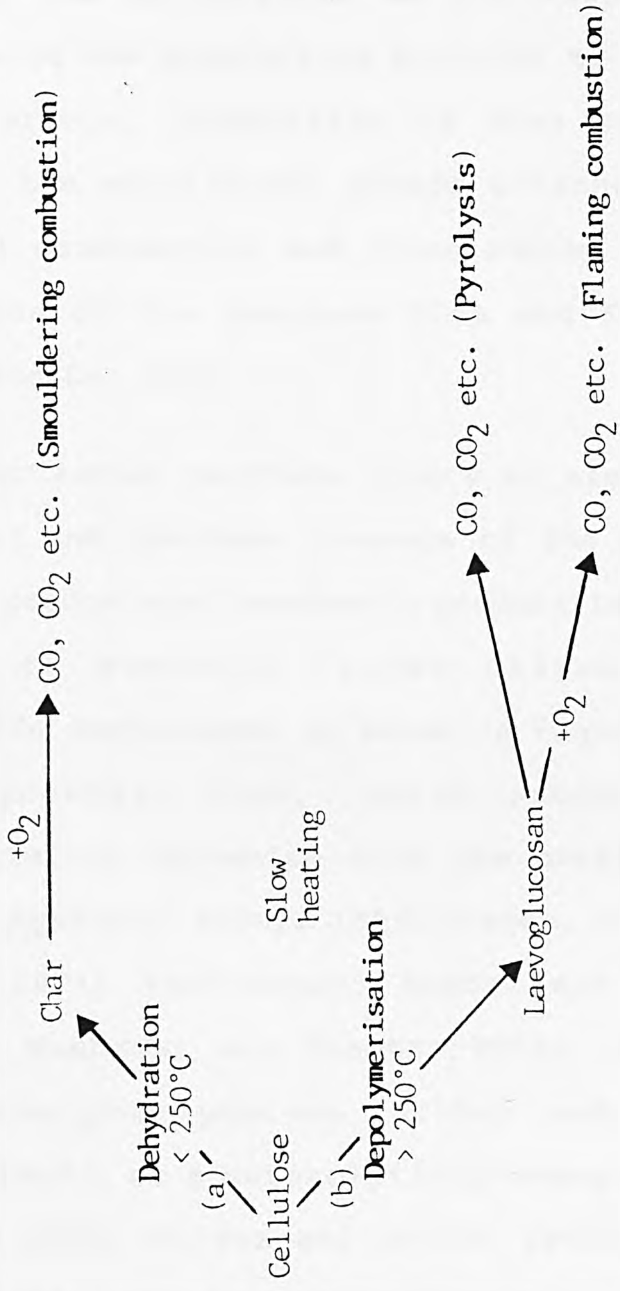
* Product of main interest

of pyrolysis as identified by gas chromatography. The yields of products, including laevoglucosan, vary markedly depending on the type and purity of the cellulose. Laevoglucosan generally accounts for about 20 wt percent of the total products (Tsuchiya and Sumi 1970), although 50 wt percent can be obtained from very pure cellulose.

Two main pathways can be recognised for the degradation of cellulose, as shown in Figure 1.11. Pathway (a) involves dehydration and the formation of carbonaceous char that could lead to localized, and relatively slow, smouldering combustion. Pathway (b) involves depolymerization of the cellulose chain to give combustible volatile products which constitute the fuel for flaming combustion. The two pathways compete for the same initial substrate, and one may predominate at the expense of the other depending on the reaction conditions.

The dehydration route, which takes place at fairly low temperatures (ca. < 250°C) can be enhanced by the addition of catalysts (Shafizadeh, Chin and DeGroot 1975; Susott, DeGroot and Shafizadeh 1975). This process involves more than simple elimination of the hydroxyl groups. Both intermolecular dehydration (resulting in crosslinking), and intramolecular dehydration occur, the latter resulting in cyclodehydration and formation of furan rings. The unsaturated volatile products formed, such as 3-deoxyglucosenone, levoglucosenone and furfural as well as

Figure 1.11 The two main modes of decomposition of cellulose

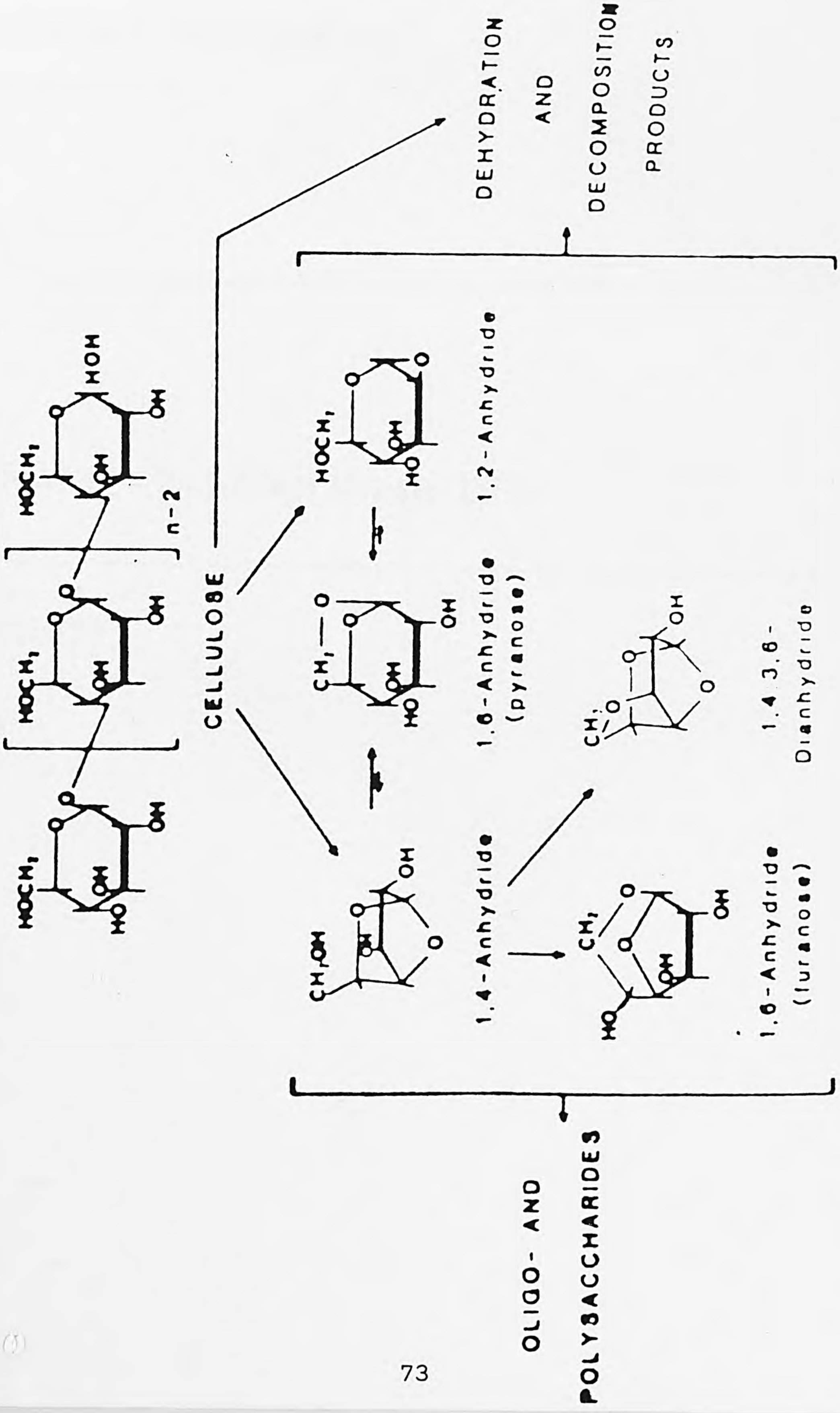


various furan derivatives, are found both in the tar and among the volatiles.

The charring reactions have been investigated using model compounds. Shafizadeh (1968) has shown that the chars are produced by the dehydration of the carbohydrate units, condensation of the unsaturated products to higher molecular weight materials, production of free radicals through cleavage of the substituent groups attached to carbon and free radical condensation and crosslinking, which result in carbonization of the residues (Lai and Shafizadeh 1974; Shafizadeh and Lai 1975).

The depolymerization reaction occurs at higher temperatures (ca. > 250°C) and involves cleavage of the glycosidic bonds to form the predominant monomeric product laevoglucosan, and a variety of randomly linked oligosaccharide and monosaccharide derivatives as shown in Figure 1.12. Cleavage of the glycosidic bond, which proceeds through a transglycosylation mechanism with the participation of one of the free hydroxyl groups (Shafizadeh, McGinnis, Susott and Tatton 1971; Shafizadeh, Susott and McGinnis 1972; Shafizadeh, Meshreki and Susott; 1973), could occur via either a homolytic process (Arthur and Hinojosa 1966; Shafizadeh 1968), or a heterolytic process (Madorsky, Hart and Strauss 1958; Kilzer and Broido 1965; Gardiner 1966; Shafizadeh 1968). The homolytic process has been suggested on the basis of the free radicals detected by e.s.r. spectroscopy of the pyrolysis products. However more recent

Figure 1.12 The decomposition of cellulose by a heterolytic mechanism to form anhydro sugars and the possible conversion of 1,4 and 1,2-anhydro sugars to laevoglucosan (1,6-anhydro-β -D-gluco pyraneose)



studies have shown that the free radicals are formed by the dehydration or degradation of the carbohydrate unit (Shafizadeh, Susott and McGinnis 1972; Shafizadeh 1968).

Most of the evidence for a heterolytic cleavage reaction has come from studies of a variety of model compounds by Golova (1957), Kislitsyn (1969, 1971) and Shafizadeh (Shafizadeh, McGinnis, Susott, Tatton 1971; Shafizadeh, Susott, McGinnis 1972; Shafizadeh, McGinnis and Philpot 1972; Shafizadeh, Lai, Susott 1972; Shafizadeh, Fu 1973; Shafizadeh, Meshreki, Susott 1973; Shafizadeh and Lai 1973; Richards and Shafizadeh 1978; Shafizadeh 1982). These studies indicate that the electron density at the glycosidic position and the configuration of the pyranose ring have a strong effect on glycosidic bond cleavage. The direction and size of these effects support a heterolytic mechanism. The most likely route involves a nucleophilic displacement of the glycosidic group by one of the ring hydroxyl groups to form an anhydro sugar as in Figure 1.12. Three types of anhydro sugar have been proposed: 1,2-, 1,4- and 1,6- (Shafizadeh 1971) as shown in Figure 1.12. Laevoglucosan (1,6-anhydro-β-D-glucopyranose) can be formed from any of these anhydro sugars or directly from cellulose.

The fate of the anhydro sugars formed from the cleavage of the glycosidic linkage in cellulose depends on the relative stability of the sugar and the prevailing conditions. The 1,2- and 1,4-anhydro sugars are easily converted into the more stable 1,6-anhydro sugars. Under vacuum, the anhydro sugars are readily removed from the heated reaction zone before they can undergo further extensive degradation and decomposition. Consequently the tar fraction of the volatile products contains predominantly a mixture of 1,6-anhydro-β-D-glucopyranose (laevoglucosan), and 1,6-anhydro-β-D-glucofuranose and further condensation products, consisting mainly of various oligo- and polysaccharides.

The effect of temperature on the range of pyrolysis products of cellulose is shown in Table 1.5. The extent of tar-forming reactions increases considerably with increasing temperature, while the production of char decreases to a value of only 3 percent at 500°C. The volatile products at intermediate temperatures are formed by dehydration, scission and fragmentation of the hexose sugar rings.

Pyrolysis of cellulose at higher temperatures (ca. 550°C) results in further degradation of the D-glucose residues to yield products of lower molecular weight as shown in Figure 1.13. These include furan, 2-furaldehyde, 5-methyl-2-furaldehyde, acetic acid, acetaldehyde, acrolein, 2-butenal, glycoxal, methanol and 2,3-butanedione (Shafizadeh 1975). These compounds are further randomized by disproportionation, decarboxylation and decarbonylation reactions to provide a mixture of products typical of pyrolytic reactions at elevated temperatures.

The thermal degradation of cellulose as described in this

Table 1.5 Effect of temperature on the products from pyrolysis of cellulose powder under vacuum[a]

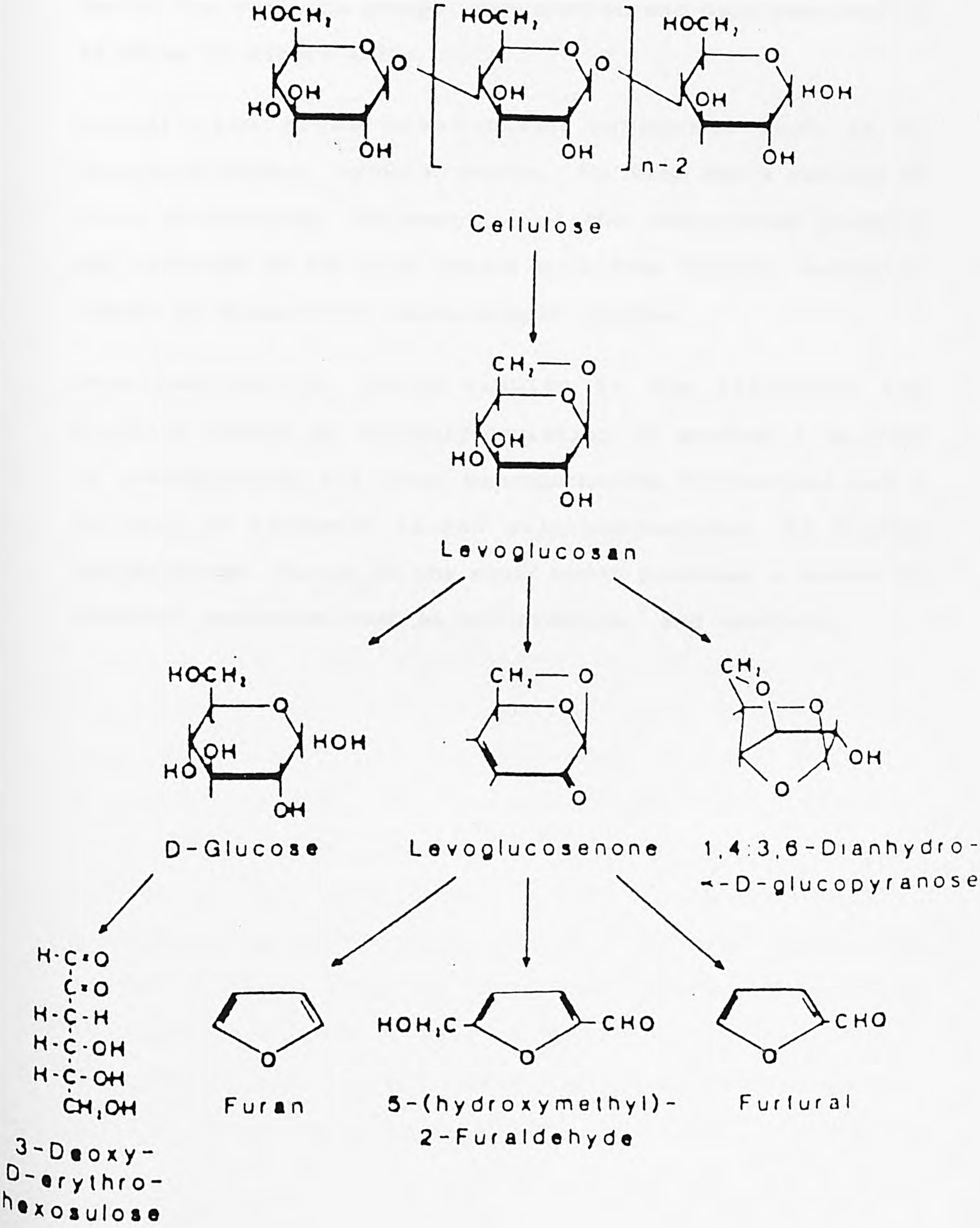
Oven temp. (°C)	Pyrolysis time (min)	Percentage yield from cellulose			
		Char	Tar	Laevo-glucosan[b]	1,6-anhydro-β-D-gluco-furanose[b]
300	180	21	60	34	4
325	60	10	70	38	-
350	30	8	70	38	4
375	10	6	70	38	-
400	5	5	77	39	4
425	4	4	78	40	4
450	3	4	78	39	4
475	3	3	80	38	4
500	3	3	81	38	4

[a] Pressure + 1.5 mm Hg

[b] This is the percentage of this compound, based on the starting cellulose content in the tar fraction.

Source: In: Cellulose Chemistry and its applications, ed. T.P.Nevell and S.H. Zeronian, 1985, p. 283

Figure 1.13 The formation of five- and six-membered ring compounds from the decomposition of cellulose



section involves a series of highly complex concurrent and consecutive reactions producing flammable volatile products and char. The reactions which occur concurrently fall into one of the two main groups, dehydration and depolymerization as shown in Figure 1.11.

Dehydration gives unsaturated compounds such as 3-deoxyglucosenone, levoglucosenone, furfural and a variety of furan derivatives. Condensation of the unsaturated products and cleavage of the side chains by a free radical mechanism leaves an essentially carbonaceous residue.

Depolymerization, which results in the flammable tar fraction occurs by transglycosylation to produce a mixture of laevoglucosan and other monosaccharide derivatives and a variety of randomly linked oligosaccharides. At higher temperatures, fusion of the sugar units produces a number of carbonyl compounds such as acetaldehyde, and acrolein.

1.3.2 Possible mechanisms of inhibition of cellulose combustion

Obvious methods of reducing the flammability of a polymeric system involve either altering the pathways by which degradation takes place so that non-flammable products are formed or alternatively preventing the flammable products produced from undergoing combustion.

In simple terms cellulose can be considered to decompose by the two principal routes described earlier, one produces a flammable tar, which derives predominantly from laevoglucosan, whereas the other leads to the formation of char and water as a result of dehydration. The prevention of laevoglucosan formation and/or the enhancement of char and water formation is therefore fundamental to reduction of the flammability of cellulose.

Madorsky (1956, 1958) investigated the rate of formation of tar during pyrolysis of cellulose and showed by infrared and mass spectrometry that laevoglucosan was the principal component of tar under the conditions used. The data obtained indicated different tar yields from different celluloses and showed that cellulose which had been substituted at the C-6 hydroxyl and more highly substituted celluloses, e.g., cellulose triacetate, yielded little or no laevoglucosan. In further work (Holmes et al. 1961, 1966; Schwenker and Pascu 1957, 1958) measurements were made of the tar and laevoglucosan yields from untreated oxidised and flame-retarded cottons and evidence was obtained of a direct proportionality between these yields and cotton flammability.

Laevoglucosan yields are strongly influenced by even trace impurities present in or added to the cellulose (Patai 1970). It has been shown that acidic impurities can either increase or decrease the percentage of laevoglucosan in the tar, depending on their concentration (Basch and Lewin 1973), while basic impurities decrease laevoglucosan formation at all levels as shown in Table 1.6.

Since flammability increases with laevoglucosan formation (Table 1.6) the observed surprising increase in the flammability of cellulose textiles treated with low concentrations of certain known flame retardants is explained (Coppick 1947; Miller 1972).

Cross-linking with formaldehyde also decreases both laevoglucosan yields and flammability (Rodrig et al. 1975). This is explained by the lower tendency of cellulose substituted in the C_2 and C_6 positions to undergo depolymerization.

Madorsky (1956) and Holmes (1961) have shown that flame retardants for cellulose generally increase the yields of water, carbon monoxide, carbon dioxide, and char, but decrease the yield of the tar fraction. This is shown by the data in Table 1.7, which demonstrate that addition of salts

Table 1.6 Effects of additives upon laevoglucosan formation and flammability of cotton

Additive	Concentration (%)	Laevoglucosan in tar (%)	Limited oxygen index (LOI)
Blank	-	22	18.10
$(NH_4)_2SO_4$	0.1	41	17.40
$(NH_4)_2SO_4$	0.2	28	18.10
$(NH_4)_2SO_4$	1.0	14	19.76
$NaHCO_3$	0.01	16	18.73
$NaHCO_3$	0.1	13	19.15
$NaHCO_3$	1.0	0	20.50

Source: A. Basch and M. Lewin (1973), Text.Res.J. 43, 693

Table 1.7 Effects of salts on vacuum pyrolysis of cotton cellulose

Sample	Temp., °C	Heating, periods min.	Weight loss %	Composition of the volatiles			
				(Tar)	(H_2O)	(CO_2)	(CO)
Cotton	280	661	70	65	27	6	2
Cotton + 7% of Na_2CO_3	251	180	37	9	59	21	11
Cotton + 0.14% of Na_2CO_3	280	149	15	21	54	13	12
Cotton + 8% of NaCl	280	120	49	12	59	15	14

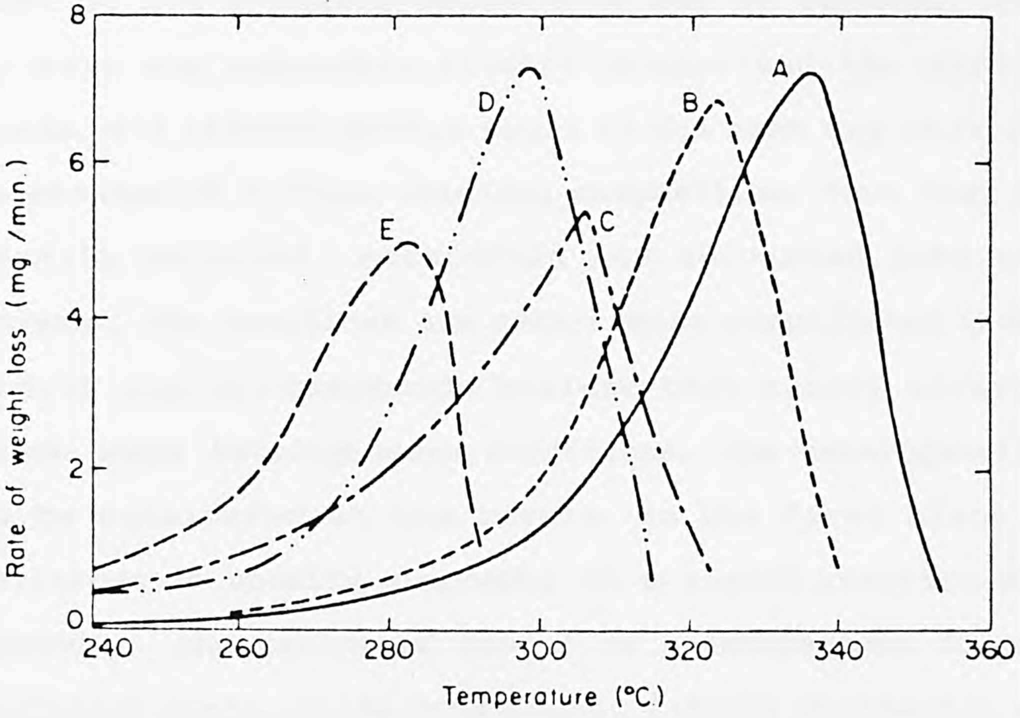
Source: S.L. Madorsky, V.E. Hart and S. Strauss (1956).
J. Res. Natl. Bur. Stud., 56, 343

not only lessens the weight loss by volatilization and increases the amount of char, but also raises the percentage of non-combustible components (water and carbon dioxide) at the expense of the combustible tar fraction. Extensive kinetic investigations have also indicated that the activation energy for the overall thermal decomposition is substantially lowered by the addition of sodium carbonate (Madorsky 1956). It is proposed that such salts catalyze the dehydration of cellulose by glycosidic bond scission. Other workers (Golova 1961, 1962) consider that inorganic salts promote the cleavage of C-C, rather than C-O, bonds.

The fact that flame retardants and salts alter the kinetics, as well as the products, of the pyrolysis reactions is confirmed by thermogravimetric and differential thermal analysis techniques (Tang and Neill 1964). Use of these methods shows that flame retardants generally lower the activation energy as well as the threshold temperature of pyrolysis. The resulting change in the nature of the pyrolysis reaction is apparent in the higher rate of volatilization at lower temperatures shown in Figure 1.14. The thermal analysis data also show that the combustion of untreated cellulose occurs over a narrow temperature range. In the presence of flame retardants, however, the process of weight loss is spread over a wider range at lower temperatures, and has a lower maximum rate.

The change in the rate of volatilization of cellulose, and the analysis of the products strongly suggest that flame

Figure 1.14 Rate of volatilization of cellulose samples



(A) = No treatment
(B) = 2% of $Na_2B_4O_7 \cdot 10H_2O$
(C) = 2% of $KHCO_3$
(D) = 2% of $AlCl_3 \cdot 6H_2O$
(E) = 2% of $NH_4H_2PO_4$

Source: W.K. Tang and W.K. Neill (1964) in F. Shafizadeh (1968), Advances in Carbohydrate Chemistry, 23, 469 retardants primarily promote dehydration and char formation in cellulose. However, there is a possibility that flame retardants also operate by affecting the decomposition of laevoglucosan and other degradation products in the tar.

The essential features of the cellulose molecule, to which most of its chemical properties may be related, are the primary and secondary alcohol groups and the glycosidic bonds. The alcohol groups react in the same way as in simple substances of similar chemical composition. Thus they may be readily oxidized, esterified and converted into ethers. However, the reactions are rather more complicated than with simple organic compounds because they nearly always take place under heterogeneous conditions. The heterogeneity has to be considered at two levels. In the first place solid cellulose is usually suspended in a liquid reaction medium. Secondly, the cellulose itself is heterogeneous in nature, different parts of its constituent fibrils displaying widely differing accessibilities to the same reagent. Thus any reactions on cotton cloth may provide a non-uniform product. The use of agents such as sodium hydroxide to swell the fibres allows greater penetration into the cellulose structure and therefore leads to a more uniform product. The glycosidic bonds are not easily broken, which is why cellulose is relatively stable under a wide range of conditions. They may, however, be broken by hydrolysis or alcoholysis and this has been used for detailed structure determination (Kennedy and White 1983).

The hydroxyl groups in the 2, 3 and 6 positions of the anhydroglucose unit are very reactive and provide sites at which cotton cellulose can be modified to give changes in certain properties.

Most commercial flame-retardant treatments are based on phosphorus and consequently the effect of the structure of phosphorus-based materials on their flame retardant action has been widely studied. Acidic phosphates have been shown to act by phosphorylation, presumably at the C-6 hydroxyl of the anhydroglucose unit (Hendrix et al. 1970). Consequently compounds which undergo esterification more readily are likely to be more effective flame retardants. Thus the temperature of decomposition of the flame retardants (Sanderson et al. 1970) and the ease of esterification (Hendrix 1972) or transesterification (Arney and Kuryla 1972) have been shown to be significant in determining the efficiency of flame retardants. The degree of phosphorus retention in the char has been shown to be closely related to the flame-retardant efficiencies of the phosphorus compounds (Drews 1974), suggesting perhaps a condensed phase mechanism of operation. It was also shown that the nature of the chars formed is independent of the chemical structure of the phosphorus compound.

There seems to be good evidence that acid-forming flame retardant compounds are effective in cellulose (Lyons 1970; Hindersinn 1977; Kishore and Mohandas 1982), while fully neutralized salts of non-volatile metals are not (Hindersinn 1977). The flame-retardant action is brought about by the catalytic dehydration of cellulose through a carbocation intermediate, identical to the dehydration of monohydric alcohols as shown below:

$$\begin{tikzcd} R_2CH\text{-}CH_2OH \arrow[r, "H^+", "\text{fast}"'] & R_2CH\text{-}CH_2OH_2{}^+ \arrow[d, "\text{slow}"] \\ & R_2CH\text{-}CH_2{}^+ + H_2O \arrow[d, "\text{fast}"] \\ & R_2C{=}CH_2 + H^+ \end{tikzcd}$$

This could also occur by esterification and subsequent decomposition of the ester to yield the acid

$$\begin{tikzcd} R_2CH\text{-}CH_2OH \arrow[r, "HOZ", "\text{(acid)}"'] & R_2CH\text{-}CH_2OZ + H_2O \arrow[d] \\ & R_2CH\text{-}CH_2{}^+ + OZ^- \arrow[d] \\ & R_2CH{=}CH_2 + HOZ \end{tikzcd}$$

The protonation mechanism, once initiated, would be expected to proceed rapidly due to the instability of the carbocation intermediate, and would be favoured by the presence of very strong acids. In contrast, the esterification reaction proceeds slowly and even in discrete steps, depending on the stability of the ester formed.

It has also been suggested (Schuyten et al 1954) that the active constituent of certain flame retardants is a Lewis acid, which either reacts directly with the cellulose or is produced under pyrolytic conditions. The Lewis acid is thought to work by trapping the volatile fragments as intermediates which undergo dehydration. Although feasible this suggestion must be an over simplification as it cannot be the only mechanism by which flame retardants are effective in cellulose, and does not account for the synergism observed when certain flame-retardant mixtures are used.

The decomposition of cellulose, although a complicated process producing a variety of products, can, by the use of flame retardants, be made to occur in such a way that non-flammable carbonaceous char is the primary product. Flame retardants are seen to have certain effects on the mechanism of decomposition of cellulose such as lowering the temperature of decomposition and thus promoting the dehydration mechanism. Favouring C-C as opposed to glycosidic C-O bond cleavage, thus reducing laevoglucosan formation, is also effective. The promotion of the dehydration mechanism at the expense of the depolymerization, tar-forming route is fundamental to the reduction of the flammability of cellulose.

1.4 Flame retardants for organic polymers

1.4.1 Historical introduction

Ever since the discovery of fire man has tended to regard it as an uncontrollable process against which he was helpless.

Throughout history, however, attempts have been made to control the force of fire. Fire's greatest enemy, water, was utilized soon after the discovery of fire. Ancient Egypt and the "cohortes vigilum" in Rome during Caesar's period both had organised fire fighters, which were the forerunners of our modern day fire-fighting service.

Preventive fire protection has also been practised. Man's concern over hazards associated with fire can be traced back to the time of alchemy and the Roman Empire. In 360 BC in the annals of Claudius a treatise on fortifications recommended that timbers should be protected against fire by painting with vinegar. In the battle for the town of Piraeus in 83 BC, wooden towers were impregnated with alum to prevent them being set alight and were successfully used without catching fire. In AD 77 Pliny the Elder described asbestos table cloths which could be cleaned by heating to red heat.

In 1638, Nicolas Sabatini suggested that clay and gypsum could be used as flame retardants for theatre scenery made of painted canvas. The first patent (No. 551), describing the treatment of textiles and paper with fire retardants was published in England in 1735 by Jonathan (Obadiah) Wilde. The mixture used consisted of alum, borax ($Na_2O.2B_2O_3.10H_2O$), vitriol (probably impure iron sulphate), or copperas ($FeSO_4.7H_2O$). In 1783, the Montgolfier brothers used a flame-retardant coating of alum on the envelope of their hot-air balloon.

The use of ammonium phosphate, still an important ingredient in several flame-retardant compositions today, was first suggested by Arfird in 1786. Shortly afterwards in France, King Louis XVIII commissioned Gay-Lussac to study means of reducing the flammability of fabrics used in theatres, as fires were of major concern to society at that time. In 1820 Gay-Lussac found that mixtures of ammonium phosphate, ammonium chloride and borax were very effective when applied to linen and jute (Gay-Lussac 1821).

In 1859, Versmann and Oppenheim studied some forty potential flame-retardant compounds and found that only ammonium phosphate, sodium ammonium phosphate, ammonium sulfate, sodium tungstate, and a mixture of ammonium phosphate and ammonium chloride were effective on cellulose (Versmann 1860; Schuyten 1954). Following this work, they also developed a process for flameproofing cellulosic fabric by the precipitation of stannic oxide on the fibres. This concept was originally patented by Versmann and Oppenheim (Versmann 1859; Anon 1925).

By this time, many inorganic salts had already been recognized to be useful flame-retardant materials. The coming of the twentieth century brought with it man's increasing concern with flammability and his attempt to impart flame retardancy not only to cotton fabric, wood and paper but also to plastics. The studies of William Henry Perkin at the turn of the century have become a milestone in the more recent history of man's desire for new methods of flameproofing and in his understanding of the underlying mechanisms of flame retardancy. His involvement in this applied work has a story behind it. In 1902 Messrs. Whipp, Brothers and Tod, the largest manufacturers of cotton flannelette in Manchester, talked him into conducting flame-retardant research, because they had become alarmed over the frequent fatalities that resulted from accidental burns to children dressed in flannelette garments. It was felt that, if something was not done, the sale of this material might be prohibited. Flannelette was popular in those days because it was cheap and shrink-resistant. Large quantities were used in children's clothing, especially in the homes of low income groups. The fabric was highly flammable on account of its nap. Perkin reasoned that a successful process would not damage the feel or durability of the cloth, cause it to become damp or make it dusty. Furthermore the colours and the design woven into the cloth or dyed or printed upon it should not be affected. Nothing of a poisonous nature (such as arsenic, antimony or lead) or anything deleterious to the skin, could be used. The fire-proofing also had to be permanent; i.e., it should not be removed even if a garment were washed fifty times or more. Finally, in order to have a wide application, the process had to be cheap. It is amazing how accurately the above requirements hold today.

Perkin's patented treatment (NON-FLAM) involved the precipitation of stannic oxide on the flannelette, although some 10,000 burning tests were needed before a satisfactory process was obtained. The presence of tin in the pores of the fabric also gave the cloth a softer and fuller feel, with increased strength apart from its flame-retardant properties. In 1912 NON-FLAM was awarded a £50 prize offered by the Daily Express for the safest cotton material available. Though Perkin's treatment had an obvious advantage over previous flame retardants cost prevented it from being widely accepted. Although the treatment was not as durable as Perkin had claimed and the material's flammability increased on exposure to light, Perkin's work did produce the first durable flame-retardant finish for cotton textiles.

In present society fire catastrophies are not a common occurrence due to the technological advances in fire fighting equipment and legislation to reduce the risk of fire. As technology and our standard of living prosper, new potential hazards arise. The use of high-rise buildings for accommodating the populus creates new and potentially lethal venues for fire catastrophes. The use of fire-resistant materials, fire alarms and sprinkler systems all help to reduce the risk of fire.

The use of new synthetic building materials, many of which are polymeric in nature and therefore potentially a fire hazard, have given rise to an industry associated with the conferment of some degree of flame retardance on new and existing materials.

1.4.2 Changing patterns of consumption of flame retardants

Figure 1.15 shows the growth in the world consumption of synthetic polymers from 1935 to the present time.

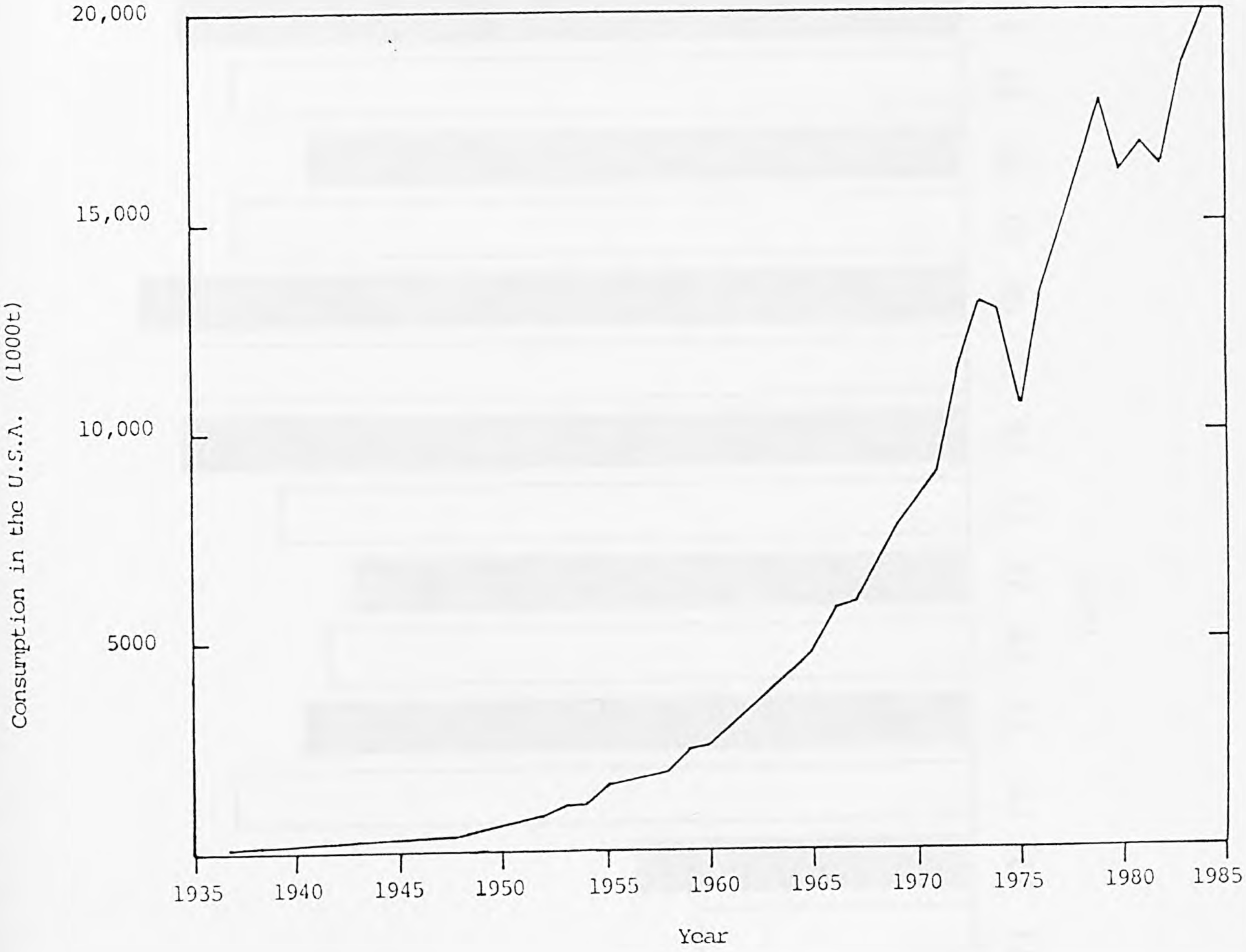
Fire performance regulations demand the frequent addition of flame retardants to polymeric materials due to their applications in house furniture and fittings, transportation and electrical appliances.

It is difficult to quote exact figures for the consumption of fire retardants since they are not listed separately in official statistics and many other sources are incomplete. However the consumption figures for flame retardants used in polymers provide a relatively accurate indication of trends. Figures 1.16 and 1.17 show the total consumption of flame retardants in the USA between 1968 and 1985.

It can clearly be seen in Figure 1.16 that there was a rather sudden increase in flame retardant consumption in 1973 to over 190,000t, due presumably to the expansion of the plastics industry which is based on petroleum-derived oil based products. Current production levels seem to have been set by this figure.

In 1974 consumption dropped and continued to do so until 1976 as a result of the first oil crisis. Government legislation in the form of the introduction of TSCA (Toxic Substances Control Act) and the removal of two major products, Dechlorane and Tris[tris (2,3 - dibromopropyl)

Figure 1.15 Total consumption of synthetic polymers in USA, 1935 - 1985



Source: H. Teitge, Kunststoffe, 70 (1980), 5, 299.

Figure 1.16 Total consumption of flame retardants for plastics in the USA, 1968 - 1985

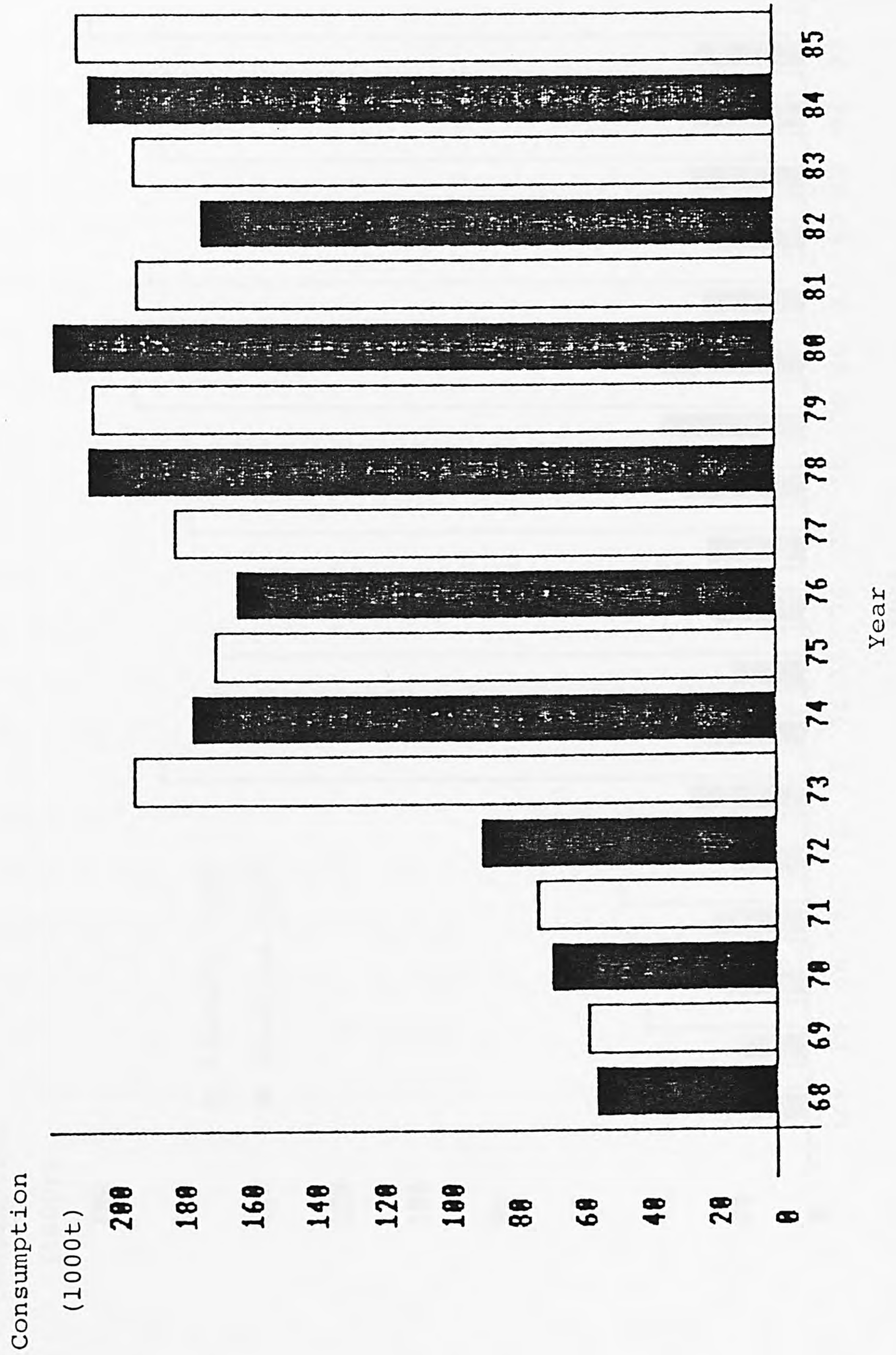
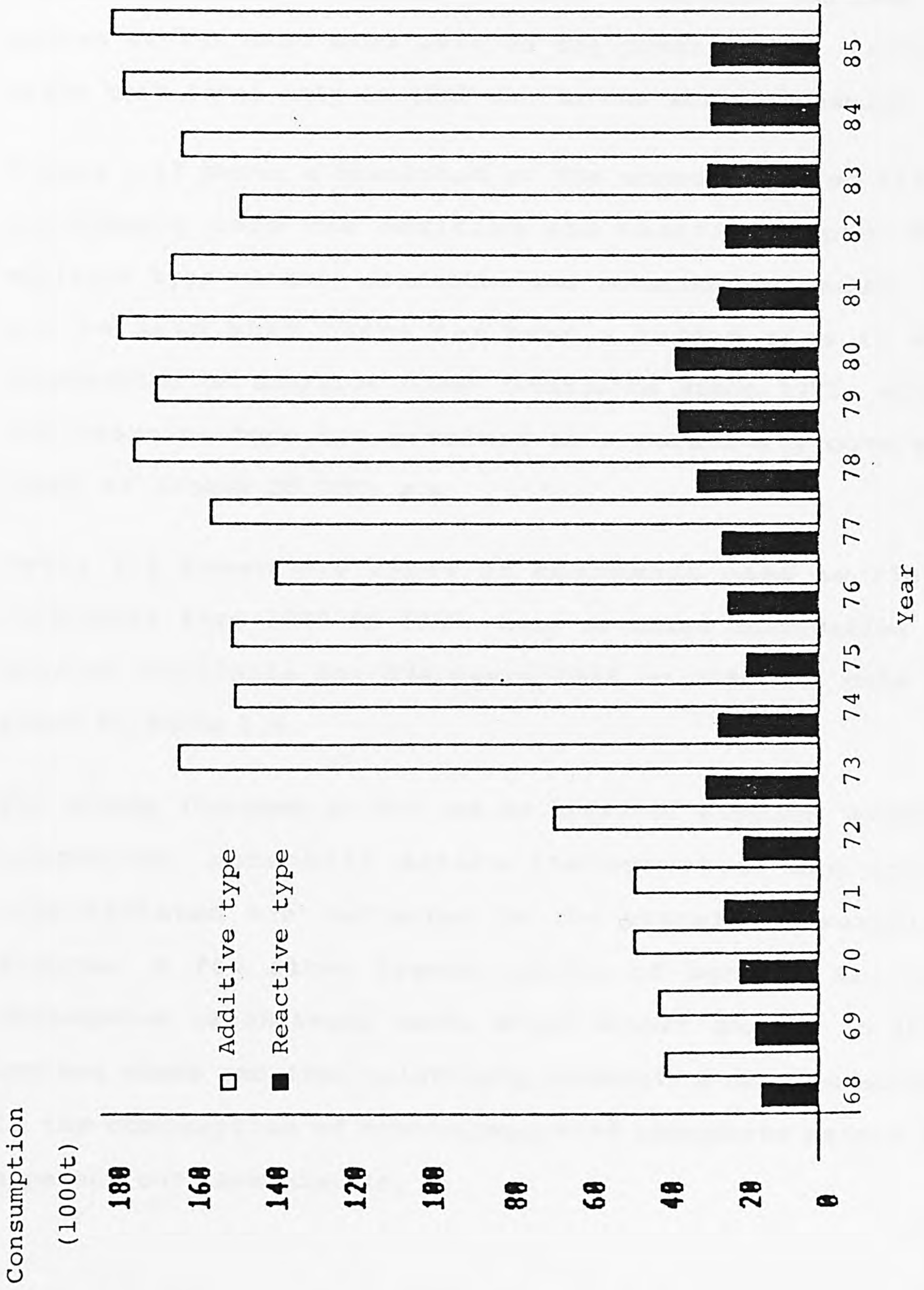


Figure 1.17 Consumption of additive and reactive flame retardants for plastics in the USA, 1968 - 1985



phosphate] from the market due to controversy, caused a further fall in consumption in 1977.

Despite the more stringent legislation constantly being introduced, the consumption of flame retardants has been in excess of 180,000t from 1977 to the present day, falling below this level only in 1982 due to the world recession.

Figure 1.17 shows a breakdown of the consumption of flame retardants into the additive and reactive types. The additive type clearly dominates the consumption market. It can be seen that there has been a sudden rise in the consumption of additive flame retardants since 1973, while the reactive type has remained at a relatively constant level of around 25,000t p.a.

Table 1.8 shows the types of compounds used as flame retardants from 1960 to 1968. More detailed information is however available for the years 1968 to 1985 and this is shown in Table 1.9.

The steady increase in the use of hydrated alumina, bromine compounds, phosphate esters (halogenated) and epoxy intermediates are reflected in the overall consumption figures. A few other trends worthy of mention are the consumption of antimony oxide which almost doubled in 1976 and has since remained relatively constant. A slow reduction in the consumption of non-halogenated phosphate esters is apparent but less visible.

Table 1.8 Consumption of flame retardants for plastics in the USA (1960 - 1968)

	Consumption (1000t)				
Type of flame retardant	1960	1963	1964	1965	1968
Additive Systems					
Antimony oxide	4.5	6.8	6.8	9.1	6.4
Chloroparaffins and chlorinated cycloaliphatics	2.7	3.6	3.1	3.1	4.5
Phosphate esters	11.8	14.0	15.4	17.3	21.4
Others[a]	0.5	0.9	0.9	0.9	2.3
TOTAL	19.5	25.3	26.8	30.4	34.6
Reactive systems					
Expoxies, Polyesters, Styrene derivatives	2.7	3.6	5.0	6.4	na
Polyurethanes	na	0.5	0.9	1.4	na
Others	3.6	4.5	5.9	7.7	na
TOTAL	6.3	8.6	11.8	15.5	na
Grand Total	25.8	33.9	38.6	45.9	-

a = includes molybdenum, zinc and other metal oxides

Source: Modern Plastics 9, 99 (1965)

Table 1.9 Consumption of flame retardants for plastics in the USA, 1968 - 1985

Type	Consumption (1000t)																	
	1968	1969	1970	1971	1972	1973	1974	1975	1976	1977	1978	1979	1980	1981	1982	1983	1984	1985
Additive Systems																		
Alumina hydrates	na	na	na	na	na	72	50	60	64	80	90	75	80	80	76	84	92	94
Antimony oxides	6.4	7.3	6.5	7	8	8.5	11	8.5	14	13	15	15	16	15	13	14	15	16
Boron compounds	0.7	0.7	1	1	2	2	4	4	5	5	5	5	5	3	4	5	5	5
Bromine compounds	na	na	na	na	3	5	6	9	10	8	13	15	17	14	11	12	15	17
Chlorinated paraffins and cycloaliphatics[a]	4.5	6.4	8	10	19	27	31	30	15	16	17	19	20	16	14	14	15	13
Phosphate esters:																		
Nonhalogenated	21.4	23	26	22.5	24.5	31	10	19	16	17	18	19	19	18	15	17	17	17
Halogenated	3.9	4.3	2.5	3	7	11	29.5	13.5	8	9	10	12	13	11	9	10	11	11
Others[b]	2.3	2.6	3	4	4.5	7	7	5	6	7	7	9	9	8	6	7	8	8
Total	39.2	40.4	47	47.5	68	163	148.5	149	138	155	175	169	179	165	148	163	178	181

Table 1.9

Type	Consumption (1000t)																	
	1968	1969	1970	1971	1972	1973	1974	1975	1976	1977	1978	1979	1980	1981	1982	1983	1984	1985
<u>Reactive systems</u>																		
Epoxy intermediates	0.7	0.8	2	1	2.5	3.5	4.5	3	5	5	5	5	5	5	8	9	11	10
Polycarbonate intermediates	na	na	na	na	0.5	1	1	0.5	1	1	2	2	2	2	2	3	3	3
Polyester intermediates	7.8	8.6	10.5	12	5	6.5	7	5	6	7	7	8	8	5	5	6	5	6
Urethane intermediates	na	na	na	na	na	1	0.5	0.5	1	1	2	2	2	1	1	1	1	1
Flexible foam	3.9	4.3	5	7	8	11	2	0.5	1	1	3	4	4					
Rigid foam						2	7	7	6	7	9	11	12	9	5	6	4	4
Others	2.0	2.3	2.5	3	3.5	4	4	2.5	3	3	3	4	4	4	3	4	4	4
Total	14.4	16	20	24	19.5	29	26	19	23	25	31	36	37	26	24	29	28	28
Grand Total	53.6	56.4	67	71.5	87.5	192	174.5	168	161	180	206	205	216	191	172	192	206	209

na = not available

Source: 1968-69: Modern Plastics 46, 95 (1969)
1970-80: Flame Retardants. Mod. Plast. Intern. 1 (1971) 9, p. 66; 2 (1972) 9, p. 72; 3 (1973) 9, p. 53; 4 (1974) 9, p. 52; 5 (1975) 11, p. 66; 6 (1976) 9, p. 42; 7 (1977) 9, p. 46; 8 (1978) 9, p. 54; 10 (1980) 9, p. 42
1981: Mod. Plast. Intern. 9, 58 (1982)
1982-83: Modern Plastics 9, 55 (1983)
1984-85: Modern Plastics 9, 65 (1985)

The consumption of chlorinated paraffins and cycloaliphatics shows clearly the effect of the oil crisis in 1974. Consumption increased considerably each year up to 1975 but suddenly dropped to half the 1975 level in 1976.

Little information is available in the literature regarding the UK or European consumption of flame retardants. Manufacturing companies in the UK are, on the whole, unwilling to provide any type of statistical data.

Tables 1.10 and 1.11 show the consumption of flame retardants in the UK and Western Europe from 1983 to 1985. They also give speculative consumptions obtained from a market research report which provided the only information and was obtained by kind donation of Frost and Sullivan Ltd.

It is shown in Table 1.12 that in 1985 the UK market accounted for approximately 30 percent of the total Western European consumption fo flame retardants. In this year, the individual UK flame retardant additives are seen to vary between 18 and 30 percent of the total European market. Boron compounds are however a notable exception, the UK accounting for 53 percent of the total European consumption. The same is true of halogen-free phosphate esters, where 40 percent of total consumption may be attributable to the UK market.

The total UK market (both additive and reactive flame retardants) is predicted to grow by 7.6 percent over the next three years and by 14.5 percent over the following five

Table 1.10 Consumption of flame retardants in the UK (1983 - 1990)

	Consumption (t)				
Type of flame retardant	1983	1984	1985	1988*	1990*
Additive					
Aluminium oxide hydrates	5500	5700	6060	6720	7400
Antimony oxides	2050	2100	2170	2380	2520
Boron compounds	1450	1500	1550	1800	2000
Bromine compounds	1050	1110	1180	1420	1580
Chloroparaffins	600	610	610	620	630
Phosphate esters,					
halogen-free	9000	9130	9210	9520	9700
halogenated	1270	1230	1200	1160	1100
Others	300	350	350	400	500
TOTAL	21220	21730	22330	24020	25430
Reactive					
Halogenated Acids	630	620	610	610	630
Phosphorus polyols	460	470	500	560	630
Brominated bisphenol A and others	1960	2080	2190	2390	2670
TOTAL	3050	3170	3300	3560	3930
GRAND TOTAL	24270	24900	25630	27580	29360

* Estimated values from market research by Frost and Sullivan Ltd.

Reproduction or use of data contained in this table is strictly prohibited without written permission of the authors Frost and Sullivan Ltd.

Table 1.11 Consumption of flame retardants in Western Europe[a] (1983- 1990)

Type of flame retardant	Consumption (1000t)				
	1983	1984	1985	1988*	1990*
Aluminium oxide hydrates	18.6	19.3	20.4	22.5	24.5
Antimony oxides	9.8	10.2	10.6	11.8	12.7
Boron compounds	2.7	2.8	2.9	3.4	3.8
Bromine compounds	5.3	5.5	5.8	7.0	7.7
Chloroparaffins	2.5	2.6	2.6	2.6	2.7
Phosphate esters,					
halogen-free	22.6	22.8	23.0	23.7	24.2
halogenated	6.9	6.8	6.7	6.6	6.1
Others	0.02	0.02	0.02	0.03	0.03
TOTAL	68.42	70.02	72.02	77.63	81.73

[a] Included are Benelux, France, Italy, United Kingdom and West Germany

* Estimated from market research by Frost and Sullivan Ltd.

Reproduction or use of data contained in this table is strictly prohibited without the written permission of the authors Frost and Sullivan Ltd.

Table 1.12 The UK consumption of flame retardants as a percentage of the Western European* markets for 1985

Type of flame retardant	Percentage
Aluminium oxide hydrates	30.0
Antimony oxides	20.5
Boron compounds	53.4
Bromine compounds	20.3
Chloroparaffins	23.5
Phosphate esters:	
halogen-free	40.0
halogenated	18.0

* Included are Benelux, France, Italy, United Kingdom and West Germany.

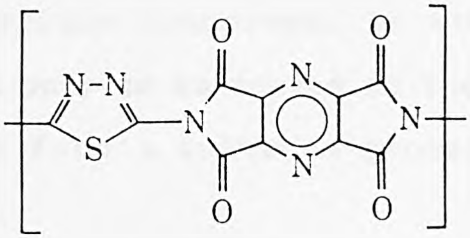
years. With this encouraging growth, the UK will maintain a 35 percent hold of the total European market.

1.4.3 Modes of action

1.4.3.1 General classification

Materials which require to be made flame-retardant are almost invariably polymeric, either natural or synthetic. Some organic polymers are however inherently more combustion resistant than others. Thus, polytetrafluoroethylene is ignited only with difficulty, whereas nitrocellulose burns explosively.

The simplest method, in principle, of reducing fire hazards is to use polymers specially designed to resist combustion (Cassidy 1980; Critchley 1983). There are several ways of synthesizing such materials. For example, compounds containing a carbon backbone can be "stiffened" by incorporating ring systems as is the case with chain polymers such as polyxylylene. Alternatively the H atoms in C-H bonds in the macromolecule can be partially or wholly replaced by atoms such as fluorine which have inherent flame-retardant properties. A further method is to use inorganic polymers with chains consisting of inorganic components and organic side groups, such as silicones or polyphosphazenes. An example of such a compound is an aromatic polyimide that does not contain any hydrogen atoms:



Compounds of this kind have excellent fire resistance but are expensive and therefore limited to speciality uses such as aerospace applications.

Most common polymeric materials in use are, however, inherently flammable and it is necessary to introduce additives to retard or inhibit their combustion. Flame-retardant additives fall into two broad classes viz. additive and reactive types. Additive flame retardants are compounds containing elements with known flame-retardant properties, such as boron, bromine, chlorine, nitrogen, phosphorus, sulphur and certain metals which are intimately mixed with the polymer concerned. Reactive flame retardants utilize the inherent flame retardance of these same elements but become an integral part of the polymer since they are present in the monomers from which the polymer is formed. An example is the use of phosphorus-containing polyols in the manufacture of polyurethanes. The majority of flame retardants used fall into one of the two main types but some are in effect intermediate between the two, as they are incorporated after the polymerization process via chemical reactions.

Additive flame retardants, which are most widely used in practice to inhibit the combustion of the commoner synthetic organic polymers, are generally incorporated throughout the polymeric materials concerned. In some cases the flame retardants need only to be coated on the external surface of the polymer to form a suitable protective barrier as is sometimes done, for example, in the case of fibres and films. Although this is frequently carried out by mechanical means, such as milling, various types of radiation can be used for the incorporation of flame retardants of this type.

This is sometimes called polymer grafting and is particularly useful for textiles (Liepins, Surles et al. 1978; Liepins, Stannett et al. 1978; Harris et al. 1980). Radiation-processing is claimed to be more economical than conventional methods of incorporation; its use reduces flammability and toxicological hazards as no solvents are required in processing. Few commercial methods based on radiation processing are, however, yet in use.

From a manufacturing point of view, the introduction of additive flame retardants undoubtedly constitutes the simplest way of making an organic polymer less flammable, because the additives can be incorporated during the final stages of production of the finished material. Some of the otherwise desirable additive flame retardants have, however, poor compatibility with the polymers into which they need to be incorporated. Furthermore, many of these compounds are appreciably volatile or subject to hydrolysis, so that their flame-retardant action may decrease with time.

Reactive flame retardants, however, need to be incorporated at a much earlier stage of manufacture but, once introduced, become a permanent part of the polymeric structure.

Both reactive and additive flame retardants often have deleterious effects on the properties of the polymers into which they are incorporated. Thus they may change the viscosity, flexibility, density, and may also increase the susceptibility of the polymers to photochemical and thermal degradation. Sometimes, too, they have deleterious effects on electrical properties, increasing the electrical conductivity to unacceptable levels. In view of the nature of some of the elements most commonly used to confer flame retardance, the combustion of polymers containing them often leads to the formation of highly toxic gaseous products as well as copious quantities of smoke. Thus, however effective flame-retardant additives may be in reducing the flammability of polymers, they are clearly not without certain disadvantages.

Turning now to the mechanisms by which flame retardants act, both additive and reactive agents may affect the various stages of the burning process in a number of different ways:

a) **Gaseous dilution modes.** Generation of large volumes of non-combustible gases may change the composition of the gaseous fuel-oxidant mixture so that it no longer lies in the flammability range.

A typical example of an additive which may act in this way is ammonium carbonate, which decomposes to form ammonia, water and carbon dioxide.

b) **Thermal modes.** Two principles are involved here. One employs the fact that certain compounds, particularly inorganic salts, decompose endothermically resulting in the removal of heat from the system as a whole. Secondly, inert "fillers", such as hydrated divided alumina act as heat sinks and thus prevent the polymer from reaching the temperature at which decomposition will occur. The flame-retardant effectiveness of fillers depends on both their heat capacity and thermal conductivity and their effects are increased considerably if they decompose endothermically.

c) **Coating modes.** As early as 1821, Gay-Lussac suggested that flame retardants work by forming a layer of fusible material on the surface of the polymer. When this melts a coating is formed which excludes the oxygen necessary for combustion to take place.

Certain boron-containing flame retardants are known to function in this way. Intumescent coatings also work in this manner but they will be dealt with in the Section 1.5.2.2.

d) **Flame inhibition modes.** The most widely accepted mechanism involves the release into the gas phase of volatile species which then inhibit the flame reactions. The precise mechanism of action of flame-speed inhibitors on premixed flames are not fully understood but such compounds must clearly interfere somehow with chain propogation reactions in the flame front. For more detail see Section 1.2.3.

1.4.3.2 Phosphorus compounds

The use of phosphorus compounds as flame retardants dates back to the time of Gay-Lussac's identification (1820) of ammonium orthophosphate as an effective agent for flame retarding hemp or linen cloth for use in theatre fabrics. Early in this century, organic derivatives of phosphorus were also found to be effective flame retardants. Simple esters of phosphoric acid were the first of these to be studied, although during the last thirty years many more sophisticated phosphorus compounds have been synthesized and evaluated as flame retardants. A variety of these are in commercial use today. They vary from compounds in the +5 oxidation state to those in the -3 state (Table 1.13).

Both additive and reactive phosphorus-based flame retardants are commercially available. One of the main applications of phosphorus additives is as plasticisers for poly (vinyl chloride). A plasticised polymer containing such additives is less flammable than when other plasticisers such as phthalates are used but is nevertheless more flammable than the unplasticised polymer.

The most extensively employed reactive flame retardants are phosphorus-containing polyols used in the manufacture of polyurethane foams. Other reactive flame retardants include vinyl and allyl phosphates (used as co-monomers with vinyl alcohol), hydroxy alkyl phosphates and phosphonates (used in condensation polymerization to form polyesters), and

Table 1.13 The variation in oxidation states of different phosphorus containing flame retardant compounds

Structure	Class	Oxidation State
$(RO)_3PO$	Phosphates	+5
$(RO)_3P$, $(RO)_2R'PO$	Phosphites and Phosphonates	+3
$(RO)R'_2PO$	Phosphinates	+1
R_3PO	Phosphine oxides	-1
R_3P or R_4P	Phosphines and phosphonium salts	-3

phosphines (used to add directly to unsaturated polymers) (Boyer and Vajda 1964; Jacques 1967; Sander and Steininger 1967a,b; 1968 a,b,c; Lyons 1970 a,b; Yokoyama 1971; Kuryla 1973; Inagaki, Tomiha and Katsuura 1974; Inagaki, Goto and Katsuura 1975; Weil 1978).

Some typical phosphorus-based flame retardants used are given in Table 1.14. This list is by no means exhaustive but emphasises that phosphorus compounds are effective flame retardants in a wide variety of polymeric systems.

The effectiveness of phosphorus as a flame retardant depends on the form in which it is present in the additive and the elements may act both in the condensed phase and in the gas phase. Under combustion conditions, phosphorus oxides, phosphoric acids may be formed (Chamberlain 1978). In the condensed phase these are known to accelerate polymer chain stripping and the consequent loss of substituent groups. Experimentally it has been shown that in the presence of additives volatile products are formed at lower temperatures. In such cases the phosphorus either produces inherently less flammable volatile products or results in a heavy vapour which "blankets" the flame and thus excludes oxygen (Benbow and Cullis 1972, 1973).

With highly hydroxylated polymers, such as cellulose, phosphorus-based flame retardants act largely, if not exclusively, in the condensed phase (Cullis and Hirschler 1981). The effectiveness of phosphorus compounds as flame

Table 1.14 Some phosphorus compounds used as flame-retardants for cellulose

Inorganic (additive)

Ammonium phosphate

Organic (additive)

Triethyl and trioctyl phosphates

Triphenyl phosphate

Tricresyl and related phosphates

Tris(2,3-dibromopropyl)phosphate

Organic (reactive)

Tetrakis hydroxymethyl phosphonium salts (THPC, THPOH)

N-hydroxymethyl-3-(dimethylphosphonopropionamide)(Pyrovatex CP)

Oligomeric vinyl phosphonates (Fyrol 76)

Source: Modified from C.F. Cullis and M.M. Hirschler.

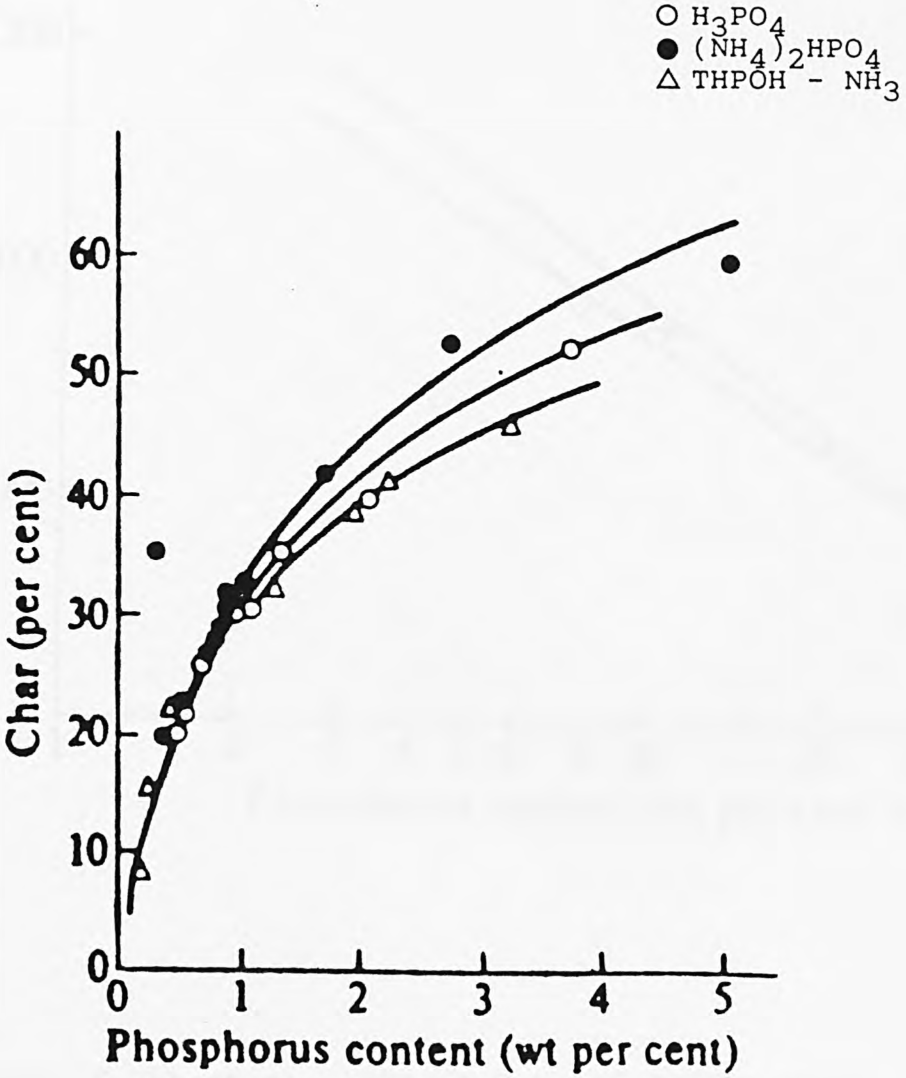
In: The Combustion of Organic Polymers, 1981, p. 262

retardants for cellulosic polymers is due to the formation of acidic species which cause dehydration of the cellulose. Acidic flame retardants are very effective, whilst neutral compounds are found to be ineffective (Hindersinn and Witschar 1978). Thus the acidic species mentioned earlier formed by combustion of phosphorus alter the mechanism of breakdown of cellulose in the condensed phase, so that the major products are char and water rather than laevoglucosan and other volatile flammable compounds (Lyons 1970).

Experimental evidence (Yeh and Barker 1971; Yeh, Birky and Huggett 1973) as seen in Figure 1.18 shows that the quantity of char formed, gives and indication of the effectiveness of phosphorus as a flame retardant. Figures 1.19 and 1.20 show that the addition of as little as one percent of phosphorus to cellulose causes a several-fold increase in char yield, which is accompanied by a decrease in the heat of combustion and in the rate of heat release (Birky and Yeh 1973).

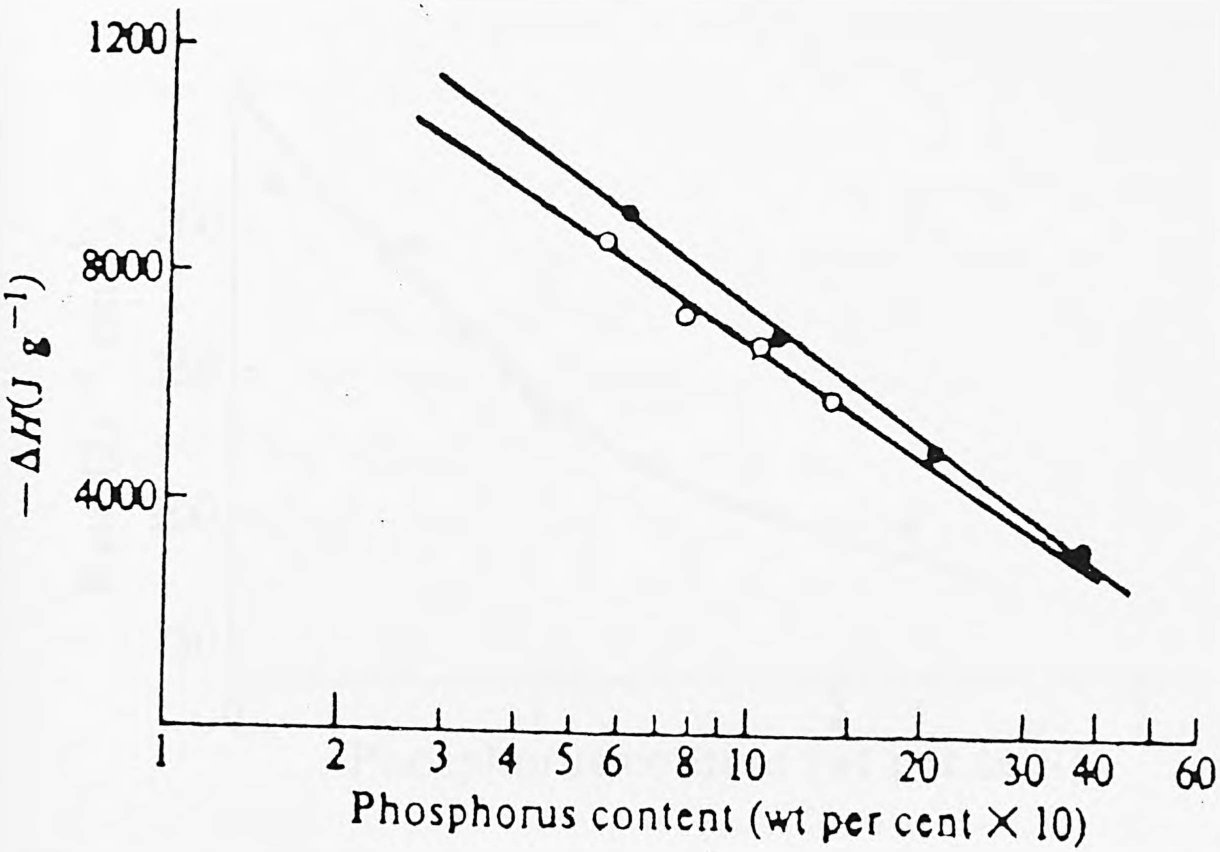
The flame-retardant efficiency of phosphorus compounds acting in the condensed phase also depends considerably on their thermal stability (Hendrix, Anderson et al. 1970; Hendrix, Bostic et al. 1970). Volatile thermally stable phosphate esters tend to be lost before they can cause dehydration. In such cases there is little or no increase in char and any inhibiting effect observed must be due to interference with the flame reactions (Lask and Wagner 1962).

Figure 1.18 Effect of phosphorus compounds on char yields from cellulose



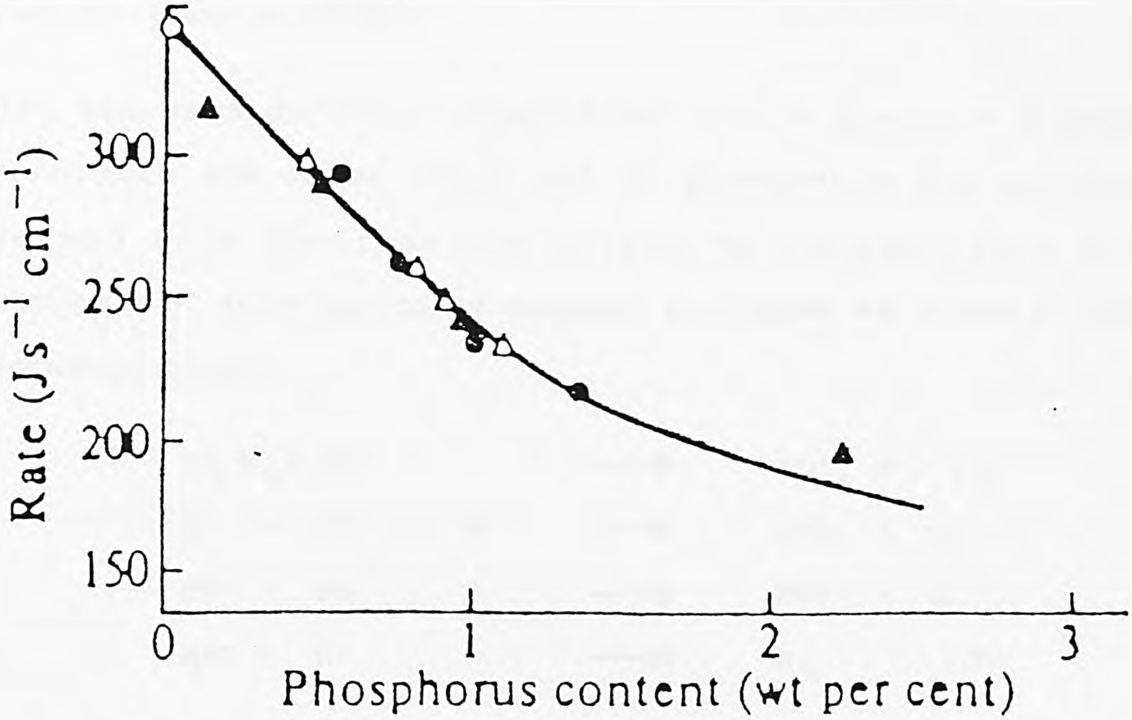
Source: After Yeh and Barker 1971; Yeh, Birky and Huggett 1973.

Figure 1.19 Variation of the heat of combustion of cotton with the amount of phosphoric acid



Source: ○ Yeh et al. 1973; ● Yeh and Barker 1971.

Figure 1.20 Effect of phosphorus compounds on the rate of heat release from cotton during combustion



Source: After Yeh et al. 1973.

○ no additive
● H_3PO_4
△ $(NH_4)_2HPO_4$
▲ THPOH-NH_3

Volatile phosphorus compounds are very efficient gas phase inhibitors in premixed flames (Palmer and Seery 1960) and certain phosphorus-containing flame retardants act in the gas phase, particularly during the combustion of hydrocarbon polymers (Lask and Wagner, 1963; Jacques 1967). Triphenyl phosphine oxide has been shown to inhibit rich methane-oxygen and hydrogen-oxygen flames by producing the $PO^{\cdot}$ radical (Hastie 1973c).

HPO has been directly identified in low pressure flames (Fenimore and Jones 1964) and is presumably the species formed from the reaction of the $PO^{\cdot}$ radical with the reactive $H^{\cdot}$ atom typically present in flames as shown in the sequence below:

$$
\begin{array}{lcl}
(C_6H_5)_3PO & \longrightarrow & PO^{\cdot},\ P^{\cdot},\ P_2 \\
H^{\cdot} + PO^{\cdot} + M & \longrightarrow & HPO + M \\
OH^{\cdot} + PO^{\cdot} & \longrightarrow & HPO + O^{\cdot\cdot} \\
HPO + H^{\cdot} & \longrightarrow & H_2 + PO^{\cdot}
\end{array}
$$

When triphenyl phosphine oxide is used in conjucntion with a polyester, it can be shown by an examination of the rate of vaporization of the additive, that inhibition occurs in the gas phase (Bostic 1972; Hastie and Blue 1973).

The use of phosphorus in different oxidation states in polyethylene results in an identical increase in the LOI value, suggesting that the same phsophorus species is produced in each case (Fenimore and Martin 1966b). With poly(ethylene terephthalate) fibres, the LOI value increases with phosphorus content for a variety of phosphorus-containing additives, and the same total content of phosphorus gives the same flame-retardant effect (Lawton and Setzer 1975).

In summary, then, phosphorus-based flame retardants seem to act largely, if not exclusively, in the condensed phase. For highly hydroxylated polymers, such as epoxy resins. the condensed phase mechanism results in the formation of carbonaceous char rather than flammable volatile decomposition products. In hydrocarbon polymers, phosphorus-based flame retardants tend to act primarily in the gas phase either by a chemical mechanism, to produce free radicals which interfere with the radical reactions responsible for flame propagation or possibly by physical mechanisms involving "blanketing" of the flame.

1.4.3.3 Bromine Compounds

Bromine is the most effective of the halogens in its flame retardant action. However until recently bromine compounds, due to their high cost and susceptibility to photochemical degradation, were less widely used than chloride compounds.

Bromine flame retardant consumption between 1980 - 1985 for plastics in the USA rose to 17 000t per annum overtaking that of chlorine which maintained an average consumption of 14 000t per annum over the same period (Modern Plastics, 1980). It is interesting to compare the changing trend in the consumption of the two halogens by examining the figures for 1977 (Modern Plastics, 1985). In that year bromine consumption was half that of chlorine, 8000 and 16 000t per annum respectively. More complete consumption figures for the respective halogen compounds are shown in Table 1.9 in Section 1.4.2.

The increased use of bromine at the expense of chlorine is partly due to the fact that much lower levels of the heavier halogen are sufficient to produce a given flame-retardant effect. The relative halogen requirements for an equivalent degree of flame retardance for various polymers are given in Table 1.15 which shows clearly that in each case less bromine is required to provide a given level of flame retardance. Indeed with polymers such as ABS and styrene, the amount of bromine required is minimal compared with that of chlorine. The use of smaller quantities of flame

Table 1.15 Relative halogen requirements for equivalent degree of flame retardancy of various polymers

Polymer	Chlorine (wt %)	Bromine (wt %)
ABS	23	3
Acrylates	20	16
Epoxies	26-30	13-15
Polyacrylonitrile	10-15	10-12
Polyolefins	40	20
Polyurethane	18-20	12-14
Unsaturated polyester	25	12-15
Polystyrene	10-15	4-5

Source: J.W. Lyons, "The chemistry and uses of fire retardants", Interscience Division of John Wiley and Sons Inc, New York (1970).

retardant is not only cost-effective but also minimizes adverse changes in the physical and mechanical properties of the polymers concerned.

Although both additive and reactive brominated flame retardants are commonly used, the additive type finds greater application due to ease of incorporation. Most bromine flame retardants tend to be per-brominated and therefore generally contain a very high percentage of the halogen. Table 1.16 lists a range of additive and reactive type flame retardants and shows that the percentage weight of bromine in the compounds listed is commonly between 55 and 80 wt percent. Aliphatic bromine compounds are in general less thermally stable than aromatic compounds.

Essentially two modes of action have been proposed for the flame-retardant action of bromine: it can act either in the condensed phase or in the gas phase.

In the condensed phase, one probable mode of action is the release of bromine atoms which remove hydrogen from the polymer chain, forming hydrogen bromide and polymer radicals. These radicals undergo either chain scission or cross-linking or react with more bromine to form a brominated polymer. Studies of the combustion of brominated polystyrenes (Volans 1967) and polyurethanes (Papa and Proops 1973) suggest that the elimination of hydrogen bromide is an important initial step and that this compound alters the mechanism of polymer decomposition in the

Table 1.16 A list of additive and reactive type bromine-containing flame retardants and their uses

Bromine Compounds	Bromine (wt %)	Polymers for which used
Additive Type		
Decabromodiphenyl oxide	83.0	Polycarbonates, polyester resins, polyolefins, ABS, PVC, polyamides
Hexabromocyclododecane	74.7	Polystyrene, polyoelfins
2,3,4,5,6-pentabromoethylbenzene	80.0	Epoxy resins, ABS, urethane foams
1,2-Bis(2,4,6-tribromophenoxy)ethane	70.0	ABS, polystyrene, polyesters
Reactive Type		
Tetrabromobisphenol-A*	58.8	Epoxy resins
Tetrabromophthalic anhydride	66.8	Polyesters
Vinyl bromide	74.7	Acrylic fibres
2,3-Dibromopropyl acrylate	58.8	Polyesters, acrylic fibres
2,3-Dibromopropyl methacrylate	55.9	Polyesters, acrylic fibres
2,4,6-Tribromophenol	72.4	Epoxy resins

* The major reactive flame retardant produced in 1980.

Source: R.E. Kirk, D.F. Othmer, Vol. 10 (1980) Encyclopedia of Chemical Technology, p. 382-386.
D.P. Miller (1980), Plastics Engineering, 29, 1972

condensed phase.

Other bromine compounds, such as decabromobiphenyl, do not produce hydrogen bromide on decomposition. Nevertheless these organic bromine compounds are still highly effective in the condensed phase. Thermogravimetric studies of decabromobiphenyl incorporated into ABS copolymer show clearly that the additive can considerably change the decomposition behaviour of the polymer (Cullis and Hirschler 1983). This suggests that it is the organic bromine compound itself which catalyses polymer decomposition by a mechanism similar to that observed for compounds which do produce hydrogen bromide.

The most widely accepted mechanism of flame retardance by bromine compounds in the gas phase involves the release of volatile species which then inhibit the flame reactions (Rosser, Wise and Miller 1959; Einhorn 1971; Fristrom and Sawyer 1971; Fristrom 1972; Hastie 1973; Petrella 1979). The precise mechanisms of action of flame-speed inhibitors are not fully understood but such compounds must clearly interfere with chain-propagation reactions in the flame. For example, hydrogen bromide, the product most likely to be formed from brominated flame retardants, reacts with radicals responsible for the propagation of combustion, e.g.

$$H^{\cdot} + HBr \longrightarrow H_2 + Br^{\cdot}$$

$$OH^{\cdot} + HBr \longrightarrow H_2O + Br^{\cdot}$$

Highly reactive species are thus replaced by the relatively unreactive bromine atom, which abstracts hydrogen from the fuel (RH) to regenerate hydrogen bromide:

$$RH + Br^{\cdot} \longrightarrow HBr + R^{\cdot}$$

Removal of $OH^{\cdot}$ radicals has a further inhibiting effect inasmuch as these radicals bring about the exothermic conversion of carbon monoxide to carbon dioxide:

$$OH^{\cdot} + CO \longrightarrow H^{\cdot} + CO_2$$

This mechanism is supported by the fact that the order of effectiveness of different halogens as flame retardants is the same as in premixed flames, where such a mechanism is known to operate. However, there are a number of difficulties about this simple explanation of the gas-phase action of bromine compounds. For example, hydrogen bromide can also be an effective promoter of low-temperature oxidation and combustion (Rust and Vaughan 1949; Allen and Tipper 1960). This is also observed for certain organic bromine compounds which evolve hydrogen bromide on decomposition (Cullis, Fish and Ward 1963).

Another more important objection to the purely chemical mechanism of action of hydrogen bromide is based on the behaviour of halocarbons such as CF_3Br, CF_2ClBr and $C_2F_4Br_2$ which are used extensively as flame suppressants (Ford 1975; Gann 1975). These compounds have high thermal stability and therefore release little, if any, hydrogen halides into the gas phase. As a consequence it would not be expected that hydrogen bromide is the active species. The contrary is true, however, and these compounds are more effective than the corresponding hydrogen halides (Creitz 1970).

An alternative theory has been put forward to explain the action of bromine compounds in purely physical terms (Larsen 1974, 1975a, b, c, 1977; Larsen and Ludwig 1979). Larsen re-examined flammability limits for halocarbons, showing that more than 70 wt percent halogen was required in a compound to prevent flame propagation and that the total amount of halogen was the only important factor. The role of the halogen was considered to be simply to increase the total mass of material which had to be vaporized (Larsen and Ludwig 1979). The theory does receive support from measurements of the flammability of polystyrene, poly (methyl methacrylate) and unsaturated polyesters, which show that the limited oxygen index (LOI) increases linearly with the total amount of bromine present but is independent of the structure of the additive (Ravey, Fischler and Kramer 1978).

Irrespective of their mode of action, bromine compounds are generally not used alone, due partly to their high cost, and in part to the deleterious effect on polymer properties of high levels of the halogen. However, various co-additives appear to modify favourably the breakdown of brominated flame retardants.

One example is provided by free radical initiators. It was first proposed that these compounds catalyse the release of hydrogen bromide from organic bromine compounds so that flames were extinguished by large-scale chemical inhibition of the gaseous oxidation reactions (Eichhorn 1964). However, it was later shown (Hindersinn 1966) that these compounds cause depolymerization of the hot polymer, so that they melt much more easily. It was then more difficult to sustain their burning, as molten material dripped away from the locality of the flame source, carrying with it heat which would otherwise have been transferred back to the polymer. A combination of tetrabromoethylene and dicumyl peroxide is a good flame retardant for polystyrene.

The effectiveness of combinations of bromine and phosphorus is well established, and is dealt with in more detail in Section 1.5.2.3.

One other class of compound frequently used as co-additives are oxides of metals, such as antimony, aluminium and iron. These oxides when used as co-additives with bromine compounds often show synergism, resulting in an overall increase in flame-retardant behaviour. The concept of synergism is discussed in considerable detail in Section 1.5.2.

Antimony oxide Sb_4O_6 when used in conjunction with halogen compounds has been shown to be a highly effective flame retardant for many polymers acting initially in the gas phase. Antimony oxyhalides and antimony halides are formed, the latter being converted in the flame to hydrogen bromide and a lower oxide, SbO, which can cause recombination of highly reactive flame species, such as $OH^{\cdot}$ and $H^{\cdot}$.

In summary then, bromine compounds are known to be some of the most effective flame retardants. These compounds act predominantly in the gas phase. One mechanism involves the reaction of highly reactive radicals with hydrogen bromide to form much less reactive bromine atoms but there is also evidence that organic bromine compounds can act as flame inhibitors probably by some physical mechanism. Evidence does exist for certain condensed phase mechanisms but these are less well established.

1.4.3.4 Nitrogen compounds

The importance of nitrogen in flame-retardant systems is well established but poorly understood. The presence of the element in organic polymers appears to confer flame-retardant properties as shown by the relatively low flammability of both natural polymers, such as leather and silk, and synthetic polymers, such as nylons, which contain the element. However, some nitrogen-containing polymers, e.g. polyurethanes, which contain only small proportions (4 to 5 wt percent) of nitrogen, are quite flammable, suggesting that the presence of nitrogen in a polymer does not necessarily result in appreciable flame retardance. The flammabilities of some nitrogen-containing polymers are shown in Table 1.17.

Little fundamental work has been carried out on nitrogen-containing flame retardants, so that little is known about their mechanism of action. Several modes of action have been suggested to account for the effectiveness of nitrogen as a flame retardant. One, which has little experimental supporting evidence is the formation of nitrogen acids (Lyons 1970), such as HNO_2 and HNO_3, formed by oxidation of the nitrogen in flame retardants. These when formed may protonate highly hydroxylated polymers such as cellulose, subsequent elimination would lead to the formation of carbocations which would in turn favour the formation of char. This ignores the well-known oxidising nature of these

Table 1.17 The flammability of some nitrogen containing polymers

Polymer	Nitrogen content (wt %)	LOI
Polyurethane foam	4.5 - 5.2	16.5
Nylon-6,6	12.4	24.0
Wool	16 - 17	23.8 - 25.2
Silk	18 - 19	> 27.0
Leather	11.0	34.8

acids. Similarly nitrogen oxides, particularly NO, which are formed by the oxidation of nitrogen, may combine with and thus destroy highly reactive radical species in the flame (Camac and Feinberg 1964; Shahed and Newhall 1971; Heywood 1971; Williams, Sarofim and Lambert 1972; Thompson, Brown and Beer 1972). Despite these suggestions the only mechanism which appears to have any experimental vailidity is the formation on decomposition of the flame retardant to produce gaseous nitrogen, which behaves as a "diluent". The flammable volatile polymer decomposition products are therefore diluted by the inert nitrogen thereby decreasing the overall flammability of the gaseous products (Chamberlain 1978). This mode of action is examined in more detail in Section 1.4.3.1. The ability to release nitrogen at elevated temperatures explains the widespread use of nitrogen compounds as spumifics in the production of intumescent coatings. The effectiveness of inorganic nitrogen compounds is shown by the use as flame retardants of $(NH_4)_2HPO_4$, $(NH_4)_2SO_4$, NH_4Br, $(NH_4)_2B_4O_7.4H_2O$, $MgNH_4PO_4.6H_2O$, and $(NH_4PO_3)_n$ (Pitts 1971). All these salts produce ammonia, which in most gaseous mixtures does not sustain combustion and acts as a "diluent" (Durrant and Durrant 1962; Little, Rose and Rose 1966). Inorganic nitrogen compounds generally contain less than 25 wt percent of ammonia by weight but metal ammine complexes of the general type $M(NH_3)NX$ are a class of compound which can contain up to 40 wt percent of ammonia as shown in Table 1.18.

Table 1.18 A series of metal ammine complexes containing high percentages of ammonia by weight

Complex	Calcd. (wt % NH_3)	N (%)
$Co(NH_3)_6Cl_3$	38.2	31.4
$[Co(NH_3)_5Cl]Cl_2$	33.9	28.0
$Co(NH_3)_6Br_3$	25.5	20.9
$Co(en)_3Cl_3 \cdot 3H_2O^*$	0.0	21.0
$[Cr(NH_3)_5Cl]Cl_2$	35.0	28.8
$Zn(NH_3)_4(BF_4)_2$	22.2	18.3
$Ni(NH_3)_6(BF_4)_2$	30.6	25.1

*en = ethylenediamine

Source: J.J. Pitts (1971), Journal of Cellular Plastics, 7, 202

One particularly effective ammine complex utilised in polyurethane foams is $Co(NH_3)_6Cl_3$ which loses 50 percent of its total weight by evolving 35 moles of non-combustible, NH_3, N_2 and NH_4Cl per 6 moles of starting compound as shown in the equation below (Pitts 1971):

$$6Co(NH_3)_6Cl_3 \xrightarrow{190 - 325^\circ C} 6CoCl_2 + 6NH_4Cl\uparrow + N_2\uparrow$$
$$+ 28NH_3\uparrow$$

A number of nitrogen-containing organic compounds are used as reactive flame retardants for certain polymers. These include triazines and isocyanates, as well as urea, guanidine and cyanuric acid derivatives (Kuryla 1973). Urea and guanidine are also used as additive-type flame retardants, often in conjunction with phosphorus, to reduce the flammability of cellulosics.

In summary, the effectiveness of nitrogen as a flame retardant is observed in several systems. However, apart from its acting as a diluent, little experimental evidence is available to support other suggested mechanisms.

1.5 Phosphorus-based Flame Retardants for cellulose

1.5.1 Phosphorus compounds as phosphorylating agents for cellulose

This Section examines phosphorylating agents for cellulose, specifically for the production of durable flame-retardant textiles; i.e. textiles which will withstand leaching, laundering and dry cleaning for the life of the material. Phosphoric acid and its ammonium salts are very effective in inhibiting the combustion of cellulose. However, since the effects produced by their deposition are temporary in nature (semi-durable) a method of binding such compounds to the cellulose molecule via phosphorylation has to be devised in order to obtain a durable flame-retardant finish.

The importance of phosphorus compounds in living systems has provoked a great deal of interest in the synthesis of phosphorylated species (Khorana 1961, Brown 1963, Clark et al. 1964). Most of the synthetic methods involve nucleophilic displacement at a phosphoryl centre by alcohols (to give phosphorus esters), by amines (to give phosphoramides) and by phosphate anions (to give di-phosphates). A general equation for this process of nucleophilic displacement at phosphorus is shown below:

$$Y^- + (HO)_2P(O)X \longrightarrow (HO)_2P(O)Y + X^-$$

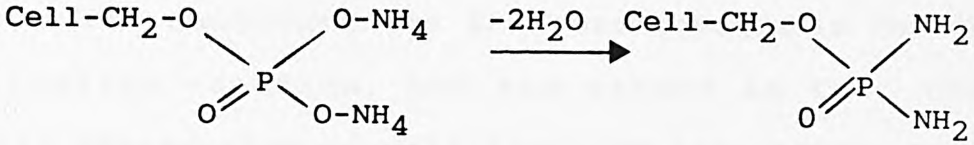
and is termed "phosphorylation" and a large number of phosphorylating agents have been discovered and classified.

The simplest phosphorylating agents are phosphoryl chlorides, such as $(RO)_2P(O)Cl$, which readily phosphorylate alcohols, amines, or phosphate anions e.g.

$$EtNH_2 + (RO)_2P(O)Cl \longrightarrow (RO)_2P(O)NHEt + HCl$$

An early review (Reid and Mazzeno 1949) has listed reagents used to phosphorylate cellulose, the OH groups of which behave like those in alcohols, as described in Section 1.3.1. These include the well established urea-phosphoric acid system (Bancroft 1948, Ford and Hall 1949) and others such as ammonium phosphate, phosphorus pentoxide and chlorides of partially esterified phosphoric acid. Phosphoric acid can be used in the form of metaphosphoric, orthophosphoric, pyrophosphoric and polyphosphoric acids and phosphorous acid can be used as orthophosphorous and pyrophosphorous acids. It appears that the valence state of the phosphorus has no effect on the phosphorylation reaction, since the esterification reaction takes place normally between 150 - 200°C, where all the acids appear to be converted to the same form.

The reaction of cellulose with urea-phosphoric acid has been thoroughly studied (Coppick and Hall 1947, Nuessle et al. 1956) and it has been shown that below 170°C an acidic monoammonium cellulose phosphate is formed. At temperatures above 170°C or after prolonged periods of curing the ammonium salt loses water:



Unlike the ammonium salt, the cellulose amidophosphate formed does not undergo ion exchange with calcium or sodium ions found in hard water. The use of more complex amines or amides, and hence bulkier side groups, also decreases the rate of exchange with such ions.

It is important that the reaction medium is not only a solvent for the acid but also a swelling agent for the cellulose. It should also remain a liquid above 140°C and be inert towards cellulose itself. At the temperature of esterification it should not decompose to form highly acidic or alkaline decomposition products. It is found that, in general, nitrogen bases with strong hydrogen-bonding groups satisfy the above requirements. The esterification reaction proceeds well in the presence of formamide, acetamide, urea, biuret, dicyandiamide and melamine. Substituted derivatives of these amides are also suitable, provided that the substituents do not affect the hydrophilic character or the hydrogen bonding capability of the molecule. Halogen, alkyl or aryl substituents affect these properties unfavourably, as demonstrated by the ineffectiveness of methyl urea. The introduction of amino or hydroxyl groups alters the weak basic character of the reaction medium and guanidine (imino urea) for example is unsuitable because it is strongly alkaline in character.

Strongly acidic conditions are the most favourable for the esterification reaction, but the danger is then that hydrolytic degradation of cellulose may take place. It is therefore necessary to buffer the system carefully in order that the esterification should proceed at an acceptable rate with minimum degradation. Such favourable conditions can be obtained by esterifying cellulose in the presence of an excess of urea. A suitably buffered system would then be composed of a mixture of urea and guanidine carbonate. Similar effects are obtained with other guanidine derivatives like dehydroxyguanidine, guanylurea, aminoguanidine and biguanidine. Since these compounds are alkaline, it is necessary to have urea in excess to provide an adequately buffered system. The resulting cellulose phosphates would be the salts of these strong bases.

Besides the urea-phosphoric acid system, several other combinations of organic compounds and inorganic acids have been suggested for the flame-retardant treatment of cellulose. Work carried out on alkali metal salts (Blanchard 1983) showed that monobasic sodium phosphate and sodium hexametaphosphate were much better than their potassium analogues. Despite this ammonium phosphate was still found to impart the greatest flame-retardant effect, again suggesting the importance of the ammonium ion.

The best overall fabric properties are achieved when the fabric is phosphorylated in the presence of urea at a 2:1 urea to phosphate ratio. The replacement of urea by other nitrogen compounds has been the subject of several patents. Among them, Loukomsky (1957) showed that treatment of cellulose with a combination of guanyl-melamine salts and pyrophosphoric acid gave a durable flame-retardant finish. The cellulosic substrate is first impregnated with guanylmelamine hydrochloride solution (obtained by the reaction of dicyandiamide with hydrogen chloride at 100 - 150°C) and then with pyrophosphoric acid. Thus water-insoluble guanylmelamine pyrophosphate is precipitated in situ within the fibre.

The use of diammonium phosphate, hexamethylenetetramine, and dicyandiamide has also been reported (Fluck and Moretti 1957). Another method which made use of cyanamide and phosphoric acid as a single-step pad-heat-cure process (curing time of 3-5 min at 130 - 150°C) resulted in durable flame retardance (O'Brien 1968). The durability of this treatment was improved by a patented process (Courtaulds 1968), which involved incorporating halogenated alkyl phosphates (e.g. a mixture of chloroethyl phosphates) in the phosphoric acid-cyanamide impregnating solution.

The replacement of urea by organic amines and a polymeric-type phosphoric acid has been suggested (Asahi 1967). The polymerized acid is polymetaphosphoric $(HOPO_2)_n$ where n=1 to 6 or higher. However it was found that if $n < 3$ the fabric had an objectionable yellow colour, which decreased as the degree of condensation of metaphosphoric acid increased. Metaphosphoric acid must be present as ammonium or organic amine (mono-, di- or trisubstituted methyl, ethyl, or propylamine or corresponding alkanolamine) salts. Certain quaternary ammonium compounds, such as tetramethyl-, tetraethyl- and tetrapropylammonium hydroxides, can be used in conjunction with the metaphosphoric acid.

Phosphoramides also phosphorylate cellulose in high yield (Nielsen 1957). Unsubstituted phosphoric triamide reacts almost quantitatively with cellulose during washing, however most of the P-N bonds cleave and yield cellulose phosphate. In contrast, substituted phosphoramides, e.g., NN'N'-trimethyl-phosphoramide, react in significantly lower yields (Lewin et al. 1973).

The use of phosphorus oxychloride (Reid and Mazzeno 1949, Nagoria 1977, Jain et al. 1985), in conjunction with pyridine as a base, has been well investigated. Although this method causes a considerable reduction in tensile strength of the cotton cloth, it does impart durable flame retardant properties (Gupta et al. 1979).

1.5.2 Synergistic interactions of phosphorus with nitrogen and halogen flame retardants

1.5.2.1 Introduction

The effect of a mixture of two or more flame retardants may be additive, synergistic or antagonistic. When the effect of two flame retardants is the sum of the effects of the two components measured independently, it is called an additive effect. Synergism is the name given to behaviour where the effect of two or more components taken together is greater than the sum of their individual effects. Conversely an antagonistic effect is one in which the flame retardance is less than that predicted on an additive basis.

The most commonly used flame retardants are mixtures based on the elements Al, B, Br, Cl, Mg, N, P, Sb, Sn and Zn. The use of several of these elements in combined form is common in commercial flame retardants and this perhaps suggests that advantage is being taken of the synergistic effects which may be observed.

In this section, synergism between phosphorus and nitrogen and between phosphorus and halogens will receive special consideration. Synergistic effects involving phosphorus and nitrogen are well substantiated for cellulose and have also been observed with polyurethane foams; but are not generally found with other polymeric systems.

1.5.2.2 Phosphorus-Nitrogen Synergism

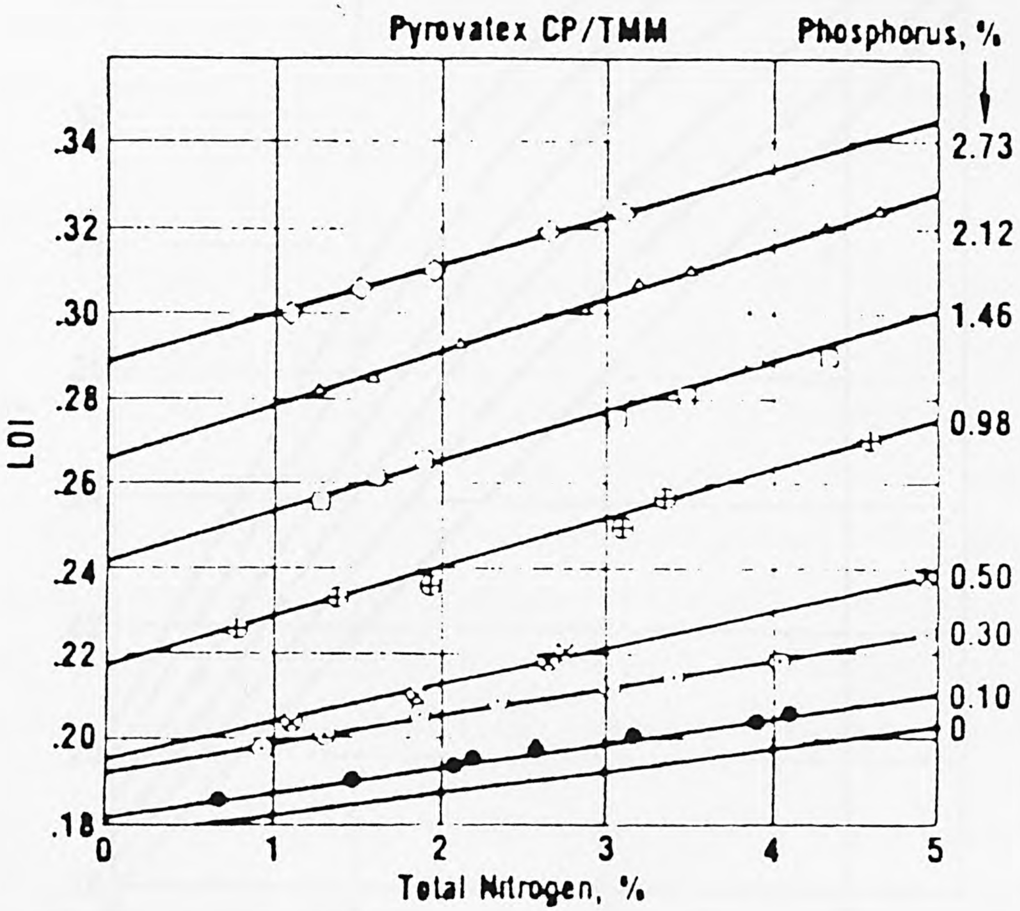
The following experimental observations with mixtures of phosphorus and nitrogen compounds suggest the existence of synergism:

(i) A combination of urea and phosphoric acid used as part of the pad-dry cure phosphorylation process showed a greater flame retardant effect at lower concentrations than either of the two compounds used alone (Little 1968).

(ii) Some of the most durable flame retardant finishes employ tetrabis(hydroxymethyl) phosphonium chloride combined with ammonia, urea or trimethylol melamine (Kuryla and Papa 1975).

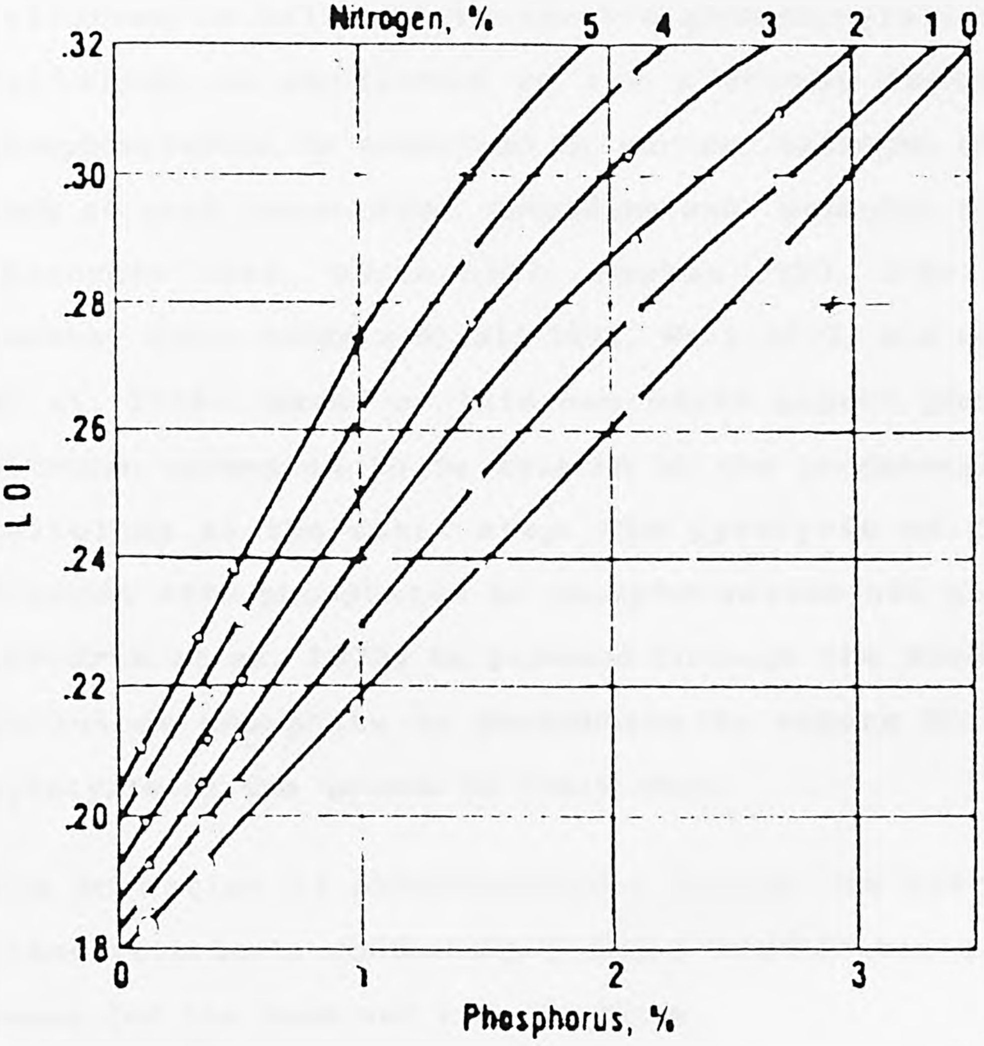
In these cases, the role of nitrogen was believed to be to strengthen the attachment of the phosphorus to the cellulose. More quantitative information regarding the interaction of phosphorus and nitrogen was obtained from a study of the interaction between Pyrovatex CP (i.e., $(CH_3O)_2P(O)CH_2CH_2CONH\text{-}CH_2OH$) and trimethylol melamine as a treatment for cotton cloth (Willard and Wondra 1970). Figure 1.21 shows Limited Oxygen Index (LOI) values plotted against percentage of phosphorus as the percentage of nitrogen is increased and Figure 1.22 shows the LOI values plotted against percentage of nitrogen as the percentage of phosphorus is increased. The increasing slope in both cases is indicative of synergism. The authors state that no

Figure 1.21 LOI (Limited oxygen index) as a function of phosphorus content at fixed nitrogen levels for pyrovatex CP/trimethylol melamine treated cotton cloth



Source: J.J. Willard and R.E. Wondra (1970) Textile Res. J., 40, 203

Figure 1.22 LOI as a function of nitrogen content at fixed phosphorus levels for pyrovatex CP/trimethylol melamine treated cotton cloth



Source: J.J. Willard and R.E. Wondra (1970)
Textile Res. J., 40, 203

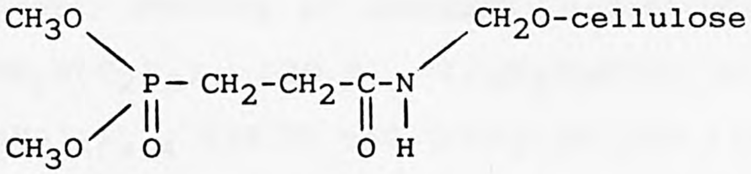
specific N/P ratio produces an optimum synergistic effect but nonetheless a maximum appears to exist with ca. 1 percent of phosphorus and 4-5 percent of nitrogen.

The flame retardant action of phosphorus compounds in cellulose is believed to involve phosphorylation of the cellulose as mentioned in the previous section. The phosphorylation is catalysed by certain nitrogen compounds, such as urea, cynanamide, guanidine and methylol melamines. (Bancroft 1948, Davis 1949, Marton 1950, O'Brien 1968, Sawhney 1971, Hendrix et al. 1972, Weil 1975, and Peppermann et al. 1976). Based on this one might expect phosphorus-nitrogen synergism to be related to the phosphorylation of cellulose as the first step. The pyrolysis of cellulose treated with phosphates or phosphoramides has been shown (Hendrix et al. 1972) to proceed through the formation of cellulose phosphate or phosphoramide esters followed by pyrolysis of the esters to yield char.

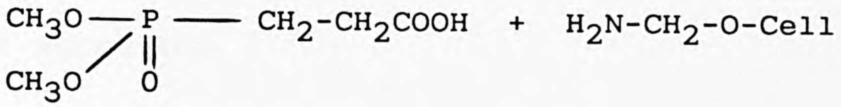
The formation of phosphoramides during the pyrolysis of flame retardants containing P and N constitutes a possible basis for the observed P-N synergism.

A study of the efficiencies of different aromatic phosphoramides in increasing char formation from cellulose indicates that these are all closely similar and much higher than for the corresponding aromatic phosphates or phosphonates (Langley et al. 1980).

When an aromatic phosphonitrile was used, the slope of LOI vs concentration was the same as for nitrogen additives not containing phosphorus, suggesting that it is the ability to form P-N bonds which is important for phosphorus-nitrogen synergism. Work carried out with both ortho and para derivatives of diphenyl-o-carbamylphenyl phosphate ($C_6H_4(CONH_2).OPO(OC_6H_5)_2$) incorporated into several thermosetting polymers, such as polyethylene (Casagrande 1986), showed an increased slope of LOI vs percentage of phosphorus, further suggesting that the use of compounds containing P-N bonds gives enhanced flame retardance. This is further confirmed by the fact that the nitrogen in N,N'-dimethylacrylamide exhibits synergism with the phosphorus in phosphorylated cellulose, while that in N-vinyl-2-pyrrolidone does not (Inagaki et al. 1976, Inagaki and Katsuura 1980). Methylol phosphopropionamides have been seen to be effective flame retardants (Bakos et al. 1982), the methylolamide end functioning as a binding site for attachment to cellulose as shown:

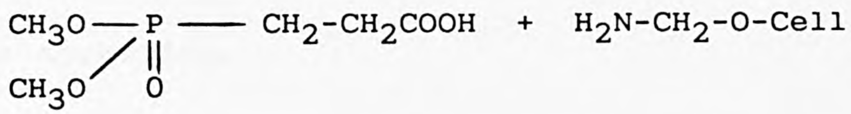


The treated cellulose has an LOI of 31.4 and after laundering the LOI of the cellulose is still above 25. It is thought that the amide linkage in the modified cellulose undergoes hydrolysis during the finishing process to yield a modified cellulose containing amino groups, i.e.,



The incorporation of amino groups into carbohydrates has been reported to lower the temperature of decomposition (Rohringer et al. 1975). The form of the nitrogen may be important as it is generally believed that both amide and amine nitrogen behave as flame retardants (Reeves et al. 1970, Drake 1976), while nitrile nitrogen, e.g. polyacrylonitrile in cellulose, does not (Drake 1976).

Very few reports of phosphorus-nitrogen synergism appear in the literature for polymers other than cellulose and most of these already contain nitrogen. In fact, with poly(methyl methacrylate) the presence of nitrogen impairs the flame retardance conferred by phosphorus (Weil 1975). This work showed that, when several pentavalent phosphates and phosphonates were used the LOI was increased from 17.3 to between 21.5 and 22.5. However when the following nitrogen-phosphorus compounds were used the LOI's were as indicated in brackets, showing an increase in flammability: $(C_2H_5O)_2 P(O) CH_2N(C_2H_5)_2$ (20.8), $(C_6H_5O_2P(O) N(CH_3)_2$ (20.4), $[PN(OC_3H_7)_2]_{3-4}$ (19.7) and $[(CH_3)_2N]_3(O)$ (19.6). This was explained by the fact that acidic phosphorus compounds change the mechanism of decomposition of poly (methyl methacrylate), so that it no longer unzips to yield monomer but instead gives char and carbon dioxide (Gruntfest and Young 1961). The nitrogen makes the phosphorus compound less acidic and thus decreases its efficiency as a catalyst for



$CH_3O-P(O)(OCH_3)-CH_2-CH_2COOH + H_2N-CH_2-O-Cell$

The incorporation of amino groups into carbohydrates has been reported to lower the temperature of decomposition (Rohringer et al. 1975). The form of the nitrogen may be important as it is generally believed that both amide and amine nitrogen behave as flame retardants (Reeves et al. 1970, Drake 1976), while nitrile nitrogen, e.g. polyacrylonitrile in cellulose, does not (Drake 1976).

Very few reports of phosphorus-nitrogen synergism appear in the literature for polymers other than cellulose and most of these already contain nitrogen. In fact, with poly(methyl methacrylate) the presence of nitrogen impairs the flame retardance conferred by phosphorus (Weil 1975). This work showed that, when several pentavalent phosphates and phosphonates were used the LOI was increased from 17.3 to between 21.5 and 22.5. However when the following nitrogen-phosphorus compounds were used the LOI's were as indicated in brackets, showing an increase in flammability: $(C_2H_5O)_2$ P(O) $CH_2N(C_2H_5)_2$ (20.8), $(C_6H_5O_2P(O)$ $N(CH_3)_2$ (20.4), $[PN(OC_3H_7)_2]_{3-4}$ (19.7) and $[(CH_3)_2N]_3(O)$ (19.6). This was explained by the fact that acidic phosphorus compounds change the mechanism of decomposition of poly (methyl methacrylate), so that it no longer unzips to yield monomer but instead gives char and carbon dioxide (Gruntfest and Young 1961). The nitrogen makes the phosphorus compound less acidic and thus decreases its efficiency as a catalyst for char formation.

Another type of phosphorus-nitrogen interaction which is not synergistic but is worthy of mention is utilised in intumescent coatings. In such systems the formation of a suitable acid catalyst such as phosphoric acid and its further action is utilized. "Intumescence" means bubbling up under the action of heat. Thus, when an intumescent coating is exposed to intense heat, it undergoes thermal decomposition resulting in the formation of acidic compounds which catalyse further breakdown of the coating. The gases released during the decomposition convert the semi-molten polymer and its residual breakdown products into a carbonaceous foam which may be many times thicker than the original coating and thus provide efficient thermal insulation for the underlying polymer.

Five important interrelated steps must occur in order for an intumescent coating to be formed (Roth and Green 1974).

1. The "intumescent catalyst" must decompose to form a suitable acid catalyst. In the case of dihydrogen ammonium phosphates, the acid is phosphoric acid.

$$NH_4H_2PO_4 \xrightarrow{\Delta} NH_3\uparrow + H_3PO_4$$

2. The phosphoric acid formed reacts with a "carbonific compound", e.g. pentaerythritol, giving a phosphorus ester.

$$C_5H_8(OH)_4 + H_3PO_4 \longrightarrow C_5H_8(OH)_4.H_3PO_4$$

3. The phosphorus ester decomposes to phosphoric acid, water and a carbonaceous char.

$$C_5H_8(OH)_4 \cdot H_3PO_4 \xrightarrow{\Delta} H_3PO_4 + H_2O + C$$

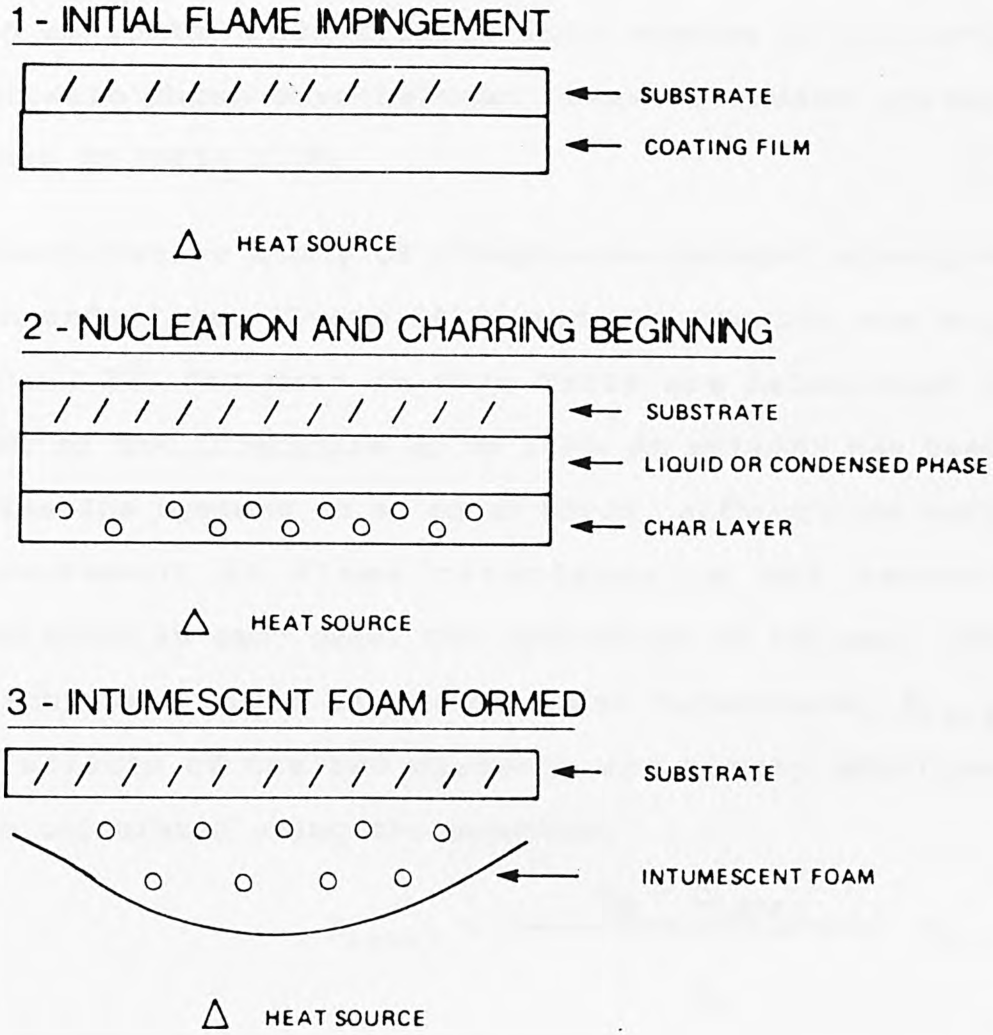
4. The resin binder softens and melts, covering the carbonaceous char and trapping the released gases.

5. The "spumific" compound or blowing agent decomposes, releasing non-flammable gases which blow the carbonaceous char into an insulating foam which protects the substrate, as shown with dicyandiamide.

$$C_2H_4N_4 \longrightarrow NH_3\uparrow + N_2\uparrow + \text{char}$$

A schematic diagram of the intumescent mechanism has been suggested by Rheineck (1972) and is shown in Figure 1.23.

Figure 1.23 Schematic representation of the intumescent mechanism for coatings



Source: Flame retardancy of polymeric materials, Vol. 4, ed. by W.C. Kuryla and A.J. Papa, p. 95.

1.5.2.3 Phosphorus-halogen synergism

Significant experimental evidence is available to show the effectiveness of combinations of phosphorus- and halogen-containing flame retardants in polymeric systems. These have been exploited industrially and a number of commercially available phosphorus-halogen flame-retardant systems are listed in Table 1.19.

A quantitative study of phosphorus-halogen synergism has been undertaken (Lyons 1970) and the results are shown in Table 1.20. The data in this Table are calculated from a study of the literature up to 1970. An attempt has been made to examine systems on an equal basis, although the method of measurement of flame retardancy is not necessarily consistent in each case. The percentage of halogen, required to achieve a given degree of flame retardance, $R_{(p+x)}$, if the effects of the two elements are simply additive, has been calculated using the equation:

$$R_{(p+x)} = \frac{Q_p - Q_{(p+x)}}{Q_p} R_x$$

where Q_p and $Q_{(p+x)}$ are the percentages of phosphorus needed with and without halogen respectively and R_x is the percentage of halogen needed alone. An assumption is made that the additivity is linear which may not be applicable in all cases. The results in Table 1.16 suggest, at first sight, synergism for all the polymers mentioned, the least

Table 1.19 A list of some fire-retardant combinations of phosphorus-halogen compounds

Phosphorus compounds	Halogen compounds	Phosphorus-halogen compounds	Polymer substrate
		tris(2,3-Dibromopropyl) phosphate	Polypropylene Polystyrene
		2-Bromoethyl diglycol phosphate	Rigid polyurethane foam
Phosphoric acid	Epichlorohydrin		Unsaturated polyesters
Phosphorines	Chloroethylene oxide		
Phosphoric acid	Dibromo succinic acid		
Diethyl-N,N-bis(2-hydroxyethyl aminomethyl phosphonate)	Dibromopentyl glycol		Flexible polyurethane foam
Tris(dipropylene glycol) phosphite			

Source: Modified from Flame Retardant Polymeric Materials, ed. by M. Lewin, S.M. Atlas and E.M. Pearce, New York, Plenum Press, 1978, p. 54

Table 1.20 Average requirements for phosphorus-bromine flame retardants to render polymers self-extinguishing

Polymer	% P	% Br	% P + Br
Polyolefins	5	20	0.5 + 7
Polyacrylates	5	16	1 + 3
Polyacrylonitrile	5	10-12	1-2 + 5-10
Polyurethane	1.5	12-14	0.5 + 4-7
Polyesters	5	12-15	2 + 6
Epoxy	5-6	13-15	2 + 5

Source: Extracted from J.W. Lyons (1970). J. Fire Flammability, 1, 302 convincing behaviour being observed with polyacrylonitrile.

On reviewing the evidence available for phosphorus-halogen synergism, Weil (1975) suggested however that combinations of the two elements exerted effects which are largely additive and that non-linearity may well be responsible for the deviations observed.

It is therefore important to elucidate the mode of action of phosphorus-halogen flame retardant mixtures. As we have seen in two of the preceding sections, phosphorus is effective mainly in the condensed phase, while bromine is effective predominantly in the gas phase. One suggestion is that, when both elements are present, phosphorus halides or oxhyhalides may be formed (Hilado 1969). These compounds are very efficient inhibitors of premixed flames (Miller 1969; Hastie 1973). However formation of such species is not favoured on equilibrium considerations.

The use of phosphorus-halogen flame retardants in flexible polyurethane foams has provided some information on the interaction of the two elements. Measurement of char yields (Papa and Poops 1972) and of the LOI showed that most of the phosphorus originally present in the polyurethane foam remains in the char. Elemental analysis of the char revealed also a surprisingly large amount of bromine, suggesting that, as with phosphorus, the bromine acts in the condensed phase.

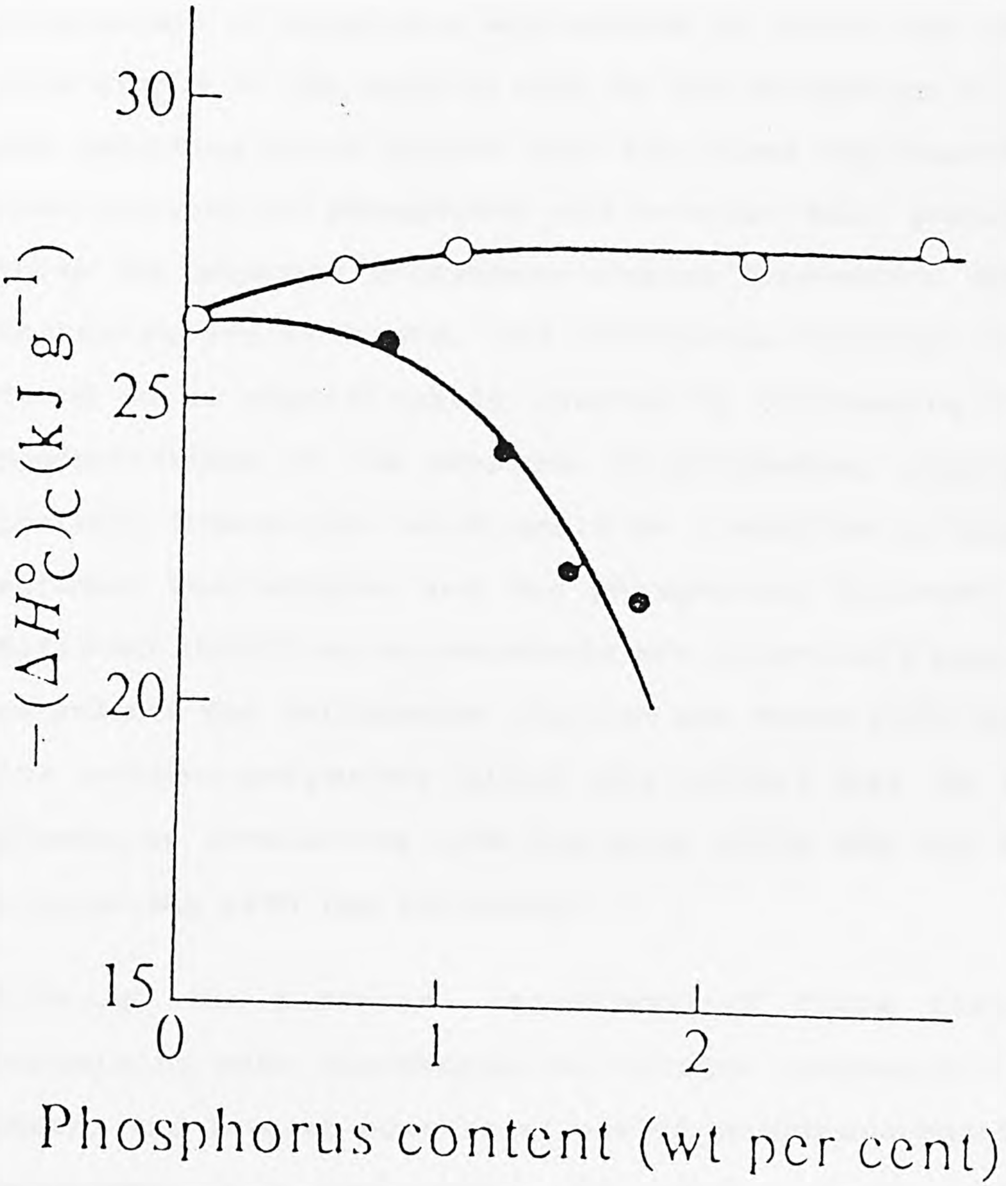
Bromine appeared to be most effective in an ionic form.

Studies of chars formed at 300°C revealed that they tended to retain ionic bromine and phosphorus, when in a 1:1 ratio, whereas with chars formed at 550°C the ratio of bromine to phosphorus was 1:3, suggesting both a structural as well as a concentration dependence.

Measurements of the effect of tris(2,3-dibromopropyl) phosphate on the combustion of poly((1,4-cyclohexylene dimethylene) terephthalate) (Bostic, Yeh and Barker 1973) have shown that not only is much more char formed in the presence of the halogen but the heat of combustion of the char decreases rapidly with increasing concentration of the phosphorus-bromine compound as shown in Figure 1.24. These results suggest that the tris(2,3-dibromopropyl) phosphate affects predominantly the condensed-phase reactions of the polymer. Similar conclusions have been reached for polyesters (Avondo, Vovelle and Delbourgo 1978) and radiolytically grafted cotton (Mey-Marom and Behar 1980) containing both phosphorus and halogens. Work carried out on the effect of phosphorus and bromine on cotton, and a 50:50 cotton-polyester blend (Johnson and Moore 1972) seems to be representative of the experimental information available as regards phosphorus-halogen synergism in cellulose. In this study diammonium phosphate was used as a model phosphorus compound and diammonium tetrabromophthlate as the bromine compound.

It was found that the burning rate of pure cotton decreased slowly with increasing percentage of bromine. The slope of

Figure 1.24 Effect of phosphorus on the heat of combustion of the char obtained from poly(1,4-cyclohexylene dimethylene) terephthalate) fibres



○ triphenyl phosphate
● tris(2,3-dibromopropyl)phosphate
After Bostic et al. 1973).

this plot was the same with or without phosphorus, suggesting no interaction between the two elements.

The overall effect of the two flame retardants thus appears to be additive. Further evidence for the absence of interaction of phosphorus and bromine on cotton was obtained from graphs of the burning rate vs the percentage of oxygen. The resulting plots showed that the lines representing two combinations of phosphorus and bromine were parallel to those for separate phosphorus-bromine treatments. With the cotton-polyester blend, the horizontal burning rate was found to be significantly lowered by increasing bromine concentrations in the presence of phosphorus, suggesting a positive interaction which could be classified as synergism between the halogen and the phosphorus. However, it is believed that bromine compounds are relatively poor flame retardants for cellulosics (Johnson and Moore 1972) and with the cotton-polyester blend the effect may be due to phosphorus interacting with the pure cotton and the bromine interacting with the polyester.

Although the potential importance of flame retardants containing both phosphorus and halogen compounds is well known, the largest commercial use of phosphorus-based flame retardants is in conjunction with poly(vinyl chloride).

Upon critical examination, few generalizations can be made regarding phosphorus-halogen synergism in polymers. Most of the work to date has shown that combinations of the two elements result in predominantly condensed-phase modes of action.

The absence of thorough quantitative and mechanistic information questions the existence of phosphorus-halogen synergism in cellulose, where phosphorus-nitrogen synergism is much better documented and understood. It is this that has largely resulted in the work described in this thesis. Possible synergistic interactions of phosphorus-nitrogen, phosphorus-bromine and phosphorus-nitrogen-bromine have been examined with a view to quantifying synergism in real terms. A quantitative method for assessing synergism has been developed and a study has been made of possible mechanistic implications of the observed flame-retardant effects of mixtures of phosphorus-, nitrogen- and bromine-containing flame retardants on cellulose in the form of cotton cloth.

Chapter 2 - Experimental

The hand that kindles cannot quench the flame

Byron, Lara Canto ii, st.11

2.1. Materials

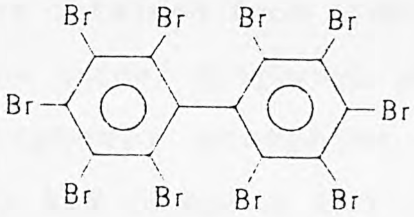
2.1.1 Polymer

Cellulose, in the form of unmercerised Egyptian cotton cloth, was kindly provided by Bide Company Limited. Weave characteristics: weight, 192 gm m^{-2}; warp threads, 3 gm cm^{-1}; weft threads, 26 gm cm^{-1}. Methyl cellulose and cellulose acetate were obtained from BDH Ltd and used without further purification.

2.1.2 Additives

2.1.2.1 Bromine compounds

Decabromobiphenyl (Adine 0102)



was kindly provided by Produits Chimiques Ugine Kuhlmann.

2.1.2.2 Nitrogen compounds

All compounds used were S.L.R. grade. Melamine was kindly donated by Imerial Chemical Industries Ltd. The following compounds were obtained from Aldrich Chemical Company and used without further purification: ethylene urea (2-imidazolidone), barbituric acid, ammonium formate, imidazole, *N*-methylimidazole. BDH Ltd provided hexamethylenetetramine.

2.1.2.3 Phosphorus compounds

Red phosphorus (98.6% P-Exolit 405), containing a small amount of di-2-ethylhexylphthalate was kindly donated by Hoechst, West Germany and was sieved to a particle size of 90μm to facilitate even coverage on cotton cloth.

The following were obtained from Aldrich Chemical Co Ltd: Triphenyl phosphine oxide, triphenyl phosphate, phosphorus oxychloride, triphenyl phosphine, dimethyl methyl phosphonate. The BDH Company Ltd supplied triphenyl phosphite, tritolyl phosphate, triphenyl phosphine.

2.1.2.4 Preparation of modified cellulose substrates for casting

Cellulose acetate and methyl cellulose, in powdered form, were dissolved in tetrahydrofuran and water respectively to allow incorporation of flame retardant additives and to facilitate casting of the polymers, into suitably rigid samples so that they could be burnt in the LOI apparatus.

Typically 10g of methyl cellulose were mixed vigorously with 150 cm^3 of distilled water and allowed to stand overnight. In the case of cellulose acetate 20g of polymer were added to 100 cm^3 of tetrahydrofuran. In both cases the resulting mixtures were left overnight to form a gel suitable for casting. Flame-retardant additives were then easily mixed with the resulting gel before it was cast. After casting, the samples were allowed to dry by slow evaporation of the solvent, taking typically 3 - 6 days.

2.1.2.5 Phosphorylation of Cellulose

The method used was one modified from Gupta et al. (1979). Typically 55g of unmercerised cotton were treated with a 2.5 percent sodium hydroxide solution for two minutes. The cloth was then washed with water, dried and cut into pieces of suitable dimensions for the LOI test allowing for minimal shrinkage of the cloth.

The cloth was placed in a 1 dm^3 reaction vessel. The vessel was fitted with a dry nitrogen inlet, a dropping funnel fitted with an equaliser, a condenser, a thermometer and a magnetic flea to facilitate gentle agitation of the mixture. In the case of microcrystalline cellulose a mechanical stirrer was found to be more efficient. 300 cm^3 of dry pyridine were added and the resulting mixture was flushed with dry nitrogen for thirty minutes. 70 cm^3 of phosphorus oxychloride were then added dropwise over one hour and the resulting solution was heated to a range of temperatures for differing periods of time in order to vary the degree of phosphorylation.

The method reported by Gupta et al. (1979) produced in practice only low levels of phosphorylation and some decomposition of the cloth. The optimum conditions for maximum phosphorylation ca. 5 wt percent, with acceptable cloth characteristics were found to be obtained by refluxing the mixture at 55°C for 72 hours. The cloth appeared yellow in colour and had lost some of its tensile strength but was quite suitable for LOI measurements.

2.1.3 Gases

Oxygen, oxygen-free nitrogen, and air were obtained from the British Oxygen Company and used without further purification.

2.1.4 Sample preparation

Additives soluble in suitable solvents were incorporated into the cotton by immersing weighed, conditioned, samples of the cotton cloth (ca. 35 gm) through solutions containing the additives using a manually-operated wringer. Solutions containing a range of weights from 2 - 25 wt percent were used in the first instance; and solutions of other concentrations were later used in the case of the additives showing the greatest flame-retardant effect. Before treatment the cotton was kept overnight in a controlled atmosphere of constant humidity (saturated sodium chloride solution). After treatment the cotton was dried in an oven at about 70°C for 7 hours to evaporate excess water. Subsequently the dried, treated samples were again kept overnight in the same controlled-humidity atmosphere.

In view of the extremely low solubility of both decambromobiphenyl and red phosphorus, these compounds were both applied directly to the treated cotton cloth via the use of a neoprene adhesive. Neoprene, a natural chlorinated rubber, was applied via a toluene solution which was allowed to evaporate fully before the deacbromobiphenyl or red phosphorus were added. The additives were then incorporated onto the cloth by means of a warm heavy iron, covered with a removeable perforated polytetrafluoroethylene sleeve to prevent adhesion of the additive to the iron itself.

2.2 Apparatus and procedure

2.2.1 The limiting oxygen index apparatus

Flammability of the cotton samples was measured using Stanton Redcroft limiting oxygen-index equipment, designed to meet ASTM D2863 specifications. The lay-out is shown schematically in Figure 2.1 and in detail in Figure 2.2. Two gas inlets at the rear of the insturment lead to two filters fitted with numerical controls. This enables the needle valves to be set very precisely. An ON-OFF lever is situated adjacent to each control needle valve in each gas line. The two separate pipes merge at a mixing chamber to give a homogeneous combined gas flow. The main portion (ca. 99.5 percent) passes directly to the principal indicating flowmeter, which is calibrated to read from 0 - 25 $dm^3 min^{-1}$ for air. From the flowmeter the gas passes directly to the mesh at the base of the test column. The small by-pass flow (ca. 0.5 percent of the total) goes to a paramagnetic oxygen analyser which produces a digital read-out of the percentage of oxygen in the gas mixture.

The instrument was connected to cylinders containing oxygen and nitrogen via a two-stage regulator, and supply pressures of 170 kPa were employed in order to achieve the required flow rates during the test.

The test column on the limiting oxygen index equipment is a heat-resistant glass tube of 75 mm minimum internal diameter

Figure 2.1 Schematic Diagram of the Limited Oxygen Index Equipment (LOI)

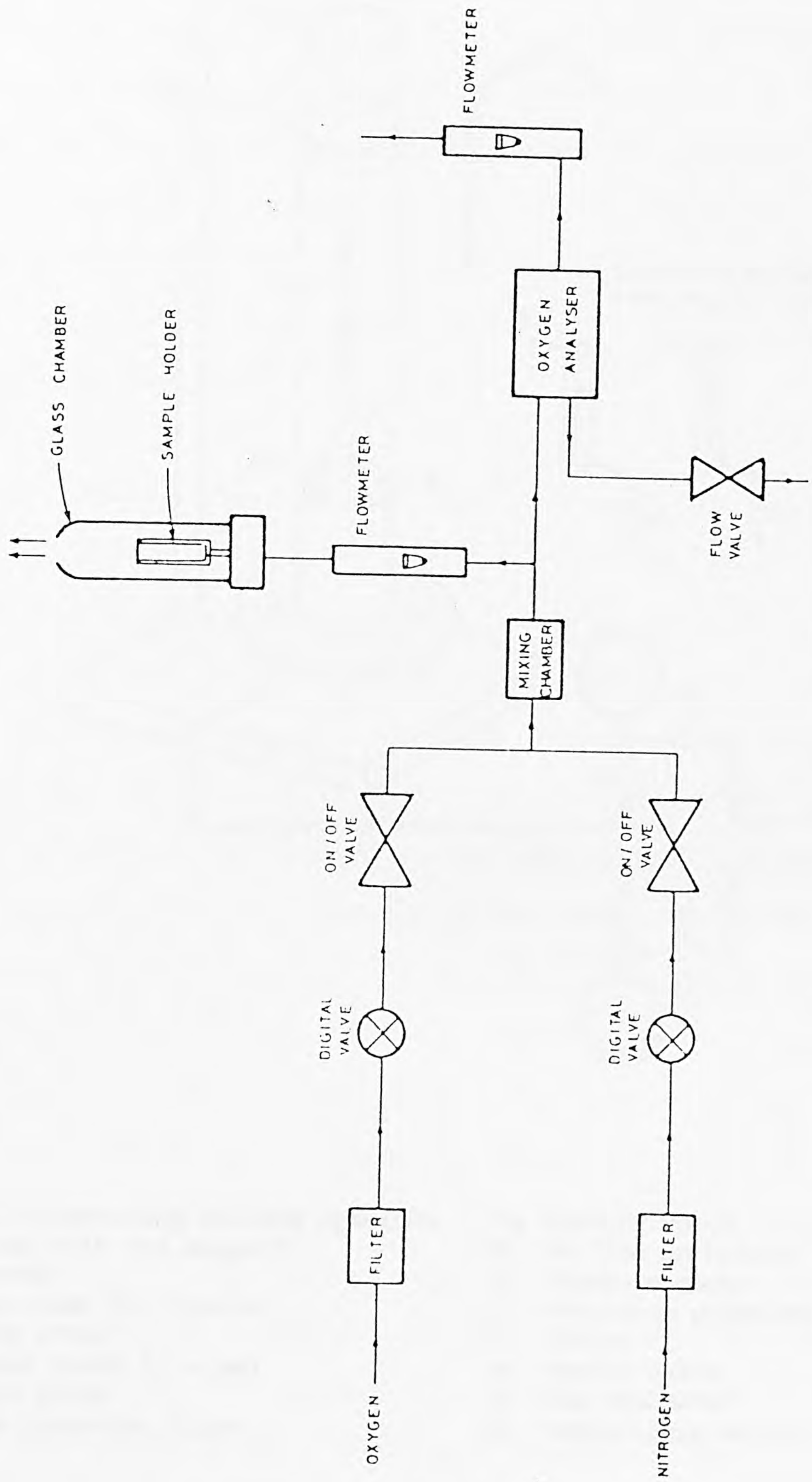
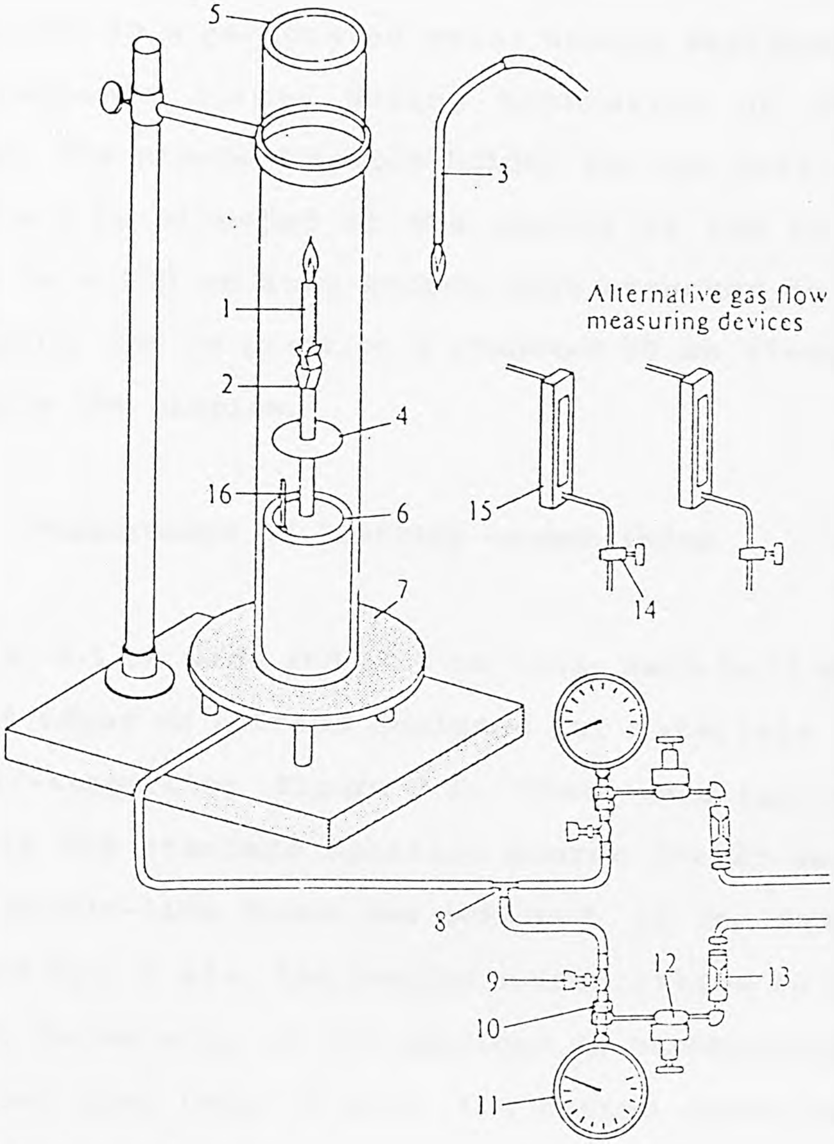


Figure 2.2 Limiting Oxygen Index (LOI) Apparatus ASTM or BS 2782-141



Key

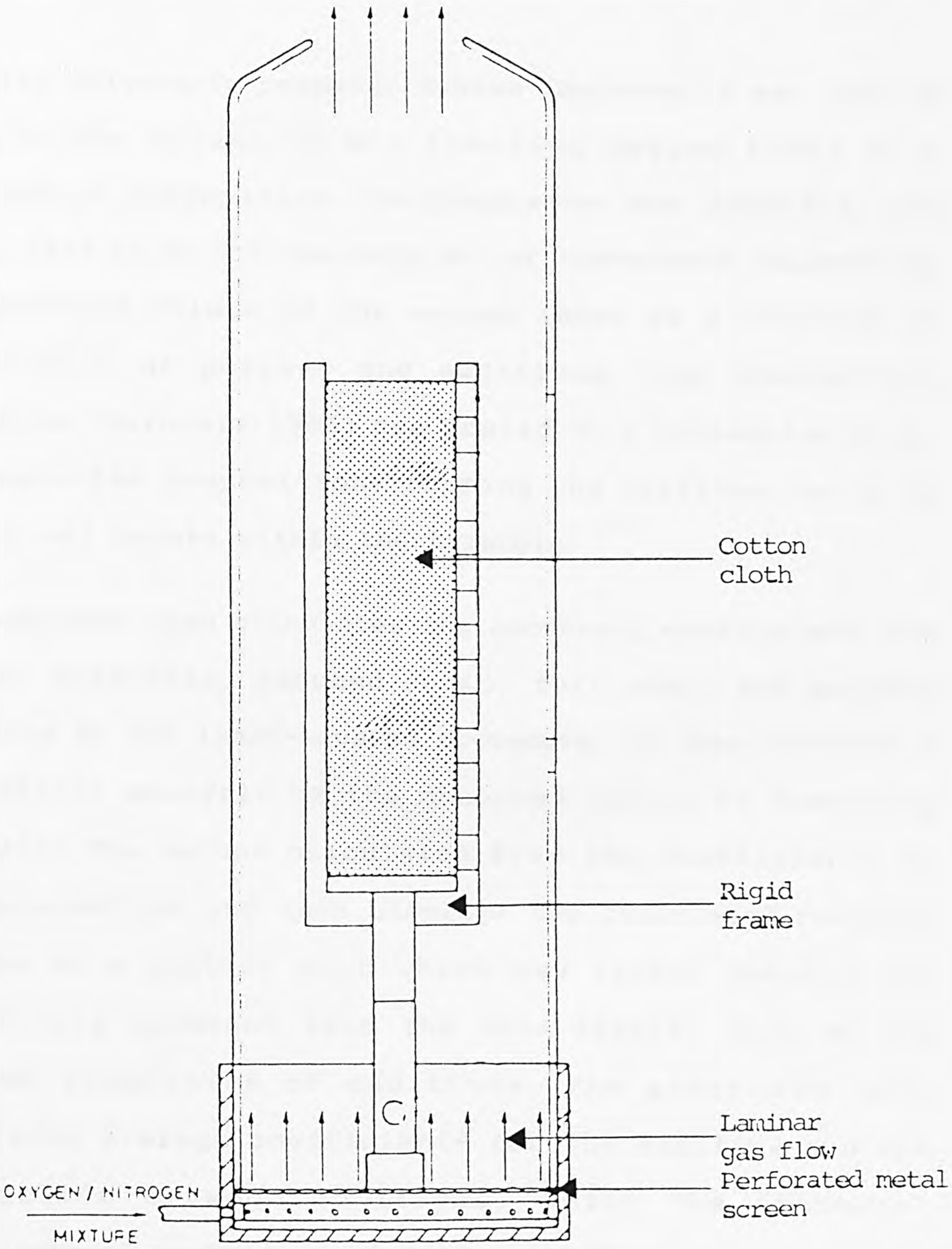
1. Self-supporting burning specimen
2. Clamp with rod support
3. Burner
4. Wire mesh for debris
5. Ring stand
6. Glass beads in a bed
7. Base plate
8. Gas premixing joint
9. Cut-off valve
10. Orifice in holder
11. Pressure gauge
12. Precision pressure regulator
13. Filter
14. Needle valve
15. Gas flowmeter
16. Temperature sensor

and 450 mm minimum height, which rests in a casing designed with special entry ports, so that the entering gas gives a laminar flow up the column (see Figure 2.3). At the base of the column is a perforated metal screen designed to catch any fragments formed during combustion of the cotton samples. The standard sample holder for non self-supporting materials is situated at the centre of the column. The burner is a 150 mm long copper tube attached to a natural gas supply; and in practice a standard 25 mm flame was used to ignite the samples.

2.2.2 Measurement of limiting oxygen index

Samples, 5.1 cm wide and 14.0 cm long, were held along both upright edges of a frame designed for materials which are not self-supporting (Figure 2.3). These were ignited at the top with the standard ignition source for 20 sec until a stable candle-like flame was obtained. If the sample burns for more than 3 min, the oxygen concentration is gradually reduced. Conversely, if the specimen is extinguished in less than that time (viz. 3 min), the oxygen concentration is increased. The procedure is continued until an oxygen concentration is reached at which extinction occurs as nearly as possible at the specified time. That oxygen concentration is then taken as the LOI value for that sample. For samples which exhibit smouldering combustion at various oxygen concentrations, the concentration of oxygen was increased until a candle-like flame was obtained and

Figure 2.3 Limited oxygen index (LOI) set-up for non-self supporting polymeric materials



that particular oxygen concentration was taken as the LOI value for that sample.

2.2.3 Computation of LOI results

The City University computer system (Honeywell) was used to analyse the values of the limiting oxygen index as a function of composition. The programme (see Appendix) was set to read in an introductory set of statements followed by the observed values of the oxygen index as a function of composition of polymer and additives. The composition variables (Kurotori 1966) are scaled to a triangular grid, with selected compositions forming the vertices, so as to include all points within the triangle.

The programme then calculates the necessary coefficients for linear, quadratic, reduced cubic, full cubic and quartic equations by the least-squares procedure. It then conducts a statistical analysis of the observed values by comparing each with the values calculated from the coefficients at that composition and then displays the calculated response surface as a contour plot which may reveal details not immediately apparent from the data itself, such as the optimum proportion of additives. The programme also calculates average coefficients for the additive and the interaction between additives, using the "integral effectiveness" techniques of Baldry (1985).

Polynominals of order 1 - 4 were tried (Scheffe 1958) and

The LOI values, in terms of composition, were represented as a map, for 9 - 10 equidistant LOI values calculated from the best-fit polynomial and plotted as contour lines of constant LOI. The correlation coefficient should approach 1.0 for a perfect fit, (it is zero if there is no correlation between LOI and the polynomial of the compositions) and for the representation of experimental data to be adequate, should be comparable with the uncertainty in LOI, which can be estimated as ±1 LOI unit. Thus, from these diagrams, the compositions at which the maximum LOI values occur can be obtained. That is to say, the diagrams give useful qualitative information such as the amounts which each component contributes to the flammability which can be found more precisely by examination of the average coefficients over the range x2 or x3 = 0 - 0.2 for each component. The degree of synergism between additives over this range is represented in the tables in the following sections.

2.2.3.1 Ternary-flame retardant system (four component)

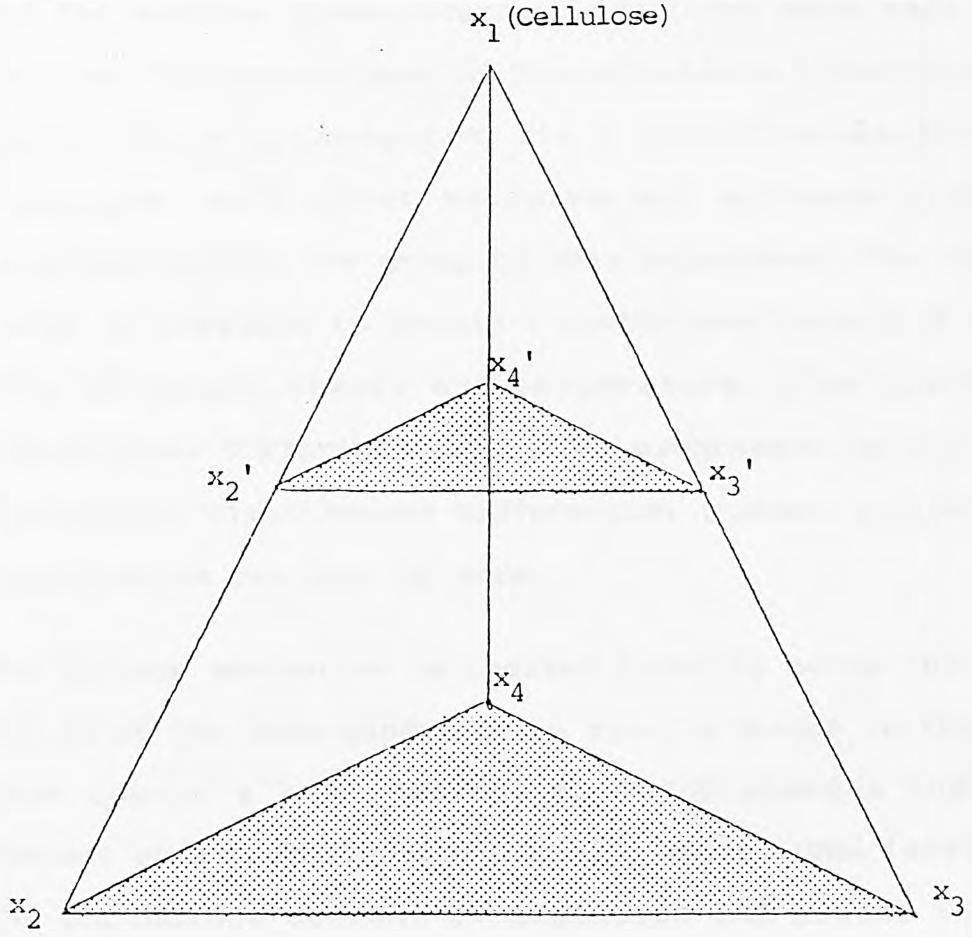
Modifications were made to the programme for the binary system (substrate plus two flame retardant additives) to allow another additive to be considered. The ternary system (substrate plus three additives) required expansion of the 3x3 matrix to a 4x4 matrix. It was also necessary to increase the dimensions as more data points would be required to facilitate the calculation of the new coefficients. A sequential F-test calculation was carried out to assess the significance of the last added variable as for the binary system.

The coefficients are defined below.

Linear	x1, x2, x3, x4
Restricted quadratic	x5=x2x3, x6=x2x4, x7=x3x4
Quadratic	x8=x1x2, x9=x1x3, x10=x1x4
Restricted reduced cubic	x11=x2x3x4
Reduced cubic	x12=x1x2x3, x13=x1x2x4, x14=x1x3x4
Restricted full cubic	x15=x2x3(x2-x3), x16=x2x4(x2-x4) x17=x3x4(x3-x4)
Full cubic	x18=x1x2(x1-x2), x19=x1x3(x1-x3), x20=x1x4(x1-x4)
Reduced cubic	x21=x1x2x3x4

The presence of an extra additive and hence an extra dimension means that the data have to be arranged in the form of a tetrahedron. The resulting contour plots of any plane parallel to the face of the tetrahedron are therefore equivalent to the previous binary plots. Interactions between additives are depicted as slices through the tetrahedron at a fixed total additive loading. Successive slices through the tetrahedron allow the building-up of a qualitative picture of any interaction in the system as shown in Figure 2.4.

Figure 2.4 The ternary flame-retardant system: cellulose plus three additives conveniently represented as a tetrahedron



If x_1 was held constant at, say, 50 percent cellulose, the plane through the triangle would be as shown at x_2', x_3' and x_4'.

If x_1 was held at zero cellulose, this would be equivalent to a binary system triangular diagram and would be represented by the base, i.e. x_2, x_3 and x_4.

2.2.4 The Mettler 2 thermobalance

Thermoanalytical studies of the degradation and oxidation of the cellulose and of the extent of interaction between it and the various flame-retardant additives were made using a Mettler "Thermoanalyser 2" thermobalance interfaced to an Apple IIe microcomputer via a U-microcomputer U-A/D interface, with other hardware and software previously developed within the group of this Department. The apparatus makes it possible to obtain a continuous record of weight, rate of weight change and temperature, when samples are heated under different temperature programmes in any desired atmosphere. Simultaneous differential thermal analysis (DTA) measurements can also be made.

The balance mechanism is located directly below the furnace and is of the beam-substitution type. A change in the sample mass causes a beam deflection which changes the output current of a photoelectric scanning system. The imbalance in the photodiode current is amplified and passed through a coil attached to the balance beam which produces the restoring force. The current in the coil is used to measure the sample mass. The balance allows taring of samples of up to 15.99 g and has three sensitivity ranges, 0-1000 mg, 0-100 mg and 0-10 mg respectively. A weight expansion unit provides greater accuracy by electronic amplification of the weight signal by a factor of ten. An accuracy of ±0.2 percent of the range can be attained for all three ranges of sample mass.

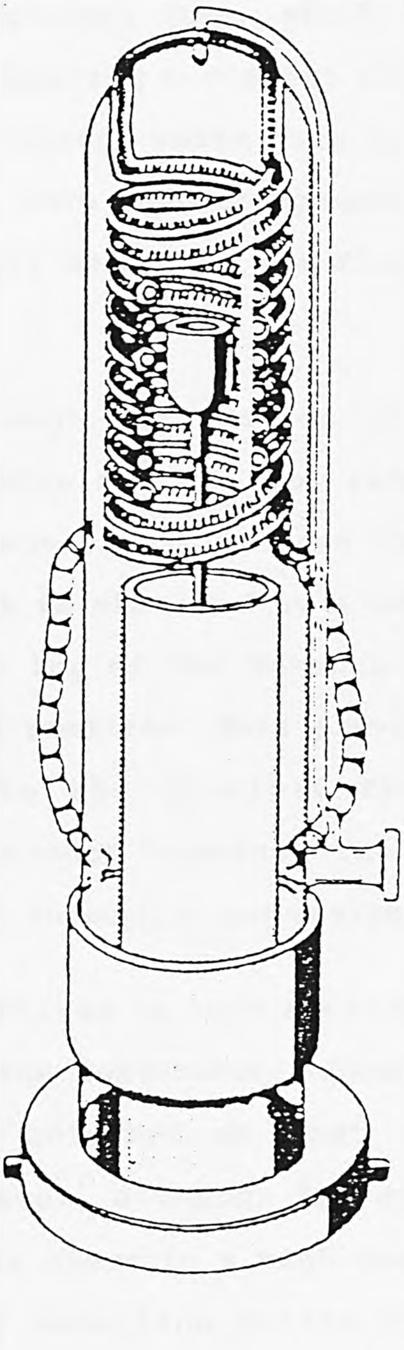
The expanded weight signal is electronically differentiated to provide the first derivative of sample weight. The most sensitive range available on the thermogravimetric (TG) unit is 0.5 mg min^{-1} for full-scale deflection. The accuracy of the instrument is ±0.4 percent in the differential thermogravimetry (DTG) range.

Temperature measurements are carried out by means of a Pt/10 percent Rh thermocouple. The hot junction is located underneath and in contact with the crucible. Temperatures can be measured with an accuracy of ±2.5° at 100°C and ±2.0° at 500°C.

The DTA unit has six ranges, 20, 50, 100, 200, 500 and 1000 V. An accuracy of ±0.2 percent over the range can be attained for all six ranges. The analog/digital conversion uses an instrumentation amplifier with linearity error 0.2 percent and a 12-bit A/D converter with maximum non-linearity 1 bit (0.024 percent full scale).

The furnace tube is of quartz and is surrounded by an aluminium reflecting shield. The heating element consists of a non-inductively wound Kanthal wire filament inside a bifilar quartz spiral (Figure 2.5). The furnace may be heated from 300 to 1000°C under computer control at a heating rate up to a maximum of ca. 500°min^{-1} (linear up to 100°min^{-1}).

Figure 2.5 Furnace showing crucible position and spiral windings of heating element

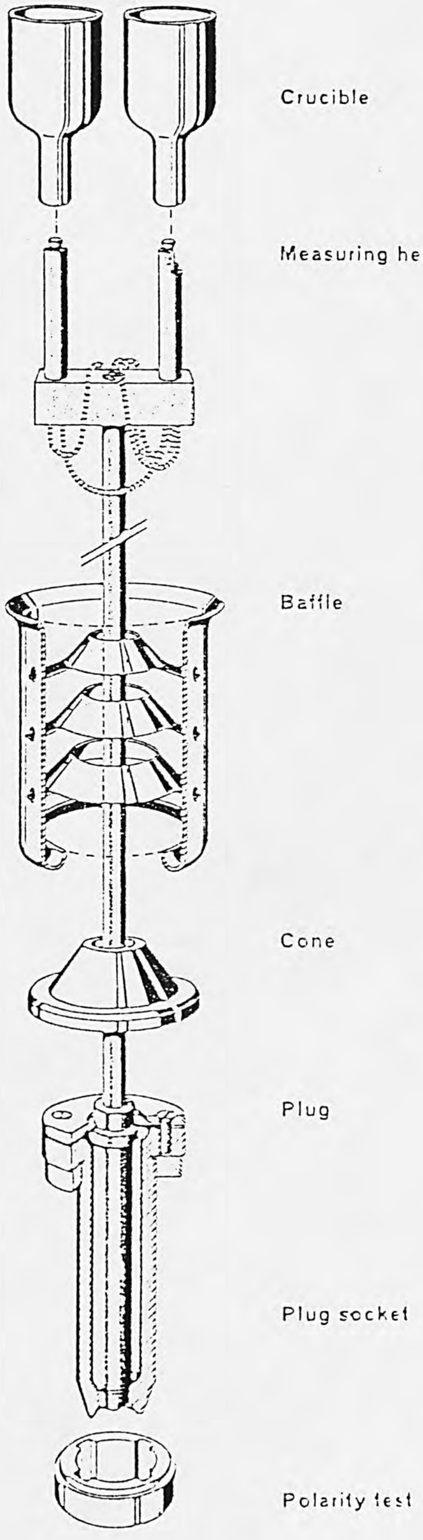


Sample holder geometry and composition are of great importance in thermal analysis. Two matched flat-bottomed platinum crucibles were used; these were 8 mm in diameter and had a short straight wall rising vertically from the bottom of the crucible. The crucibles were supported on a sintered four-hole capillary tube, which had a cross-piece 270 mm from the end, bearing two short alumina pegs, 11 mm apart. Special metal bands, which have no influence on the accuracy of weighing, were used to connect the thermocouple leads from the crucible holder to the fixed balance housing (Figure 2.6).

The flow of gas through the furnace is controlled by a pressure-regulating valve and the flow rate is metered by a "rotameter". The passage of gas between the balance housing and the reaction area is shielded by a metal baffle which rests in a socket on top of the balance housing when the crucible holder is in position. This prevents any substance which may fall from the crucible from entering and contaminating the balance housing. The gas leaving the furnace can be passed through a gas analyser if required.

The limits of error stated in this section for the various channels other than the temperature channel are lower than those which can be obtained on most other commercial thermobalances. However, although the data points can be read off the recorder chart to a high degree of accuracy, this is impaired by base-line drifts caused by defects inherent in the instrument design. The base-line drift in

Figure 2.6 Crucible holder assembly for thermoanalysis



the weight channel is caused by buoyancy effects due to the heating. In some other commercial thermobalances this has been overcome by use of two matched furnaces, one for each arm of the balance, and by symmetrical design of the balance. In the Mettler "Thermoanalyser 2" thermobalance, most of the base-line drift finishes by the time the sample reaches 75 - 100°C. The extent of this drift can be as high as 0.15 mg, which corresponds to 1.66 percent in a sample of 9 mg weight. From 100 to 1000°C, the base-line rises approximately linearly at ca. 0.03 mg/100°C.

Base-line drift also occurs on the DTA channel, which leads to errors in calculations of the peak areas of thermal changes. Because the sample is supported on a long rod inside the furnace, it is impossible to align the crucible with the axis of the furnace. As a result there is a difference in temperature between the sample and reference crucibles, which causes the base-line drift. High heating rates increase the effect significantly. Base-line drift in DTA would be reduced if a furnace with a more even temperature distribution were used.

Block schematic diagrams of the balance mechanism and of the recording and electric systems are shown in Figures 2.7 and 2.8 respectively.

Figure 2.7 Block Schematic Diagram of the Balance Mechanisms

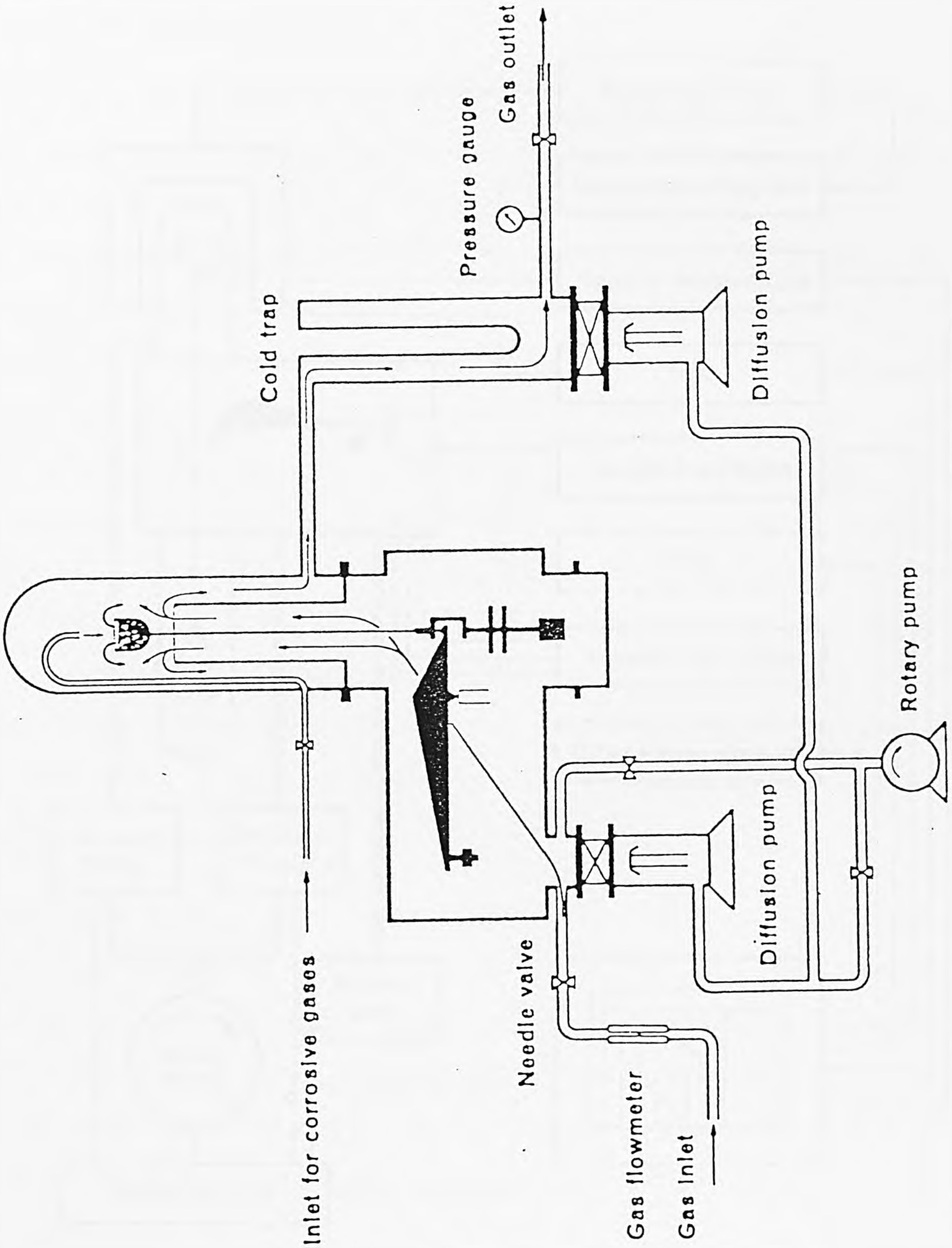
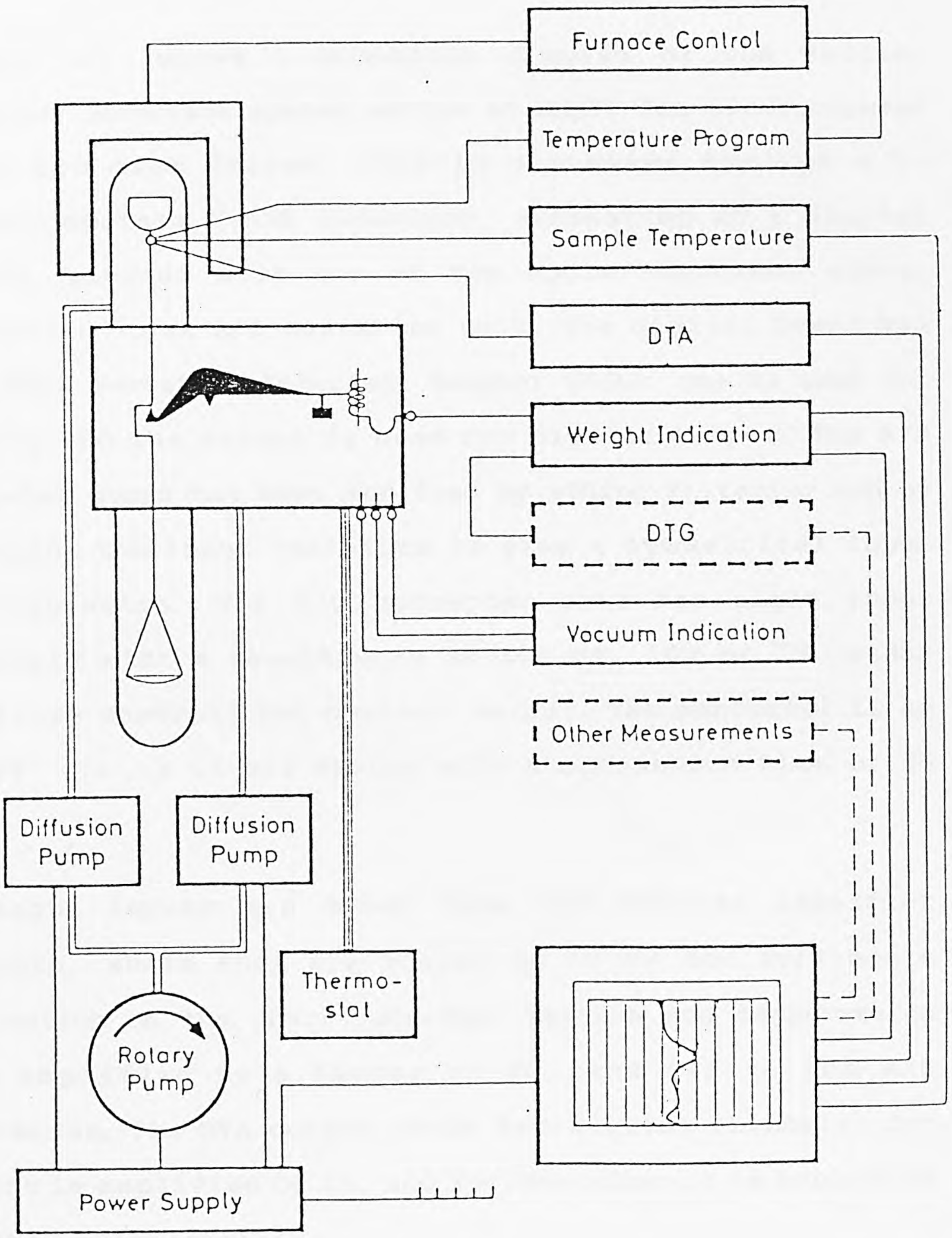


Figure 2.8 Block Schematic Diagram of the Balance Mechanism and the Recording and Electric Systems



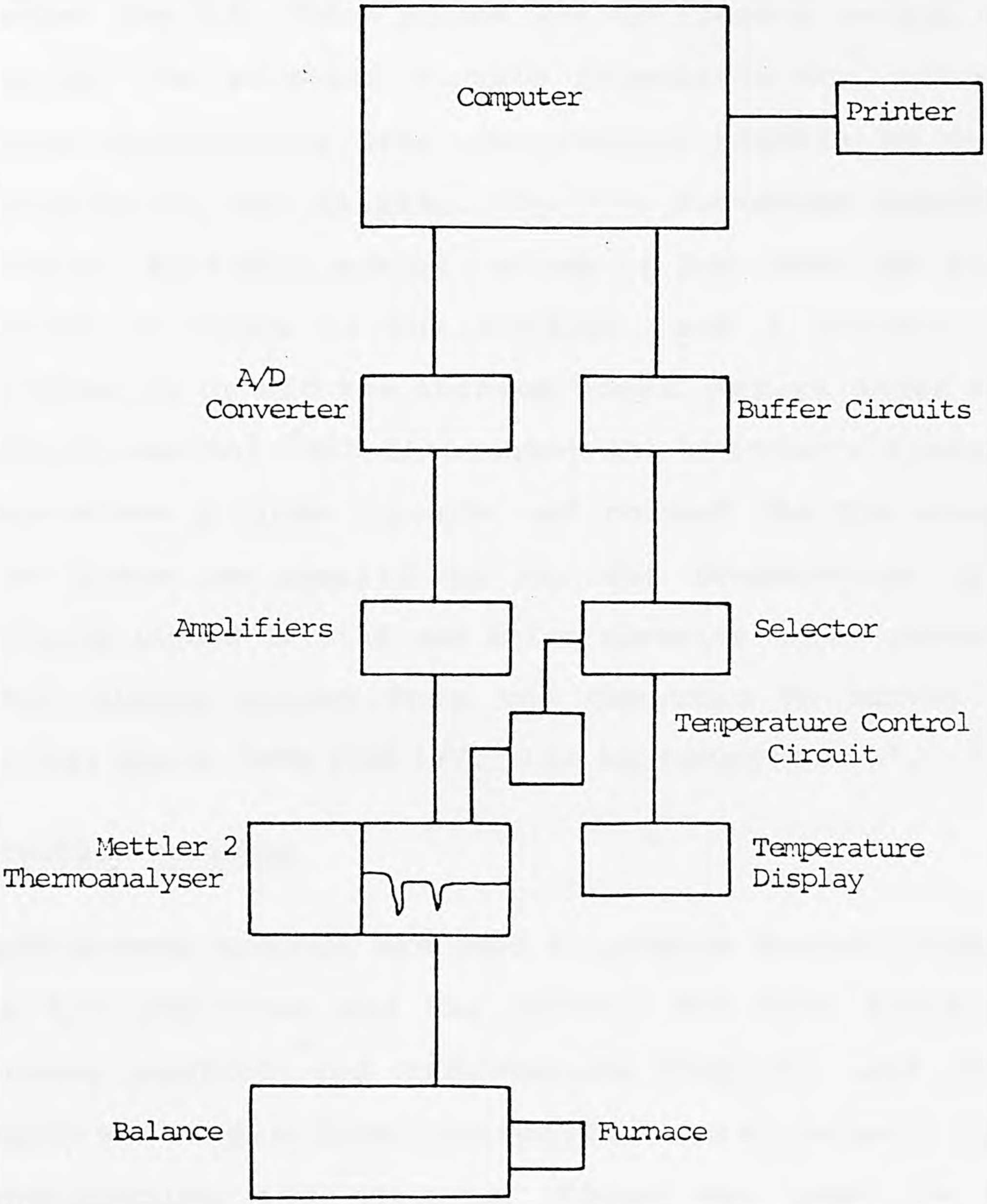
2.2.4.1 Mettler Thermobalance - Apple IIe computer interface set-up

Interface hardware:

Figure 2.9 shows a schematic diagram of the Mettler computer interface system versus an Apple IIe microcomputer with two disc drives. This is connected through a U-Microcomputers U-A/D interface, consisting of a digital board, plugged into one of the Apple expanison slots, connected to an A/D converter unit. The digital board has two 6522 Versatile Interface Adaptor (VIA); one is used for timing and the second is used for digital output. The A/D computer board has been modified by adding filtering and by changing the input resistors to give a symmetrical input configuration. The A/D converter unit has eight input channels with a sensitivity of 100 mV, 10V or 1V (under software control) for maximum output. The converter is an AD574, i.e., a 12-bit device with a conversion time of 25 μs.

Analogue inputs are taken from the Mettler amplifier outputs, where they are scaled to 10 mV for full-scale deflection on the chart recorder. Weights and temperatures are amplified by a factor of 10, and fed to the A/D converter. The DTA output feeds two digital channels; for one it is amplified by 25, and for the other it is amplified by 0.5.

Figure 2.9 Schematic Diagram of Mettler 2 - Apple IIe Computer Interface System



Digital outputs from the computer are used for furnace control and to display the approximate temperature. The computer sends alternatively control codes and data: control codes determine whether the furnace is switched on or off, whether the display is showing figures or is blank, and whether the data which follow are for furnace control or for display. The selector circuit interprets the codes, and routes appropriate data and control signals to the D/A converter or the display. The D/A converter provides a voltage, suitably scaled, which is fed into the furnace control circuits of the Mettler, and a voltage which switches on or off the furnace power. Relays added to the Mettler control unit disconnect the Mettler's timing and temperature program circuits and connect the D/A converter when power is applied to it. The temperature display contains liquid crystal and drive circuits which convert the 9-bit binary output from the computer to binary-coded decimal scale from 0 to 1275°C in increments of 5°.

Interface software

Machine-code routines are used to provide control signals to the A/D converter and the control and data signals for furnace control and temperature display, and further routines handle data collection, preliminary signal conditioning and storage. These are used in three programmes: (i) real-time graphical display of input data, for initial setting up, (ii) reading and averaging data provided by standard input conditions for calibration purposes, and (iii) control and data collection during normal running of the Mettler. Program (ii) produces a file of calibration data which are used by program (iii) to convert digital input to numerical data. Program (iii) samples data continuously and writes an appropriate selection of such data to one or more data discs.

Further programs deal with the data stored on discs: (i) a plotting program produces suitably scaled plots of any two of the data items; (ii) a printing program produces a complete listing of the data stored in a particluar disc file. A listing of the main program routines is given in the Appendix.

2.2.5 Procedure for thermoanalysis

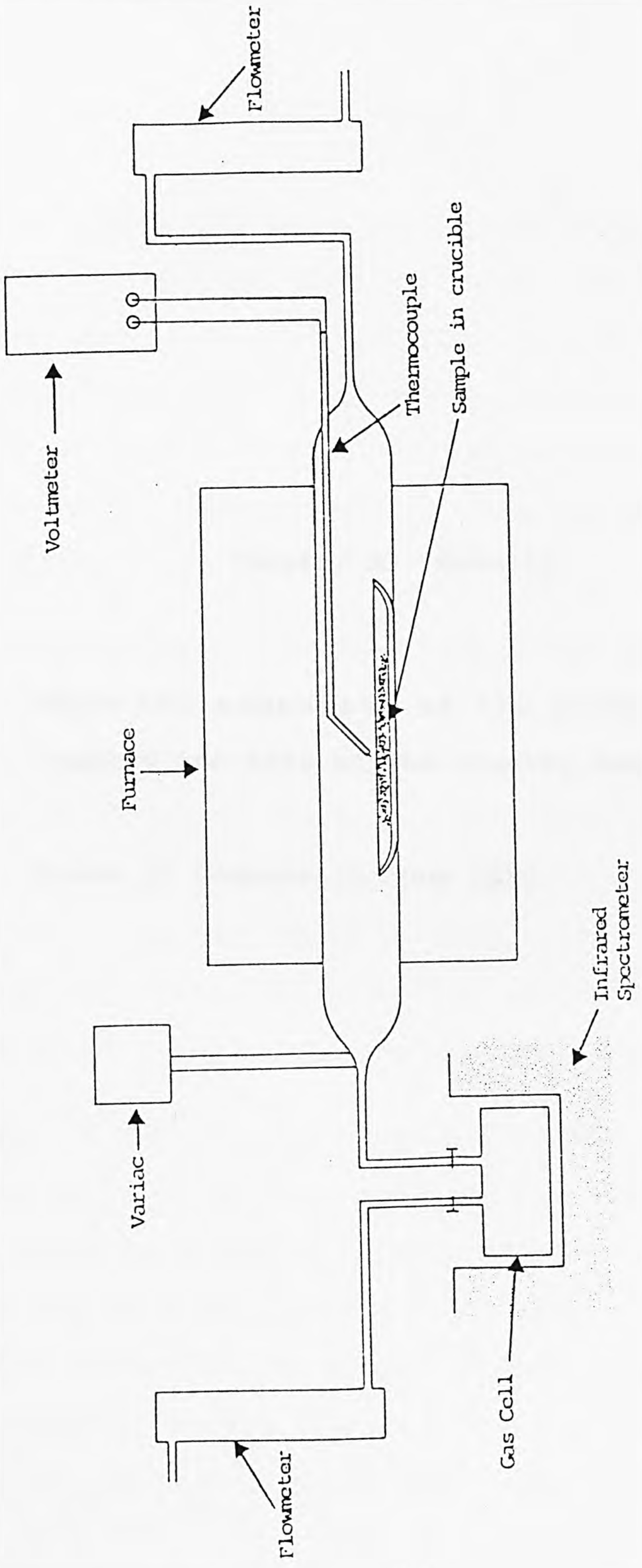
After the recorder had been switched on, the air flow rate was set at 60 cm^3 min^{-1} for a sample weight of between 8 and 10 mg. Small circles of cotton cloth (weighing ca. 4 mg) were cut via a paper hole punch from the centre of the cotton sample and placed in the crucible. The range shift on the DTG panel was set on manual and a sensitivity of 5mg min^{-1} per full scale deflection was used throughout. The range used for differential thermal analysis was 200 μV, and for temperature readings it was 10mV; the heating rate used throughout was 5° min^{-1}. The results of thermogravimetric and differential thermal analysis runs were printed by means of the computer software mentioned previously.

2.2.6 Infrared measurement of gaseous combustion products

A silica tube, 40 cm in length and 2.5 cm in diameter, was mounted horizontally in an electric furnace capable of reaching temperatures of 700°C with the heating rate controlled by a Variac as shown in Figure 2.10. A suitable Variac setting was chosen such that a heating rate of 6°/min was achieved over the main decomposition range of interest. For cellulose this was 150 - 480°C.

The flow rate of gaseous air or nitrogen was 60 or 100 cm^3 min^{-1} and was measured with a flowmeter. The gaseous products were carried from the furnace by a ball-and-socket connection to a 10 cm path length gas cell fitted with sodium chloride windows. The temperature of the furnace was measured by means of a chrome/alumel thermocouple and the mV output was converted into the temperature equivalent. A total sample size of 1g was used routinely and placed in a ceramic combustion boat which was located centrally in the furnace. Typically 10 - 15 wt per cent of flame retardant was used. Comparisons were made between the two flow rates and this gave complementary information to facilitate the identification and presence of the species observed. The gas phase infrared spectra were recorded on a Perkin Elmer 257 grating infrared spectrometer with air as the reference material.

Figure 2.10 Apparatus for Gas-phase Infra-red Identification of Gaseous Combustion Products



Chapter 3 - Results

Upon the education of the people of this country the fate of the country depends.

House of Commons 15 June 1874

3.1 The effects of red phosphorus and other additives on the thermal behaviour of cellulose

3.1.1 Effects on Flammability

Figure 3.1 shows the effect of temperature on the LOI of cotton cloth on its own over the range 15 - 140°C. It can be seen that, as the cellulose approaches its temperature of decomposition, the LOI falls progressively as less oxygen is required to sustain combustion. These results agree with those found for other textiles (e.g. Hendrix, Drake and Reeves 1970).

It can be seen that the LOI of conditioned cotton cloth, measured at room temperature, is 18.2 and the results in Table 3.1 show that the addition of red phosphorus raises the value to 23.1 at a loading of 16 wt percent, an increase of approximately 5 LOI units. Above this loading the red phosphorus causes the cloth to catch fire as it is ignited during the LOI measurement, so that there is little further increase in LOI with increasing phosphorus concentration.

In order to obtain a more significant decrease in flammability than is possible with red phosphorus alone, studies were also made of the effects of a number of nitrogen and halogen co-additives. The nitrogen compounds used were melamine, ammonium formate, ethylene urea, hexamethylenetetramine, N-methylimidazole and barbituric acid, and the halogen compound was decabromobiphenyl.

Figure 3.1 The effect of temperature on the flammability of cellulose-cotton cloth

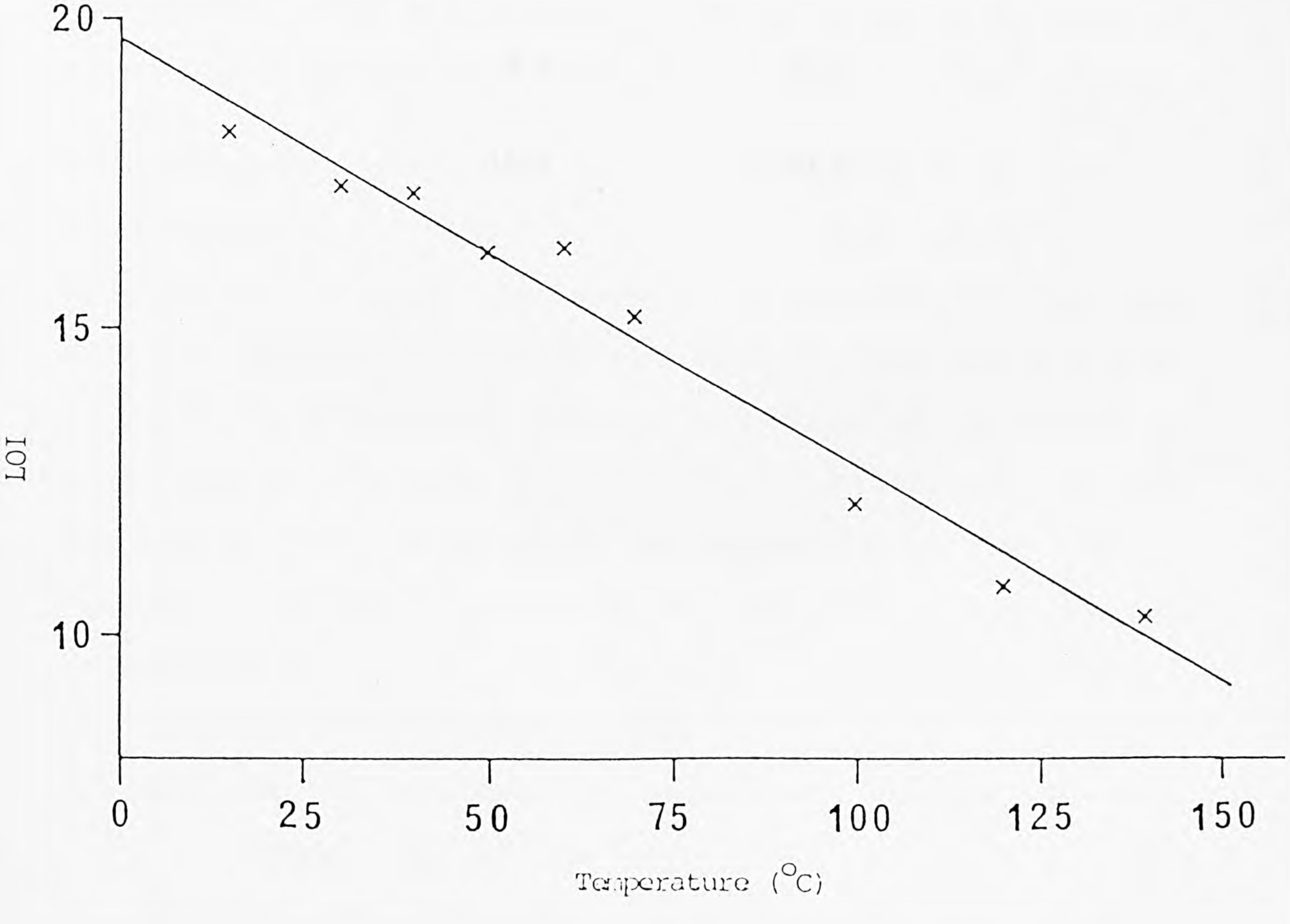


Table 3.1 The effect of red phosphorus on the flammability of cotton cloth

Red phosphorus (wt %)	LOI
0	18.2
3.0	20.3
9.8	22.7
16.4	23.1

Melamine was shown, however, to be far more effective than the other nitrogen compounds, which will be dealt with later. Most measurements were therefore made with melamine.

Although a very large number of results was obtained (102) the general findings are illustrated by the few typical examples shown in Table 3.2. Thus addition of 13 wt percent decabromobiphenyl further raises the LOI of a cellulose - red phosphorus system to 24.6, whereas melamine at a loading of 14.9 wt percent increases it to 26.3. Combinations of decabromobiphenyl and melamine with red phosphorus result in an even greater rise to 27.2.

Measurements were also made of the effect of varying compositions of the cellulose - red phosphorus - decabromobiphenyl and cellulose - red phosphorus - melamine systems. Compositions were chosen such that they could be fitted to a contour map or triangular diagram of predetermined vertices. Only equilateral triangles were used in order to facilitate visual interpretation of the results. Typically compositions were spread over the ranges bounded by the points:

A: 100 wt percent cellulose

B: 75 wt percent cellulose, 25 wt percent red phosphorus (additive x_1),

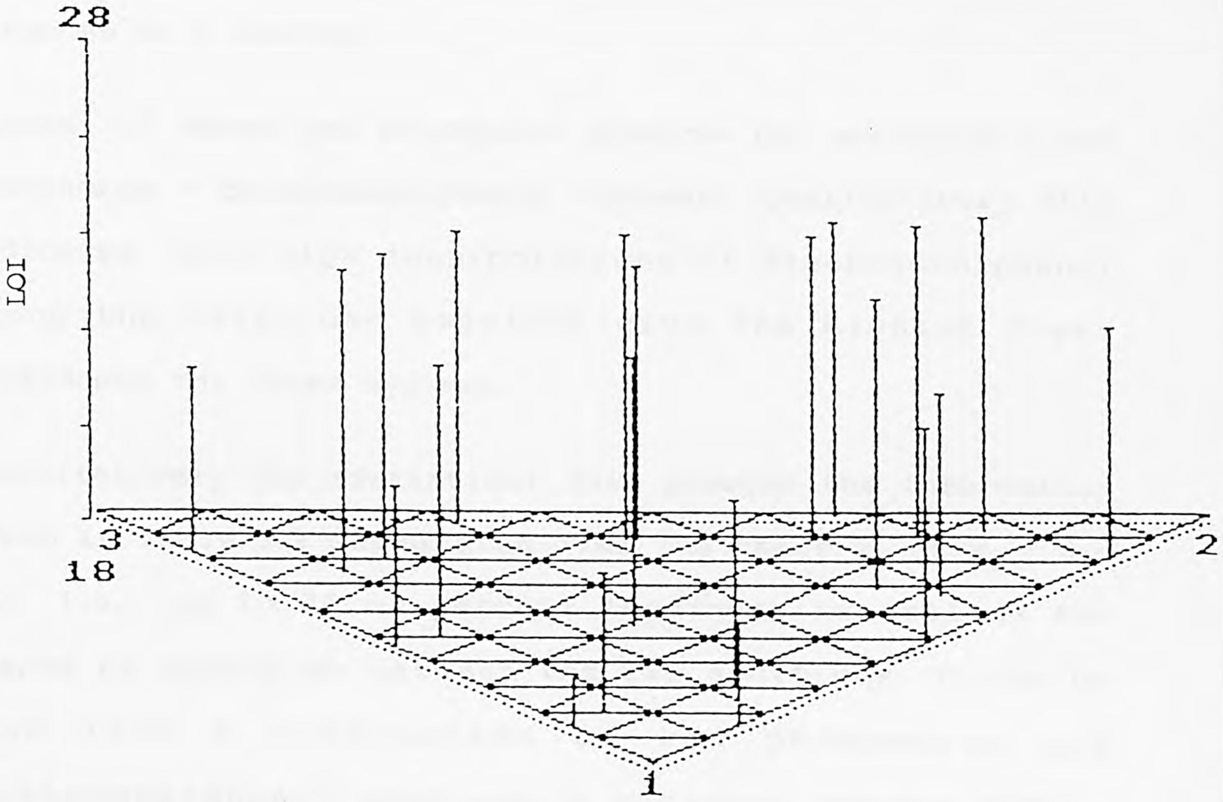
C: 75 wt percent cellulose, 25 wt percent decabromobiphenyl (additive x_2),

Figure 3.2 thus shows compositions for a total additive

Table 3.2 The effect of decabromobiphenyl and **melamine** on the flammability of the cellulose - red phosphorus system

Red phosphorus (wt %)	Decabromobiphenyl (wt %)	Melamine (wt %)	LOI
-	-	-	18.2
9.8	-	-	22.7
8.5	13.0	-	24.6
(-	12.8	-	21.6)
9.2	-	11.3	26.3
(-	-	14.9	21.7)
(-	7.5	11.6	26.1)
8.1	8.1	7.2	27.2

Figure 3.2 Triangular diagram showing individual LOI values as bars above a plane with respect to concentration of individual additives for the red phosphorus - decabromobiphenyl system



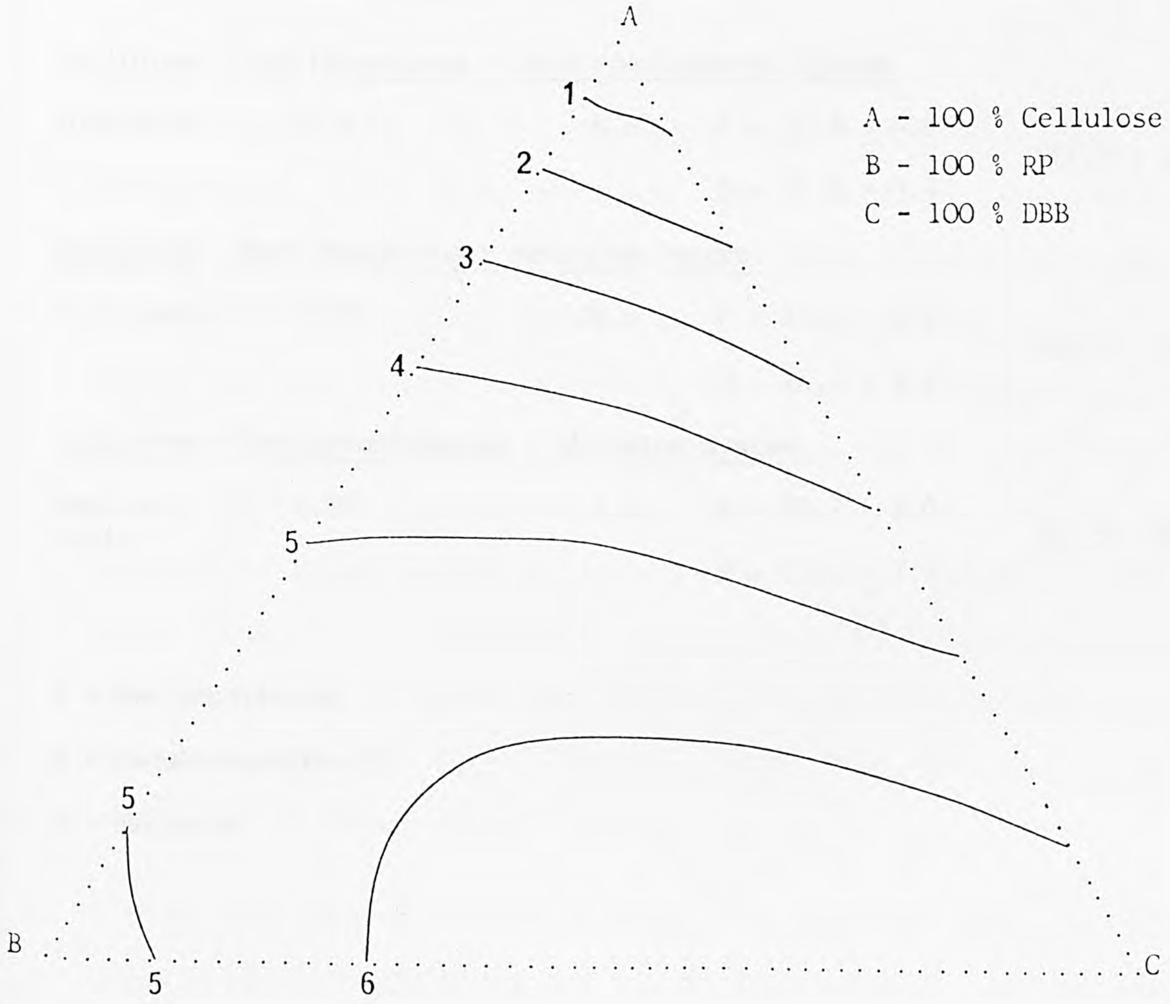
Vertex 1 is Cellulose (cotton cloth)
Vertex 2 is 25% Red phosphorus in cellulose
Vertex 3 is 25% Decabromobiphenyl in cellulose

loading of 25 wt percent. These data were fitted by the polynomial function described in Section 2.2.3 and the coefficients for linear, quadratic, reduced cubic and full cubic equations were calculated by the least-squares procedure. The computer programme used then conducts a statistical analysis of the observed values by comparing each with the values calculated from the coefficients at that particular composition and then plots the calculated response as a contour.

Figure 3.3 shows the triangular diagram for cellulose - red phosphorus - decabromobiphenyl systems. Qualitatively this indicates that high incorporations of decabromobiphenyl along the cellulose baseline give the highest flame retardance for these systems.

Quantitatively the statistical data provide the information given in Table 3.3 calculated over the range x_1 or x_2 = 0 - 0.2, i.e., up to 20 wt percent loadings, as well as the degree of synergism between the two additives. It can be seen that a combination of red phosphorus and decabromobiphenyl produces a somewhat greater flame-retardant effect than would be expected from the individual contributions of the two constituents on their own. The degree of synergism is 141.7 ± 62.5 which, for a loading of 10 wt percent of each additive, is equivalent to a rise of 1.4 LOI units. The individual components also contribute to the overall increase in LOI. In the case of the cellulose - red phosphorus - decabromobiphenyl system, red phosphorus

Figure 3.3 Triangular diagram showing variation of LOI with composition for cellulose - red phosphorus - decabromobiphenyl systems



LOI values: 0 = 18.2, 1 = 19.2, 2 = 20.2, 3 = 21.2, 4 = 22.2, 5 = 23.2, 6 = 24.2, 7 = 25.2, 8 = 26.2, 9 = 27.2, 10 = 28.2.

Table 3.3 Quantitative data for cellulose - binary additive systems containing red phosphorus - decabromobiphenyl and melamine

Order	Root Mean square difference (σ)	Sequential F-test ratio	Average coefficents over range 0-0.2	Synergism
Cellulose - Red Phosphorus - Decabromobiphenyl System				
Quadratic	0.71	6.6	P = 37.8 ± 4.6	141.7 ± 62.5
			B = 27.5 ± 3.9	
Cellulose - Red Phosphorus - Melamine System				
Full cubic	0.70	26.4	P = 35.4 ± 6.8	235.0 ± 116.6
			N = 24.3 ± 5.6	
Cellulose - Decabromobiphenyl - Melamine System				
Reduced cubic	0.89	1.4	B = 20.7 ± 8.0	301.2 ± 95.8
			N = 27.1 ± 7.9	

P = Red phosphorus

B = Decabromobiphenyl

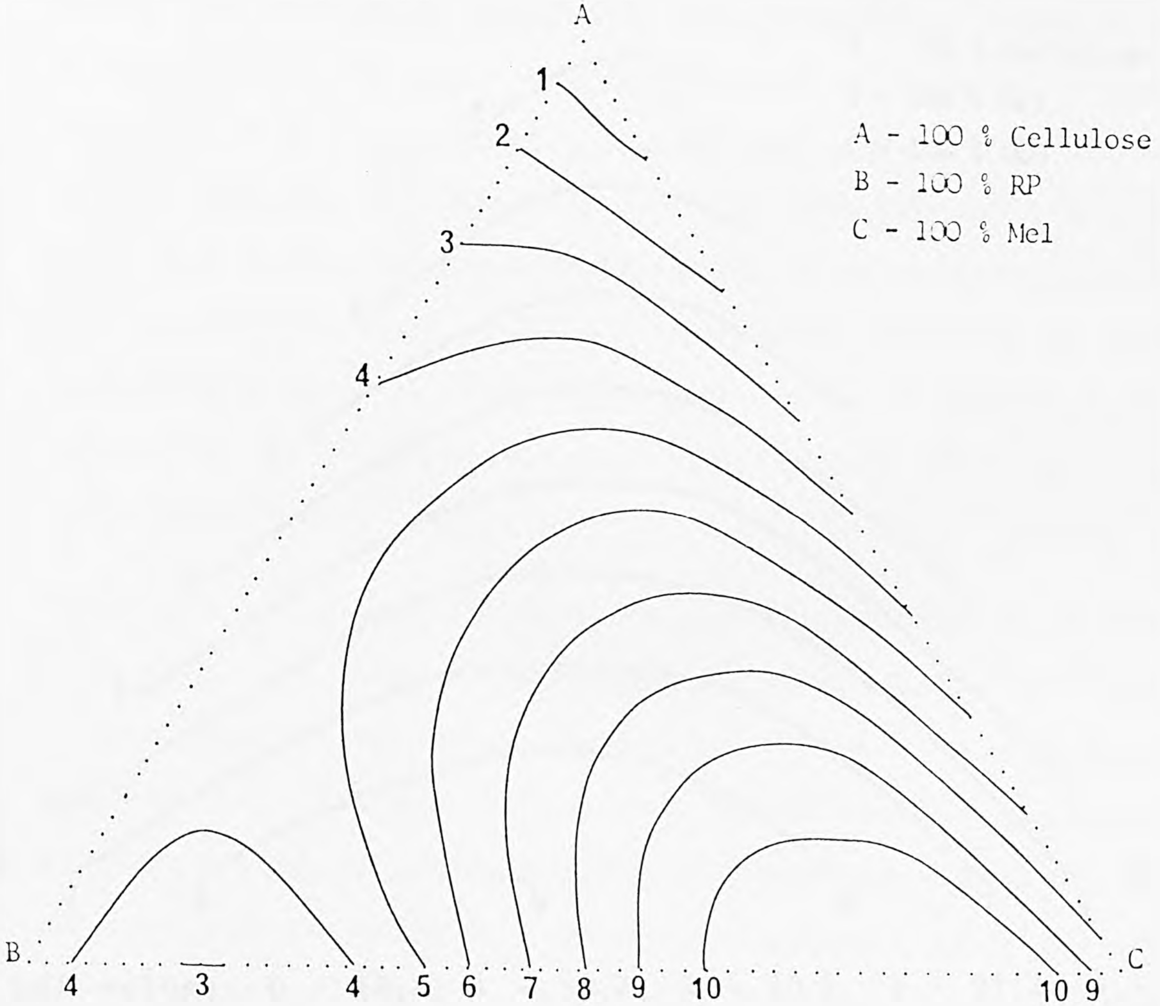
N = Melamine

contributes a rise of 3.8 LOI units and decabromobiphenyl a rise of 2.8 units (Table 3.3) at a loading of 10 wt percent of each additive. Thus the total effect is the summation of these including the synergism factor of 1.4 to give a value of 8.0 LOI units. Table 3.2 shows that the system raises the LOI by 6.4 LOI units which is comparable to the calculated value of 8.0 LOI units.

Figure 3.4 shows the triangular diagram for cellulose - red phosphorus - melamine systems. Qualitatively this shows a region of high flame retardance at high melamine loadings along the cellulose baseline. At high red phosphorus loadings the flame retardancy is seen to decrease, as is observed experimentally. Quantitative data are given in Table 3.3 for which it can be seen that there is a reasonably good degree of synergism with a value of 235.0 ± 116.6. This also shows that a combination of red phosphorus and melamine produces the greatest flame-retardant effect, raising the LOI by 11 points and thus being the most effective system studied during this work.

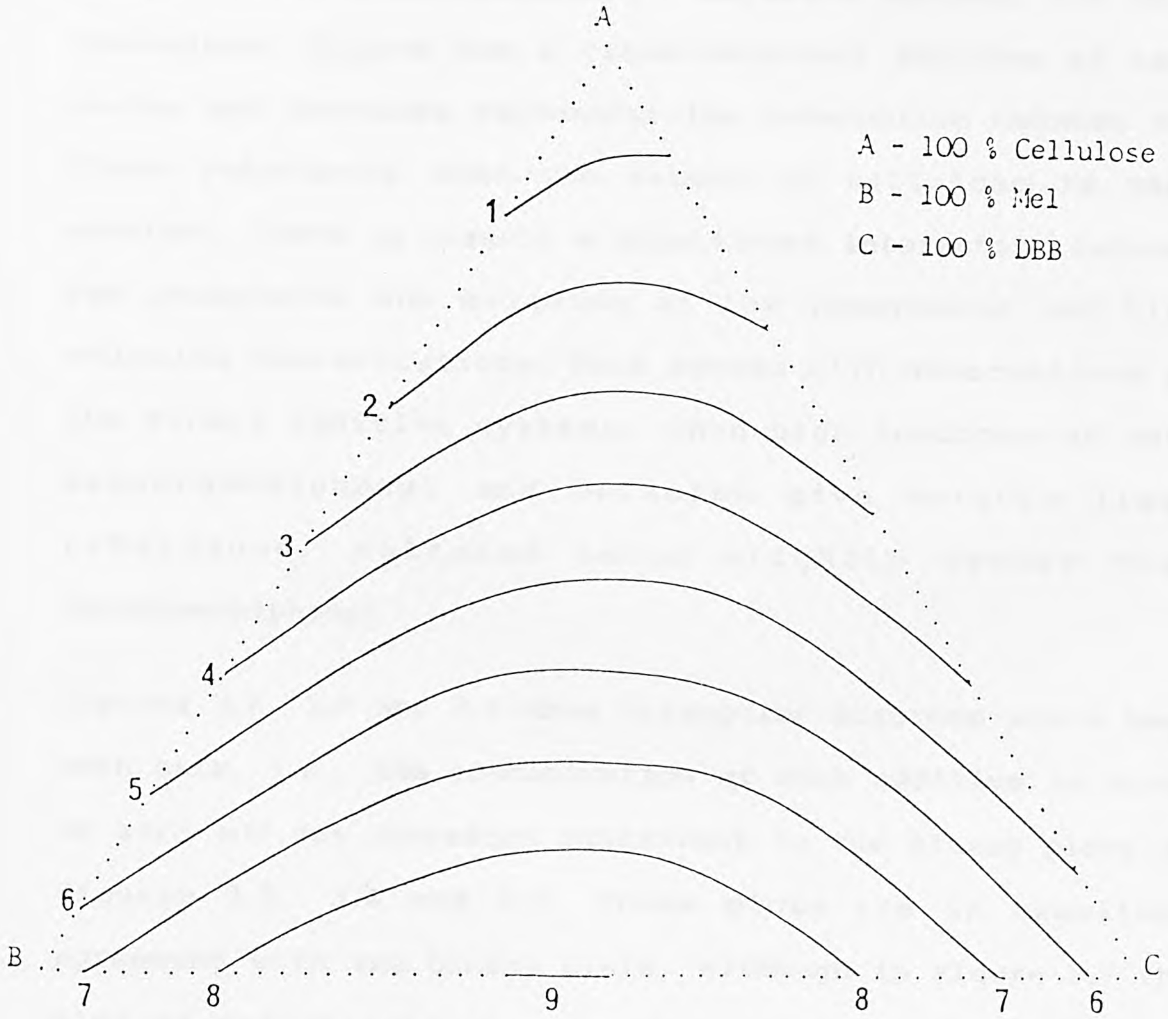
Figure 3.5 shows the triangular diagram for the cellulose binary additive mixture of decabromobiphenyl and melamine. Qualitatively the diagram shows that melamine is a slightly more effective flame retardant than decabromobiphenyl at higher loadings. A degree of synergism is evident due to the increase in LOI along the cellulose baseline. This is further confirmed by quantitative data given in Table 3.3, which show a value of 301.0 ± 95.8 for the synergistic

Figure 3.4 Triangular diagram showing variation of LOI with composition for cellulose - red phosphorus - melamine systems



LOI values: 0 = 18.2, 1 = 19.2, 2 = 20.2, 3 = 21.2, 4 = 22.2, 5 = 23.2, 6 = 24.2, 7 = 25.2, 8 = 26.2, 9 = 27.2, 10 = 28.2.

Figure 3.5 Triangular diagram showing variation of LOI with composition for cellulose - melamine - decabromobiphenyl systems



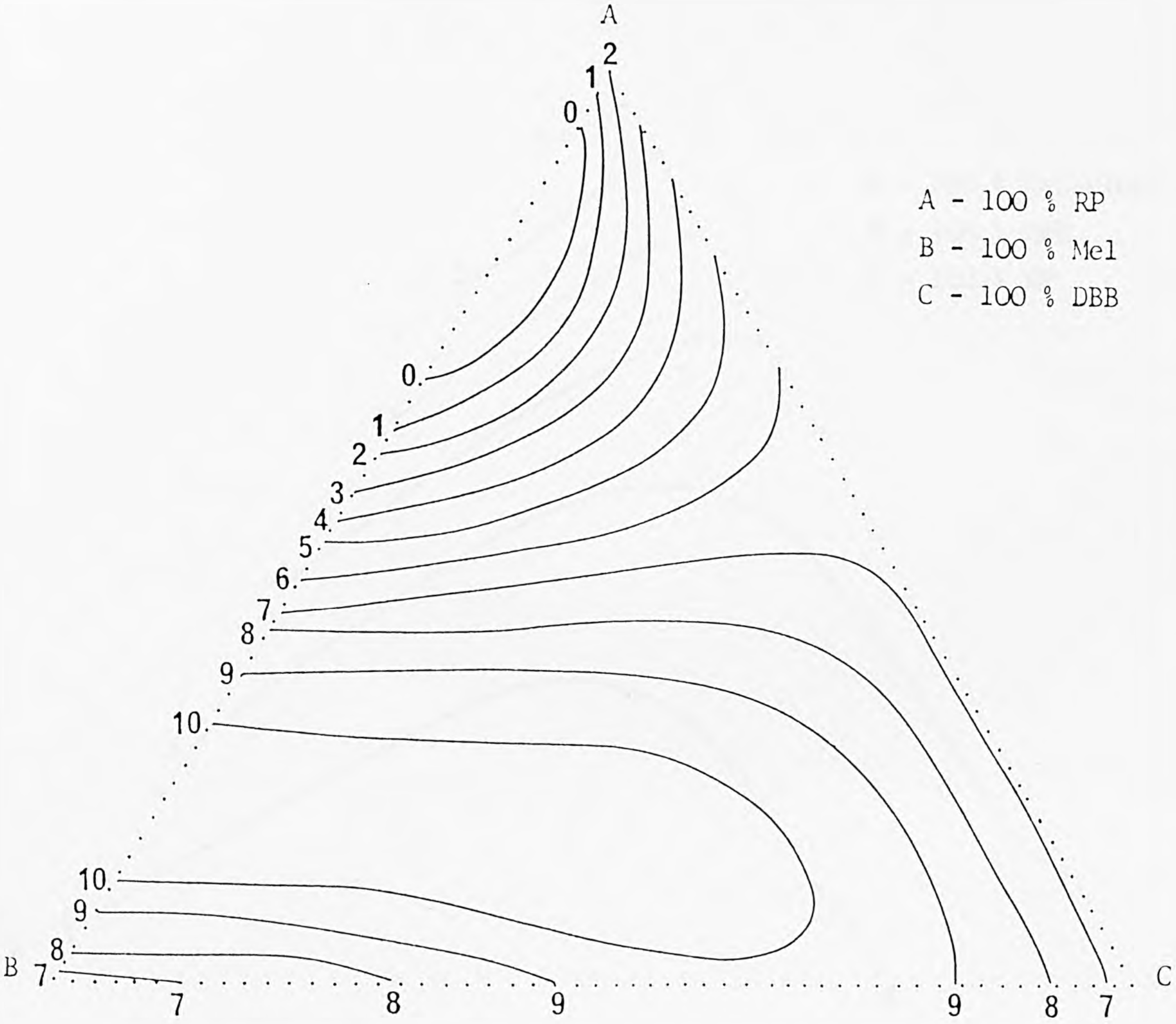
LOI values: 0 = 18.2, 1 = 19.2, 2 = 20.2, 3 = 21.2, 4 = 22.2, 5 = 23.2, 6 = 24.2, 7 = 25.2, 8 = 26.2, 9 = 27.2, 10 = 28.2.

interaction. In the case of the cellulose ternary additive system the data have to be arranged in the form of a tetrahedron. Any given triangular diagram would then represent a face of the tetrahedron.

Figure 3.6 shows the triangular diagram for cellulose - red phosphorus - decabromobiphenyl - melamine systems. The two-dimensional diagram has a flame-retardant additive at each vertex and therefore represents the interaction between the flame retardants when the amount of cellulose is kept constant. There is clearly a significant interaction between red phosphorus and melamine at low phosphorus and high melamine concentrations. This agrees with observations on the binary additive systems, when high loadings of both decabromobiphenyl and melamine give notable flame retardance, melamine being slightly better than decabromobiphenyl.

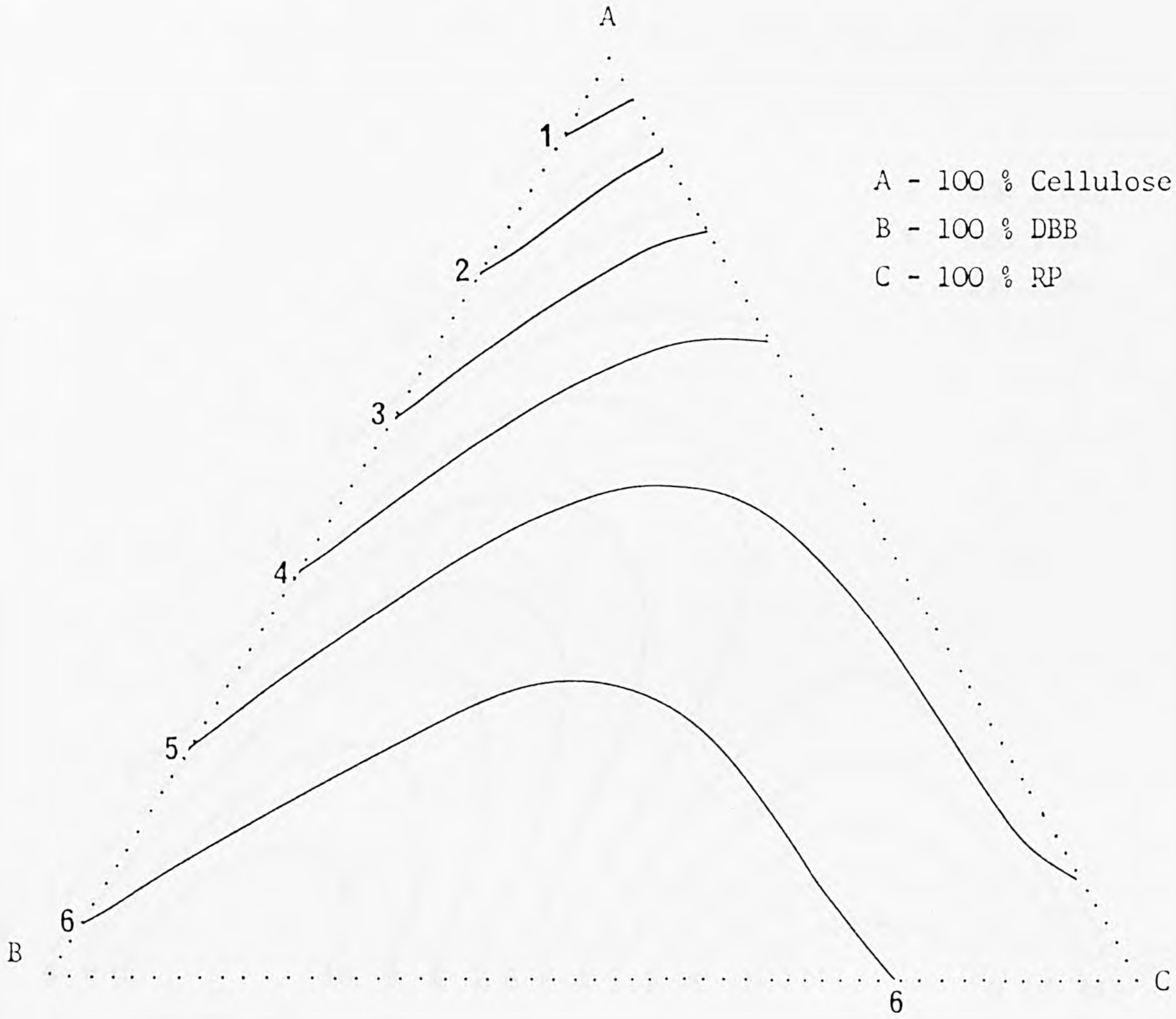
Figures 3.7, 3.8 and 3.9 show triangular diagrams which keep each axis, i.e., the concentration of each additive in turn, at zero and are therefore equivalent to the binary plots in Figures 3.3, 3.4 and 3.5. These plots are in excellent agreement with the binary plots, although in Figure 3.7 the plot of red phosphorus - decabromobiphenyl is the least representative showing a slightly lower contour than expected. This may be due to a lack of data at high phosphorus loadings.

Figure 3.6 Triangular diagram showing variation of LOI with composition for red phosphorus - decabromobiphenyl - melamine ternary additive systems



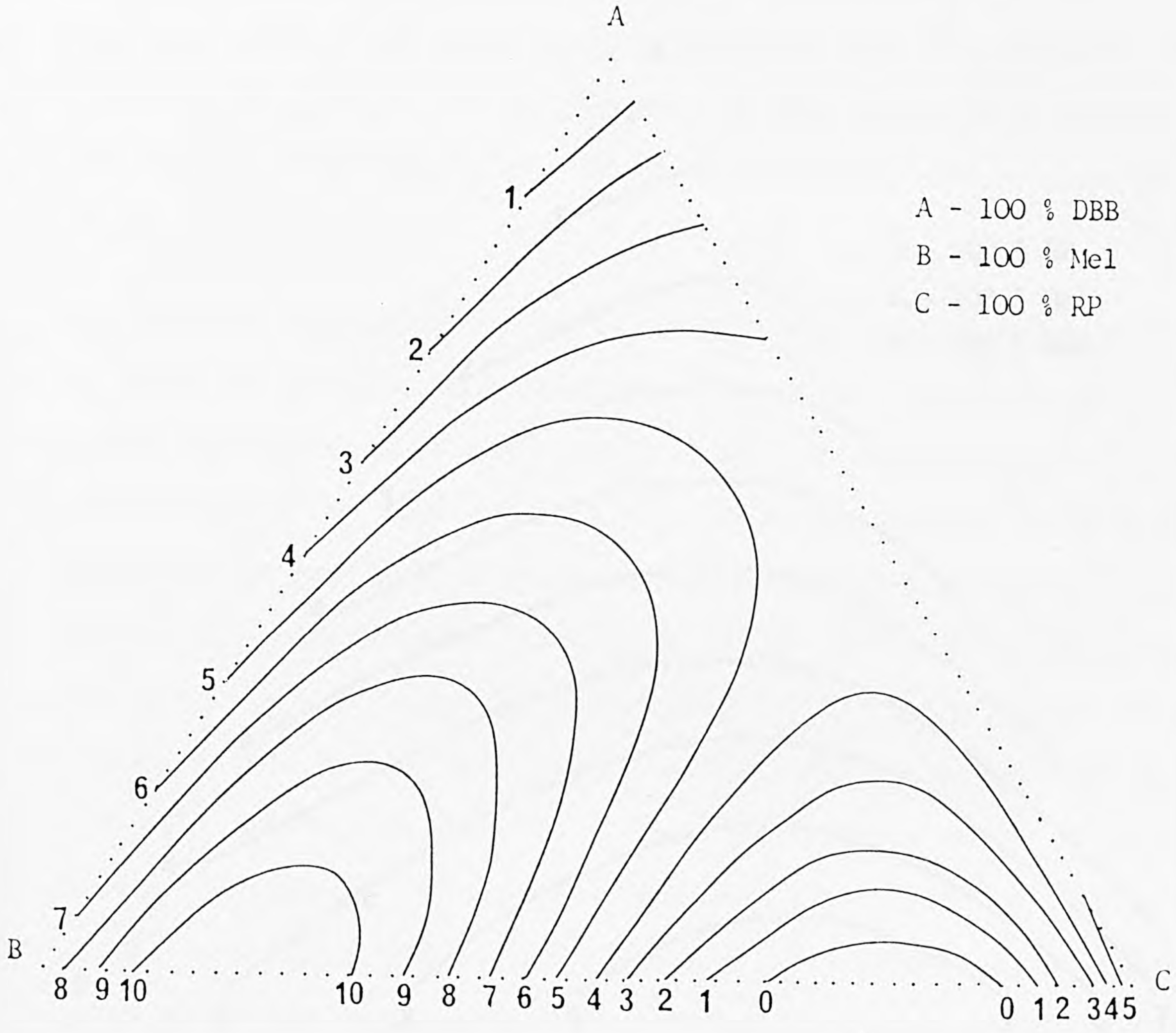
LOI values: 0 = 18.2, 1 = 19.2, 2 = 20.2, 3 = 21.2, 4 = 22.2, 5 = 23.2, 6 = 24.2, 7 = 25.2, 8 = 26.2, 9 = 27.2, 10 = 28.2.

Figure 3.7 Triangular diagram showing variation of LOI with composition for the cellulose - ternary additive system - red phosphorus - decabromobiphenyl - melamine: projection of face with melamine held constant at zero



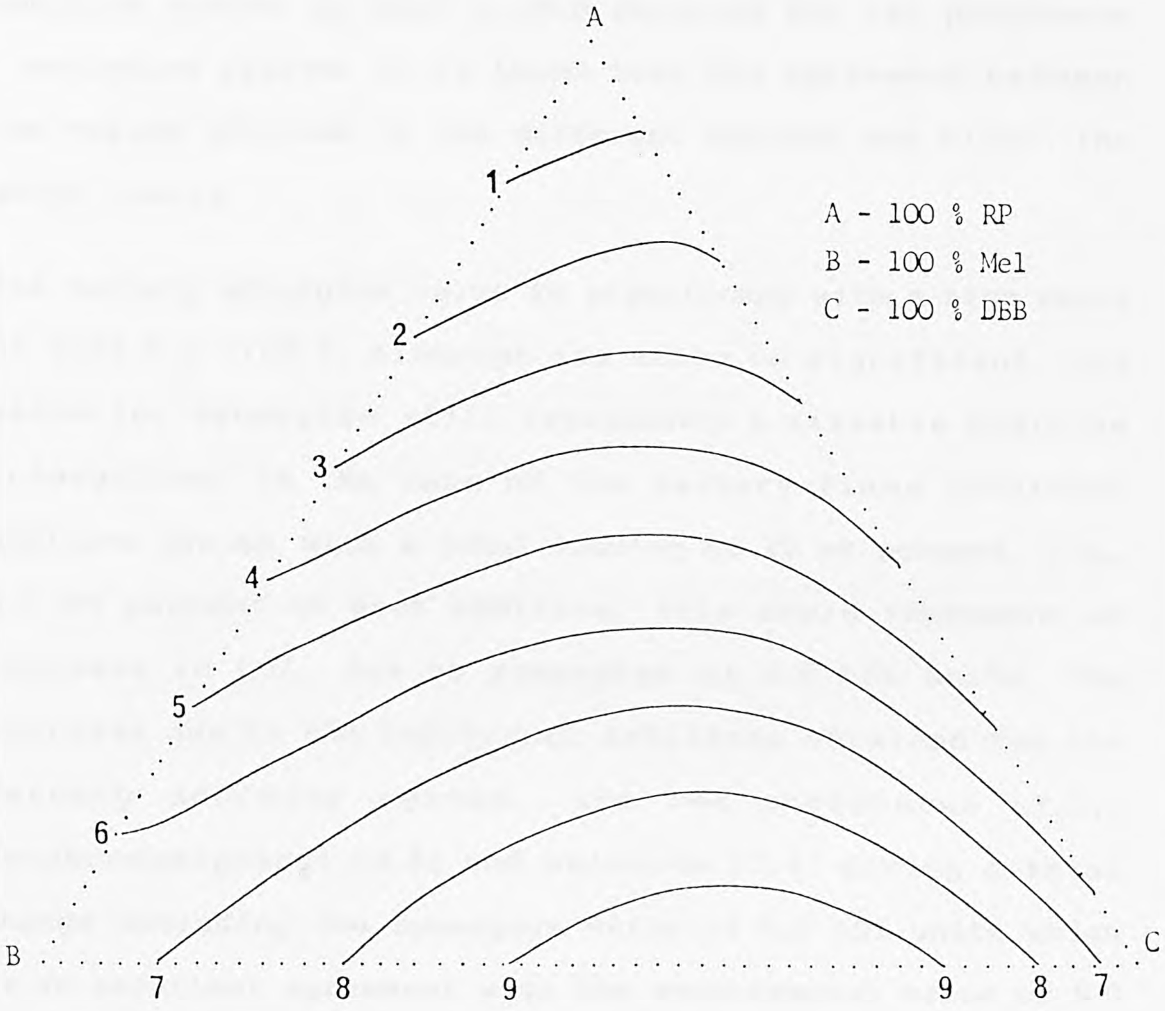
LOI values: 0 = 18.2, 1 = 19.2, 2 = 20.2, 3 = 21.2, 4 = 22.2, 5 = 23.2, 6 = 24.2, 7 = 25.2, 8 = 26.2, 9 = 27.2, 10 = 28.2.

Figure 3.8 Triangular diagram showing variation of LOI with composition for the cellulose - ternary additive system - red phosphorus - decabromobiphenyl - melamine: projection of face with decabromobiphenyl held constant at zero



LOI values: 0 = 18.2, 1 = 19.2, 2 = 20.2, 3 = 21.2, 4 = 22.2, 5 = 23.2, 6 = 24.2, 7 = 25.2, 8 = 26.2, 9 = 27.2, 10 = 28.2.

Figure 3.9 Triangular diagram showing variation of LOI with composition for the cellulose - ternary additive system - red phosphorus - decabromobiphenyl - melamine: projection of face with red phosphorus held constant at zero



LOI values: 0 = 18.2, 1 = 19.2, 2 = 20.2, 3 = 21.2, 4 = 22.2, 5 = 23.2, 6 = 24.2, 7 = 25.2, 8 = 26.2, 9 = 27.2, 10 = 28.2.

Table 3.4 shows the quantitative data for cellulose - red phosphorus - decabromobiphenyl - melamine ternary flame retardant system. On examination of the coefficients for each additive, it can be seen that they are in reasonable agreement with the values shown earlier in Table 3.3. The highest synergism value for a binary flame retardant additive system is 336.7 ± 68.8 obtained for red phosphorus - melamine system. It is found that the agreement between the values obtained in the different systems are within the error limits.

The ternary synergism value is significant with a high value of 3053.9 ± 1105.7. Although the error is significant, the value for synergism still represents a sizeable positive interaction. In the case of the ternary flame retardant additive system with a total loading of 20 wt percent, i.e., 6.7 wt percent of each additive, this would represent an increase in LOI, due to synergism of 0.9 LOI units. The increase due to the individual additives obtained for the ternary additive system, are red phosphorus (3.3), decabromobiphenyl (2.5) and melamine (2.4) giving a total change including the synergism value of 9.1 LOI units which is in excellent agreement with the experimental value of 9.0 LOI units obtained for the ternary additive system shown in Table 3.2.

Figures 3.10 and 3.12 show cross-sectional slices through the tetrahedron which correspond to constant values of coordinate x_1, i.e., cellulose at 0.25, 0.5 and 0.75 which

Table 3.4 Quantitative data for the cellulose - ternary flame-retardant additive mixtures of red phosphorus - decabromobiphenyl - melamine and a summary of data obtained for the cellulose binary flame-retardant mixtures

R.M.S. difference (σ) = 0.9

Sequential F-test ratio = 38.2

Average coefficient over range 0 - 0.2

Individual flame retardant additives:

Red phosphorus	32.9 ± 5.2
Decabromobiphenyl	25.3 ± 4.8
Melamine	24.0 ± 4.9

Binary flame retardant additive combinations:

Red phosphorus/Decabromobiphenyl	184.2 ± 71.1
Red phosphorus/Melamine	336.7 ± 68.8
Decabromobiphenyl/Melamine	265.6 ± 71.4

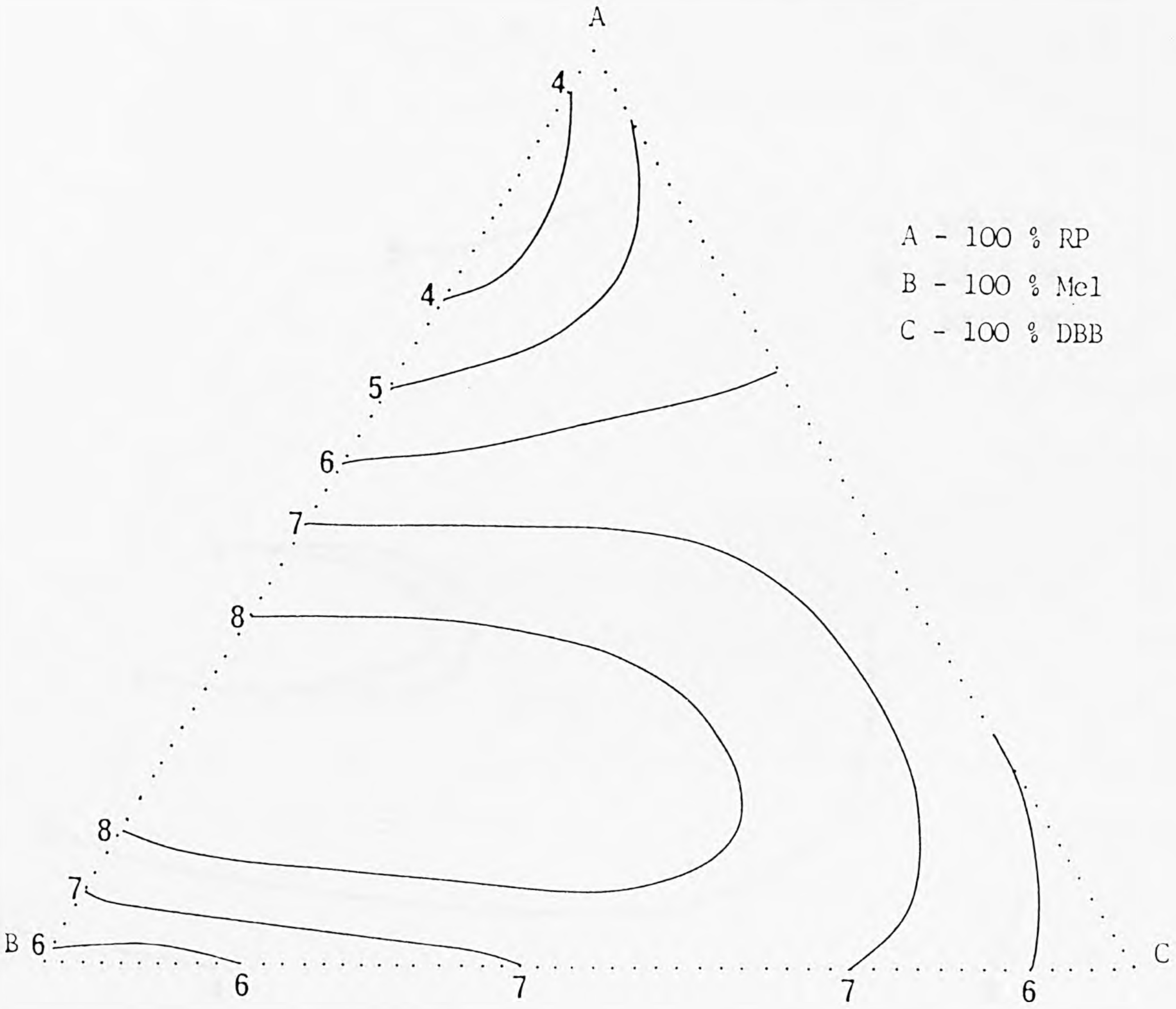
Ternary flame retardant additive combinations:

Red phosphorus/Decabromobiphenyl/Melamine	3053.9 ± 1105.7

Summary of flame retardant additive combinations obtained from binary systems:

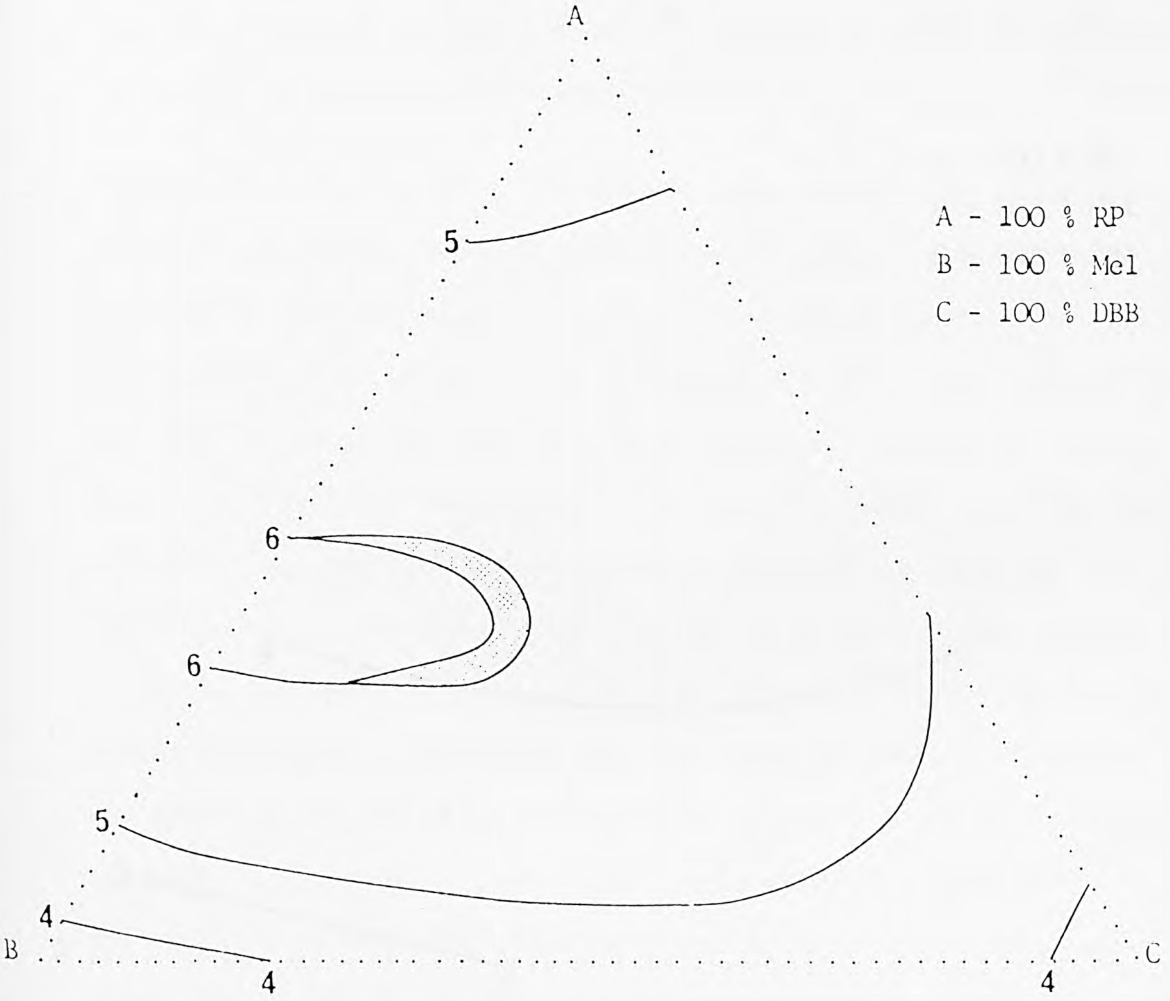
Red phosphorus/Decabromobiphenyl	141.7 ± 62.5
Red phosphorus/Melamine	301.2 ± 95.8
Decabromobiphenyl/Melamine	235.0 ± 116.6

Figure 3.10 Triangular diagram representing a slice through the tetrahedron with cellulose being held constant at 81.25% and showing the variation of LOI with composition for the cellulose - ternary additive system - red phosphorus - decabromobiphenyl - melamine



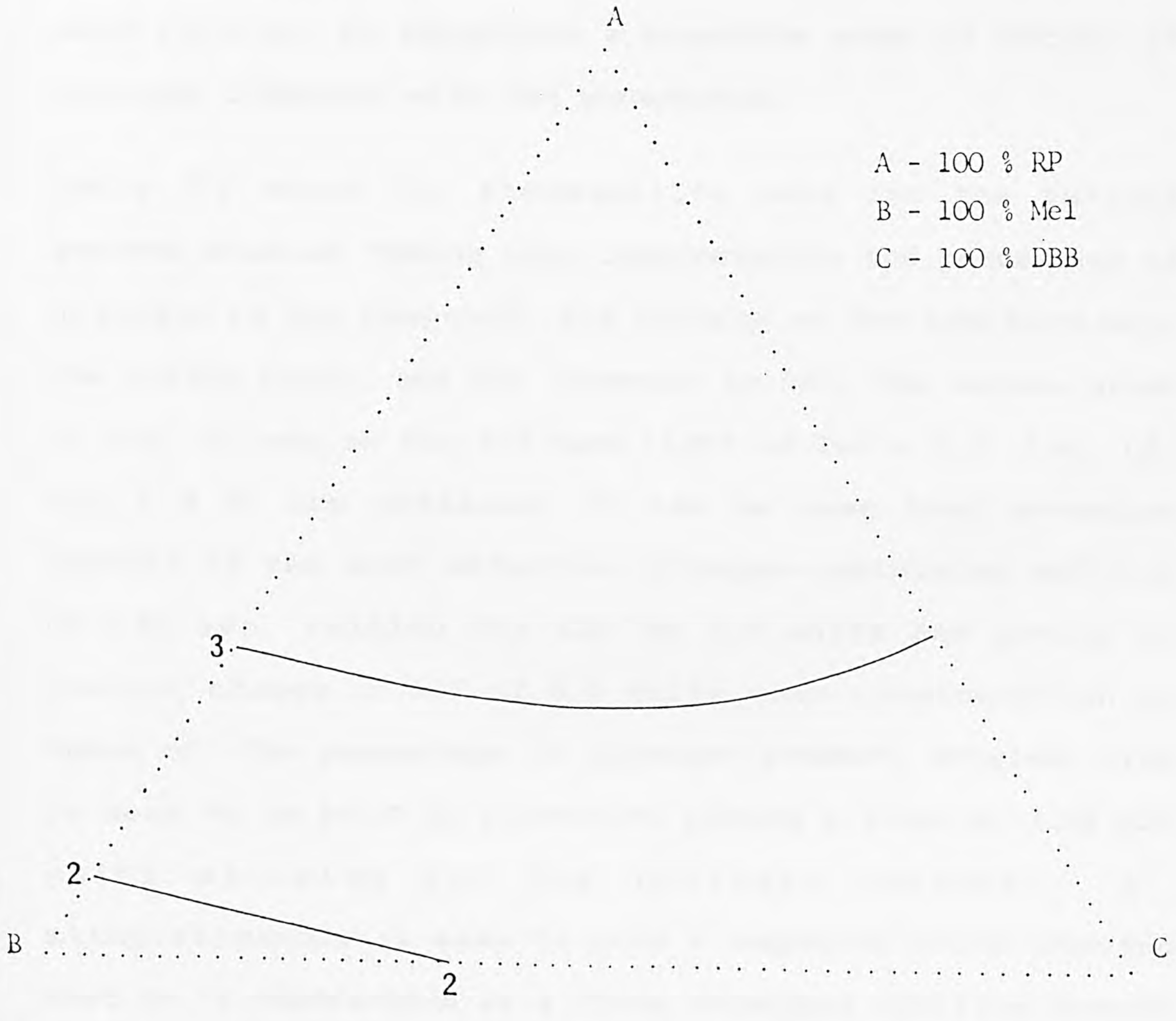
LOI values: 0 = 18.2, 1 = 19.2, 2 = 20.2, 3 = 21.2, 4 = 22.2, 5 = 23.2, 6 = 24.2, 7 = 25.2, 8 = 26.2, 9 = 27.2, 10 = 28.2.

Figure 3.11 Triangular diagram representing a slice through the tetrahedron with cellulose being held constant at 87.50%, and showing the variation of LOI with composition for the cellulose ternary additive system - red phosphorus - decabromobiphenyl - melamine



LOI values: 0 = 18.2, 1 = 19.2, 2 = 20.2, 3 = 21.2, 4 = 22.2, 5 = 23.2, 6 = 24.2, 7 = 25.2, 8 = 26.2, 9 = 27.2, 10 = 28.2.

Figure 3.12 Triangular diagram representing a slice through the tetrahedron with cellulose being held constant at 93.75%, and showing the variation of LOI with composition for the cellulose - ternary additive system - red phosphorus - decabromobiphenyl - melamine



LOI values: 0 = 18.2, 1 = 19.2, 2 = 20.2, 3 = 21.2, 4 = 22.2, 5 = 23.2, 6 = 24.2, 7 = 25.2, 8 = 26.2, 9 = 27.2, 10 = 28.2.

at a 25 wt percent loading total of additive corresponds to cellulose values of 81.25, 87.5 and 93.75 percent. These triangular diagrams indicate that increased flame retardance occurs at high loadings of the three additives.

As mentioned earlier, melamine produced the greatest flame retardant effects. However, other nitrogen compounds were used in order to ascertain a possible mode of action of nitrogen compounds with red phosphorus.

Table 3.5 shows the flammability data for the various systems studied. Taking into consideration the percentage of nitrogen in the compound, the loading of the additive onto the cotton cloth, and the increase in LOI, the values given in the column on the extreme right of Table 3.5, i.e., (Δ LOI / % N) are obtained. It can be seen that ammonium formate is the most effective nitrogen-containing additive on its own, raising the LOI by 1.2 units and giving an overall change in LOI of 0.6 units when consideration is taken of the percentage of nitrogen present. Ethylene urea is seen to be half as effective giving a rise of 0.38 LOI units allowing for the nitrogen content. N - methylimidazole is seen to give a negative value showing that it is ineffective as a flame retardant additive causing an actual increase in the flammability of cellulose.

When the nitrogen compounds are used in conjunction with red phosphorus further reductions in flammability are found.

Both ammonium formate and barbituric acid give significant

Table 3.5 The effect of different nitrogen compounds - red phosphorus systems on the flammability of cellulose - cotton cloth

Nitrogen compound	Nitrogen additive (wt %)	Phosphorus additive (wt %)	Amount of Nitrogen in compound (%)	Equivalent amount of Nitrogen (%N)*	LOI	ΔLOI / %N
-	-	9.8	-	-	22.7	-
Ethylene urea	15.5	-	32.6	3.4	19.5	0.38
	15.2	10.6		3.3	22.3	1.20
Barbituric acid	14.7	-	24.1	3.2	18.8	0.19
	13.1	9.2		2.9	23.2	1.70
N-methylimidazole	17.8	-	34.1	6.1	17.3	-0.15
	16.4	8.1		5.6	20.4	0.40
Ammonium formate	9.0	-	22.2	2.0	19.4	0.60
	11.4	5.1		2.5	25.0	2.72
Hexamethylenetetramine	10.0	-	40.0	4.0	18.8	0.15
	9.2	7.8		3.7	22.8	1.24
Melamine	14.9	-	66.6	9.9	21.7	0.35
	11.3	9.2		7.5	26.3	1.08

* Equivalent amount of nitrogen calculated by multiplying the wt percent of additive by the amount of nitrogen in the compound.

increases in the LOI values corrected to take into consideration the nitrogen content of the system. N - methylimidazole, which causes an increase in flammability when used alone, results in a favourable reduction in flammability when combined with red phosphorus.

Quantitative data for these systems are given in Table 3.6 and these show that hexamethylenetetramine and ethylene urea give the greatest degree of synergism in agreement with the earlier flammability findings. The synergism value for N - methylimidazole and barbituric acid are negative and therefore represent an antagonistic interaction which agrees with the flammability data showing that these additives are ineffective flame retardants.

In summary then it can be said that red phosphorus has a limited effect in reducing the flammability of cellulose - cotton cloth. By the addition of decabromobiphenyl and melamine this can be raised further, melamine being the better of the two. Combination of all three flame retardant additives only slightly increases the LOI value. The red phosphorus - melamine system is thus the most effective flame retardant combination for cellulose - cotton cloth studied in this work.

Table 3.6 Quantitative data for the various nitrogen compounds - red phosphorus cellulose systems

Nitrogen compound	R.M.S. difference (σ)	Coefficients	Synergism
Ethylene urea	0.72	N = 3.5 ± 4.9 P = 35.1 ± 5.4	203.9 ± 79.0
Barbituric acid	1.07	N = 7.4 ± 6.5 P = 33.9 ± 6.6	- 44.2 ± 17.0*
N - methylimidazole	1.03	N = -2.4 ± 8.9 P = 38.9 ± 10.0	- 72.2 ± 30.0*
Ammonium formate	1.3	N = 38.6 ± 8.6 P = 38.5 ± 8.0	308.4 ± 38.0*
Hexamethylenetetramine	0.6	N = 6.2 ± 3.7 P = 37.9 ± 3.2	331.7 ± 50.3

* Values obtained by graphical method.

3.1.2 Simultaneous thermal analysis measurements

Cellulose breaks down in two stages, a very fast main decomposition stage at about 325°C, and a much slower stage at around 460°C, identifiable as the carbon burn off (CBO) stage and accounting for about 18 percent of the weight loss (see Figure 3.13 and Table 3.7).

Cellulose in the form of microcrystalline powder undergoes its main decomposition at a slightly lower temperature of 310°C (Table 3.7) and the second stage occurs at a slightly higher temperature of 473°C. The CBO for microcrystalline cellulose is slightly higher, giving a value of 20 percent. This difference is due to the physical nature of the respective samples. In fact varying weights of the same sample also result in appreciable differences and can again be explained in terms of physical effects.

The thermal analysis of red phosphorus on its own shows that it undergoes a significant (ca. 16.1 wt percent) increase in weight at about 420°C (see Figure 3.14) which is presumably due to its reaction with oxygen to form a moderately volatile oxidised species such as phosphorus pentoxide. When red phosphorus is added to cellulose the first weight loss stage of cellulose occurs at a slightly lower temperature (see Figure 3.15). The CBO stage occurs, however, at a significantly higher temperature, the maximum rate being observed at 648°C as opposed to 464°C for cellulose alone (see Table 3.7). The CBO stage produces 30.6 percent carbon

Figure 3.13 Simultaneous thermal analysis plots for cellulose in the form of cotton cloth

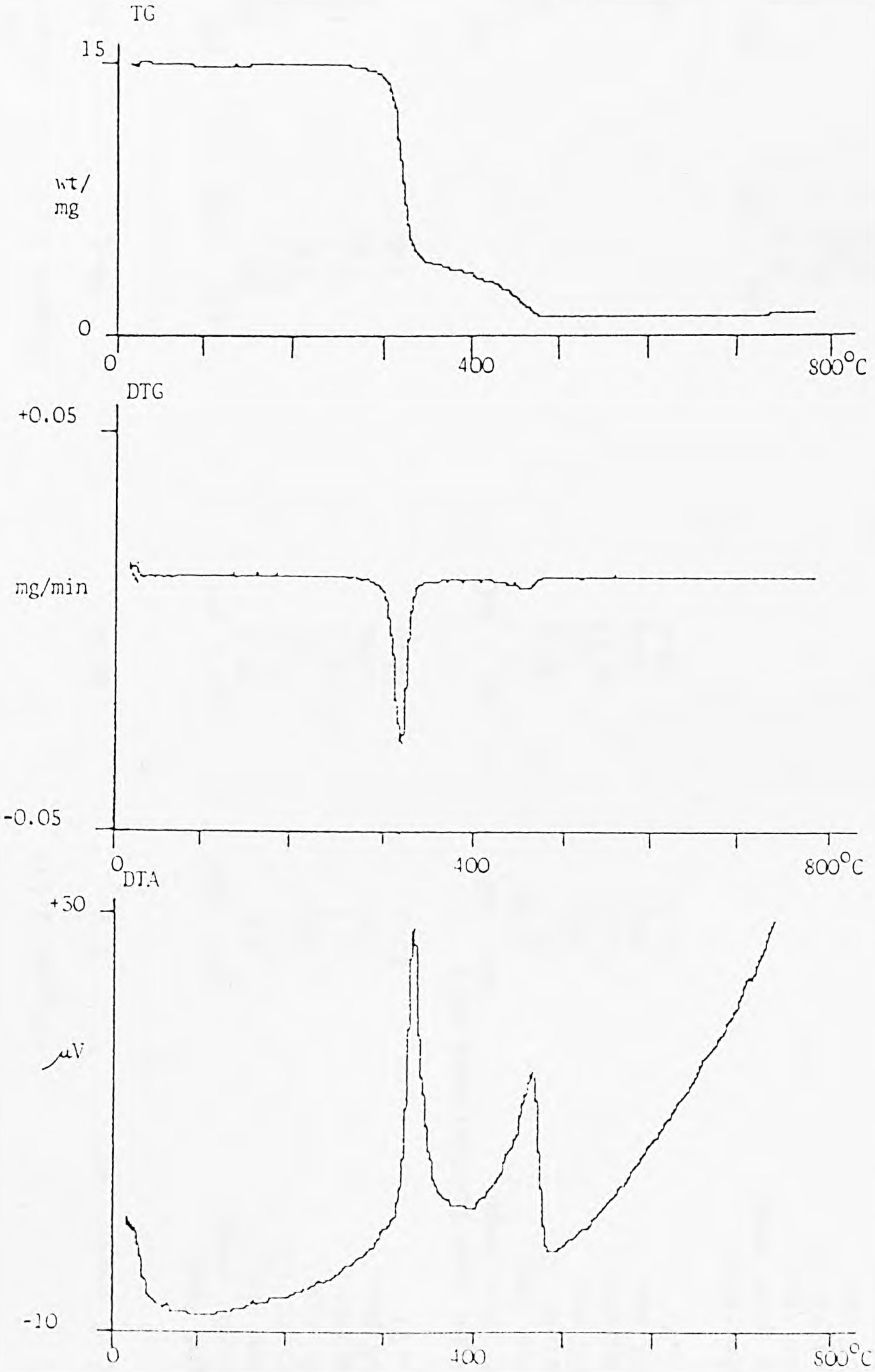


Table 3.7 Thermal analysis data for cellulose - red phosphorus systems

Sample Name	Cotton cloth (Figure 3.13)	Microcrystalline cellulose	Red phosphorus (Figure 3.14)	Cellulose powder + 15 wt % red phosphorus (Figure 3.15)
Initial wt of sample (mg)	7.9	82.4	52.1	91.1
First weight loss				
Temp of weight range	287 - 349	287 - 371	432 - 538	236 - 325
Weight value (mg)	5.6	59.1	44.1	46.6
Loss in weight (%)	70.6	71.7	84.7	51.2
Temp of DTG max	320	328	470	298
DTG max (mg/min)	-1.9	-14.3	-3.9	-14.7
Temp of DTA max	330	354	470	205
DTA max (μV)	21.3	66.6	148	
Second weight loss (carbon burn off)				
Temp of wt loss range	366 - 477	380 - 560		591 - 731
Weight value (mg)	1.42	16.7		23.7
Loss in weight (%)	18.0	20.2		30.6
Temp of DTG max	460	464		648
DTG max (mg/min)	-0.12	-0.83		-2.3
Temp of DTA max	460	464		632
DTA max (μV)	10.5	58.4		16.7
Weight gain stage				
Temp of wt gain range			196 - 419	330 - 427
Weight gain (mg)			8.4	5.6
Gain in weight (%)			16.1	6.2
Temp of DTG max			365	350
DTG max (mg/min)			2.9	0.58
Temp of DTA max			364	332
DTA max (μV)			0.08	205

Figure 3.14 Thermal analysis plots for red phosphorus on its own

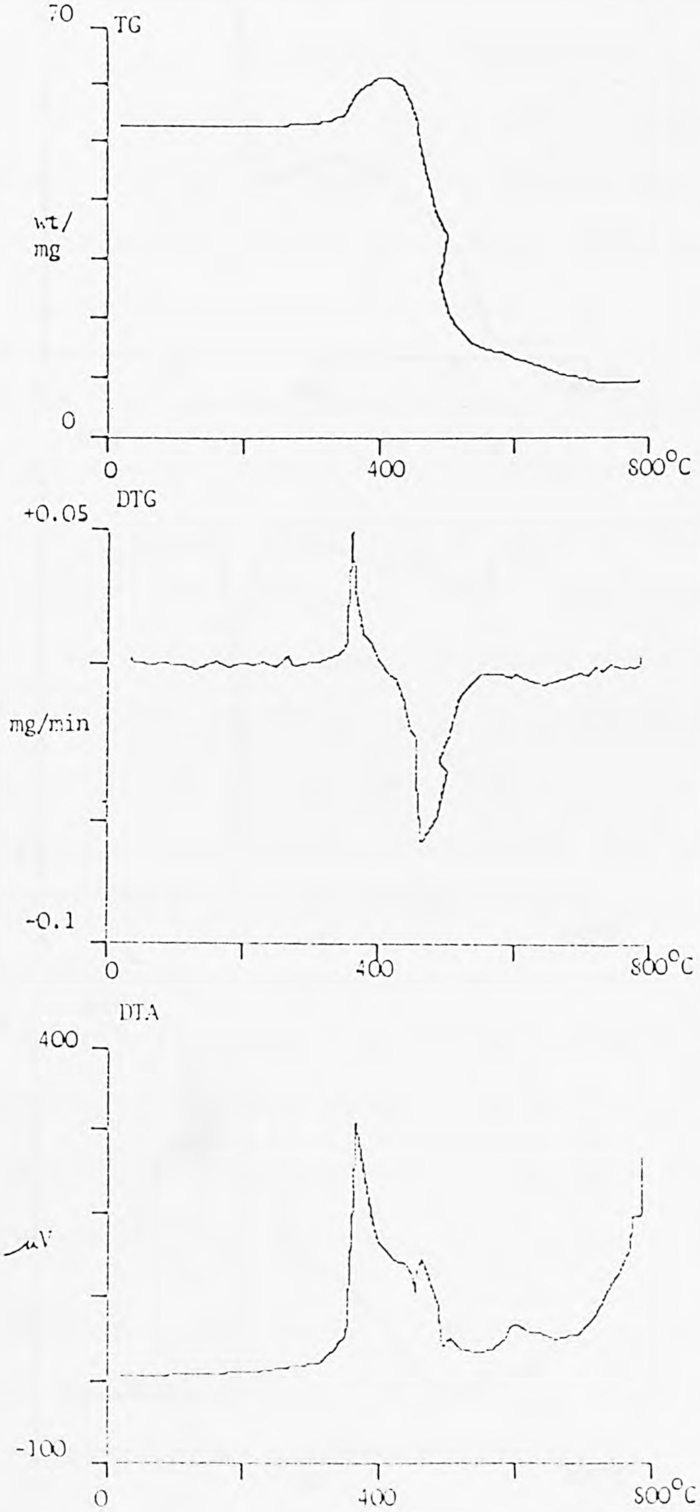
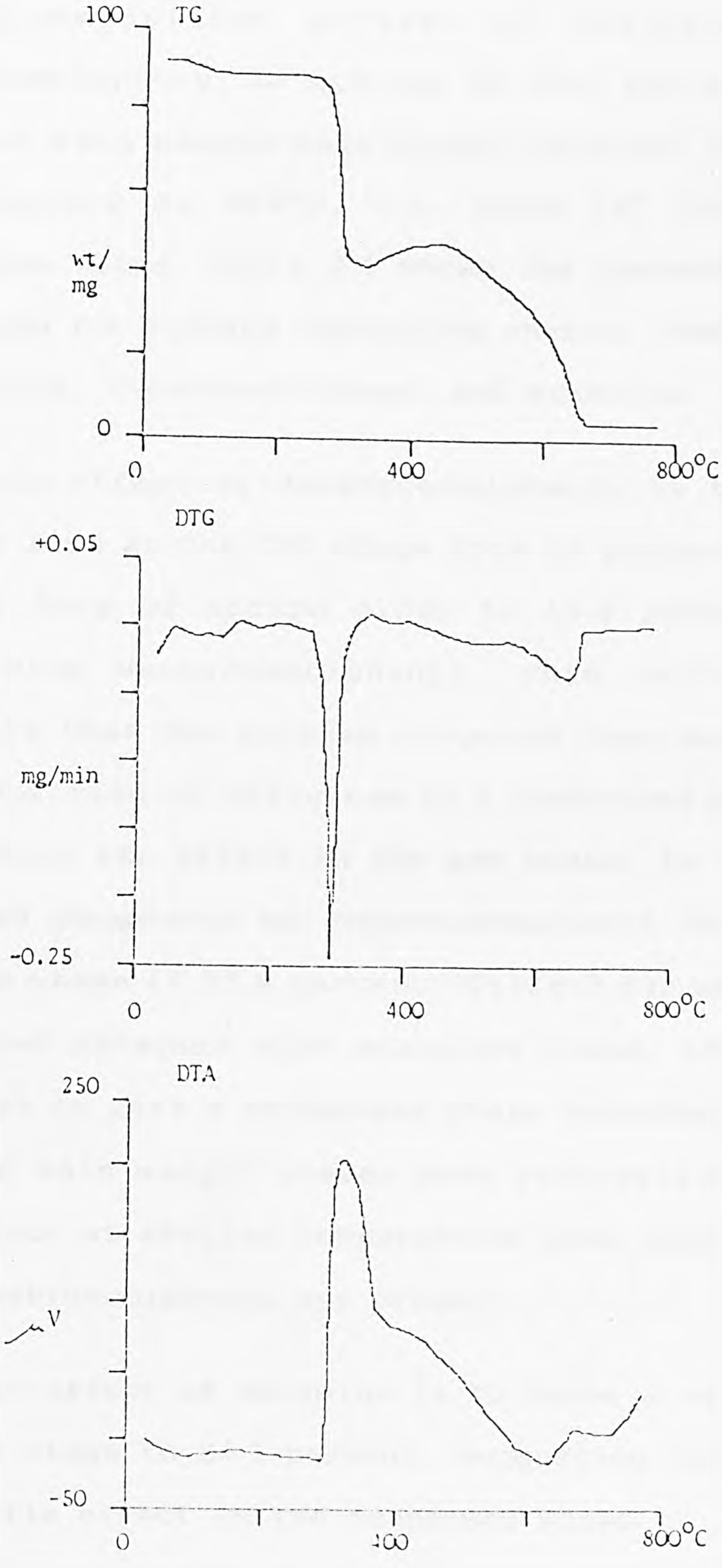


Figure 3.15 **Thermal analysis plots of microcrystalline cellulose and 15 wt percent red phosphorus**



which is significantly greater than that from cellulose alone.

The decomposition pattern of cellulose containing decabromobiphenyl is similar to that for cellulose alone, i.e. two main weight loss stages. However the first weight loss occurs at 306°C, i.e. some 15° lower than with cellulose alone. Table 3.8 shows the percentage loss at the CBO stage for systems containing various combinations of red phosphorus, decabromobiphenyl and melamine.

The main effect of decabromobiphenyl is to decrease the weight loss at the CBO stage from 18 percent for cellulose in the form of cotton cloth to 12.8 percent for cotton containing decabromobiphenyl. This decrease in weight suggests that the halogen compound does not influence the decomposition of cellulose by a condensed phase mechanism but exerts its effect in the gas phase. In the presence of both red phosphorus and decabromobiphenyl the weight loss at the CBO stage is 25.4 percent (Table 3.8), which is greater than that obtained with cellulose alone, and this suggests at least in part a condensed phase dehydration mechanism. The two main weight losses seen with cellulose on its own take place at similar temperatures when both red phosphorus and decabromobiphenyl are present.

The main effect of melamine is to cause a small increase in the CBO stage to 24.1 percent, suggesting that this additive has little effect in the condensed phase.

Table 3.8 Summary of the percentage loss at the carbon burn off (CBO) stage for the cellulose - binary and ternary additive mixtures of red phosphorus - decabromobiphenyl - melamine systems

Red phosphorus (wt %)	Decabromobiphenyl (wt %)	Melamine (wt %)	CBO (%)
-	-	-	18.0
-	-	-	20.2*
10	-	-	25.6
-	10	-	12.8
-	-	10	24.1
9	9	-	25.4
10	-	10	26.1
-	10	10	25.5
10	10	10	29.2*

* Microcrystalline cellulose, rather than cotton cloth.

In the presence of both red phosphorus and melamine the weight loss at the CBO stage is 27.2 percent which is an increase on the value for cellulose on its own. However the increase is not as pronounced as when red phosphorus is used alone. Presumably this is due to the presence of melamine in the system, which only results in a relatively small increase in the CBO stage when used on its own with cellulose. This suggests that a red phosphorus - melamine mixture also promotes dehydration. The main effect of decabromobiphenyl was to cause a drop in the percentage loss at the CBO stage from 18 percent for untreated cotton cloth to 12.8 percent.

In the case of melamine as an additive the CBO stage resulted in an increase to 24.1 wt percent. A combination of the two additives increased the loss in weight slightly to 25.5 wt percent suggesting a degree of dehydration due presumably to the presence of melamine.

For the cellulose - red phosphorus - decabromobiphenyl - melamine system, analysis was carried out using a sample of microcrystalline cellulose as opposed to cotton cloth in order to study a homogeneous mixture with all three addiives in equal concentrations. The results show that the two main weight losses are similar to those for cellulose itself. The first weight loss occurs at a slightly lower temperature than with cellulose on its own and the second weight loss occurs some 40° higher.

The weight loss at the CBO stage is 29.2 percent which should be compared with 20.2 percent (Table 3.8) for a sample of microcrystalline cellulose of similar size. The significant increase in weight loss at the CBO stage suggests a dehydration mechanism due presumably to the presence of red phosphorus and/or melamine, as decabromobiphenyl has been shown earlier to cause a decrease in the CBO stage.

Other nitrogen compounds were also studied and their effects on the CBO with and without red phosphorus present are shown in Table 3.9. All the compounds used caused an increase in the weight loss at the CBO stage, this being most noticeable for N - methylimidazole and ammonium formate which increase the weight loss compared with that for cellulose on its own, by about 7 percent. This suggests that they are effective as dehydrating agents in the condensed phase.

In combination with red phosphorus, ethylene urea and ammonium formate cause a reduction in the CBO stage suggesting that they do not function as flame retardants entirely by a condensed phase dehydration mechanism but may be partly effective by some other mechanism.

The CBO value for these systems has shown itself to be the most informative quantity for evaluating whether the flame-retardant additives exert their effects in the condensed phase or the gas phase. Both red phosphorus and melamine on

Table 3.9 Summary of the percentage loss at the carbon burn off (CBO) stage for various nitrogen compound - red phosphorus systems on cotton cloth

Nitrogen compound	Ammonia gas produced on decomposition	Nitrogen (wt %)	Phosphorus* (wt %)	CBO (%)
-		-	-	18.0
-		-	15.0	30.6
Ethylene urea	yes	10.0	-	19.1
		16.0	7.0	17.5
Barbituric acid	trace	10.4	-	21.0
		13.4	9.4	27.1
N-methyl imidazole	no	7.4	-	24.9
		16.4	8.1	38.6
Ammonium formate	yes	9.0	-	24.8
		13.0	7.0	27.4
Hexamethylenetetramine	yes	14.0	-	22.0
		11.0	11.0	26.6
(Melamine	yes	10.0	-	24.1)
		10.0	10.0	26.1)

* Values quoted may contain a percentage attributable to the oxidised species of red phosphorus and therefore the amount of carbon may be lower than these figures suggest.

their own cause an increase in the CBO value, red phosphorus being considerably better than melamine. This suggests that both additives exert their effect by a condensed phase mode of action. Decabromobiphenyl, in contrast, causes a significant reduction in the CBO stage. Combinations of flame retardant additives further suggest such modes of action. However, a red phosphorus melamine - combination causes a smaller reduction compared with that for red phosphorus alone, showing that phosphorus - melamine mixtures are less effective dehydrating agents for cellulose than phosphorus on its own.

3.1.3 Gas Phase Infrared Spectroscopy

Figure 3.16 shows the gas phase spectrum resulting from heating a cellulose sample between 485 and 515°C. Cellulose undergoes decomposition at 340°C to form mainly carbon dioxide (2330 cm^{-1}), carbon monoxide (2120 cm^{-1}), and water. The latter compound, with its characteristic broad band between 3400 and 3600 cm^{-1}, appears as a maximum at a higher temperature of 450°C. Figure 3.17 shows the gas phase spectrum of the same sample at about 420°C between 1900 and 625 cm^{-1}. Two broad peaks are visible centering around 1650 and 1050 cm^{-1}. The band at 1650 cm^{-1} is probably due to the OH bend from water. Further peaks are also visible at 1400 and 1200 cm^{-1} but they are not as clearly defined. They may be indicative of laevoglucosan (1,6-anhydro-β-D-glucopyranose), a likely decomposition product of cellulose which also has absorptions centering at 1640 and 1050 cm^{-1} as seen in Figure 3.18.

Red phosphorus, when heated in a nitrogen atmosphere, produced no observable gaseous species. Yellow phosphorus is formed which spontaneously ignites on coming into contact with air to form phosphorus pentoxide. Figure 3.19 shows infrared spectra of red phosphorus heated in air at ca. 500 and 540°C in the range of 1800 - 626 cm^{-1}. This spectrum shows clearly three absorptions at 940, 1035 and 1175 cm^{-1}. On comparison with that of phosphoric acid (Figure 3.20), it can be seen that there is a good deal of similarity between

Figure 3.16 Gas phase infrared spectrum of cellulose heated to a temperature of 485 - 515°C in the region 4000 - 2000 cm^{-1}

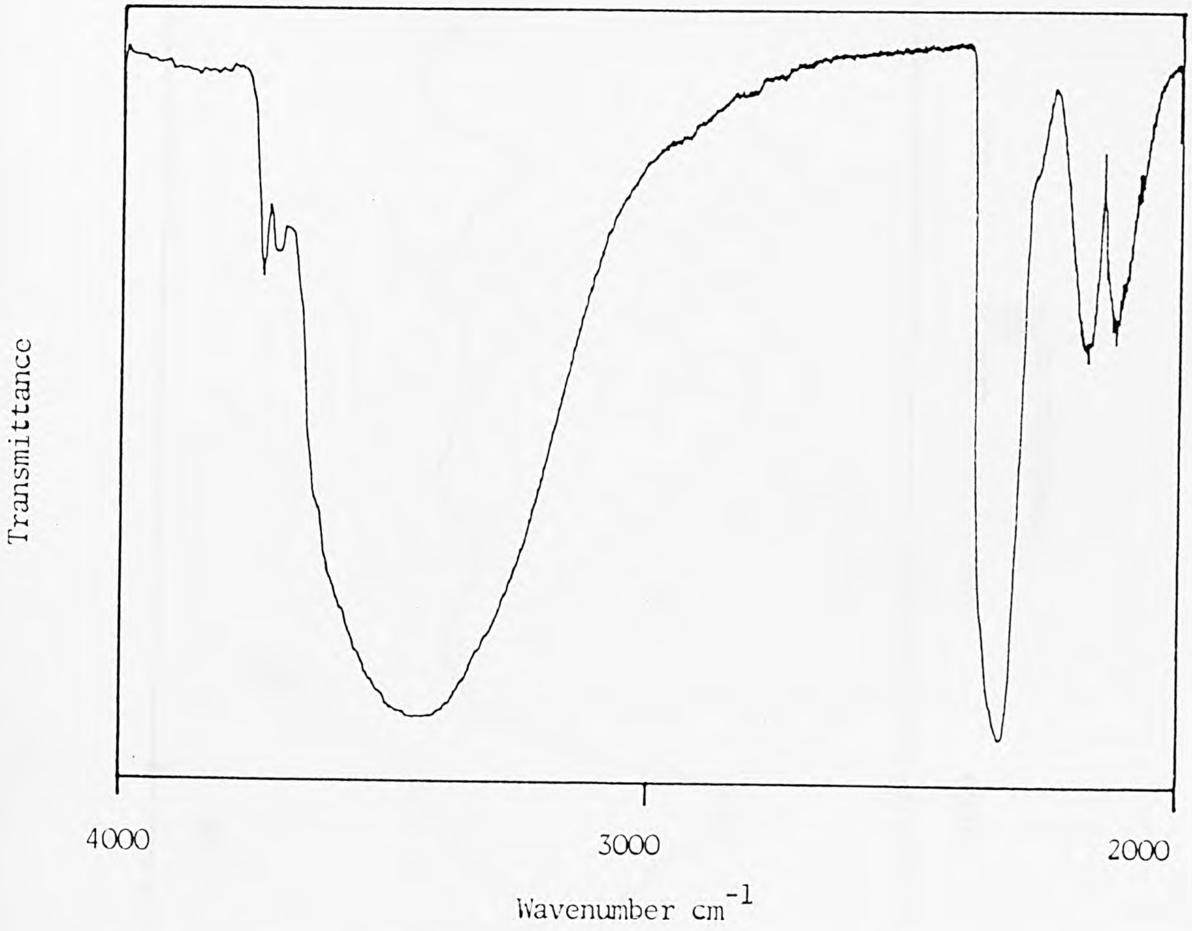


Figure 3.17 Gas phase infrared spectrum of cellulose at about 420°C over the 1900 - 625 cm^{-1} region

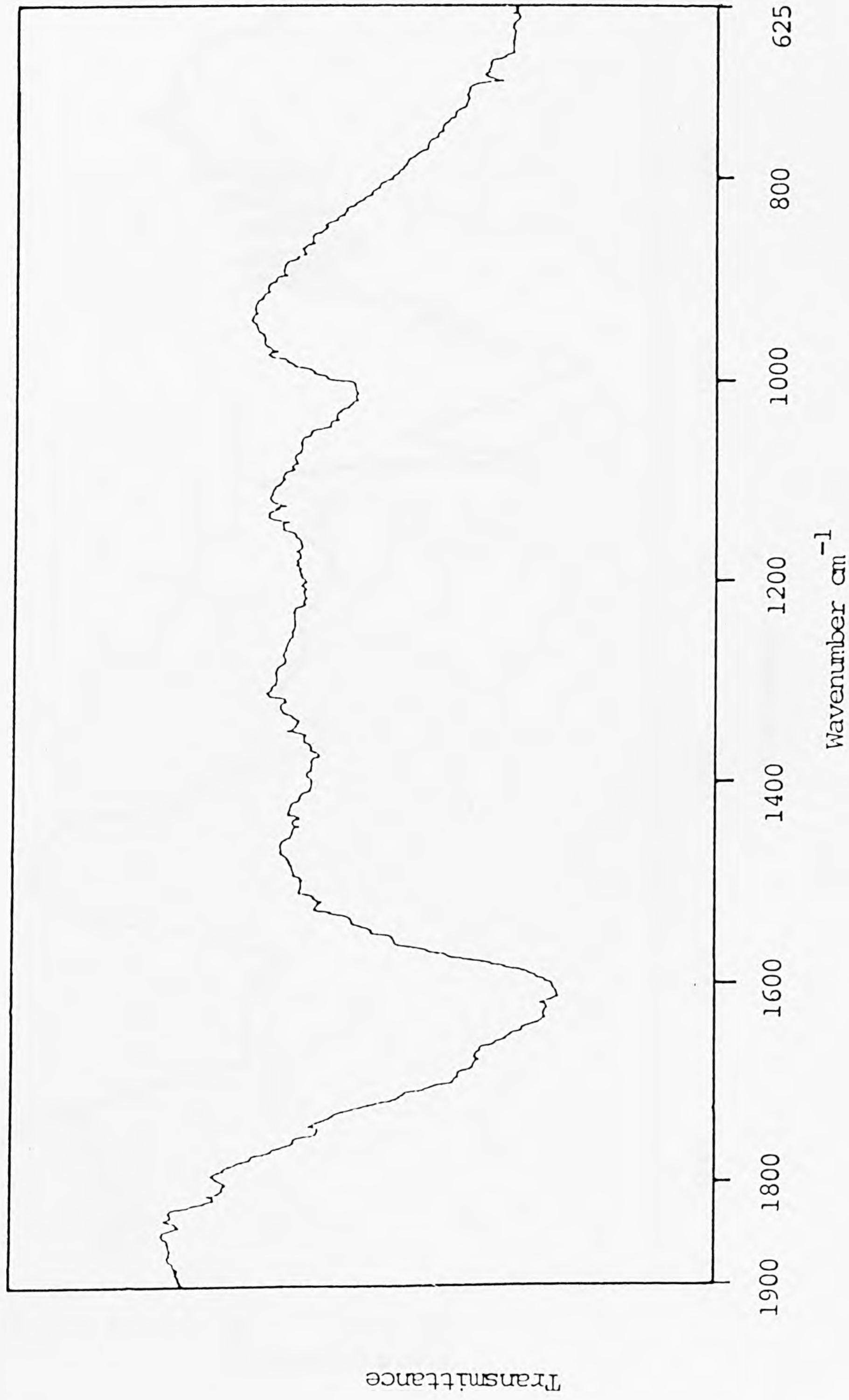


Figure 3.18 Infrared spectrum (KBr disc) of laevoglucosan supplied by Sigma Chemical Co. over the region 1900 - 625 cm^{-1}

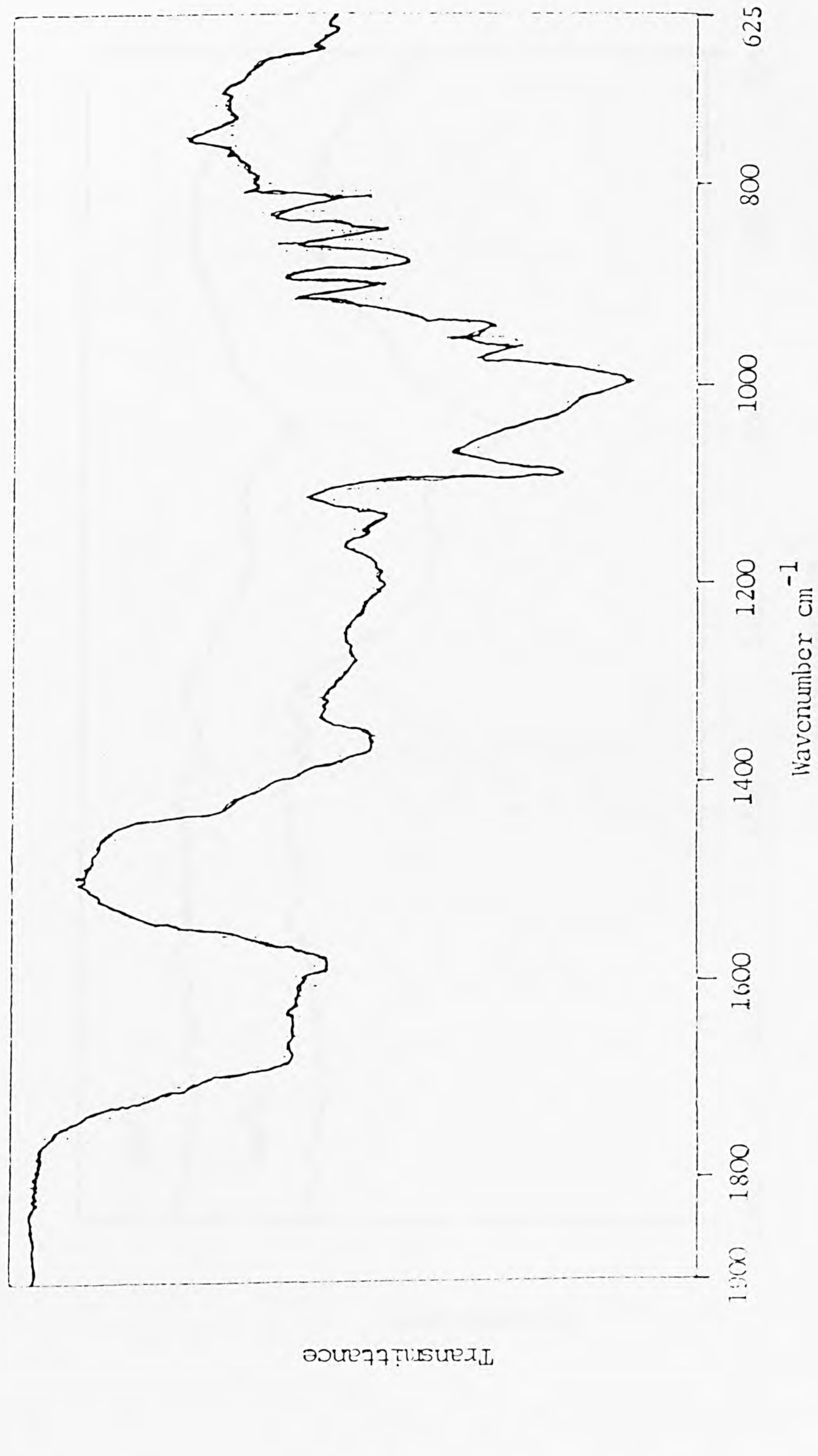


Figure 3.19 Gas phase infrared spectra of red phosphorus heated in air at 500 and 540°C over the region 1800 and 625 cm^{-1}

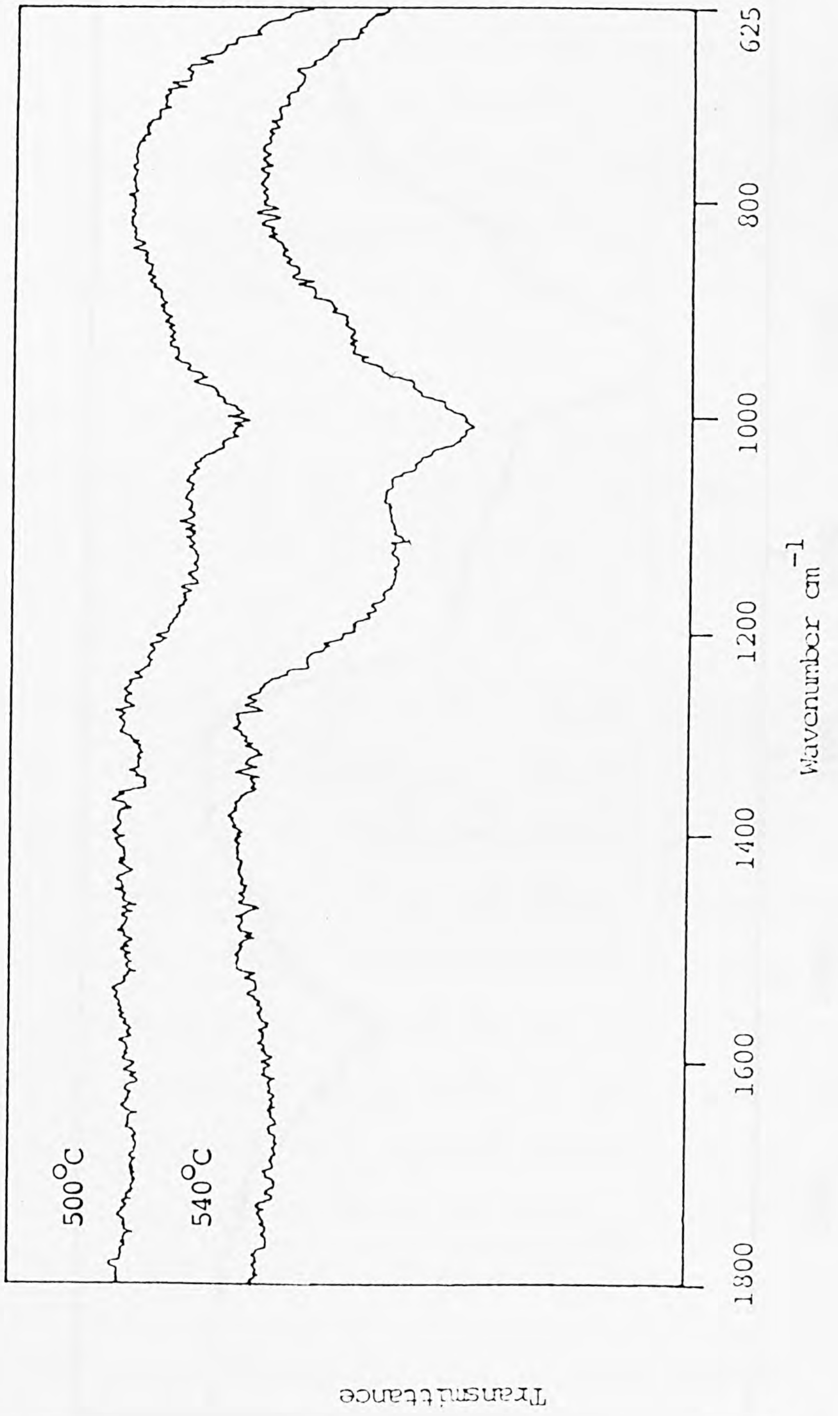
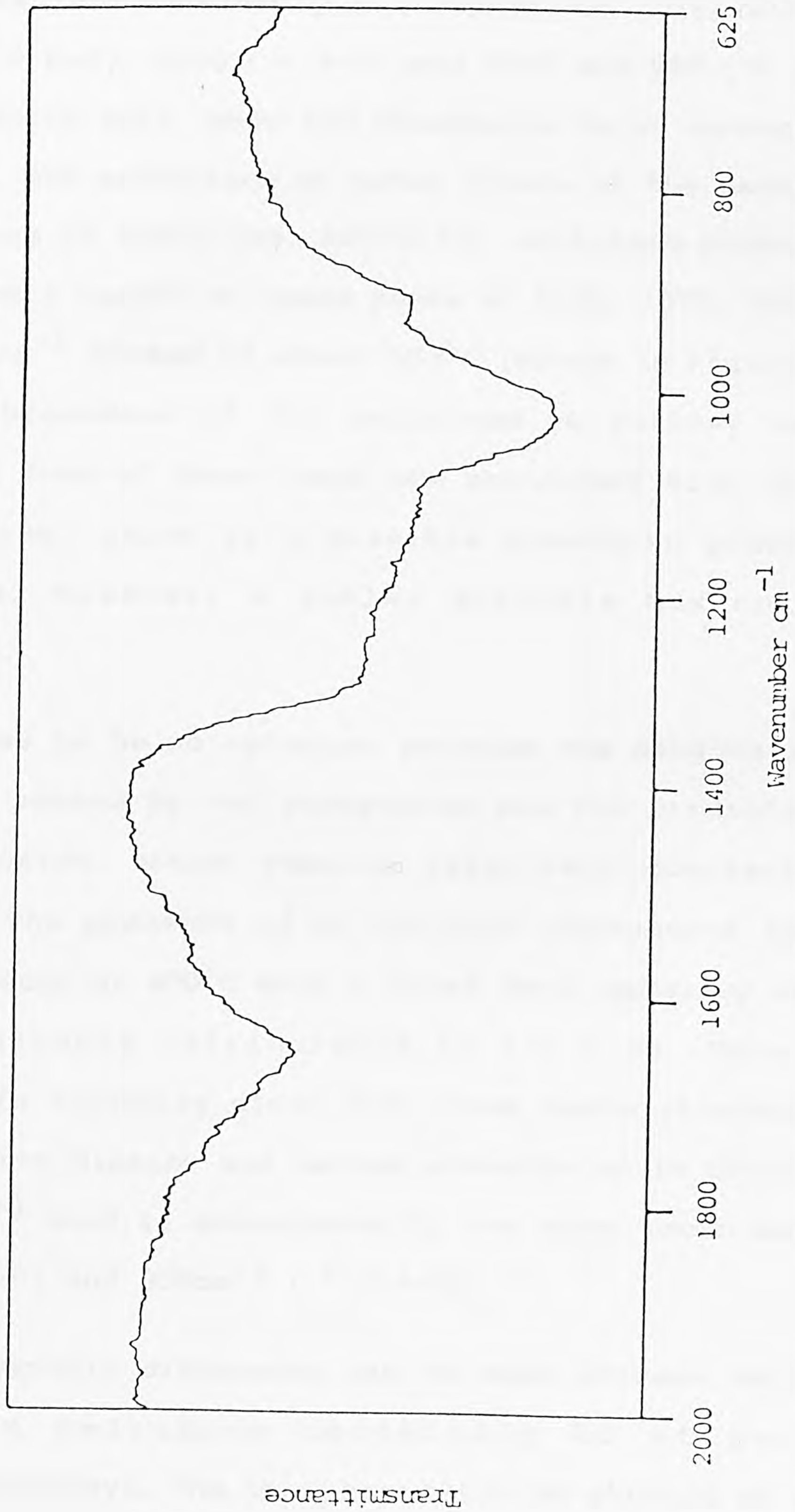


Figure 3.20 This film spectrum of phosphoric acid $(H_3PO_4)_n$ on a sodium chloride plate over the region 2000 - 625 cm^{-1}

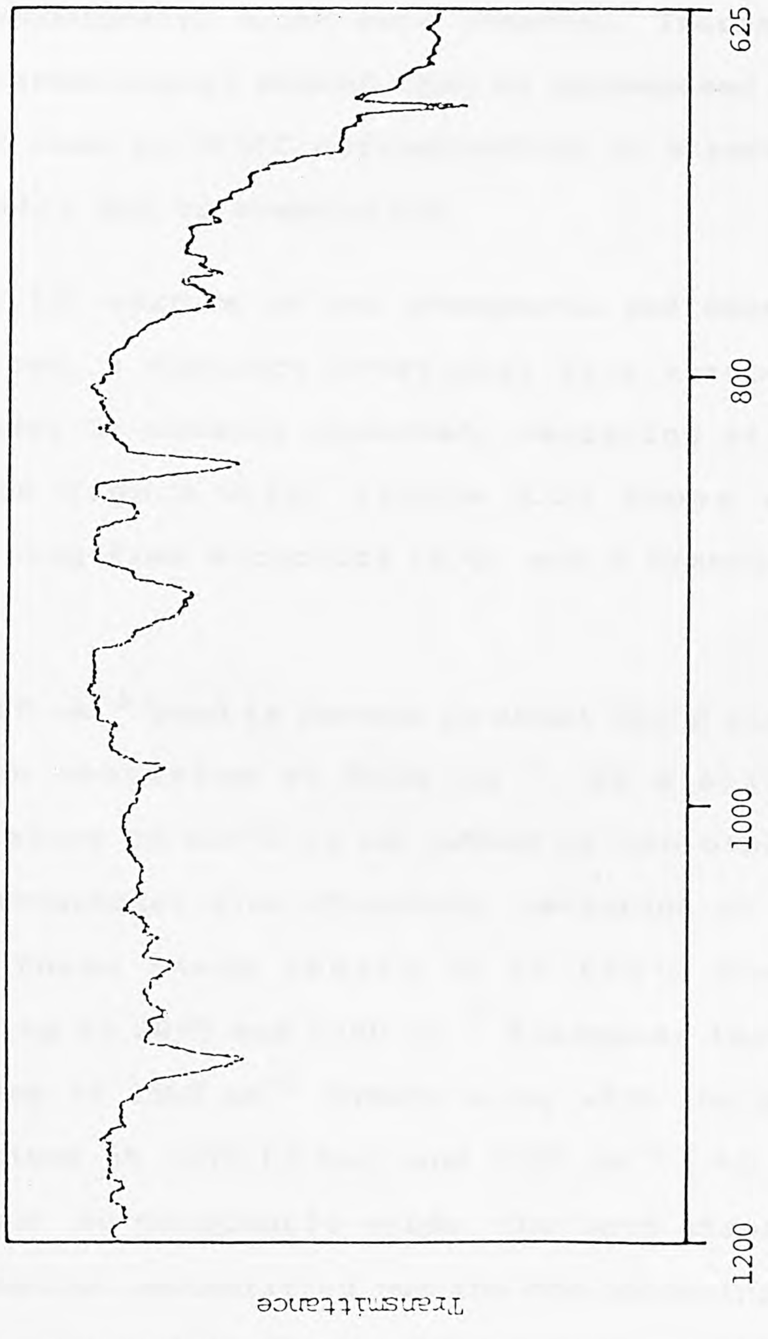


the two spectra between 1400 and 625 cm^{-1} with a slight shift to lower frequency in the case of phosphoric acid. These peaks have been assigned (Chapman and Thirlwell 1964) to 1250 (ν P=O), 1040 (ν P-O) and 1007 and 885 (ν O-P-O) for phosphoric acid. When red phosphorus is in contact with cellulose, the production of water occurs at the much lower temperature of 300°C (cf. 450°C for cellulose alone). The presence of a number of small peaks at 1110, 1070, 980, 890, 830, 750 cm^{-1} formed at about 250°C (shown in Figure 3.21) suggests breakdown of the cellulose to smaller organic molecules. Some of these bands are coincident with those of acetaldehyde, which is a possible breakdown product of cellulose. However, a fuller analysis has not been undertaken.

There seems to be no relation between the dehydration of cellulose caused by red phosphorus and the production of carbon dioxide, which remains relatively constant once produced. The presence of an oxidised phosphorus species seems to occur at 400°C with a broad band appearing at 1040 cm^{-1} presumably attributable to (ν P-O). This band increases in intensity along with other bands attributed to water, carbon dioxide and carbon monoxide up to 570°C when the 1040cm^{-1} band is accompanied by two other broad bands at 1250 (ν P=O) and 900cm^{-1} (ν O-P-O).

Little observable difference can be seen between cellulose alone and cellulose containing 20 wt percent decabromobiphenyl. The characteristic OH stretch of water

Figure 3.21 Gas phase infrared spectrum of cellulose - red phosphorus system at 250°C over the range 1200 - 625 cm^{-1}



from the decomposition of cellulose is clearly visible at 450°C along with that of the other cellulose breakdown products, i.e. carbon dioxide and carbon monoxide. No breakdown products due to the decomposition of decabromobiphenyl alone were observed. Thermal analysis of decabromobiphenyl showed that it decomposes with only one weight loss at 373°C corresponding to a zero order rate, presumably due to evaporation.

When a 1:1 mixture of red phosphorus and decabromobiphenyl is heated, a distinct rotational fine structure (P and R branches) is clearly observed, centering at 2560 cm^{-1} as seen in Figure 3.22. Figure 3.23 shows another band containing fine structure (P,Q, and R branches) at 1360 cm^{-1}.

The 1360 cm^{-1} band is formed at about 390°C along with an OH stretch centering at 3400 cm^{-1}. At a slightly higher temperature of 420°C it is joined by two other bands with clear rotational fine structure, centering at 2890 and 2560 cm^{-1}. These bands remain up to 645°C when the bands centering at 2890 and 1360 cm^{-1} disappear leaving the band centering at 2560 cm^{-1} intact along with the characteristic absorptions at 1250 (ν P=O) and 1050 cm^{-1} (ν P-O) previously assigned to phosphoric acids. The band structure at 1360 cm^{-1} remains unidentified but the one centering at 2560 cm^{-1} may be assigned to HBr (ν 2559)(Blinder 1969), a likely decomposition product of decabromobiphenyl in an atmosphere where water is present.

Figure 3.22 Gas phase infrared spectrum of a 1:1 mixture of red phosphorus and decabromobiphenyl over the range 4000 - 2000 cm^{-1}

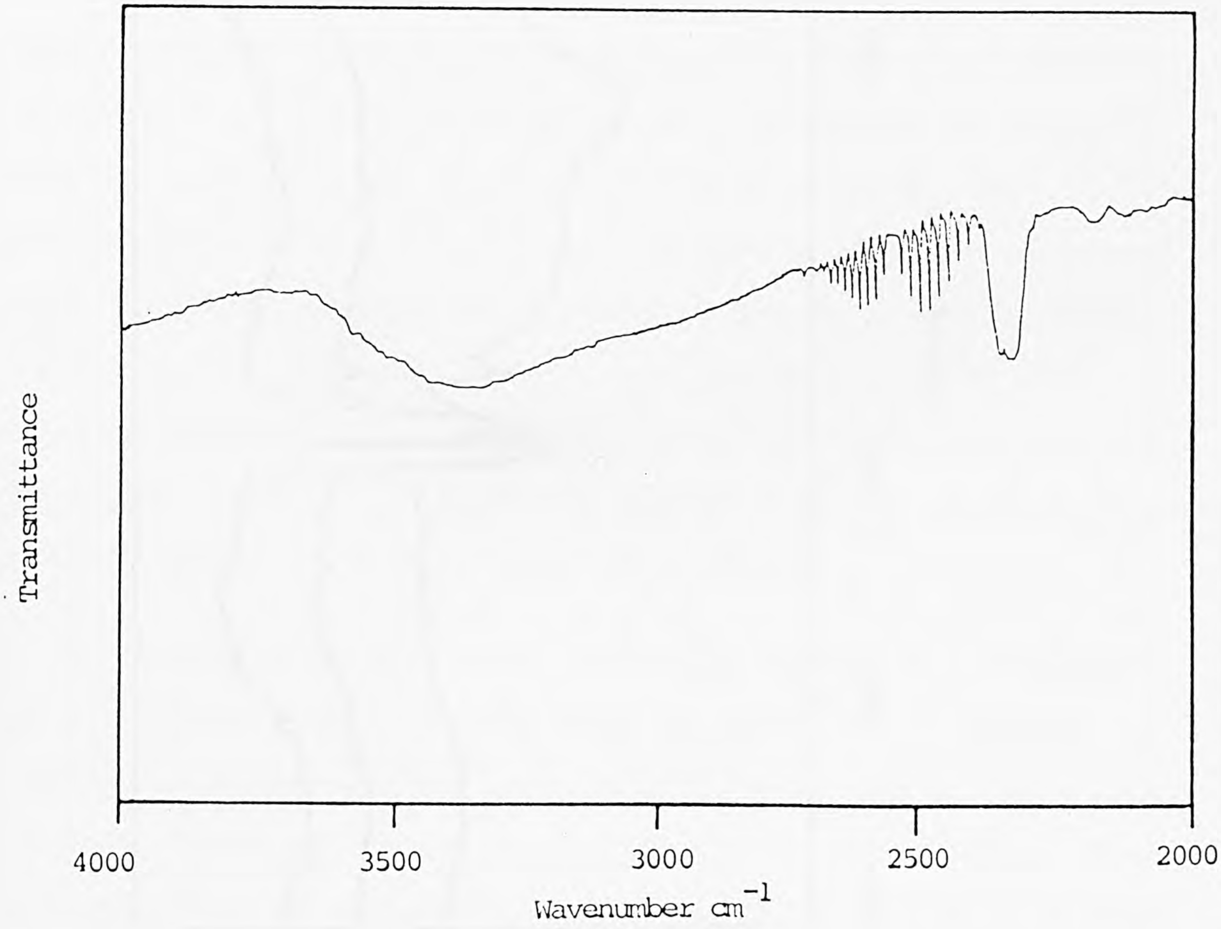
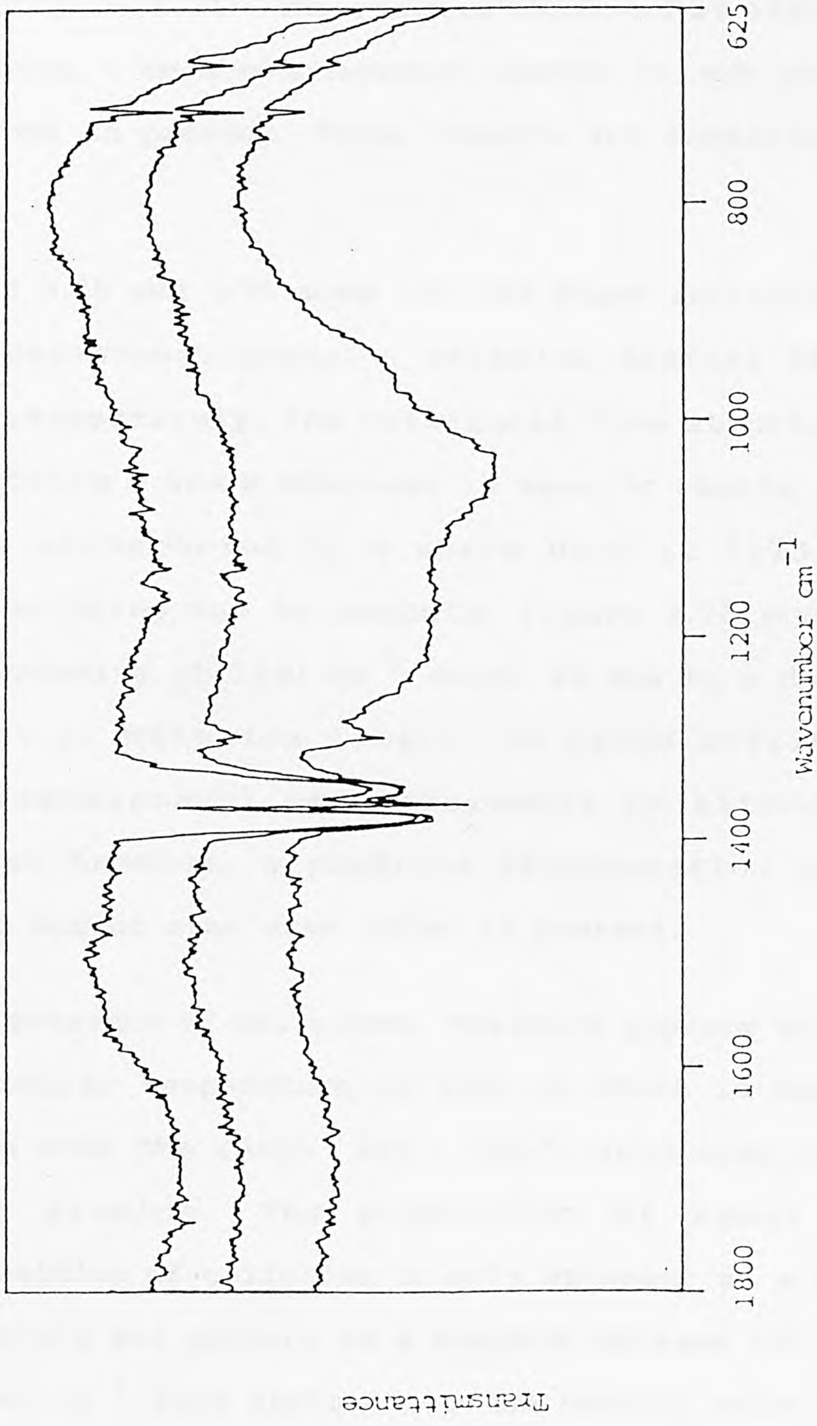


Figure 3.23 Gas phase infrared spectrum of a 1:1 mixture of red phosphorus and decabromobiphenyl over the range 1800 - 625 cm^{-1}



In the presence of cellulose, the red phosphorus - decabromobiphenyl mixture exhibits the characteristic cellulose decomposition products of water, carbon dioxide and carbon monoxide, along with a band centering at 1310 cm^{-1} (Figure 3.24). The species observed at 1360 in the red phosphorus - decabromobiphenyl system is not observed when cellulose is present. These results are summarised in Table 3.10.

Figures 3.25 and 3.26 show the gas phase infrared spectra of a 1:1 decabromobiphenyl - melamine mixture at 400°C and 600°C respectively. The rotational fine structure showing distinctive P and R branches is seen to centre at 950 cm^{-1} and is accompanied by a sharp band at 1625 cm^{-1}, both features being due to ammonia. Figure 3.26 shows a broad band centering at 1440 cm^{-1} which is due to a decomposition product of melamine itself. No bands attributable to decabromobiphenyl are observable in either spectrum; hydrogen bromide, a possible decomposition product, is clearly absent even when water is present.

In the presence of cellulose, melamine appears to break down at a similar temperature to that at which it decomposes on its own over the range 360 - 400°C producing ammonia and carbon dioxide. The production of water from the decomposition of cellulose is only apparent at a much higher temperature and appears as a maximum between 550 and 600°C. The 1640 cm^{-1} band assigned to the bending mode of water is not visible until 400°C.

Figure 3.24 Gas phase infrared spectrum of cellulose - red phosphorus - decabromobiphenyl system over the range 1900 - 625 cm^{-1}

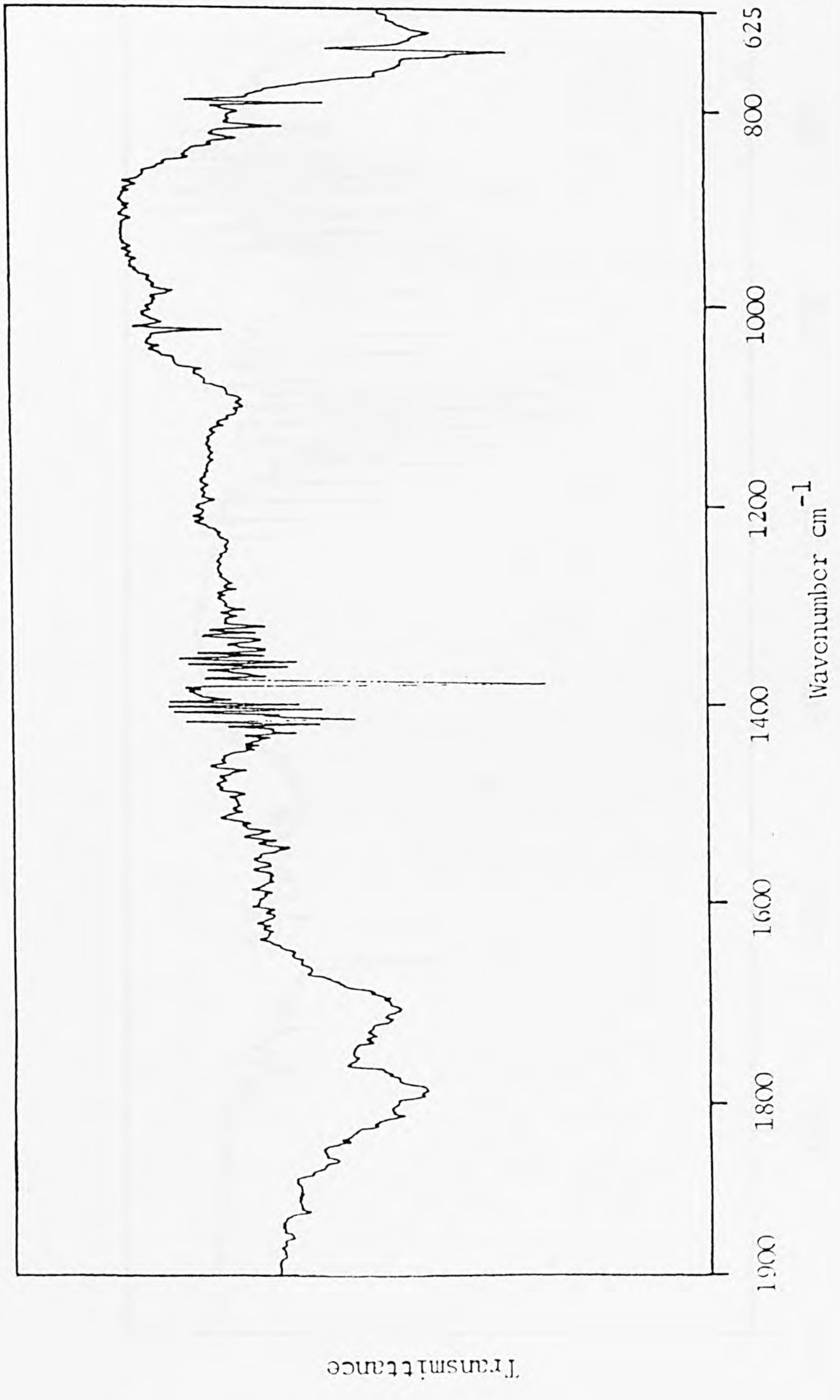


Figure 3.25 Gas phase infrared spectrum of a 1:1 decabromobiphenyl - melamine mixture at 400°C over the range 2000 - 625 cm^{-1}

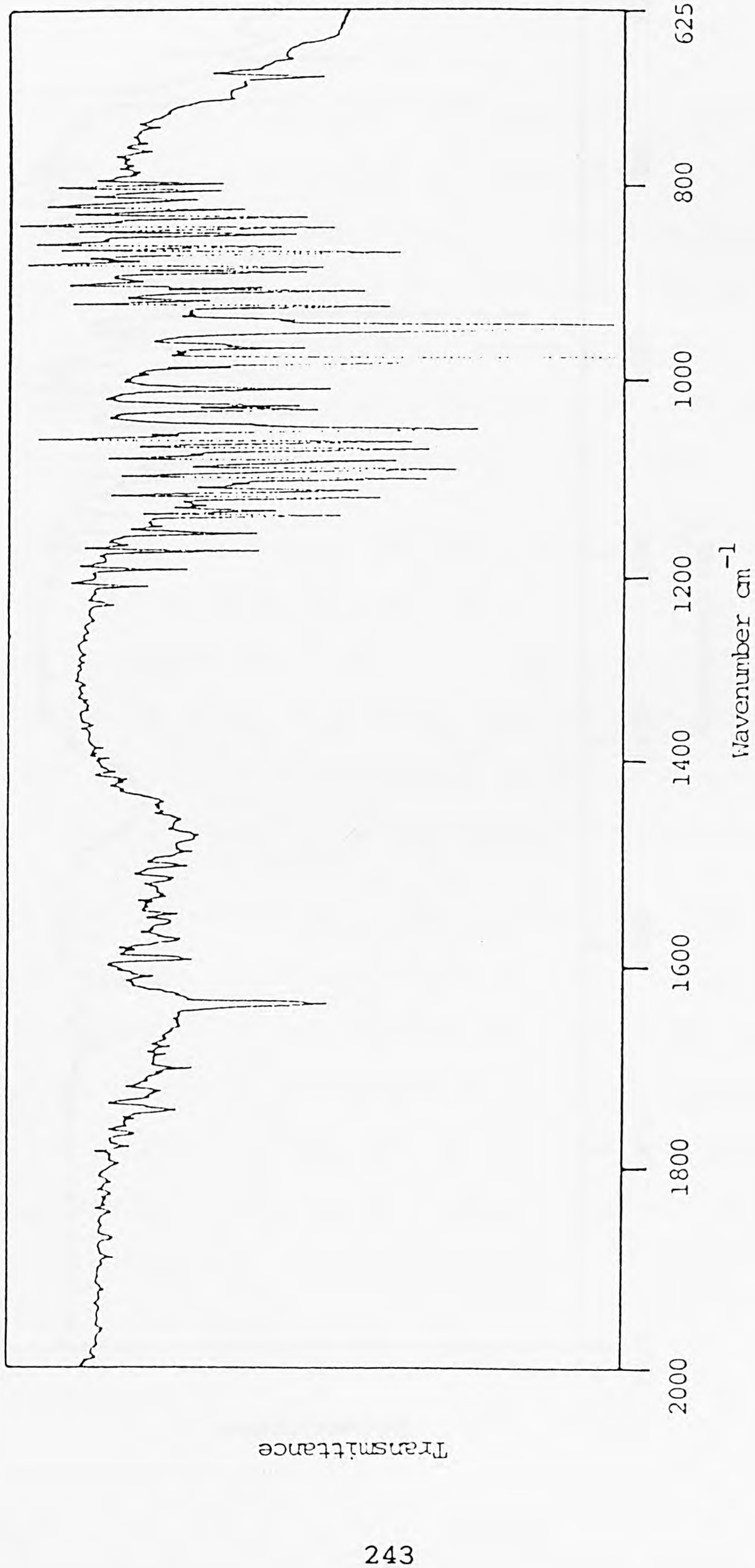
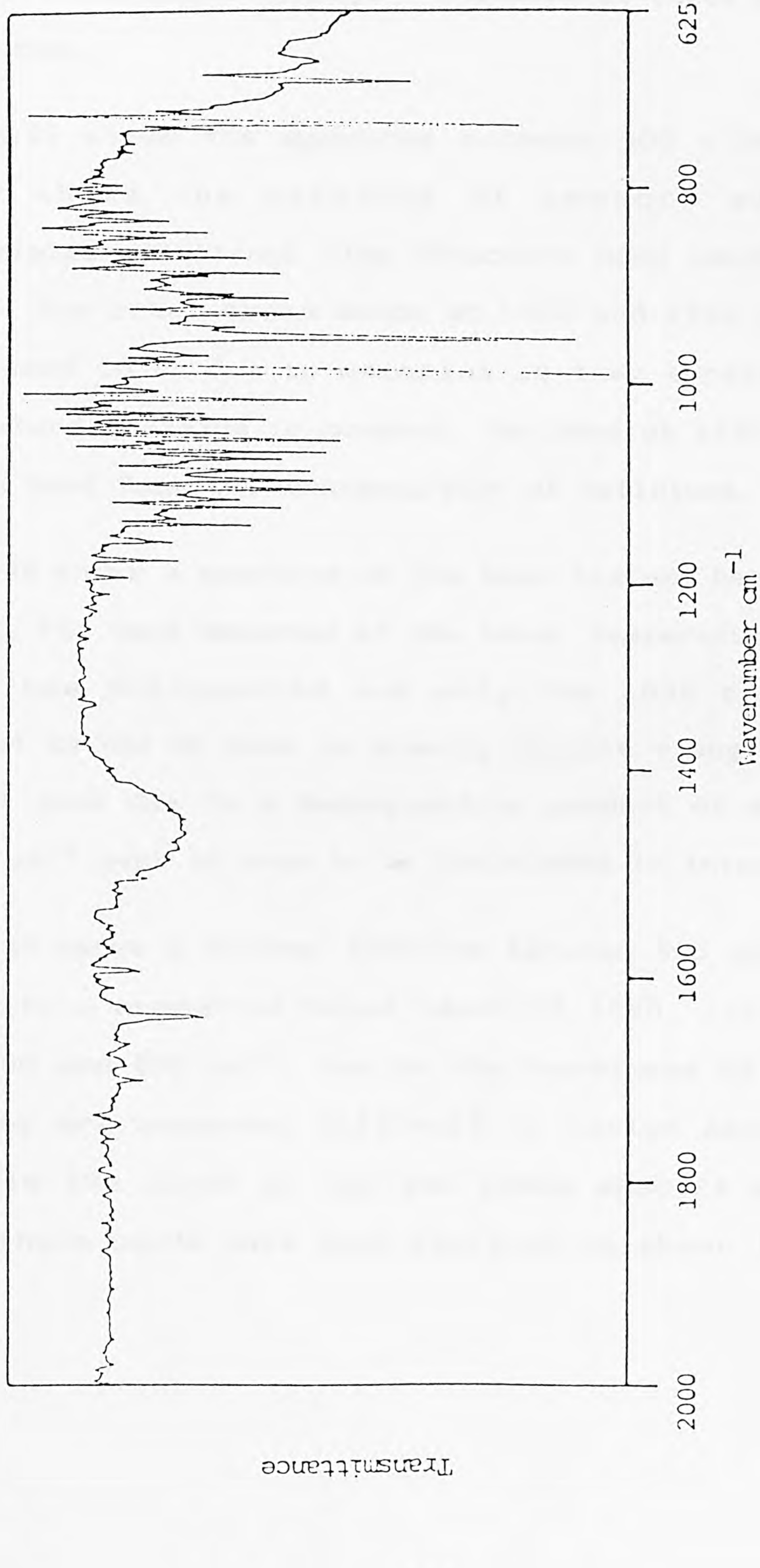


Figure 3.26 Gas phase infrared spectrum of a 1:1 decabromobiphenyl - melamine mixture at 600°C over the range 2000 - 625 cm^{-1}



Figures 3.27, 3.28 and 3.29 show the infrared spectra over the 2000 - 625 cm^{-1} range for a mixture of cellulose - red phosphorus - decabromobiphenyl - melamine at three different temperatures.

Figure 3.27 shows the spectrum between 300 - 360°C and clearly shows the presence of ammonia with its characteristic rotational fine structure band centering at 950 cm^{-1}. Two other broad bands at 1450 and 1550 cm^{-1} are also assumed to be due to melamine as they appear in all spectra where melamine is present. The band at 1630 cm^{-1} is due to OH bend from the decomposition of cellulose.

Figure 3.28 shows a spectrum of the same mixture between 545 and 565°C. The band observed at the lower temperature due to ammonia has disappeared and only the 1630 cm^{-1} band attributed to the OH band is clearly visible along with the 1450 cm^{-1} peak due to a decomposition product of melamine. The 1450 cm^{-1} peak is seen to be diminished in intensity.

Figure 3.29 shows a further spectrum between 560 and 590°C and depicts a number of broad bands at 1640, 1550, 1450, 1250, 1100 and 875 cm^{-1}. Due to the broadness of certain bands they are somewhat difficult to assign accurately. However in the light of the gas phase spectra examined earlier these bands have been assigned as shown in Table 3.10.

Figure 3.27 An infrared spectrum of a cellulose - red phosphorus - decabromobiphenyl - melamine between 300 - 360°C over the range 2000 - 625 cm^{-1}

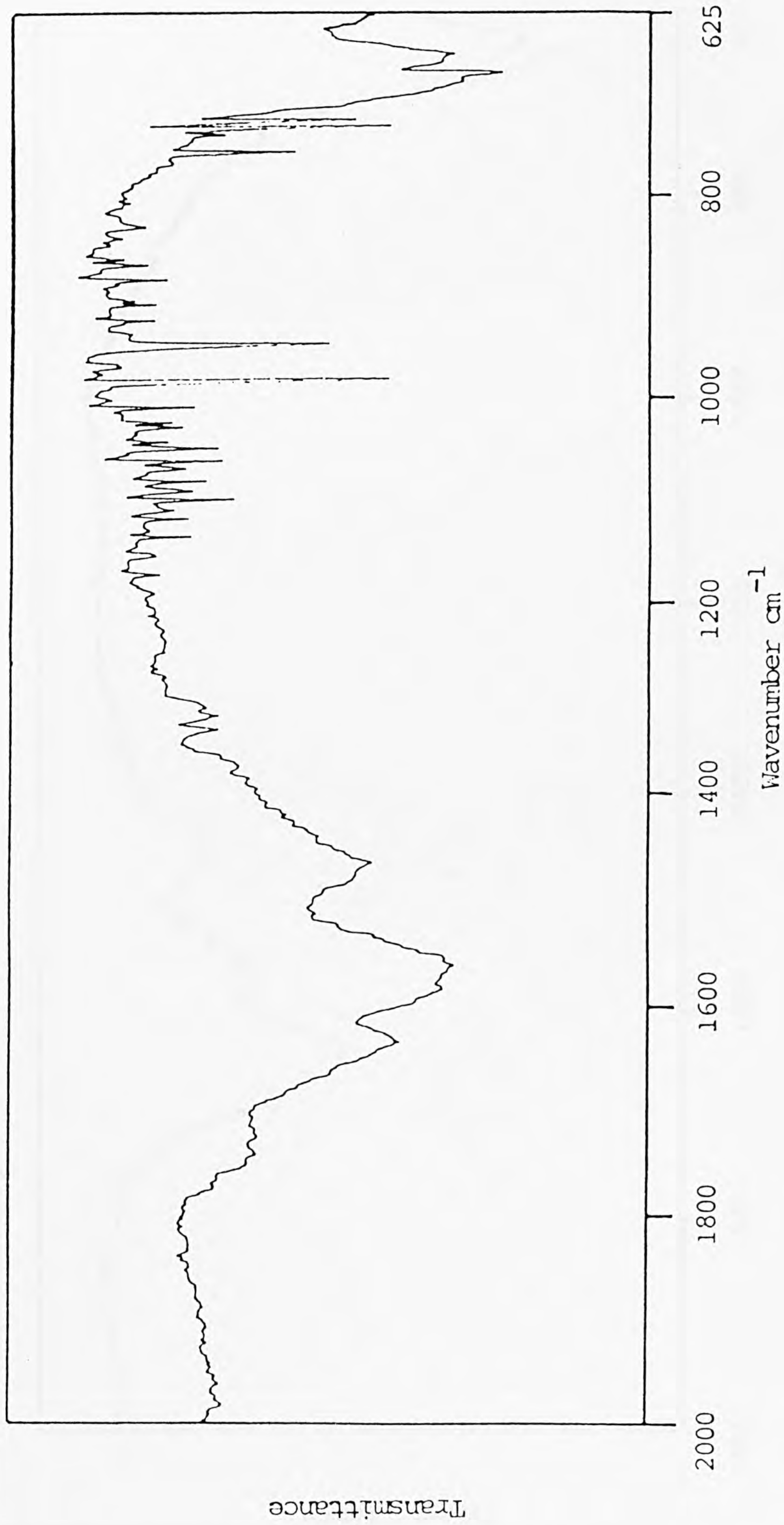


Figure 3.28 An infrared spectrum of a cellulose - red phosphorus - decabromobiphenyl - melamine between 545 - 565°C over the range 2000 - 625 cm^{-1}

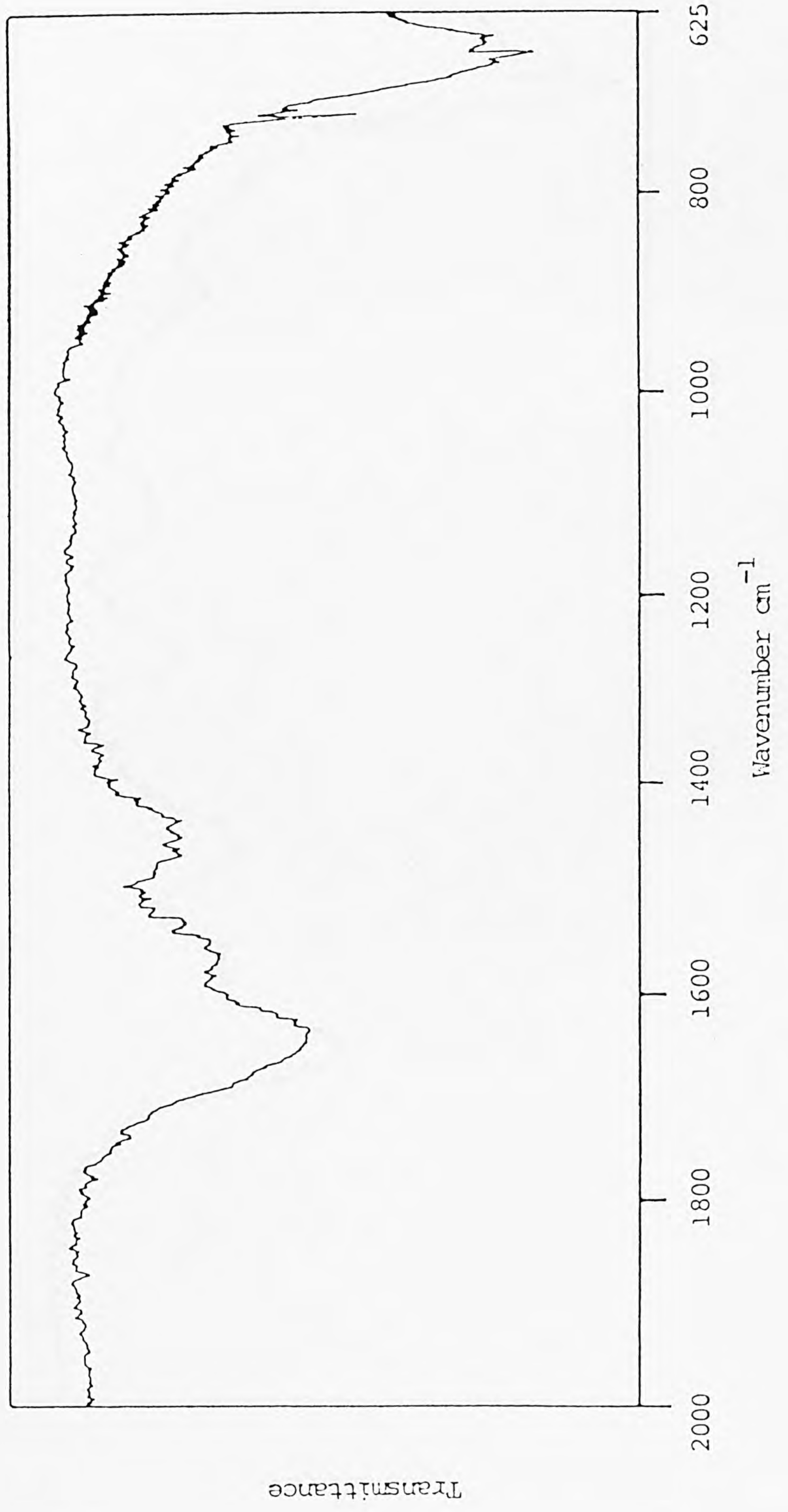


Figure 3.29 An infrared spectrum of a cellulose - red phosphorus - decabromobiphenyl - melamine between 560 - 590°C over the range 2000 - 625 cm^{-1}

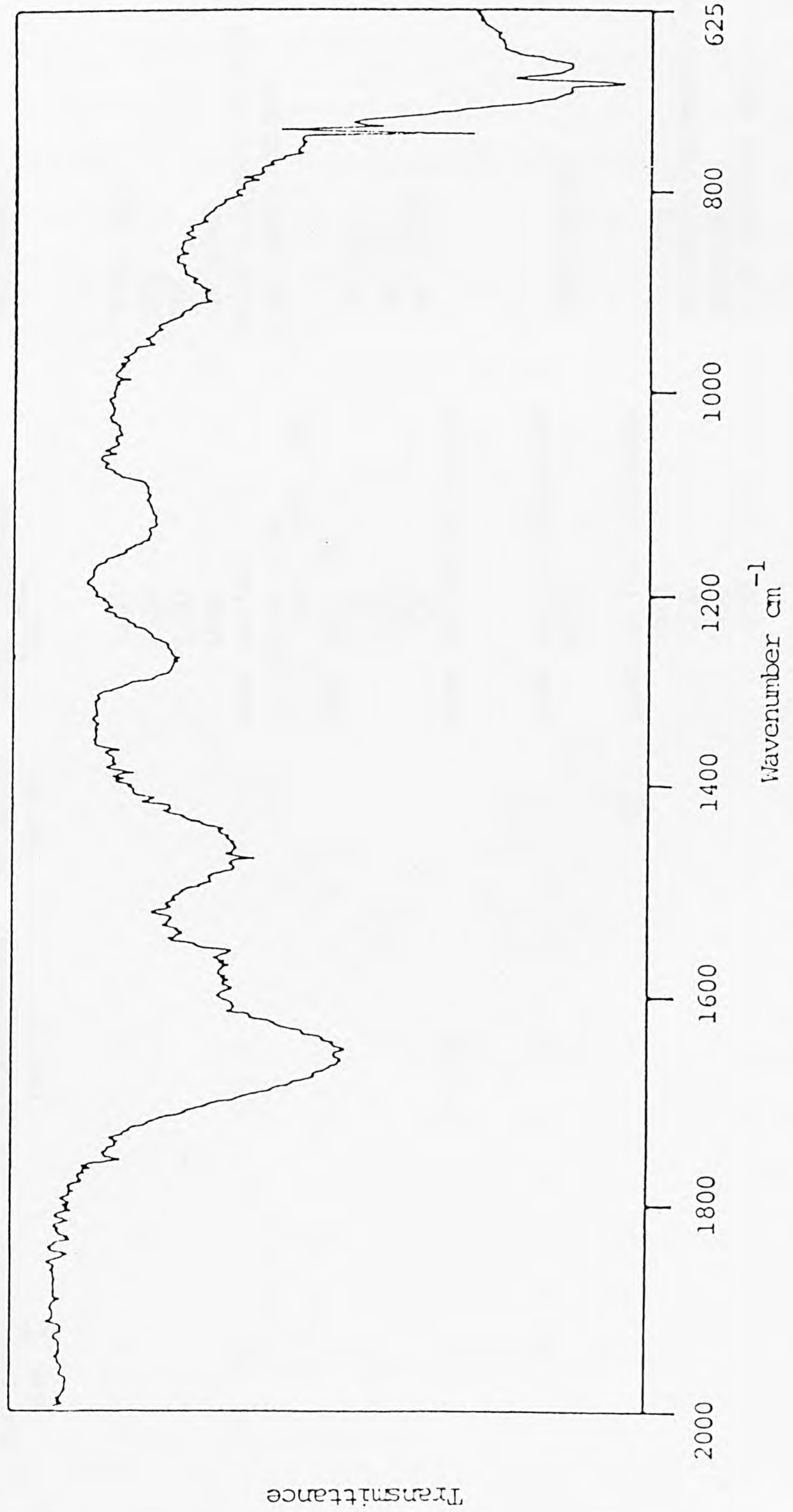


Table 3.10 Summary of infrared spectroscopic data for the cellulose - binary and ternary systems of red phosphorus - **decabromobiphenyl** - melamine

Red phosphorus (wt %)	Decabromobiphenyl (wt %)	Melamine (wt %)	Bands observed (cm^{-1})	Assignment
-	-	-	3400	ν OH (H_2O)
			2330	CO_2
			2120	CO
			1640	OH bend
10	-	-	same as for cellulose plus 1110, 1070, 1020, 980 890, 830, 750	small organic molecules e.g. acetaldehyde
			1250	ν P=O
			1040	ν P-O
			900	ν O-P-O
-	10	-	same as for cellulose	
10	10	-	same as for cellulose	
			1310	unassigned
-	-	10	same as for cellulose	
			1625	NH_3
			1550	melamine decomposition products
			1450	
			950	P,R branches NH_3
10	10	10	same as for cellulose	
			1640	OH bend
			1550	melamine decomposition products
			1450	
			1250	oxidised P species ν P=O
			1100	oxidised P species ν P-O
			875	oxidised P species ν O-P-O

Gas phase infrared spectroscopy shows thus that cellulose - flame retardant additive systems are remarkably complex producing a number of different species and hence are difficult to interpret fully. It can be seen that both red phosphorus and melamine cause a reduction in the temperature at which water, a main decomposition product of cellulose undergoing dehydration is produced. Decabromobiphenyl has little if any effect on the temperature or products of the decomposition of cellulose.

3.2 The effect of other phosphorus compounds on the thermal behaviour of cellulose

3.2.1 Effects of tritolyl phosphate on the flammability of cellulose - decabrombiphenyl - melamine systems

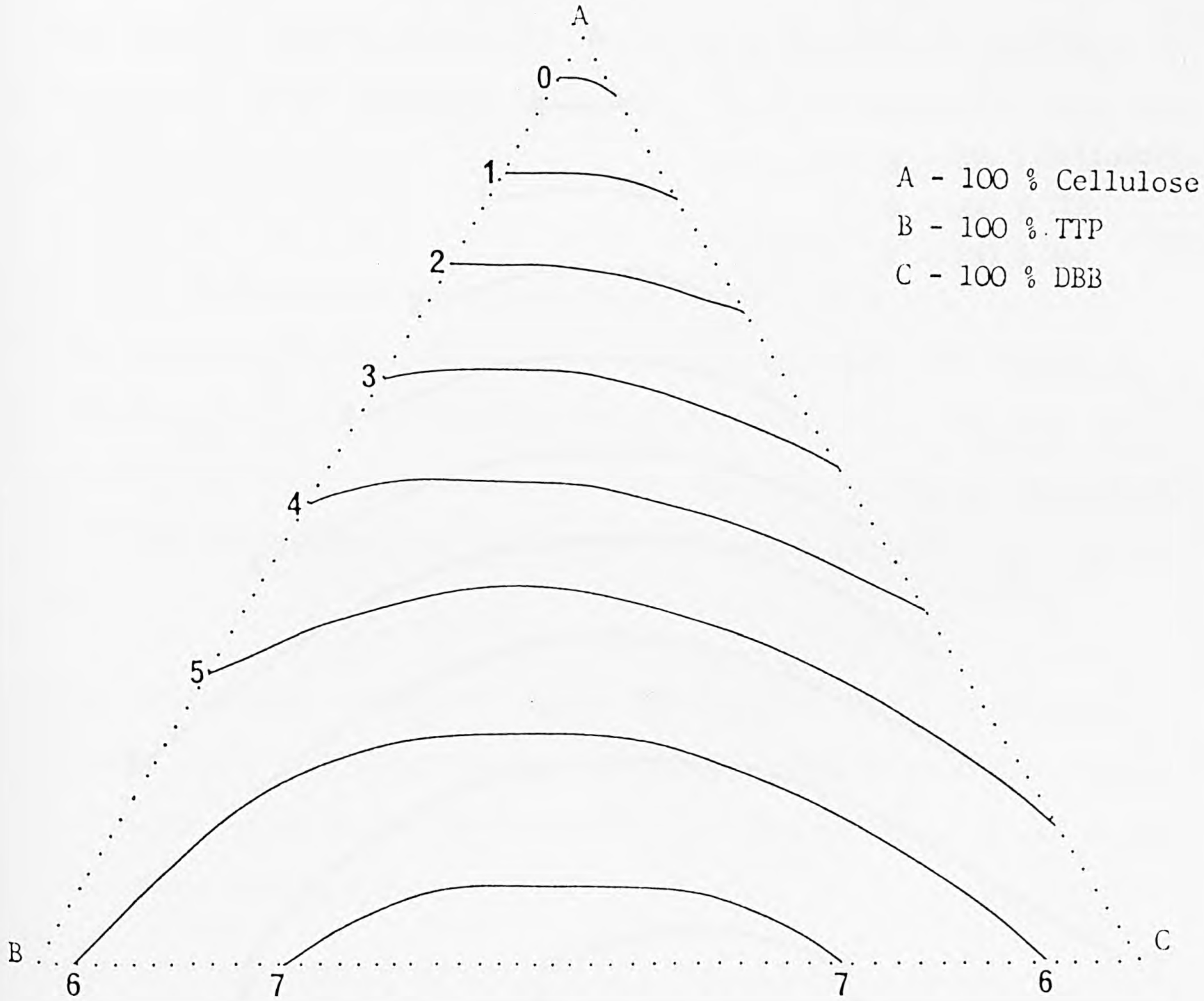
Table 3.11 shows the effect of tritolyl phosphate both on its own and in conjunction with decabromobiphenyl and melamine on the flammability of cotton. Tritolyl phosphate raises the LOI for pure cellulose from 18.2 to 23.9 at a high loading of 30.7 wt percent, showing that this compound is relatively effective on its own. Measurements were then made of the LOI of varying other combinations of tritolyl phosphate and decabromobiphenyl incorporated onto cotton cloth and the results were plotted in the form of a triangular diagram (Figure 3.30). Qualitatively the diagram shows a region of high flame retardancy along the cellulose baseline with a maximum at about 50 weight percent of each additive.

The effect on the flammability of cotton of mixtures of tritolyl phosphate and melamine was also studied, as melamine had been shown to impart a reasonable degree of additional flame retardancy when used in conjunction with red phosphorus (Table 3.2). Figure 3.31 shows a triangular diagram for the tritolyl phosphate - melamine system. Qualitatively the diagram shows a similar region of flame retardancy along the cellulose baseline to that for tritolyl

Table 3.11 The effect of tritolyl phosphate on the flammability of cellulose

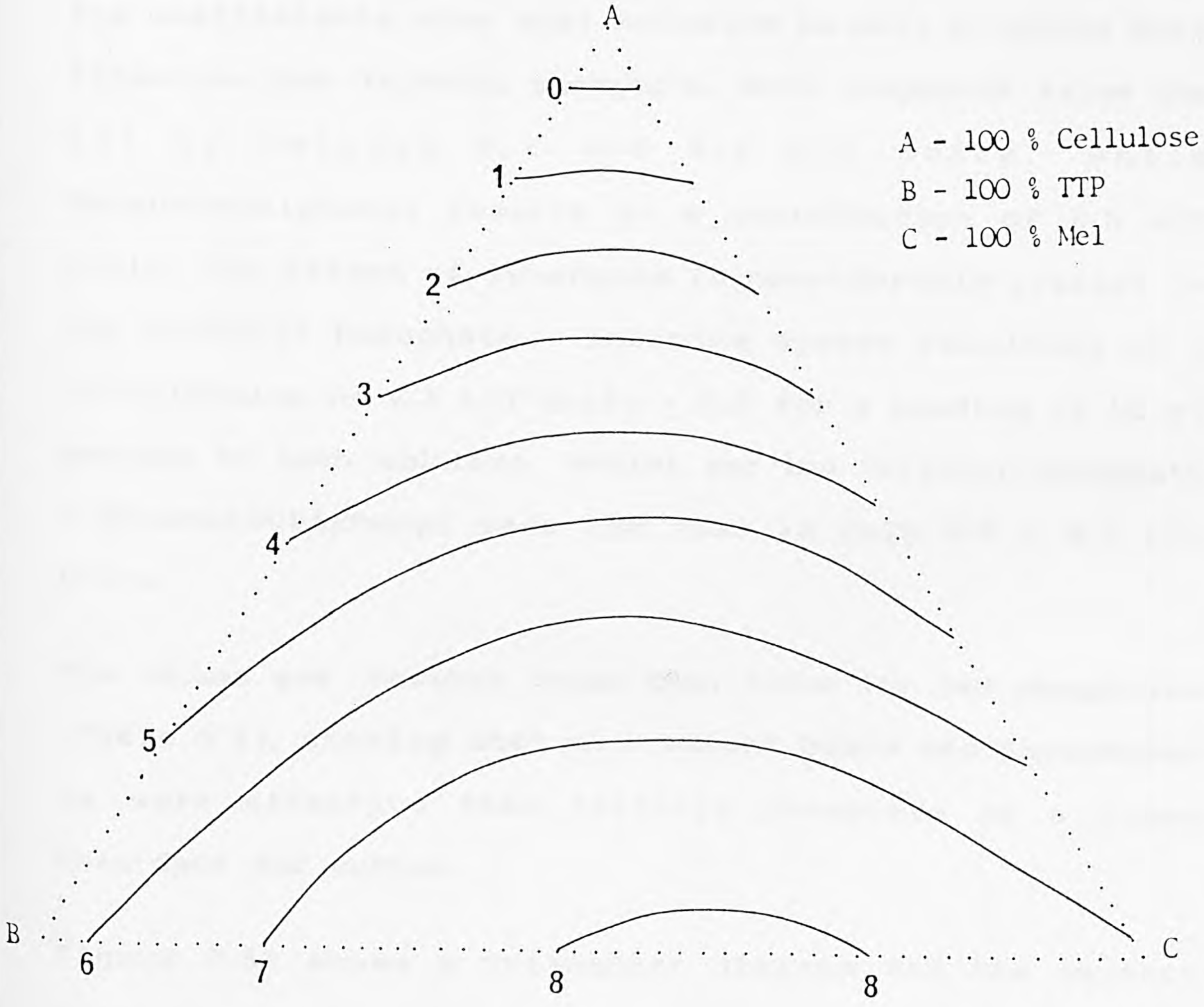
Tritolyl phosphate (wt %)	Decabromobiphenyl (wt %)	Melamine (wt %)	LOI
-	-	-	18.2
3.7	-	-	18.3
10.3	-	-	21.0
30.7	-	-	23.9
-	12.8	-	21.6
-	-	14.9	21.7
11.2	9.2	-	24.5
16.8	-	15.0	26.4
-	8.8	8.5	23.5
8.6	5.9	7.9	25.5

Figure 3.30 Triangular diagram showing variation of LOI with composition for cellulose - tritolyl phosphate - decabromobiphenyl systems



LOI values: 0 = 18.2, 1 = 19.2, 2 = 20.2, 3 = 21.2, 4 = 22.2, 5 = 23.2, 6 = 24.2, 7 = 25.2, 8 = 26.2, 9 = 27.2, 10 = 28.2.

Figure 3.31 Triangular diagram showing variation of LOI with composition for cellulose - tritolyl phosphate - melamine systems



LOI values: 0 = 18.2, 1 = 19.2, 2 = 20.2, 3 = 21.2, 4 = 22.2, 5 = 23.2, 6 = 24.2, 7 = 25.2, 8 = 26.2, 9 = 27.2, 10 = 28.2.

phosphate - decabromobiphenyl (Figure 3.30). In this case however the maximum is shifted slightly towards the melamine axis and it can be seen that melamine is more effective than tritolyl phosphate because there is a greater increase of LOI along the melamine axis. Quantitative data are given in Table 3.12.

The coefficients show that melamine is only slightly more effective than tritolyl phosphate. Both compounds raise the LOI by between 3.1 and 3.5 LOI units, while decabromobiphenyl results in a contribution of 2.6 LOI units. The extent of synergism is considerably greater in the tritolyl phosphate - melamine system resulting in a contribution of 2.1 LOI units ± 0.7 for a loading of 10 wt percent of each additive, whilst for the tritolyl phosphate - decabromobiphenyl case the rise is only 0.8 ± 0.3 LOI units.

The values are however lower than those for red phosphorus (Table 3.3), showing that on a weight basis red phosphorus is more effective than tritolyl phosphate as a flame retardant for cotton.

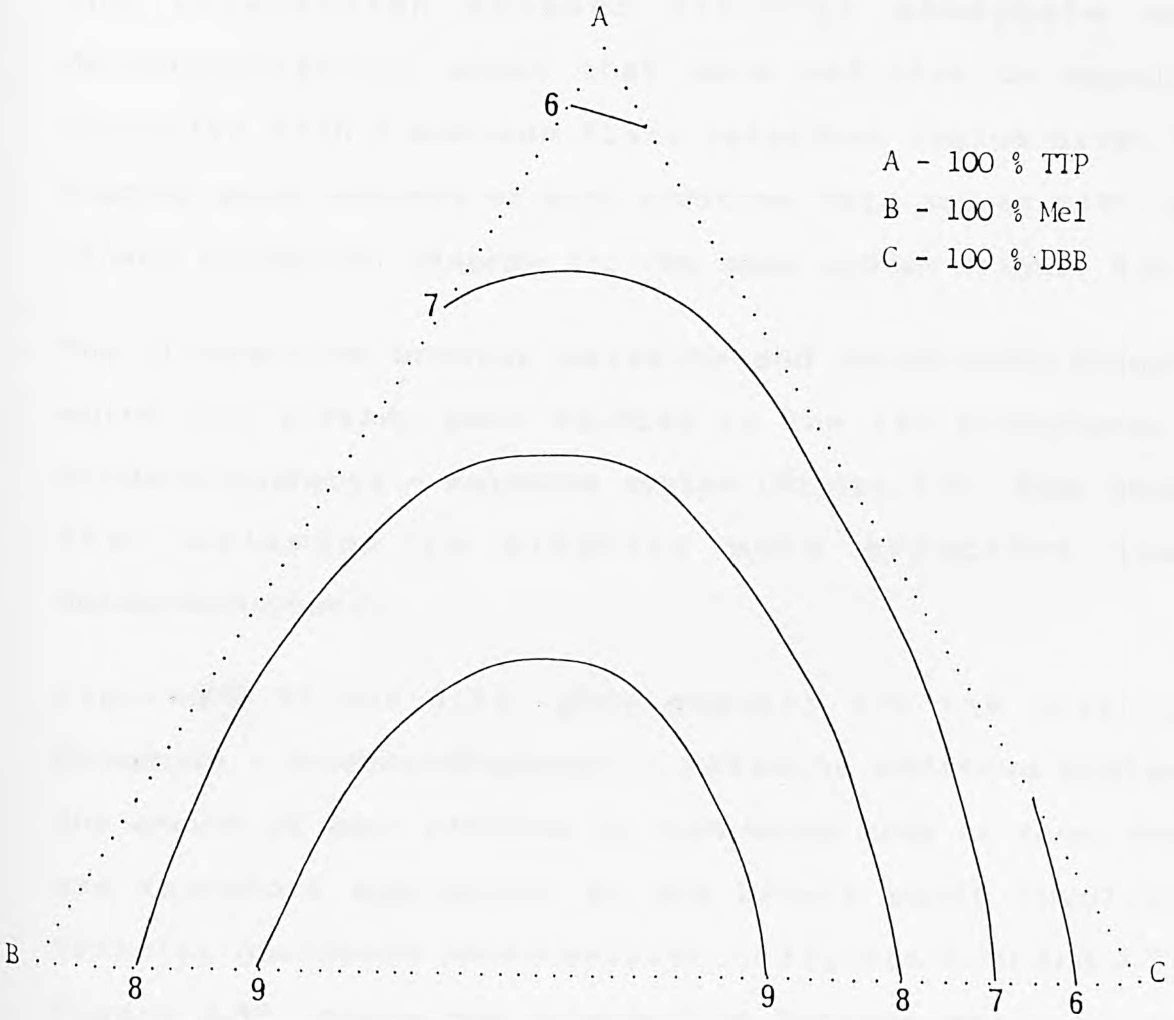
Figure 3.32 shows a triangular diagram for the ternary additive tritolyl phosphate - decabromobiphenyl - melamine systems, obtained from the ternary additive - four component program with one of these additives at each vertex. This therefore indicates the interaction between the various additives when the amount of cellulose is kept constant. The

Table 3.12 Quantitative data for the cellulose binary flame retardant combinations of tritolyl phosphate - decabromobiphenyl - melamine systems

Order	Root mean square difference (σ)	Sequential F-test ratio	Average coefficients over range 0 - 0.2	Synergism
Tritolylphosphate - decabromobiphenyl Reduced cubic	0.7	4.0	P = 31.0 ± 4.1 B = 25.6 ± 4.1	84.4 ± 34.2
Tritolylphosphate - Melamine Reduced cubic	0.6	4.8	P = 32.6 ± 4.2 N = 34.9± 4.9	208.5 ± 68.1

P = Tritolylphosphate
B = Decabromobiphenyl
N = Melamine

Figure 3.32 Triangular diagram showing variation with composition for tritolyl phosphate - decabromobiphenyl - melamine ternary additive system



LOI values: 0 = 18.2, 1 = 19.2, 2 = 20.2, 3 = 21.2, 4 = 22.2, 5 = 23.2, 6 = 24.2, 7 = 25.2, 8 = 26.2, 9 = 27.2, 10 = 28.2.

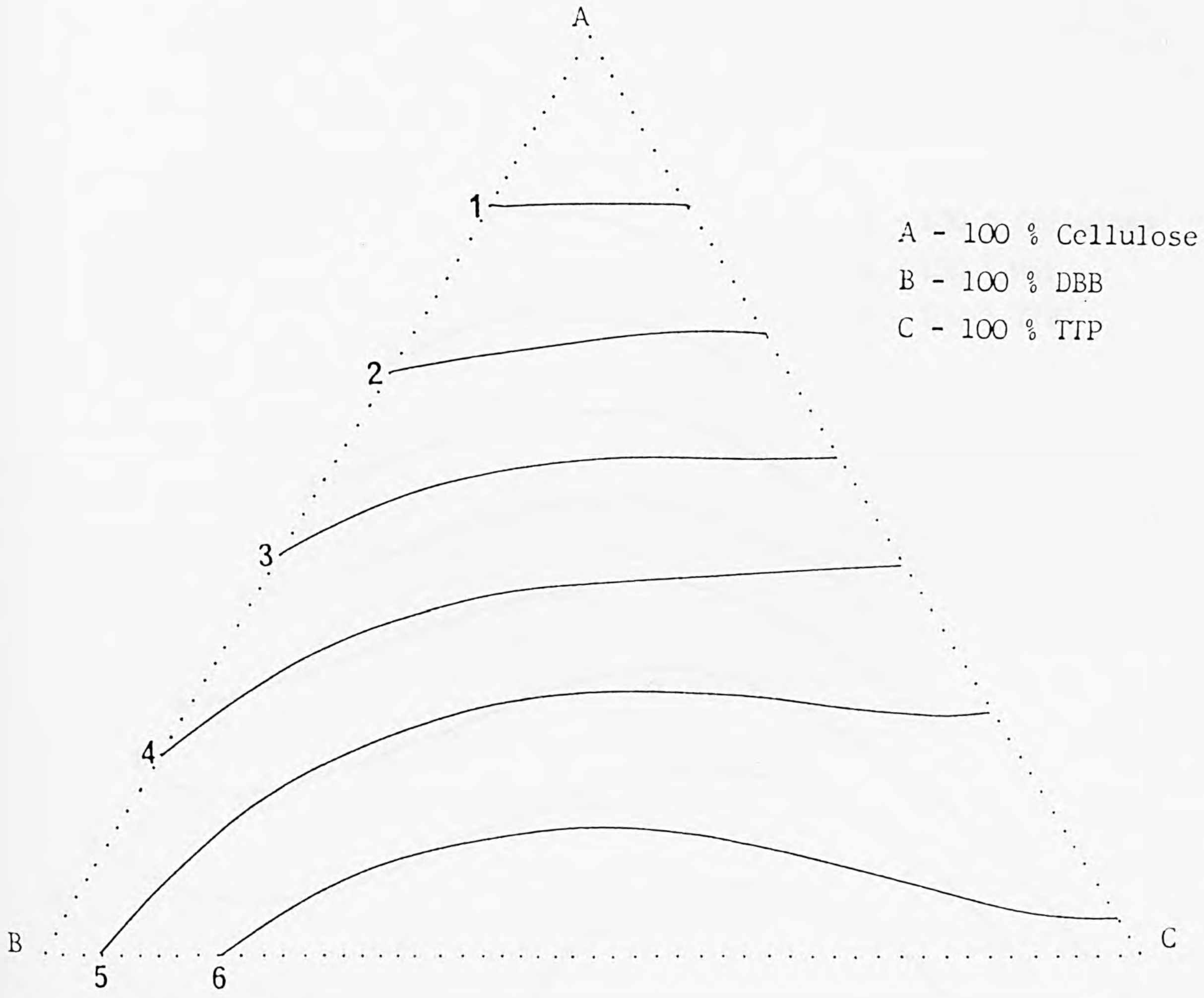
diagram shows a significant interaction between tritolyl phosphate and melamine when they are present in almost equal proportions. This agrees with results obtained for the binary additive, tritolyl phosphate - melamine system (Figure 3.31). The binary diagram shows more clearly that melamine is in fact more effective than tritolyl phosphate. The interaction between tritolyl phosphate and decabromobiphenyl shows that each additive is equally effective with a maximum flame retardant region given by roughly equal amounts of each additive. This agrees with the binary triangular diagram for the same system (Figure 3.30).

The interaction between melamine and decabromobiphenyl, which had already been studied in the red phosphorus - decabromobiphenyl - melamine system (Figure 3.5), also shows that melamine is slightly more effective than decabromobiphenyl.

Figures 3.33 and 3.34 show results for the tritolyl phosphate - decabromobiphenyl - melamine additive system, the amount of each additive in turn being kept at zero; they are therefore equivalent to the binary plots involving tritolyl phosphate shown earlier in Figures 3.30 and 3.31. Figure 3.35 shows the interaction between melamine and decabromobiphenyl and the results agree reasonably well with those in Figure 3.5.

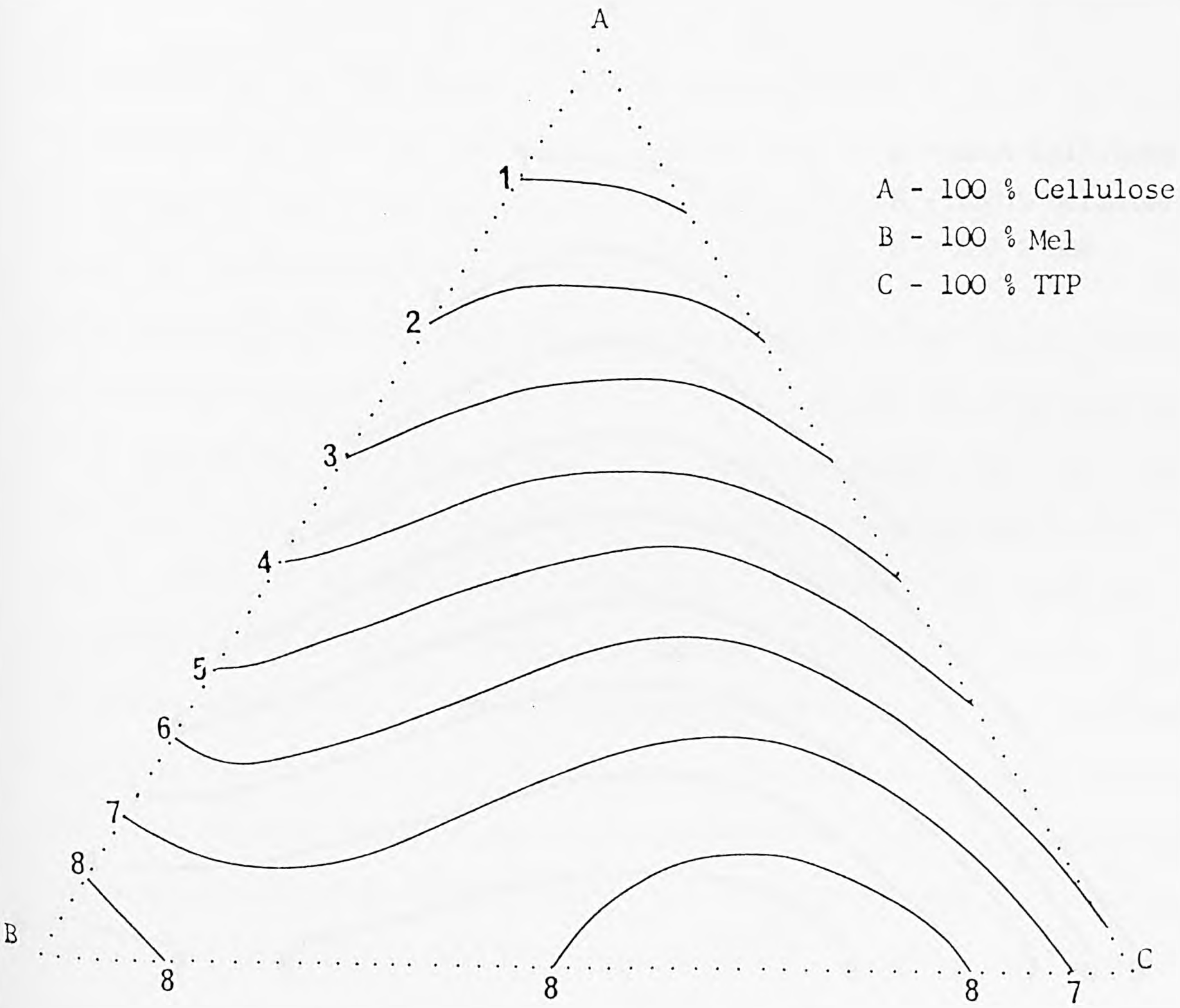
Critical comparison of Figures 3.31 and 3.34 which relate to the interaction between tritolyl phosphate and melamine

Figure 3.33 Triangular diagram showing variation of LOI with composition for the cellulose ternary additive system - tritolyl phosphate - decabromobiphenyl - melamine with melamine held constant at zero



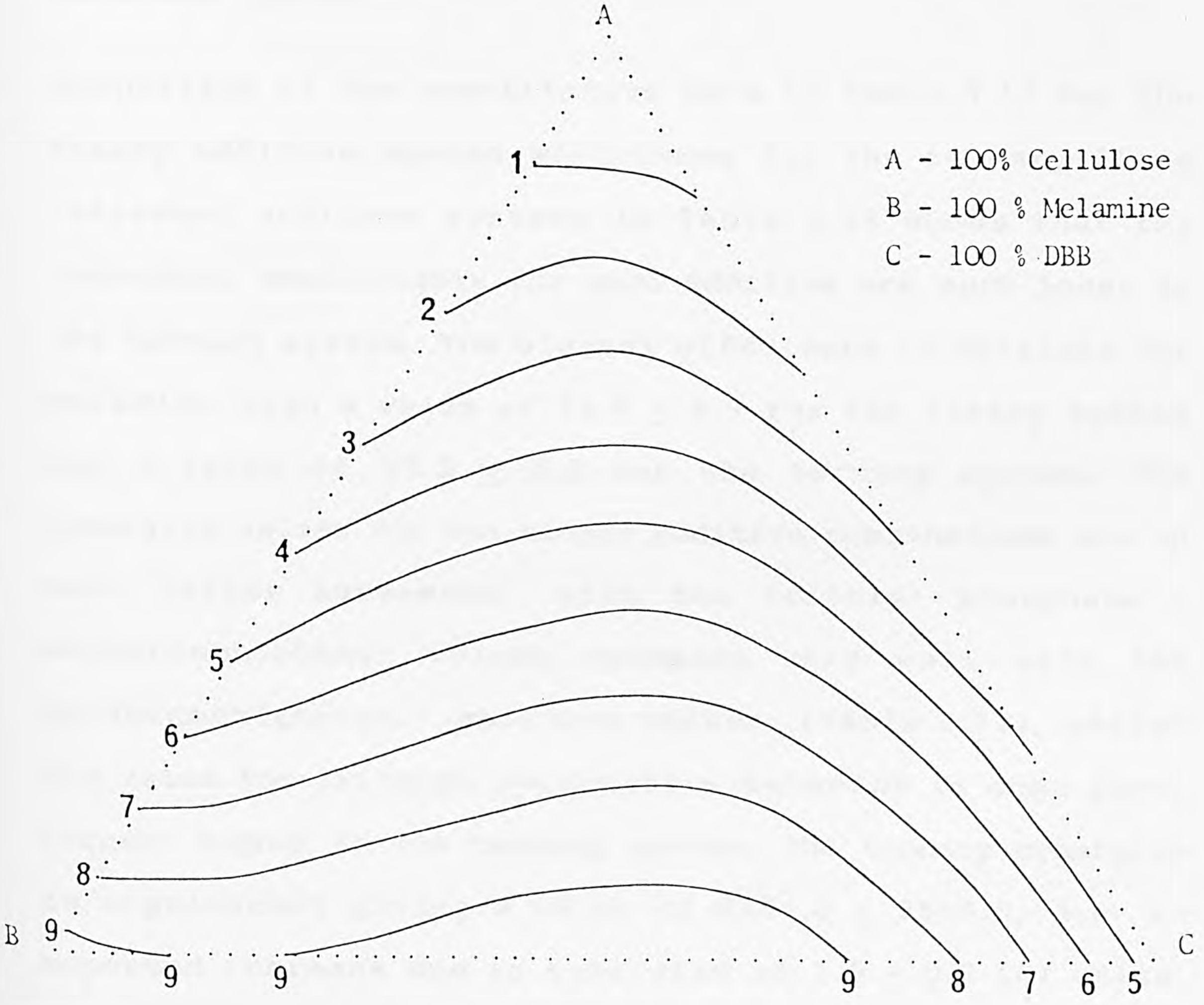
LOI values: 0 = 18.2, 1 = 19.2, 2 = 20.2, 3 = 21.2, 4 = 22.2, 5 = 23.2, 6 = 24.2, 7 = 25.2, 8 = 26.2, 9 = 27.2, 10 = 28.2.

Figure 3.34 Triangular diagram showing variation of LOI with composition for the cellulose ternary system - tritolyl phosphate - decabromobiphenyl - melamine with decabromobiphenyl held constant at zero



LOI values: 0 = 18.2, 1 = 19.2, 2 = 20.2, 3 = 21.2, 4 = 22.2, 5 = 23.2, 6 = 24.2, 7 = 25.2, 8 = 26.2, 9 = 27.2, 10 = 28.2.

Figure 3.35 **Triangular diagram showing variation of LOI with composition for the cellulose - ternary additive system tritolyl phosphate - decabromobiphenyl - melamine with tritolyl phosphate held constant at zero**



LOI values: 0 = 18.2, 1 = 19.2, 2 = 20.2, 3 = 21.2, 4 = 22.2, 5 = 23.2, 6 = 24.2, 7 = 25.2, 8 = 26.2, 9 = 27.2, 10 = 28.2.

reveals a slightly different increase in the flame retardant contour. Triangular diagrams for tritolyl phosphate - decabromobiphenyl systems (Figures 3.30 and 3.33) agree better, despite a lower contour in the ternary additive system.

Table 3.13 gives quantitative data for the ternary flame retardant system.

Comparison of the quantitative data in Table 3.12 for the binary additive system with those for the ternary flame retardant additive systems in Table 3.13 shows that the individual coefficients for each additive are much lower in the ternary system. The biggest difference is obtained for melamine with a value of 34.9 ± 4.9 for the binary system and a value of 27.3 ± 5.2 for the ternary system. The synergism values for the binary additive combinations are in much better agreement, with the tritolyl phosphate - decabromobiphenyl values agreeing very well with the decabromobiphenyl - melamine values (Table 3.12), whilst the value for tritolyl phosphate - melamine is some forty percent higher in the ternary system. The ternary synergism is significant giving a value of 4234.0 ± 2699.0, i.e. an expected increase due to synergism of 1.3 ± 0.8 LOI units. The error is relatively large, but the value does represent a sizeable positive interaction between the three flame retardant additives. The increase in LOI due to the individual coefficients for each additive are tritolyl phosphate (2.5), decabromobiphenyl (2.0) and melamine

Table 3.13 Quantitative data for the cellulose - ternary flame retardant system of tritolyl phosphate - decabromobiphenyl - melamine for the reduced quartic model

Root mean square difference (σ) = 0.7

Sequential F-test = 3.7

Average coefficients over the range 0 - 0.2

Individual flame-retardant additives

Tritolylphosphate = 24.8 ± 4.6

Decabromobiphenyl = 19.8 ± 5.1

Melamine = 27.3 ± 5.2

Binary flame-retardant additive combinations:

Tritolylphosphate - Decabromobiphenyl = 81.6 ± 54.6

Tritolylphosphate - Melamine = 191.2 ± 68.7

Decabromobiphenyl - Melamine = 302.2 ± 63.4

Ternary flame-retardant additive combinations:

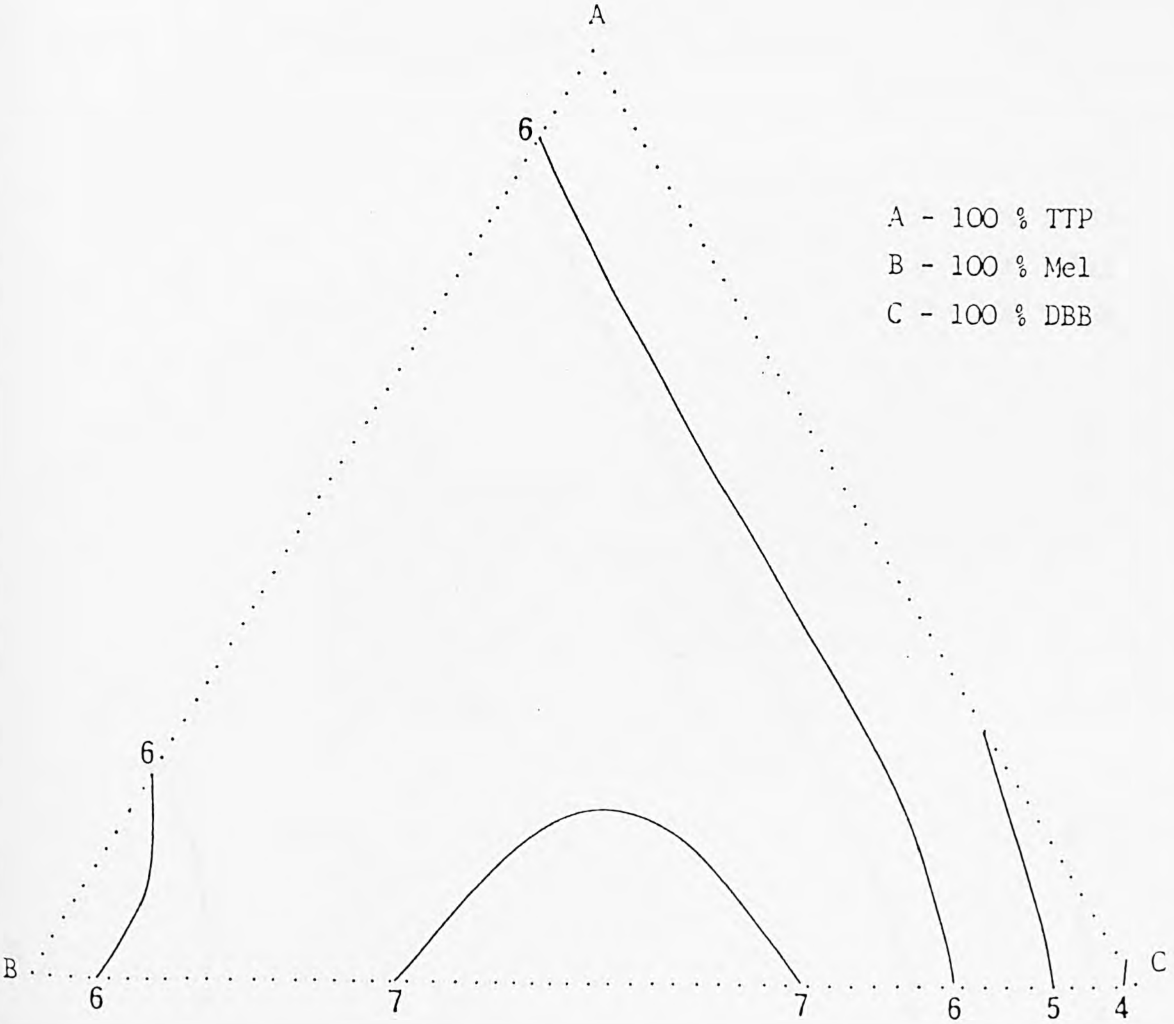
Tritolylphosphate - Decabromobiphenyl - Melamine = 4234.0 ± 2699.0

(2.7)(Table 3.13). This gives a total change of 8.5 LOI units which is in quite good agreement with the experimentally determined value of 7.3 LOI units obtained for the ternary additive system (Table 3.10).

Slices through the tetrahedron at representative cross sectional values are shown in Figures 3.36 to 3.38. Each slice represents a situation when the percentage of cellulose is kept constant at values of 81.25, 87.50 and 93.75 respectively. As expected, the effectiveness of the additives increases as the loading is increased over the range examined.

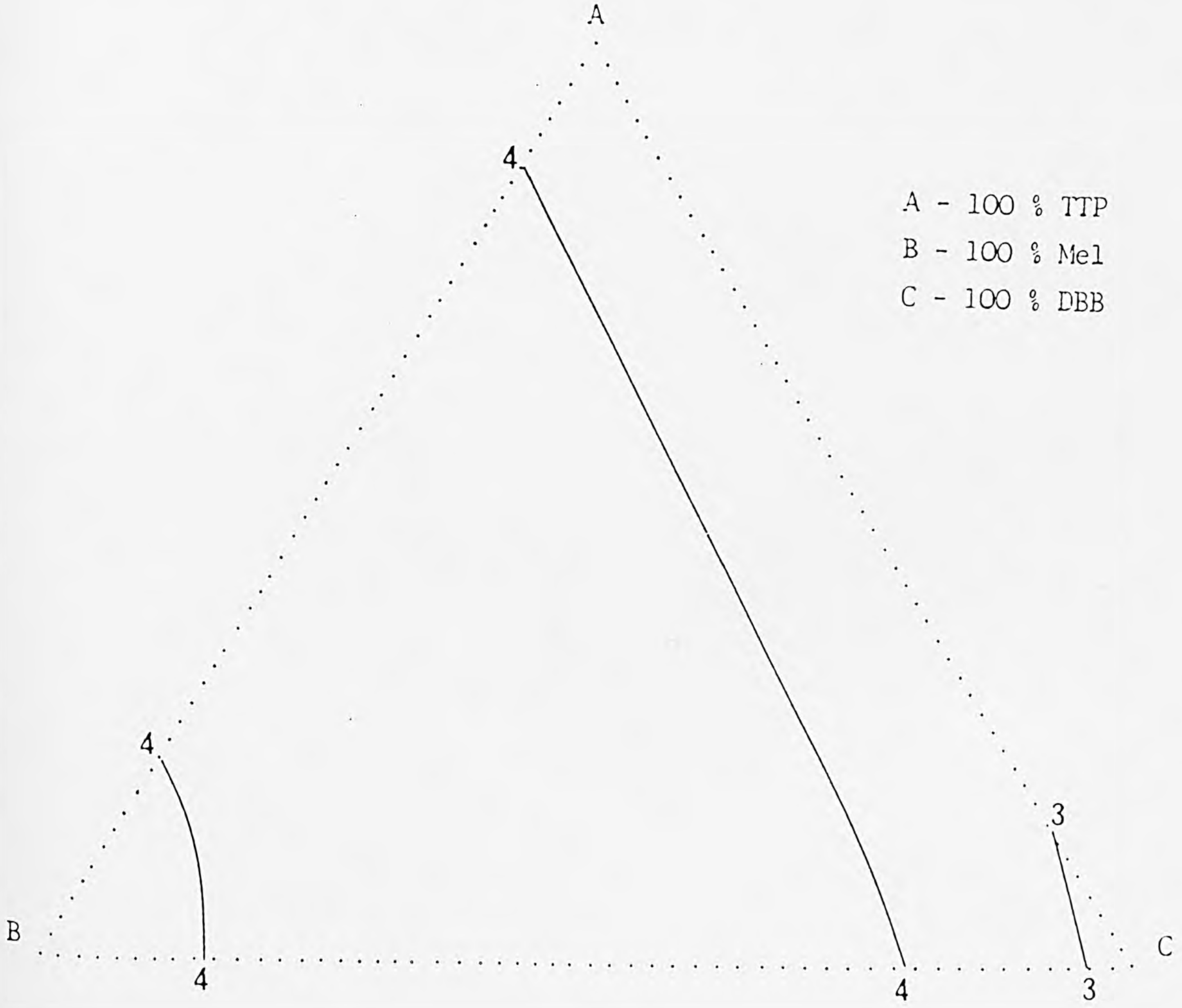
In summary then, tritolyl phosphate causes a small reduction in the flammability of cellulose - cotton cloth. It is not, however, as effective as red phosphorus when used at a similar loading but since it contains very little phosphorus (8.4 percent) it is more effective on the basis of the percentage weight of phosphorus. The combination of tritolyl phosphate with decabromobiphenyl and melamine causes a further reduction in the flammability of cellulose, a tritolyl phosphate - melamine combination showing an effect similar to that for the red phosphorus - melamine system.

Figure 3.36 Triangular diagram showing a slice through the tetrahedron with cellulose being held constant at 81.25 percent showing the variation of LOI with composition for the cellulose - ternary additive system - tritolyl phosphate - decabromobiphenyl - melamine



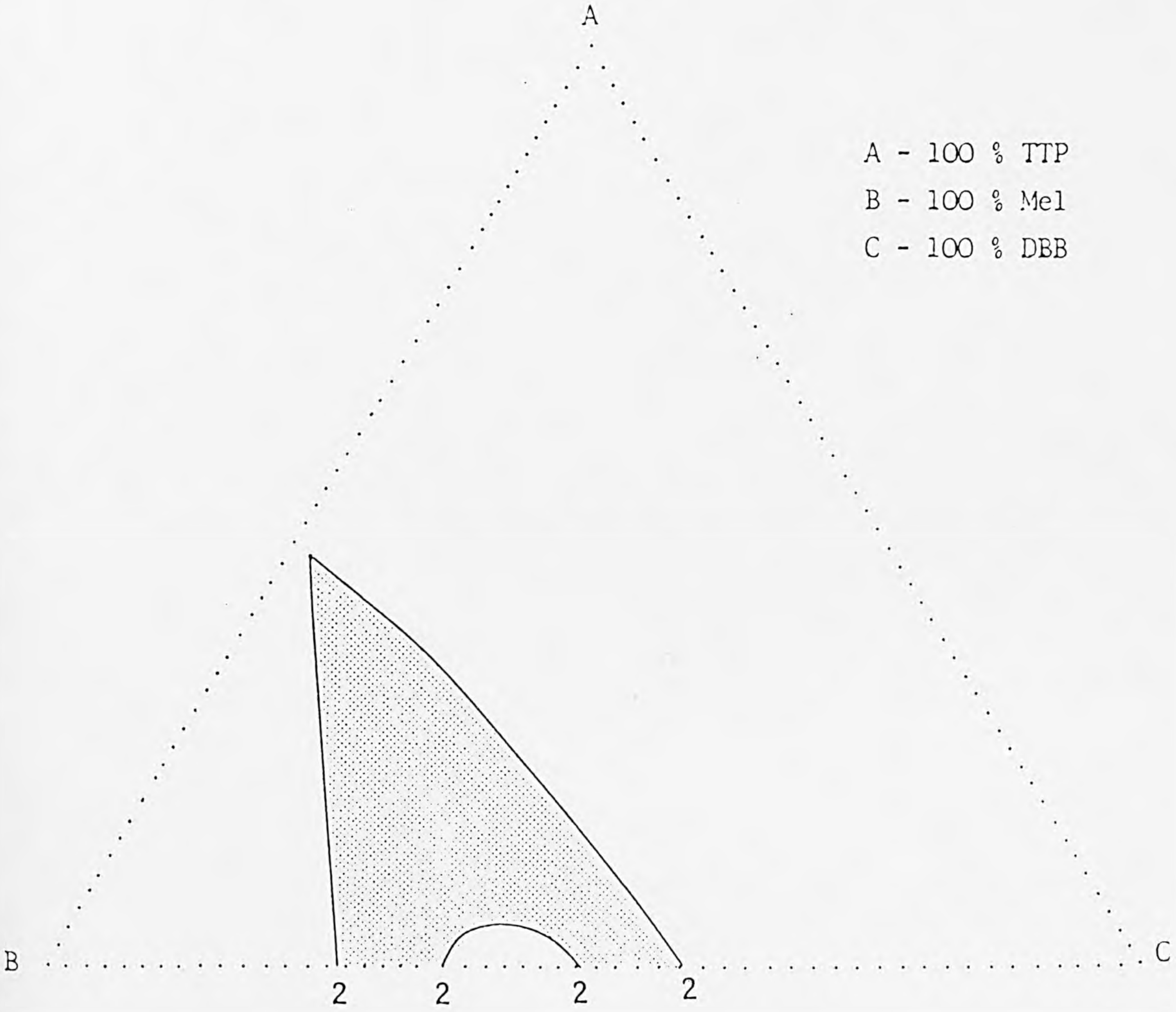
LOI values: 0 = 18.2, 1 = 19.2, 2 = 20.2, 3 = 21.2, 4 = 22.2, 5 = 23.2, 6 = 24.2, 7 = 25.2, 8 = 26.2, 9 = 27.2, 10 = 28.2.

Figure 3.37 Triangular diagram showing a slice through the tetrahedron with cellulose being held constant at 87.50 percent showing the variation of LOI with composition for the cellulose - ternary additive system - tritolyl phosphate - decabromobiphenyl - melamine



LOI values: 0 = 18.2, 1 = 19.2, 2 = 20.2, 3 = 21.2, 4 = 22.2, 5 = 23.2, 6 = 24.2, 7 = 25.2, 8 = 26.2, 9 = 27.2, 10 = 28.2.

Figure 3.38 Triangular diagram showing a slice through the tetrahedron with cellulose being held constant at 93.75 percent showing the variation of LOI with composition for the cellulose - ternary additive system - tritolyl phosphate - decabromobiphenyl - melamine



LOI values: 0 = 18.2, 1 = 19.2, 2 = 20.2, 3 = 21.2, 4 = 22.2, 5 = 23.2, 6 = 24.2, 7 = 25.2, 8 = 26.2, 9 = 27.2, 10 = 28.2.

3.2.2 Simultaneous thermal analysis of a cellulose - tritolyl phosphate systems containing decabromobipnenyl and / or melamine system

Figure 3.39 shows the TG trace for a cellulose - tritolyl phosphate system. There is a significant weight loss between 200 and 270°C. This represents approximately 11 percent of the total weight and is therefore presumably attributable to the loss of tritolyl phosphate from the cloth. The second and third weight loss stages correspond with the two weight losses which occur during the decomposition of cellulose on its own. However, both these weight losses occur at temperatures some 20° higher than for cellulose alone. The weight loss at the CBO stage is reduced slightly from 18.0 percent for cellulose alone to 17.0 percent indicating that tritolyl phosphate does not promote dehydration of the cellulose. These data are summarised in Table 3.14.

In the presence of both tritolyl phosphate and melamine a slightly higher initial weight loss of 14 percent is observed at 240°C. The second and third weight losses agree well with those for cellulose. The weight loss at the CBO stage is 21.0 percent which is slightly higher than for cellulose alone (Table 3.14). The presence of melamine has been shown previously to increase the weight loss at the CBO stage (Table 3.8). Thus tritolyl phosphate alone causes a reduction at the CBO stage and therefore does not catalyse dehydration. When tritolyl phosphate is used in combination

Figure 3.39 Thermogravimetric (TG) trace of cellulose cotton cloth containing 10 wt percent tritolyl phosphate

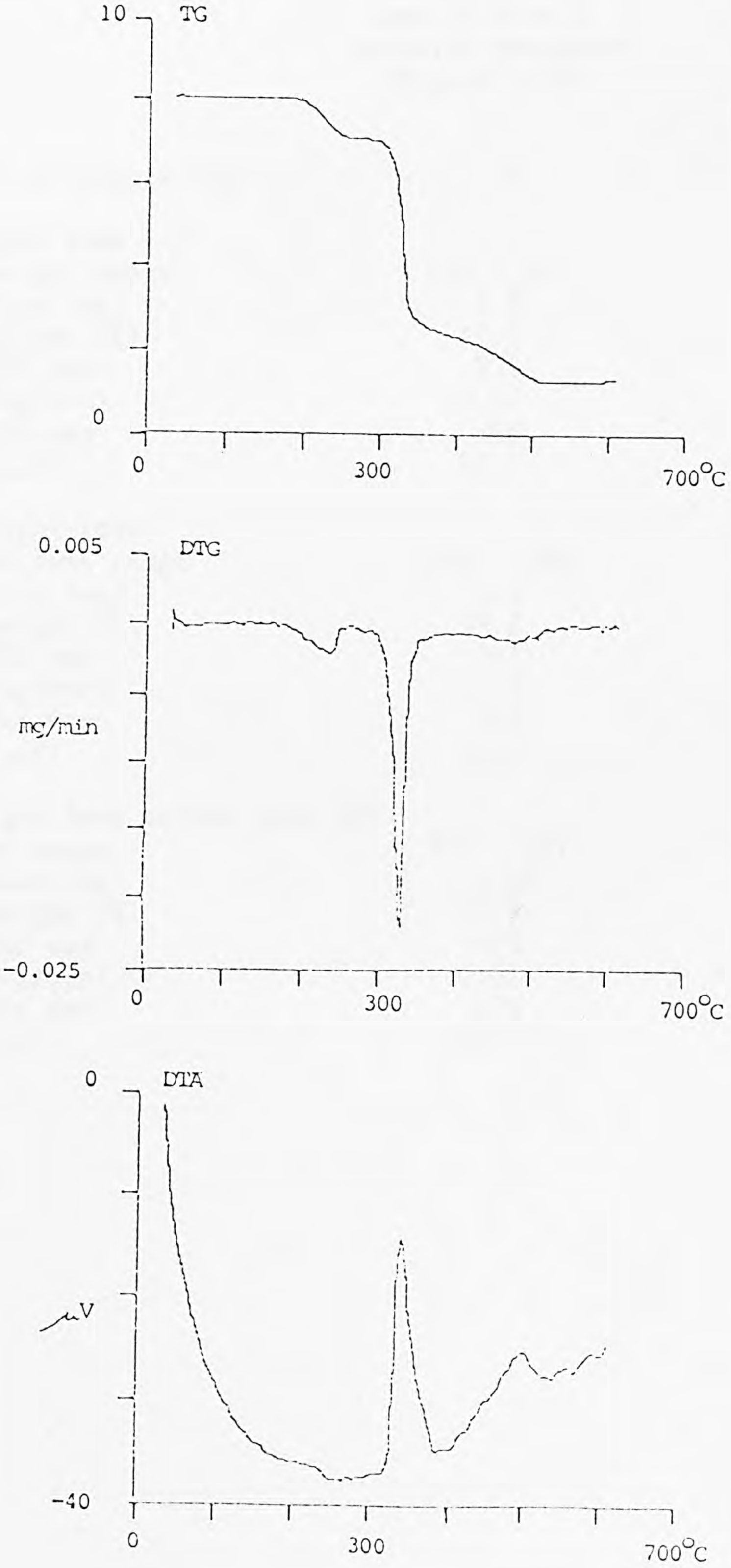


Table 3.14 Thermal analysis data for cellulose - tritolyl phosphate - melamine systems

Sample Name	Cotton cloth and 15.8 wt % tritolyl phosphate (Figure 3.39)	Cotton cloth and 6.1 wt % tritolyl phosphate and 12.6 wt % melamine
Initial wt of sample (mg)	7.6	7.6
First weight loss		
Temp of weight range	229 - 274	167 - 272
Weight value (mg)	0.8	1.1
Loss in weight (%)	11.2	14.4
Temp of DTG max	239	210
DTG max (mg/min)	-0.12	-0.09
Temp of DTA max	268	221
DTA max (μV)	37.7	40.9
Second weight loss		
Temp of wt loss range	294 - 360	303 - 361
Weight value (mg)	4.5	3.8
Loss in weight (%)	59.2	49.6
Temp of DTG max	337	322
DTG max (mg/min)	-1.3	-1.07
Temp of DTA max	344	332
DTA max (μV)	14.4	2.6
Third weight loss carbon burn off		
Temp of wt range	373 - 501	371 - 556
Weight value (mg)	1.09	1.7
Loss in weight (%)	15.9	21.0
Temp of DTG max	479	481
DTG max (mg/min)	-0.07	-0.08
Temp of DTA max	474	500
DTA max (μV)	28.4	31.6

with melamine, there is a minimal increase in the CBO stage, suggesting that some dehydration takes place.

3.2.3 Effects of phosphorus compounds in different oxidation states on the flammability of cellulose in the absence or presence of melamine

Table 3.15 shows the effects of a range of phosphorus compounds of different oxidation states on the flammability of cotton cloth.

It can be seen that tritolyl phosphate and triphenyl phosphine are almost equally effective in reducing the flammability of cellulose on the basis of percentage weight of phosphorus, with values of 3.0 and 2.9 for Δ LOI / % P, i.e., taking into consideration the loading of the particular additive and the amount of phosphorus in the compound. Triphenyl phosphite is slightly less effective with a value of 2.6. Red phosphorus, which contains at least 99 percent of the element, is evidently relatively ineffective as a flame retardant additive.

Table 3.16 shows the effects of some phosphorus compound - melamine mixtures on the flammability of cotton cloth. In the presence of melamine the flammability of cellulose is in general further reduced by all of the phosphorus compounds except triphenyl phosphite. The reduction in flammability of most systems seems to be achieved by ratios of phosphorus : nitrogen, of approximately 1:2. Triphenyl phosphine is however more effective in a 2:1 ratio. Table 3.17 shows the quantitative data for these systems.

Table 3.15 **The effect of a range of phosphorus compounds in different oxidation states on the flammability of cellulose**

Phosphorus compound	Oxidation stage	Phosphorus Additive (wt %)	Amount of Phosphorus in compound (%)	Equivalent amount of Phosphorus* (%)	LOI	Δ LOI / %P
-		-	-	-	18.2	-
Tritolyl phosphate	+5	17.4	8.4	1.5	22.7	3.0
Dimethyl methyl phosphonate	+3	11.9	25.0	3.0	24.1	2.0
Triphenylphosphite	+3	16.0	10.0	1.6	22.3	2.6
Red phosphorus	0	16.4	99.0	16.2	23.1	0.3
Triphenyl phosphine oxide	-1	13.5	11.2	1.5	20.9	1.8
Triphenyl phosphine	-3	10.9	11.8	1.3	22.0	2.9

* Equivalent amount of phosphorus calculated by multiplying the wt percent of additive by the amount of phosphorus in the compound.

Table 3.16 The effect of phosphorus - melamine combinations on the flammability of cellulose

Phosphorus compound	Phosphorus (wt %)	Equivalent amount of phosphorus (%)	Melamine (wt %)	LOI	LOI / %P
-	-	-	-	18.2	-
-	-	-	7.6	21.7	-
-	-	-	14.9	25.1	-
Tritolyl phosphate	6.1	0.51	12.6	24.8	12.9
Dimethyl methyl phosphonate	6.5	1.63	10.2	27.6	5.8
Red phosphorus	9.2	9.10	11.3	26.3	0.9
Triphenyl phosphite	9.3	0.93	10.6	26.1	8.5
Triphenyl phosphine oxide	5.8	0.65	9.2	23.7	8.5
Triphenyl phosphine	13.8	1.63	5.8	24.4	3.8

Table 3.17 Quantitative data for the cellulose - phosphorus additive - melamine systems

Phosphorus compound	Order	σ	Coefficients P = phosphorus additive N = melamine	Synergism
Tritolyl phosphate*	RC	0.71	P = 24.8 ± 4.6 N = 27.3 ± 5.2	191.2 ± 68.7
Dimethyl methyl phosphonate	RC	0.60	P = 46.5 ± 5.4 N = 21.9 ± 5.0	733.7 ± 141.1
Triphenyl phosphite	Q	0.74	P = 45.0 ± 10.9 N = 23.5 ± 6.3	570.0 ± 140.0
Triphenyl phosphine oxide	Q	0.61	P = 18.3 ± 5.8 N = 21.4 ± 5.1	419.8 ± 135.4
Triphenylphosphine	Q	0.56	P = 28.8 ± 6.4 N = 22.1 ± 4.8	141.8 ± 134.5

RC = reduced cubic

Q = quadratic

* Values taken from data obtained for ternary flame retardant system (cf. Table 3.10)

There seems to be a reasonable correlation between the degree of synergism and the reduced flammability of the mixtures. This can be seen for the dimethyl methyl phosphonate - melamine system which has a synergism value of 733.7 ± 141.1, the largest value in Table 3.17, and also the highest LOI value of 27.6. The synergism value for triphenyl phosphine has a significant error and therefore the synergism is not very conclusive in this case.

In summarizing the effectiveness of the phosphorus compounds studied, tritolyl phosphate and triphenyl phosphine are on the basis of the percentage weight of phosphorus the most effective additives. The addition of melamine causes a further reduction in flammability in all systems studied.

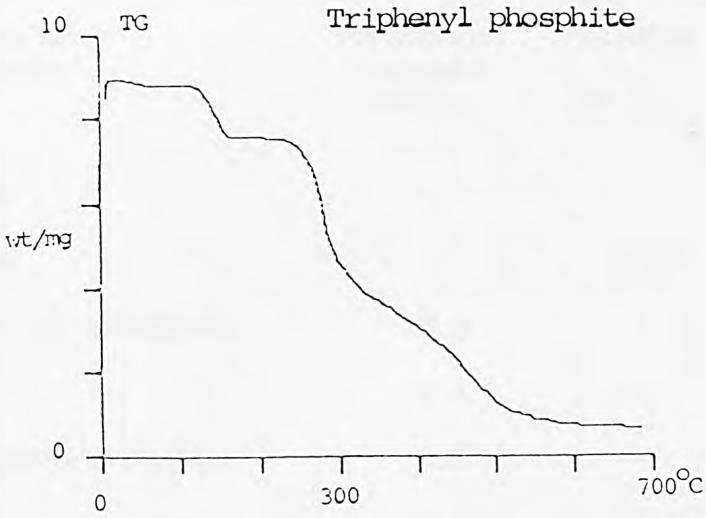
3.2.4 Simultaneous thermal analysis of cellulose - melamine systems containing various phosphorus compounds.

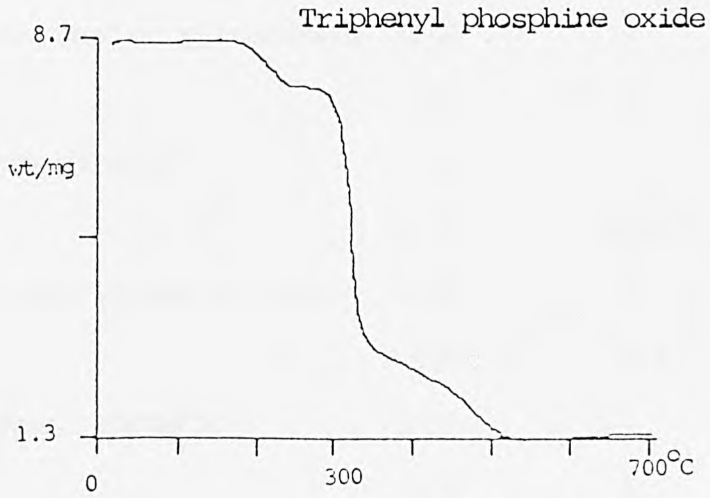
Figure 3.40 shows TG traces for cellulose - triphenyl phosphite, cellulose - triphenylphosphine oxide and cellulose - triphenyl phosphine systems. Each of the additives shows an additional weight-loss stage occurring prior to the two weight losses attributable to the decomposition of cellulose. A cellulose - dimethylmethylphosphonate mixture produces a TG trace similar to that of cellulose on its own.

Table 3.18 shows the percentage loss at the CBO stage for the phosphorus - melamine systems studied. All the phosphorus compounds produce an increase in weight at the CBO stage above the value of 18 percent for cotton cloth alone, except triphenyl phosphine oxide which shows a small reduction. The increases observed at the CBO stage for most of the phosphorus compounds studied, (e.g. 34 percent for triphenyl phosphite and 32 percent for dimethyl methylphosphonate) suggest that these phosphorus compounds promote dehydration of the cellulose.

On comparison of the percentage loss at the CBO stage and the flammability results given in Table 3.16, the least effective phosphorus compound in reducing the flammability of cellulose is triphenyl phosphine oxide, which also produces the least char, and is therefore likely to bring

Figure 3.40 Weight loss trace for samples of cellulose - cotton cloth containing triphenyl phosphite, triphenyl phosphine oxide and triphenyl phosphine


Triphenyl phosphite


Triphenyl phosphine oxide

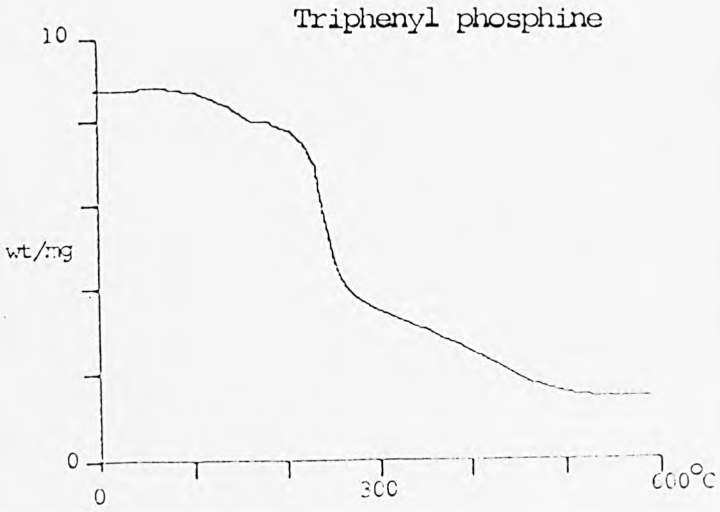

Triphenyl phosphine

Table 3.18 Summary of the percentage loss at the carbon burn off (CBO) stage for various phosphorus compound - melamine systems on cotton cloth

Phosphorus Compound	Phosphorus Compound (wt %)	Melamine (wt %)	CBO (%)	Δ CBO / wt % P
None	-	-	18.0	-
None	-	10.0	24.2	0.62
Tritolyl phosphate	15.8	-	15.9	-0.13
	6.1	12.6	27.5	-
Triphenylphosphite	16.0	-	34.2	1.01
-	9.3	10.6	38.6	-
Dimethylmethyl phosphonate	11.8	-	31.8	1.17
	6.5	10.2	35.8	-
Red phosphorus	15.0	-	30.6	0.84
	10.0	10.0	26.1	-
Triphenyl phosphine oxide	13.5	-	16.9	-0.09
	5.8	9.2	17.8	-
Tsiphenyl phosphine	10.8	-	23.0	0.46
	6.5	8.7	21.9	-

about its effects in the gas phase.

In the case of the cellulose - phosphorus - melamine systems, both triphenyl phosphite and dimethyl methyl phosphonate, when combined with melamine, result in an increase at the CBO stage. The triphenyl phosphine oxide - melamine mixture undergoes a decrease (less than 1 percent) compared with melamine on its own and triphenyl phosphine also shows a decrease from 23 to 21.9 percent.

In summary, all the phosphorus compounds studied cause an increase in the CBO stage, except triphenyl phosphine oxide which shows a very small decrease. The addition of melamine to cellulose - phosphorus additive systems causes an increase in the CBO as is seen for triphenylphosphite and dimethylmethylphosphonate and a slight decrease for triphenyl phosphine and triphenyl phosphine oxide.

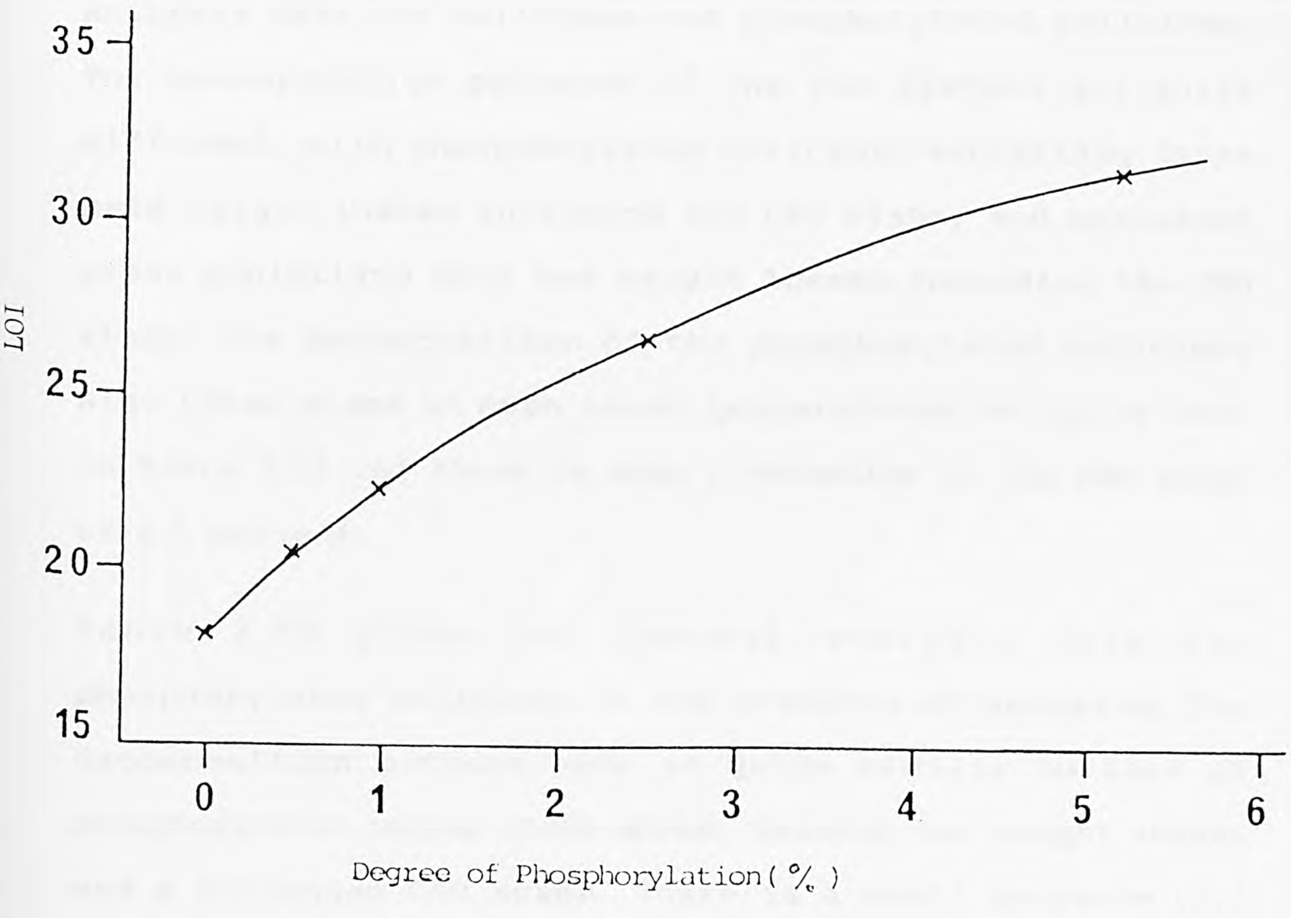
3.3 The effects of chemical modification on the thermal behaviour of cellulose

3.3.1 Effect of phosphorylation on flammability

Figure 3.41 shows the effect of phosphorylation of cellulose on the LOI over the range 0.5 - 5.2 wt percent phosphorus. As can be seen the higher the degree of phosphorylation the greater is the flame retardant effect. At 5.2 wt percent phosphorus the LOI increases from 18.2 to 31.5, an increase of 13.3 LOI units.

With the addition also of 5 wt percent melamine to cotton containing 5.2 wt percent phosphorus, the LOI increases still further to 35.0. A similar loading of melamine to non-phosphorylated cotton gives a rise of only 1.7 LOI units, suggesting a strong synergistic action between nitrogen and phosphorus.

Figure 3.41 The effect of phosphorylation on the flammability of cellulose-cotton cloth



3.3.2 Simultaneous thermal analysis of phosphorylated cellulose in the absence and presence of melamine

The TG trace in Figure 3.42 shows that the main decomposition of phosphorylated cotton cloth occurs much more slowly than that of cellulose on its own and does not start to take place below ca. 280°C. The trace shows however that this decomposition involves two distinct weight losses at 320 and 460°C. Table 3.19 gives a comparison of thermal analysis data for cellulose and phosphorylated cellulose. The decomposition patterns of the two systems are quite different, with phosphorylated cellulose exhibiting three main weight losses including the CBO stage, and cellulose alone exhibiting only two weight losses including the CBO stage. The decomposition of the phosphorylated cellulose also takes place at much lower temperatures as can be seen in Table 3.19 and there is also a reduction in the CBO stage of 4.5 percent.

Table 3.20 gives the thermal analysis data for phosphorylated cellulose in the presence of melamine. The decomposition pattern here is quite similar to that of phosphorylated cotton cloth alone, showing two weight losses and a prolonged CBO stage. There is a small increase (2.4 percent) in the CBO stage with the addition of melamine, suggesting that melamine may be acting at least in part via a condensed-phase mechanism. Thermal analysis shows that the decomposition of phosphorylated cotton cloth is quite

Figure 3.42 Simultaneous thermal analysis plots for phosphorylated cotton cloth containing 5.2 wt percent phosphorus

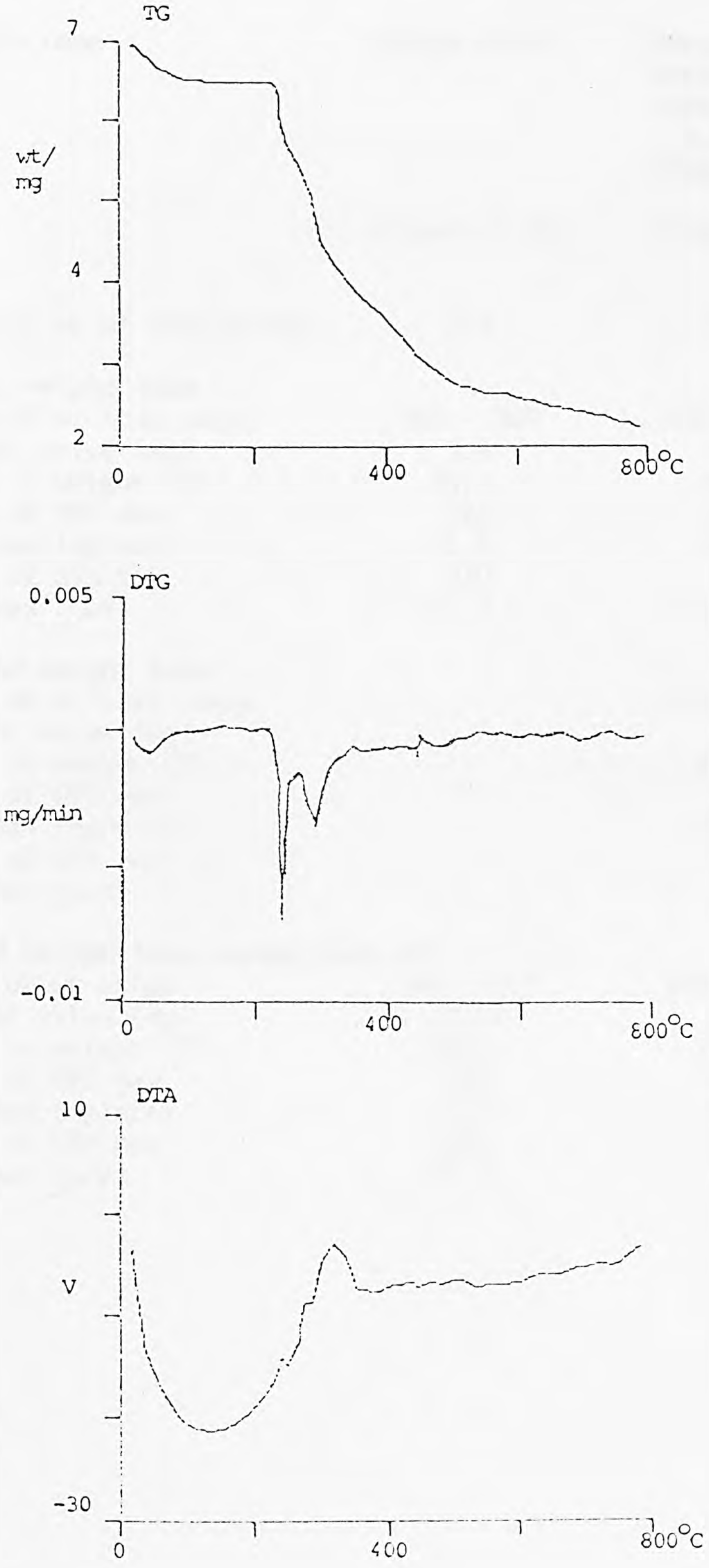


Table 3.19 Thermal analysis data for phosphorylated cellulose

Sample name	Cotton cloth	Phosphorylated cotton cloth containing 5.2 wt% phosphorus
	(Figure 3.10)	(Figure 3.42)
Initial wt of sample (mg)	7.9	6.9
First weight loss		
Temp of wt loss range	287 - 349	230 - 273
Weight value (mg)	5.6	1.04
Loss in weight (%)	70.6	15.1
Temp of DTG max	320	247
DTG max (mg/min)	-1.9	-0.43
Temp of DTA max	330	247
DTA max (μV)	21.3	14.1
Second weight loss		
Temp of wt loss range		273 - 350
Weight value (mg)		1.49
Loss in weight (%)		21.7
Temp of DTG max		296
DTG max (mg/min)		-0.22
Temp of DTA max		324
DTA max (μV)		2.8
Third weight loss carbon burn off		
Temp of wt range	366 - 477	396 - 517
Weight value (mg)	1.42	0.88
Loss in weight (%)	18.0	13.6
Temp of DTG max	460	449
DTG max (mg/min)	-0.12	-0.06
Temp of DTA max	460	450
DTA max (μV)	10.5	7.1

Table 3.20 Thermal analysis data for phosphorylated cellulose in the presence of melamine

Sample name	Phosphorylated cotton cloth containing 5.2 wt % phosphorus and 7.7 wt % melamine
Initial wt of sample (mg)	7.7
First weight loss	
Temp of wt loss range	190 - 271
Weight value (mg)	2.1
Loss in weight (%)	28.0
Temp of DTG max	245
DTG max (mg/min)	-0.64
Temp of DTA max	255
DTA max (µV)	20.4
Second weight loss	
Temp of wt loss range	271 - 357
Weight value (mg)	1.3
Loss in weight (%)	17.2
Temp of DTG max	299
DTG max (mg/min)	-0.15
Temp of DTA max	392
DTA max (µV)	0.1
Third weight loss	Carbon burn off
Temp of wt range	392 - 564
Weight value (mg)	1.05
Loss in weight (%)	16.0
Temp of DTG max	474
DTG max (mg/min)	-0.05
Temp of DTA max	564
DTA max (µV)	13.9

different from that of cellulose on its own. The presence of the phosphorus slightly reduces the amount of char formed, but the addition of melamine slightly increases the char yield.

3.3.3 Effects of red phosphorus and melamine on the flammability of cellulose acetate and methyl cellulose

The effect of red phosphorus and melamine on the flammability of cellulose acetate, methyl cellulose and cellulose is shown in Table 3.21. The change in LOI (Δ LOI) from the value for the base polymer gives an indication of the relative effectiveness of each of the flame retardant combinations. It can be seen that the effect of red phosphorus in reducing the flammability of cellulose acetate is to raise the LOI to 22.0 at a loading of 5.2 wt percent, with little further increase when the loading of red phosphorus is doubled. Melamine at a similar loading raises the LOI to 20.0 and is therefore not as effective as red phosphorus. However doubling the melamine concentration (to 11.1 wt percent) results in a further rise in the LOI. A slight synergistic effect is seen when the two additives are used at a loading of 5.2 wt percent each, although at a loading of 10 wt percent each antagonism rather than synergism is observed. With methyl cellulose, red phosphorus is the most effective additive, raising the LOI by 3.1 units at a 5 wt percent loading compared with an increase of 0.5 LOI units for melamine at a similar loading. At a 20 wt percent loading red phosphorus raises the LOI by 7.3 units, while melamine gives a minimal increase of 3.3 units. When the two additives are used together at low concentrations (5 wt percent), a small degree of synergism is seen, and this increases with 10 wt percent of each additive.

Table 3.21 The effect of red phosphorus - melamine on the flammability of some modified cellulose systems

Substrate	Red phosphorus (wt %)	Melamine (wt %)	LOI	Δ LOI
Cellulose acetate	-	-	19.0	-
	5.2	-	22.0	3.0
	11.1	-	22.4	3.4
	-	5.2	20.0	1.0
	-	11.1	21.5	2.5
	5.5	5.5	23.5	4.5
	10	10	23.0	4.0
	2.7	7.6	22.0	3.0
	7.6	2.7	21.8	2.8
Methyl cellulose	-	-	16.2	-
	5	-	19.3	3.1
	10	-	21.6	5.4
	20	-	23.5	7.3
	-	5	16.7	0.5
	-	10	17.1	0.9
	-	20	19.5	3.3
	5	5	20.0	3.8
	10	10	24.3	8.1
	14	14	24.3	8.1
Cellulose	-	-	18.2	-
	9.8	-	22.7	4.5
	16.4	-	23.1	4.9
	-	7.6	21.0	2.8
	-	14.9	21.7	3.5
	-	20.3	25.1	6.9
	6.0	7.0	24.4	6.2
	12.1	11.2	22.2	4.0

3.3.4 Simultaneous thermal analysis of cellulose acetate - red phosphorus - melamine and methyl cellulose - red phosphorus - melamine systems

Table 3.22 shows the percentage weight loss at the CBO stage for cellulose acetate, methyl cellulose and cellulose when various loadings of red phosphorus and melamine are used. In all cases red phosphorus causes an increase in the CBO stage, suggesting that it is acting in the condensed phase. The increase is most noticeable with methyl cellulose where the CBO stage is increased from 23.3 percent for the polymer on its own to 35.3 percent when it contains 20 wt percent red phosphorus.

Melamine also increases the CBO stage for the polymers the greatest effect being with cellulose itself. Combinations of both red phosphorus and melamine also cause an increase in the CBO stage.

If an attempt is made to correlate char yields with flammabilities for the systems studied, it would be expected that, as the char yield increases, the flammability of the system would decrease. The results show that there is a relationship between char production and flammability of these systems. Methyl cellulose, for example, is seen to produce the largest amount of char with red phosphorus and also shows the greatest flame retardant effect. Melamine in contrast causes only a small increase in the CBO value for cellulose acetate and results in a correspondingly small

Table 3.22 Summary of the percentage weight loss at the carbon burn off (CBO) stage for cellulose acetate, methyl cellulose and cellulose substrates with red phosphorus - melamine flame retardant additives

Substrate	Red phosphorus (wt %)	Melamine (wt %)	CBO (%)	△CBO / wt % P or N
Cellulose acetate	-	-	16.1	-
	20	-	25.4	0.47
	-	10	17.9	0.09
	10	10	21.7	-
Methyl cellulose	-	-	23.3	-
	20	-	35.3	0.60
	-	20	28.1	0.24
	16	16	28.2	-
Cellulose	-	-	18.0	-
	10	-	25.6	0.76
	-	10	24.1	0.61
	10	10	27.2	-

Values quoted may contain a percentage attributable to the oxidised species of red phosphorus and therefore the amount of carbon may be lower than these figures suggest.

rise in the LOI value.

In summary then, the thermal analysis data show that red phosphorus and melamine increase the char yield for both methyl cellulose and cellulose acetate, the greatest effect being found with red phsophorus on cellulose acetate. When the two additives are combined an overall further increase in char yields occurs for both polymers.

3.3.5 Gas phase infrared spectroscopy of cellulose acetate - red phosphorus - melamine and methyl cellulose - red phosphorus - melamine systems

Cellulose acetate on its own decomposes at about 310°C to form acetic acid, carbon monoxide and carbon dioxide. The infrared spectra produced (Figures 3.43 and 3.44) are indicative of the acetic acid dimer with two characteristic intense bands at 1300 and 1425cm^{-1}. The maximum production of acetic acid occurs at about 420°C.

When red phosphorus is present, the formation of acetic acid monomer seems to occur at a much lower temperature i.e. 230°C, and a maximum is observed at 330°C where the acid is almost entirely in the dimeric form. No peaks associated with the oxidation of red phosphorus are evident and the acetic acid dimer spectrum is dominant even at 550°C.

When melamine is present the acetic acid monomer is visible at 220°C and the dimer is formed at 280°C. At about the same temperature water is produced with its characteristic stretching vibration as shown in Figure 3.45. The production of water seems to reach a maximum at 360°C above which it decreases slightly but remains a dominant feature of the spectrum up to 550°C. The absence of any vibrations due to the presence of ammonia is noticeable but not entirely surprising due to the large amount of water produced. When both red phosphorus and melamine are present, the acetic acid monomer appears at 145°C (Figure 3.46), which is a much

Figure 3.43 Gas phase infrared spectrum of cellulose acetate at 350 - 400°C over the range 4000 - 1600 cm^{-1}

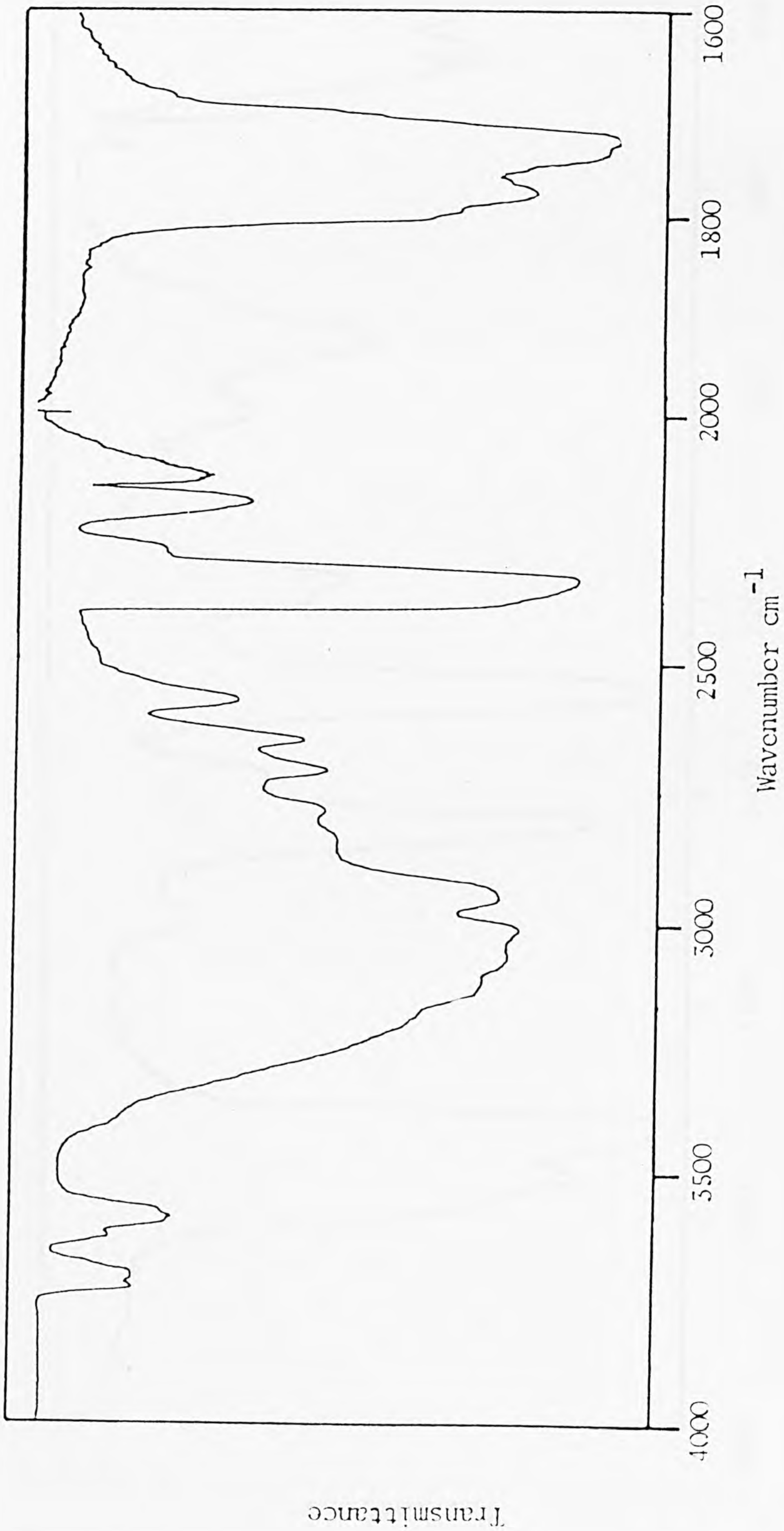


Figure 3.44 Gas phase infrared spectrum of cellulose acetate at 350 - 400° C over the range 2000 - 625 cm^{-1}

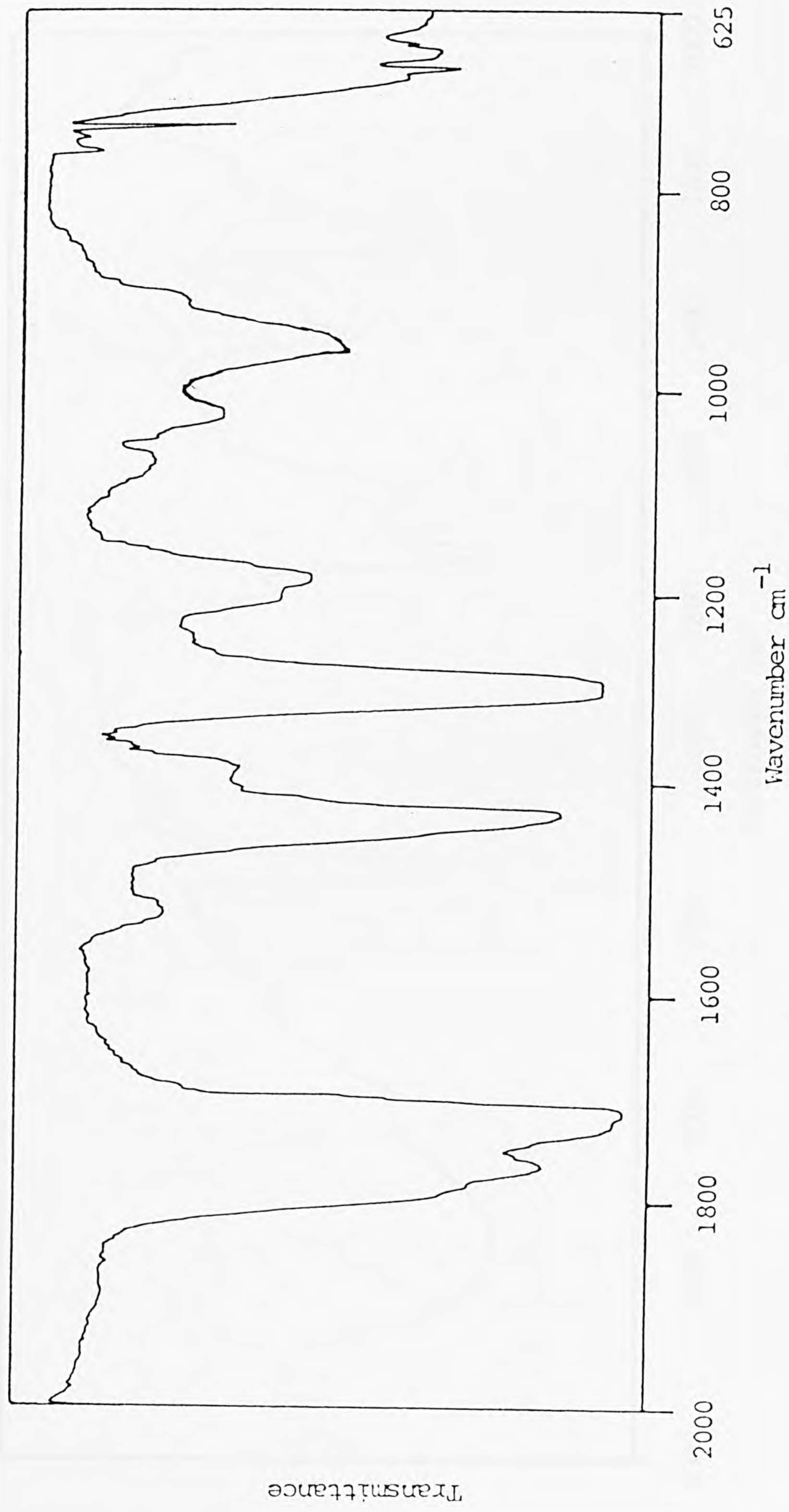


Figure 3.45 Gas phase infrared spectrum of cellulose acetate containing 11 wt percent melamine at 465°C over the range 4000 - 1000 cm^{-1}

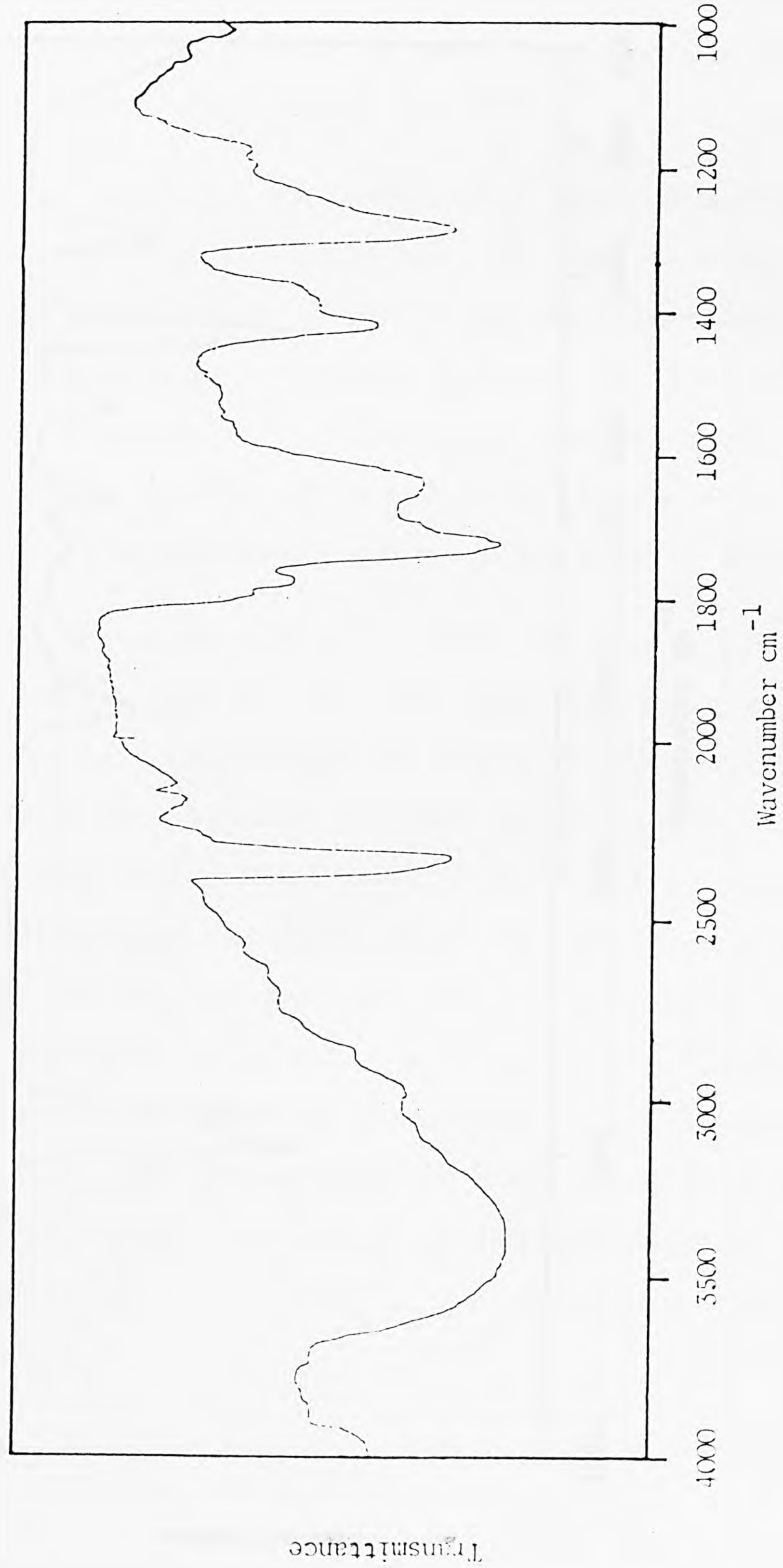
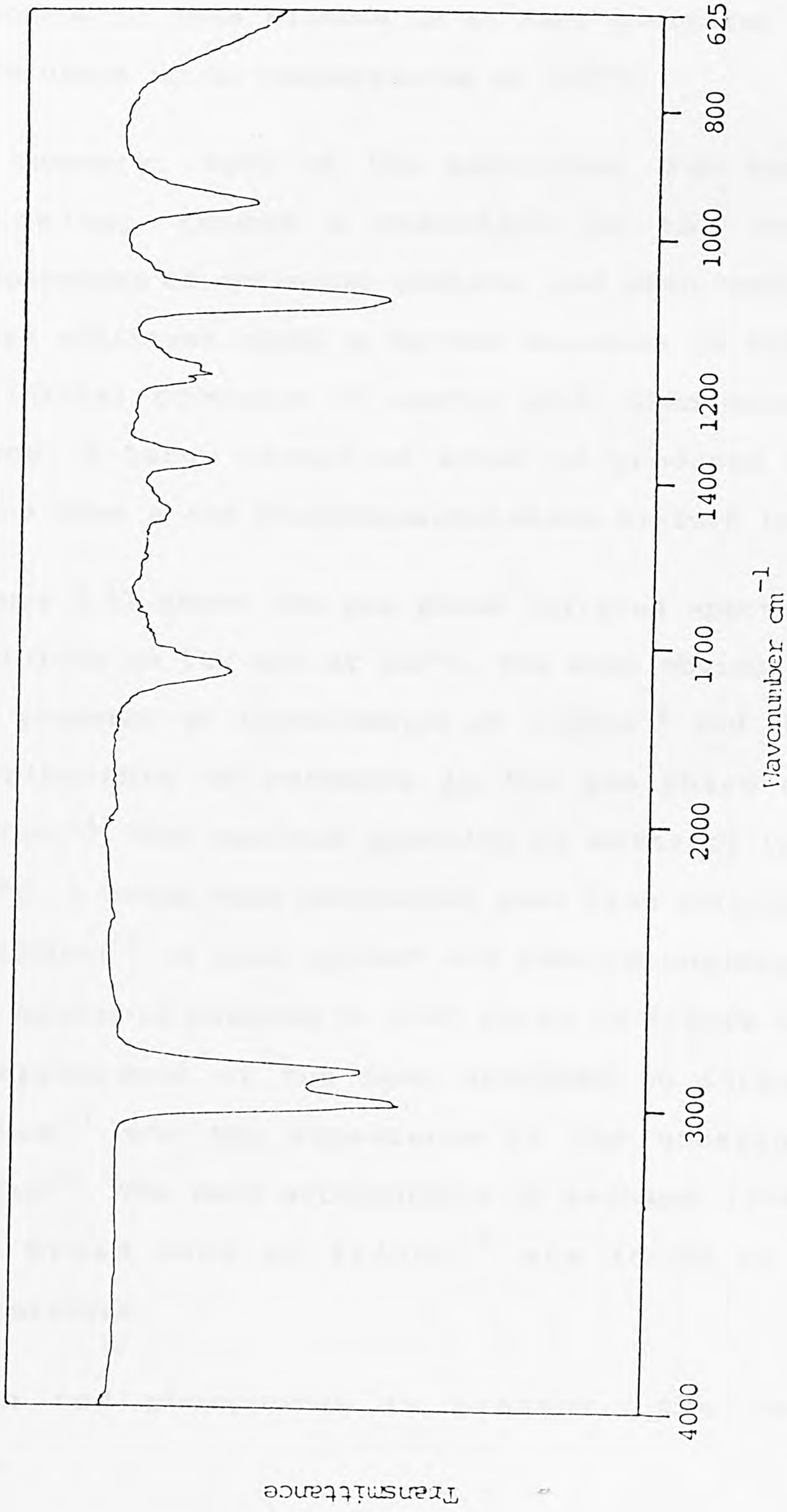


Figure 3.46 Infrared spectrum of cellulose acetate containing red phosphorus and melamine (10 wt percent each) at 220°C over the range 4000 - 625 cm^{-1} showing the presence of the acetic acid monomer



lower temperature than when melamine was present on its own and the dimer is visible at 340°C. The production of water is not observed, nor is the presence of ammonia. The spectrum of this mixture is in fact dominated by the acetic acid dimer up to temperatures of 620°C.

In summary, each of the additives, red phosphorus and melamine, causes a reduction in the decomposition temperature of cellulose acetate, and when combined together these additives cause a further decrease in the temperature of initial formation of acetic acid. When melamine is used alone, a large amount of water is produced which is not found when a red phosphorus/melamine mixture is used.

Figure 3.47 shows the gas phase infrared spectrum of methyl cellulose on its own at 320°C. The most obvious features are the presence of formaldehyde at 1750cm^{-1} and the absorption attributable to methanol in the gas phase centering at 1040cm^{-1}. The maximum quantity of methanol is produced at 360°C. A broad band containing some fine structure centering at 1200cm^{-1} is also evident and remains unassigned. At 420°C the spectrum changes to that shown in Figure 3.48 with the disappearance of the peak assigned to formaldehyde at 1750cm^{-1} and the appearance of the unassigned peak at 1200cm^{-1}. The band attributable to methanol (1040cm^{-1}) and a new broad band at 1640cm^{-1} are found at the higher temperature.

When red phosphorus is present, the formation of

Figure 3.47 Gas phase infrared spectrum of methyl cellulose at 320°C over the range of 2000 - 600 cm^{-1}

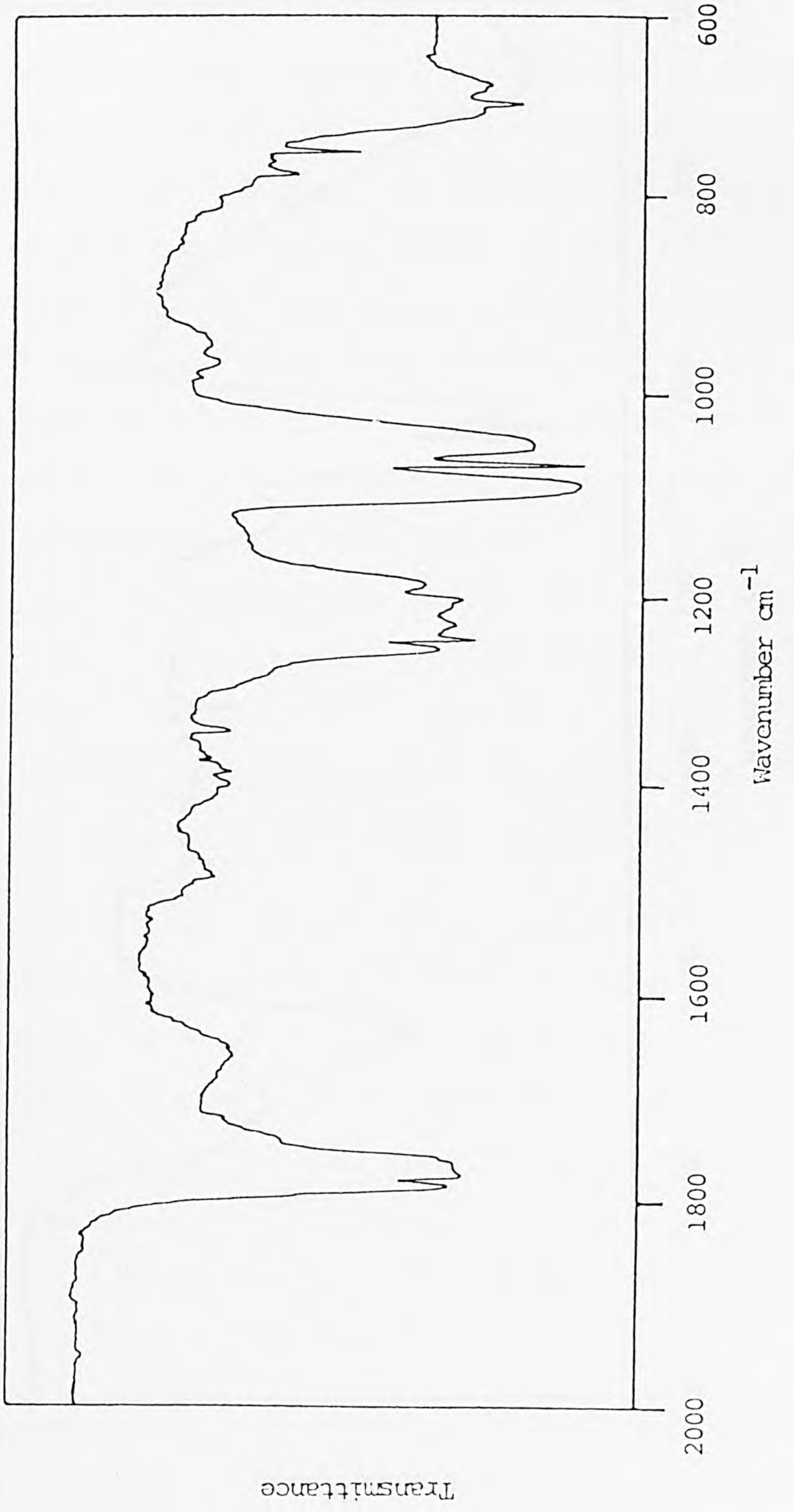
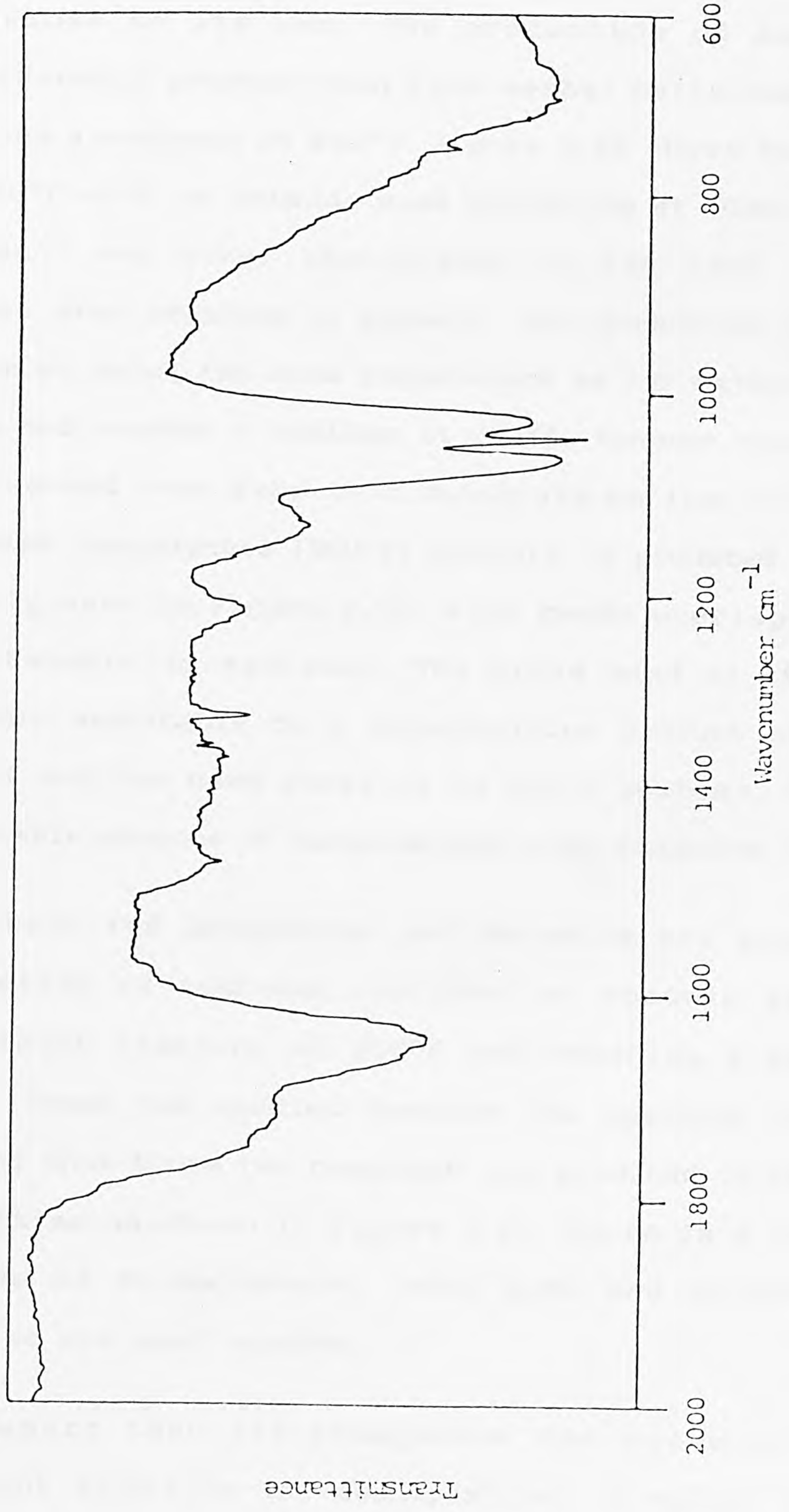


Figure 3.48 Gas phase infrared spectrum of methyl cellulose at 420°C over the range 2000 - 600 cm^{-1}



formaldehyde is first observed at 250°C and methanol is seen at 310°C, a slightly lower temperature than for methyl cellulose on its own. The production of methanol is considerably greater than from methyl cellulose alone and reaches a maximum at 440°C. Figure 3.49 shows the spectrum at 450°C with an intense peak centering at 1030cm^{-1} due to methanol and other absorptions in the 1300 - 1450cm^{-1} region. When melamine is present, the production of methanol occurs at about the same temperature as for methyl cellulose alone and reaches a maximum at 390°C. However more methanol is produced than from this substrate on its own. At about the same temperature (390°C) ammonia is produced and can be clearly seen in Figure 3.50, with bands overlapping those attributable to methanol. The broad band at 1625cm^{-1} is probably ascribable to a decomposition product of melamine itself and has been observed in other systems. There is a noticeable absence of formaldehyde when melamine is present.

When both red phosphorus and melamine are present, the production of methanol and that of ammonia seem to be coincident starting at 310°C and reaching a maximum at 440°C. These two species dominate the spectrum throughout, showing that these two compounds are produced in significant quantities as shown in Figure 3.51. There is a noticeable absence of formaldehyde, when both red phosphorus and melamine are used together.

In summary then red phosphorus and melamine have no important effect on the decomposition of methyl cellulose.

Figure 3.49 Gas phase infrared spectrum of methyl cellulose containing 20 wt percent red phosphorus at 450°C over the range 2000 - 600cm^{-1}

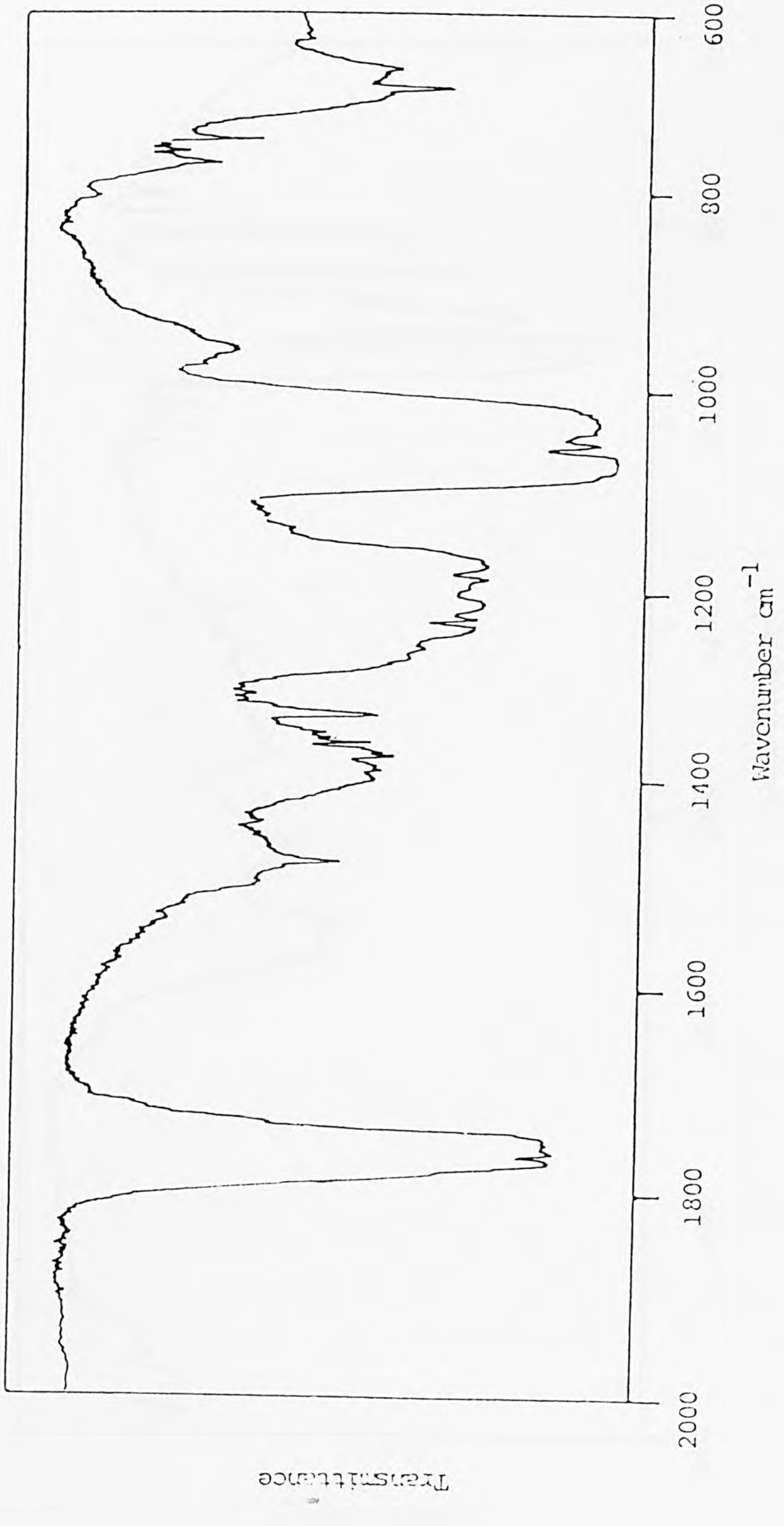


Figure 3.50 Gas phase infrared spectrum of methyl cellulose containing 20 wt percent melamine at 460°C over the range 2000 - 600cm^{-1} showing the absorptions due to methanol and ammonia in the 800 - 1150cm^{-1} region

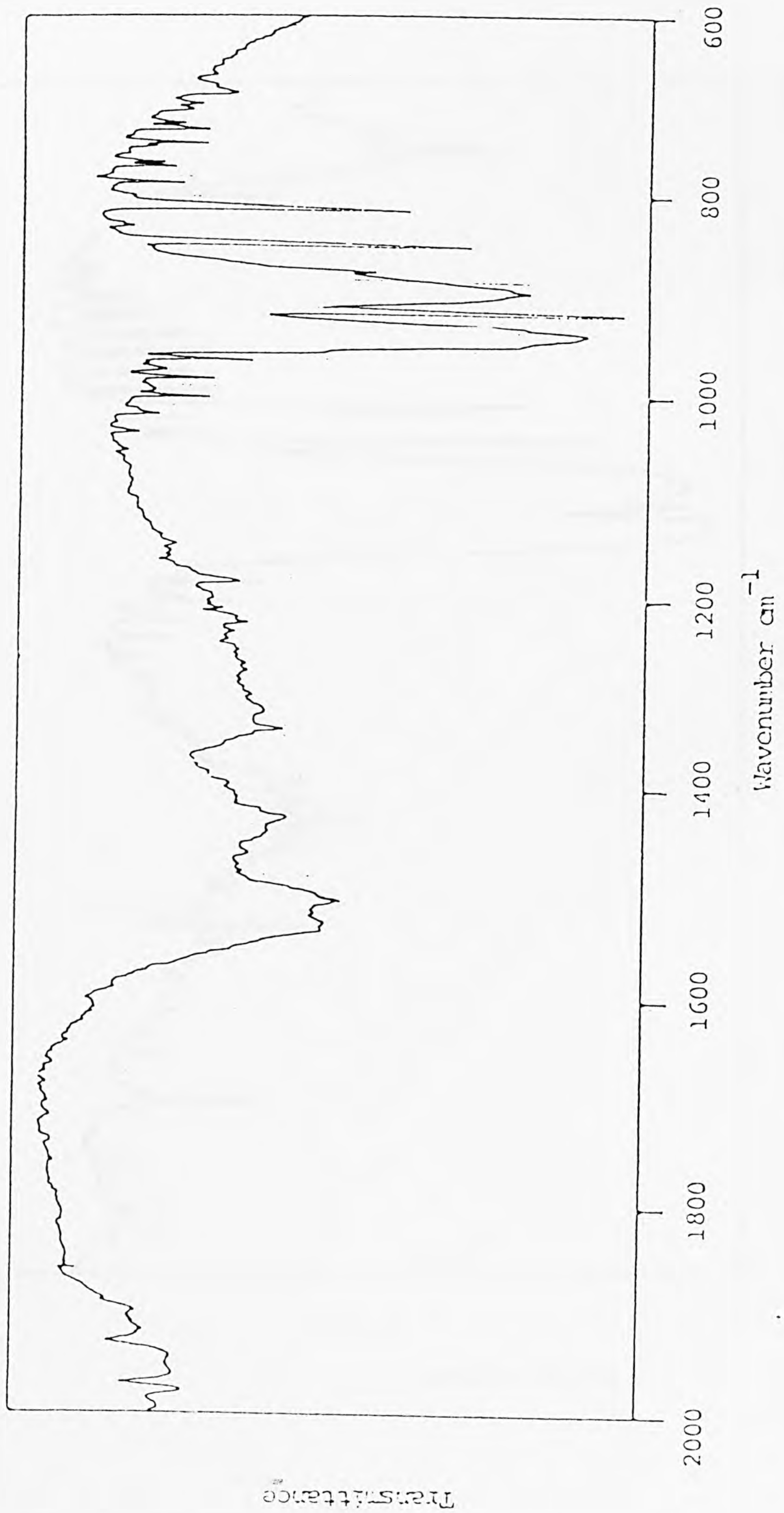
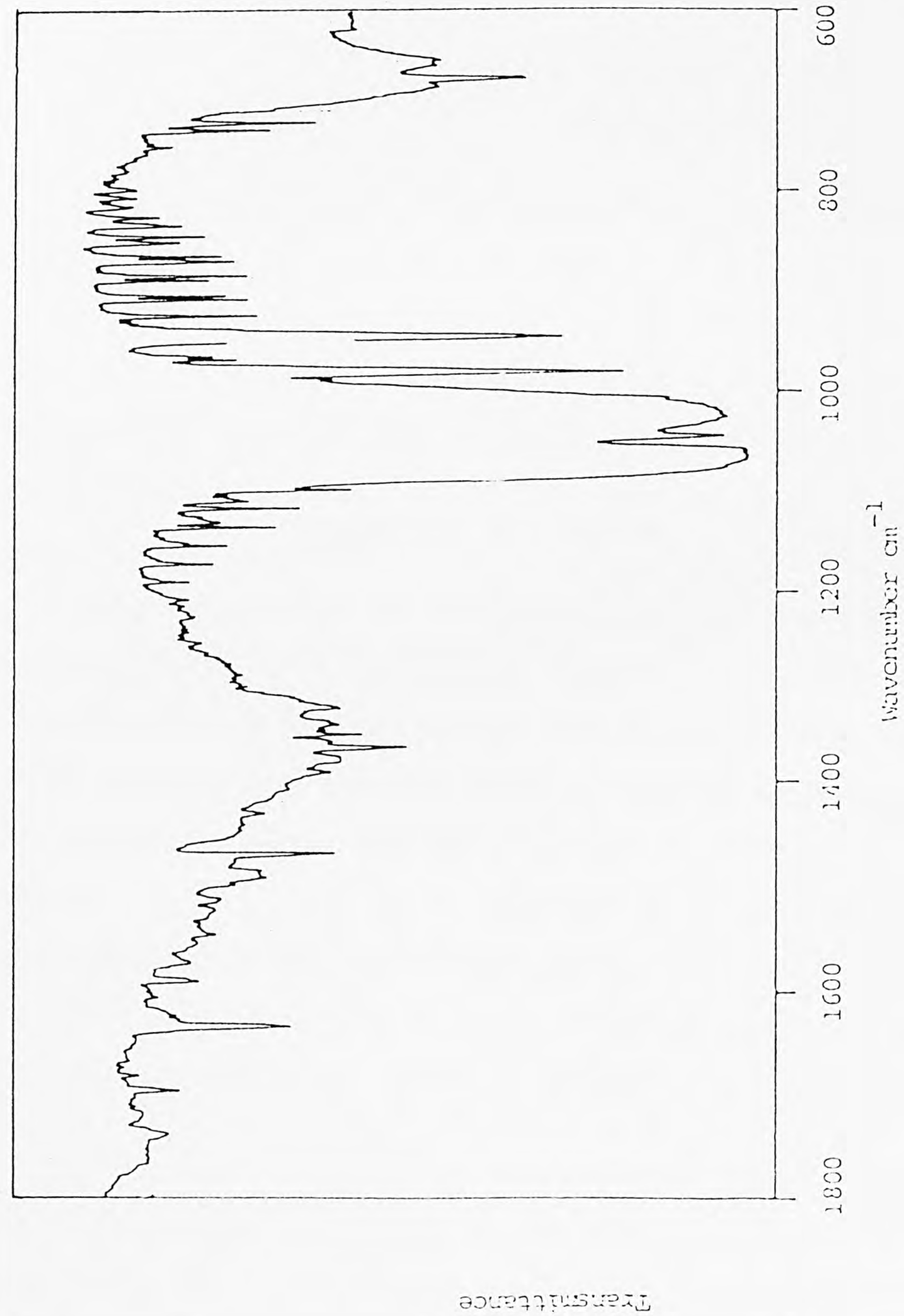


Figure 3.51 Gas phase infrared spectrum of methyl cellulose containing red phosphorus and melamine (10 wt percent each) at 490°C over the range 1800 - 600cm^{-1}



Red phosphorus causes a slight reduction in the temperature at which methanol is produced. Both red phosphorus and melamine seem to cause an increased formation of methanol.

Chapter 4 - Discussion

Read not to contradict and confute, nor to believe and take for granted, nor to find talk and discourse, but to weigh and consider.

Francis Bacon 1561-1626

4.1 Introduction

Cotton has supplied man with fibre from before written history to the present day, where it can be regarded almost as a necessity of everyday life. Although widely used, however, cotton creates a flammability problem with an LOI varying between 16 and 19 depending on the tightness of the weave and the water content.

Since Gay-Lussac's systematic study of flame-retardant additives to theatre canvas in 1820, it is clear that the flammability of cotton cloth can be reduced, thus creating a safer material resulting in increased usage. There are two principal ways in which it is possible to impart flame-retardant characteristics to cotton cloth and other cellulosic materials. One is to alter the route by which cellulose breaks down (Section 1.3). Cellulose can undergo depolymerisation to form laevoglucosan and other flammable products, or dehydration to form carbon and water. Positive encouragement of the dehydration route at the expense of depolymerisation will cause a decrease in the ease with which cellulose burns. The other method is to incorporate flame-retardant additives which on decomposition act in the gas phase and interfere with flame reactions.

It is the formation of phosphorus acids - which are good dehydrating agents (Lyons 1970b and Weil 1975) - that made Gay-Lussac's mixture of ammonium phosphate, ammonium chloride and borax an effective flame retardant for canvas.

Phosphorus in other forms, often combined with co-additives, is also effective as a flame retardant, suggesting that it is the presence of phosphorus in some particular state that provides the flame-retardant effect.

One aim of this work has been to try and determine to what extent the form in which phosphorus is present is important and to examine whether its effect can be enhanced. Many of the common phosphorus-based flame retardants contain only a small proportion of phosphorus together with relatively large amounts of carbon, hydrogen and oxygen. Elemental phosphorus is clearly the form which is, in principle, capable of producing the greatest effect if phosphorus itself is the active species. Red phosphorus has been shown to be effective in several nitrogen-containing thermoplastics such as polyurethanes (Piechota 1965), and ABS (Broadbent and Hirschler 1984). This form of phosphorus has also been shown to exhibit useful flame-retardant properties when incorporated into oxygenated polymers (Granzow and Cannolongo 1976; Granzow, Ferrillo and Wilson 1977; Ballistreri, Foti, Montaudo, Scamporrino, Arnesano and Calgari 1981; Ballistreri, Montaudo, Puglisi, Scamporrino, Vitalini and Calgari 1983) and polystyrene (Cullis, Hirschler and Tao 1986).

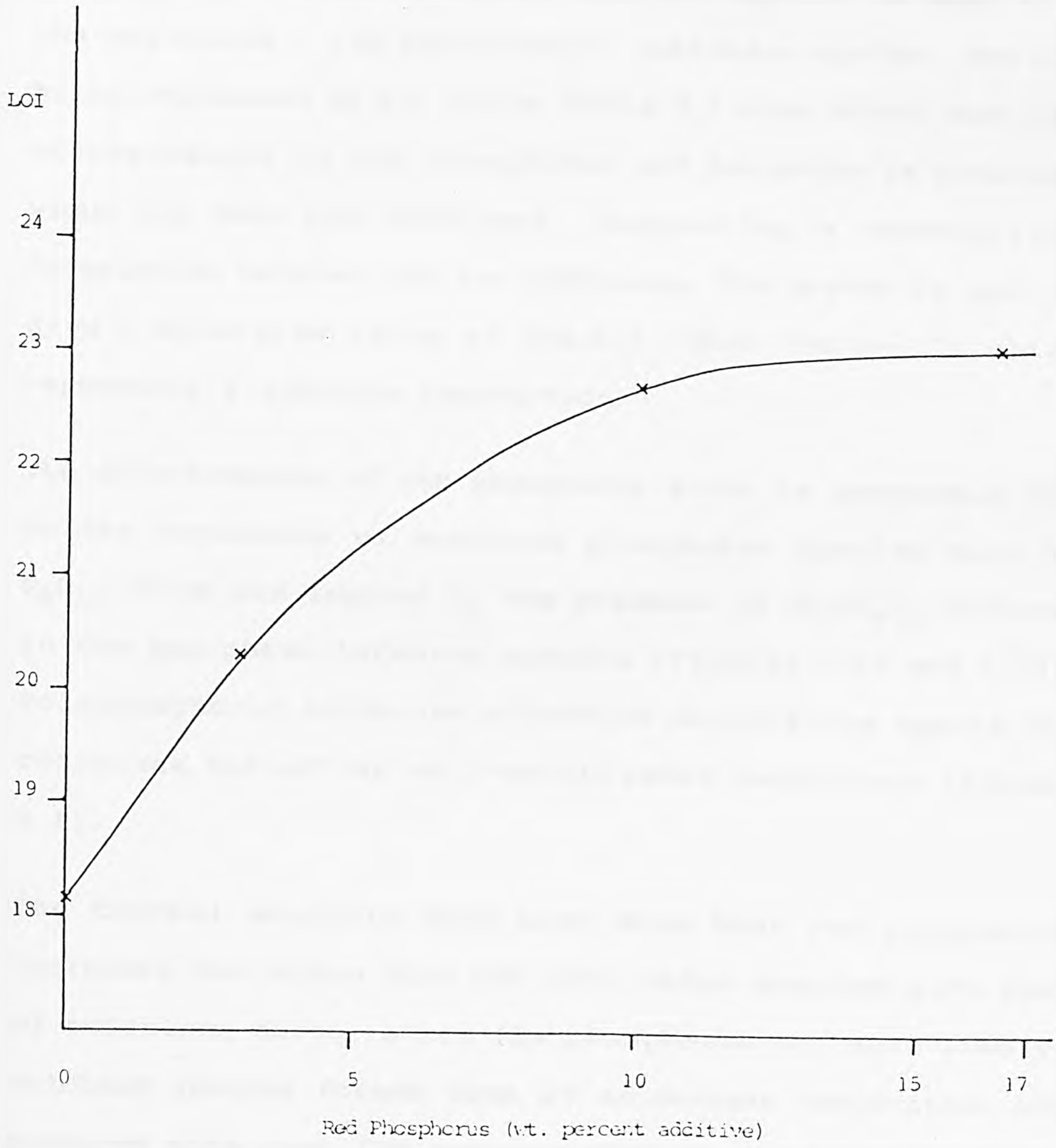
It is with this in mind that the present study was undertaken, the initial investigation being concerned with the effect of red phosphorus on the flammability of cellulose-cotton cloth.

4.2 The flame retardant effectiveness of red phosphorus in the absence and presence of co-additives

Red phosphorus was applied to cellulose - cotton cloth by a hot iron technique as described in Section 2.1.4. On account of the method employed the additive was effectively incorporated onto only one side of the material. Figure 4.1. shows a graph of LOI against red phosphorus concentration.

The figure shows a levelling off at high concentrations of red phosphorus which is quite typical for flame-retardant additives generally where an optimum effectiveness is reached. In the case of red phosphorus, however, this effect occurs because the particles of red phosphorus come so close together that the flame front spreads across the cloth via the phosphorus. Thus red phosphorus at high loadings dominates the system and the presence of the cotton cloth is effectively ignored. This is borne out further by the flammability data represented as a triangualr diagram for the cellulose - red phosphorus - melamine system (Figure 3.4). The diagram shows a region of high flammability at high loadings of red phosphorus. However at loadings of between 3 and 16 wt percent the presence of red phosphorus does reduce the flammability of cellulose effectively, a loading of 9.8 wt percent increasing the LOI by 4.5 units. The diagram also shows a degree of synergism between the two additives shown by the increase in LOI along the cellulose baseline.

Figure 4.1 The effect of red phosphorus on the flammability of cellulose - cotton cloth



In combination with other additives the flammability of cellulose - red phosphorus is further reduced and Table 4.1 shows the LOI values of some cellulose - red phosphorus - decabromobiphenyl - melamine systems. The greatest flame-retardant effect for a binary additive mixture is seen with the cellulose - red phosphorus - melamine system, the LOI being increased by 8.1 units. Table 4.1 also shows that the effectiveness of red phosphorus and melamine is greatest when the two are combined, suggesting a synergistic interaction between the two additives. The system is seen to give a synergism value of 235.0 ± 116.6 (Table 3.3) which represents a sizeable interaction.

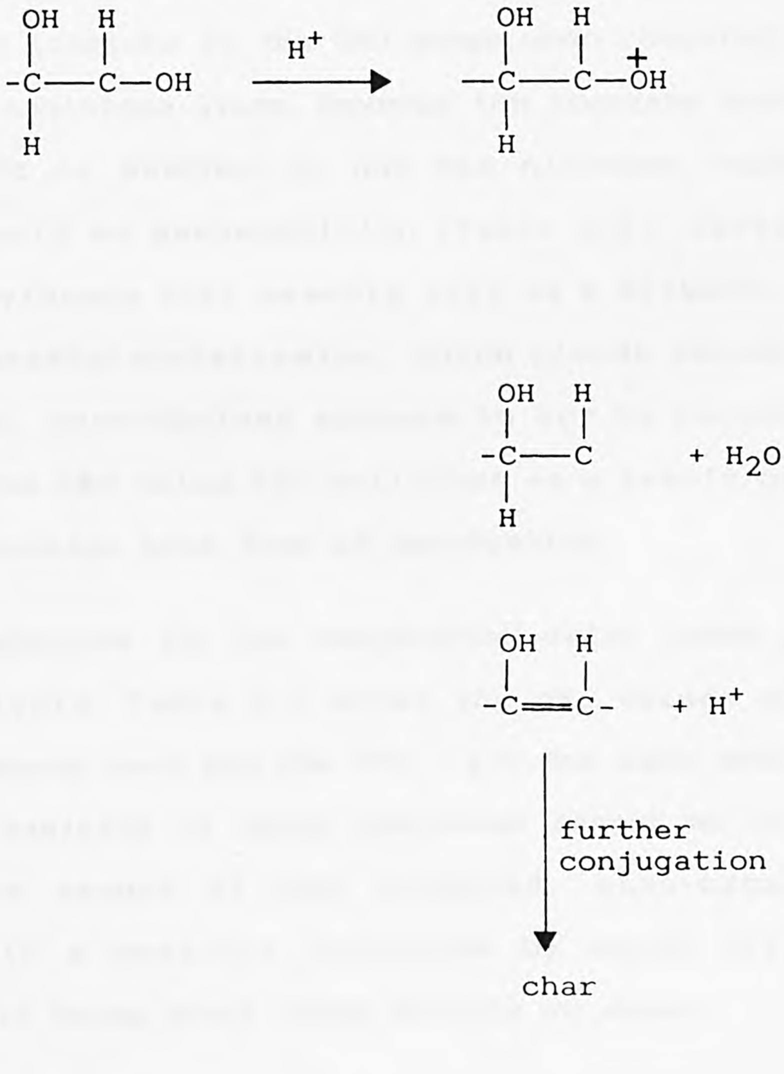
The effectiveness of red phosphorus alone is presumably due to the formation of oxidised phosphorus species such as P_4O_{10} which are implied by the presence of $(H_3PO_4)_n$ observed in the gas phase infrared spectra (Figures 3.19 and 3.20). Polyphosphoric acids are effective dehydrating agents for cellulose and act by well-established mechanisms (Scheme 4.1).

The thermal analysis data also show that red phosphorus increases the carbon burn off (CBO) value compared with that of cellulose alone, since the phosphorus or, more likely, oxidised species formed from it encourages dehydration and produces more char. CBO values quoted when red phosphorus is present may include a contribution from the oxidised species of red phosphorus, and therefore the values may be slightly lower than the figures suggested.

Table 4.1 The effect of red phosphorus on the flammability of cellulose in the absence and presence of co-additives

Red phosphorus (wt %)	Decabromobiphenyl (wt %)	Melamine (wt %)	LOI
-	-	-	18.2
9.8	-	-	22.7
-	12.8	-	21.6
-	-	7.6	21.0
9.2	-	11.3	26.3
3.6	-	20.9	29.6
6.9	-	18.7	29.5
3.6	-	18.8	28.5
5.8	-	13.3	28.0
8.3	13.0	-	24.6
-	7.5	11.6	26.1
8.1	8.1	7.2	27.2

Scheme 4.1 Dehydration of cellulose by phosphoric acid via an acid-catalysed dehydration mechanism



Melamine also increases the weight loss accompanying the CBO stage, suggesting that it too promotes dehydration. This is further supported by the infrared spectroscopic evidence of a lower temperature for the production of water. Melamine has been shown to break down to give ammonia, which although flammable itself (in pure oxygen), can nevertheless act, during the combustion of cellulose, as a diluent and thus reduce the overall flammability of the system.

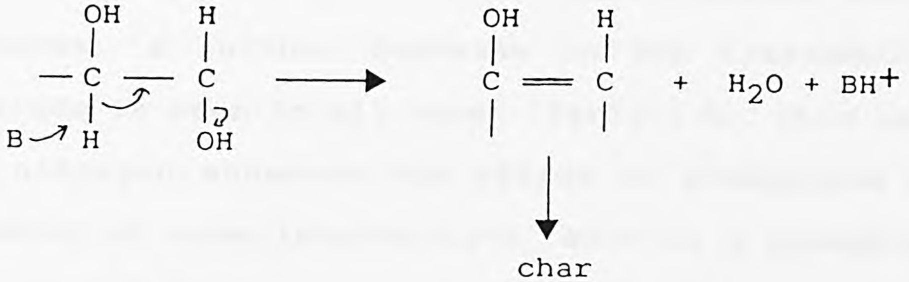
Table 4.2 shows that all the nitrogen compounds when used alone cause an increase in the CBO stage when compared with the value for cellulose alone. However the increase seems to be independent of whether or not the nitrogen compound produces ammonia on decomposition (Table 3.9). Certainly there is no evidence that ammonia acts as a diluent. For example, hexamethylenetetramine, which yields ammonia on decomposition, nevertheless appears to act by causing an increase in the CBO value for cellulose as a result of its ability to encourage some form of dehydration.

A possible mechanism for the dehydration which takes place is base catalysis. Table 4.2 shows the pK_a values of the nitrogen compounds used and the CBO / % N for each additive. Although the basicity of these compounds cannot be related easily to the amount of char produced, base-catalysed dehydration is a possible mechanism by which nitrogen compounds could bring about these effects as shown:

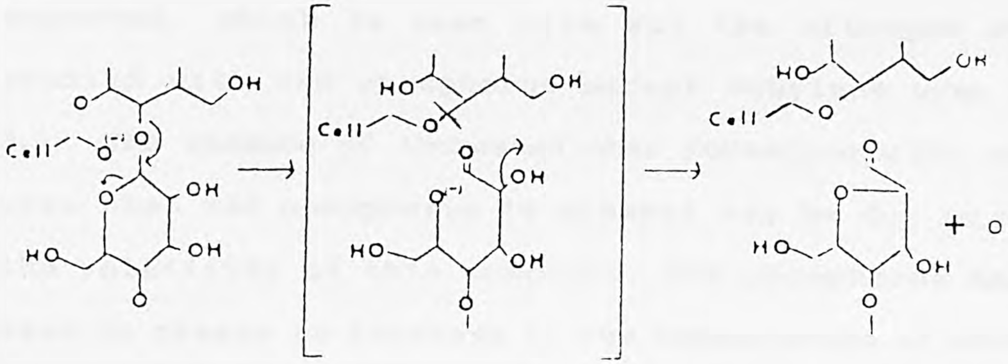
Table 4.2 The pK_a values of different nitrogen compounds and their relation to the CBO stage for cellulose

	pKa	Δ CBO / % N
Melamine	5.0	0.61
Ethylene urea	4.8	0.11
Barbituric acid	8.4	0.29
N-methyl imidazole	7.3	0.93
Ammonium formate	3.8*	0.75
Hexamethylenetetramine	6.3	0.29

* value quoted for formic acid.



Another possibility of base catalysed dehydration is by attack from an adjacent cellulose chain. This results in the formation of a double bond which would allow further conjugation and char formation.



When red phosphorus is combined with nitrogen-containing additives, a further decrease in the flammability of cellulose is seen in all cases (Table 3.5). This suggests that nitrogen enhances the effect of phosphorus by the formation of some intermediate, such as a phosphoramide ($P(O)(NH_2)_3$). Such compounds and chemically related species have been shown to confer excellent flame retardant characteristics on cellulose (Drews, Yeh and Barker 1973). Such compounds would generally be expected to be effective in the condensed phase and work carried out has shown that their volatility has an important influence on their effectiveness (Drews and Barker 1973). If such compounds bring about their effect in the condensed phase via a dehydration mechanism, an increase in the CBO value would be expected, which is seen with all the nitrogen systems studied with red phosphorus except ethylene urea (Table 3.9). The absence of increased char formation with ethylene urea when red phosphorus is present may be due in part to the volatility of this compound. Red phosphorus has been seen to create an increase in the temperature at which the CBO stage takes place for cellulose (Table 3.7). This increase in the temperature of decomposition of cellulose and the relative volatility of ethylene urea may hinder the formation of a phosphoramide and hence cause a small reduction in the CBO value (Table 3.9).

N-methylimidazole, which does not produce ammonia, and barbituric acid, which produces only trace quantitities of this gas, cause marked increases in the CBO stage when they are combined with red phosphorus, suggesting an entirely condensed-phase mode of action. Since a dehydration mechanism is possibly one of the most important routes for reducing the flammability of cellulose, these additives would be expected to be effective flame retardants. In fact, analysis of flammability data for these systems (Table 3.6) suggests a small degree of antagonism.

It is clear from these investigations that, although an increase in the CBO stage is a strong indication of a dehydration mechanism, this may not reduce the flammability of the cellulose per se and other reactions may also take place, probably in the gas phase, resulting in a reduction in the flammability of cellulose. This is a strikingly different finding from previously reported works which have concluded that there is a direct relationship between reduced flammability and char yield. The investigations carried out in this work have shown that the dependancy is not as simple as perhaps was thought earlier.

Hydrogen bromide is known to be a gas-phase inhibitor of flame reactions (Rosser, Inami and Wise 1966; Fristrom 1972; Petrella 1979) and decabromobiphenyl is therefore likely to bring about its effect in the gas-phase. Indeed decabromobiphenyl causes a considerable reduction in the CBO stage of cellulose, so that an entirely gas-phase mode of flame retardant action is possible. This has also been seen with decabromobiphenyl oxide, which causes a similar reduction in the CBO value of cotton cloth (Khattab 1985).

Combinations of all three flame-retardant additives, viz. red phosphorus, decabromobiphenyl and melamine, cause a further reduction in flammability, increasing the LOI of cellulose to a maximum value of 27.2. The quantitative data (Table 3.4) indicate a significant degree of synergism of 3053.9 ± 1105.7. The CBO stage shows an increase from 20.2 to 29.2 but little information can be obtained about the way(s) in which the ternary additive mixture acts due to the complexity of the situation. It is likely, from information obtained for the individual flame retardants, that red phosphorus is effective in the condensed phase promoting dehydration and decabromobiphenyl is active in the gas phase. Melamine has been shown to be effective in the condensed phase since it increases the CBO stage but it also produces ammonia gas which may act as a diluent and therefore exerts some of its effect in the gas phase.

4.3 Advantages of using organic phosphorus compounds as flame retardants

4.3.1 The flame-retardant effectiveness of soluble phosphorus compounds in the absence and presence of co-additives

Although red phosphorus is quite effective as a flame retardant for some forms of cellulose, it is not particularly suitable for cotton cloth due to its physical form. If used commercially it would be necessary to use a strong adhesive to bind the red phosphorus to the cloth and this would limit its use to a restricted number of applications. However, in the present work, neoprene was found to be a suitable adhesive and due to the low concentration needed did not appreciably alter the flammability of the cellulose. It was suggested in Section 4.2 that the active species formed from red phosphorus during combustion are essentially polyphosphoric acids $(H_3PO_4)_n$. These compounds are viscous liquids, the physical state of which may govern their effectiveness.

With this in mind it was decided to investigate a phosphate which was soluble only in organic solvents. Tritolyl phosphate was considered to be a suitable compound as it is soluble in acetone thus allowing easy incorporation into the cotton cloth.

A loading of 10.3 wt percent of tritolyl phosphate on cellulose - cotton cloth gives a LOI value of 21.0. When this is compared with the effect of red phosphorus at a similar loading of 9.8 wt percent for which the LOI is 22.7, it is clear that tritolyl phosphate is not nearly as effective a flame retardant as elemental phosphorus. At a much higher loading of tritolyl phosphate of 30.7 wt percent, the LOI is increased to 23.9 but a direct comparison with the effect of red phosphorus at such loadings is not possible for the reasons outlined in Section 4.2. It appears that, when tritolyl phosphate and red phosphorus are used at similar loadings, red phosphorus is a more effective flame retardant on a weight percent additive basis. However, since tritolyl phosphate contains only 8.4 percent phosphorus, this latter compound has a greater effect on the basis of percentage weight of phosphorus.

In summary, then, tritolyl phosphate is seen to be more effective than elemental phosphorus on a percentage weight of phosphorus basis as tritolyl phosphate contains only 8.4 percent phosphorus per mole.

The coefficients of synergism (Table 4.3) for the red phosphorus - melamine and tritolyl phosphate - melamine systems show that, within experimental error, the values are similar and that the two forms of phosphorus are almost equally effective on a weight basis.

Tritolyl phosphate decreases the CBO value from 18.0 for

Table 4.3 The flammability coefficients of synergism for the cellulose - phosphorus - nitrogen co-additive systems

Systems	Synergism value
Cellulose - RP - DBB	141.7 ± 62.5
Cellulose - RP - N	235.0 ± 116.6
Cellulose - DBB - N	301.2 ± 95.8
Cellulose - TTP - DBB	84.4 ± 34.2
Cellulose - TTP - N	208.5 ± 68.1
Cellulose - RP - DBB - N	3053.9 ± 1105.7
Cellulose - TTP - DBB - N	4234.0 ± 2699.0

DBB = decabromobiphenyl
N = melamine
RP = red phosphorus
TTP = tritolyl phosphate

cellulose alone to 15.9 for cellulose with a 10 wt percent loading of tritolyl phosphate. This implies that the phosphate does not bring about its effect via a dehydration mechanism which is the way in which elemental phosphorus is ultimately believed to work. Tritolyl phosphate must therefore function in the gas phase. Tritolyl phosphate may be quite effective as an inhibitor of gas phase reactions either by functioning as a blanketing agent due to its ability to form a dense vapour or behaving as an inert gas and acting as a diluent. The blanketing effect of tritolyl phosphate has been observed with several thermoplastics and may be attributable in part to its high density and thermal stability (Fenimore and Jones 1966).

On examination of the first weight loss of tritolyl phosphate on cellulose (Table 3.14), it can be seen that it is equivalent to 11.2 percent of the total weight. The actual loading of tritolyl phosphate was 10 wt percent, which suggests that, by 250°C, i.e. some time before the main decomposition of cellulose takes place, the tritolyl phosphate is lost into the gas phase.

If the phosphorus species has to be in an acidic form in order to promote dehydration as shown by Scheme 4.1, then it is not surprising that tritolyl phosphate is not a particularly effective dehydrating agent. Tritolyl phosphate could form an acidic species by an ester interchange reaction, which is known to take place with phosphorus esters between 150 and 200°C, i.e.

$$\text{cell-OH} + (\text{ArO})_3\text{P=O} \longrightarrow \text{cell-O-}\overset{\text{OAr}}{\underset{\text{OAr}}{\text{P}}}\text{=O} + \text{ArOH}$$

The cellulose phosphate produced could then lose a $(ArO)_2PO_2H$ forming a dehydrated cellulose which would then form char. The fact that tritolyl phosphate, when used alone on cellulose, does not increase the CBO value suggests that the ester interchange reaction, although feasible, does not take place. A possible explanation for this could be that the bulky tolyl groups may sterically hinder the molecule and prevent the phosphorylation reaction from taking place. With this in mind, triethyl phosphate was used and despite having a boiling point of 215°C evaporated from the cloth during drying at 40°C preventing further investigations being carried out. The above reaction could be catalyzed by an amine such as melamine which would bring about its effect via a phosphoramide as mentioned in Section 4.2. Since the CBO value for the tritolyl phosphate - melamine system is seen to increase from 18.0 for cellulose alone to 21.0, this is quite a feasible explanation.

The effect of tritolyl phosphate on the flammability of cellulose shows that this compound on its own does not promote char formation but that the phosphorus in it must be in a particular form in order to take part in a dehydration mechanism. It has already been suggested that the active species may be a phosphoramide. With this in mind it was decided to investigate a number of phosphorus compounds in different oxidation states to study whether this is a factor contributing to their ability to react with an amine such as melamine and thus form the phosphorus - nitrogen compounds responsible for conferring flame retardance on cellulose.

4.3.2 The flame-retardant effectiveness of phosphorus compounds in various oxidation states in the absence and presence of melamine

A series of phosphorus compounds was chosen to investigate the dependence of flame-retardant effectiveness on oxidation state. These were all soluble in volatile organic solvents in order to facilitate their incorporation onto the cotton cloth. The variation in oxidation state of the phosphorus compounds allowed an examination of the importance of both the total phosphorus content (% P) and the chemical structure of the additive as factors affecting the flammability. For example, triphenyl phosphine oxide, and triphenyl phosphite contain similar amounts of phosphorus, between 10 and 12 wt percent, but the phosphorus is in different oxidation states.

The effects of the different phosphorus compounds on the flammability of cellulose are shown in Table 3.15. Tritolyl phosphate and triphenyl phosphine are seen to be almost equally effective on a percentage phosphorus basis with Δ LOI/% P values of 3.0 and 2.9 respectively; triphenyl phosphite is the next best additive with a Δ LOI/% P value of 2.6. Table 3.15 also shows that there is little correlation between the phosphorus oxidation state and effectiveness as a flame retardant. This contrasts with other work carried out on urethane foam (Piechota 1965), which showed that the amount of phosphorus present in the system was important. However the phosphorus content is not the only important factor with cellulose.

It is likely that the effectiveness of triphenyl phosphite and dimethyl methyl phosphonate is due to the ability of these compounds to be converted to acidic species via an ester interchange reaction of the type described in Section 4.3.1. The resulting species could then act as dehydrating agents for cellulose. For example the pK_a for $(OH)_2POH$, a likely decomposition product of the reaction, is 2.1. It is known that, of the compounds in question, phosphites are most susceptible to this type of interchange reaction (O'Brien 1960).

Table 3.15 shows that tritolyl phosphate, triphenyl phosphine, triphenyl phosphite and dimethyl methyl phosphonate are effective flame retardants for cellulose. If the CBO values in the presence of these compounds are examined (Table 3.18), it can be seen that tritolyl phosphate and triphenyl phosphine oxide produce little char whilst triphenyl phosphite and dimethyl methyl phosphonate show significant char formation. This suggests that tritolyl phosphate and triphenyl phosphine oxide bring about their effect in the gas phase, whilst triphenyl phosphite and dimethyl methyl phosphonate act in the condensed phase by an ester interchange reaction.

The effectiveness of tritolyl phosphate has been attributed to its ability to act as a blanketing agent or diluent and therefore bring about its effect in the gas phase as discussed in Section 4.3.1.

Triphenyl phosphine is also seen in Table 3.18 to increase char formation and therefore must be effective in the condensed phase causing dehydration. It is however unable to phosphorylate cellulose and therefore must bring about its effect via an alternative mechanism to the ester interchange reaction occurring with triphenyl phosphite and dimethyl methyl phosphonate. If the thermoanalytical weight loss trace (Figure 3.40) for triphenyl phosphine and cellulose is compared with that for cellulose alone, it can be seen clearly that the main decomposition of cellulose takes place some 60° lower. This may be due to the species being partially oxidised when triphenyl phosphine is present. This temperature reduction implies catalysis of the breakdown mechanism resulting in an increase in char which suggests that this is due to dehydration.

The addition of melamine to the different cellulose - phosphorus systems causes a general reduction in flammability, as shown by the LOI data in Table 3.16 and the quantitative data for phosphorus - melamine synergism in Table 3.17. The presence of nitrogen bases is known to accelerate the phosphorylation of cellulose as it provides a better leaving group for the ester interchange reaction.

Table 3.18 shows that triphenyl phosphite and dimethylmethyl phosphonate, when combined with melamine, cause significant increases in the CBO value, suggesting a dehydration mechanism. These compounds are able to take part in an ester interchange reaction.

The effectiveness of triphenyl phosphite and dimethylmethyl phosphonate have already been attributed to an ester interchange reaction and such reactions are catalysed by bases such as melamine. This is in fact seen by further increases in the CBO values to 38.6 and 35.8 respectively for the two compounds. The small increase in the CBO value for tritolyl phosphate when melamine is present is due presumably to the presence of melamine, which has been shown (Table 3.8) to promote the dehydration of cellulose.

Triphenyl phosphine oxide causes very small changes in the CBO value, suggesting that it is not particularly effective in the condensed phase and must therefore bring about its effect mainly in the gas phase. Triphenyl phosphine oxide is known to produce $PO^{\cdot}$, $P^{\cdot}$ and P_2 species (Hastie 1973a), which, if formed, could act as gas phase radical scavengers causing the removal of $H^{\cdot}$ and $OH^{\cdot}$ which are highly reactive species formed in flames as shown:

$$(C_6H_5)_3PO \longrightarrow PO^{\cdot},\ P^{\cdot} \text{ and } P_2$$

$$H^{\cdot} + PO^{\cdot} + M \longrightarrow HPO + M$$

$$OH^{\cdot} + PO^{\cdot} \longrightarrow HPO + O^{\cdot\cdot}$$

$$HPO + H^{\cdot} \longrightarrow H_2 + PO^{\cdot}$$

The thermograms of cellulose - triphenyl phosphite - melamine, cellulose - triphenyl phosphine oxide and cellulose - triphenyl phosphine - melamine mixtures are shown in Figure 3.40. When melamine is present together with triphenyl phosphine oxide, the decomposition temperature of the system is decreased by some 35° which may account for the enhancing effect of melamine (Table 3.16). The temperature of the main weight loss stage of triphenyl phosphine is increased by about 40° by the presence of melamine, thus perhaps explaining why this compound is relatively inefficient at promoting dehydration.

The results for triphenyl phosphine oxide acting on cellulose contrast with the effect of this same phosphorus compound on polyester, where 50 percent of the triphenyl phosphine oxide was lost prior to the breakdown of the polymer. Thus it is relatively ineffective as a flame retardant (Bostic 1972, Hastie and Blue 1973).

Melamine, which is seen to decrease the decomposition temperature of triphenyl phosphine oxide, thus enables the phosphorus compound to form active gas phase species at a temperature commensurate with the decomposition temperature of cellulose. Hence the species can be effective gas phase radical scavengers. The effectiveness of this system is also reflected in a relatively large synergism value of 419.8 ± 135.4 (Table 3.17), showing the effectiveness of these two additives when used together.

4.4 The flame retardant effect of red phosphorus on chemically modified forms of cellulose

Some of the phosphorus additives described in Section 3.2.3 are believed to operate by phosphorylating cellulose which is suggested to be one of the principal ways to reduce its flammability. With this in mind, it was decided to examine this process in more detail.

The phosphorylation of cellulose was carried out by the procedure described in Section 2.1.2.5. This gave up to 5 wt percent phosphorus content, which shows that the structure of cellulose is relatively stable to chemical attack, with only a small percentage of accessible sites undergoing phosphorylation. Figure 3.41 shows clearly that phosphorylation of cellulose - cotton cloth causes a reduction in its flammability and this seems to be dependent on the degree of phosphorylation. The LOI of cotton containing 5.2 wt percent phosphorus was 31.5, an increase of 13.3 units which is the greatest reduction in flammability of any of the systems studied in this work.

The TG trace shown in Figure 3.42 for phosphorylated cellulose agrees well with similar work carried out by Jain et al. (1985), showing rather indistinct weight loss stages. The DTG trace in Figure 3.42 shows two distinct weight loss stages, compared with the three stages observed by Jain et al. (1985). The first peak observed by these workers occurs at about 140°C and is due presumably to loss of absorbed water whereas the other two sharp peaks observed are in good agreement with those in Figure 3.42. Compared with cellulose the DTG and DTA maxima for the two peaks of phosphorylated cellulose are shifted to lower temperatures, the first peak by some 50 - 60° (Table 3.19), and also broadened slightly. This suggests a lower activation energy, and is indicative of a change of mechanism of decomposition. This is further borne out by the CBO value for phosphorylated cellulose which shows a reduction from 18.0 for cellulose alone to 13.6 for phosphorylated cellulose. Phosphorylated cellulose, having its C(6) position blocked, cannot rearrange on decomposition to form laevoglucosan. If dehydration of the molecule does not take place, which is suggested by the reduction in the CBO value, the only alternative explanation is that dephosphorylation takes place. This process would produce $P^{\cdot}$, $PO^{\cdot}$ and P_2 species which are known to be effective as gas-phase radical scavengers. Further support for this suggestion comes from elemental analysis, which shows that very little phosphorus remains in the char after decomposition.

The addition of 5 wt percent melamine to the phosphorylated cotton containing 5.2 wt percent phosphorus causes a further increase in the LOI to 35.0, suggesting a synergistic interaction between phosphorus and nitrogen. An increase in the CBO value over that of cellulose phosphate of 2.4 percent also occurs suggesting that melamine may act to some extent by a condensed phase mechanism involving base catalysis as described in Section 4.2. Melamine has also been shown to be effective in the gas phase (Section 4.2), as it produces ammonia gas which may act as a diluent.

The effect of nitrogen bases such as melamine is generally thought to be the catalysis of the phosphorylation of cellulose. In the case of cellulose phosphate this reaction has already taken place and the observed synergistic effect seen when melamine is present must be due to some alternative mechanism. The relatively small increase in the CBO value when melamine is present with cellulose phosphate compared to the effect of melamine on cellulsoe alone (cf. Table 3.9) suggests that, although some condensed phase dehydration mechanism occurs, it is not particularly important as regards causing a further reduction in flammability.

In summary, melamine incorporated into phosphorylated cotton cloth at a relatively low loading results in a highly flame-retardant material. The system must act essentially in the gas phase for the following reasons:

i) there is a decrease in the CBO value

ii) no significant amount of phosphorus is retained in the char.

The formation of a combination of ammonia and gas-phase phosphorus species may account for the strong synergistic interaction between phosphorus and nitrogen observed in this system.

An alternative method of blocking the cellulose C(6) position to prevent laevoglucosan formation and hence provide information on the mode of action of flame-retardant additives for cellulose involves formation of a cellulose ester and a cellulose ether.

Cellulose acetate and methyl cellulose are both important polymers and have commercial uses. These materials allow easy incorporation of flame retardant additives, producing homogenous mixtures when cast from suitable solvents, which could then be used for LOI measurements as self-supporting samples. Table 3.21 gives the flammability results for cellulose, cellulose acetate and methyl cellulose, with and without red phosphorus and melamine present. It can be seen that the flammability of the individual polymers reflects the ease of removal of the substituent to give char, i.e. methyl cellulose is the most flammable of the polymers as methanol is a relatively poor leaving group whereas acetate is the best leaving group and cellulose acetate is the least flammable polymer.

The difference in structure of modified celluloses with the blocked C(6) position results in a different method of decomposition as compared with cellulose. It is likely that deacetylation is the initial step of decomposition in the case of cellulose acetate (Scotney 1972). Elimination of all three acetate groups would cause complete disintegration of the ring unit. However analysis of the tarry material produced on decomposition suggests a process which keeps the basic ring system of the polymer intact suggesting scission of the 1,4 glycosidic bonds as seen with cellulose itself. The constituents of the tar formed from cellulose triacetate differ from those of an acetylated laevoglucosan (Madorsky, Hart and Straus 1958) thus it seems that some unsaturation deriving from the loss of acetate groups is a necessary precursor to the chain-scission process. A suggested mechanism for the decomposition of cellulose acetate is shown in Scheme 4.2.

It can be seen that red phosphorus at a loading of about 10 wt percent affects the flammability of the various polymers in the following order;

methyl cellulose > cellulose > cellulose acetate

with Δ LOI results of 5.4, 4.5 and 3.4.

With melamine at a similar loading, the order is

cellulose > cellulose acetate > methyl cellulose

giving values of 3.5, 2.5 and 0.9.

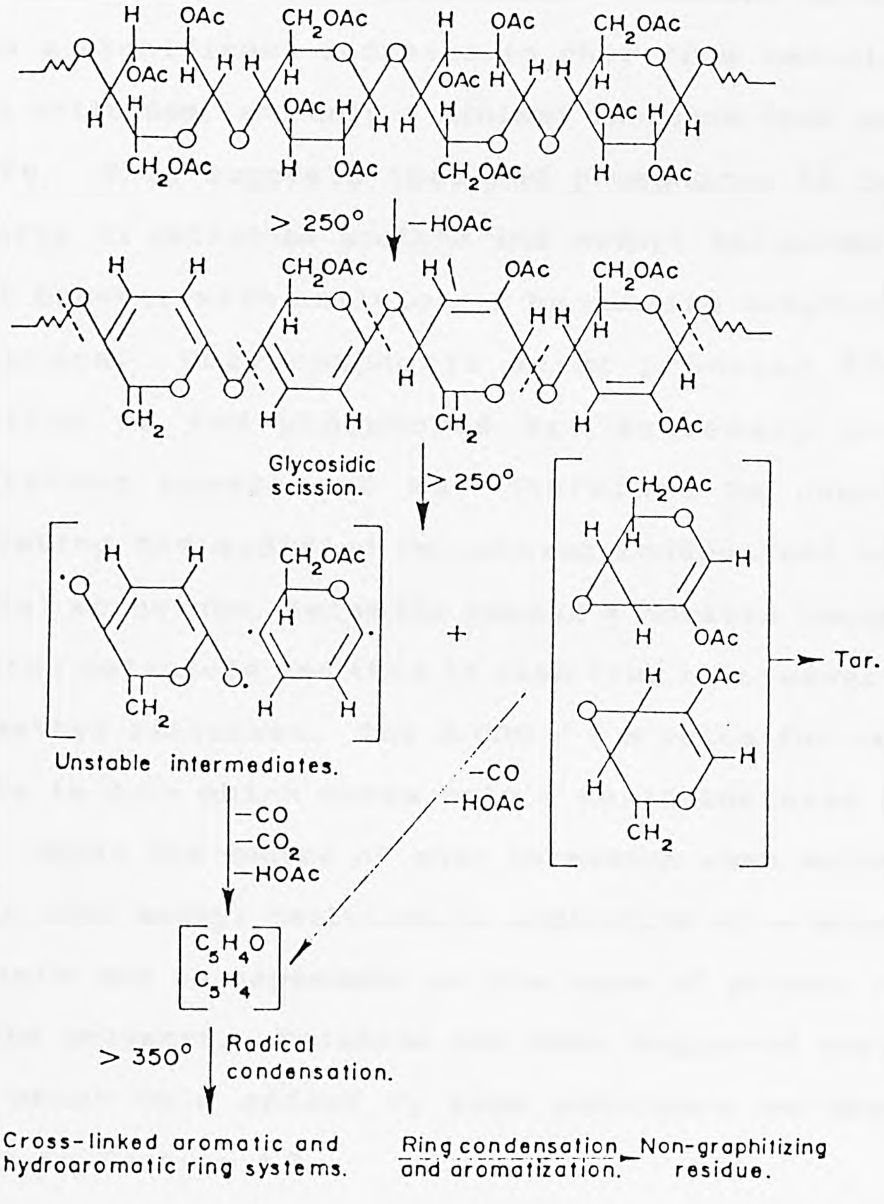
With the two additives each at a ca. 10 wt percent loading the order is;

cellulose acetate >> cellulose > methyl cellulose

giving values of 8.1, 4.0 each respectively.

The results show that red phosphorus is effective in both cellulose and cellulose acetate. A combination of the two additives shows that significant synergism exists between red phosphorus and melamine in methyl cellulose.

Scheme 4.2 Proposed mechanism of thermal degradation of cellulose triacetate

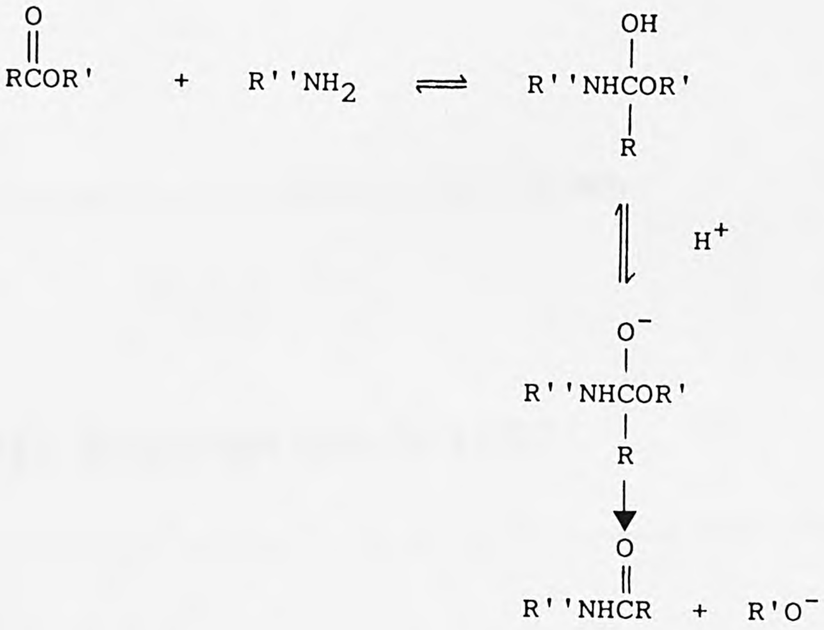


Source: A. Scotney (1972), Eur. Polymer Jour., 8, 190.

The CBO values in Table 3.22 show that red phosphorus increases the char yields from all three cellulosic polymers, with methyl cellulose showing the greatest effect of the two substituted celluloses. Melamine in contrast causes a significant increase in char from cellulose and methyl cellulose, and only a minimal increase from cellulose acetate. This suggests that red phosphorus is behaving similarly in cellulose acetate and methyl cellulose to the way it behaves with cellulose , by causing dehydration to take place. Polyphosphoric acids produced from the oxidation of red phosphorus are extremely powerful dehydrating agents and may therefore be capable of dehydrating the modified celluloses independent of their chemical structure. Melamine causes a notable increase in char from cellulose and this is also true to a lesser extent with methyl cellulose. The Δ CBO / % N value for celluose acetate is 0.09 which shows only a small increase in char yield. Again the degree of char formation when melamine is present with methyl cellulose is indicative of a dehydration mechansim and is dependent on the ease of proton removal from the polymers. Melamine has been suggested earlier to bring about this effect by base catalysis as described earlier in Section 4.2.

Esters are known to react with ammonia and amines to form amides (Scheme 4.3), and with cellulose acetate, acetamide is a likely product from the reaction. Amides have characteristic infrared peaks in the carbonyl region which

Scheme 4.3 **A reaction scheme to show the effect of ammonia or amines on esters to form amides**



are shifted slightly compared with an aliphatic carbonyl, C=O stretch due to the presence of the nitrogen atom. Figure 3.45 shows a definite band at 1775 cm^{-1}, slightly higher than the carbonyl stretch of acetic acid which appears at 1730 cm^{-1}. The formation of acetamide which has a boiling point of 221°C and would therefore be relatively volatile may account for the small increase in the CBO value when melamine is used with cellulose acetate. Red phosphorus and melamine, when used separately and in combination with each other, cause a reduction in temperature at which cellulose acetate forms acetic acid suggesting that they are both responsible for a condensed phase mode of action.

Ethers do not react with ammonia or amines in the same way as esters and therefore the formation of such a product cannot take place. The effectiveness of melamine in reducing the flammability of methyl cellulose may be due to a base catalysed dehydration mechanism. The addition of both red phosphorus and melamine alone, and together to methyl cellulose causes increased production of methanol, as detected by infrared spectroscopy. Red phosphorus does cause a reduction in the breakdown temperature of methyl cellulose, suggesting it has a significant effect on the decomposition in the condensed phase. The addition of melamine has no effect on the temperature at which methanol is produced, suggesting it is perhaps effective in the condensed phase but by a different mechanism from red phosphorus. A combination of the two additives causes no significant change in the CBO value but does cause the absence of formaldehyde, a product visible when the two additives are used separately. The production of formaldehyde is due to the further oxidation of methanol. The absence of this oxidation when both red phosphorus and melamine are present suggests that a combination of the two additives results in the formation of an intermediate, such as a phosphoramide, which may account for the observed P-N synergism in this system.

4.5 Conclusions

The work described in this thesis has been concerned with various ways in which phosphorus compounds bring about their flame-retardant effect on cellulose cotton cloth.

Many of the common phosphorus - based flame retardants contain only small proportions of phosphorus, together with large amounts of other elements. Elemental red phosphorus is clearly a form which is, in principle, capable of producing the greatest-flame retardant effect if phosphorus itself is the active species. Investigations showed that this form of phosphorus had a number of practical limitations and, in order to alleviate, these a number of soluble phosphorus compounds were examined. In addition, various nitrogen-containing co-additives were studied to see whether these enhanced the effect of the phosphorus, and the mechanism of the interactions between the additives was investigated.

The present work has shown that the system which has provided the greatest reduction in flammability of cotton cloth has been that of phosphorylated cellulose with melamine as a co-additive. The importance of the phosphorylation reaction has been examined in some detail by considering a number of different phosphorus compounds which are capable of phosphorylating cellulose either by forming phosphorus acids, as is the case with red phosphorus, or by taking part in an ester interchange reaction, as occurs with dimethyl methyl phosphonate and triphenyl phosphite. Other additives, such as triphenyl phosphine, triphenyl phosphine oxide and tritolyl phosphate, have been found not to take part in such reactions to form cellulose phosphate but to bring about their effect by alternative mechanisms in the gas phase. Thus they may behave as radical scavengers or in the case of tritolyl phosphate as a blanketing agent.

The further reduction in flammability caused by the addition of melamine to phosphorylated cotton cloth demonstrates the effectivenesss of combined phosphorus - nitrogen systems. It seems that nitrogen may act by some alternative mechanism to that of catalysis of phosphorylation via a phosphoramide intermediate.

A number of nitrogen compounds have been investigated in the presence and absence of phosphorus compounds. All those examined except ethylene urea have been shown to be effective in the condensed phase and to promote char formation, and a base-catalysed mechanism has been postulated. Although a number of these nitrogen-containing compounds produced ammonia on decomposition, no evidence was obtained to suggest that the diluent action of this compound when released into the gas phase is responsible for their flame - retardant effect. An unexpected observation with some of the systems studied was that increased char formation need not necessarily cause a reduction in flammability. N-methylimidazole, in particular, showed this behaviour.

Synergism between phosphorus and nitrogen systems has been investigated in both a qualitative and a quantitative manner, with red phosphorus and melamine showing the greatest interaction. The effectiveness of nitrogen compounds on polymer systems containing phosphorus-based flame retardants has been attributed to the former catalyzing phosphorylation reactions by forming a condensed phase intermediate such as a phosphoramide. This is demonstrated by both triphenyl phosphite and dimethyl methyl phosphonate which show further reductions in flammability, as well as increased char formation, when melamine is present. However, melamine also enhances the effect of any cellulose phosphate formed so that the reduction in flammability need not imply a greater degree of phosphorylation. Evidence also exists for phosphorus - nitrogen synergism in systems which are effective in the gas phase, such as tritolyl phosphate - melamine.

The importance of condensed phase mechanisms of flame-retardant action was also shown in systems involving modified forms of cellulose. Red phosphorus promotes char formation with these polymers, suggesting the greater effectiveness of polyphosphoric acids as dehydrating agents for cellulose. Melamine also appears to be effective in base - catalyzed dehydration as is also seen with cellulose.

This work has shown that a number of phosphorus and nitrogen additives have succesfully reduced the flammability of the cellulosic materials studied. However their modes of action are quite complicated and the systems concerned may function in either the condensed or the gas phase, or in both.

Appendix

Program for binary flame retardant additive system - 3 components

```
10 common x(100,15),xt(15,100),xtx(15,15),y(100),xty(15),beta(15),
15 & cc(2,3),yc(100),ec(100)
20 dimension vbl(2,15),sp(100,10),xc(10,7),xv(3,3),
25 & vtitle(9),AK(7,10)
30 INTEGER VTL(15),VTM(15)
35 character*80 title,vtitle,vbl*60
40 data xc/1.,2*0.,2*.5,0.,.333333,.666667,
50     & 2*0.166666,0.000000,1.000000,0.000000,0.500000,0.000000,0.500000,
60     & 0.333333,0.166666,0.666666,0.166666,2*0.000000,1.000000,0.000000,
70     & 2*0.500000,0.333333,2*0.166666,0.666666,3*0.000000,0.250000,
80     & 2*0.000000,3*0.111111,0.027778,4*0.000000,0.250000,0.000000,
90     & 2*0.111111,0.027778,0.111111,5*0.000000,0.250000,0.111111,
100     & 0.027778,2*0.111111,6*0.000000,0.037037,3*0.018518/
105 &,vbl/'xo1 = ',' ','xo2 = ',' ','xo3 = ',' ','xo4 = ','xo1 * xo2','xo5 = ',
106 &'xo1 * xo3','xo6 = ','xo2 * xo3','xo7 = ','xo1 * xo2 * xo3',
107 &'xo8 = ','x01*x02(x01-x02)','x09=','x03*x01(x03-x01)','x010=
108 &','x02*x03(x02-x03)','x011 =','x01*x02(x01**x02**2-3*x01*x02)'
109 &,'x012=','x01*x03(x01**2+x03**2-3*x01*x03)','x013=','x02*x03
110 & (x02**2+x03**2-3*x02*x03)','x014=','x01*(x02**2)*x03',
111 &'x015=','x01*x02*(x03**2)'/
119 41 FORMAT(/30x,/'MATRICE X'/30X,9('-')///13x,'x01',9x,'x02',9x,'x03',
120     & 9x,'x04',9x,'x05',9x,'x06'//(10x,6(F8.6,4x)))
130   72 FORMAT(//30X,'VECTOR XPRIM Y'/30X,15('-')//10X,3(E12.6,1X)//)
140   61 FORMAT(30X,'MATRICE XPRIM X'/30X,15('-')//15X,'X01',10X,'X02',10X,
150     & 'X03',10X,'X04',10X,'X05',10X,'X06'//(10X,6(E12.6,1X)))
160   71 FORMAT(//30X,'VECTOR XPRIM Y'/30X,15('-')//10X,6(E12.6,1X)//)
170   81 FORMAT(30X,'MATRICE (XPRIM X)-1'/30X,19('-')//15X,'X01',10X,'X02',
180     & 10X,'X03',10X,'X04',10X,'X05',10X,'X06'//(10X,6(E12.6,1X)))
190   91 FORMAT(1X,29X,'MODEL POLYNOMIAL OF DEGREE 2'///31X,'MIXTURE OF 3
200    & CONSTITUENTS'/31X,'SPECIFICATION OF VARIABLES :'/)
210 42 FORMAT(/30X,'Input Data'/10X,'No.',7X,'LOI',10X,
215      &'xo1',11X,'xo2',11x,'xo3')
220 43 FORMAT(/30X,'Original Input Data'/10X,'No.',7X,'LOI',10X,
221    &'xo1',11x,'xo2',11x,'xo3')
223 433 FORMAT(/30X,'Original Input Data'/10X,'No.',7X,'Ds',10X,
224      &'xo1',11X,'xo2',11X,'xo3')
227 443 FORMAT(I12,F11.3,3F14.6)
230   62 FORMAT(30X,'MATRICE XPRIM X'/30X,15('-')//15x.'X01',10X,'X02',10X,
240     & 'X03'//(10X,3(E12.6,1X)))
250   82 FORMAT(30X,'MATRICE (XPRIM X)-1'/30X,19('-')//15X,'X01',10X,'X02',
260     & 10X,'X03'//(10X,3(E12.6,1X)))
270  991 FORMAT(1X,29X,'MODEL POLYNOMIAL OF DEGREE 1'///31X,'MIXTURE OF 3
280    & CONSTITUENTS'/31X,'SPECIFICATION OF VARIABLES :'/)
290 10 Format(V)
300   11 FORMAT('1',30X,'LINEAR REGRESSION OF MULTIPLE-MIXTURES'/30X,39('-'
310    & )//30X,A80)
320 12 format(A80)
330 20 format(A60)
340 21 format(30x,'Composition Variables:',3(/35x,A60))
350 30 format(7(30X,A6,A60/))
355 31 format(3(30X,A6,A60/2(36x,A60/)),4(30X,A6,A60/))
360   40 FORMAT(/30X,'MATRICE X'/30X,9('-')///13X,'X01',9X,'X02',9X,'X03',
370    & 9X,'X04',9X,'X05',9X,'X06',9X,'X07'//(10X,7(F8.6,4X)))
380   50 FORMAT('1',/30X,'VECTOR Y' /30X,9('-')//10X,10(F5.2,3X)//)
390   60 FORMAT(30X,'MATRICE XPRIM X'/30X,15('-')//15X,'X01',10X,'X02',10X,
400    & 'X03',10X,'X04',10X,'X05',10X,'X06',10X,'X07'//(10X,7(E12.6,1X)))
410   70 FORMAT(//30X,'VECTOR XPRIM Y'/30X,15('-')//10X,7(E12.6,1X)//)
420   80 FORMAT(30X,'MATRICE (XPRIM X)-1'/30X,19('-')//15X,'X01',10X,'X02',
430    & 10X,'X03',10X,'X04',10X,'X05',10X,'X06',10X,
440    & 'X07'//(10X,7(E12.6,1X)))
450  90 FORMAT(1X,29X,'REDUCED CUBIC MODEL'///31X,'MIXTURE OF 3 CONSTITUEN
460    & TS'/31X,'SPECIFICATION OF VARIABLES :'/)
470  994 FORMAT(12X,'X07',8X,E12.6,5X,E12.6)
480   94 FORMAT(10X,'COEFFICIENTS'/10X,12('-')/10X,'VARIABLE',6X,'COEFFICIE
490    & NT',5X,'SIGMA-SQUARE'/(12X,'X0',I2,8X,E12.6,5X,E12.6))
500 96 format('1',9x,'Calculated LOI Values:'/10x,21('-')/10x,'Number',5x,
510 & 'Observed LOI',4x,'Calculated LOI',4x,'Difference'/(11x,I3,5x,F12.6,
520 & 5x,F12.6,5x,F12.6))
530   51 FORMAT(20A4)
540 52 format('    Plot of: ',A80)
550   53 FORMAT(5X,'LINEAR MODEL',3X,10(F5.2,3X))
560   54 FORMAT(5X,'QUADRATIC MODEL',3X,10(F5.2,3X))
570   55 FORMAT(5X,'CUBIC MODEL',3X,10(F5.2,3X))
580   97 FORMAT('1')
590 120 read(5,20,end=1000) (vbl(2,i),i=1,3)
592 read(5,12,end=1000) title
593 do 699 i=1,3
594 do 699 j=1,3
595 699 xv(i,j)=xc(i,j)
```

```
write(6,11) title
write(6,21) (vbl(2,i),i=1,3)
read(5,10) ymin,pas,nin,nout
READ (5,10) IAVC,B,CSUB
NINM=NIN-1; NINP=NIN+1
ninmm = nin - 2
if(nin) ,,701
read(5,10)(y(i),i=1,10)
do 700 i=1,10
if(nin.eq.-2) y(i)=1691.*(1.95424-alog10(y(i)))
do 700 j=1,7
700 x(i,j)=xc(i,j)
iin=10;    Det=1.
go to 710
701 if(ninm)710,7011,7012
7011 write(6,43)
go to 7013
7012 write(6,433)
7013 do 703 iin=1,100
read(5,10) y(iin),(x(iin,j),j=1,3)
write(6,443) iin,y(iin),(x(iin,j),j=1,3)
if(y(iin).lt.0.) go to 704
xtot=x(iin,1)+x(iin,2)+x(iin,3)
do 702 i=1,3
702 x(iin,i)=x(iin,i)/xtot
if(nin.eq.3) y(iin)=1691.*(1.95424-alog10(y(iin)))
703 continue
704 read(5,10)((xv(i,j),j=1,3),i=1,3)
iin=iin-1
do 705 i=1,3
xtot=xv(i,1)+xv(i,2)+xv(i,3)
do 705 j=1,3
705 xv(i,j)=xv(i,j)/xtot
call coord(xv,Det)
if(Det.ne.0.) go to 707
write(6,706)
706 format(' Incorrectly chosen vertices - coordinate conversion not ',
&'possible.'/' Vertices placed at 100% of each component')
go to 710
707 call conv(iin)
write(1,703)((100.*xv(i,j),vbl(2,j),j=1,3),i=1,3)
703 format(3(F9.4,'% ',A60/2(' + ',F9.4,'% ',A60/)))
rewind 1
read(1,12)(vtitle(i),i=1,9)
rewind 1
write(6,709) (vtitle(i),i=1,9)
709 format(' Composition Limits:'/' x(1) = ',A60/2(6X,A60/),' x(2) = ',A60,
&/2(6X,A60/),' x(3) = ',A60/2(6X,A60/))
710 write(6,991)
if (nin.le.0.or.Det.eq.0.) write(6,30)((vbl(i,j),i=1,2),j=1,3)
if(nin.gt.0.and.Det.ne.0.) write(6,31)(vbl(1,j),(vtitle(i),i=3*j-2,
&3*j),j=1,3)
if(nin.lt.0.or.nin.gt.1) write(6,44)
44 FORMAT(/30X,'Input Data'/10X,'No.',7X,'Ds',10X,
    &'xo1',11X,'xo2',11X,'xo3')
610 if(ninp.ne.0.and.ninmm.ne.0) write(6,42)
  write(6,442)(i,y(i),(x(i,j),j=1,3),i=1,iin)
442 FORMAT(I12,F11.2,3F14.6)
A=0
IF (XV(2,2).EQ.XV(3,3).AND.XV(2,3).EQ.0.AND.XV(3,2).EQ.0) A=XV(2,2)
IF (A.EQ.0.OR.B.EQ.0) IAVC=0
if(iavc.eq.1) call setk(a,b,ak)
6101 if(iavc.eq.2.and.b.ne.0) call setk2(b,ak)
620 call jmtra(iin,3,nin)
630 call jmprod(1,iin,3)
635 if(nout.eq.1) write(6,62)((xtx(i,j),j=1,3),i=1,3)
call minv(3,determ,vtl,vtm)
640 call jmprod(2,iin,3)
if(nout.ne.1) go to 645
write(6,72)(xty(i),i=1,3)
write(6,32)((xtx(i,j),j=1,3),i=1,3)
645 call jmprod(3,iin,3)
ssl=0.;lastn=0
call calcul(3,iin,vr,ssl,lastn)
if(iavc.eq.1) call avcoeff(iavc,b,3,ak,vr)
if(iavc.eq.2) call ternco(b,csub,3,ak,vr)
if(iavc.eq.3) call avincco(a,b,csub,3,ak,vr)
680 write(6,94)(i,beta(i),sqrt(vr*xtx(i,i)),i=1,3)
690 if(nin) 693,692,691
691 if(ninm) ,692,693
692 if(nout.ne.0) write(6,96)(i,y(i),yc(i),ec(i),i=1,iin)
go to 694
693 if(nout.ne.0) write(6,996)(i,y(i),yc(i),ec(i),i=1,iin)
996 FORMAT('1',9X,'Calculated Ds values:'/10X,21('-')/10X,'Number',5X,
    & 'Observed Ds ',4X,'Calculated Ds ',4X,'Difference'/(11X,I3,5X,F12.6,
    & 5X,F12.6,5X,F12.6))
```

```
1000 694 if(nout.ne.0) write(6,97)
1030 if(nout.ne.0) write(6,52) title
1040 call scale(ymin,pas,iin,ym,yinc)
1042 if(nout.eq.3) call plot(ym,yinc,iin,nout,1,xv,nin)
1044 if(nout.eq.3) write(6,97)
1046 if(nout.eq.3) write(6,52) title
1050 call plot(ym,yinc,iin,nout,3,xv,nin)
1055 iv=6
1057 110 if(iin.le.iv) go to 220
1060 write(6,11) title
1062 if(iv.eq.6)write(6,91)
1063 if(iv.eq.7)write(6,90)
1064 if(iv.eq.10)write(6,111)
1065 if(iv.eq.15)write(6,112)
1068 111 format(30X,' FULL CUBIC MODEL'///31X,' Mixture of
1070 & 3 constituents'/31x,' Specification of variables')
1072 112 format(30X,' QUARTIC MODEL'///31X,' Mixture of
1074 & 3 constituents'/31x,' Specification of variables')
1080 if(nin.eq.0.or.Det.eq.0.)write(6,30)((vbl(i,j),i=1,2),j=1,iv)
1081 if(ninp.eq.0.or.Det.eq.0.) write(6,30) ((vbl(i,j),i=1,2),j=1,iv)
1082 if(nin.ne.0.and.ninp.ne.0.and.Det.ne.0.) write(6,31)(vbl(1,j),(vtitle(i),
1083 i=3*j-2,3*j)),j=1,3),((vbl(i,j),i=1,2),j=4,iv)
1085 if(nout.ne.1) go to 520
1090 510 if(iv.eq.6)write(6,41)((x(i,j),j=1,6),i=1,iin)
1095 if(iv.eq.7)write(6,40)((x(i,j),j=1,7),i=1,iin)
1100 515 write(6,50)(y(i),i=1,iin)
1130 520 call gmtra(iin,iv,nin)
1170 call gmprod(1,iin,iv)
1180 530 if(nout.eq.1.and.iv.eq.6)write(6,61)((xtx(i,j),j=1,6),i=1,6)
1190 if(nout.eq.1.and.iv.eq.7)write(6,60)((xtx(i,j),j=1,7),i=1,7)
1200 540 call minv(iv,determ,vtl,vtm)
1240 550 call gmprod(2,iin,iv)
1245 if(nout.ne.1) go to 570
1250 560 if(iv.eq.6) write(6,71)(xty(i),i=1,6)
1255 if(iv.eq.7) write(6,70)(xty(i),i=1,7)
1260 if(iv.eq.6) write(6,81)((xtx(i,j),j=1,6),i=1,6)
1265 if(iv.eq.7) write(6,80)((xtx(i,j),j=1,7),i=1,7)
1300 570 call gmprod(3,iin,iv)
1320 call calcul(iv,iin,vr,ssl,lastn)
1330 if(iavc.eq.1) call avcoeff(iavc,b,iv,ak,vr)
1340 if(iavc.eq.2) call ternco(b,csub,iv,ak,vr)
1345 if(iavc.eq.3) call avincco(a,b,csub,iv,ak,vr)
1350 580 write(6,94)(i,beta(i),sqrt(vr*xtx(i,i)),i=1,iv)
1351 590 if(nin) 593,592,591
1352 591 if(ninm) ,592,593
1353 592 if(nout.ne.0) write(6,96)(i,y(i),yc(i),ec(i),i=1,iin)
1354 go to 594
1355 593 if(nout.ne.0) write(6,996)(i,y(i),yc(i),ec(i),i=1,iin)
1400 594 if(nout.ne.0) write(6,97)
1430 if(nout.ne.0) write(6,52) title
1440 call scale(ymin,pas,iin,ym,yinc)
1450 call plot(ym,yinc,iin,nout,iv,xv,nin)
1460 if(iv.eq.15) go to 220
1470 if(iv.eq.10) iv=15
1480 if(iv.eq.7) iv=10
1490 if(iv.eq.6) iv=7
1500 go to 110
1850 220 do 250 i=1,15
1890       BETA(I)=0.0
1900  250 CONTINUE
1910       GO TO 120
1920 1000 call lpconv
1925 stop
1930       END
1940 subroutine scale(ymin,pas,iin,ym,yinc)
1950 common x(100,15),dummy(1725),y(100),dummy2(39),yc(100)
1960 ym=ymin;  yinc=pas
1970 if(ymin.ge.0..and.pas.gt.0.) return
1980 ym=100.;  yx=0.
1990 do 101 i=1,iin
1995 if(x(i,1).lt.0..or.x(i,2).lt.0..or.x(i,3).lt.0.) go to 101
2000 if(y(i).gt.yx) yx=y(i)
2010 if(yc(i).gt.yx) yx=yc(i)
2020 if(y(i).lt.ym) ym=y(i)
2030 if(yc(i).lt.ym) ym=yc(i)
2040 101 continue
2050 if(ymin.gt.ym.and.ymin.lt.yx) ym=ymin
2060 ydiff=(yx-ym)/10.
2070 do 102 i=1,4
2080 ysc=aint(ydiff)+1.
2090 if(ydiff.ge.5.) ysc=10.
2100 if(ydiff.ge.1.) go to 103
2110 102 ydiff=ydiff*10.
```

```
2120 103 if(pas.le.0.) yinc=ysc/10.**(i-1)
2130 if(ymin.lt.0.) ym=yinc*aint(ym/yinc)
2140 return
2150 end
2540 subroutine gmtra(n,m,nin)
2550 common a(100,15),r(15,100),dummy(15,15),y(100)
2560 do 10 i=1,n
2570 do 10 j=1,m
2580 10 r(j,i)=a(i,j)
2582 if(nin.eq.0.or.nin.eq.1) return
2584 do 11 i=1,n
2586 do 11 j=1,m
2588 11 if(y(i).ne.0) r(j,i)=1E6*r(j,i)/y(i)/y(i)
2590 return
2600 end
2650 subroutine gmprod(ncalc,n,m)
2660 common x(100,15),xt(15,100),xtx(15,15),y(100),xty(15),beta(15)
2665 if(ncalc.ne.1) go to 12
2670 do 11 i=1,m
2675 do 11 j=1,m
2680 xtx(i,j)=0.
2690 do 11 k=1,n
2700 11 xtx(i,j)=xtx(i,j)+xt(i,k)*x(k,j)
2710 return
2720 12 if(ncalc.ne.2) go to 14
2730 do 13 i=1,m
2740 xty(i)=0.
2750 do 13 k=1,n
2760 13 xty(i)=xty(i)+xt(i,k)*y(k)
2770 return
2780 14 do 15 i=1,m
2790 beta(i)=0.
2795 do 15 k=1,m
2798 15 beta(i)=beta(i)+xtx(i,k)*xty(k)
2800       RETURN
2810       END
2820 subroutine minv(n,d,l,m)
2825 common dummy(3000),xtx(15,15)
2830 dimension a(225),l(15),m(15)
2831 ia=0
2832 do 5 i=1,n
2834 do 5 j=1,n
2836 ia=ia+1
2838 5 A(ia)=xtx(j,i)
2840CC         SEARCH FOR LARGEST ELEMENT
2850       D=1.0
2860       NK=-N
2870       DO80 K=1,N
2880       NK=NK+N
2890       L(K)=K
2900       M(K)=K
2910       KK=NK+K
2920       BIGA=A(KK)
2930       DO 20 J=K,N
2940       IZ=N*(J-1)
2950       DO 20 I=K,N
2960       IJ=IZ+I
2970    10 IF( ABS(BIGA)-ABS(A(IJ))) 15,20,20
2980    15 BIGA=A(IJ)
2990       L(K)=I
3000       M(K)=J
3010    20 CONTINUE
3020CC
3030CC         INTERCHANGE ROWS
3040CC
3050       J=L(K)
3060       IF(J-K)35,35,25
3070    25 KI=K-N
3080       DO 30 I=1,N
3090       KI=KI+N
3100       HOLD=-A(KI)
3110       JI=KI-K+J
3120       A(KI)=A(JI)
3130    30 A(JI)=HOLD
3140CC         INTERCHANGE COLUMNS
3150CC
3160CC
3170    35 I=M(K)
3180       IF(I-K) 45,45,38
3190    38 JP=N*(I-1)
3200       DO 40 J=1,N
```

```
3210          JK=NK+J
3220          JI=JP+J
3230          HOLD=-A(JK)
3240          A(JK)=A(JI)
3250       40 A(JI)=HOLD
3260CC
3270CC          DIVIDE COLUMN BY MINUS PIVOT (VALUE OF PIVOT ELEMENT
3280CC          IS CONTAINED IN  BIGA)
3290CC
3300       45 IF(BIGA) 48,46,48
3310       46 D=0.0
3320          RETURN
3330       48 DO 55 I=1,N
3340          IF(I-K) 50,55,50
3350       50 IK=NK+I
3360          A(IK)=A(IK)/(-BIGA)
3370       55 CONTINUE
3380CC
3390CC          REDUCE MATRIX
3400CC
3410          DO 65 I=1,N
3420          IK=NK+I
3430          HOLD=A(IK)
3440          IJ=I-N
3450          DO 65 J=1,N
3460          IJ=IJ+N
3470          IF(I-K)60,65,60
3480       60 IF(J-K)62,65,62
3490       62 KJ=IJ-I+K
3500          A(IJ)=HOLD*A(KJ)+A(IJ)
3510       65 CONTINUE
3520C   C
3530CC          DIVIDE  ROW  BY  PIVOT
3540CC
3550          KJ=K-N
3560          DO 75 J=1,N
3570          KJ=KJ+N
3580          IF(J-K)70,75,70
3590       70 A(KJ)=A(KJ)/BIGA
3600       75 CONTINUE
3610CC
3620CC          PRODUCT OF PIVOTS
3630CC
3640          D=D*BIGA
3650CC
3660CC          REPLACE PIVOT BY RECIPROCAL
3670CC
3680          A(KK)=1.0/BIGA
3690       80 CONTINUE
3700CC
3710CC          FINAL ROW AND COLUMN INTERCHANGE
3720CC
3730          K=N
3740      100 K=(K-1)
3750          IF(K) 150,150,105
3760      105 I=L(K)
3770          IF(I-K) 120,120,108
3780      108 JQ=N*(K-1)
3790          JR=N*(I-1)
3800          DO 110 J=1,N
3810          JK=JQ+J
3820          HOLD=A(JK)
3830          JI=JR+J
3840          A(JK)=-A(JI)
3850      110 A(JI)=HOLD
3860      120 J=M(K)
3870          IF(J-K)100,100,125
3880      125 KI= K-N
3890          DO 130 I=1,N
3900          KI=KI+N
3910          HOLD=A(KI)
3920          JI=KI-K+J
3930          A(KI)=-A(JI)
3940      130 A(JI)=HOLD
3950          GO TO 100
3955 150 ij=0
3960 do 161 i=1,n
3962 do 161 j=1,n
3964 ij=ij+1
3966 161 xtx(j,i)=A(ij)
3968 return
3970          END
3980 subroutine calcul(n,iin,vr,ssl,lastn)
3990 common a(100,15),xt(15,100),dum1(225),c(100),dum2(15),B(15),dum3(9),d(100),
3995 se(100)
```

```
4000    92 FORMAT('1',9X,'STATISTICS'/10X,11('-')/10X,'RESIDUAL VARIANCE',
4010 & 6X,E12.6/10X,'R.m.s. difference',6X,F12.6/10X,         'DEGREES OF FREE
4020     & DOM',12X,I2/10X,'REGR.CORR.COEFFICIENT',2X,E12.6//)
4030    93 FORMAT(10X,'ANALYSIS OF VARIANCE'/10X,20('-')/10X,'SOURCE',5X,
4040     & 'DOF      DIFF-OF-SUM       MEAN SQUARE',6X,'F-TEST RATIO'/10X,
4050     & 'ERROR',6X,I2,5X,E12.6,6X,E12.6/10X,'REGRESSION',1X,I2,5X,E12.6,
4060     & 6X,E12.6,6X,E12.6//)
4070       sumy=0.0
4075 sumw=0.
4080       sumy2=0.0
4085 sumy0=0.
4090       sumy02=0.0
4095 sce=0.;swe=0.
4100 do 190 i=1,iin
4102 w=0.
4104 do 191 j=1,3
4106 191 w=w+xt(j,i)
4110       D(I)=0.0
4120       DO 192 J=1,N
4130       D(I)=D(I)+B(J)*A(I,J)
4140  192 CONTINUE
4150       E(I)=C(I)-D(I)
4155 sumw=sumw+w
4160       sumy2=sumy2+C(I)*C(I)*w
4170       sumy=sumy+C(I)*w
4175 sumy0=sumy0+D(i)*w
4180       sumy02=sumy02+D(I)*D(I)*w
4185 sce=sce+e(i)*e(i) ;swe=swe+e(i)*e(i)*w
4190  190 CONTINUE
4210 scr=sumy02-sumy0*sumy0/sumw
4215 nl=iin-n
4220 vr=sce/nl; wvr=swe/nl
4230       SCM=SCR/(FLOAT(N))
4240 ratio=scm/wvr
4250 wvr=wvr*iin/sumw
4260 ecvr=sqrt(wvr)
4270 R2=scr/(sumy2-sumy*sumy/sumw)
4280  200 write(6,92)wvr,ecvr,nl,r2
4285 write(6,94) vr,sqrt(vr)
4286  94 format(10X,'(unweighted values: variance ',E12.6,' r.m.s. difference '
4287 &,F12.6,')')
4290  210 WRITE(6,93)NL,SWE,wvr,N,SCR,SCM,RATIO
4292 sse=scr-ssl;ne=n-lastn;ssem=sse/ne;Fseq=ssem/wvr/sumw*iin
4294 write(6,95) ne,sse,ssem,Fseq
4295 vr=wvr
4296 lastn=n;ssl=scr
4298 95 format(//10X,"Sequential F-test for extra variables added in this step"
4299 &/10X,"Extra degrees of freedom ",I2,"  extra sum of squares ",E12.6,
4300 &" mean ",E12.6/10X,"F-test ratio ",F14.6)
4305 RETURN
4310      END
4320 subroutine plot(ym,yinc,iin,nout,ncoeff,xv,nin)
4330 common x(100,15),dummy(1725),y(100),dummy2(15),beta(15)
4340 dimension ppos(51,101),pc(11),yval(11),ycal(2,101),xa(15)
4345 &,xv(3,3)
4350 character*1 ppos,pc
4360 data pc/'0','1','2','3','4','5','6','7','8','9','x'/
4362 ninp = nin + 1
4363 ninmm = nin - 2
4365 if(nout.eq.0) return
4370 if(ncoeff.eq.3) write(6,300)
4380 300 format(' Linear Model')
4390 if(ncoeff.eq.6) write(6,301)
4400 301 format(' Quadratic Model')
4410 if(ncoeff.eq.7) write(6,302)
4420 302 format(' Reduced Cubic Model')
4422 if(ncoeff.eq.10) write(6,330)
4424 330 format(' Full Cubic Model')
4426 if(ncoeff.eq.15) write(6,331)
4428 331 format(' Quartic Model')
4430 if(ninp.eq.0) write(6,3031) ym,yinc,(xv(1,i),i=1,3)
4432 3031 FORMAT(' Min. Ds = ',F8.3,', Increment = ',F7.3,8X,'x(1) = 1.00, (',
4433       &3F8.4,')')
4435 if(ninmm.eq.0) write(6,3031) ym,yinc,(xv(1,i),i=1,3)
4436 if(ninp.ne.0.and.ninmm.ne.0) write(6,303) ym,yinc,(xv(1,i),i=1,3)
4440 303 format(' Min. LOI = ',F8.3,', Increment = ',F7.3,8x,'x(1) = 1.00 , (',
4445 &3F8.4,' )')
4450 if(nout.eq.2.and.ncoeff.eq.3) write(6,304)
4460 304 format(' * = position of data point')
4470 yval(1)=ym
4480 do 305 i=2,11
4490 305 yval(i)=yval(i-1)+yinc
```

```
do 307 i=1,51
do 306 j=1,101
306 ppos(i,j)=' '
ppos(i,i)='.';    ppos(i,102-i)='.'
307 ppos(1,2*i+1)='.'
do 308 i=1,51,5
ppos(i,i)='+';    ppos(i,102-i)='+'
308 ppos(1,2*i-1)='+'
nfirst=0.;   ny=1
if(ncoeff.eq.1) go to 323
do 315 line =1,51
do 310 ip=line,102-line
xa(1)=(line-1)/50.; xa(3)=(ip-line)/100.; xa(2)=1.-xa(1)-xa(3)
xa(4)=xa(1)*xa(2); xa(5)=xa(1)*xa(3); xa(6)=xa(2)*xa(3)
xa(7)=xa(1)*xa(2)*xa(3); xa(8)=xa(4)*(xa(1)-xa(2))
xa(9)=xa(5)*(xa(3)-xa(1)); xa(10)=xa(6)*(xa(2)-xa(3))
xa(11)=xa(4)*(xa(1)*xa(1)+xa(2)*xa(2)-3.*xa(4))
xa(12)=xa(5)*(xa(1)*xa(1)+xa(3)*xa(3)-3.*xa(5))
xa(13)=xa(6)*(xa(2)*xa(2)+xa(3)*xa(3)-3.*xa(6))
xa(14)=xa(2)*xa(7);   xa(15)=xa(3)*xa(7)
ycal(ny,ip)=0.
do 309 j=1,ncoeff
309 ycal(ny,ip)=ycal(ny,ip)+xa(j)*beta(j)
do 310 j=1,11
if(abs(ycal(ny,ip)-yval(j)).lt.yinc/50.) ppos(line,ip)=pc(j)
310 continue
do 314 j=1,11
if(line.eq.51) go to 312
do 311 ip=1+line,102-line
y1=ycal(ny,ip)-yval(j) ;  a1=abs(y1)
y2=ycal(ny,ip-1)-yval(j); a2=abs(y2)
if(a1.eq.0..or.a2.eq.0.) go to 311
if(y1/a1.eq.y2/a2) go to 311
if(a1.lt.a2) ppos(line,ip)=pc(j)
if(a1.gt.a2) ppos(line,ip-1)=pc(j)
311 continue
312 if(nfirst.eq.0) go to 314
do 313 ip=line,102-line
y1=ycal(ny,ip)-yval(j);    a1=abs(y1)
y2=ycal(3-ny,ip)-yval(j); a2=abs(y2)
if(a1.eq.0..or.a2.eq.0.) go to 313
if(y1/a1.eq.y2/a2) go to 313
if(a1.lt.a2) ppos(line,ip)=pc(j)
if(a1.gt.a2) ppos(line-1,ip)=pc(j)
313 continue
314 continue
nfirst=1;    ny=3-ny
315 continue
323 if((nout.ne.2.or.ncoeff.ne.3).and.ncoeff.ne.1) go to 317
do 316 i=1,iin
ix=int(50.*x(i,1)+100.*x(i,3)+1.5)
iy=int(50.*x(i,1)+1.5)
if(nout.eq.2.and.iy.ge.1.and.iy.le.51.and.ix.ge.iy.and.ix.le.(102-iy))
&ppos(iy,ix)='*'
ival=int(y(i)/yinc-ym/yinc+1.5)
if(nout.eq.3.and.iy.ge.1.and.iy.le.51.and.ix.ge.iy.and.ix.le.(102-iy))
&ppos(iy,ix)=pc(ival)
316 continue
317 do 318 i=1,51
ip=52-i
318 write(6,319)(ppos(ip,j),j=1,101)
319 format(10x,101A1)
write(6,320)(0.1*i,i=1,10)
320 format(9x,'0.0',10(7x,F3.1)/5x,'x(2) = 1.00',90x,'x(3) = 1.00')
write(6,322) ((xv(i,j),j=1,3),i=2,3)
322 format(2x,'(',3F8.4,')',70x,'(',3F8.4,')')
if(ninp.eq.0) write(6,3211) (pc(i),yval(i),i=1,11)
3211 FORMAT(' Ds Values: ',9(A1,' = ',F7.2,'; ')/A1,' = ',F7.2,';
       &  ',A1,' = ',F6.2)
if(ninp.ne.0.and.ninmm.ne.0) write(6,321) (pc(i),yval(i),i=1,11)
321 format(' LOI Values: ',9(A1,' = ',F7.2,'; ')/A1,' = ',F7.2,'; ',
&A1,' = ',F8.2)
return
end
subroutine coord(A,Det)
common dummy(3355),c(3,3)
dimension a(3,3),d(4)
amult=-1.
do 601 i=1,3
do 601 j=1,3
amult=-amult
n=0
```

```
5300 do 600 id=1,3
5310 do 600 jd=1,3
5320 if(id.eq.i.or.jd.eq.j) go to 600
5330 n=n+1
5340 d(n)=a(id,jd)
5350 600 continue
5360 601 c(j,i)=amult*(d(1)*d(4)-d(2)*d(3))
5370 det = a(1,1)*c(1,1)+a(1,2)*c(2,1)+a(1,3)*c(3,1)
5380 if(det.eq.0.) return
5390 do 602 i=1,3
5400 do 602 j=1,3
5410 602 c(i,j)=c(i,j)/det
5420 return
5430 end
5440 subroutine conv(iin)
5450 common x(100,15),dummy(1855),c(3,3)
5460 dimension xt(3)
5470 do 605 ir=1,iin
5480 do 603 i=1,3
5490 603 xt(i)=x(ir,i)
5500 do 604 i=1,3
5510 x(ir,i)=0.
5520 do 604 j=1,3
5530 604 x(ir,i)=x(ir,i)+c(j,i)*xt(j)
5540 x(ir,4)=x(ir,1)*x(ir,2); x(ir,5)=x(ir,1)*x(ir,3); x(ir,6)=x(ir,2)*x(ir,3)
5545 x(ir,7)= x(ir,1)*x(ir,2)*x(ir,3); x(ir,8)= x(ir,4)*(X(IR,1)
5546 & -X(IR,2))
5548 X(IR,9)=X(IR,5)*(X(IR,3)-X(IR,1))
5549 X(IR,10)=X(IR,6)*(X(IR,2)-X(IR,3))
5550 X(IR,11)=X(IR,4)*(X(IR,1)*X(IR,1)+X(IR,2)*X(IR,2)-3*X(IR,4))
5560 X(IR,12)=X(IR,5)*(X(IR,1)*X(IR,1)+X(IR,3)*X(IR,3)-3*X(IR,5))
5565 X(IR,13)=X(IR,6)*(X(IR,2)*X(IR,2)+X(IR,3)*X(IR,3)-3*X(IR,6))
5570 X(IR,14)=X(IR,2)*X(IR,7)
5580 605 X(IR,15)=X(IR,3)*X(IR,7)
5590 return
5600 end
5610 SUBROUTINE SETK(A,B,AK)
5620 DIMENSION AK(7,16)
5630 DO 1 I=1,3
5640 DO 1 J=1,15
5650 1 AK(I,J)=0
5660 IF (A.EQ.B) GOTO 2
5670 Q=B/A; R=1./B; S=A/B/B
5680 AK(1,1)=-R; AK(2,1)=-R; AK(1,2)=R; AK(2,3)=R
5690 AK(1,4)=R-R*2*Q/3; AK(2,5)=AK(1,4)
5700 AK(1,8)=R*(1.-2*Q+Q*Q); AK(2,9)=-AK(1,8)
5710 AK(1,11)=R*(1.-4*Q+5*Q*Q-2*Q*Q*Q); AK(2,12)=AK(1,11)
5720 AK(3,6)=S*S*Q**4; AK(3,7)=AK(3,6)-4*AK(3,6)*Q/5
5730 AK(3,14)=2*AK(3,6)*Q/5-AK(3,6)*Q*Q/3;AK(3,15)=AK(3,14)
5740 RETURN
5750 2 AK(1,1)=-1/B; AK(2,1)=-1/B; AK(1,2)=1/B; AK(2,3)=1/B
5760 AK(1,4)=1./3./B; AK(2,5)=AK(1,4)
5770 AK(3,6)=1/B/B; AK(3,7)=0.2/B/B
5780 AK(3,14)=AK(3,6)/15; AK(3,15)=AK(3,14)
5790 RETURN
5800 END
5810 SUBROUTINE AVCOEFF(IAVC,B,ncoeff,ak,vr)
5820 COMMON DUM(3000), XTX(15,15), DUM2(115), BETA(15)
5830 DIMENSION AK(7,16), CAVG(3),TEMP(15,3),CVNEW(3,3)
5840 IF (IAVC.EQ.0) RETURN
5846 IF (IAVC.EQ.2) CALL SETK2(B,AK)
5850 DO 2 I=1,3
5860 CAVG(I)=0
5870 DO 2 J=1,NCOEFF
5880 CAVG(I)=CAVG(I)+AK(I,J)*BETA(J)
5890 TEMP(J,I)=0
5900 DO 1 K=1,NCOEFF
5910 1 TEMP(J,I)=TEMP(J,I)+XTX(J,K)*AK(I,K)
5920 2 CONTINUE
5930 DO 4 I=1,3
5940 DO 4 J=1,3
5950 CVNEW(I,J)=0
5960 DO 3 K=1, NCOEFF
5970 3 CVNEW (I,J)=CVNEW(I,J)+AK(I,K)*TEMP(K,J)
5980 4 CONTINUE
5990 WRITE (6,5) B,(CAVG(I),SQRT(CVNEW(I,I)*VR), I=1,3)
6000 5 FORMAT (10X,'AVERAGE COEFFICIENTS OVER RANGE OF',
6010 \026& 'x2 OR x3 = 0 TO ', F8.5//15x, 'COMPONENT 2',
6020 & F12.5,'S.D.', F12.5/15x, 'COMPONENT 3', F12.5,'S.D.',
6030 & F12.5/15X,'* SYNERGISM *', F15.5,'S.D.',F15.5)
6040 RETURN
6050 END
6099 SUBROUTINE SETK2 (B,AK)
```

```
6100 DIMENSION AK(7,16)
6110 BR=1/B; BR2=BR*BR
6120 DO 1 J=1,3
6130 AK(J,1)=-BR; AK(J,J+1)=BR
6140 1 ak(j+3,j+4)=br2
6150 AK(7,8)=BR2*BR; AK(7,15)=2*AK(7,8)/7
6160 AK(7,16)=AK(7,15)
6170 RETURN
6180 END
6200 SUBROUTINE TERNCO(B,CSUB,N,AK,Var)
6210 COMMON DUMMY(3000), OLDX(15,15),DUMMY2(115),OLDBETA(15)
6220 DIMENSION AK(7,16),CAVG(7),TEMP(16,7),CVNEW(7,7),BETA(16),
6230 &XTX(16,16)
6240 BETA(1)=CSUB; XTX(1,1)=0; NCOEFF=N+1
6250 DO 10 I=1,15
6260 BETA(I+1)=OLDBETA(I); XTX(I+1,1)=0; XTX(1,I+1)=0
6270 DO 10 J=1,15
6280 XTX(I+1,J+1)=OLDX(I,J)
6290 10 CONTINUE
6310 DO 1 I=1,7
6320 1 cavG(I)=0
6330 DO 3 I=1,7
6340 DO 3 J=1,NCOEFF
6350 CAVG(I)=CAVG(I)+AK(I,J)*BETA(J)
6360 TEMP (J,I)=0
6370 DO 2 K=1,NCOEFF
6380 2 TEMP (J,I)=TEMP(J,I)+XTX(J,K)*AK(I,K)
6390 3 CONTINUE
6400 DO 5 I=1,7
6410 DO 5 J=1,7
6420 CVNEW(I,J)=0
6430 DO 4 K=1,NCOEFF
6440 4 CVNEW(I,J)=CVNEW(I,J)+AK(I,K)*TEMP(K,J)
6450 5 CONTINUE
6460 WRITE(6,6)B, (CAVG(I), SQRT(CVNEW(I,I)*VAR),I=1,7)
6470 6 FORMAT(/10X, 'AVERAGE COEFFICIENTS OVER RANGE OF
6480 & X2, X3, X4=0 TO ',F8.5/15X,' TYPE VARIABLE VALUE S.D.'/
6490 & 15X,'LINEAR  2', 2F12.5/ 24X,' 3 ', 2F12.5/
6500 &24X, '4', 2F12.5/15X, ' BINARY 2-3 ', 2F12.5/22X, ' 2-4',
6510 &2F12.5/22X, ' 3-4 ',2F12.5/15X, ' TERNARY    ',2F12.5)
6520 RETURN
6530 END
6540 subroutine avincco(a,bmax,binc,ncoeff,ak,vr)
6550 dimension ak(7,16),ak2(7,16)
6560 b=0.
6570 do 1 i=1,7
6580 do 1 j=1,16
6590 1 ak2(i,j)=0.
6600 2 bbef=b; bbsq=b*b
6610 b=b+binc
6620 if(b.gt.bmax) return
6630 bsq=b*b
6640 do 3 i=1,7
6650 do 3 j=1,16
6660 3 ak(i,j)=ak2(i,j)
6670 call setk(a,b,ak2)
6680 do 4 i=1,2
6690 do 4 j=1,16
6700 4 ak(i,j)=(bsq*ak2(i,j)-bbsq*ak(i,j))/(bsq-bbsq)
6710 do 5 j=1,16
6720 5 ak(3,j)=(bsq*bsq*ak2(3,j)-bbsq*bbsq*ak(3,j))/(bsq*bsq-bbsq*bbsq)
6730 write (6,6) b
6740 6 format(//10x,'Overall coefficients at b = ',F8.5)
6750 call avcoeff(1,b,ncoeff,ak2,vr)
6760 write(6,7) bbef,b
6770 7 format(//10x,'Incremental coefficients over range b =',F8.5,' to',
6780 & F8.5)
6790 call avcoeff(1,b,ncoeff,ak,vr)
6800 goto 2
6810 end
```

Program for ternary flame retardant additive system - 4 components

```
10 COMMON X(500,21),W(500),XTX(21,21),Y(500),XTY(21),BETA(21),
20 &CC(4,4),YC(500)
30 DIMENSION VBL(21),XV(4,4),VTITLE(4),NPLOT(8),NC(20),XP(20),
40 &IV(8),ORDER(8),YMIN(20),YSTEP(20),YTYPE(3),AK(7,21)
50 CHARACTER*80 TITLE,VTITLE,VBL,ORDER*30,YTYPE*8
60 DATA IV/4,7,10,11,14,17,20,21/,VBL/' ',' ',' ',' ','X02*X03',
70 &'X02*X04','X03*X04','X01*X02','X01*X03','X01*X04',
80 &'X02*X03*X04','X01*X02*X03','X01*X02*X04','X01*X03*X04',
90 &'X02*X03(X02-X03)','X02*X04(X02-X04)','X03*X04(X03-X04)',
100 &'X01*X02(X01-X02)','X01*X03(X01-X03)','X01*X04(X01-X04)',
110 &'X01*X02*X03*X04'/,ORDER/'LINEAR MODEL','RESTRICTED QUADRATIC MODEL',
120 & 'QUADRATIC MODEL','RESTRICTED REDUCED CUBIC MODEL',
130 &'REDUCED CUBIC MODEL','RESTRICTED FULL CUBIC MODEL',
140 &'FULL CUBIC MODEL','REDUCED QUARTIC MODEL'/,YTYPE/'LOI','DS'
141 &,'DS DATA'/
150 1 READ (5,2,END=100) TITLE
160 2 FORMAT (A80)
170 Read (5,2,end=100)(vtitle(i),i=1,4)
180 write (6,3) title
190 3 Format('1',30x,'LINEAR REGRESSION OF FOUR COMPONENT MIXTURES'
200 &/30X,41('-')//30X,A80)
210 write(6,4) (i,vtitle(i), i=1,4)
220 4 FORMAT (//'COMPONENTS: Z',I1,'=',A80,3(/13X,'Z',I1,"=',A80)
230 &//'(N.B. COMPONENT Z1 IS ASSUMED TO BE THE SUBSTRATE,')
240 READ (5,5)NIN, NOMAX
245 READ(5,5) IAVC,B
250 5 FORMAT(V)
260 IF (NIN.LT.0.OR.NIN.GT.2.)NIN=0
270 IF (NOMAX.LT.1.OR.NOMAX.GT.8)NOMAX=8
280 READ (5,5)(NPLOT(I),I=1,NOMAX)
290 DO 6 I=1,20
300 READ(5,5) NC(I),XP(I),YMIN(I),YSTEP(I)
310 IF (NC(I).LE.0.OR.NC(I).GT.4) GOTO 7
320 6 CONTINUE
330 7 IF (I.NE.20) NPT=I-1
340 DO 8 I=1,NOMAX
350 IF (NPLOT(I).GT.NPT) NPLOT(I)=NPT
360 8 CONTINUE
370 READ (5,5) ((XV(I,J), I=1,4),J=1,4)
380 DO 10 J=1,4
390 SUM=0
400 DO 9 I=1,4
410 9 SUM=SUM+XV(I,J)
420 DO 10 I=1,4
430 10 XV(I,J)=XV(I,J)/SUM
440 CALL COORD (XV,DET)
450 IF (DET.NE.0) GOTO 14
460 WRITE (6,11)((XV(I,J),I=1,4),J=1,4)
470 11 FORMAT(10X,'INCORRECTLY CHOSEN VERTICES - COORDINATE
480 & CONVERSION NOT POSSIBLE'/10X,'VERTICES ATTEMPTED:',4(/20X,4F10.5)
490 &/10X,'VERTICES FOR CALCULATION PLACED AT 100% OFF EACH COMPONENT'
500 &/10x,'NO PLOTS')
510 DO 12 I=1,4
520 DO 12 J=1,4
530 CC(I,J)=0
531 IF (I.EQ.J) CC(I,J)=1
532 12 XV(I,J)=CC(I,J)
540 do 13 i=1,nomax
550 13 NPLOT(I)=0
560 14 WRITE (6,15) YTYPE(NIN+1)
570 15 FORMAT (30X,'ORIGINAL INPUT DATA'/10X,'NO.',A8,
580 &'COMPOSITION VARIABLES')
590 DO 18 IIN=1,500
600 READ (5,5) Y(IIN), (X(IIN,I), I=1,4)
610 IF (Y(IIN).LT.0) GOTO 20
620 WRITE (6,19) IIN, Y(IIN), (X(IIN,I), I=1,4)
630 SUM=0
640 DO 16 I=1,4
650 16 SUM=SUM+X(IIN,I)
660 DO 17 I=1,4
670 17 X(IIN,I)=X(IIN,I)/SUM
680 18 CONTINUE
690 19 FORMAT (10X,I4,5F10.5)
700 IIN=IIN+1
710 20 IIN=IIN-1
720 CALL CONV(IIN)
722 A=0
723 IF(XV(2,2).EQ.XV(3,3).AND.XV(3,3).EQ.XV(4,4))A=XV(2,2)
724 DO 301 I=2,4
```

```
725 DO 201 J=2,4
726 IF(I.NE.J.AND.XV(I,J).NE.0) A=0
727 201 CONTINUE
728 IF (A.EQ.0.OR.B.EQ.0) IAVC=0
729 IF(IAVC.NE.0) CALL SETK (A,B,AK)
730 IF (NIN.NE.2) GOTO 22
740 DO 21 I=1,IIN
750 21 Y(I)=1891*(1.95424-ALOG10(Y(I)))
770 22 WRITE(6,23)
780 23 FORMAT('1',10X,'COORDINATES OF VERTICES')
790 DO 25 J=1,4
800 WRITE (6,26)J
810 DO 24 I=1,4
820 if(XV(I,J).NE.0)WRITE (6,27) 100*XV(I,J),VTITLE(I)
830 24 CONTINUE
835 ENCODE (VBL(J),28)(XV(I,J),I,I=1,4)
840 25 CONTINUE
850 26 FORMAT (/10X,'Z',I1,'=')
860 27 FORMAT (15X,F9.4,'%',A80)
861 28 FORMAT (3(F9.6,'*Z',I1,'+'),F9.6,'*Z',I1)
880 IF (NIN.GT.0) GOTO 30
890 DO 29 I=1,IIN
900 29 W(I)=1
910 GOTO 32
920 30 DO 31 I=1,IIN
930 31 W(I)=1E6/Y(I)/Y(I)
940 32 IF(NIN.EQ.2) NT=2
950 IF (NIN.LT.2) NT=NIN+1
960 WRITE(6,33) YTYPE(NT)
970 33 FORMAT(20X,'INPUT DATA'//10X,'NO.',A8,' X01  X02  X03  X04')
980 DO 34 I=1,IIN
990 34 WRITE (6,35) I,Y(I),(X(I,J),J=1,4)
1000 35 FORMAT (10X,I4,5F11.6)
1010 SSL=0; LASTN=0
1020CC        LEAST SQUARE CALCULATION BEGINS HERE * * * *
1030 DO 53 IORD=1,NO MAX
1035 IF (IV(IORD).GE.IIN-1) GOTO 100
1040 DO 41 I=1, IV(IORD)
1050 DO 41 J=1, IV(IORD)
1160 XTX(I,J)=0
1170 DO 40 K=1,IIN
1180 40 XTX(I,J)=XTX(I,J)+X(K,I)*X(K,J)*W(K)
1190 41 CONTINUE
1200 DO 43 I=1,IV(IORD)
1210 XTY(I)=0
1220 DO 42 K=1,IIN
1230 42 XTY(I)=XTY(I)+X(K,I)*Y(K)*W(K)
1240 43 CONTINUE
1250 CALL MINV(IV(IORD),DET)
1255 IF (DET.EQ.0) GOTO 90
1260 DO 45 I=1,IV(IORD)
1270 BETA(I)=0
1280 DO 44 K=1,IV(IORD)
1290 44 BETA (I)=BETA(I)+XTX(I,K)*XTY(K)
1300 45 CONTINUE
1310 CALL CALCUL(IV(IORD),IIN,VR,SSL,LAST N)
1315 CALL AVCOEFF(IAVC,B,IV(IORD),AK,VR)
1320 WRITE (6,46) ORDER(IORD)
1340 46 FORMAT ('1',20X,A30)
1350 WRITE (6,47)(I,VTITLE(I),I=1,4)
1360 47 FORMAT (//20X,'COMPONENTS'/4(/10X,'Z',I1,'=',A80))
1370 WRITE (6,48)(I,VBL(I),I=1,IV(IORD))
1380 48 FORMAT(//20X,'VARIABLES:'/(/10X,'X0',I2,'=',A80))
1390 WRITE(6,49)(I,BETA(I),SQRT(VR*XTX(I,I)),I=1,IV(IORD))
1400 49 FORMAT (//20X,'COEFFFICIENTS'/20X,12('-')/10X'VARIABLE',
1410 &6X,'COEFFFICIENT',10X,'S.D.'/(11X,'X0',I2,8X,E12.6,5X,E12.6))
1420 WRITE(6,50)YTYPE(NT),YTYPE(NT),YTYPE(NT),
1430 &((J,Y(J),YC(J),Y(J)-YC(J)),J=1,IIN)
1440 50 format('1',9X,'CALCULATED',A5,'VALUES:'//10X,'NUMBER',
1450 &6X,'OBSERVED',A5,3X,'CALCULATED',A5,3X,'DIFFERENCE'/
1460 &(11X,I3,5X,F12.6,5X,F12.6,5X,F12.6))
1470 IF(NPLOT(IORD).EQ.0)GOTO 53
1480 DO 52 I=1,NPLOT(IORD)
1490 WRITE (6,51) TITLE,ORDER(IORD),NC(I),XP(I)
1500 51 FORMAT ('1',9X,A80/10X'PLOT OF\027',A30,'WITH X0',I1,
1510 &'HELD CONSTANT AT',F8.6)
1520 CALL SCALE(YMIN(I),YSTEP(I),IIN,YM,YINC)
1530 CALL PLOT (YM,YINC,IIN,IV(IORD),XV,NIN,NC(I),XP(I))
1540 52 CONTINUE
1550 53 CONTINUE
1560 100 STOP
```

```
1561 90 WRITE(6,91)
1562 91 FORMAT ('LEAST SQUARES MATRIX IS SINGULAR')
1563 GOTO 100
1570 END
1940 subroutine scale(ymin,pas,iin,ym,yinc)
1950 COMMON X(500,21),DUMMY(941),Y(500),DUMMY2(58),YC(500)
1960 ym=ymin;  yinc=pas
1970 if(ymin.ge.0..and.pas.gt.0.) return
1980 ym=100.;   yx=0.
1990 do 101 i=1,iin
1995 if(x(i,1).lt.0..or.x(i,2).lt.0..or.x(i,3).lt.0.) go to 101
2010 if(yc(i).gt.yx) yx=yc(i)
2020 if(y(i).lt.ym) ym=y(i)
2030 if(yc(i).lt.ym) ym=yc(i)
2040 101 continue
2050 if(ymin.gt.ym.and.ymin.lt.yx) ym=ymin
2060 ydiff=(yx-ym)/10.
2070 do 102 i=1,4
2080 ysc=aint(ydiff)+1.
2090 if(ydiff.ge.5.) ysc=10.
2100 if(ydiff.ge.1.) go to 103
2110 102 ydiff=ydiff*10.
2120 103 if(pas.le.0.) yinc=ysc/10.**(i-1)
2130 if(ymin.lt.0.) ym=yinc*aint(ym/yinc)
2140 return
2150 end
2820 SUBROUTINE MINV(N,D)
2825 common dummy(11000),xtx(21,21)
2830 dimension a(441),l(21),m(21)
2831 ia=0
2832 do 5 i=1,n
2834 do 5 j=1,n
2836 ia=ia+1
2838 5 A(ia)=xtx(j,i)
2840CC       SEARCH FOR LARGEST ELEMENT
2850       D=1.0
2860       NK=-N
2870       DO80 K=1,N
2880       NK=NK+N
2890       L(K)=K
2900       M(K)=K
2910       KK=NK+K
2920       BIGA=A(KK)
2930       DO 20 J=K,N
2940       IZ=N*(J-1)
2950       DO 20 I=K,N
2960       IJ=IZ+I
2970    10 IF( ABS(BIGA)-ABS(A(IJ))) 15,20,20
2980    15 BIGA=A(IJ)
2990       L(K)=I
3000       M(K)=J
3010    20 CONTINUE
3020CC
3030CC       INTERCHANGE ROWS
3040CC
3050       J=L(K)
3060       IF(J-K)35,35,25
3070    25 KI=K-N
3080       DO 30 I=1,N
3090       KI=KI+N
3100       HOLD=-A(KI)
3110       JI=KI-K+J
3120       A(KI)=A(JI)
3130    30 A(JI)=HOLD
3140CC       INTERCHANGE COLUMNS
3150CC
3160CC
3170    35 I=M(K)
3180       IF(I-K) 45,45,38
3190    38 JP=N*(I-1)
3200       DO 40 J=1,N
3210       JK=NK+J
3220       JI=JP+J
3230       HOLD=-A(JK)
3240       A(JK)=A(JI)
3250    40 A(JI)=HOLD
3260CC
3270CC       DIVIDE COLUMN BY MINUS PIVOT (VALUE OF PIVOT ELEMENT
3280CC       IS CONTAINED IN  BIGA)
3290CC
```

```
3300    45 IF(BIGA) 43,46,48
3310    46 D=0.0
3320       RETURN
3330    48 DO 55 I=1,N
3340       IF(I-K) 50,55,50
3350    50 IK=NK+I
3360       A(IK)=A(IK)/(-BIGA)
3370    55 CONTINUE
3380CC
3390CC       REDUCE MATRIX
3400CC
3410       DO 65 I=1,N
3420       IK=NK+I
3430       HOLD=A(IK)
3440       IJ=I-N
3450       DO 65 J=1,N
3460       IJ=IJ+N
3470       IF(I-K)60,65,60
3480    60 IF(J-K)62,65,62
3490    62 KJ=IJ-I+K
3500       A(IJ)=HOLD*A(KJ)+A(IJ)
3510    65 CONTINUE
3520C   C
3530CC       DIVIDE  ROW  BY  PIVOT
3540CC
3550       KJ=K-N
3560       DO 75 J=1,N
3570       KJ=KJ+N
3580       IF(J-K)70,75,70
3590    70 A(KJ)=A(KJ)/BIGA
3600    75 CONTINUE
3610CC
3620CC       PRODUCT OF PIVOTS
3630CC
3640       D=D*BIGA
3650CC
3660CC       REPLACE PIVOT BY RECIPROCAL
3670CC
3680       A(KK)=1.0/BIGA
3690    80 CONTINUE
3700CC
3710CC       FINAL ROW AND COLUMN INTERCHANGE
3720CC
3730       K=N
3740   100 K=(K-1)
3750       IF(K) 150,150,105
3760   105 I=L(K)
3770       IF(I-K) 120,120,108
3780   108 JQ=N*(K-1)
3790       JR=N*(I-1)
3800       DO 110 J=1,N
3810       JK=JQ+J
3820       HOLD=A(JK)
3830       JI=JR+J
3840       A(JK)=-A(JI)
3850   110 A(JI)=HOLD
3860   120 J=M(K)
3870       IF(J-K)100,100,125
3880   125 KI= K-N
3890       DO 130 I=1,N
3900       KI=KI+N
3910       HOLD=A(KI)
3920       JI=KI-K+J
3930       A(KI)=-A(JI)
3940   130 A(JI)=HOLD
3950       GO TO 100
3955 150 ia=0
3960 do 161 i=1,n
3962 do 161 j=1,n
3964 ia=ia+1
3966 161 xtx(j,i)=A(ia)
3968 return
3970       END
3980 SUBROUTINE CALCUL (N,IIN,VR,SSL,LASTN)
3990 COMMON A(500,21),W(500),DUM1(441),C(500),DUM2(21),B(21),
3991& DUM3(16),D(500)
4000    92 FORMAT('1',9X,'STATISTICS'/10X,11('-')/10X,'RESIDUAL VARIANCE',
4010 & 6X,E12.6/10X,'R.m.s. difference',6X,F12.6/10X,       'DEGREES OF FREE
4020     & DOM',12X,I2/10X,'REGR.CORR.COEFFICIENT',2X,E12.6//)
4030    93 FORMAT(10X,'ANALYSIS OF VARIANCE'/10X,20('-')/10X,'SOURCE',5X,
4040     & 'DOF      DIFF-OF-SUM       MEAN SQUARE',6X,'F-TEST RATIO'/10X,
4050     & 'ERROR',6X,I2,5X,E12.6,6X,E12.6/10X,'REGRESSION',1X,I2,5X,E12.6,
```

```
4060     & 6X,E12.6,6X,E12.6//)
4070         sumy=0.0
4075 sumw=0.
4080         sumy2=0.0
4085 sumy0=0.
4090         sumy02=0.0
4095 sce=0.;swe=0.
4100 do 190 i=1,iin
4110         D(I)=0.0
4120         DO 192 J=1,N
4130         D(I)=D(I)+B(J)*A(I,J)
4140  192 CONTINUE
4150 E=C(I)-D(I)
4155 sumw=sumw+w(I)
4160         sumy2=sumy2+C(I)*C(I)*w(I)
4170         sumy=sumy+C(I)*w(I)
4175 sumy0=sumy0+D(i)*w(I)
4180         sumy02=sumy02+D(I)*D(I)*w(I)
4185 SCE=SCE+E*E ;SWE=SWE+E*e*w(i)
4190  190 CONTINUE
4210 scr=sumy02-sumy0*sumy0/sumw
4215 nl=iin-n
4220 vr=sce/nl;  wvr=swe/nl
4230         SCM=SCR/(FLOAT(N))
4240 ratio=scm/wvr
4250 wvr=wvr*iin/sumw
4260 ecvr=sqrt(wvr)
4270 R2=scr/(sumy2-sumy*sumy/sumw)
4280  200 write(6,92)wvr,ecvr,nl,r2
4285 write(6,94) vr,sqrt(vr)
4286  94 format(10X,'(unweighted values: variance ',E12.6,' r.m.s. difference '
4287 &,F12.6,')')
4290  210 WRITE(6,93)NL,SCE,wvr,N,SCR,SCM,RATIO
4292 sse=scr-ssl;ne=n-lastn;ssem=sse/ne;Fseq=ssem/wvr*sumw/iin
4294 write(6,95) ne,sse,ssem,Fseq
4295 vr=wvr
4296 lastn=n;ssl=scr
4298 95 format(//10X,"Sequential F-test for extra variables added in this step"
4299 &/10X,"Extra degrees of freedom ",I2,"  extra sum of squares ",E12.6,
4300 &" mean ",E12.6/10X,"F-test ratio ",F14.6)
4305 RETURN
4310        END
4320 SUBROUTINE PLOT(YM,YINC,IIN,NCOEFF,XV,NIN,NC,XP)
4330 COMMON X(500,21),DUMMY(941),Y(500),DUMMY2(21),BETA(21)
4340 dimension ppos(51,101),pc(11),yval(11),ycal(2,101),xa(21)
4345 &,xv(4,4),NV1(4),NV2(4),NV3(4)
4350 character*1 ppos,pc
4360 data pc/'0','1','2','3','4','5','6','7','8','9','X'/,NV1/2,1,
4361 &1,1/,NV2/3,3,2,2/,NV3/4,4,4,3/
4370 IF(XP.EQ.1)RETURN
4430 IF(NIN.GT.0) WRITE (6,3031) YM,YINC,NV1(NC),1-XP
4432 3031 FORMAT ('MIN. DS = ',F8.3,', INCREMENT = ',F7.3,8X,'X(',I1,')
44338 =',F8.4)
4436 IF(NIN.EQ.0) WRITE (6,303) YM,YINC,NV1(NC),1-XP
4440 303 FORMAT('MIN. LOI = ',F8.3,',INCREMENT = ',F7.3,8X,'X(',I1,')
4445 & =', F8.4)
4470 yval(1)=ym
4480 do 305 i=2,11
4490 305 yval(i)=yval(i-1)+yinc
4500 do 307 i=1,51
4510 do 306 j=1,101
4520 306 ppos(i,j)=' '
4530 ppos(i,i)='.';    ppos(i,102-i)='.'
4540 307 ppos(1,2*i+1)='.'
4550 do 308 i=1,51,5
4560 ppos(i,i)='+';    ppos(i,102-i)='+'
4570 308 ppos(1,2*i-1)='+'
4580 nfirst=0.;   ny=1
4585 if(ncoeff.eq.1) go to 317
4590 do 315 line =1,51
4600 DO 310 IP=LINE,102-LINE
4610 XA(NV1(NC))=(1-XP)*(LINE-1)/50
4611 XA(NV2(NC))=(1-XP)*(IP-LINE)/100
4612 XA(NC)=XP;XA(NV3(NC))=1-XA(NV1(NC))-XA(NV2(NC))-XP
4630 CALL XFUNCS(XA)
4640 ycal(ny,ip)=0.
4650 do 309 j=1,ncoeff
4660 309 ycal(ny,ip)=ycal(ny,ip)+xa(j)*beta(j)
4670 do 310 j=1,11
4680 if(abs(ycal(ny,ip)-yval(j)).lt.yinc/50.) ppos(line,ip)=pc(j)
4690 310 continue
4700 do 314 j=1,11
```

```
4710 if(line.eq.51) go to 312
4720 do 311 ip=1+line,102-line
4730 y1=ycal(ny,ip)-yval(j) ;  a1=abs(y1)
4740 y2=ycal(ny,ip-1)-yval(j); a2=abs(y2)
4745 if(a1.eq.0..or.a2.eq.0.) go to 311
4750 if(y1/a1.eq.y2/a2) go to 311
4760 if(a1.lt.a2) ppos(line,ip)=pc(j)
4770 if(a1.gt.a2) ppos(line,ip-1)=pc(j)
4780 311 continue
4790 312 if(nfirst.eq.0) go to 314
4800 do 313 ip=line,102-line
4810 y1=ycal(ny,ip)-yval(j);    a1=abs(y1)
4820 y2=ycal(3-ny,ip)-yval(j); a2=abs(y2)
4825 if(a1.eq.0..or.a2.eq.0.) go to 313
4830 if(y1/a1.eq.y2/a2) go to 313
4840 if(a1.lt.a2) ppos(line,ip)=pc(j)
4850 if(a1.gt.a2) ppos(line-1,ip)=pc(j)
4860 313 continue
4870 314 continue
4875 NFIRST =1; NY=3-NY
4880 315 CONTINUE
4950 317 do 318 i=1,51
4960 ip=52-i
4970 318 write(6,319)(ppos(ip,j),j=1,101)
4980 319 format(10X,101A1)
4990 WRITE(6,320)(0.1*I,I=1,10), NV3(NC),1-XP,NV2(NC),1-XP
5000 320 FORMAT(9X,'0.0',10(7X,F3.1)/5X,'X(',I1,')=',F8.4,86X,
5005 & 'X(',I1,')=',F8.4/)
5010 if(nin.gt.0) write(6,3211) (pc(i),yval(i),i=1,11)
5012 3211 FORMAT(' Ds Values: ',9(A1,' = ',F7.2,'; ')/A1,' = ',F7.2,';
5013        &  ',A1,' = ',F6.2)
5016 if(nin.eq.0) write(6,321) (pc(i),yval(i),i=1,11)
5020 321 format(' LOI Values: ',9(A1,' = ',F7.2,'; ')/A1,' = ',F7.2,'; ',
5030 $A1,' = ',F3.2)
5040 return
5050 end
5220 SUBROUTINE COORD(A,DET)
5230 COMMON DUMMY(11000),XTX(21,21),DUMMY2(542),C(4,4)
5240 DIMENSION A(4,4)
5250 DO 601 I=1,4
5260 DO 600 J=1,4
5270 600 XTX(I,J)=A(I,J)
5280 601 CONTINUE
5290 CALL MINV(4,DET)
5300 IF(DET.EQ.0)RETURN
5310 DO 602 I=1,4
5320 DO 602 J=1,4
5330 602 C(I,J)=XTX(I,J)
5335 RETURN
5337 END
5440 SUBROUTINE CONV(IIN)
5450 common x(500,21),dummy(1483),c(4,4)
5460 DIMENSION XF(21)
5470 DO 605 IR=1,IIN
5480 DO 604 I=1,4
5490 XF(I)=0
5500 DO 604 J=1,4
5510 604 XF(I)=XF(I)+C(I,J)*X(IR,j)
5520 CALL XFUNCS(XF)
5530 DO 607 I=1,21
5540 607 X(IR,I)=XF(I)
5550 605 CONTINUE
5560 RETURN
5570 END
5580 SUBROUTINE XFUNCS(XF)
5590 DIMENSION XF(21)
5600 INDEX=4
5610 DO 606 I=2,3
5620 DO 606 J=I+1,4
5630 INDEX=INDEX+1
5640 606 XF(INDEX)=XF(I)*XF(J)
5650 DO 607 J=2,4
5660 INDEX=INDEX+1
5670 607 XF(INDEX)=XF(1)*XF(J)
5680 INDEX=INDEX+1
5690 XF(INDEX)=XF(2)*XF(3)*XF(4)
5700 DO 608 I=2,3
5710 DO 608 J=I+1,4
5720 INDEX=INDEX+1
5730 608 XF(INDEX)=XF(1)*XF(I)*XF(J)
5740 DO 609 I=2,3
5750 DO 609 J=I+1,4
```

```
5760 INDEX=INDEX+1
5770 609 XF(INDEX)=XF(I)*XF(J)*(XF(I)-XF(J))
5790 DO 610 J=2,4
5800 INDEX=INDEX+1
5810 610 XF(INDEX)=(XF(1)*XF(J))*(XF(1)-XF(J))
5820 INDEX=INDEX+1
5830 XF(INDEX)=XF(1)*XF(2)*XF(3)*XF(4)
5840 RETURN
5850 END
5999 SUBROUTINE SETK(A,B,AK)
6000 DIMENSION AK(7,21)
6020 DO 1 I=1,7
6030 DO 1 J=1,21
6040 1 AK(I,J)=0
6050 IF(A.EQ.B) GOTO 3
6060 R=1./A; Q=B/A; RQ=R*R
6070 DO 2 J=1,3
6080 AK(J,1)=-R; AK(J,J+1)=R; AK(J+3,J+4)=RQ
6090 AK (J,J+7)=R*(1-2*Q/3); AK(J,J+17)=R*(1-2*Q+Q*Q)
6100 2 AK (J+3,J+11)=RQ*(1-4*Q/5)
6110 AK(7,11)=R*RQ; AK(7,21)=AK(7,11)*(1-6*Q/7)
6120 RETURN
6130 3 BR=1/B; BR2=BR*BR
6140 DO 4 J=1,3
6150 AK(J,1)=-BR; AK(J,J+1)=BR; AK(J,J+7)=BR/3
6160 AK(J+3,J+4)=BR2
6170 4 AK(J+3,J+11)=BR2/5
6180 AK(7,11)=BR*BR2; AK(7,21)=AK(7,11)/7
6190 RETURN
6200 END
6210 SUBROUTINE AVCOEFF (IAVC,B,NCOEFF,AK,VAR)
6220 COMMON DUMMY(11000),XTX(21,21), DUMMY2(521),BETA(21)
6230 DIMENSION AK(7,21), CAVG(7), TEMP(21,7), CVNEW(7,7)
6240 IF (IAVC.EQ.0) RETURN
6250 DO 1 I=1,7
6260 1 CAVG(I)=0
6270 DO 3 I=1,7
6280 DO 3 J=1,NCOEFF
6290 CAVG(I)=CAVG(I)+AK(I,J)*BETA(J)
6300 TEMP(J,I)=0
6310 DO 2 K=1, NCOEFF
6320 2 TEMP (J,I) = TEMP(J,I)+XTX(J,K)*AK(I,K)
6330 3 CONTINUE
6340 DO 5 I=1,7
6350 DO 5 J=1,7
6360 CVNEW(I,J)=0
6370 DO 4 K=1,NCOEFF
6380 4 CVNEW(I,J)=CVNEW(I,J)+AK(I,K)*TEMP(K,J)
6390 5 CONTINUE
6400 WRITE (6,6) B, (CAVG(I), SQRT(CVNEW(I,I)*VAR), I=1,7)
6410 6 FORMAT (/10X, ' AVERAGE COEFFICIENTS OVER RANGE OF
6420 &X2, X3, X4 = 0 TO  ', F8.5/15X, 'TYPE VARIABLE VALUESS.D.'/
6430 &15X, 'LINEAR 2 ',2F12.5/ 24X, ' 3 ', 2F12.5/
6440 &24X, ' 4 ',2F12.5/15X, 'BINARY 2-3', 2F12.5/22X,' 2-4',2F12.5/
6450 & 22X,' 3-4', 2F12.5/15X, 'TERNARY    ', 2F12.5)
6460 RETURN
6470 END
```

References

References

Allen, E.R. and Tipper, C.F.H. (1960). Proc. Roy. Soc. Lond. **A258**, 251.

Anon (1925). Nature, **116**, 415.

Arney, W.C. and Kuryla, W.C. (1972). J. Fire Flammability, **3**, 183.

Arthur, J.C. and Hinojosa, O. (1966). Text. Res. Jour., 36, 385.

Avondo, G., Vovelle, C. and Delbourgo, R. (1978). Combust. Flame, **31**, 7.

Bakos, D., Kosik, M., Antos, K. Karolyova, M. and Vyskocil, I. (1982). Fire and Materials, **6**, 10.

Ballistreri, A., Foti, S., Montaudo, G., Scamporrino, E., Arnesano, A. and Calgari, S. (1981). Makromolek. Chem., **182**, 1301.

Ballistreri, A., Montaudo, G., Puglisi, C., Scamporrino, E., Vitalini, D. and Calgari, S. (1983). J. Polym. Sci., Polym. Chem., **21**, 679.

Bancroft, J. and Sons Co. (1948). Br. Pat. 604, 197.

Barnard, J.A. and Bradley, J.N. (1985). Flame and Combustion, 2nd ed., Chapman-Hall, p. 149.

Basch, A.,and Lewin, M (1973). Text. Res. J., **43**, 693.

Bauer, R.G. (1978). "Fire Retardant Polymers: A review", Journal of Fire Retardant Chemistry, **5**: 200-221.

Baulch, D.L., Drysdale, D.D., Horne, D.G. and Lloyd, A.C. (1972). Evaluated Kinetic Data for High Temperature Reactions, Cleveland, Ohio, Chemical Rubber Publishing Co., Vol. 1.

Becker, W. (1975). VFDB - 2 Forsch. Techn. Brandschutz, 24, **1**, p.4.

Benbow, A.W. and Cullis, C.F. (1972). In: Proc. 2nd Int. Conf. on non-flammability of Plastics, Wool and Textiles, Strbske Pleso, Czechoslovakia, 1972, Bratislava, Dom Techniky, p. 45.

Birky, M.M. and Yeh, K.N. (1973). J. Appl. Polym. Sci., 17, 239.

Blanchard, E.J., and Harper, R.J. (1983). Journal of Coated Fabrics, **12**, 213.

Blazej, A. and Kosik, M. (1985). In: Cellulose and its derivatives - Chemistry, Biochemistry and applications, (eds. J.F. Kennedy, G.O. Phillips, D.J. Wedlock and P.A. Williams), Chichester, Ellis Horwood.

Blinder, S.M. (1969). Advanced Physical Chemistry. A summary of modern theoretical principles. London, Macmillan, p. 450.

Bostic, J.E. (1972). Ph.D. Thesis. Clemson, S.C., Clemson Univ.

Bostic, J.E., Yeh, K.N. and Barker, R.H. (1973). J. Appl. Polym. Sci., **17**, 471.

Boyer, N.E., and Vajda, A.E. (1964). Soc. Plast. Eng. Trans., **4**,(1), 45.

Bradley, J.N. (1969). Flame and Combustion Phenomena, London, Methuen.

Brit. Pat. 604, 197 (1948) (to Joseph Bancroft & Sons Co.).

Broadbent., J.R.A. and Hirschler, M.M. (1984). Eur. Polym. Jour., **20**, 1087.

Brooks, J.D. and Taylor, G.H. (1968). In Chemistry and Physics of Carbon, Vol. 4 (ed. P.L. Walker), p. 243, New York, Marcel Dekker.

Brown, D.M. (1963). In: Advances in Organic Chemistry, (eds. R.A. Raphael, E.C. Taylor and H. Wynberg), New York, Wiely Interscience, p. 75.

Bulewicz, E.M., and Padley, P.J. (1963). Ninth International Symposium on Combustion, New York, Academic Press, p. 638.

Burge, S.J. and Tipper, C.F.H. (1969). Combust. Flame, 13, 495.

Calcote, H.F. (1957). Combustion and Flame, **13**, 495.

Camac, M. and Feinberg, R. M. (1967). Proc. 11th Int. Symp. on Combustion, Pittsburgh, Pa., Combustion Institute, p. 557.

Cameron, G.G. (1972). In The Mechanisms of pyrolysis, oxidation and burning of organic materials, Gaithersburg, Md., Oct. 1970 (ed. L.A. Wall). Nat. Bur. Stand. (U.S.), Spec. Publ. 357, p. 61.

Carabine, M.D., Cullis, C.F. and Groome, I.J. (1968). Proc. Roy. Soc. London, **A306**, 41.

Casagrande, F. (1986). Personal communication.

Cassidy, P.E. (1980). "Thermally Stable Polymers", New York, Marcel Dekker.

Chamberlain, D.L. (1978). In: Flame Retardancy of Polymeric Materials, (eds. W.C. Kuryla and A.J. Papa), New York, Marcel Dekker, Vol. 3, p. 109.

Chamberlain, D.L. (1978). In: Flame Retardancy of Polymeric Materials, (eds. W.C. Kuryla and A.J. Papa), New York, Marcel Dekker, Vol. 4, pp. 104, 109.

Chandler, S.E. (1979). Building Research Information Paper (IP 20/29).

Chedaille, J. and Braud, Y. (1972). Industrial Flames, Measurement in Flames, Edward Arnold Pub., Vol. 1.

Clark, T.C. and Dove, J.E. (1973). Can. J. Chem., **54**, 2147 and **51**, 2155.

Clark, V.M., Hutchinson, D.W., Kirby, A.J. and Warren, S.G. (1964). Angew. Chem., Int. Ed. Eng., **3**, 678.

Coppick, S. (1947). Flameproofing Textile Fabrics (ed. R.W. Little,) ed. pp. 50-54. A.C.S. Monograph Series, New York, Van Nostrand Reinhold.

Coppick, S. and Hall, W.P. (1947). Flameproofing Textile Fabrics, (ed. R.W. Little), New York, Reinhold Publishing Co., p. 179.

Creitz, E.C. (1970). J. Res. Nat. Bur. Stand. **65A**, 389.

Creitz, E.C. (1970). J. Res. Nat. Bur. Stand. **74A**, 521.

Critchley, J.P., Knight, G.J. and Wright, W.W. (1983). "Heat-Resistant Polymers", New York, Plenum Press.

Cullis, C.F., Fish, A. and Ward, R.B. (1963). Proc. Roy. Soc. London, **A276**, 527.

Cullis, C.F. and Hirschler, M.M. (1981). In: The Combustion of Organic Polymers, Oxford, Clarendon Press.

Cullis, C.F. and Hirschler, M.M. (1983). Polymer, **24**, 834.

Cullis, C.F., Hirschler, M.M. and Tao, Q.M. (1986). Eur. Polym. J., **22**, 161.

Davis, F.V., Findlay, J. and Rogers, E. (1949). J. Text. Inst., **40**, T839.

Drake, G.L. (1976). Textile Chem. Color., **8**, 184.

Drews, M.J. and Barker, R.H. (1973). in Abstracts of Papers presented, 165th National Meeting, ACS, Dallas Tex.,

Drews, M.J. and Barker, R.H. (1974). J. Fire Flammability, **5**, 116.

Drews, M.J., Yeh, K. and Barker, R.H. (1973). Textilveredlung, **8**, 180.

Durrant, P.J. and Durrant, B. (1962). In: Introduction to Advanced Inorganic Chemistry, New York, Wiley, p. 689.

Eichhorn, J. (1964). J. Appl. Polym. Sci., **8**, 2497.

Einhorn, I.N. (1971). J. Macromol. Sci., Rev. Polym. Tech., D**1**,(2) 113.

Emmons, H.W. (1973). Heat Transfer, p. 145.

Ernst, J., Wagner, H.G. and Zellner, R. (1978). Ber. Bunsenges. Phys. Chem., **82**, 409.

Feilchenfield, H., Jolles, Z.E. and Meisel, D. (1970). Combust. Flame, **15**, 247.

Fenimore, C.P. and Jones, G.W. (1961). J. Phys. Chem., 65, 1532.

Fenimore, C.P. and Jones, G.W. (1961). J. Phys. Chem., 65, 2200.

Fenimore, C.P. and Jones, G.W. (1963). Combust. Flame, 7, 323.

Fenimore, C.P. and Jones, G.W. (1964). Combust. Flame, 8, 133.

Fenimore, C.P. and Jones, G.W. (1966). Combust. Flame 10, 295.

Fenimore, C.P. and Martin, F.J. (1966). Combust. Flame, 10, 135.

Fish, A., Franklin, N.H., and Pollard, R.T. (1963). J. Appl. Chem., **13**, 506.

Fitzer, E., Mueller, K. and Schaefer, W. (1971). In Chemistry and Physics of Carbon, Vol. 7 (ed. P.L. Walker), p. 237. New York, Marcel Dekker.

Fluck, L.A. and Moretti, L.J. (1957). U.S. Pat.2,784,159.

Ford, C.L. (1975). In: Halogenated Fire Supressants (ed. R.G. Gann), Am. Chem. Soc. Symp. Ser. No 16, p. 1. Am. Chem. Soc., Washington, D.C.

Ford, F.M. and Hall, W.P. (1949). U.S. Pat. 2,482,755.

Friedmann, R. (1977). In Fire Standards and Safety (ed. A.F. Robertson), Am. Soc. Test. Mater. Spec. Tech. Publ., 614, p. 91.

Fristrom, R.M. and Sawyer, R.F. (1971). Flame inhibition chemistry. In: Proc. 37th AGARD Conf. No 84 on Aircraft fuels, Lubricants and Fire Safety (AGARD - CP - 84 - 71), Section 12, Brussels, NATO.

Fristrom, R.M. (1972). In: The mechanisms of pyrolysis, oxidation and burning of organic materials, Gaithersburg, Md., Oct. 1970 (ed. L.A. Wall). Nat. Bur. Stand. (U.S.) Spec. Publ. 357, p. 131.

Fryburg, G. (1950). Review of literature pertinent to fire extinguishing agents and basic mechanisms involved in their action. NACA Tech. Noxe. TN 2102.

Furgeson, G.E. (1933). Fire Gases, NFPA Quarterly, October.

Gann, R.G. (1975), In: Halogenated Fire Supressants (ed. R.G. Gann), Am. Chem. Soc. Symp. Ser. No 16, p. 318. Am. Chem. Soc., Washington, D.C.

Gardiner, D. (1966). J. Chem. Soc., 1473.

Garner, F.H., Long, R., Graham, A.J., and Badakhshan, A. (1975). Proc. 6th Int. Symp. on Combustion, p. 802, New York, Reinhold.

Gaydon, A.G. and Wolfhard, H.G. (1979). In: Flames - Their Structure, Radiation and Temperature, Chapman and Hall.

Gay-Lussac, J.L. (1821). Ann. Chim., **2**, (18), 211

Golova, O.P., Epshtein, V.Y. and Durynina, L.I. (1961). Vysokomolekul. Soedin., **3**, 536.

Golova, O.P. and Krylova, R.G. (1957). Dokl. Akad. Nauk. S.S.S.R., **116**, 419; Chem. Abstracts, **52**, 4974 (1958).

Golova, O.P., Pakhomov, A.M. and Andrievskaya, E.A. (1957). Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk., 1499.

Gruntfest, I.J. and Young, E.M. (1961). Prepr., Am. Chem. Soc., Div. Org. Coat. Plast. Chem., **21**, 113.

Granzow, A. and Cannelongo, J.F. (1976). J. Appl. Polm. Sci., **20**, 689.

Granzow, A., Ferrillo, R.G. and Wilson, A. (1977). J. Appl. Polym. Sci., **21**, 1687.

Grassie, N. (1972). In Polymer Science (ed. A.D. Jenkins), Chap. 22, p. 1443, London, North-Holland.

Gupta, J.C., Bhatnagar, S., Lal, K. and Bhatnagar, H.L. (1979). Indian Journal of Textile Research, **4**, 43.

Harris, J.A., Keating, E.J., and Goynes, W.R. (1980). J. Appl. Poly. Sci., **25**, 2195.

Hastie, J.W. (1973). Combust. Flame, **21**, 49.

Hastie, J.W. (1973a). J. Res. Nat. Bur. Stand., **77A**, 733.

Hastie, J.W. and Blue, G.D. (1973). In: 165th Am. Chem. Soc. National Meeting, Dallas, April 1973, Fire Retardancy Studies on Polyester Systems at the Molecular Level, Div. Org. Coat. Plast. Chem., Paper 86. Am. Chem. Soc., Washington, D.C.

Hendrix, J.E., Anderson, T.K., Clayton, T.J., Olson, E.S. and Barker, R.H. (1970). J. Fire Flammability, **1**, 107.

Hendrix, J.E., Bostic, J.E., Olsen, E.S. and Barker, R.H. (1970). J. Appl. Polym. Sci., **14**, 1701.

Hendrix, J.E., Drake, G.L. and Reeves, W.E. (1970). Text. Res. Jour., 360.

Hendrix, J.E., Drake, G.L., and Barker, R.H. (1972). J. Appl. Polym. Sci., **16**, 257.

Hengemihle, F., McGinnis, G.D., Prince, S. and Templeton, C. (1984). In: J. of Anal. and Appl. Pyrolysis. **6**, 317.

Heywood, J.B. (1971). AIAA/AAE 7th Propulsion Joint Specialist Conf., Salt Lake City, Utah, 1971, AIAA Pap. No. 71-712.

Hilado, C.J. (1969). Flammability Handbook for Plastics. Stamford, CT., Technomic.

Hindersinn, R.R. (1966). Polymer Conf. Ser., Wayne State Univ., Detroit, Mich.

Hindersinn, R.R. (1977). Fire retardancy, Enyclopedia of Polymer Science and Technology, New York, Wiley, Supplement, Vol. 2, pp. 270 - 339.

Hindersinn, R.R. and Wagner, G.M. (1967). Encyclopedia of Polymer Science and Technology, Vol. 7, Interscience, New York.

Hindersinn, R.R. and Witschard, G. (1978). In: Flame retardancy of polymeric materials, (eds. W.C. Kuryla and A.J. Papa), New York, Dekker, Vol. 4, p. 1.

Holmes, F.H. and Shaw, C.J.G. (1961). J. Appl. Chem., 11, 210.

Holmes, F.H., Byrne, F.A. and Gardiner, D. (1966). J. Appl. Chem., **16**, 81.
Home Office: Fire Statistics United Kingdom 1983.

Inagaki, N. and Katsuura, K. (1980). J. Polym. Sci., Polym. Chem. Edn., **18**, 441.

Inagaki, N., Nakumara, S., Asai, H., and Katsuura, K. (1976). J. Appl. Polym. Sci., **20**, 2829.

Inagaki, N., Tomiha, K. and Katsuura, K. (1974). Polymer, 15, 335.

Inagaki, N., Goto, K. and Katsuura, K. (1975). Polymer, 16, 641.

Jacques, J.K. (1967). Trans. J. Plast. Inst. (Conf. Suppl. No. 2), 33.

Jain, R.K., Lal, K. and Bhatnagar, H.L. (1985). J. Appl. Polym. Sci., **30**, 897.

Johnson, J.R. and Moore, D.R. (1972). Paper given at Division of Cellulose, Wool and Fiber Chemistry, 164th ACS National Meeting, New York.

Jost, W., Schecker, H.G. and Wagner, H.G. (1965). Z. Phys. Chem. (Neue Folge), **45**, 47.

Kashiwaga, T., MacDonald, B.W., Isuda, H. and Summerfield, M. (1971). In: 13th International Symposium on Combustion, Salt Lake City, The Combustion Institute, p. 1073.

Kennedy, J.F., and White, C.A. (1983). Bioactive Carbohydrates, Chichester, Ellis Horwood Ltd., pp. 66-69.

Khorana, H.G. (1961). Some Recent Developments in the Chemistry of Phosphate Esters of Biological Interest, New York, Wiley.

Kilzer, F.J. and Broido, A. (1965). Pyrodynamics, 2, 151.

Kishore, K. and Mohandas, K. (1982). Fire and Materials, 6, 54.

Kislitsyn, A.N. and Rodionova, Z.M. (1969). Sb. Tr. Tsent. Nauchn.-Issled. Inst. Lesokhim. Prom., 20, 4.

Kislitsyn, A.N., Rodionova, Z.M., Savinykh, V.I. and Guseva, A.V. (1971). Zh. Prikl. Khim., **44**, 2518.

Klemm, R.B., Tanzawa, T., Skolnik, E.G. and Michael, J.V. (1981). 18th Symposium (International) on Combustion, p. 785.

Kurotori, I.S. (1966). Industr. Qual. Control. 592.

Kuryla, W.C. (1973). In: Flame retardancy of polymeric materials, (eds. W.C. Kuryla and A.J. Papa), New York, Marcel Dekker, Vol. 1, p. 1.

Kuryla, W.C. (1973). In: Flame Retardancy of Polymeric Materials, (eds. W.C. Kuryla and A.J. Papa), New York, Marcel Dekker, Vol. 4, p. 109.

Kuryla, W.C. and Papa, A.J. (1975). Flame Retardancy of Polymeric Materials, New York, Marcel Dekker, Vol. 3.

Lai, Y.Z. and Shafizadeh, F. (1974). Carbohydr. Res., 38, 177.

Langley, J.T., Drews, M.J. and Barker, R.H. (1980). J. Appl. Polym. Sci., **25**, 243.

Larsen, E.R. (1974). J. Fire and Flammability/Fire Retardant Chemistry, **1**, 4.

Larsen, E.R. (1975a). In: Halogenated Fire Supressants (ed. R.G. Gann), Am. Chem. Soc. Symp. Ser. No 16, p. 376.

Larsen, E.R. (1975b). J. Fire Flammability/Fire Retardant Chem. **2**, 5 and 209.

Larsen, E.R. (1976). A.C.S. Organic Coatings and Plastics Chemistry Preprints 36, **2**, 310.

Larsen, E.R. (1977). 32nd Ann. Tech. Conf. Reinforced Plastics/Composites Inst., Soc. Plast. Ind. **17B**, 1. Soc. Plast. Ind., New York.

Larsen, E.R. and Ludwig, R.B. (1979). J. Fire Flammability, **10**, 69.

Lask, G. and Wagner, H.G. (1963). Proc. 8th Int. Symp. on Combustion, Baltimore, Md., Williams and Wilkins, p. 432.

Lawton, E.L. and Setzer, C.J. (1975). In: Flame-retardant polymeric materials, (eds. M. Lewin, S.M. Atlas and E.M. Pearce), New York, Plenum Press, p. 193.

Lewin, M., Atlas, S.M., and Pearce, E.M. (1978). "Flame Retardant Polymeric Materials", Vol. II, p. 183, New York, Plenum Press.

Lewin, M, Isaacs, P, Stevens, C. and Sello, S.B. (1973). Textilveredlung, **8** (3), 158-161.

Liepins, R., Surles, J.R., Morsoff, N. and Stannett, V. (1977). J. Appl. Poly. Sci., **21**, 2592.

Liepins, R., Stannett, V., Surles, J.R., Morsoff, N. and Day, F.H. (1978). Prog. Polym. Sci., **6**, 1.

Little, R.W., Rose, A. and Rose, E. (1966). In: The Condensed Chemical Dictionary, New York, Reinhold Pub. Co., 7th ed., p. 54-55.

Little, R.W. (1968). Combust. Flame, **12**, 191.

Loukomsky, A.M. (1957). U.S. Pat. 2,779,691.

Lyons, J.W. (1970). In: The Chemistry and Uses of Fire Retardants, New York, Wiley - Interscience.

Lyons, J.W. (1970**a**). The chemistry and uses of fire retardants. New York, Wiley - Interscience.

Lyons, J.W. (1970**b**). J. Fire and Flammability, **1**, 302.

Madorsky, S.L. (1964). Thermal degradation of organic polymers, New York, Wiley.

Madorsky, S.L., Hart, V.E. and Strauss, S. (1956). J. Res. Natl. Bur. Std., **56**, 343;

Madorsky, S.L., Hart, V.E. and Strauss, S. (1958). J. Res. Natl. Bur. Std., **60**, 343.

McCarter, R.J. (1977). J. Consum. Prod. Flammability., **4**, 346.

McGinnis, G.D. and Parikh, S. (1973). Carbohydr. Res., 31, 183.

Mey-Marom, A. and Behar, D. (1980). J. Appl. Polym. Sci., **25**, 691.

Miller, B. and Turner, R. (1972). Text. Res. J., **42**, 629.

Moussa, N.A., Toong, T.Y. and Garris, C.A. (1977). In: Proc 16th Int. Symp. on Combustion, p. 1447, Pittsburgh, The Combustion Institute.

Marton, T.H. (1950). Br. Pat. 634, 690 (to Courtaulds Ltd.).

Nagoni, H.B. (1977). Man Made Textiles in India, **8**, 405.

Nevell, T.P. (1985). In: Cellulose Chemistry and its applications, (eds. T.P. Nevell and S.H. Zeronian), Chichester, Ellis Horwood.

Nielsen, M.L. (1957). Text. Res. J., **27**, 603-610.

Nuessle, A.C., Ford, F.M., Hall, W.P. and Lippert, A.L. (1956). Text. Res. J., **26**, 32-39.

O'Brien, R.D.O. (1960). Toxic Phosphorus Esters, New York, Academic Press.

O'Brien, S.J. (1968). Text. Res. J., **38**, 256-266.

O'Mara, M.M. (1977). Pure. Appl. Chem. **49**, 649.

Palmer, H.B. (1974). In: Combustion technology: some modern developments (eds. H.B. Palmer and J.M. Beer), New York, Academic Press, p. 1.

Palmer, H.B. and Seery, D.J. (1960). Combust. Flame, **4**, 213.

Papa, A.J. and Proops, R. (1973). A New Mechanism of flame retardancy for polyurethanes, J. Appl. Polym. Sci., **17**, 2463-2483.

Papa, A.J. and Proops, W.R. (1972). J. Appl. Polym. Sci., **16**, 2361.

Patai, S. and Halpern, Y. (1970). Isr. J. Chem., **8**, 655.

Pearce, E.M., Shalaby, S.W. and Barker, R. H. (1975). In: Flame-retardant polymeric materials (eds. M. Lewin, S.M. Atlas and E.M. Pearce), New York, Plenum Press, Vol. 2, p. 239

Pepperman, A.B., Margavio, M.F. and Vail, S.L. (1976). J. Fire Retardant Cham., **3**, 276.

Petrella, R.V. (1979). J. Fire Flammability, **10**, 52.

Piechota, H. (1965). J. Cell. Plast., **1**, 186.

Pitts, J.J. (1971). J. Cell. Plast., **7**, 202.

Pitts, J.J. (1973). In: Flame Retardancy of Polymeric Materials, (eds. W.C. Kuryla and A.J. Papa), New York, Marcel Dekker, Vol. 1, p. 133.

Ravey, M., Fischler, Th. and Kramer, M. (1978). Fire Mater., **2**, 34.

Ravey, M. and Fischler, Th. (1978). Fire Mater., **2**, 80.

Reeves, W.A., Perkins, R.M., Piccolo, B. and Drake, G.L. (1970). Text. Res. J., **40**, 223.

Reid, J.D. and Mazzeno, L.W. (1949). J. Ind. and Eng. Chem., **41**, 2828-2831.

Richards, G.N. and Shafizadeh, F. (1978). Aust. J. Chem., 31, 1825.

Rodrig, H., Basch, A. and Lewin, M. (1975). J. Polym. Sci., Polym. Chem. Ed., **13**, 1921.

Rogers, F.E., Ohlemiller, T.J., Kurtz, A. and Summerfield, M. (1978). J. Fire Flammability, **9**,5.

Rohringer, P., Stensby, P. and Adler, A. (1975). Text. Res. J., **45**, 586.

Rosser, W.A., Wise, H., and Miller, J. (1959). Proc. 7th Int. Symp. on Combustion, 175. London, Butterworth.

Rosser, W.A., Inami, S.H., and Wise, H. (1966). Combust. Flame, **10**, 287.

Roth, P. and Just, Th. (1975). Ber. Bunsenges. Phys. Chem., 79, 682.

Roth, P. and Just, Th. (1977). Ber. Bunsenges. Phys. Chem., 81, 572.

Rust, F.F. and Vaughan, W.E. (1949). Ind. Eng. Chem., **41**, 2595.

Sander, M. and Steininger, E. (1967**a**). J. macromol. Sci., Rev. macromol. Chem. C., **1**, 7.

Sander, M. and Steininger, E. (1967**b**). J. macromol. Sci., Rev. macromol. Chem. C., 1, 91.

Sander, M. and Steiniger, E. (1968**a**). J. macromol. Sci., Rev. macromol. Chem. C., 2,1.

Sander, M. and Steininger, E. (1968**b**). J. macromol. Sci., Rev. macromol. Chem. C., 2, 33.

Sander, M. and Steininger, E. (1968**c**). J. macromol. Sci., Rev. macromol. Chem. C., 2, 57.

Sanderson, W.A., Mueller, W.A. and Swidler, R. (1970). Text. Res. J., **40**, 217.

Sawyer, R.F. (1971). In: Combustion-generated pollution (ed. E.S. Starkman), New York, Plenum Press, p. 60.

Sawhney, V.R. (1971). Synergism in Flame Retardance, at Stevens Institute of Technology, New Jersey, Hoboken.

Scheffe, H. (1958). J. Royal Statistical Soc., 20B, 344.

Schuyten, H.A., Weaver, J.W. and Reid, J.D. (1954). Advan. Chem. Ser., 9, 7.

Schuyten, H.A., Weaver, J.W. and Reid, J.D. (1954). Fire Retardant Paints, Advances in Chemistry Series A.C.S., Washington D.C., 1954, pp. 7 - 20.

Schwenker, R.F. and Pascu, E. (1957). Ind. Eng. Chem., 2, 83.

Schwenker, R.F. and Pascu, E. (1958). Ind. Eng. Chem., 3, 50, 91.

Scotney. A. (1972). Eur. Polymer. Jour. 8, 190.

Semenov, N.N. (1958). Some problems in chemical kinetics and reactivity (Trans. M. Boudant). Princeton, N.J., Princeton Univ. Press.

Shafizadeh, F. (1968). Adv. Carbohydr. Chem., 23, 419.

Shafizadeh, F. (1971). Adv. Carbohydr. Chem., 26, 297.

Shafizadeh, F. (1971). J. Polymer. Sci., Poly. Chem. Edn., 36, 21.

Shafizadeh, F., McGinnis, G.D., Susott, R.A. and Tatton, H.W. (1971). J. Org. Chem., 36, 2813.

Shafizadeh, F., Lai, Y.Z. and Susott, R.A. (1972). Carbohydr. Res., 25, 387.

Shafizadeh, F., McGinnis, G.D. and Philpot, C.W. (1972). Carbohydr. Res., 25, 23.

Shafizadeh, F., Susott, R.A. and McGinnis, G.D. (1972). Carbohydr. Res., 22, 63.

Shafizadeh, F. and Fu, Y.L. (1973). Carbohydr. Res., 29, 113.

Shafizadeh, F. and Lai, Y.Z. (1973). Carbohydr. Res., 31, 57.

Shafizadeh, F., Meshreki, M.H. and Susott, R.A. (1973). J. Org. Chem., 38, 1190.

Shafizadeh, F. (1975). Appl. Polym. Symp., 28, 153.

Shafizadeh, F. (1975). Jour. Appl. Polym. Sci. Appl. Polym. Symp., **28**, 153.

Shafizadeh, F., Chin, P.S. and DeGroot, W.F. (1975). J. Fire and Flammability, Fire Retardant Chemistry, **2**, 195.

Shafizadeh, F. and Lai, Y.Z. (1975). Carbohydr. Res., **40**, 263.

Shafizadeh, F. (1982). J. Anal. Appl. Pyrolysis, **3**, 283.

Shahed, S.M. and Newhall, H.K. (1971). Combust. Flame, **17**, 131.

Simmons, R.F. and Wolfhard, H.F. (1955). Trans. Faraday Soc., **51**, 1211.

Simmons, R.F. and Wolfhard, H.F. (1956). Trans. Faraday Soc., **52**, 53.

Skinner, G.B. (1961). Survey of Chemical fire aspects of flame extinguishment. ASO Tech. Dept. G1 - 408.

Spindler, K.G. and Wagner, H. (1982). Ber. Bunsenges. Phys. Chem., **86**, 119.

Stuetz, D.E., Di Edwardo, A.H., Zitomer, F., and Barnes, B.P. (1970). 28th Mtg of the Society of Plastics Engineers (SPE - ANTEC). **16**, Soc. Plastics Engineers, Brookfield, C.T.

Susott, R.A., DeGroot, W.F. and Shafizadeh, F. (1975). J. Fire and Flammability, **6**, 311.

Tang, W.K. and Neill, W.E. (1964). J. Polymer Sci., **C6**, 65.

Thompson, D., and Brown, T.D., Beer, J.M. (1972). Combust. Flame, **19**, 69.

Troitzsch, J. (1983). "International Plastics Flammability Handbook", Munich, Hanser.

Tsuchiya, Y. and Sumi, K. (1970). J. Appl. Polym. Sci., **14**, 2003.

Vandooren, J. and Van Tiggelen, P.J. (1981). 18th Symposium (International) on Combustion, p. 473.

Versmann, F. and Oppenheim, A. (1859). British Pat. 2077.

Versmann, F. and Oppenheim, A. (1860). J. Prakt. Chem., 80. 433 Rept. (1859). British Association for the Advancement of Science.

Volans, P. (1967). J. Trans. Plast. Inst. (Conf. Suppl. No. 2), 47.

Walker, J. (1978). Sci. American, 4, 235, p. 154.
Wall, L.A. (1972). In the Mechanisms of pyrolysis, oxidation and burning of organic materials, Gaithersburg, Md., 1970, (ed. L.A. Wall), Nat. Bur, Sond. Spec. Publ., 357, p. 74.

Warnatz, J. (1984). In: Combustion Chemistry, (ed. W.C. Gardiner Jr.), New York, Springer-Verlag.

Weil, E.D. (1975). In: Flame Retardancy of Polymeric Materials (ed. W.C. Kuryla and A.J. Papa). New York, Marcel Dekker, Vol. 3, pp. 185-243.

Weil, E.D. (1978). In: Flame-retardant polymeric materials, (eds. M. Lewin, S.M. Atlas and E.M. Pearce), New York, Plenum Press, Vol. 2, p. 103.

Westenberg, A.A. and Fristrom, R.M. (1961). J. Phys. Chem., **65**, 591.

Williams, G.C., Sarofim, A.F. and Lambert, N. (1972). In: Emissions from Continuous Combustion Systems (eds. W. Cornelius and W.G. Agnew), New York, Phenum Press, p. 141.

Willard, J.J. and Wondra, R.E. (1970). Text. Res. J., **40**, 203.

Wines, R.A., Watermeier, L.A. and Strehlow, R.A. (1959). J. Phys. Chem., **63**, 989.

Wise, H. and Rosser, W.A. (1963). Proc. 9th Int. Symp. on Combustion, p. 733. London, Butterworths.

Wong, E.L. and Potter, A.E. (1963). J. Chem. Phys., 39, 2211.

Yeh, K.N., and Barker, R.H. (1971). Text. Res. J., **41**, 932.

Yeh, K.N., Birky, M.M. and Huggett, C. (1973). J. Appl. Polym. Sci., **17**, 255.

Yokoyama, M. (1971). Int. Chem. Eng., **11**, (1), 152.