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Citation: Tao, Q. M. (1987). Effects of Phosphorus - Halogen - Nitrogen Systems on the Combustion of Some Thermoplastic Polymers. (Unpublished Doctoral thesis, The City University)

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	QUEI MEI TAO	
	for the degree of Doctor of Philosophy	
	at The City University	
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Acknowledgment

I am indebted to many people for the help and advice they have given me in the preparation of this book. I would like to thank them as follows:

First and foremost, I would like to thank Professor [redacted] for his help and advice throughout the project.

To

and

my family

I would like to thank Mr. [redacted] for his help and advice in the preparation of this book. I would like to thank Mr. [redacted] for his help and advice in the preparation of this book. I would like to thank Mr. [redacted] for his help and advice in the preparation of this book.

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Acknowledgment

I am indebted to many people for the help that they have given me in producing this work and I would like to thank them as follows.

First and foremost, I would like to thank Professor Cullis for his considerable help, patience and guidance throughout the project.

Many thanks to [REDACTED] for his invaluable advice and discussions. I would also like to extend my thanks to [REDACTED] for his guidance in the early stages of the work.

I would like to thank [REDACTED] for the microanalytical work, [REDACTED] for the glassblowing work and my colleagues in Combustion Research for providing a pleasant atmosphere in which to work.

I am greatly indebted to my very good friends, [REDACTED] for their great kindness and encouragement, and for seeing me through some very difficult times.

Finally, I am especially grateful to my family for their support and understanding.

April 1987

Q.M.T

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ABSTRACT

An investigation has been made of the effectiveness of red phosphorus, used in conjunction with decabromobiphenyl and various nitrogen compounds, in conferring flame retardance and smoke suppression on some thermoplastic polymers (poly(vinyl chloride), polystyrene, poly(methyl methacrylate) and high-density polyethylene). Studies have also been made of the effects of other phosphorus-based additives, such as triethyl phosphate and tritolyl phosphate.

The Introduction opens with an account of the historical development and usage of synthetic organic polymers in some major countries. The hazards associated with polymer combustion and some common standard tests for measuring the flammability and smoke-forming tendency of polymers are described. General mechanisms of polymer combustion and techniques available for the study of polymer decomposition are then reviewed. Finally, an outline is given of some general principles and of different classes of compounds used to decrease flammability and smoke formation.

In the Experimental Section, the sources of the polymers and additives and the procedure used in the preparation of polymer-additive samples are described, followed by details of the apparatus and procedure used in the measurement of flammability and smoke production. An account is also given of the computer method used to fit polynomial functions to the flammability and smoke production data and to present the data in the form of triangular contour plots. The experimental set-up and procedure for making thermoanalytical and infrared spectroscopic measurements are then described, as is the procedure used in the preparation of polymer samples for microanalytical measurements.

The Results Section gives an account of measurements made of the flammability and smoke-forming tendency of polymers containing combinations of the various additives and the results are presented mainly in the form of triangular diagrams. With all the polymers studied, a greater-than-additive effect on flammability is observed with red phosphorus and melamine, red phosphorus and urea, and red phosphorus and guanidine carbonate. Two other nitrogen compounds, barbituric acid and benzotriazole were also used to help to elucidate the mechanisms involved. Finally, results of thermoanalytical, microanalytical and infrared spectroscopic measurements show the extent to which phosphorus is oxidised and the way in which the other additives break down.

In the Discussion Section, possible mechanisms are suggested to account for the effects of the additives on the flammability and smoke-forming tendency of the polymers. As regards flame retardance, decabromobiphenyl is found to act mainly in the gas phase, whereas red phosphorus functions principally in the condensed phase, by enhancing melting and dripping or char formation, or by stabilising the polymer. Melamine, urea and guanidine carbonate act mainly in the gas phase, by releasing ammonia which serves as a diluent. Mechanisms are also discussed for the phosphorus-bromine, phosphorus-nitrogen, bromine-nitrogen, and phosphorus-bromine-nitrogen interactions observed with some of the polymers.

INTRODUCTION

1. INTRODUCTION.

1.1. The Polymer Industry.

1.1.1. Historical Development.

The synthetic polymer industry had its inception in the work of Braconnot in France in 1833 and of Schoenbein in Switzerland in 1845, through their discoveries relating to the preparation of cellulose nitrate. In 1870, a material formed from cellulose nitrate and camphor was developed by J.W. Hyatt and within two years, this product, termed "celluloid", became a commercial success. However, the first industrially successful thermosetting polymer was the phenolic resin, called Bakelite, developed by Baekeland in 1909. This stimulated research into other resins giving rise to the development of urea-formaldehyde and melamine-formaldehyde resins.

The decade 1930-40 saw the initial industrial development of today's major thermoplastics, namely polystyrene (PS), poly(vinyl chloride) (PVC), polyethylene (PE), polypropylene (PP) and poly(methyl methacrylate) (PMMA). The styrene monomer from which polystyrene is produced was first isolated in 1831 but it was thirty-eight years before the ethyl benzene process, now used in its manufacture, was developed. It was not until 1937, i.e. sixty-eight years

later, that polystyrene was introduced commercially. Industrial interest in PVC also commenced at about this time and today, PVC is one of the two largest tonnage polymeric materials, the other being polyethylene. Polyethylene was discovered by Imperial Chemical Industries (I.C.I.) in 1934, and in 1939, just before the Second World War, it started to be manufactured on a commercial scale. During this period, I.C.I. also marketed poly(methyl methacrylate).

The onset of war brought synthetic polymers more into demand, largely as substitutes for materials, such as rubber and gutta percha, which were in short supply. In the United States of America, the crash programme leading to the large-scale production of synthetic rubbers resulted in extensive research into the chemistry underlying the formation of polymers. New materials also emerged. Nylon was first made in 1941 and at the same time, polytetrafluoroethylene (PTFE) was discovered. Interesting developments were also taking place in the field of thermosetting resins. Experiments in polyester laminated resins and epoxy resins were also taking place during this period. Between 1945 and 1955, high-impact polystyrene was one of the few new polymers to be introduced commercially but there was a noticeable improvement in the quality of existing polymeric materials and an increase in the range of grades of such materials.

In the mid-1950's, a number of new thermoplastics became available and these had some very valuable properties. High-density polyethylene (HDPE), produced by the Phillips and Ziegler processes, was marketed and this was followed by the discovery and rapid exploitation of polypropylene. More specialised materials also became available, including the acetal resins, first introduced by Du Pont, and the polycarbonates, developed simultaneously but independently in the United States and Germany. Further developments involving the high-impact polystyrenes led to the development of acrylonitrile-butadiene-styrene (ABS) polymer.

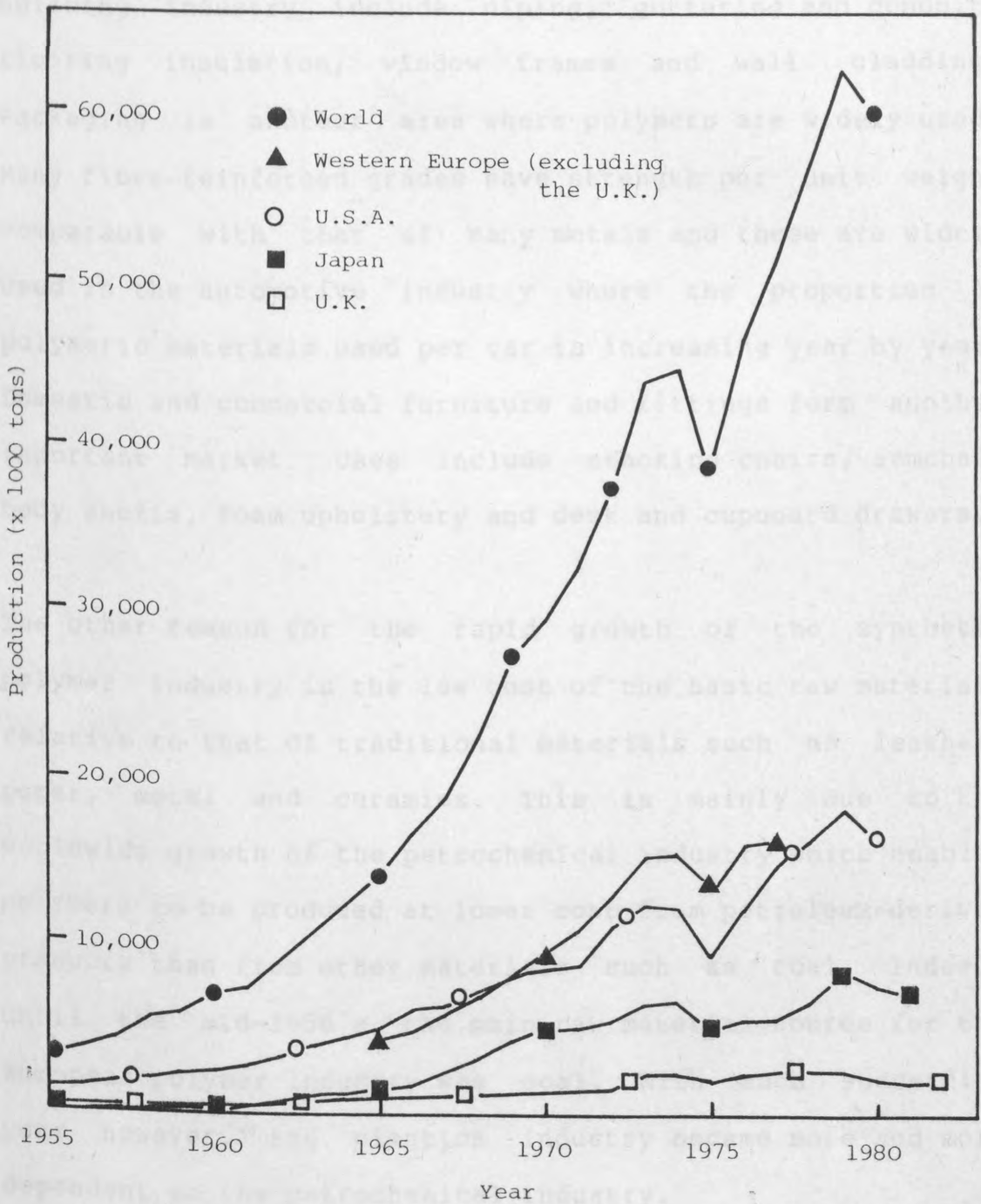
1.1.2. The Usage of Synthetic Organic Polymers.

The spectacular growth of the synthetic polymer industry since 1955 is illustrated in Fig. 1.1. The world's production increased from 3.3 million tons in 1955 to a staggering 60 million tons in 1980. The U.S.A. is the largest producer in the world, Japan the second largest and West Germany the third largest, with the U.K. in seventh place after the U.S.S.R., France and Italy.

The reasons for the spectacular growth of the synthetic polymer industry between 1945 and 1973 lie in the interaction of two main factors. The first is the growing understanding of the characteristics and capabilities of polymeric materials. Vast improvements have been made on previous existing types and, with better processing equipment, applications of polymers have increased tremendously. Most polymeric materials can be fabricated at quite low temperatures, so that the energy requirements for processing are low and, since polymers generally have low densities, costs of transportation and general handling are also relatively low. Through the development of such techniques as injection moulding, it is possible to make highly complex parts in one operation without the need for assembly work. Many polymers are superb electrical insulators and have good insulation characteristics at high frequencies. In view of their toughness, durability and

Figure 1.1

World production of synthetic polymers.



Sources : Japan Plastics Industry Annual,
Modern Plastics International,
British Plastics,
Business Monitor PQ 276.1.

flexibility, many polymers have found wide applications in the electrical and electronic industries. Their uses in the building industry include piping, guttering and conduit, flooring insulation, window frames and wall cladding. Packaging is another area where polymers are widely used. Many fibre-reinforced grades have strength per unit weight comparable with that of many metals and these are widely used in the automotive industry where the proportion of polymeric materials used per car is increasing year by year. Domestic and commercial furniture and fittings form another important market. Uses include stacking chairs, armchair body shells, foam upholstery and desk and cupboard drawers.

The other reason for the rapid growth of the synthetic polymer industry is the low cost of the basic raw materials relative to that of traditional materials such as leather, paper, metal and ceramics. This is mainly due to the worldwide growth of the petrochemical industry which enabled polymers to be produced at lower cost from petroleum-derived products than from other materials such as coal. Indeed, until the mid-1950's, the main raw material source for the European polymer industry was coal. With each succeeding year however, the plastics industry became more and more dependent on the petrochemical industry.

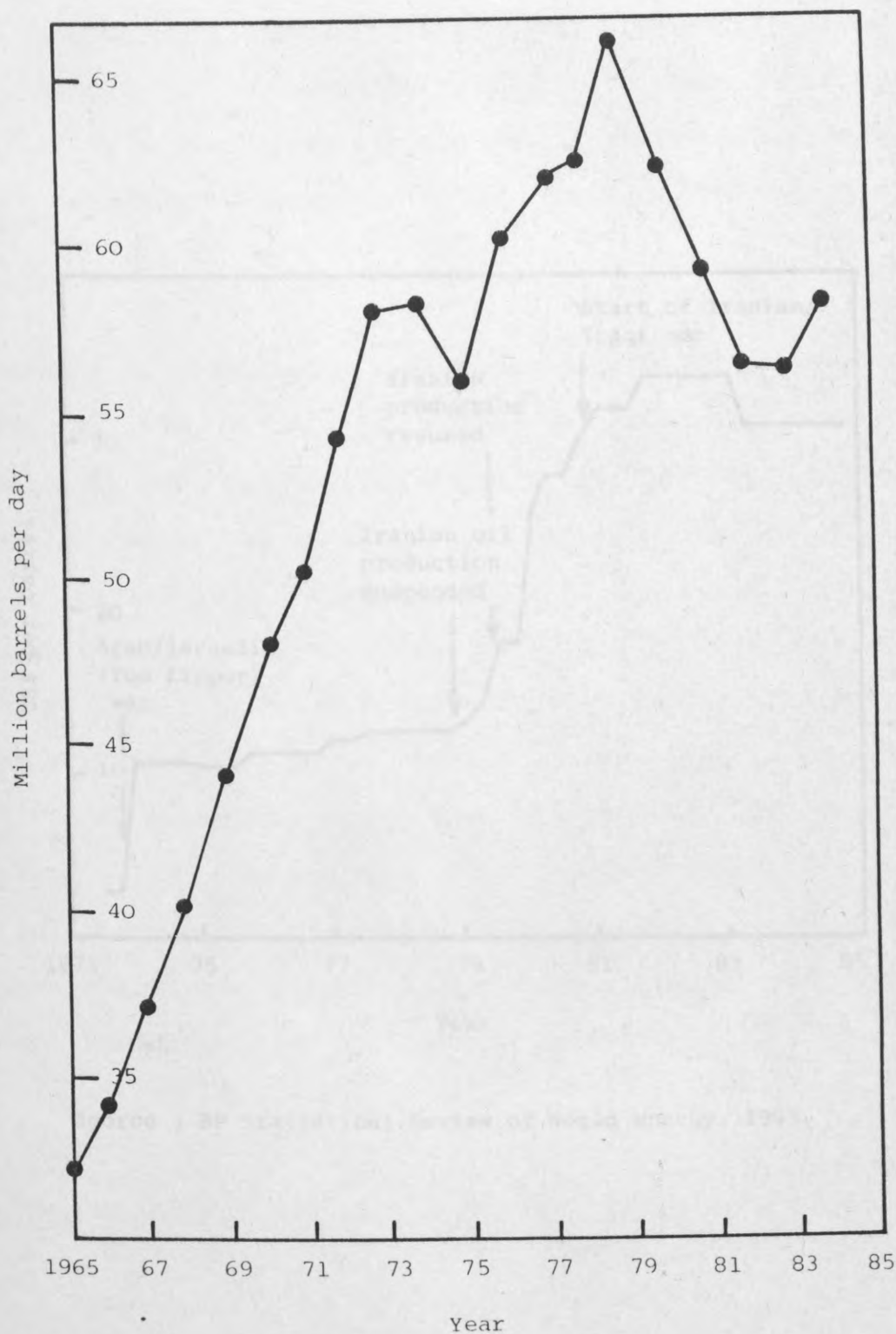
It was in 1973 that the disadvantages of the integration of the polymer industry with the oil industry first became

apparent. Up to 1980, the Middle East produced almost one third of the world's oil and as much as 85% of this was exported to the rest of the world. Saudi Arabia and Iran between them accounted for about 60% of the total oil production in the Middle East. The world was to experience its first oil crisis when war broke out between the Arabs and the Israelis at the end of 1973. For the first time, the world's oil production became static and eventually took a plunge downwards in 1975 (Fig. 1.2). The price of oil rose from US\$2.80 per barrel in October 1973 to a staggering US\$10.84 in January 1974 (Fig. 1.3). This inevitably affected the polymer industry, causing the first overall reduction in growth in its entire history (Fig. 1.1). The oil and polymer industries were to face a second crisis when hostility and unrest escalated in the Middle East in the late 1970's.

The revolution in Iran, the second largest producer in the Middle East, took place at the end of 1979. Its oil production was suspended for a year and, when it resumed, the price again escalated, this time from US\$18 a barrel to US\$26. The situation worsened further when the Iran-Iraq war started towards the end of 1981. The effect of these events was reflected in the statistics, where a second drop in the world's production of polymers was recorded.

The U.S.A. is the largest producer and consumer of polymers

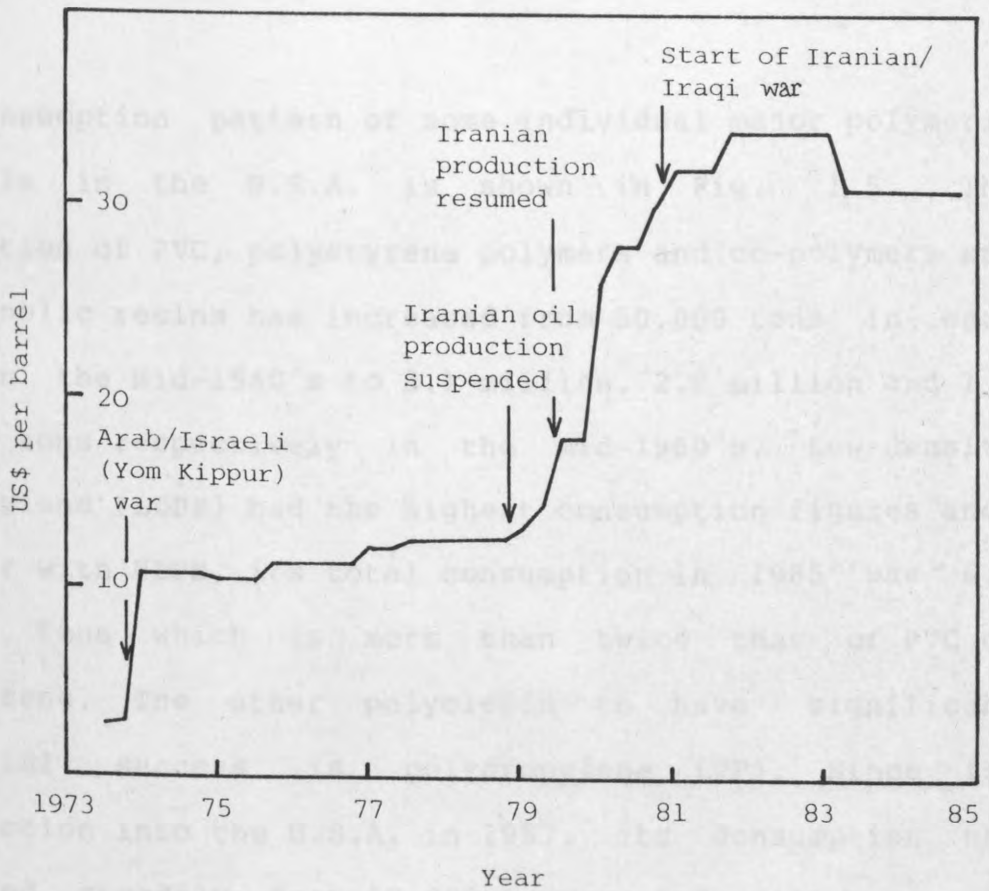
Figure 1.2
World production of oil.



Source : BP Statistical Review of World Energy, 1985.

Figure 1.3

Saudi Arabia's crude (light) prices 1973-1984.



Source : BP Statistical Review of World Energy, 1985.

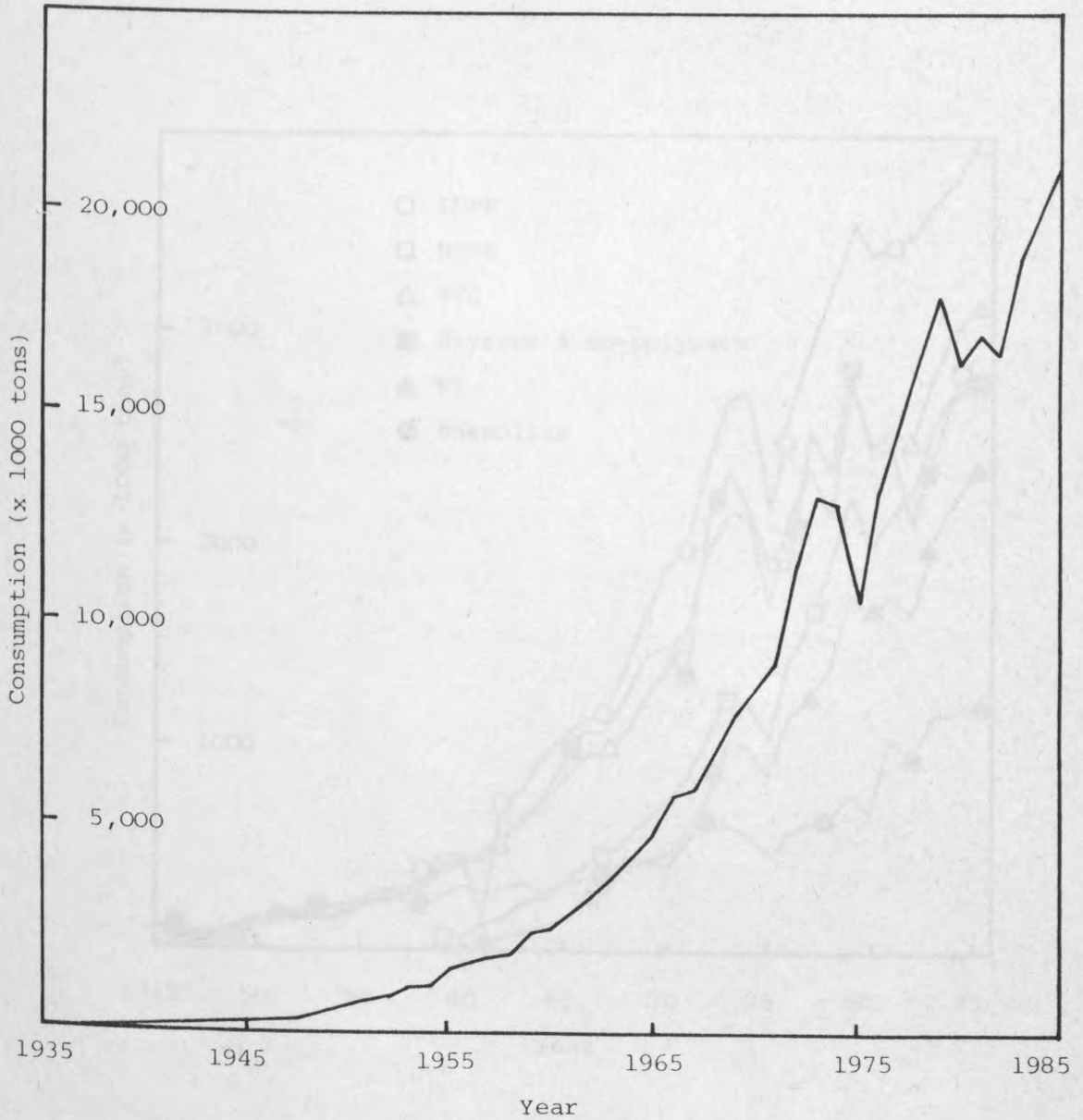
in the world. In the last twenty years, it has recorded a four-fold increase in its consumption which was a mere 5 million tons in 1964 (Fig. 1.4). The U.S.A. imports about 30% of its oil and the effects of the oil crises are evident in the consumption pattern (Fig. 1.4). However, 1983 and 1984 saw a growth in consumption after almost three years of recession. In fact, 1985 was the best year the U.S.A. has had, with an annual consumption of polymers of 21 million tons.

The consumption pattern of some individual major polymeric materials in the U.S.A. is shown in Fig. 1.5. The consumption of PVC, polystyrene polymers and co-polymers and the phenolic resins has increased from 50,000 tons in each case in the mid-1940's to 3.1 million, 2.8 million and 1.2 million tons respectively in the mid-1980's. Low-density polyethylene (LDPE) had the highest consumption figures and, together with HDPE, its total consumption in 1985 was 6.9 million tons which is more than twice that of PVC or polystyrene. The other polyolefin to have significant commercial success is polypropylene (PP). Since its introduction into the U.S.A. in 1957, its consumption has increased steadily from 50,000 tons to 2.3 million tons in 1985.

Japan, which imports almost all its oil, recorded a drop of

Figure 1.4

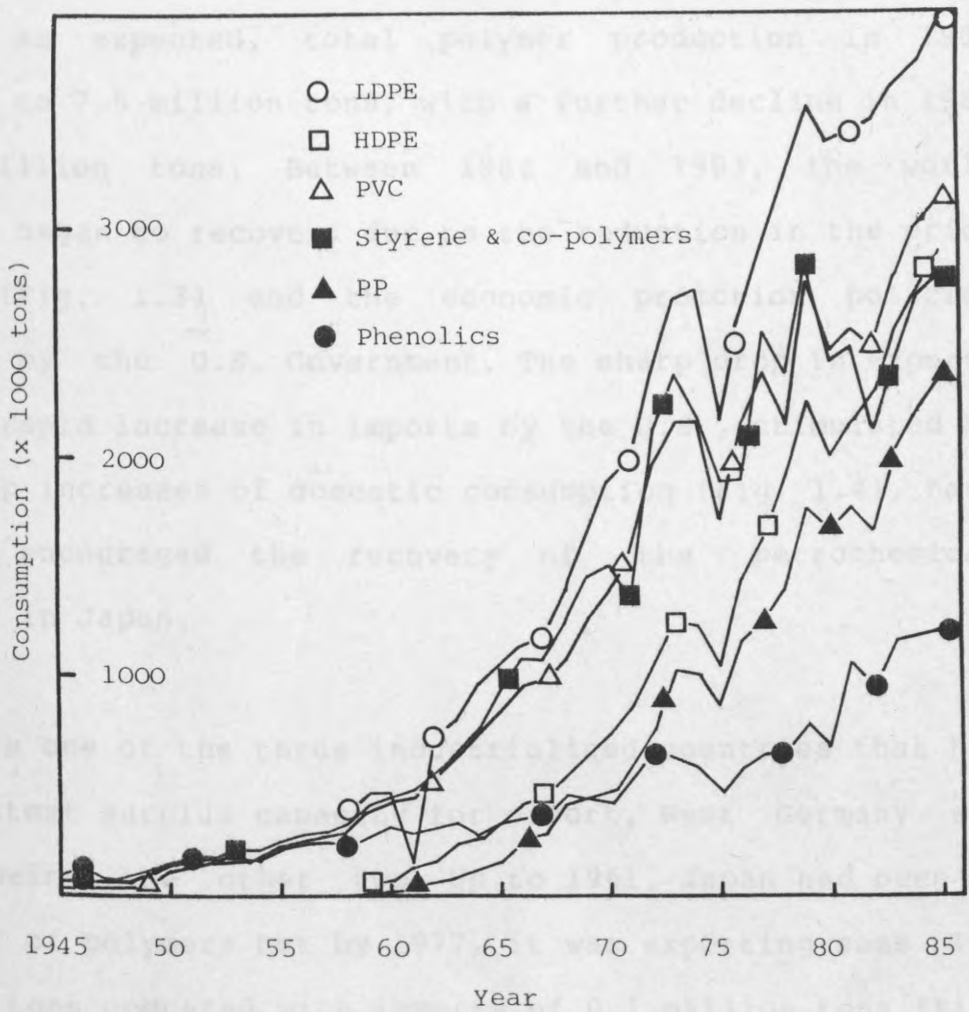
Total consumption of synthetic polymers in the U.S.A.



Source : Modern Plastics International.

Figure 1.5

Consumption of specific polymers in the U.S.A.



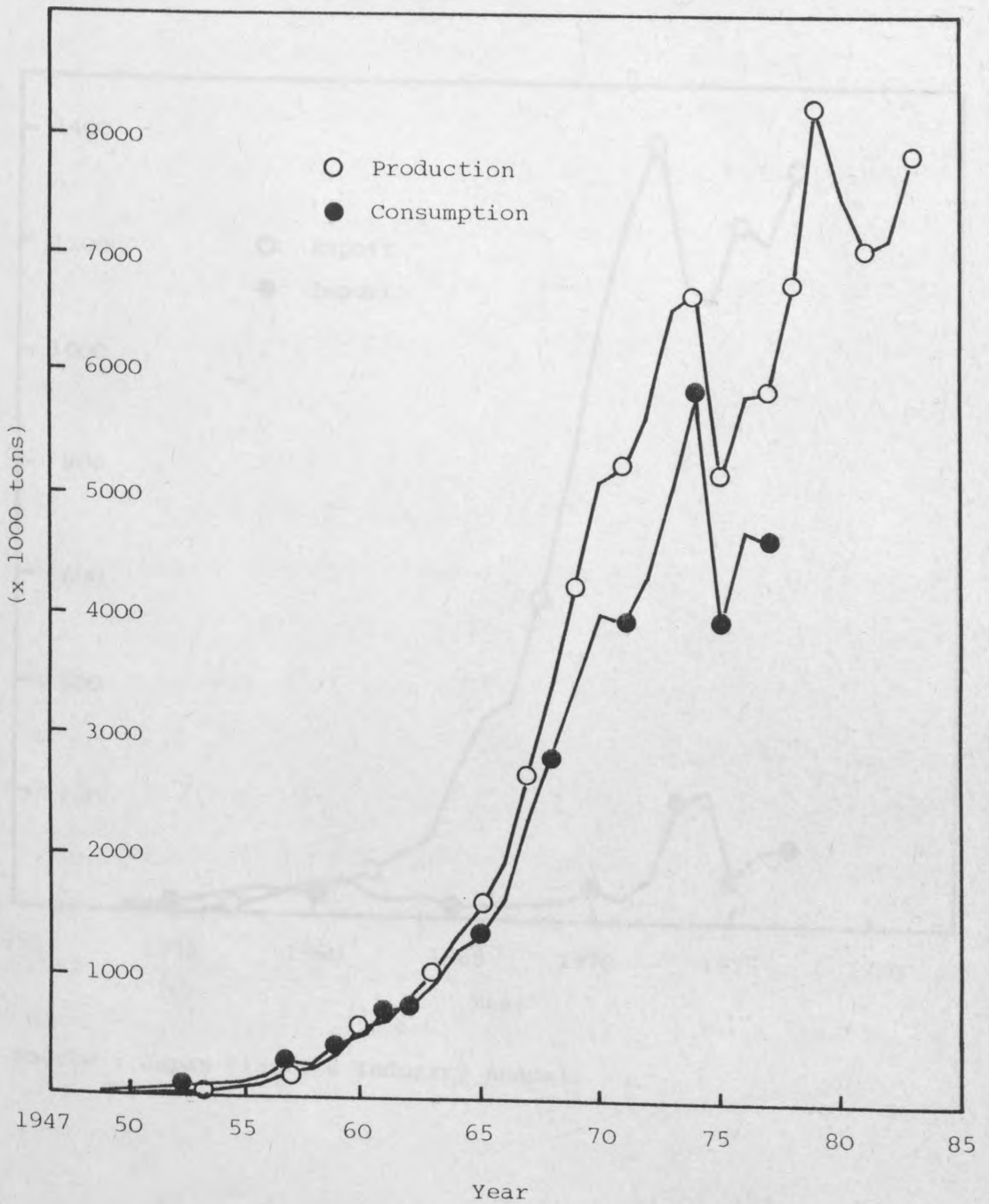
Source : Modern Plastics International.

23% in its production of polymers in 1975, 8.4% in 1980 and 6.4% in 1981, compared with each previous year (Fig. 1.6). Over the last thirty-five years, Japan has increased its production from 20,000 tons in 1950 to its highest ever value at 8.2 million tons in 1979. The mini-boom in 1979 was caused by speculative buying of raw materials by polymer manufacturers and distributors resulting from the second oil crisis. As expected, total polymer production in 1980 declined to 7.5 million tons, with a further decline in 1981 to 7.0 million tons. Between 1982 and 1983, the world economy began to recover, due to the reduction in the price of oil (Fig. 1.3) and the economic promotion policies adopted by the U.S. Government. The sharp drop in exports and the rapid increase in imports by the U.S., stimulated by the sharp increases of domestic consumption (Fig. 1.4), have greatly encouraged the recovery of the petrochemical industry in Japan.

Japan is one of the three industrialised countries that has the greatest surplus capacity for export, West Germany and Italy being the other two. Up to 1961, Japan had been an importer of polymers but by 1977, it was exporting some 1.3 million tons compared with imports of 0.1 million tons (Fig. 1.7). Today, almost 50% of the polymeric materials imported by Asian countries come from Japan. However, Europe and the U.S.A. each has a 15% share of the market. In 1973, a drop in export was recorded due to the shortage of supplies of

Figure 1.6

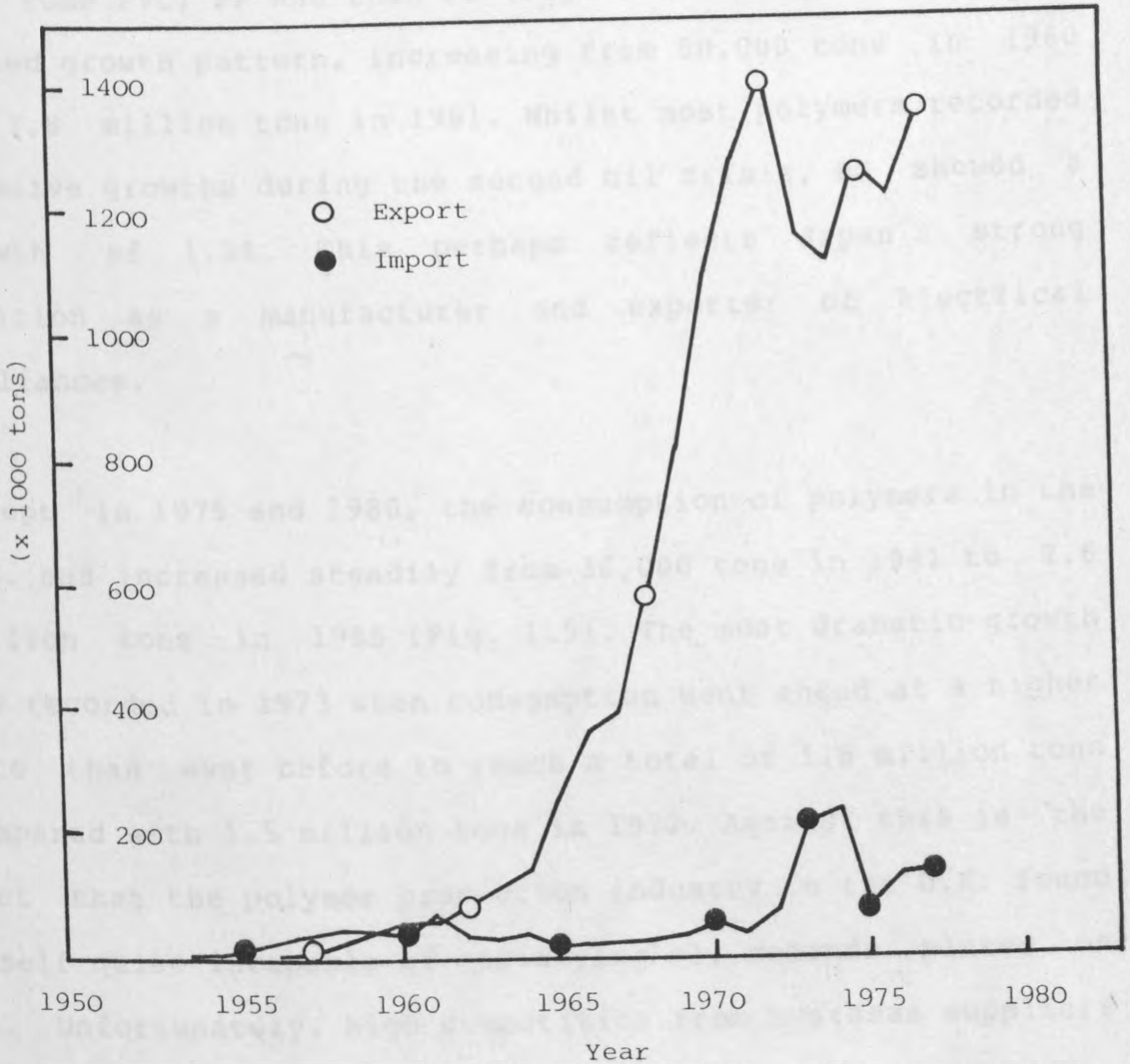
Total production and consumption of synthetic polymers in Japan.



Source : Japan Plastics Industry Annual.

Figure 1.7

Import and export of synthetic polymers by Japan.



Source : Japan Plastics Industry Annual.

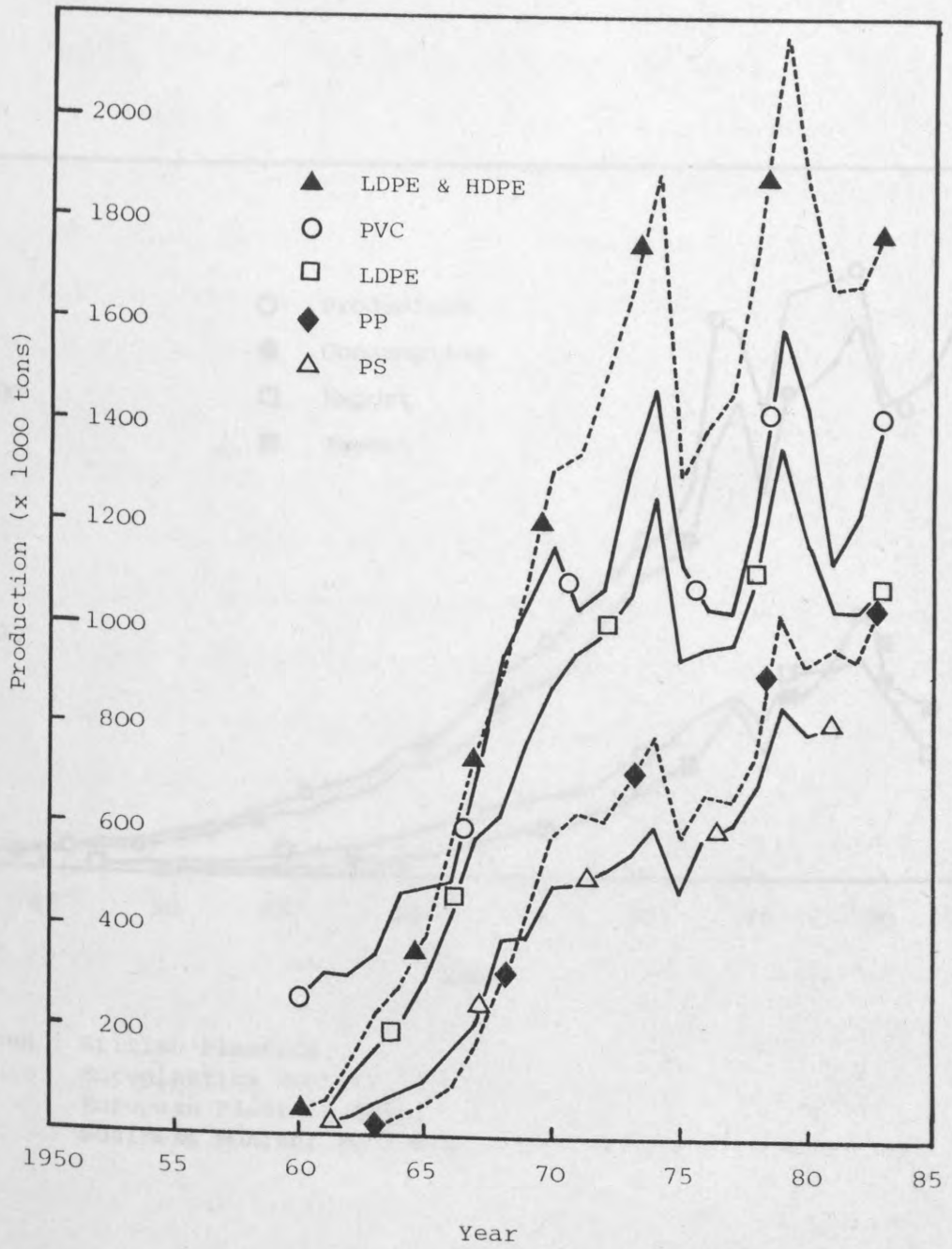
polymeric materials and to the business recession in South East Asia in 1974. To cope with the short supply conditions, imports were increased during 1973 to as much as three times those of 1972.

In Japan, polyethylene has the highest production output. Next come PVC, PP and then PS (Fig. 1.8). PE showed the most marked growth pattern, increasing from 50,000 tons in 1960 to 1.8 million tons in 1981. Whilst most polymers recorded negative growths during the second oil crisis, PS showed a growth of 1.5%. This perhaps reflects Japan's strong position as a manufacturer and exporter of electrical appliances.

Except in 1975 and 1980, the consumption of polymers in the U.K. has increased steadily from 36,000 tons in 1941 to 2.6 million tons in 1985 (Fig. 1.9). The most dramatic growth was recorded in 1973 when consumption went ahead at a higher rate than ever before to reach a total of 1.8 million tons compared with 1.5 million tons in 1972. Against this is the fact that the polymer production industry in the U.K. found itself quite incapable of satisfying all demands placed on it. Unfortunately, high competition from overseas suppliers of raw materials kept the U.K. price levels depressed to the point at which they were only marginally profitable and certainly too low to justify further investment. This made the U.K. increasingly dependent on imported materials and in

Figure 1.8

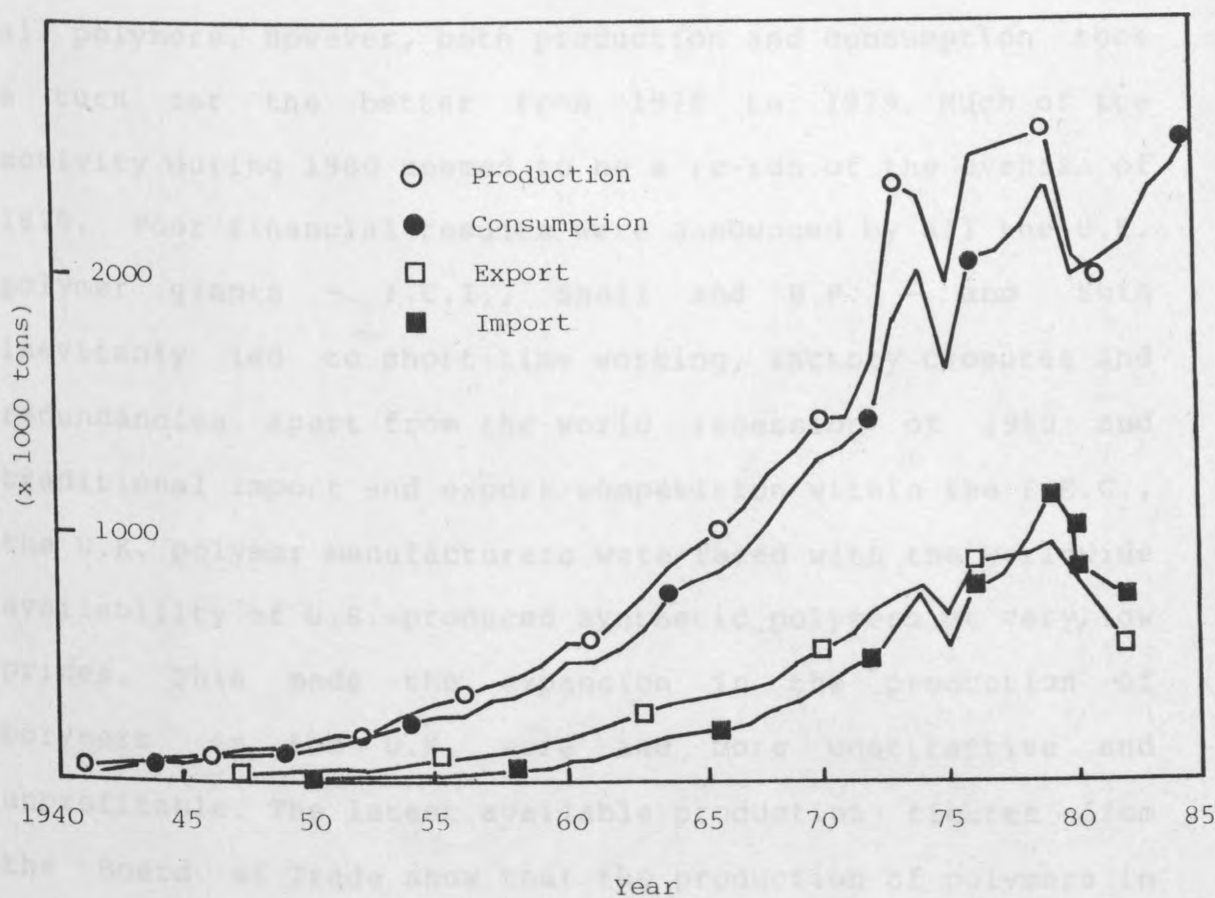
Production of specific polymers in Japan.



Source : Japan Plastics Industry Annual.

Figure 1.9

Import, export and total production and consumption
of synthetic polymers in the U.K.



Sources : British Plastics,
Europlastics Monthly,
European Plastics News,
Business Monitor PQ 276.1.

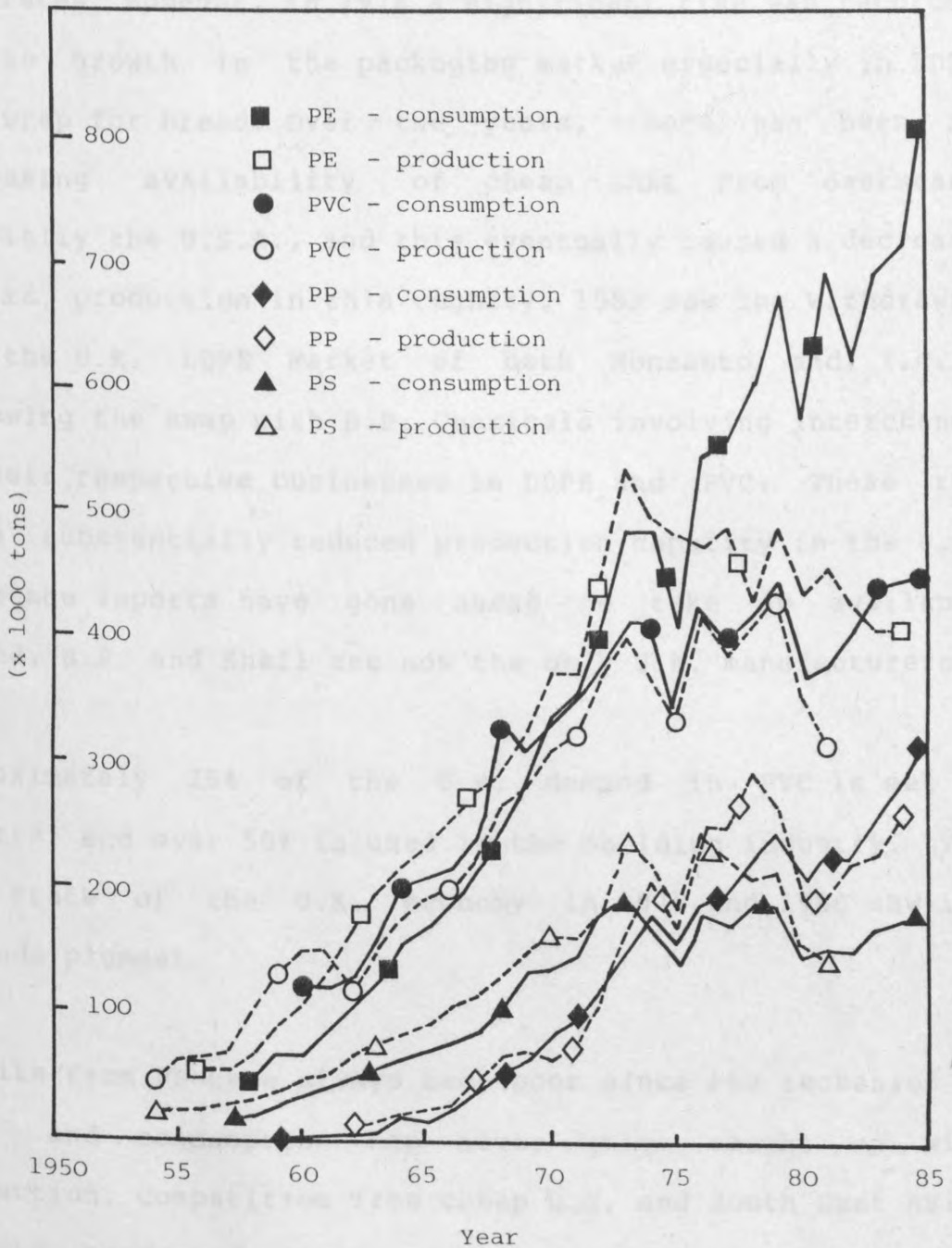
1973, for the first time, imports nearly equalled exports (Fig. 1.9). In fact, in 1978, imports overtook exports and have continued to do so ever since.

Deepening recession during 1975, together with continuing inflation and rising oil prices, combined to create a severe decline in demand (by 15-20%) in the U.K. for practically all polymers. However, both production and consumption took a turn for the better from 1976 to 1979. Much of the activity during 1980 seemed to be a re-run of the events of 1975. Poor financial results were announced by all the U.K. polymer giants - I.C.I., Shell and B.P. - and this inevitably led to short-time working, factory closures and redundancies. Apart from the world recession of 1980 and traditional import and export competition within the E.E.C., the U.K. polymer manufacturers were faced with the worldwide availability of U.S.-produced synthetic polymers at very low prices. This made the expansion in the production of polymers in the U.K. more and more unattractive and unprofitable. The latest available production figures from the Board of Trade show that the production of polymers in the U.K. in 1981 was as low as that in 1975, even though home consumption has been increasing steadily since 1981.

The production and consumption patterns of some major polymers in the U.K. are illustrated in Fig. 1.10. PE shows the most outstanding growth in consumption, increasing from

Figure 1.10

Production and consumption of specific polymers in the U.K.



Sources : British Plastics,
Europlastics Monthly,
European Plastics News,
Business Monitor PQ 276.1.

60,000 tons in 1960 to 820,000 tons in 1985. As a result of the 1975 oil crisis, there was a sharp drop in the demand for large blow-moulded containers, such as drums, barrels and crates. However, in 1976 a significant rise was recorded due to growth in the packaging market especially in LDPE film wrap for bread. Over the years, there has been an increasing availability of cheap LDPE from overseas, especially the U.S.A., and this eventually caused a decrease in its production in this country. 1982 saw the withdrawal from the U.K. LDPE market of both Monsanto and I.C.I. following the swap with B.P. Chemicals involving interchange of their respective businesses in LDPE and PVC. These two moves substantially reduced production capacity in the U.K. and hence imports have gone ahead to take up available demand. B.P. and Shell are now the only U.K. manufacturers.

Approximately 25% of the U.K. demand in PVC is met by imports and over 50% is used in the building industry. The bad state of the U.K. economy in 1975 and 1980 saw its demands plummet.

Profits from PP have always been poor since the recession in 1980 and consumption has never quite caught up with production. Competition from cheap U.S. and South East Asian imports presented little incentive for the raw material manufacturers to return to their original capacities, let alone increase it.

The main market sectors of polystyrene are toys, consumer durables, general packaging, radio and T.V. cabinets. 1982 saw a rapid decline in the toy market, more and more toys then being made abroad. One good area in the polystyrene field was direct gassed PS for meat trays in supermarkets and fast food outlets but this was insufficient to alter the PS consumption situation. In fact, in 1980, B.P. ceased its production arrangements with Monsanto, and Shell mothballed a certain amount of PS capacity. At least in the immediate future, U.K. processors are expected to continue importing their raw materials.

The synthetic polymer industry has become a mature industry where economies of scale appear to have reached a limiting value and improvements to existing manufacturing methods tend to have marginal effects. Taking these factors and past experiences into consideration, it can be said that the future growth of the polymer industry is highly dependent on the global economic situation.

1.2. The Involvement of Polymers in Fires.

1.2.1. Hazards Associated with Polymer Combustion.

1.2.1.1. Introduction.

In a real fire situation, a number of factors can be responsible for the death or serious incapacitation of persons in or near a fire. The main contributory factors include direct destruction of tissue, extremely high temperatures, oxygen deficiency, presence of smoke, presence of toxic gases and development of fear. Up to the time of the Second World War, most materials susceptible to combustion were either natural substances, such as wood or leather, or were produced from them. However, with the growing importance of synthetic polymers in the clothing, household, construction and transportation industries, there has been an increase in the danger of the consequences of fire not encountered before and this is especially true as regards the production of toxic gases.

Perhaps the first awareness of the serious hazards caused by the thermal decomposition products of synthetic polymers was caused by the Cleveland Clinic fire of 1929 in which 125 people died. Analysis of the fatal casualty pattern showed that most of the deaths were due to the production of carbon monoxide and nitrogen oxides from burning X-ray films and

not to the fire directly. Generally, when polymeric materials are heated and burn, smoke and other pyrolysis and combustion products will be evolved. Depending on the material, the temperature and the absence and presence of oxygen, a variety of toxic gases may also be formed. These gases include carbon monoxide, hydrogen cyanide, hydrogen chloride, sulphur dioxide and nitrogen dioxide, various fluorinated compounds and other gases which are not always easily identified. In recent years, the awareness of the fire hazards caused by synthetic polymers has stimulated the development of a variety of flame retardants to reduce the burning potential of such materials. However, the inclusion of these compounds in polymers has introduced some of the toxicological implications not previously realised.

The effects of flame, hot gases, smoke and toxic gases will be discussed in Sections 1.2.1.3., 1.2.1.4., 1.2.1.5. and 1.2.1.6. respectively.

1.2.1.2. U.K. Statistics on Types of Injuries Sustained.

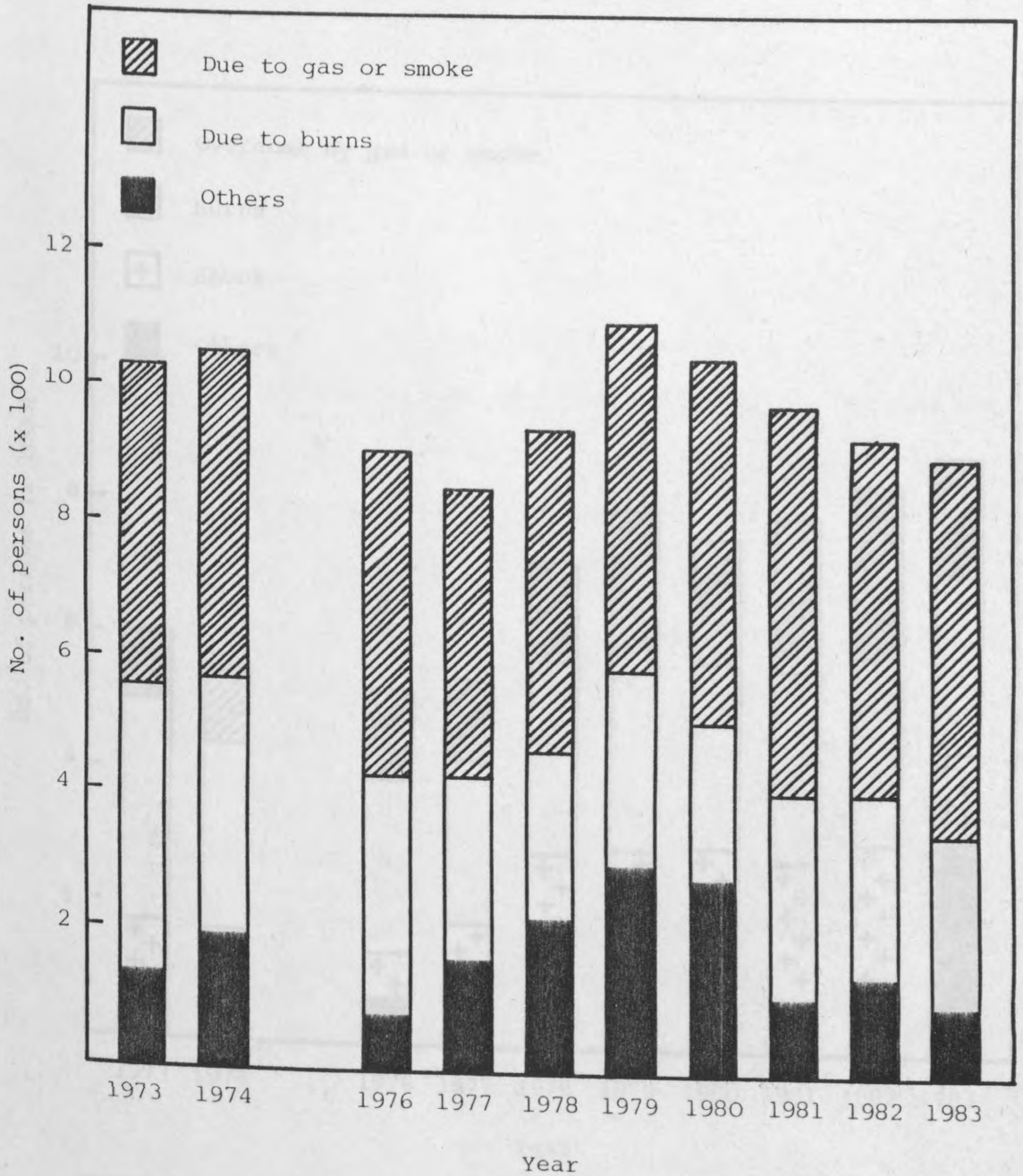
Generally, the exposure of humans to the various combustible and non-combustible gases as well as the particulates in the smoke produced in the event of a fire can result in cases of toxicity ranging from irritant effects to death. In statistical terms, the actual lethality of smoke and toxic gases may be more important than the effects of the flame

itself. Indeed, the most recent survey of fire statistics conducted by the Home Office (1984) covering the period from 1973 to 1983 revealed that gas and smoke caused more deaths than flame. The number of fatalities overcome by gas or smoke rose from 474 in 1973 to 553 in 1983, while the annual number of deaths recorded as due to burns fell from 420 in 1973 to between 230 and 300 over the last five years (Fig. 1.11). In fact, the percentage of fatalities overcome by gas or smoke has increased continuously from 45.5% in 1973 to the highest ever value of 61.2% in 1983. The decrease in the proportion of deaths due to burns is less consistent. In 1973, 40.4% of deaths were caused by burns compared with 27.6% in 1983.

Since 1979, the number of fatal casualties has been decreasing and in 1983, it had fallen back to the level of the mid-1970's. However, the number of non-fatal casualties from fire has not shown the same tendency to decline as has that of fatal casualties (Fig. 1.12). In fact, it has increased from 8,230 in 1978 to 10,004 in 1983, the highest yet recorded. This may be attributed in part to the revised reporting procedures introduced in 1978 which are thought to give a more representative view. In particular, casualties suffering from minor injuries, such as shock, are now taken into account. Among the non-fatal casualties, the proportions of different types of injury sustained changed considerably over the period 1973 to 1983. Further insight

Figure 1.11

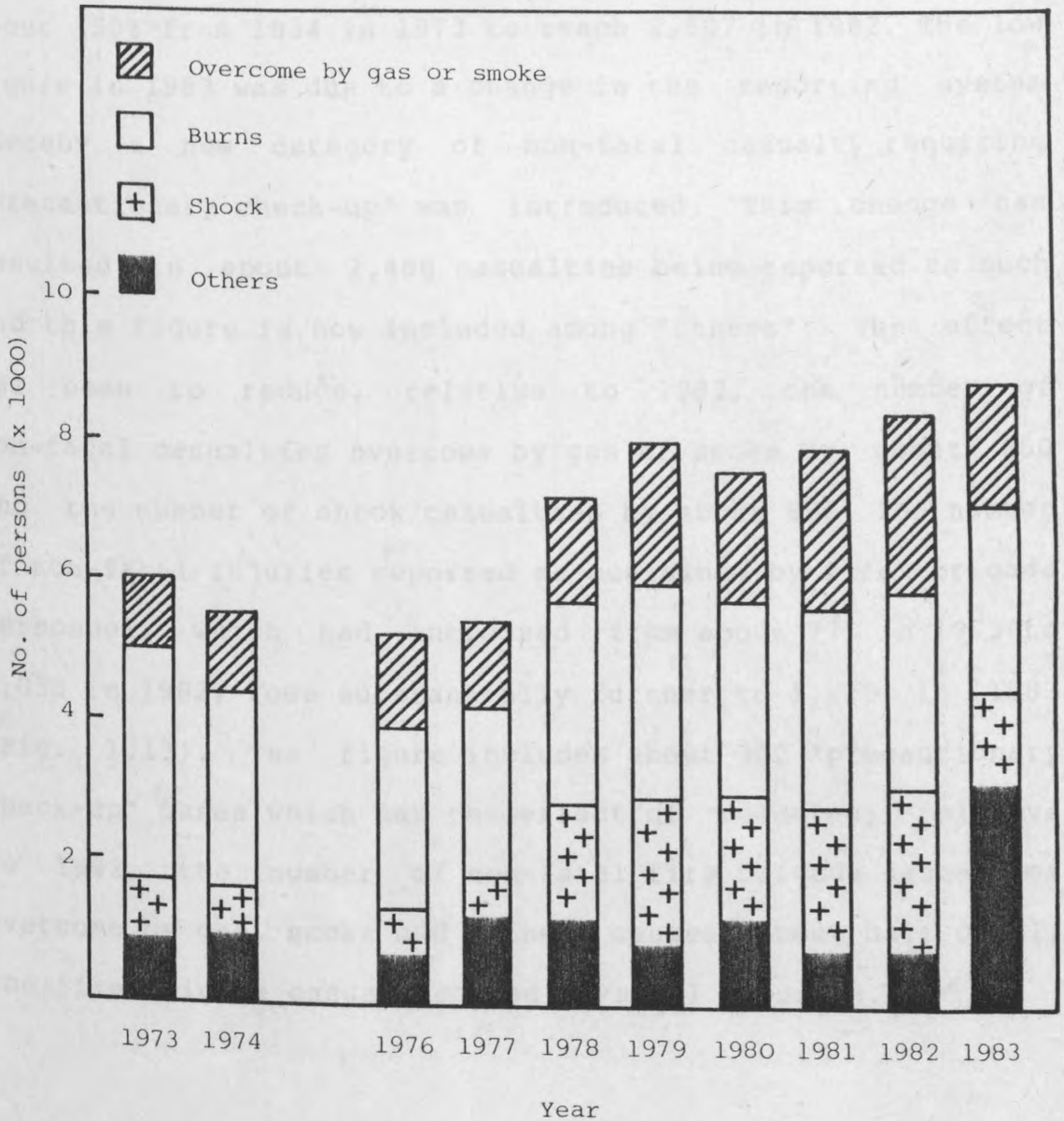
Fatal casualties from fires - by cause of death (1973-1983).



Source : Fire Statistics, U.K. 1983, Home Office.

Figure 1.12

Non-fatal casualties from fires - by nature of injury (1973-1983)
(excluding fire brigade casualties).

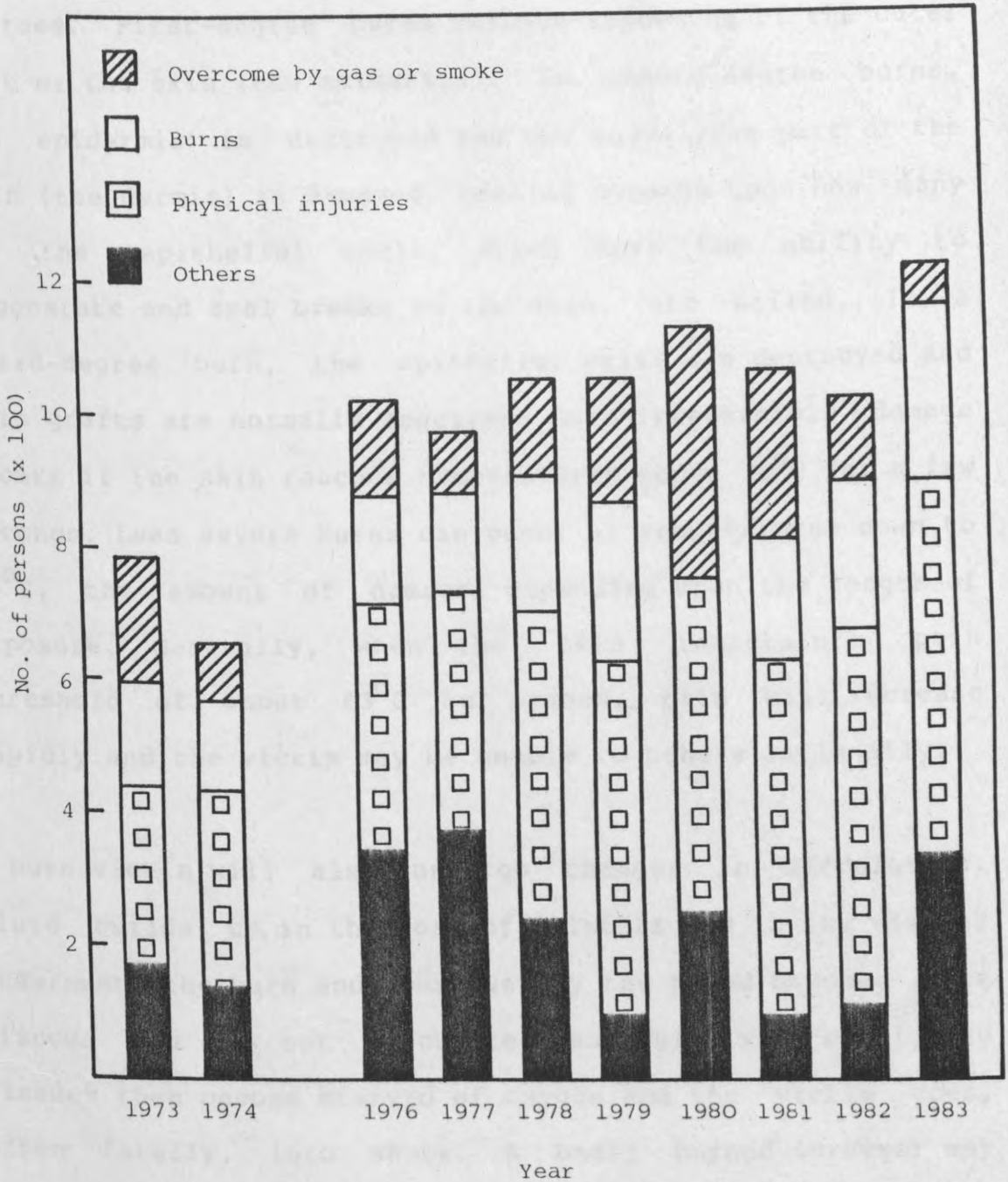


Source : Fire Statistics, U.K. 1983, Home Office.

into the changing patterns can be gained by looking at the fire brigade and non-fire brigade casualties separately. In the case of non-fire brigade casualties, the most numerous category of casualties reported were those due to burns and since 1976, this figure appears to have remained constant. Casualties recorded as overcome by gas or smoke increased by about 150% from 1034 in 1973 to reach 2,507 in 1982. The low figure in 1983 was due to a change in the reporting system whereby a new category of non-fatal casualty requiring "precautionary check-up" was introduced. This change has resulted in about 2,400 casualties being reported as such and this figure is now included among "others". The effect has been to reduce, relative to 1982, the number of non-fatal casualties overcome by gas or smoke by about 850 and the number of shock casualties by about 800. The number of non-fatal injuries reported as sustained by fire brigade personnel, which had increased from about 775 in 1973 to 1,028 in 1982, rose substantially further to 1,210 in 1983 (Fig. 1.13). The figure includes about 300 "precautionary check-up" cases which has the effect of reducing, relative to 1982, the number of non-fatal fire brigade casualties overcome by gas, smoke and "other" causes. About half of all the fire brigade casualties had physical injuries.

Figure 1.13

Non-fatal fire brigade casualties from fires - by nature of injury (1973- 1983).



Source : Fire Statistics, U.K. 1983, Home Office.

1.2.1.3. Effects of Flame.

Direct contact with flames or heat radiated from flames causes burns to the skin. Skin burns are classified by degrees. First-degree burns involve reddening of the outer part of the skin (the epidermis). In second-degree burns, the epidermis is destroyed and the underlying part of the skin (the dermis) is damaged. Healing depends upon how many of the epithelial cells, which have the ability to regenerate and seal breaks in the skin, are killed. In a third-degree burn, the epithelial cells are destroyed and skin grafts are normally required. Such irreversible damage occurs if the skin reaches temperatures above 70°C for a few seconds. Less severe burns can occur at temperatures down to 43°C , the amount of damage depending upon the length of exposure. Generally, when the skin temperature pain threshold of about 43°C is passed, pain will increase rapidly and the victim may be unable to behave rationally.

A burn victim will also undergo changes in circulation. Fluid builds up in the form of blisters and in the tissues underneath the burn and consequently the blood becomes more viscous and is not circulated as quickly as usual. The tissues then become starved of oxygen and the victim goes, often fatally, into shock. A badly burned survivor may succumb to infection or may develop kidney, brain, heart, lung or stomach damage.

1.2.1.4. Effects of Hot Gases.

Heat radiated from flames also causes the temperature of the surrounding gases in the atmosphere to rise and, when these hot gases are inhaled, they cause the respiratory tract to become inflamed and congested, often resulting in suffocation of the victim. If a person survives serious injury of this kind, he may die later from subsequent infection or pneumonia. The effects of combustion gases, in particular toxic ones, will be discussed in greater detail in Section 1.2.1.6.

1.2.1.5. Effects of Smoke.

The principal hazard of smoke is that it obscures the vision of occupants in a building and thus hinders their escape. It also prevents fire fighters from locating and extinguishing the fire. In the early stages of fire, smoke does not usually contain a sufficiently high concentration of toxic gases to be lethal, but very often its blinding and irritating effects cause the occupants to panic and become disorientated; the delay in escaping allows the concentrations of the gases to build up to levels that are fatal. Smoke includes particulate matter and various toxic compounds. Depending on the size of the particles contained in it, smoke may be absorbed from lung tissue into the blood stream. It may also be trapped in lung tissue. In this case

it may either be absorbed and slowly destroyed by phagocytes or remain indefinitely. Chronic effects of these "non-removed" particulates lodged in lung tissue over long periods could lead to malignant tissues. Acute cases of smoke inhalation can of course lead to suffocation due to the dense build-up of material which prevents absorption of oxygen.

1.2.1.6. Effects of Toxic Gases.

Besides being absorbed into the blood stream, toxic gases can also act as a primary irritant on the skin, or on mucous membranes. They may act as sensitive agents producing antibodies to antigens. If exposure to similar agents is repeated, these gases may be absorbed in very low concentrations, producing no definite signs and symptoms of toxicity but nevertheless affecting mental functions.

The hazards and various symptoms associated with toxic gases have been reviewed in great detail by Autian (1970) and Hilado (1974). The following discussion covers some of the more important toxic gases associated with polymer decomposition and combustion and the effects of, and symptoms due to, such gases are given in Table 1.1.

Carbon dioxide is not generally considered toxic. However, it overstimulates the respiratory system if inhaled in

Table 1.1

Effects of some common fire gases on humans.

Compound and highlights of its physiological effects.	T.L.V. ^a (ppm)
---	---------------------------

Carbon monoxide.

Exposure to CO at concentrations of 200 to 300 ppm for 2 hours can cause headache and unconsciousness. Other symptoms include nausea, hallucination and collapse. Concentrations of 12,000 ppm can cause death in a matter of minutes.

50

Carbon dioxide.

Inhalation of CO₂ at concentrations of 10 % causes headaches, dizziness and unconsciousness as well as other symptoms. Higher concentrations (above 20%) can lead to narcosis, immediate unconsciousness and death by suffocation.

5,000

Oxygen.

O₂ at concentrations of only 12 to 15% causes shortness of breath, headache, dizziness, quick fatigue upon exertion and loss of muscular coordination. At concentrations between 6 and 8%, collapse and unconsciousness occur but rapid treatment can prevent death. Death can intervene in 6 to 8 minutes if the concentration falls below 6%. Even if death does not occur due to low levels of oxygen in the immediate atmosphere, denial of sufficient oxygen to brain tissue even for short periods of time produces irreparable brain damage.

-

a : Threshold limiting value is the maximum permissible concentration for indefinite exposure. These values depend on experience and must always be considered as subject to revision.

Hydrogen cyanide.

Concentrations above 20 ppm in the air are considered to be dangerous to health. Initial inhalation of the vapours of HCN causes a reflex stimulation of breathing which in turn will lead to greater concentrations of the gas entering the body. Within a very short time, the person becomes unconscious, and if not removed from the source, will suffer certain death.

10

Hydrogen chloride.

Hydrogen chloride combines with water to form hydrochloric acid. It is less corrosive than sulphuric acid and does not produce a severe tissue response on skin but does cause destructive damage to mucous membrane. If inhaled, the upper respiratory tract will be severely damaged and this may lead to asphyxiation and death. Short exposure of 1000 to 2000 ppm leads to lung oedema.

5

Hydrogen fluoride.

Hydrogen fluoride combines with water to form the highly corrosive hydrofluoric acid. Inhalation of this compound produces serious damage to the mucous membranes in the respiratory tract, which may lead to death. At 120 ppm and above, exposure for one minute can cause conjunctival and respiratory irritation.

3

Hydrogen sulphide.

Concentrations as low as 50 ppm generally cause toxic symptoms and exposure to concentrations of 2000 ppm or more paralyses the olfactory nerves so that victims can no longer smell the gas. Lower levels in the air (200 ppm and below) can be extremely dangerous to mucous membranes through the irritant properties of the gas. It can cause headaches, nausea, confusion and weakness and may even lead to unconsciousness. Because of the rapid metabolism of the compound, death can be prevented if the persons are removed from the source of the exposure. Death is generally due to central respiratory paralysis.

50

Sulphur dioxide.

This is a pungent and heavy gas and combines with water to form sulphur oxy-acids which in turn produce extremely irritant response in contact with the skin. Mucous membrane, particularly in the respiratory tract and in the eye, is highly susceptible to the irritant effects. Exposure to high concentrations of the gas (600 to 800 ppm) leads to death most likely due to asphyxiation. Chronic exposure to SO₂ appears to have greater toxic effects upon those with cardiorespiratory diseases than those not suffering from these ailments.

5

Nitrogen oxides.

Both NO and NO₂ are toxic gases. Lethal effects occur in a relatively short time when the level of these gases in the atmosphere reaches 250 ppm. Lower concentrations, if inhaled for several hours, can lead to death. These compounds are also marked irritants, in particular to mucous membranes, and thus, when inhaled, they damage tissue in the respiratory tract. When absorbed, nitric oxide will react with oxyhaemoglobin producing methaemoglobin. A combination of the accumulation of liquids in the lungs as well as the production of methaemoglobin will lead to death.

5

Ammonia.

This gas is highly irritant at concentrations well below lethal levels and this is particularly true in the case of the mucous membrane of the respiratory tract. Exposure to 5,000 to 10,000 ppm of ammonia for 30 minutes may, however, be very harmful.

25

Acrolein.

This is a yellowish, flammable liquid with a pungent odour. At a concentration of 5.5 ppm, it can cause intense irritation of mucous membranes. Exposure to 10 ppm and above for a short time can be fatal.

0.1

Tolylene diisocyanate.

This causes intense irritation, coughing, spasms of the bronchi and tracheitis lasting several hours after exposure to a concentration of only 1.3 ppm.

0.02

significantly high concentrations, causing an abnormally high intake of other gases resulting in toxic or lethal effects which would not otherwise have been encountered. At a concentration of 20%, carbon dioxide causes asphyxia and death in a matter of minutes.

Carbon monoxide is considered to be the most common cause of fire deaths (Birky et al. 1979; Harland & Woolley 1979). It is a colourless and odourless gas which is readily formed in poorly ventilated fires. Carbon monoxide is absorbed through the lungs into the blood, where it reacts with the haemoglobin to form carboxyhaemoglobin, reducing the amount of haemoglobin available for the transportation of oxygen. Carbon monoxide combines with haemoglobin about 250 times more readily than oxygen, so that even low concentrations can be dangerous. Carbon monoxide is one of the commonest causes of anoxia.

Another very important toxic gas is hydrogen cyanide. Its primary function is to inactivate certain enzymes in the body which will then prevent utilisation of oxygen by the tissue. Initial inhalation of hydrogen cyanide causes a reflex stimulation of breathing which in turn leads to a greater concentration of gas entering the body within a short period of time. The person becomes unconscious and, if not removed from the source, can die in minutes.

Other toxic gases such as hydrogen chloride, hydrogen fluoride, sulphur dioxide, acrolein and ammonia, are generally classified as sensory irritants, which are basically irritants of the upper respiratory tract. These compounds cause difficulty in breathing and affect one or more typical reflex actions associated with stimulation of trigeminal endings, like burning sensation in the nose or eyes, moist facial skin, sneezing, coughing and eye-watering. Other gases act as pulmonary irritants which affect the lower respiratory tract by increasing respiratory rates as a result of stimulation or sensitisation of various nerve endings in the lungs. Such action usually does not cause any pain. Nitrogen oxides are the most likely pulmonary irritants present in fire situations. Many such irritants have the combined effects of sensory irritants. Nitrogen oxides, sulphur dioxide, acrolein and ammonia are classified as respiratory irritants and bronchioconstrictors (chemicals that induce increased resistance to air-flow in the lungs). Other examples of such irritants are hydrogen sulphide and tolylene diisocyanate (TDI). Gases such as sulphur dioxide, hydrogen sulphide and ammonia have very strong and distinctive smells (but exposure to high concentrations of H_2S paralyses the olfactory nerves so that people are unable to smell it) and they cause extreme irritation at concentrations well below lethal levels.

1.2.2. Measurement of Polymer Flammability.

1.2.2.1. Introduction.

No two fires follow exactly the same course so that it is unlikely that any simple or single test can be designed to predict the actual fire performance of a material in a real fire. However, if a representative scale test is carried out under known conditions, typical of a specific real fire situation, it is possible to relate the fire performance using a given method to a real fire situation. At present, most of the standard tests developed to assess the flammability of polymeric materials are carried out on relatively small scales, mainly because it is much more economical than using large-scale tests. Furthermore, while small-scale tests do not simulate the situation in a large fire, they can nevertheless give information about the relative behaviour of different materials. The general lack of correlation of most small-scale tests with actual fire situations has led to an uncertainty concerning the interpretation and meaning of the test results. This in turn has created considerable pressure on both commercial and government agencies to develop large-scale tests that would give a more realistic evaluation of real fire hazards. In recent years, considerable research has gone into the understanding and prediction of fires by using computer modelling (Schultz 1985). However in order to set up

mathematical models, assumptions and estimates have to be made and most of these can be provided by conducting small-scale tests.

When designing a test to assess the flammability of a material, it is necessary that the conditions used are standardised to resemble closely certain features of one or more of the stages of combustion. Indeed, most of the standard tests developed by the American Society for Testing Materials (ASTM) and the British Standards Institution (BSI) are concerned with the initiation and early stages of development of a fire. This involves the use of methods to evaluate the ease with which the material can be ignited initially, the rate at which heat is released from the surface of the material, the rate at which the material burns and the performance of materials under actual conditions of use. Perhaps the most important individual test is the one concerned with the determination of the limiting oxygen concentration necessary to sustain a flame. This method provides a useful comparative quantitative measure of polymer flammability on a laboratory scale.

The tests described in the following Sections are some of the most commonly used ones adopted by the ASTM, BSI and Underwriters Laboratories (UL).

1.2.2.2. Spread of Flame Tests.

The majority of tests involving the combustion of polymeric materials are concerned with the determination of the extent and time for which a material will burn after being ignited in a standard way. Different tests have been devised to evaluate the flammability of polymeric materials depending on their nature, shape, form and size. Many of these tests differ in the angle at which the sample is held.

ASTM D635 : Test method for rate of burning and / or extent of burning of self-supporting polymers in a horizontal position.

This method provides a standard test for obtaining comparative data on moderately fire-retardant polymers in the form of bars, moulded or cut from sheets, and plates or panels that are tested in a horizontal position. A 25 mm high flame is brought into contact with a specimen of dimensions 125 mm x 12.5 mm x 12.5 mm for 30 s. The procedure is repeated until 3 specimens have burned to the gauge mark previously drawn 100 mm from the ignition end of the specimen, or until 10 specimens have been tested. The average burning rate (ABR) is calculated (in cm min^{-1}) by dividing 10 cm by the time (in min). The average time of burning (ATB) and average extent of burning (AEB) are given

by:

$$\text{ATB} = \frac{\sum (t-t')}{\text{no. of specimens}}$$

$$\text{AEB} = \frac{\sum (l_0-l)}{\text{no. of specimens}}$$

where t is the time (in s) taken for the flame to extinguish or for any part of the burning edge to reach the gauge mark; t' is the time (in s) taken for the specimen to ignite; and l is the length (in cm) measured from the gauge mark to the remaining unburned edge.

The most serious deficiencies of this method are that it fails to measure the actual fire hazard or to distinguish between polymers that do not drip and those that melt as the flame progresses down the sample in the process. Highly flammable polymers that drip can give misleading results in this test as the falling drips can carry away the burning polymer and thus remove the heat which would otherwise be fed back to the unburnt polymer to enhance further combustion.

Subsequently, ASTM D3801, a revised version which combines the best features of the UL 94 horizontal burning test, and the established ASTM D635 method has been developed. This will be described later.

UL 94 : Tests for flammability of polymeric materials for use as parts in electrical devices and appliances.

This is an important standard test for classifying polymeric materials used for building construction or furnishing. Five different tests are described in this standard; one horizontal burning test, three vertical burning tests and one flame spread index test.

The horizontal burning test and the flame spread index test are similar to ASTM D635 (described earlier) and ASTM E162 respectively.

The vertical burning test method has assumed overriding importance over the other two because it is considered to be a more severe method of testing. The vertical burning tests described in this standard are carried out in a draught-free flame test chamber similar to the one used in ASTM D3713. The test specimen, 125 mm x 12 mm and of maximum thickness 12 mm, is supported vertically by its upper end and is ignited at its lower end for 10 s by a Bunsen burner with a 9 mm blue flame. If flaming or glowing combustion stops within 30 s after removal of the flame, the specimen is reignited for 10 s. The duration of flaming or glowing is again noted. A layer of surgical cotton, placed 300 mm below the sample, collects any drippings from the burning specimen and if the cotton ignites, the drippings are considered

significant. Flammability ratings of V-0, V-1 and V-2 are applied to the materials tested depending on their behaviour during the test. Table 1.2 summarises the test requirements. In addition to the above ratings, a material can also be classified with a flammability rating of 5-V which involves a more stringent test. The dimensions of the test specimen are the same and a Tirrill burner with a flame height of 125 mm is used to ignite the specimen from an angle of 20° from the vertical for 5 s and removed for another 5 s. This procedure is repeated until the specimen has been subjected to 5 applications of the test flame. Materials that undergo shrinkage, elongation or melting are tested further using the same set-up except that the specimens of dimensions 153 mm x 153 mm are tested in both vertical and horizontal positions and with the flame applied from various positions. Materials are classified 94 5-V when none of the test specimens drip or burn with flaming and / or glowing combustion for more than 60 s after the fifth application of the flame. Finally, flammability ratings of VTM-0, VTM-1 and VTM-2 are applied to very thin materials and their test requirements are similar for solid materials which are given in Table 1.2.

Table 1.2

UL 94 vertical burning test
for classifying polymeric materials.

Classification	^a 94 V-0	^a 94 V-1	^a 94 V-2
Total flaming combustion for 10 flame applications (maximum, seconds)	50	250	250
Individual flaming time (maximum, seconds)	10	30	30
Glowing combustion time (seconds)	30	60	60
Drippings that flare up	None	None	Allowed but must only burn briefly

a : The same requirements apply to the vertical burning test for very thin materials. In this case, the flammability ratings are 94 VTM-0, VTM-1 and VTM-2.

1.2.2.3. Ignitability Tests.

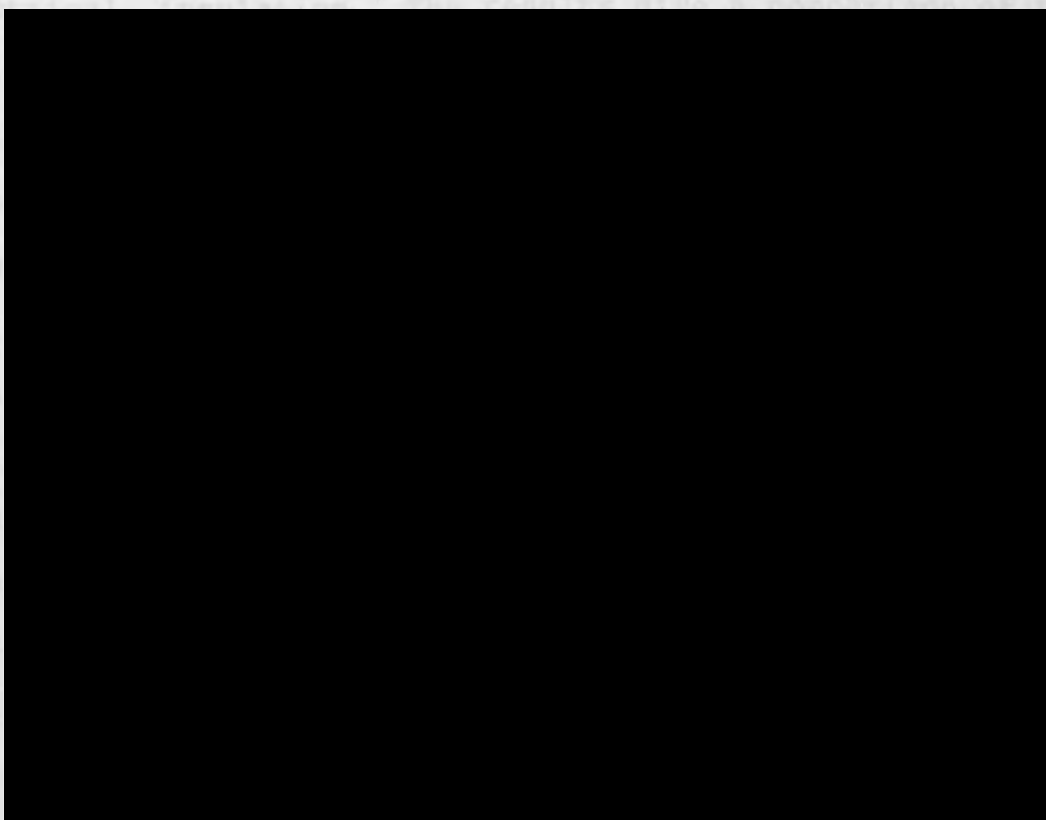
Most organic materials will ignite if they are provided with a sufficient quantity of heat in the presence of a suitable amount of oxidant for a sufficient period of time. If all but one of these conditions are kept constant, a comparative study of the ease with which some of these materials ignite can be achieved. Thus ease of ignition can be evaluated from the amount of heat required under fixed conditions of oxygen concentration and time; from the amount of oxygen required under fixed conditions of heat and time; or from the amount of time required under fixed conditions of heat and oxygen concentration.

ASTM D1929 : Test method for ignition properties of polymers.

This test, sometimes called the Setchkin test, provides a small-scale laboratory test for the determination of the self-ignition and flash-ignition temperatures of polymers using a hot-air ignition furnace as a heat source (Fig. 1.14). The sample, in the form of pellets or sheets of polymer, is placed in a steel pan which can be raised and lowered to a given depth in the furnace by means of a support rod. Chromel-alumel thermocouples, T-1, T-2 and T-3, are situated in the test chamber in such a way that T-1 measures the temperature of the sample, T-2, that of the air flowing past the specimen and T-3, that of the heating coil. The test

Figure 1.14

Cross-section of the hot air ignition furnace for ASTM D1929.



procedure is quite complex but gives accurate and reproducible results.

ASTM D229 : Testing rigid sheet and plate materials used for electrical insulation.

This standard test consists of two tests which evaluate the burning rate and flame resistance of materials used for electrical insulation. The results give a comparison of the ignition resistance of materials and the extent of burning if ignition does occur. The first part of the test is intended primarily as a relatively simple control test for screening materials that are flame resistant. The samples, held in a horizontal position, are twice exposed to a gas flame for 30 s and are then classified according to the duration of sustained flaming combustion. Thus, the longer the specimen burns, the less flame-resistant it is. The second part of the standard is more complex and requires more precise control of test conditions. The materials tested may be compared for resistance to ignition by determination of ignition time and for burning, from the burning time. The sample is ignited with a spark generated from a heating coil of nickel-chromium wire maintained at $860 \pm 5^{\circ}\text{C}$ and situated close to the sample. The ignition time is recorded as the time taken for the spark to cause ignition. The spark is left for another 30 s and the burning time is then the time for which the sample continues to burn after removal of the heat source.

1.2.2.4. Heat Release Tests.

These tests provide a measure of the amount of heat produced by the material in the process of burning. This measure is generally relative and is used simply for purposes of comparison with other materials.

There is no national standard test specifically designed for measuring heat contributions but both the ASTM E84 25 ft tunnel test and the ASTM E162 radiant panel test do in fact determine the temperature rise of the resulting product gases. They are essentially tests for surface flame spread and ASTM E84 will be described later.

U.S. Factory Mutual Engineering has developed a test which uses a calorimeter with a 1200 mm x 1200 mm sample mounted on its roof. The sample is exposed to the main fire exposure burners fuelled by gasoline. After the sample is burnt, it is replaced by a non-combustible material such as asbestos and the burners, fuelled by propane this time, are adjusted to reproduce the time-temperature curve produced by the burning specimen. The extra heat added then equals the heat contributed by the original combustible specimen.

The U.S. National Bureau of Standards has also devised a heat-release rate calorimeter which uses a combustion chamber lined with three side walls which are gas-fired

ceramic radiant panels and the temperature of which can be varied between 627 and 1027°C to produce the desired irradiation of the specimen. The specimen is held vertically at the centre of the combustion chamber with its front surface exposed to the radiant panels and its back surface cooled by a water-cooled brass block, simulating a construction material such as a wall in a burning room. Air for combustion passes up through the porous plate in the floor of the combustion chamber. The hot gases from the combustion chamber then pass into the control chamber. The temperature of the gases entering the mixing chamber situated above the control chamber is kept constant by controlling the gas flow into the auxiliary burner in the control chamber. The heat produced by the burning specimen is compensated by a reduction in the heat produced by the burner.

1.2.2.5. Fire Performance Tests.

These tests are generally used to classify materials under actual use conditions. They generally require large samples and test equipment and can be very expensive to carry out.

ASTM E84 : Method for surface burning characteristics of building materials.

This test, also known as the Steiner Tunnel Test, is used to evaluate rates of flame spread, fuel contribution and density of smoke formation under realistic fire conditions with known heat input. The apparatus consists of a 7.6 m long tunnel with a 450 mm x 300 mm cross-section. The sample, 7.3 m x 0.5 m, is mounted on the roof and exposed to flames from two gas burners situated at one end of the tunnel for 10 min, while the maximum extent of flame spread and the temperature down the tunnel are observed. Smoke evaluation and heat contribution from the sample are measured by a photo-electric cell and thermocouple installed in the exhaust stack downstream from the test sample. The flame spread is calculated on an arbitrary scale upon which asbestos board and red oak have been assigned values of 0 and 100 respectively. One major deficiency of this test is that highly flammable polymers with a tendency to drip have been passed by this test as non-combustible. In spite of this drawback, this test will continue to be used to evaluate the flame spread and smoke emission of foamed polymers until a more meaningful test is developed.

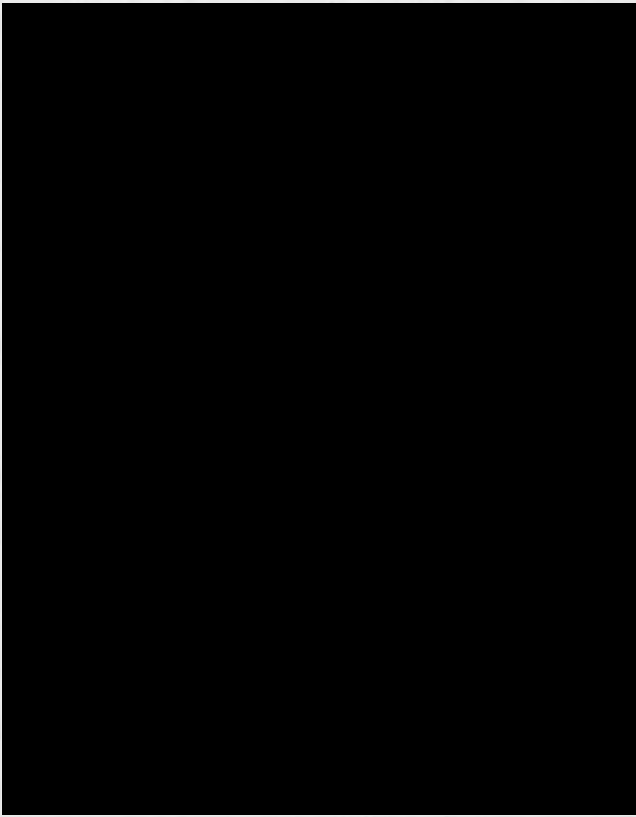
BS 476 Part 6 : Method of test for fire propagation of building materials.

This test provides a means of comparing the heat contribution of different combustible building materials, in particular, wall and ceiling linings. The apparatus, shown in Fig. 1.15, consists of a cast iron combustion chamber lined with asbestos millboard of a specified density, thermal conductivity and thermal capacity. It has one face that can be replaced by the specimen holder and an opposite face that has an air inlet and mica window for observation purposes. A thermocouple-lined steel chimney is situated at the top face of the chamber. The specimen is initially placed in position, the chamber is closed and the gas jets are ignited. After 165 s, the specimen is subjected to electric radiation lasting 135 s. At the end of this time, the power is reduced from 1,800 to 1,500 watts and held constant for 20 min. Temperature readings are obtained either continuously or at specified time intervals for the three samples and then plotted together with a calibration curve for the apparatus. The performance index (I) is defined as follows:-

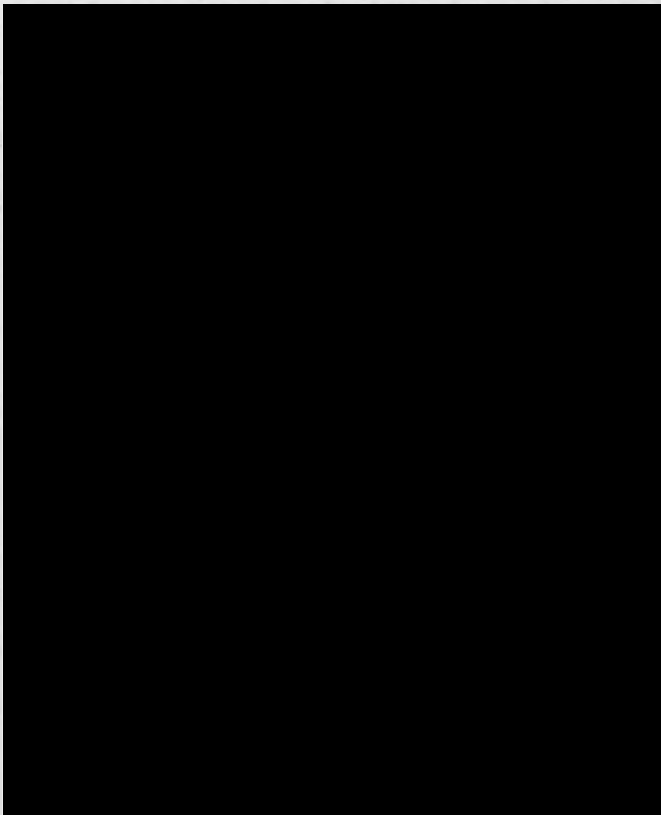
$$I = \sum_{0.5m}^{3m} \frac{T_s - T_c}{10t} + \sum_{4m}^{10m} \frac{T_s - T_c}{10t} + \sum_{12m}^{20m} \frac{T_s - T_c}{10t}$$

Figure 1.15

Test apparatus for BS 476 Part 6.



(a) Front



(b) Rear

where t is the time (in min) from which the readings are first taken. T_s and T_c are the temperature rise (in $^{\circ}\text{C}$) of the flue gases for the test sample and calibration sample respectively. In computations, only the positive values of $T_s - T_c$ are used.

$\frac{T_s - T_c}{10t}$

1.2.2.6. Oxygen Concentration Tests.

All the methods described so far involve the assessment of properties of a material in terms of its ignitability, spread of flame and heat release. Another important property of a polymeric (or indeed other) material that can be used to evaluate its flammability is the minimum oxygen concentration which is needed in an otherwise inert gaseous medium to enable sustained burning to take place after ignition. The oxygen index or limiting oxygen index (LOI) is defined as 100 times the ratio of the minimum amount of oxygen corresponding to sustained burning after ignition to the total amount of gas in the corresponding atmosphere :

$$\text{LOI} = \frac{\text{O}_2}{\sum_j [\text{gas}]_j} \times 100$$

The original concept for such a flammability test came from Simmons and Wolfhard (1957) and it was later developed and applied to organic polymers by Fenimore and Martin (1966a),

thus forming the basis of an ASTM standard.

ASTM D2863 : Method for minimum oxygen concentration to support candle-like combustion of polymers.

This test is a procedure for determining the relative flammability of a polymer by measuring the minimum concentration of oxygen in a flowing mixture of oxygen and nitrogen that will support flaming combustion. The test apparatus is shown in Fig. 1.16 and its layout is shown schematically in Fig. 1.17. The equipment consists of two sections: a gas-metering system and a test column. In the metering system, the flow of each gas is accurately measured before the streams are mixed and fed into the base of the column. The instrument is connected to cylinders containing oxygen and nitrogen via a two-stage regulator, and supply pressures of 170 kPa are used in order to achieve the required flow rates during the test. Two gas inlets at the rear of the instrument lead to two filters fitted with numerical controls, which enable the needle valve to be set very accurately. An on-off lever is situated adjacent to each control needle valve in each gas line. From the mixing chamber the homogeneous gas mixture passes directly through a flowmeter which is calibrated to read from 0-25 dm³ min⁻¹. A small by-pass flow is fed directly to a paramagnetic oxygen analyser which produces direct digital readout of the percentage of oxygen in the gas mixture.

Figure 1.16

Test apparatus for ASTM D2863

(for self-supporting (a) & non-self-supporting (b) polymeric materials).

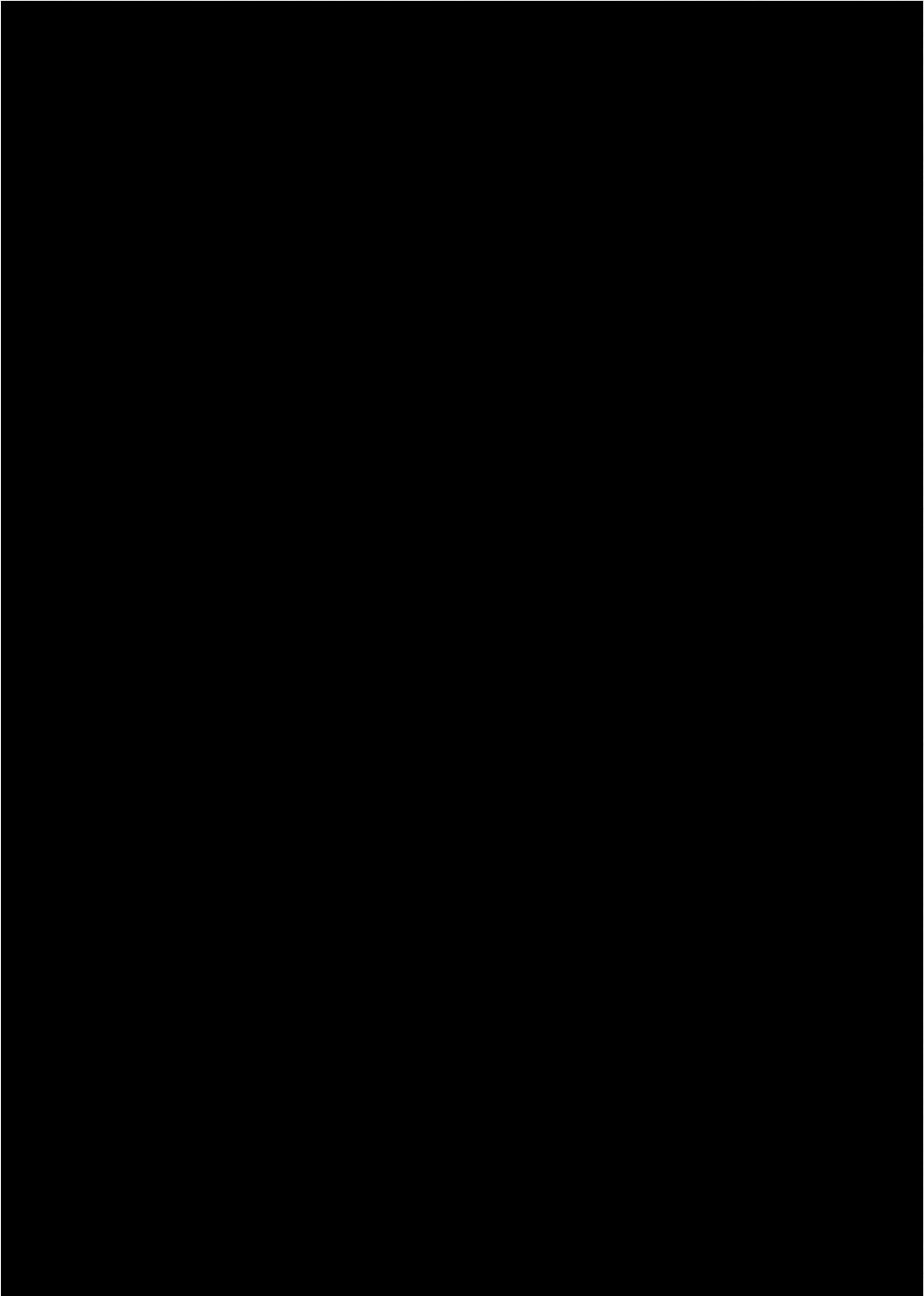


(a)

(b)

Figure 1.17

Schematic representation of the LOI equipment.



The test column is made of heat-resistant glass tubing of prescribed dimensions (75 mm minimum internal diameter and 450 mm minimum height). At the bottom of the column there are special entry ports which produce a laminar flow for gases entering the column, while a perforated metal screen is placed to catch any fragments or burning droplets formed during the combustion of polymer samples and to mix and distribute evenly the gases entering the tube. The vertically positioned specimen is supported by a clamp (Fig. 1.16a) or for thin films or thin sheets, by a frame (Fig. 1.16b), and exposed to an ignition flame at its top. A standard igniter (a copper tube with an orifice of diameter 1-3 mm, from which a gas flame 20-40 mm long can be obtained) is used to ignite the sample.

The total gas flow rate is maintained at $18 \text{ litres min}^{-1}$. If ignition occurs and the sample burns for 3 min or longer, the oxygen concentration is gradually reduced. Conversely, if the sample does not ignite or is extinguished in less than 3 min, the oxygen is gradually increased. This procedure is continued until an oxygen concentration is reached at which the flame is extinguished as near as possible to the specified time and length and this is taken as the LOI.

Table 1.3 shows values of LOI for some polymeric materials. The precision and reproducibility of the results as obtained by this LOI method have led to its wide acceptance as a test for flammability of polymers.

Table 1.3

LOI values of some polymeric materials.

Material	LOI	Reference
Polyurethane foam	16.5	Pitts 1972
Cotton	16-17	Tesoro 1975
SBR foam	16.9	Isaacs 1970
Polybutadiene foam	17.1	Isaacs 1970
Natural rubber foam	17.2	Isaacs 1970
Poly(methyl methacrylate) (Plexiglas)	17.3	Fenimore & Martin 1966a,b
Polyethylene (Allied Chem. 1220)	17.4	Fenimore & Martin 1972
Polyethylene (Phillips Marlex 5002)	17.4	Fenimore & Martin 1972
Polypropylene (Hercules Profax 6505)	17.4	Fenimore & Martin 1972
Polystyrene (Shell 325)	17.8	Isaacs 1970
Polyacrylonitrile	18.0	Van Krevelen 1976
SAN	18.0	Nelson & Webb 1975
Polybutadiene	18.3	Nelson & Webb 1973
ABS	18.3-18.8	Nelson & Webb 1975
Cotton (loosely woven)	18.5	Fenimore & Martin 1972
Polyisoprene	18.5	Van Krevelen 1977
Rayon	18.7-18.9	Isaacs 1970
Cellulose	19.0	Van Krevelen 1977
SAN	19.1	Isaacs 1970
Epoxy resin	19.8	Nelson & Webb 1975
PET	20.0	Imhof & Stueben 1973
Polyester fabric	20.6	Isaacs 1970
Phenolic resin	21.0	Nelson & Webb 1975
Poly(vinyl alcohol) (Dupont Elvanol 70-05)	22.5	Fenimore & Martin 1966a,b
Poly(butylene terephthalate)	23.2	Nelson & Webb 1973
Nylon-6,6	24-29	Nelson & Webb 1973
Nylon-6,12	25.0	Nelson & Webb 1975
Nylon-6	25-26	Nelson & Webb 1973
Wool	25.2	Benisek 1975
Polysulphone	30-32	Imhof & Stueben 1973
Phenol-formaldehyde resin	35	Van Krevelen 1977
Neoprene	40.0	Van Krevelen 1977
Alkyd resin (Phenco 1504-136636)	41.0	Isaacs 1970
Poly(vinylidene fluoride)	43.7	Fenimore & Martin 1972
PVC (rigid)	45-49	Nelson & Webb 1975
Poly(vinylidene chloride) (Dow, Saran)	60.0	Fenimore & Martin 1972
Polychlorotrifluoroethylene	95.0	Bauer 1978
PTFE (Dupont, Teflon)	95.0	Fenimore & Martin 1972

1.2.3. Measurement of Smoke.

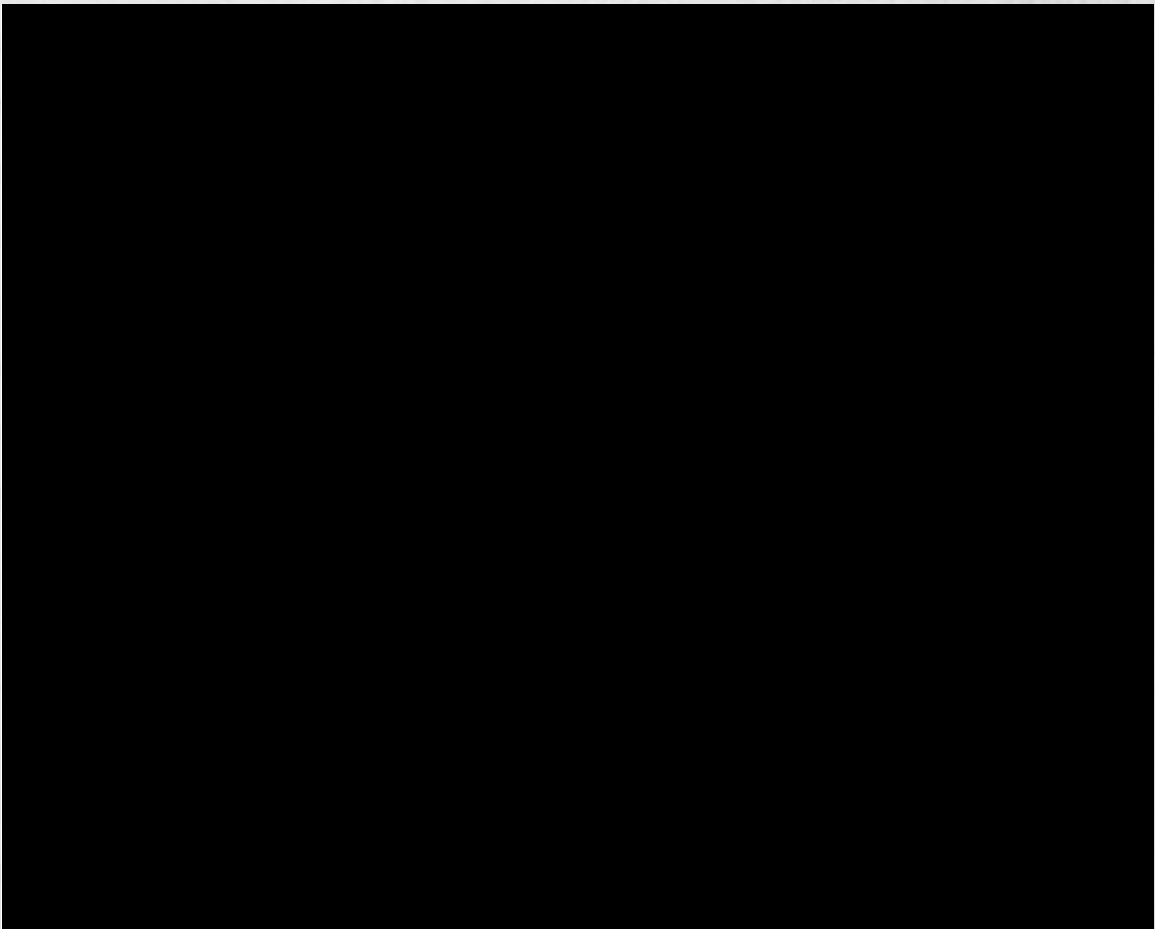
Tests for smoke evolution generally involve the measurement of the fraction of light absorbed or obstructed by smoke evolved from a decomposing or burning material. The degree of obscuration is a function of the number and size of the smoke particles, their refractive index, their rate of movement, the extent of ventilation, the distance of travel of light, the size and shape of the specimen, the humidity, the temperature, and the oxygen supply. Other methods involve the trapping and gravimetric determination of smoke particles evolved from the combustion or pyrolysis of polymeric materials.

ASTM D2843 : Test method for density of smoke from the burning or decomposition of polymers.

This method was first developed from the original Rohm and Haas XP2 apparatus. It measures the loss of light transmission when a standard specimen is burned in a test chamber under standard conditions. The apparatus used is shown in Fig.1.18. A specimen of dimensions, 25.4 mm x 25.4 mm x 6.2 mm, is supported between two metal screens and ignited with a propane burner operating at 276 kPa for 4 min. For materials that drip excessively, an auxiliary burner is provided to ensure the complete combustion of the drippings. The specimen is ignited at the same time as the

Figure 1.18

Test apparatus for ASTM D2863.



standard burner, the flame of which is directed at the centre of a metal dripping collector tray. Smoke density is measured by a photo-electric cell across a 305 mm light path. An illuminated "EXIT" sign situated at the rear wall of the test chamber is observed every 15 s in order to evaluate "visibility" in relation to the measured values of light absorption. In addition, the time taken for the sample to burst into flames, the time taken for the flame to be extinguished, and any general characteristics of the burning process e.g. melting, dripping or charring, are noted. The maximum smoke density (MSD), measured in conjunction with the corresponding time on the light absorption versus time curve, and the smoke density rating (SDR), which is the ratio of the area under the curve to the total area multiplied by a factor of 100, are then determined. High smoke-producing compositions will yield SDRs of 90% or greater, while low smoke-producing compositions will have ratings in the range of 30-40%.

ASTM E662 : Method for specific optical density of smoke generated by solid materials.

This method is basically the U.S. National Bureau of Standards' smoke density chamber test, which measures the attenuation of a light beam by smoke accumulation in a closed chamber due to non-flaming pyrolytic decomposition and flaming combustion. Tests BS6401 and NES711 are similar

to this standard test. A diagram of the test chamber is shown in Fig.1.19. A specimen of dimensions 75 mm X 75 mm is mounted within a holder which exposes an area measuring 65 mm x 65 mm. The holder can accommodate specimens up to 25 mm thick. For non-flaming combustion, an electrically-heated radiant energy source is used; this is mounted within an insulated ceramic tank and positioned to produce an irradiance level of 2.5 W cm^{-2} (averaged over the central 38 mm diameter area of the specimen). For flaming combustion, a burner with six small pilot flamelets is used to ignite the base of the specimen. This application of flame, in addition to the specified irradiance level from the heating element, constitutes the flaming combustion exposure. Light transmission is measured by a photometric system with a vertical light path. The specific optical density (D_s) is calculated from the light transmission measurements according to the equation:

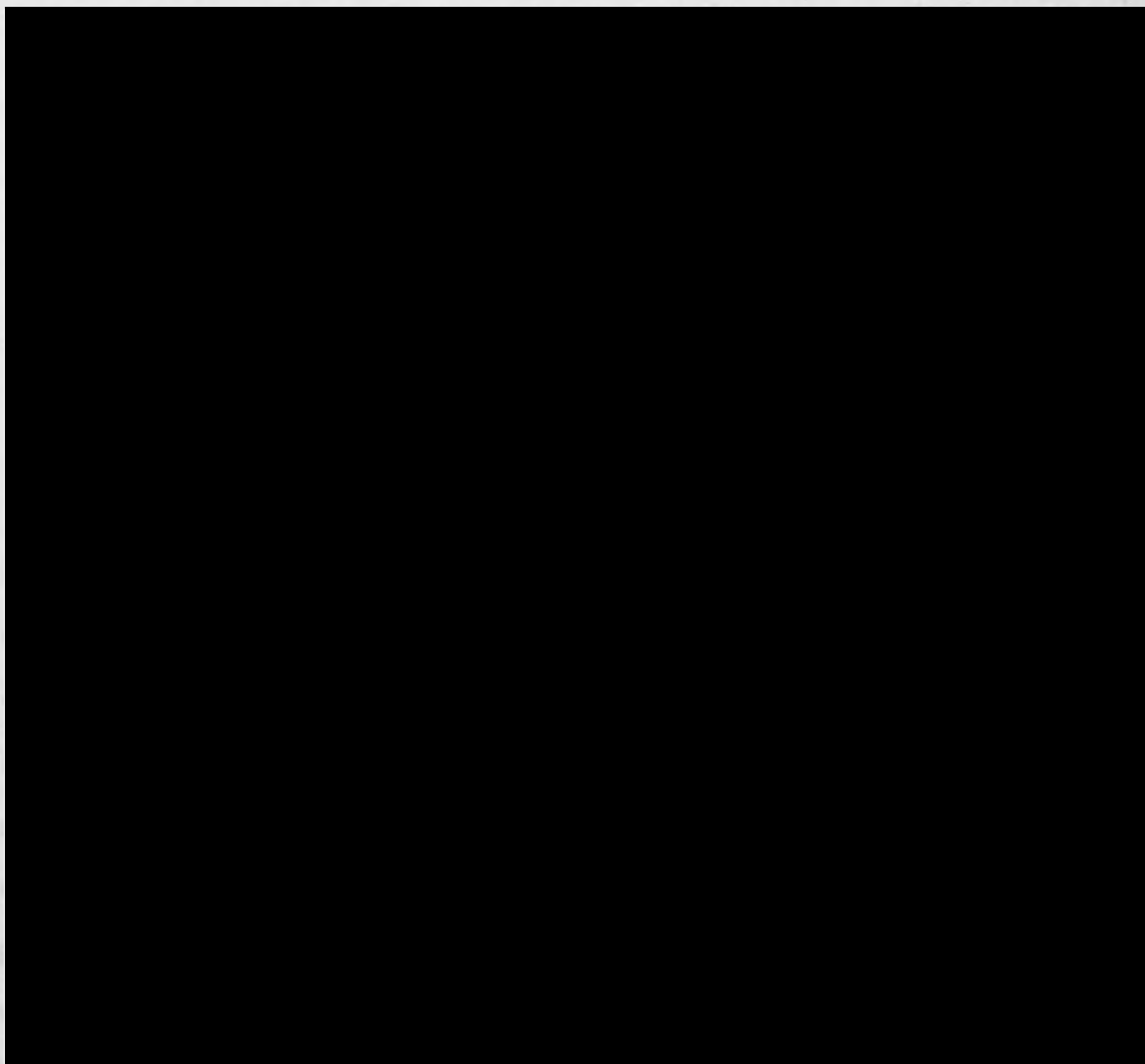
$$D_s = \frac{V}{LA} \log_{10} \frac{100}{T\%}$$

where T is the minimum transmittance, V is the volume of the chamber, L is the length of the light path and A is the area of the exposed specimen. This method is more versatile than ASTM D2843 in that it can measure the smoke density under flaming and smouldering conditions and allows the ventilation and air flow to be regulated. Another advantage

Figure 1.19

Test apparatus for ASTM E662.

ASTM D4109 - Method for gravimetric determination of smoke
particulates from combustion of polymeric
materials.

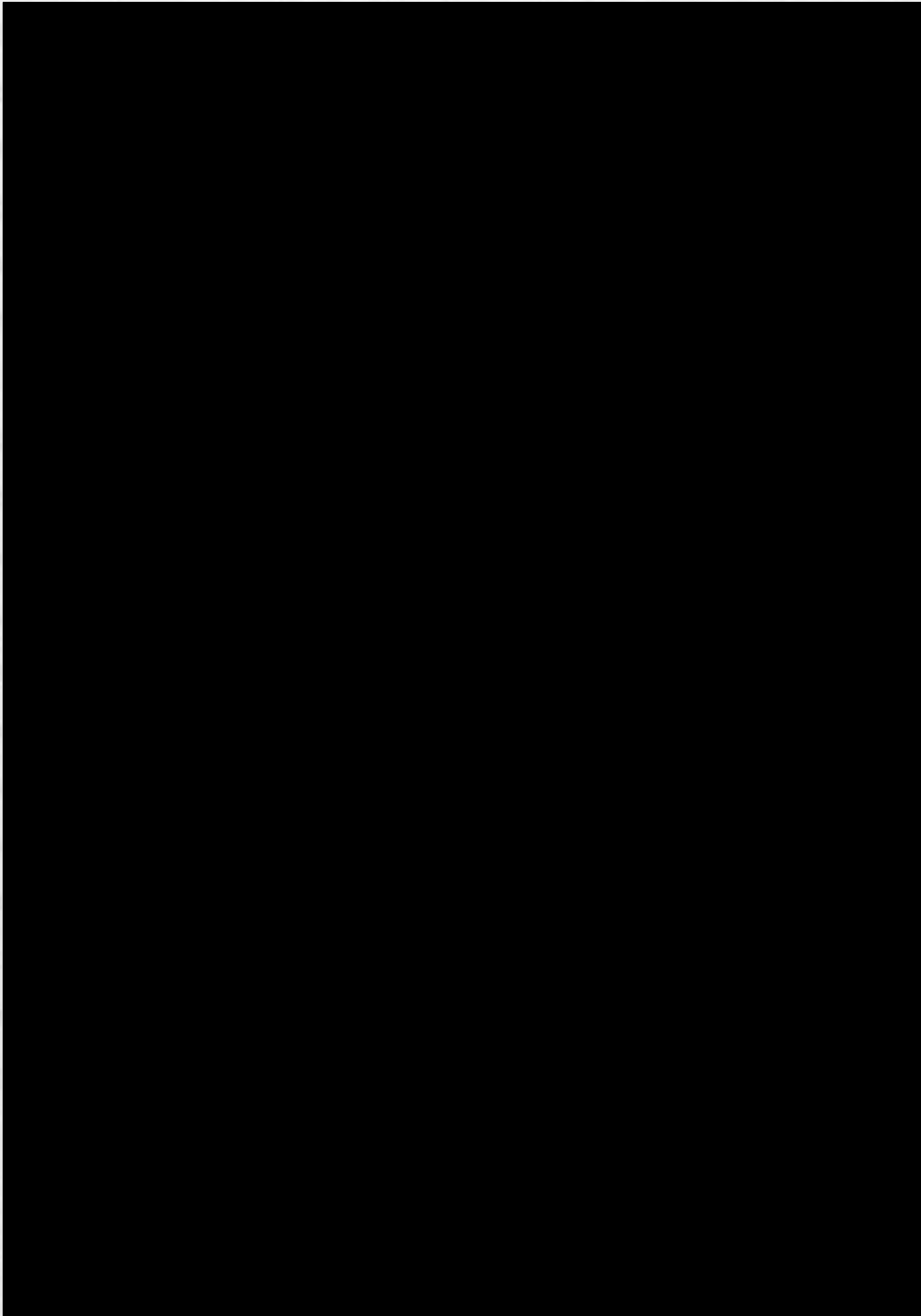


is its vertical photometer which reduces measurement errors as a result of smoke stratification.

ASTM D4100 : Method for gravimetric determination of smoke particulates from combustion of polymeric materials.

This method uses an Arapahoe system which consists of a combustion chamber, ignition source, chimney, particulate filtration system, a decharring roll-mill and a propane-nitrogen gas source (Fig.1.20). A standard size pre-weighed specimen in an enclosed test chamber is ignited with a propane-fuelled micro Bunsen burner for 30 s, with air for combustion passing through the chamber at a controlled rate. At the end of 30 s, the ignition flame is extinguished and the air flow is allowed to continue for a further 30 s. A high-capacity vacuum source above the combustion chamber draws the smoke particulates towards the filter system which collects the particulates in a pre-weighed glass-fibre filter. The remaining specimen and filter are then removed and weighed. Char is mechanically or manually removed from the burned sample and the sample is reweighed. Smoke particulate and char mass are calculated by difference and expressed as percentages of the total amount of sample burned.

1.3.4. Measurement of Toxicity



1.2.4. Measurement of Toxicity.

In Sections 1.2.1.5. and 1.2.1.6., the hazards of smoke and toxic gases have been discussed in some detail and the ways in which smoke can be measured have also been described in Section 1.2.3. It is important to remember that the test methods used in the measurement of smoke do not provide information about the toxic and irritating effects of smoke which, in some real fire situations, can be more hazardous than its light obscuration (Birky 1973). Indeed, the importance of such toxicity tests has been realised in recent years and, at present, no less than fifteen standard methods have been developed in various countries to determine the toxicity of combustion and pyrolysis products. A list of these is given in Table 1.4. However, only four of these test methods will be described in this Section. Most of these tests are applied to animals (rats or mice) and the results are currently reported in a variety of formats and chemical units. One of the most important parameters in the measurement of toxicity is the "end point", which may be irritation, incapacitation, morbidity, mortality or other manifestations of toxicity. The quantification of toxic potency may be expressed as :

LC₅₀, which is the concentration of a material in the atmosphere of the test chamber (mg/l) which when inhaled by animals will produce death in 50% of them in a specified period of time;

Table 1.4

Methods used to determine the
toxicity of combustion and pyrolysis products.

Test method	Reference
1. Carnegie Mellon Institute of Research (CMIR) method.	Gad & Smith 1983
2. Dow Chemical Company test method.	Potts & Lederer 1977
3. Federal Aviation Administration (FAA) method.	Crane <u>et al.</u> 1977
4. Federal Republic of Germany (DIN) method.	Hofmann & Oettel 1974 Kimmerle 1974
5. Japanese Combustion Toxicity test method.	Tsuchiya 1977
6. Harvard Medical School test method.	Robinson <u>et al.</u> 1977
7. McDonnell-Douglas Corporation test method.	Gaume 1980
8. National Bureau of Standards (NBS) method.	Levin <u>et al.</u> 1982
9. Radiant Furnace test method.	Alexeeff & Packham 1984
10. Stanford Research Institute International test method.	Dilley <u>et al.</u> 1979
11. University of Michigan test method.	Cornish <u>et al.</u> 1975
12. University of Pittsburgh (PITT) test method.	Alarie & Anderson 1979
13. University of San Francisco (USF) method.	Hilado & Schneider 1979
14. University of Tennessee test method.	Autian, Nunez & Hung 1976 Autian <u>et al.</u> 1978
15. University of Utah test method.	Hartzell & Packham <u>et al.</u> 1976 Farrer & Galster 1980

LD₅₀, which is the lethal dose producing death in 50% of animals in a specified period and expressed as weight of gases inhaled per kg of body weight;

LT₅₀, which is the time at which 50% of animals die at LC₅₀ sample weight, or the sample weight nearest above it;

RD₅₀, which is the concentration of smoke producing a 50% decrease in respiratory rate;

or time-to-incapacitation (t_i) or time-to-death (t_d).

Federal Republic of Germany (DIN) Method.

This German Draft Test (DIN 53436) uses a 1300 mm long quartz combustion tube with an outside diameter of 39 mm and a moveable annular electric oven which moves along the tube in the direction opposite to the flow of air. The test specimens, cut so as to have an equal volume or weight per unit length, are heated in the quartz tube at different constant furnace temperatures. The mixture of air and combustion products from the tube, cooled and further diluted by a secondary stream of air, pass through an animal exposure chamber. This DIN method may be used to assess the relative toxicities of combustion products of a material formed at different temperatures or to compare the relative toxicities of combustion atmospheres produced by different materials. One serious limitation is that the highest temperature that can be achieved in the furnace is 600°C,

although temperatures in real fires can easily exceed this.

Federal Aviation Administration Method.

This method utilises a Lindberg tube furnace which can be heated at a rate of $40^{\circ} \text{ min}^{-1}$ up to a limiting temperature of 800°C . An animal exposure chamber constructed of PMMA is connected to the furnace with two 1 in. glass tubes which provide a closed recirculation system for the thermal decomposition products. The recirculated system maintains an oxygenated atmosphere in the furnace, moves the products into the exposure chamber and dilutes and cools them. Subsequently, the design and operational parameters of this method have been modified and improved. The Lindberg furnace has been replaced by a 6 in. long, ultra-low mass, cylindrical electric heater and the diameter of the combustion tube has been increased from 1 to 2 in. This change allows a choice of constant or linearly increasing temperature profiles at rates up to $100^{\circ} \text{ min}^{-1}$. Tests can now be carried out for non-flaming and flaming combustion, with auto or pilot ignition. The sample size can be varied which means that the LC_{50} value can be determined. A photometer for continuous measurement and recording of smoke density has also been added.

University of San Francisco Method.

This method was developed by Hilado and Schneider (1979) and also uses a Lindberg horizontal tube furnace to decompose the material to be evaluated. A hemispherical 4.2-litre animal exposure chamber is constructed of PMMA and consists of a removeable upper dome section and a lower base section. This chamber is similar to that designed and developed by the National Aeronautics and Space Administration (NASA). The tests can be carried out at either fixed or linearly increasing furnace temperatures. In the fixed temperature test, the furnace is preheated to one of seven fixed temperatures at 100° intervals between 200 and 800°C . In the other case, the furnace is heated at a rate of $40^{\circ}\text{min}^{-1}$ until it reaches the maximum temperature attainable in the Lindberg furnace, which is 800°C . This temperature is maintained until the end of the test which lasts 30 min. This test system may be operated under either static or dynamic conditions. The latter is achieved by pumping a continuous flow of air into the otherwise closed end of the pyrolysis tube. The modified procedure allows varying quantities of materials to be evaluated and, in addition to time-to-incapacitation and time-to-death of the materials, the dose-response relationships and LC_{50} and LT_{50} values can be determined. This modified procedure has been referred to as the Dome Chamber Toxicity Test Method.

University of Pittsburgh Test Method.

This is the third test discussed in this Section to use the Lindberg tube furnace. Weighed samples are heated in the furnace from room temperature at a rate of $20^{\circ} \text{ min}^{-1}$ with air flowing through the furnace for the entire heating period. Before the thermal decomposition products enter the animal exposure chamber, they are cooled and diluted with cold dried air from a side stream, which enters the 60-cm quartz tube connecting the exposure chamber to the furnace. Each material was evaluated in a series of experiments in which either the quantity of material burnt or the air flow rate was varied in order to produce different smoke concentrations. In this test method, each material is evaluated for toxic effects of the combustion products by the use of five toxicity end points. These are sensory irritation, which is related to the RD_{50} value; lethality, expressed in LC_{50} values; stress, which is related to changes in the heart rate, blood pressure and blood vessel size; asphyxiant effects, produced by gases, such as carbon monoxide and hydrogen cyanide, and evaluated from characteristic alteration of the respiratory pattern of the animal as well as by the absence of body movement; and finally, systemic effects, which are evaluated from histopathological examination of major organs of exposed animals. The object of using a variety of end points is to get a better assessment of the separate and distinct effects

of different toxic components of smoke.

Summary of Toxicity Tests.

A summary of these four principal laboratory test methods is given in Table 1.5. Each of these methods has the capability for measuring carbon monoxide, carbon dioxide and oxygen and, depending on the nature or chemical structure of the test material, other selected gases also. It is apparent from this summary that there are many similarities, yet significant differences, among the four test methods. It is not possible, however, to relate the results of one test to those of another, because the combustion of a material and the production of toxic gases from it have been shown to be dependent on temperature (Gad & Smith 1983; Levin et al. 1982), presence of flame (Alexeeff & Packham 1984; Levin et al. 1982) and possibly also oxygen availability at the site of combustion and sample configuration. These factors may change the composition of toxic gases and influence the rate of sample weight loss, thus changing the animals' exposure to smoke. Furthermore, none of these test methods replicate the rapidly changing conditions and resultant combustion atmospheres produced in a real fire. However, each method will provide information on the toxicity of the combustion products evolved from various test specimens and it is up to experts to select the appropriate method or methods for any particular application and to interpret the data properly.

Table 1.5

Summary of principal toxicity tests.

<u>Method</u>	<u>Combustion device</u>	<u>Furnace temperature</u>	<u>Air flow</u>	<u>Quantity of material</u>	<u>Exposure mode</u>	<u>Exposure duration</u>	<u>Toxicity measurement</u>	<u>Chemical analyses</u>
DIN	moveable annular tube furnace	fixed, 200-600°C	dynamic	fixed, same volume or weight	head-only or whole body	30 min	a. LC ₅₀ (30 min + 14d)	CO, CO ₂ , O ₂ selected gas, COHb
FAA	tube furnace	fixed, 625°C	static, recirculating	fixed, 0.75g	whole body	30 min	b. t _i and c. t _d (and LC ₅₀)	CO, CO ₂ , O ₂ , HCN, selected gases
(modified)		(or linearly increasing, 200-800°C)		(varied to obtain LC ₅₀)				
PITT	tube furnace	linearly increasing to 600°C above 0.2% wt loss temperature except for determination of sensory irritation	dynamic	varied	head-only	30 min from 0.2% wt loss except for determination of sensory irritation	e. RD ₅₀ , LC ₅₀ (30 min + 10 min), f. SI, asphyxiation range, histopathology, g. LT ₅₀	CO, CO ₂ , O ₂ , HCN, selected gases
USF	tube furnace	fixed or linearly increasing, 200-800°C	static or dynamic	fixed, 10g	whole-body	30 min	t _i & t _d	CO, CO ₂ , O ₂ , selected gases
(modified)				(varied to obtain LC ₅₀)			(& LC ₅₀)	

a. LC₅₀; the concentration of a material in the atmosphere inhaled by animals which will produce death in 50% of animals in a specified period.

b. t_i ; time-to-incapacitation.

c. t_d ; time-to-death.

d. RD₅₀; the concentration of smoke that produces a 50% decrease in respiratory rate of animals.

e. SI ; stress index.

f. LT₅₀; the time at which 50% of animals die at LC₅₀ sample weight, or the sample weight nearest above it.

1.3. The Combustion of Organic Polymers.

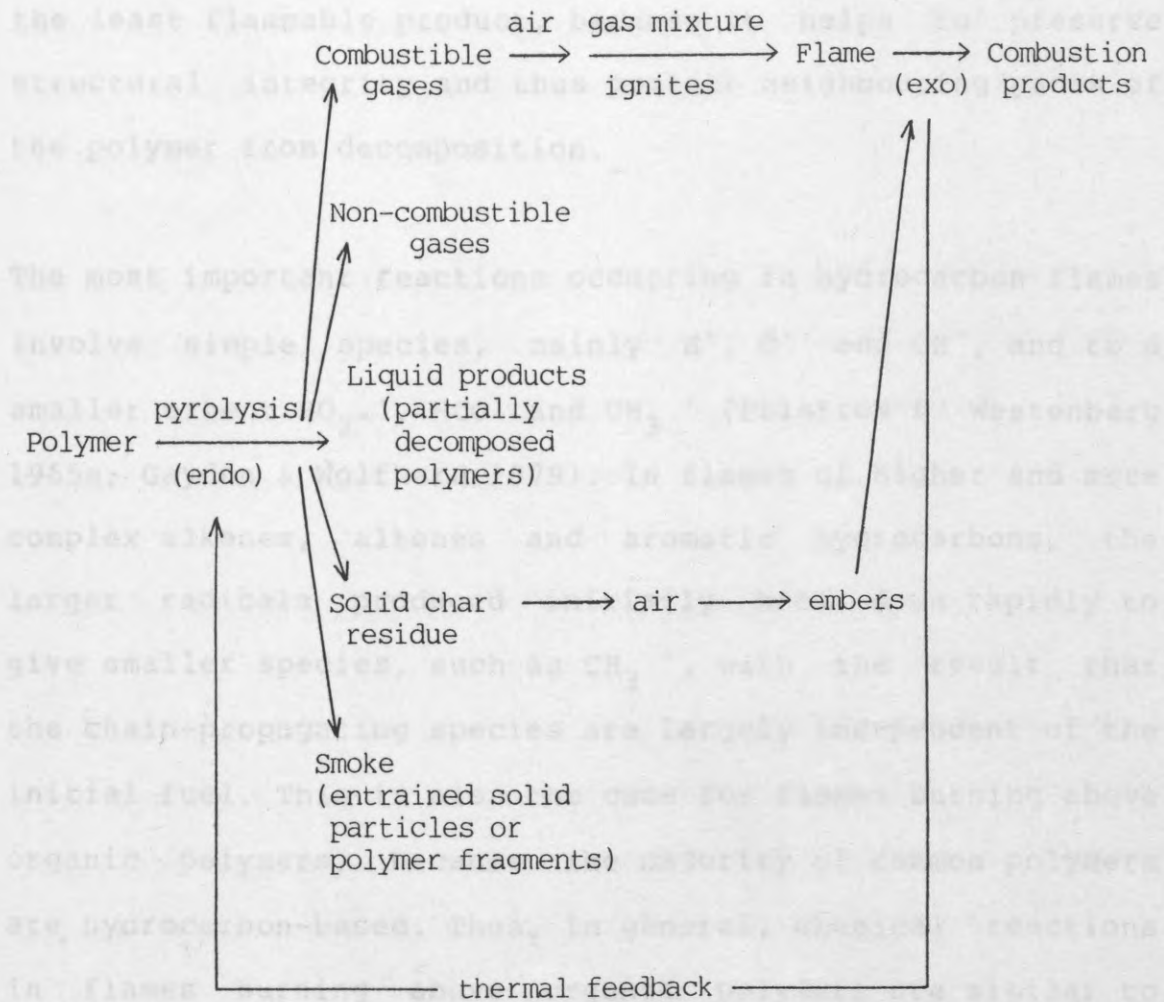
1.3.1. General Mechanisms.

1.3.1.1. Introduction to the Combustion Process.

All organic polymers will burn under appropriate experimental conditions and their combustion is invariably a complex process which involves a number of interrelated stages, some of which are still largely uninvestigated. A schematic diagram of the processes involved in the combustion of a polymer is given in Fig. 1.21. Thus in the sustained flaming combustion, which occurs with many thermoplastics, the polymer may be envisaged as first undergoing decomposition in the condensed phase to form volatile products, which mix with air and may then form a flammable mixture. This mixture enters the flame zone above the decomposing polymer where it burns in the gas phase, yielding the final combustion products, which are generally carbon oxides and water, and liberating heat. To complete the cycle, some of this heat is conducted, and to a smaller extent radiated, back to the polymer where it causes evolution of a further supply of volatile products. Thus, the production of large volumes of highly combustible gases will clearly facilitate the flaming combustion of a polymer, provided that the composition of the resulting gaseous fuel-oxidant mixture lies within the flammability limits.

Figure 1.21

The processes involved in the combustion of a polymer.



However, even the formation of non-combustible gaseous products tends to break up the polymer structure, so that small fragments of decomposing solid material become entrained in the escaping combustion gases, later appearing in the flame as soot. Liquid products are not as readily combustible as gaseous products but liquids tend to spread heat to adjacent parts of the polymer. A solid residue is the least flammable product, because it helps to preserve structural integrity and thus protect neighbouring parts of the polymer from decomposition.

The most important reactions occurring in hydrocarbon flames involve simple species, mainly $H^\cdot$, $O^\cdot$ and $OH^\cdot$, and to a smaller extent $HO_2^\cdot$, $HCO^\cdot$ and $CH_3^\cdot$ (Fristrom & Westenberg 1965a; Gaydon & Wolfhard 1979). In flames of higher and more complex alkanes, alkenes and aromatic hydrocarbons, the larger radicals produced initially break down rapidly to give smaller species, such as $CH_3^\cdot$, with the result that the chain-propagating species are largely independent of the initial fuel. This is also the case for flames burning above organic polymers, because the majority of common polymers are hydrocarbon-based. Thus, in general, chemical reactions in flames burning above organic polymers are similar to those in hydrocarbon flames.

However, the nature of the chemical reactions in hydrocarbon flames depends on the fuel : oxidant ratio. Thus, in fuel-

lean alkane-oxygen diffusion flames, $\text{OH}^{\bullet}$ radicals are the main species which attack the fuel (Fristrom & Westenberg 1965a). As the mixture becomes more fuel-rich, $\text{H}^{\bullet}$ atoms progressively replace $\text{OH}^{\bullet}$ radicals.

When the fuel is in considerable stoichiometric excess, the principal final products are carbon monoxide, hydrogen, water and solid carbon, some of which generally appear as soot. Products may also be formed containing heteroelements present in the original fuel.

Thus, in general, flames above burning organic polymers do not differ greatly in their chemistry from flames of simple hydrocarbons, although they are highly dependent on the nature of the gaseous oxidant.

1.3.1.2. Smoke Formation from Organic Polymers.

It has been seen in Section 1.2.1.5. that smoke formed in a fire can pose a serious threat to human life. It is clearly important to study the mechanism of formation of smoke before steps can be taken to achieve its suppression.

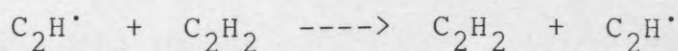
At low temperatures, combustion either does not take place or is severely limited. At higher temperatures and in the absence of sufficient oxygen, smoke constituents are formed, particularly as soot in the flame zone. Smoke is the name

given to the airborne solid and liquid products formed during the incomplete combustion of a mixture of fuel and air. Soot is the name given to the carbon-like particles in smoke.

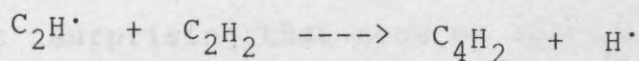
Numerous studies have been made of carbon formation in hydrocarbon premixed and diffusion flames (Clarke et al. 1946; Fenimore, Jones & Moore 1957). Since flames above burning organic polymers are usually hydrocarbon flames, these studies are relevant to the study of carbon formation from polymers.

One of the best descriptions of the overall mechanism of soot formation has been given by Lawson and Kay (1975) and is shown in Fig. 1.22. The initial aliphatic pyrolysis products are split into smaller fragments which, in the absence of oxygen, may react to form aromatic compounds or conjugated polyenes. Ultimately these intermediates undergo dehydrogenation and condense further. The conjugated polyenes can form soot by two routes; they may condense and undergo dehydrogenation to form soot directly, or they may cyclise to form polycyclic aromatic compounds, which then contribute to soot formation (Green et al. 1976). The aromatic pyrolysis products are converted to condensed polyaromatic compounds in the gas phase where they undergo dehydrogenation to form soot.

However, another theory of soot formation assumes that acetylene is first formed as an intermediate and that this gives soot via polyacetylenes. Acetylene is the commonest stable intermediate found in rich premixed hydrocarbon flames. Thus this compound or products derived from it are obvious precursors of soot (Porter 1953), although acetylene itself does not readily form soot. The primary product of acetylene pyrolysis is vinylacetylene (C_4H_4) (Cullis & Franklin 1964), which does not take part in the process of carbon formation (Cullis, Read & Trimm 1967; Cullis & Read 1970). Rich flames of acetylene also produce diacetylene (C_4H_2) and other polyacetylenes (C_6H_2 and C_8H_2), which are more likely to be involved in the formation of carbon than is acetylene itself. However, there is no evidence that the growth of polyacetylenic species is sufficiently fast to account for the almost instantaneous growth of carbon particles in sooting flames. The reason for this slow growth is that the hydrogen abstraction reaction :



competes effectively with chain-lengthening hydrogen transfer reactions such as:



(Cullis, Hucknall & Shepherd 1973; Cullis 1976). Besides,

most hydrocarbons give carbon more readily than does acetylene itself.

Another theory postulates that soot is formed from polyaromatics with acetylene as an intermediate. Benzene flames are known to give large amounts of soot. In premixed acetylene-oxygen flames, benzene is present together with diacetylene (C_4H_2) and polyacetylenes (C_6H_2 , C_8H_2 etc.) (Bonne et al. 1965; Homann 1967a,b, 1972; Homann & Wagner 1967). Various polycyclic aromatic hydrocarbons are also found in rich premixed acetylene and ethene flames (Crittenden & Long 1973). Polycyclic aromatic hydrocarbons, such as pyrene, phenanthrene and anthracene, have also been detected in soot from methane flames (D' Alessio et al. 1975, 1977). These relatively stable compounds probably eventually become adsorbed on the surface of growing soot particles. One of the attractions of this mechanism is the close similarity between the dimensions of the benzene ring and those of the carbon rings in graphite.

The extent of smoke formation is dependent on various factors, such as the nature of the fuel, the availability of oxygen, heat intensity, geometry of the sample and whether flaming or smouldering combustion is involved. Thus it is perhaps not surprising that none of the above theories can adequately describe the process of soot formation.

The tendency of a wide range of organic compounds to form soot in both premixed and diffusion flames has been quantitatively evaluated by Calcote and Manos (1983). Earlier work carried out by Clarke et al. (1946) showed that the amount of soot formed from hydrocarbon fuels in diffusion flames increases approximately in the order:

styrene (ABS) and styrene-butadiene copolymers
alkanes < alkenes < dienes < benzenes < naphthalenes

In most cases, the tendency to form carbon from a homologous series of organic compounds decreases with increasing molecular weight, although the reverse holds with alkanes. Aliphatic straight-chain compounds have a smaller tendency to yield carbon than the isomeric branched-chain compounds. Moreover, the more highly branched the compound, the greater is the tendency to form soot; the position of the branching does not seem to matter. Thus, although the C/H ratio is one of the principal factors controlling the tendency to carbon formation, the compactness of the molecules concerned also plays an important part.

The differing chemical structure of individual polymers results in the formation, during pyrolysis, of products which also contribute in varying degrees to smoke formation. Imhof and Stueben (1973) carried out an extensive investigation into smoke formation from a large number of polymeric materials and found that purely aliphatic

polymers, like polyethylene and polypropylene, which break down to yield mainly alkanes and alkenes, produce relatively little smoke. Polymers with aliphatic chains but aromatic side-chains, which decompose primarily to aromatic hydrocarbons, produce large amounts of smoke. These include polystyrene and its co-polymers, acrylonitrile-butadiene-styrene (ABS) and styrene-acrylonitrile (SAN) which, on pyrolysis, depolymerise to styrene monomers and oligomers. Polymers with aromatic groups in the main polymer chain, which undergo crosslinking and hence give rise to substantial amounts of carbonaceous char, yield intermediate quantities of smoke.

Thermoplastics, such as polyacrylates and polyacetals, produce limited amounts of smoke due to their high oxygen content. They form almost exclusively oxygen-containing, non-aromatic decomposition products even under smouldering conditions. Polyamides decompose by statistical chain scission to nitrogen-containing and oxygen-containing products which escape into the gas phase as ammonia, nitriles, amines, cyclic ketones and esters. In accordance with the finding that practically no aromatic products are formed, only small amounts of smoke are evolved.

It is well known that the presence of halogens considerably enhances smoke production and indeed poly(vinyl chloride) has the highest smoke-forming tendency of all organic

polymers. On pyrolysis, hydrogen chloride is first eliminated giving rise to unsaturated structures in the carbon chain. Some of the polyenes pass into the gas phase where they undergo dehydrogenation and cyclisation to form aromatic hydrocarbons which are known to contribute to soot formation. This effect is even greater in the case of plasticised PVC due the presence of large amounts of aromatic plasticisers. However, there is an optimum amount of chlorine which causes smoke formation. Thus poly-(vinylidene chloride) (PVDC) which contains 73.2 wt % chlorine produces less smoke than PVC which contains 56.8 wt % chlorine. This is because, on thermal decomposition of PVDC, hydrogen chloride is eliminated and leaves a virtually hydrogen-free carbon backbone which constitutes a residual char rather than smoke.

In contrast to thermoplastics, thermosets undergoing pyrolysis and combustion result in minimal smoke formation. The reason for this is that, due to their crosslinked structure, thermosets are liable to char and thus liberate few gaseous decomposition products. However, a few thermosetting plastics that contain aromatic structures do tend to give smoke. In particular, unsaturated polyester resins crosslinked with polystyrene bridges evolve styrene as the main decomposition product. Epoxy resins based on bisphenol A also have a fairly strong tendency to generate smoke.

Phenolic resins decompose by random chain scission to yield mainly formaldehyde, phenol and other oxygen-containing fragments, such as acetone and alcohols. They have a smaller tendency to give smoke because substantial amounts of carbonaceous char are formed on decomposition and only small amounts of aromatic compounds are liberated into the gas phase. Nitrogen-containing thermosets, such as urea and melamine resins, also have a strong tendency to char and hence smoke formation from them is small.

Polymers resistant to high temperatures contain mainly aromatic groups in the main polymer chain with no or few readily oxidisable side groups. Under the influence of heat, these polymers retain their structure and finally char to graphite-like networks. Only limited amounts of gaseous decomposition products are formed, so that no significant amounts of smoke are evolved during combustion of these materials. Polyethersulphones, polyimides and polyphenylene oxides are examples of high temperature-resistant polymers (Brydson 1975).

1.3.1.3. Toxic Gas Formation from Organic Polymers.

The formation of toxic gases is another danger associated with the combustion of organic polymers with or without the addition of flame retardants. Many, if not most, of the flame retardants used today are toxic as such. Whilst

complete combustion of organic materials leads to the formation of simple molecules, such as carbon dioxide, water, nitrogen oxides, sulphur dioxide and hydrogen halides, some of which are nevertheless very toxic, incomplete combustion leads to the production of more complex and noxious materials, as well as the simple but highly poisonous hydrogen cyanide and carbon monoxide. The sources of some of these harmful gases is given in Table 1.6.

NO _x and other oxides of nitrogen	Produced in the combustion of coal, lignite, oil, and other fuels containing nitrogen in large quantities (e.g., waste and cellulose).
H ₂	Produced in the combustion of organic materials containing hydrogen (e.g., coal, oil, and cellulose).
HCl	From the combustion of PVC, chlorinated polyethylene, and other chlorinated polymers.
Other halogen acid gases	From the combustion of halogenated polymers (e.g., PVC, PTFE, and other halogenated polymers).
SO ₂ , SO ₃ , CS ₂	From the combustion of sulfur-containing materials (e.g., coal, oil, and sulfur).
Acrolein	From the combustion of organic materials (e.g., coal, oil, and cellulose).
Isocyanates such as toluene-2,4-diisocyanate (TDI)	From the combustion of organic materials (e.g., coal, oil, and cellulose).

Table 1.6

Sources of some toxic decomposition
gases from the combustion of organic polymers.

Gas	Source
CO, CO ₂	From all organic polymers.
HCN	From the combustion of various organic polymers such as wool, silk, nylon, polyacrylonitrile and polyurethane in varying amounts.
NO ₂ and other oxides of nitrogen	Produced in small quantities from wool, leather and most other nitrogen containing polymers and in larger quantities from cellulose nitrate and celluloid.
NH ₃	Produced in small quantities from the combustion of wool, silk, nylon and melamine.
HCl	From the burning of PVC, chlorinated acrylics and materials containing chlorinated flame retardants.
Other halogen acid gases	From the combustion of fluorinated polymers such as polytetrafluoroethylene and flame-retardant materials containing bromine.
SO ₂ , H ₂ S, CS ₂	From vulcanised rubbers, wool and sulphur-containing polymers like polysulphones.
Acrolein	From the pyrolysis of polyolefins and cellulosics at lower temperatures (400°C).
Isocyanates such as toluene-2,4-diisocyanate (TDI)	From urethane isocyanate polymers.

1.3.2. Mechanism of Breakdown of Selected Polymers.

1.3.2.1. Poly(vinyl chloride).

When PVC is heated in nitrogen between 200 and 300°C, hydrogen chloride is rapidly eliminated, producing conjugated polyene sequences in the polymer chains. A second loss due to carbonisation of the dehydrochlorinated residue is observed between 400 and 450°C (Winslow, Baker and Yager 1956). During this stage, a vast array of aliphatic and aromatic hydrocarbons, of which benzene is one of the most abundant individual constituents, is also formed. The products of decomposition of PVC in helium and in air are shown in Table 1.7 (Tsuchiya & Sumi 1967). The results show that the main decomposition product is hydrogen chloride, almost all the chlorine in the polymer being converted to HCl. Benzene is formed in both inert atmospheres and air but CO and CO₂ are of course formed only in air. The highest concentration of CO is found at 600°C; the amount is smaller at 850°C on account of further oxidation of CO to CO₂. Other than CO and CO₂, the volatile decomposition products of PVC formed in the two different atmospheres appear to be qualitatively similar. Tsuchiya and Sumi (1967) suggest that the decomposition mechanism is essentially non-oxidative, although it is not clear from their work at which stage CO and CO₂ are formed.

Table 1.7

Thermal decomposition products of PVC.

Products (Wt.%)	350°C		600°C		850°C	
	He	Air	He	Air	He	Air
HCl	53.2	47.2	55.5	46.0	57.9	40.6
CO	-	1.0	-	35.6	-	16.6
CO ₂	-	1.7	-	40.8	-	54.8
H ₂	-	-	0.06	0.16	0.47	0.50
CH ₄	-	-	1.0	1.7	3.2	3.4
C ₂ H ₄	-	-	0.52	0.63	2.5	1.3
C ₂ H ₆	-	-	0.69	0.14	0.32	0.06
C ₆ H ₆	5.9	5.4	5.6	4.7	5.9	3.1
C ₆ H ₅ CH ₃	0.05	-	0.67	0.22	0.87	0.89
Residue	37.4	40.2	6.3	2.4	5.1	-

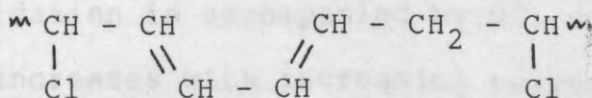
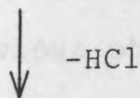
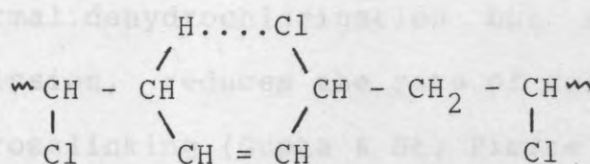
Reference: Tsuchiya & Sumi (1967).

The mechanism of decomposition of PVC is still controversial. In addition to a free-radical mechanism, ionic and molecular mechanisms have been proposed. As support for a free-radical mechanism, the following observations have been advanced, namely: (a) the rate of degradation is increased in the presence of radical initiators (Arlman 1954; Stapfer & Granick 1971); (b) the presence of radicals can be detected by ESR spectroscopy (Geddes 1967; Gupta & St. Pierre 1970) and (c) radical traps have a retarding effect (Papko & Padov 1974; Myakov & Troitskii 1962). However, using the same techniques, other workers have reported contradictory results (Baum 1961; Ayrey et al. 1974). The main support for an ionic mechanism arises from observations that: (a) the rate of dehydrochlorination in solution is influenced by the nature and dielectric constant of the solvent (Braum & Bender 1969; Zafar & Mahmood 1976) and (b) the degradation is catalysed by hydrogen chloride (Mayer et al. 1965), other acids (Wolkober 1962), strong bases (Bengough & Sharpe 1963; Shindo & Hirai 1972) and some metal salts (Baum 1961; Troitskaya & Troitskii 1966).

It is generally agreed that the hydrogen chloride evolved catalyses further degradation (Thallmaier & Braun 1967). Longer polyenes are formed in the presence of HCl than in its absence and it has been suggested, on the basis of this and other evidence, that the polyenes are involved in the

catalytic process, though the exact nature of the HCl catalysis is not known. Results of degradation experiments carried out in a tritium-labelled HCl atmosphere indicate a fast isotope exchange between the polymer and the labelled HCl, and a mechanism involving protonation of polyenes was proposed (Nagy et al. 1980).

Based on the observation that allylic chlorides with a cis configuration undergo faster HCl elimination than the corresponding trans isomers (Robinson et al. 1978), Amer and Shapiro (1980) proposed a unified mechanism for an overall process consisting of three stages. Initially, a single C=C double bond in a cis configuration is generated randomly via a radical or unimolecular process, followed by 1,4-elimination of HCl via a six-centred cyclic transition state, yielding a diene:



polymer. In addition to HCl, other volatile products, e.g. water, are formed.

The mechanism of the thermo-oxidative degradation of PVC is not known in detail, but the main features are as follows (Nagy et al. 1978): (a) primary loss of HCl and polyene formation are similar processes in the presence and absence of oxygen; (b) the polyene radicals are oxidised in a fast radical reaction; (c) the peroxy products formed decompose rapidly and (d) the radicals formed during the oxidation of polyenes and decomposition of peroxides attack intact monomer units and initiate further evolution of HCl.

1.3.2.2. Polystyrene.

Whereas the early steps in the thermal degradation of PVC have been extensively investigated, secondary processes, such as crosslinking, formation of aromatic volatiles and, in the presence of oxygen, oxidation of polyenes, have received little attention. Studies of the isothermal pyrolysis at 580°C of a mixture of non-deuterated and deuterated PVC (O'Mara 1970; 1977) show that benzene is formed by a mechanism involving intramolecular cyclisation. It has also been shown that other volatile aromatic products, like indene, naphthalene, toluene and methyl-naphthalene, are formed exclusively from non-crosslinked segments of the decomposing PVC chains (Lattimer, Kroenke and Backderf 1982). In the presence of oxygen, other reactions of the polyenes result in the formation of

peroxides and smaller amounts of hydroperoxides.

In spite of the considerable volume of work on the subject, the mechanism of the thermal and thermo-oxidative degradation of PVC is still not completely understood or established; a considerable amount of research is still being carried out to elucidate the fundamental processes in degradation. The ultimate aim for this research is to obtain a polymer with greatly enhanced stability. Detailed reviews of the degradation of PVC have been carried out by Tudos, Kelen and Nagy (1979) and Hjertberg and Sorvik (1984).

1.3.2.2. Polystyrene.

With polystyrene, no appreciable amounts of volatile products are formed below 300°C, although there is a well-defined decrease in molecular weight. Pyrolysis of polystyrene under vacuum at temperatures in the range 300-380°C results in the formation of 43% volatile materials composed mainly of styrene with traces of ethylene, benzene, toluene and ethylbenzene, and 57% of less volatile materials (Madorsky 1964). This latter fraction contains a mixture of dimers, trimers and tetramers with some remaining polymer. Using field ionisation mass spectrometry (FI-MS) and GLC, Brauman et al. (1983) have identified the volatile products of the radiant pyrolysis of polystyrene in nitrogen (Table 1.8). The volatile products are formed by a free-radical

Table 1.8

Volatile products from radiant
pyrolysis of polystyrene in nitrogen.

Product	Total detected (%)
Styrene	41.4
Dimer	11.7
Trimer	24.1
Tetramer	1.4
Pentamer	0.7
Hexamer	0.1
Heptamer	0.1
Toluene	trace
Ethylbenzene	trace
Benzaldehyde	trace
α -methylstyrene	trace
Total	79.5

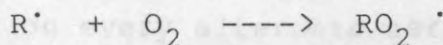
Reference: Brauman et al. (1983).

mechanism (Jellinek & Spencer 1952) and their rate of formation is proportional to the number of chain ends (Madorsky et al. 1962; Cameron 1967). The oligomeric fragments are produced by intramolecular hydrogen transfer and this is confirmed by the higher yields of monomers formed from poly(α -deuterostyrene), as compared with those from the unlabelled polymer (Wall, Brown & Hart 1955).

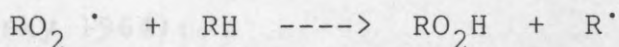
The mechanism of scission of the main polymer chain is not entirely clear. However, a unified mechanism, which assumed chain-end initiation, intermolecular transfer and bimolecular termination, has been proposed (Gordon 1957, 1961; Madorsky et al. 1962; Cameron, Meyer & McWalter 1978). It is interesting to note that polystyrenes formed by free-radical mechanisms are less thermally stable than those resulting from anionic polymerisations (Cameron & Kerr 1968) and the results indicate the presence of a small amount of very labile structures distributed randomly within the polymer chains. However, it has been shown that these structures are not head-to-head groups, peroxides, branch points, or unsaturated structures (Cameron & Kerr 1970; Cameron & McWalter 1982). It has also been proposed by Cameron et al. (1984) that anionically prepared polystyrenes undergo chain scission in a simple random manner. For thermally polymerised polystyrenes, very rapid scission of a small number of "weak links" occurs during the early stages of degradation. The later stages are believed to occur as a result of chain-

end initiation and subsequent unzipping (Grassie & Kerr 1959).

In the presence of air, however, very much higher rates of degradation are observed (Jellinek 1952). Oxidative degradation of polystyrene is a free-radical reaction, the rate of which is strongly influenced by light, heat, oxygen concentration and impurities. The main propagation occurs in two steps:



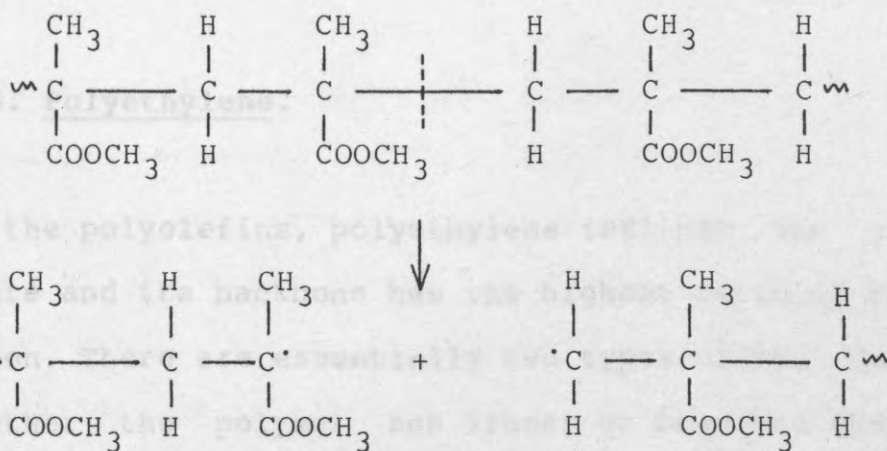
and



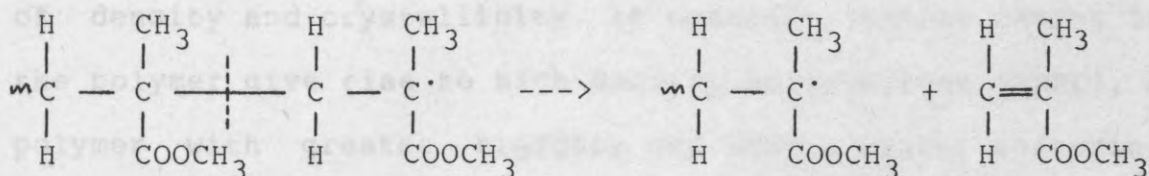
Decomposition of the hydroperoxide is catalysed by metal ion impurities and this, together with the chain reaction itself, is responsible for the high rate of polymer oxidation. Infrared analysis of thermally oxidised polystyrene has shown the presence of ketones, esters or peroxides, as well as of ether or hydroxy groups (Beachell & Nemphos 1957). A large number of volatile products are found, including water, carbon dioxide, carbon monoxide, hydrogen, styrene, xylenes and ethyl, propyl and butyl alcohols. The residue is highly crosslinked (Achhammer et al. 1952; Wall & Tyron 1962).

1.3.2.3. Poly(methyl methacrylate).

On pyrolysis in the temperature range 150-500°C, PMMA breaks down to yield almost 100% monomer (Votinov et al. 1942; Grassie & Melville 1947, 1949a,b). This mechanism involves random scission of the polymer chains, followed by a process of depolymerisation, where the monomers split off the chain ends one at a time (Grassie & Melville 1947, 1949a,b). The scissions are not accompanied by hydrogen transfer at the site of scission on account of steric hindrance of the CH₃ and COOCH₃ groups on every alternate tertiary carbon. Every scission therefore results in the formation of two free radicals (Madorsky 1964):



The free radicals then unzip to yield monomers:



Once formed, the free radicals undergo a rapid succession of β -scission reactions before they have a chance to vaporise. Thus only monomer is formed.

The thermo-oxidative decomposition mechanism of PMMA, on the other hand, is not fully understood. However, it has been reported that oxygen accelerates degradation, probably by the formation of peroxides and hydroperoxides (Bresler et al. 1958). Recent studies showed that the thermo-oxidative degradation of PMMA is greatly affected by impurities (Kashiwagi et al. 1985). Using purified samples, Kashiwagi et al. (1985) found that oxygen stabilises PMMA at low temperatures (200-250°C) but destabilises it at higher temperatures (300-350°C).

1.3.2.4. Polyethylene.

Of all the polyolefins, polyethylene (PE) has the simplest structure and its backbone has the highest ratio of hydrogen to carbon. There are essentially two types of PE, depending on whether the polymer has linear or branched chains. In low-density polyethylene (LDPE), the presence of branches reduces the ability of polymer chains to pack together closely and regularly and this in turn results in a lowering of density and crystallinity. In contrast, linear chains in the polymer give rise to high-density polyethylene (HDPE), a polymer with greater rigidity and thus a higher softening

temperature than LPDE.

In inert atmospheres, both types of PE start to crosslink at temperatures between 200 and 290°C. LDPE starts to decompose at 360°C, whereas HDPE starts to decompose at temperatures 20° higher than LDPE. Above 450°C, complete disintegration of both polymers occurs by random chain scission, yielding a spectrum of saturated and unsaturated fragments of varying molecular weights (Oakes & Richards 1949). The pyrolysis products of HDPE are given in Table 1.9 and a quantitative analysis of some of these products is shown in Fig. 1.23 (Tsuchiya & Sumi 1968). Owing to difficulties in the analysis of a large number of components present in small quantities, only C₁ to C₆ hydrocarbons have been identified.

From their studies, Wall and Straus (1960) proposed a free-radical mechanism for the thermal degradation of PE. In the initiation step, free radicals are formed by the random rupture of C-C bonds in the polymer chain. The presence of tertiary carbon atoms in LDPE drastically alters the probabilities of cleavage of the different C-C bonds. Thus, those bonds in a β -position with respect to the tertiary carbon are more easily broken, so that many more random scissions occur compared with those in HDPE (Seeger & Barrall 1975). This explains why LDPE is less stable than HDPE.

Table 1.9

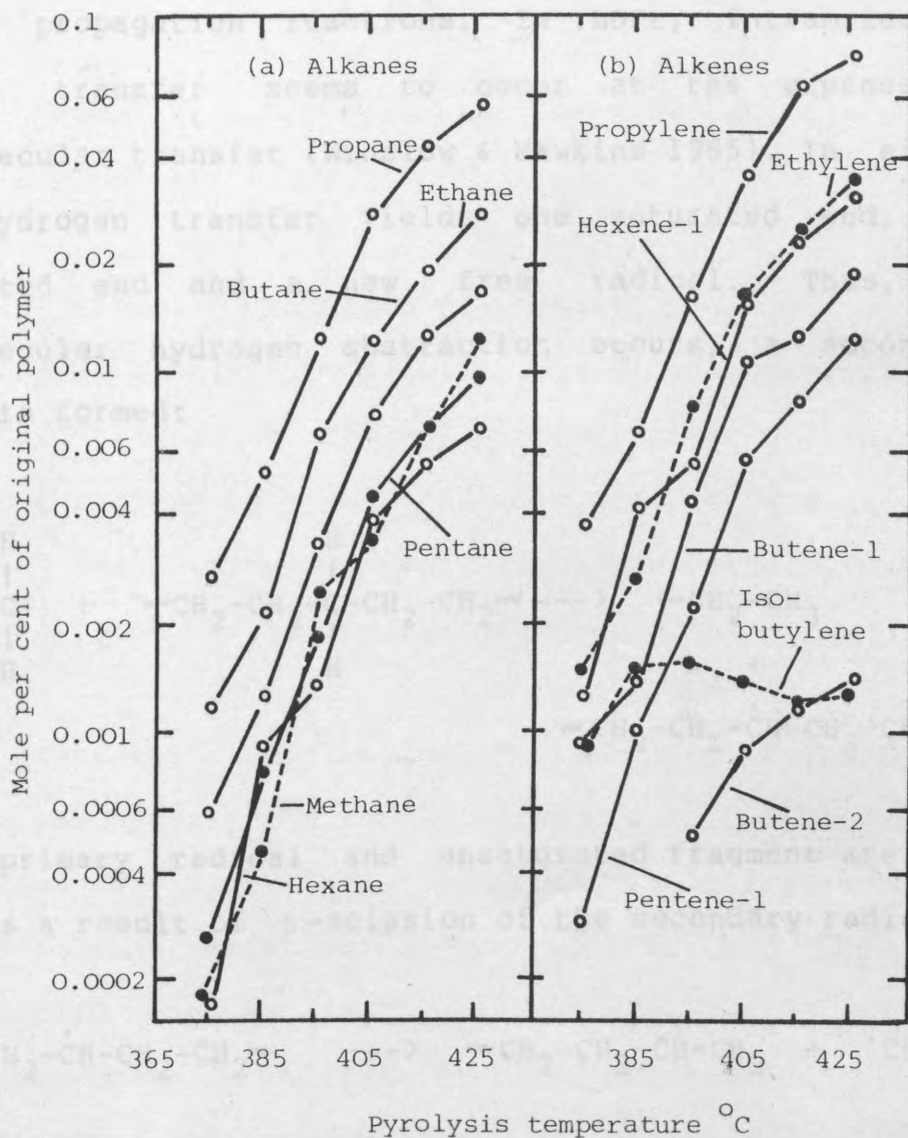
Identification of decomposition products of high-density polyethylene by gas chromatography.

Alkane	Alkene
methane	
ethane	ethene
propane	propene
2-methyl propane	2-methyl propene
butane	1-butene 2-butene, cis 2-butene, trans
2-methylbutane	2-methyl-1-butene 3-methyl-1-butene
pentane	1-pentene 2-pentene, cis 2-pentene, trans 1,3-pentadiene, cis 1,3-pentadiene, trans 1,4-pentadiene
2-methylpentane	2-methyl-1-pentene 4-methyl-1-pentene 4-methyl-2-pentene, cis
hexane	1-hexene

Reference: Tsuchiya & Sumi (1968).

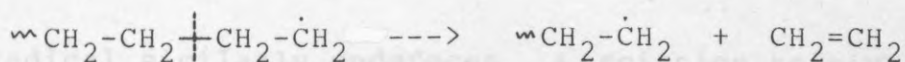
Figure 1.23

Quantitative analysis of some decomposition products of HDPE.

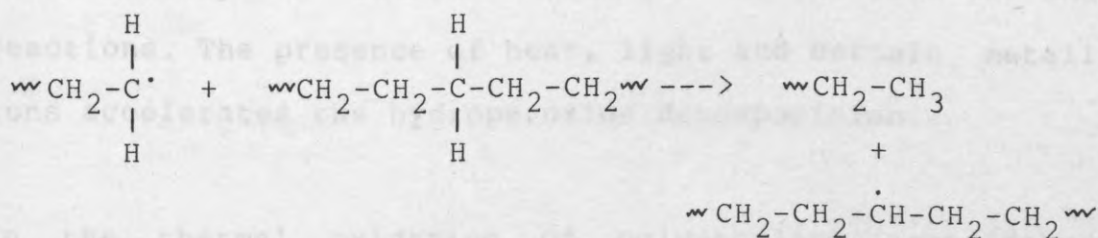


Reference : Tsuchiya & Sumi (1968).

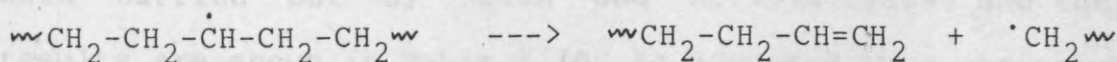
The initiation step is followed by a chain-propagation step, which results in the formation of monomers at free-radical ends of polymer chains:



However, hydrogen transfer reactions occur in competition with the propagation reactions. In LDPE, intramolecular hydrogen transfer seems to occur at the expense of intermolecular transfer (Winslow & Hawkins 1965). In either case, hydrogen transfer yields one saturated end, one unsaturated end and a new free radical. Thus, if intermolecular hydrogen abstraction occurs, a secondary radical is formed:

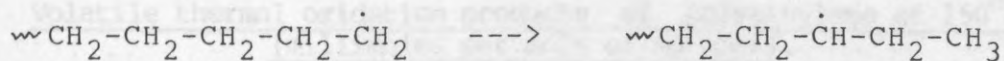


A new primary radical and unsaturated fragment are then formed as a result of β -scission of the secondary radical:

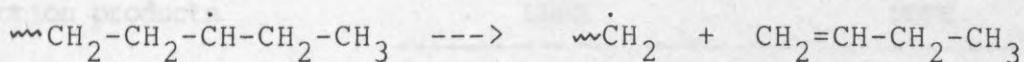


In the other case where intramolecular hydrogen abstraction

occurs, a secondary radical is formed:



This radical similarly undergoes β -scission to give:



Finally, termination occurs when two free radicals combine to form one polymer chain.

Like polystyrene, degradation of polyethylene is catalysed by oxygen (Carabine et al. 1968, 1971) and proceeds via a free-radical mechanism. The main product is a hydroperoxide which decomposes to free radicals to initiate the chain reactions. The presence of heat, light and certain metallic ions accelerates the hydroperoxide decomposition.

In the thermal oxidation of polyethylene, acetaldehyde, formaldehyde, acetic and formic acids and acetone are formed (Bevilacqua et al. 1964). Quantitative analyses of the volatile thermal oxidation products of LDPE and HDPE have been carried out by Reich and Stivala (1969) and their results are shown in Table 1.10. As expected, the principal volatile degradation products are water and carbon oxides.

Table 1.10

Volatile thermal oxidation products of polyethylene at 150°C
(millimoles per mole of monomer).

Reaction products	Time of oxidation (h)			
	LDPE		HDPE	
	4	8	4	8
Acids, considered on the basis of COOH	9-12	18-20	7-9	9-12
Esters, considered on the basis of OCOCH_3	None	None	None	None
Unsaturated compounds (Bromine number)	3.0-3.6	None	2.0-2.6	None
Peroxides, considered on the basis of active oxygen	0.6-1.0	1.0-1.1	0.5-0.6	0.4-0.5
Aldehydes:				
Formaldehyde	1.9-2.4	3.4-4.0	1.2-1.8	1.8-2.6
Acetaldehyde	1.4-1.5	1.2-1.8	0.9-1.4	0.5-0.8
Water	150-200	200-230	190-240	290-305
Carbon dioxide	13-15	-	20-25	-
Carbon monoxide	3-5	-	6-10	-
Hydrogen	-	-	3.7-4.3	-

Reference: Reich & Stivala (1969).

1.3.3. Techniques Available for Study of Polymer Decomposition.

1.3.3.1. Thermogravimetry.

There are essentially two types of thermogravimetric analysis (TGA) methods. One procedure involves the recording of the change in weight of the sample as a function of time at a constant temperature and is called isothermal thermogravimetry. The other, called dynamic or non-isothermal thermogravimetry, consists of recording the change of weight of the sample as a function of both temperature and time as the temperature is raised at a known heating rate.

Experiments involving isothermal weight-loss measurements ideally require instantaneous heating of the polymer sample to the desired temperature, which is impossible to achieve in practice. Thus, the major cause of error in this method is associated with the time taken for the sample to attain the required temperature and the weight losses occurring during the heating-up period. Most present-day equipment incorporates the continuous measurement and recording of weight. Thermobalances, containing sophisticated electronic parts, are normally based on the null-point principle. Basically, this entails the measurement of the force required to keep the sample in the same position in the furnace, thus ensuring isothermal conditions for

decomposition of the polymer. Often the time derivative of the sample weight is recorded simultaneously, this being known as differential thermogravimetry (DTG). Since the gaseous products of polymer decomposition may be corrosive, owing perhaps to the presence of additives in the polymer, it is sometimes necessary to keep such products away from metal parts and some modern commercial thermobalances are modified to achieve this.

Factors, such as sample size and geometry, shape of crucible containing the sample, heating rate and changing density of the ambient atmosphere, can affect the results. Reliable thermoanalytical information can generally be obtained only from measurements on small polymer samples; for use of such samples ensures a uniform temperature throughout the sample by avoiding anisotropic temperature gradients which might be caused by the exothermicity or endothermicity of processes involved or by slow diffusion of volatile products. When the kinetics of a reaction are determined under isothermal conditions, the normal kinetic equations are used and the activation parameters are obtained at different temperatures. Unlike the isothermal method, the non-isothermal method may require only one run to determine the temperature dependence of the rate of volatilisation of a sample over various temperature ranges. Non-isothermal thermogravimetry is also able to record any premature reactions during "heat-up" time, which would otherwise be

undetected if the isothermal technique was used. However, to obtain meaningful kinetic data from the non-isothermal method, very precise temperature control must be achieved. Facilities for using linear heating rates are available with most currently available thermobalances and can be employed for continuous recording of weight and rate of weight change in thermogravimetric analysis.

There are many different ways in which the kinetics of polymer decomposition can be deduced from thermogravimetric data (Wendlandt 1974). Critical assessment and comparison of the different methods have been carried out by various workers (Flynn & Wall 1966; Sestak 1966; MacCallum & Tanner 1970). Sestak (1966) has given major attention to the mathematical description of individual methods and has investigated both the experimental and analytical errors in the production of kinetic data. Inherent errors in several methods of mathematical analysis were evaluated by comparing the values of the kinetic parameters obtained from each method with the corresponding values for a theoretical TG curve computed from chosen kinetic data. The reason for the wide variation of activation energies of a given polymeric material obtained by various workers using different methods is due to the lack of uniformity in the experimental conditions. The procedural variables associated with thermal analysis also have a major influence on the mode of degradation, thereby altering the kinetics of reaction.

1.3.3.2. Differential Thermal Analysis (DTA) and Differential Scanning Calorimetry (DSC).

DTA is an example of a non-isothermal method in which the sample under test is heated in a crucible simultaneously with an inert standard substance, chosen to match the thermal properties of the material being investigated, which is placed in an identical crucible. Generally, when organic polymeric materials are tested, the reference crucible is left empty as it is almost impossible to find a suitable reference material. The reason is that, when polymers decompose, the composition of the sample, and hence its heat capacity, changes continuously. The thermal effects due to chemical reactions or phase changes occurring within the sample can be described by DTA by continuous measurement of the temperature differences between the two crucibles. If the object is to determine only changes in heats of reaction, e.g. the effects thereon of additives present in the polymer, then a comparison of the areas under the DTA peaks will yield the required information (Murphy 1964). If, however, the purpose is to measure absolute heats of fusion or volatilisation of a polymer, calibration needs to be carried out (Garn 1968), generally by use of a pure inorganic salt with a melting point as near as possible to the reaction temperature of the polymer. Peak areas corresponding to the polymer reaction can be compared with those representing thermal effects of known magnitude. The

slope of DTA curves is sensitive to sample characteristics, such as particle size, thermal conductivity, heat capacity, packing density, swelling or shrinking, mass of sample, nature of diluents and degree of crystallinity (Wendlandt 1974). This method is particularly useful for the determination of oxygen uptake by polymers prior to ignition. It can also provide information about the heat content of a polymer when it ignites.

DSC is similar to DTA but instead of measurements being made of the temperature difference between two crucibles, the quantity measured is the heat needed to be supplied to or removed from the sample in order to keep its temperature equal to that of the standard. A comprehensive review of the use of DTA and DSC in the study of polymers containing flame retardants has been carried out by Bhatnagar and Vergnaud (1983).

1.3.3.3. Thermomechanical Analysis and Dynamic Mechanical Analysis.

In contrast to the previous thermoanalytical methods which measure mainly chemical effects, thermomechanical analysis (TMA) monitors changes in a physical or mechanical property. This involves placing a flat quartz probe on the sample as the temperature is varied. As the sample expands or contracts, the probe will rise or fall, permitting

measurement of the coefficient of thermal expansion. Another method uses a pointed probe under load to detect the onset of deformation. These methods can also detect glass and melting transitions, especially those of components which are present in a polymer at low levels, like rubber in ABS or in impact polystyrene. The reason is that the thermal effect involves a small percentage change in the specific heat, while there may be an order of magnitude change in the elastic modulus. TMA also provides useful information on samples which cannot be isolated from a matrix, such as a thin polyethylene coating on a paper cup (Krause et al. 1983).

Dynamic mechanical analysis (DMA) uses a larger sample than TMA and is therefore usually operated at a low rate of heating. This technique measures the dynamic modulus and / or damping of a substance under oscillatory load, as a function of temperature. The sample is oscillated at its resonant frequency and an amount of energy, equal to that lost by the sample, is added to each cycle to keep the sample in oscillation at constant amplitude. The logarithm of this extra energy is called damping. The oscillating frequency decreases steadily as the temperature increases, but does so more rapidly as transition occurs. At each transition, whether of a glassy or crystalline nature, damping gives a peak. DMA is a very effective and sensitive method of detecting the presence of low levels of components

in a polymer matrix. ... full-scale fires, are available. At the end of the trapping TMA and DMA cannot, of course, provide sufficient information about the chemical changes occurring within polymers at temperatures high enough for extensive decomposition to take place.

1.3.3.4. Techniques used in the Analysis of Decomposition Products.

A better understanding of the mechanisms of polymer reactions and of the effects that modifications and additives have on such reactions can be achieved by analysing the nature and amounts of the various products formed. Thus, with both isothermal and non-isothermal techniques, the volatile products derived from the polymer can be analysed directly by means of gas chromatography (GC) and / or mass spectrometry (MS). However, the main drawback of direct analysis of degradation products by MS is that it can be applied only to degradation under vacuum. Furthermore, unless high resolution MS is used, identification of products is limited to those that have unique mass spectral features and can be distinguished within a mixture. Nevertheless, it is also possible to incorporate into the basic thermal analysis equipment some suitable means of trapping or collecting the degradation products as they are evolved from the sample. Many different

types of trap, including some that can collect samples from full-scale fires, are available. At the end of the trapping period, the trap is removed and the contents are subjected to analysis. TGA-MS has been used in the study of a number of polymeric systems, including PVC, PMMA, polyurethane and polystyrene (Sakamoto et al. 1972; Kleineberg et al. 1974; Korobeinichev et al. 1975). Where the degradation is carried out under isothermal conditions, it is possible to monitor the evolution of products, normally the final reaction products, with time. However, if non-isothermal methods are used, the analysis yields a relationship between the evolved products and the temperature of degradation.

Pyrolysis-gas chromatography (PGC) is a convenient technique for the analysis of the volatile products formed from very small polymer samples. This technique involves heating the sample very rapidly to a given temperature simply to gasify it and the pyrolysis products are then analysed by GC. It has been shown that PGC can yield a characteristic chromatographic spectrum of the pyrolysis products of a sample, which can be used in its direct identification (Groten 1964).

Direct pyrolysis-mass spectrometry is another technique where the direct identification of a sample is possible from its "finger-print" spectrum. This technique is superior to PGC in that the mass spectrometer can analyse samples in the

microgram range and cuts down the analysis time from 1 or 2 hours to 1 to 2 minutes per sample. The most important point is that the ion source is under vacuum, and on account of the very small sample size, the pyrolysis products are able to leave the pyrolysis zone faster, thereby reducing the chances of secondary reactions.

With the development of fast-scanning mass spectrometers, the advantages of interfacing the techniques of gas chromatography and mass spectroscopy were soon realised. In principle, a gas chromatograph - mass spectrometer (GC-MS) system could take a complex mixture, separate it into its individual components and then analyse these individually. In polymer degradation studies, the gases are first trapped in a low-temperature or absorbent trap and then transferred to the injection port of the gas chromatograph (Gardner & Browner 1980). Thus, the thermal degradation of polymers under conditions of flaming combustion can also be studied. GC-MS is also used in the study of the kinetics and mechanisms of polymer reactions (Sykes & Young 1977).

Differential condensation is another analytical technique commonly applied to the separation of the volatile products of polymer degradation. It is a trapping method that separates volatile materials on the basis of vapour pressure. The system consists of a number of cold traps,

each kept at a different temperature and connected in series. Four or five traps are usually used and maintained at temperatures of 0, -45, -75, -100 and -196°C. The volatile products pass through the 0°C trap and all materials condensable at this temperature are collected. The remainder of the vapour then passes from one trap to another at a lower temperature until all the condensables are collected. At the end of the experiment, the contents of each trap are analysed. Subsequently, this method was improved and modified by McNeill (McNeill 1966, 1967; McNeill & Neil 1969; McNeill et al. 1977) and this technique is now called thermal volatilisation analysis (TVA). TVA involves the controlled heating of a sample in a tube under continuous evacuation. By constantly monitoring the pressure of the system, a Pirani gauge will detect an increase in the pressure when volatile products are evolved during the decomposition of the sample. The pressure rises and then falls as the volatile products are evacuated and / or collected in the cold trap. The pressure, as measured by the millivolt output of the Pirani gauge, is recorded as a function of temperature. Depending on the mechanism of degradation, one or more peaks may be observed. The main advantage of TVA over TGA is the efficient removal of products as they are formed, so that secondary reactions are prevented or at least minimised. However, the non-linear response of the gauges to pressure and variations in behaviour from one substance to another mean that

calibration must be carried out for each type of sample tested.

Besides all the methods described above, many general analytical techniques can be adapted to study the thermal behaviour of polymers. For example, gaseous products can be analysed by infrared spectroscopy and valuable information on solid residues remaining at the completion of thermal decomposition can be obtained from elemental analysis and X-ray diffraction analysis.

Additional information on the kinetics and mechanisms of polymer decomposition can also be obtained by studying the concentration and nature of flame species. One difficulty involved in the measurement of the concentration of such species is connected with their recombination at solid surfaces. However, three of the methods most widely used for such determinations are electron spin resonance (ESR) spectroscopy (Fristrom & Westenberg 1965b), MS (Hastie 1973b) and emission spectroscopy (Jessen & Gaydon 1967; 1969). The ESR method has been applied to many common species in flames, e.g. $H^{\bullet}$, $O^{\bullet\bullet}$, $OH^{\bullet}$, halogen atoms, etc., their relative concentrations being determined by comparison of their paramagnetic behaviour with that of stable species such as O_2 (Noda et al. 1980a,b; 1983a,b). The rate constants for initiation, propagation and termination reactions in solid polyolefins at moderate temperatures have

1.4. Flame Retardancy and Smoke Suppression.
been determined using ESR combined with infrared spectroscopic techniques (Garton et al. 1979).

1.4.1. Classes of Flame Retardants.

Further information about reactions of atoms and radicals involved in flames can be obtained by techniques, such as flash-photolysis or shock-tube studies, where these species can be generated under more favourable conditions for study of their reaction kinetics.

Thus, besides the various forms of thermal analysis, techniques such as MS, PGC, TVA, ESR, emission spectroscopy and flash photolysis are also available to elucidate the mechanisms of polymer combustion.

breakdown which leads eventually to the products involved in flame propagation. In general, however, materials resistant to high temperatures are difficult to produce. Very expensive to produce and often do not possess the necessary performance characteristics. The drastic growth in the synthetic organic polymer industry is due primarily to the cheapness, easy processability, wide range of properties and desirable physical and chemical properties of the industry's products. This approach is not usually feasible for a practicable one and, in general, additives are incorporated into the common organic polymers which are normally not flameable materials in order to confer flame retardancy.

1.4. Flame Retardants and Smoke Suppressants.

1.4.1. Classes of Flame Retardants.

It has already been seen (Section 1.3) that the burning of an organic polymer is a very complex process involving a number of interrelated and interdependent stages. It is apparent therefore that it should be possible, in principle, to inhibit the combustion of polymers at one or more of these constituent stages.

Thus, for example, polymers can be designed so that they are thermally very stable; this will prevent their initial breakdown which leads eventually to the products involved in flame propagation. In general, however, materials resistant to high temperatures are difficult to process, very expensive to produce and often do not possess the necessary performance characteristics. The drastic growth in the synthetic organic polymer industry is based primarily on the cheapness, easy processability, high versatility and desirable physical and chemical properties of the industry's products. This approach is not usually therefore a practicable one and, in general, additives are incorporated into the commoner organic polymers (which are nearly all flammable materials) in order to confer some degree of flame retardance.

The two main classes of flame retardants used in synthetic organic polymers are the reactive and additive types. Existing polymers can be modified by replacement of one or more of the unsubstituted reactant monomers normally used by a substituted monomer containing heteroelements with known flame-retardant properties. The substituted monomers are then known as reactive flame retardants and the heteroelements become an integral part of the resulting polymer structure. These new functional groups are incorporated directly into the polymer structure during the polymerisation process. The main advantage here is the permanence of the fire retardancy imparted. However, it is often difficult in this way to incorporate sufficiently large amounts of heteroelements into the polymer structure to give significant flame retardance. Reactive flame retardants are primarily used in unsaturated polyesters, epoxy resins and polyurethane foams.

It is also possible to have flame retardants which react with the polymer rather than with the monomer. In polymers such as cellulose, flame retardants are often grafted on by radiation. For example, cotton fibres exposed to high-energy radiation and then contacted with a solution of vinyl phosphonate oligomer and N-methylolacrylamide yielded a grafted product with good flame resistance (Arthur 1973; 1985).

In other cases, compounds known to confer some degree of flame retardance can be intimately mixed with existing polymers to provide an optimum balance of flame retardance, physical and chemical properties and cost. In this case, the compounds do not react chemically with the polymers and are known as additive flame retardants. The main advantage of this class of fire retardant is that the additive can be incorporated during the final stages of production of the finished material. However, some desirable additive flame retardants are not readily compatible with the polymers into which they are to be introduced, making incorporation difficult. In contrast to reactive flame retardants, migration of the additive flame retardant out of the polymer can occur, causing its effectiveness to decrease with time. Additive flame retardants are generally used for thermoplastics.

Both reactive and additive flame retardants often have deleterious effects on the properties of the polymers into which they are incorporated. Thus, mechanical properties of the polymer such as toughness, rigidity, elasticity and density may be changed adversely. Additives may also increase the susceptibility of the polymer to photochemical and thermal degradation. Other important characteristics such as electrical and optical properties may also be adversely changed.

1.4.2. Modes of Action of Flame Retardants.

1.4.2.1. Introduction.

Flame retardants can function in a variety of ways for both flaming and non-flaming combustion. It is difficult to ascribe a single mode of action to a particular additive, since the combustion process is complex and involves many individual stages which can occur simultaneously. Indeed, many flame retardants appear to be capable of functioning by several different mechanisms, often depending on the nature of the organic polymer.

Inhibition of flaming combustion can be effected both in the gas phase and in the condensed phase. In the gas phase, the flame retardant may cause a reactive gaseous compound to be released into the combustion zone where it interferes with the flame reactions, replacing highly reactive free radicals by less active ones. Alternatively, the flame retardant may evolve a fine "mist" of small particles which interfere with flame propagation by acting as "third bodies" which facilitate free-radical recombination and hence chain termination. In other cases, the flame retardant may, on decomposition, release relatively large quantities of an inert gas which dilutes the fuel and perhaps also decreases the temperature of the gaseous products, giving rise to a gaseous fuel-oxidant mixture no longer capable of flame

propagation. In other words, the effect of the diluent is to cause the composition of the mixture to fall below its lower flammability limit, so that flame can no longer propagate. In other cases, additives interfere with reactions in the condensed phase. Thus inert solids, generally known as fillers, exert a completely different mode of action when they are incorporated into polymers. When these solids are present in considerable quantity, they can, partly by virtue of their heat capacity, prevent polymers from reaching temperatures at which they undergo significant breakdown to yield combustible gaseous products. Fillers that undergo endothermic decomposition are even more effective. Flame retardancy can also be achieved by covering the surface of the polymer with a non-flammable coating which excludes the gaseous oxidant from the surface of the polymer and also helps to insulate the polymer from the source of heat, thus preventing its thermal decomposition. In some cases, a protective layer of foam-like char can be formed when certain compounds, initially incorporated into or coated on the surface of the polymer, react with other materials in the condensed phase at high temperatures. Such compounds are known as intumescent flame retardants. However, in other cases, where the non-flammable protective layer is applied directly onto the surface of the polymer, a non-intumescent coating is said to have been used.

Other additives act not by interfering with either gas-phase

or condensed-phase reactions but rather by preventing the transfer of the heat of combustion back to the unburnt polymer. Thus, if the burning melt of a polymer drips away, it can carry with it a substantial proportion of the heat which would otherwise be fed back to the polymer, causing further decomposition. Melting can be facilitated by compounds which promote depolymerisation of the polymer. Thus, if such compounds are incorporated into the polymer, they can effectively inhibit its combustion. In principle, ready melting decreases flammability but in practice, droplets of burning molten polymer may spread the fire. Another method of preventing combustion which is associated with heat transfer effects is to coat or construct the polymer in such a way that, when it burns, incandescent sections disintegrate from the original polymer. In effect, much of the associated heat is removed from the combustion zone. This mechanism is known as ablation.

In principle, it is possible to inhibit non-flaming (i.e. smouldering) combustion either by retarding or preventing the initial breakdown of the polymer to form char or by interfering with the further combustion of this char. Flame retardants which affect polymer decomposition would be expected to act in the condensed phase. The possible mechanisms are clearly similar to those which apply in the case of flaming combustion and may involve, for example, chemical inhibitors or inert fillers. Intumescent coatings

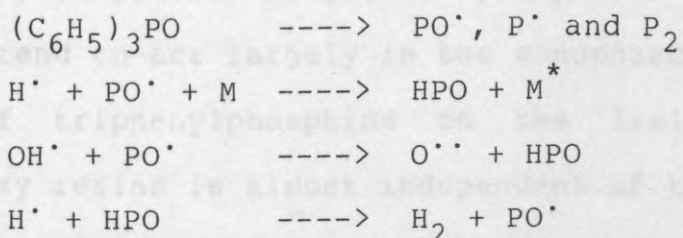
are all able to slow down or even completely prevent such decomposition. On the other hand, additives which interfere with the combustion of the carbonaceous char can do so by virtue of their effects on reactions taking place either in the solid phase or in the surrounding gas phase. However, the normal flame retardants used to prevent flaming combustion appear to have no effect on smouldering combustion. In general, only boric acid and phosphates are useful for preventing after-glow; they probably interfere with the solid phase reactions which lead to the formation of carbon oxides, inhibiting either the initial production of surface oxides or the highly exothermic conversion of CO to CO₂.

1.4.2.2. Phosphorus-based Flame Retardants.

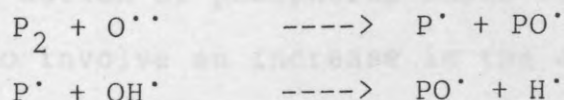
Inorganic and organic phosphorus compounds are used in the flame retardation of many polymers and both additive and reactive flame retardants are commercially available. Some typical phosphorus-based flame retardants are ammonium phosphate, triethyl and trioctyl phosphates, triphenyl phosphine oxide and didecyl phosphonate. Phosphorus compounds are used mainly in highly oxygenated polymers such as cellulose but their largest single commercial application is as plasticisers for PVC. Reactive phosphorus flame retardants are used almost exclusively in polyurethane foams where they have been found to be especially effective in

reducing flammability by encouraging char formation (Piechota 1965; Papa & Proops 1972).

Evidence for phosphorus-containing flame retardants being effective in the gas phase was provided by Hastie (1973c) and Granzow (1978). Hastie (1973c) reported that compounds such as triphenyl phosphine oxide decompose in methane and hydrogen flames to form P_2 , $PO^\cdot$ and $PO_2^\cdot$ as the main species, together with smaller amounts of $P^\cdot$ and HPO . A reaction scheme involving these species and leading to H atom recombination is as follows:



Other likely reactions are :



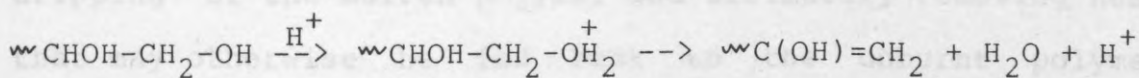
The species HPO has been identified spectroscopically in low-pressure fuel-rich hydrogen flames containing phosphorus (Fenimore & Jones 1964). This confirmed earlier observations by Palmer and Seery (1960), who found phosphorus compounds to be among the most efficient gas-phase inhibitors in

premixed flames.

Certain phosphate esters which appear to be stable under flame conditions (Gruntfest & Young 1961) may inhibit the combustion of non-hydroxylated polymers, in particular thermoplastics, by a largely physical gas-phase mechanism, in which oxygen is excluded by the formation of a heavy blanket of vapour over the flame (Benbow & Cullis 1972, 1973). In such cases, none of the phosphorus can be detected in the solid polymer residue.

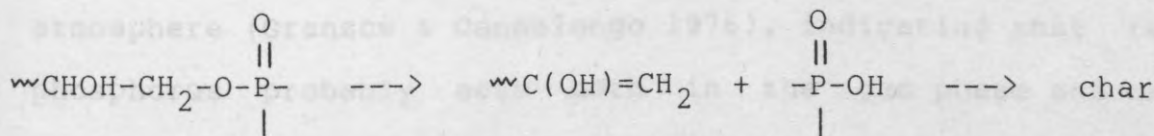
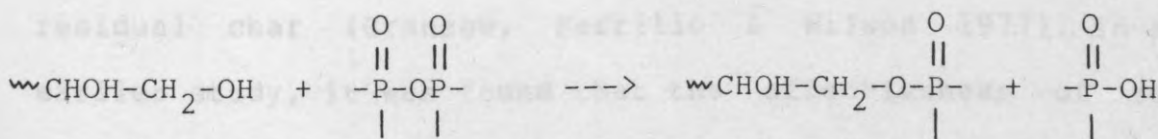
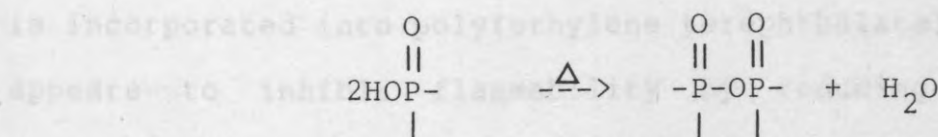
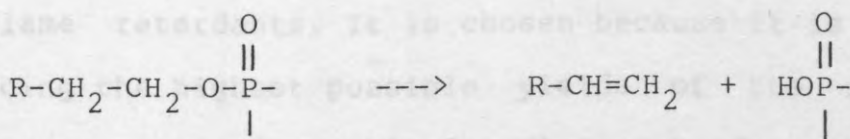
In highly hydroxylated polymers, phosphorus-based flame retardants tend to act largely in the condensed phase. Thus the effect of triphenylphosphine on the limiting oxygen index of epoxy resins is almost independent of the nature of the gaseous oxidant, which strongly suggests that this additive acts in the condensed phase (Martin & Price 1968). In poly(ethylene terephthalate) and poly(methyl methacrylate), the action of phosphorus-based flame retardants has been shown to involve an increase in the amount of residue formed and a decrease in the amount of combustible volatiles (Gruntfest & Young 1961; Avondo et al. 1978; Granzow 1978). As mentioned earlier, phosphorus-based flame retardants appear to enhance the formation of char in polyurethane foams and experiment shows that a substantial fraction of the phosphorus is retained in the char (Piechota 1965; Papa & Proops 1972).

In cellulosic materials too, phosphorus acids thermally generated by the breakdown of phosphorus-based flame retardants, alter the mechanism of decomposition of the polymer in the condensed phase. The principal products are changed from laevoglucosan and other volatile flammable compounds to carbonaceous char (Lyons 1970b). The formation of char involves either the loss of water in an acid-catalysed elimination reaction of the pyrolysing substrate:



(Danbow & Callis 1975).

or elimination via esterification by polyphosphoric acids (Hindersinn & Witschard 1978):



In both cases crosslinking then occurs, accompanied by skeletal rearrangement (Weil 1975).

Phosphorus-based flame retardants tend to be less effective in polymers like polystyrene, because such polymers do not readily undergo charring. However, there is evidence that some phosphorus-containing additives act by catalysing thermal breakdown of the polymer melt, thus enhancing dripping of the molten polymer and ultimately removing heat that may otherwise be fed back to the unburnt polymer (Benbow & Cullis 1975).

Recently, there has been considerable interest in the use of elemental red phosphorus to study the effects of phosphorus-based flame retardants. It is chosen because it is capable of producing the highest possible yields of the reactive phosphorus species responsible for flame retardance. When it is incorporated into poly(ethylene terephthalate) (PET), it appears to inhibit flammability by reducing the rate of thermal decomposition of PET and increasing the amount of residual char (Granzow, Ferrillo & Wilson 1977). In an earlier study, it was found that the effectiveness of red phosphorus was reduced when the sample was burned in a N_2O atmosphere (Granzow & Cannelongo 1976), indicating that red phosphorus probably acts both in the gas phase and the condensed phase. However, this is inconclusive because the possibility was not considered that the effective flame

retardants are oxidised phosphorus species, the formation of which is also sensitive to the oxidant. The results of separate studies of the flame-retardant action of red phosphorus in polyacrylonitrile, polyethylene and ABS gave similar indications (Peters 1979; Ballistreri et al. 1983b; Broadbent & Hirschler 1984). Phosphorus oxides produced during the combustion of polyacrylonitrile containing red phosphorus appear to act as strong dehydrating agents, promoting the carbonisation of the polymer substrate (Dany et al. 1976).

In summary, with hydrocarbon-based thermoplastics, phosphorus-based flame retardants tend to act primarily in the gas phase, either by a chemical mechanism, i.e. forming species that interfere chemically with the flame reactions, or by a physical mechanism, i.e. blanketing the flame with its vapour, according to their thermal or oxidative stability. With cellulose and other oxygenated organic polymers, phosphorus compounds exert their inhibiting influence mainly in the condensed phase by encouraging the formation of carbonaceous char rather than of flammable gaseous decomposition products.

1.4.2.3. Halogen-based Flame Retardants.

Both chlorine and bromine compounds are widely used as flame retardants for organic polymers. Bromine is generally more effective than chlorine owing to its weaker bonding to carbon. Neither fluorine nor iodine compounds interfere effectively with the combustion of polymers at the temperatures concerned. Fluorine is too strongly bonded to carbon, whereas iodine is so loosely bound that it is liberated even before the polymer starts to decompose. Aliphatic halogen compounds decompose at lower temperatures than their aromatic counterparts, so that they are generally more effective. Alicyclic halogen compounds are intermediate in their influence.

The flame retardant effectiveness of chlorine is evident in the relatively low flammability of chlorine-containing organic polymers. Poly(vinylidene chloride), which contains 73.2 wt % chlorine, has an LOI of 60 and PVC, which contains 56.8 wt % chlorine, has an LOI of 43. Chlorine compounds are widely used as reactive flame retardants in the manufacture of polyesters, epoxy resins and polyurethanes; epichlorohydrin, tetrachlorophthalic anhydride and 1,1-dichloroethene are some examples. Chlorine-based additive flame retardants are, however, used primarily in the form of chlorinated high molecular weight paraffins, derivatives of hexachlorocyclopentadiene, hexachloroethane and methyl pentachlorostearate.

Inorganic chlorine compounds are also available commercially and these are usually used to confer flame retardance on cellulosic materials. Examples of these are magnesium chloride, used in conjunction with magnesium oxide, aluminium chloride, ammonium chloride and zinc chloride. The mechanisms of action of these compounds have yet to be established. However, some of these are Lewis acids and they may act by catalysing dehydration of the cellulose.

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It is generally accepted that, when chlorine-based flame retardants are incorporated into thermoplastics, they act mainly in the condensed phase, probably as a result of their ability to cause dehydrochlorination of the chlorinated polymer and hence formation of char. Thus, measurements of the limiting oxygen indices and limiting nitrous oxide indices for chlorinated polyethylenes show similar dependence on chlorine content, suggesting that chlorine exerts its flame retardant influence primarily in the condensed phase (Fenimore & Martin 1966a; Fenimore & Jones 1966). Furthermore, addition of relatively large amounts of gaseous chlorine or hydrogen chloride to the atmosphere above the burning polymer did not affect the limiting oxygen index.

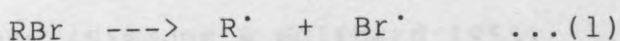
and the bromine does not abstract hydrogen from the fuel.

On a weight basis, bromine compounds are more effective than chlorine compounds but they are considerably more expensive and generally less stable both thermally and photo-

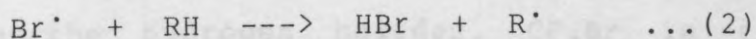
chemically. Bromine compounds, such as decabromobiphenyl, decabromobiphenyl ether, tetrabromobutane and hexabromocyclododecane, are used as additive flame retardants in organic polymers. Examples of bromine-based reactive flame retardants are 2,3-dibromo-1-propanol, tetrabromobisphenol A and tetrabromophthalic anhydride. Very few inorganic bromine compounds have been used but amongst these may be mentioned ammonium bromide, which is used mainly in cellulose (Pitts 1973).

Brominated flame retardants are generally considered to act largely through inhibition of gas-phase reactions (Fryburg 1950; Creitz 1970; Lyons 1970a; Avondo et al. 1978). The most widely accepted mechanism of action of bromine compounds is the release into the gas phase of hydrogen bromide which then inhibits the flame reactions by reacting with $\text{OH}^\cdot$ and $\text{H}^\cdot$ radicals responsible for the propagation of combustion.

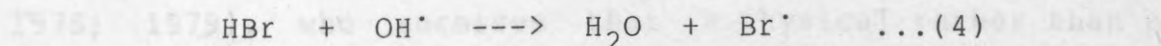
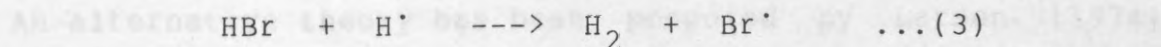
Initially, the flame retardant breaks down:



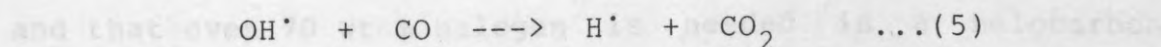
and the bromine atom then abstracts hydrogen from the fuel, RH , to form hydrogen bromide:



which in turn reacts with the chain carriers involved in flame propagation:



Thus the highly reactive $\text{H}^{\bullet}$ and $\text{OH}^{\bullet}$ radicals are replaced by the relatively unreactive bromine atom. The HBr consumed is regenerated as shown in equation (2). The removal of $\text{OH}^{\bullet}$ radicals has an additional inhibiting effect inasmuch as these radicals are involved in the very exothermic oxidation of carbon monoxide to carbon dioxide:



Although the mechanism was originally proposed to explain the inhibiting effect of halogen compounds on premixed hydrocarbon flames, its validity in polymer diffusion flames is supported by the fact that the order of effectiveness of different halogens as flame retardants is the same as in premixed flames (Garner et al. 1957), where such a mechanism is believed to operate (Simmons & Wolfhard 1955).

Despite the considerable amount of data supporting the gas-phase mode of inhibiting action of hydrogen bromide, it was found that halocarbons, such as CF_3Br , were more effective than the hydrogen halides. CF_3Br is thermally

stable at flame temperatures so that bromine atoms are not expected to be the primary decomposition product.

An alternative theory has been proposed by Larsen (1974; 1975; 1979), who surmises that a physical rather than a chemical mechanism lies behind the flame-retardant effect of bromine compounds. Re-examination of published data revealed that the relative effectiveness of the various halogens as flame inhibitors was directly proportional to the ratio of their atomic weights:

$$F : Cl : Br : I = 1 : 1.9 : 4.2 : 6.7$$

and that over 70 wt % halogen is needed in a halocarbon before any significant flame retardance is observed. Indeed, the effectiveness of halogen compounds in inhibiting combustion is believed to be dependent on the total amount of halogen present and not on its nature. For halocarbons containing over 72 wt % of halogen, the heat of combustion decreases with increasing halogen content, while the heat of volatilisation remains constant. The flammability limits were found to be a function of the heat capacities of the inert gas present and of the fuel or oxygen in excess of that required by the stoichiometry of the combustion process (Larsen 1975). The role of the halogen is therefore simply to increase the total mass of material which must be vaporised in order to give the same heat flux from the flame

to the fuel.

This theory receives support from the finding that the limiting oxygen indices of several types of polymer increase linearly with the total amount of bromine present but are independent of the structure of the additive and hence of the ease with which hydrogen bromide is liberated (Ravey, Fischler & Kramer 1978; Ravey & Fischler 1978).

Generally, halogenated compounds are more widely used in conjunction with other additives, such as phosphorus compounds and metal oxides, in particular, antimony trioxide, rather than on their own. Their effectiveness is also sometimes considerably increased by free-radical initiators, which cause depolymerisation of the hot polymer, giving a more fluid melt. Dripping occurs and takes with it heat that could otherwise be used to cause further decomposition of the polymer (Hindersinn 1966; Fenimore 1968).

There has been considerable speculation about the synergistic effect of phosphorus and halogens as flame retardants in polymers (Lyons 1970b). Originally, it was thought that phosphorus halides and oxyhalides might be formed and interfere in some way in the combustion process (Hilado 1974). Since they have higher boiling points and higher specific gravities than the hydrogen halides, it was

argued that the chances of their remaining in the flame zone to cause gas-phase inhibition would be enhanced. However, bond energy considerations do not favour the formation of such species (Lyons 1970b; Weil 1975). In addition, the reaction of alkyl halides with phosphonate esters was found to lead to a simple alkyl group exchange and the production of a new halogen compound rather than the postulated phosphorus halide. Without more experimental support, phosphorus-halogen synergism cannot be accepted. In general, it seems likely that the halogens cause some gas-phase inhibition which occurs in addition to the mainly condensed-phase mechanism involved when phosphorus compounds are used on their own (Weil 1975). The deviations observed can be accounted for by the inherent non-linearity of these systems.

The mechanism of action of antimony trioxide - halogen systems will be discussed in Section 1.4.2.5.

Thus, in summary, chlorine-based flame retardants appear to act mainly in the condensed phase by causing dehydrogenation of the polymer and enhancing char formation. With regards to bromine-based flame retardants, they are effective mainly in the gas phase, as a result of liberation of hydrogen bromide which destroys reactive $H^{\bullet}$ and $OH^{\bullet}$ radicals responsible for the propagation of combustion.

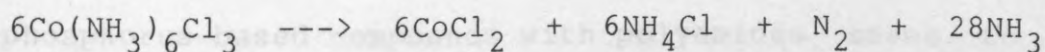
1.4.2.4. Nitrogen-based Flame Retardants.

Wool, silk, leather and other related natural polyamides contain nitrogen in their structures and are known to have low flammability. In general, the nitrogen content appears to be related to the flammability, an increase in nitrogen content resulting in a decrease in flammability. However, synthetic polymers, such as polyacrylonitrile and polyurethane, which also contain nitrogen are not so resistant to combustion, showing that the chemical structure is also important.

A number of nitrogen compounds are used in the flame retardance of synthetic as well as natural polymers. These include triazines and isocyanates as well as urea, guanidine and cyanuric acid derivatives (Kuryla 1973). Very little is known about the mechanism of action of these nitrogen-containing flame retardants. However, many of these nitrogen compounds decompose to release nitrogen, which can act as a diluent in the flame zone, thereby making the volatile decomposition products less flammable (Chamberlain 1978).

Ammonium salts and metal-amine complexes are the other main types of nitrogen-containing flame retardants used. Ammonium sulphate used in conjunction with ammonium phosphate is commonly used in the fight against forest and bush fires in the U.S.A. and ammonium carbonate is extensively used in dry

powder fire extinguishers. On thermal decomposition, most of these compounds liberate ammonia, the release of which dilutes the gaseous decomposition products, making them less flammable. One particularly effective metal-ammine flame retardant, used in flexible polyurethane foams, is the hexamminecobalt(III) chloride complex $\text{Co}(\text{NH}_3)_6\text{Cl}_3$ (Pitts 1973), which produces a large volume of diluent gases on decomposition:



On their own, nitrogen compounds are not very effective flame retardants but when they are used with phosphorus compounds, synergistic effects can be observed. Evidence for phosphorus-nitrogen synergism was obtained from the experimental finding that the minimum amount of phosphorus required to reduce the flammability of cotton decreased with increasing amounts of nitrogen present (Tesoro 1970).

Hendrix et al. (1972) have shown that the pyrolysis of cellulose treated with phosphates or phosphoramides proceeds through the formation of cellulose phosphate or phosphoramidate esters followed by breakdown of the ester to yield dehydrated cellulose char, thereby reducing the yield of laevoglucosan. Earlier work on textiles has also shown that nitrogen compounds, such as urea, cyanamide, guanidine and methylol melamines, can accelerate the phosphorylation

of cellulose (Bancroft & Sons 1948; Davies et al. 1949; Morton & Ward 1950; O'Brien 1968). It is thus generally believed that, in cellulose, nitrogen and phosphorus compounds can react to form P-N species which are better phosphorylating agents than phosphoric acids.

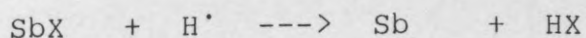
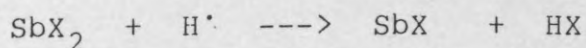
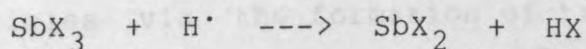
Although phosphorus-nitrogen synergistic effects are well established and proven for cellulose, they may not exist for other polymers. However, the mechanism of flame retardance by phosphorus-based compounds with polyamides seems to be the same as for cellulose (Crawshaw et al. 1973; Benisek 1975). The synergistic effects of phosphorus and nitrogen also appear in polyurethane. Studies show that acidic products formed from the decomposition of the phosphorus compound enhance the formation of a stable insulating char and the amounts of volatile decomposition products formed are decreased (Piechota 1965; Papa & Proops 1972).

Thus, it is generally believed that nitrogen-containing flame retardants act by releasing nitrogen, or in some cases ammonia, which functions as a diluent. When they are used with phosphorus compounds, synergistic effects can be observed, especially in cellulose.

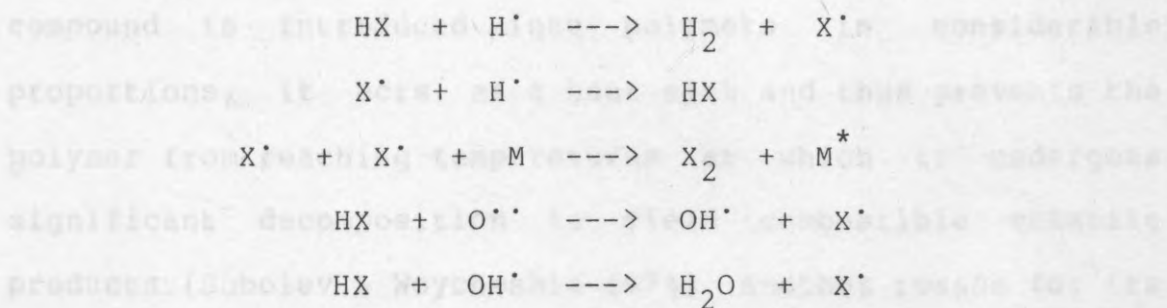
1.4.2.5. Other Flame Retardants.

Apart from compounds containing phosphorus, chlorine, bromine and nitrogen, flame retardants based on boron, aluminium and antimony are widely used. To a lesser extent, certain compounds of zinc, tin, molybdenum and sulphur are used in some polymers, sometimes as partial replacements for other flame retardants.

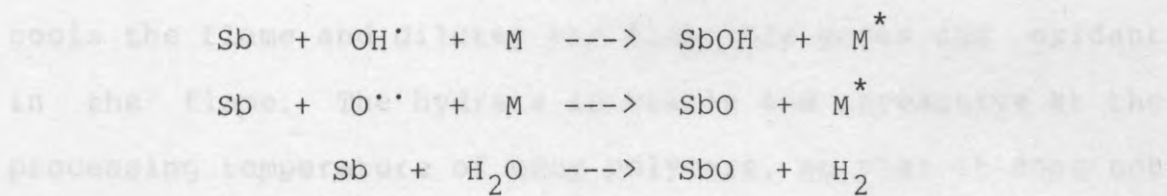
The high levels of halogenated organic compounds required to impart flame retardancy to polymers often adversely affect their physical properties. However, this problem may be overcome to a certain extent by the addition of compounds that behave synergistically. Antimony trioxide is one such compound. Combinations of antimony trioxide and halogen compounds are primarily used as flame retardants in polymers, such as ABS, polyethylene, polypropylene, polystyrene and unsaturated polyesters. When used on its own, antimony trioxide has little or no effect. The mechanism of action of antimony trioxide - halogen systems proposed by Hastie (1973a) involves the formation of the corresponding antimony trihalides which decompose in a stepwise manner and may participate directly in the inhibition reactions as follows:



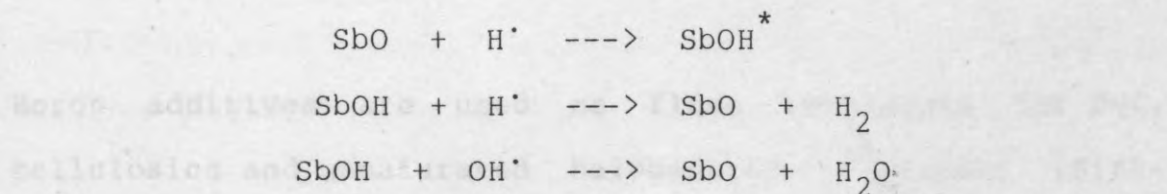
The HX formed can then interfere with the radical chains responsible for flame propagation:



The Sb atoms can also destroy the active free radicals:



These reactions generate SbO and SbOH which can subsequently react with and so destroy the radicals responsible for flame propagation:



Solid SbO is believed to enter the reaction zone as a "mist" of fine particles via the formation of transient species such as SbOH.

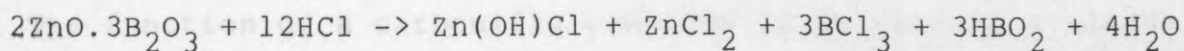
The only aluminium compound of any commercial significance

in flame retardancy is aluminium oxide trihydrate. Its main use is in unsaturated polyesters, polyurethane foam, polypropylene and phenolic and epoxy resins. When this low-cost compound is introduced into polymers in considerable proportions, it acts as a heat sink and thus prevents the polymer from reaching temperatures at which it undergoes significant decomposition to yield combustible volatile products (Sobolev & Woycheshin 1974). Another reason for its effectiveness as a flame retardant is its ability to undergo an endothermic reaction by losing water to form anhydrous alumina (Connolly and Thornton 1965). On release, the water cools the flame and dilutes the flammable gases and oxidant in the flame. The hydrate is stable and unreactive at the processing temperature of many polymers, so that it does not lose water during processing. Hydrated alumina is also used as a secondary synergist to improve the flame retardance of polymer systems that already contain antimony trioxide, zinc borate or some phosphorus-containing flame retardants (Kaufman et al. 1978).

Boron additives are used as flame retardants for PVC, cellulosics and unsaturated halogenated polyesters (Kirk-Othmer 1980). Boric acid and borax are found to be effective condensed-phase flame retardants in polyhydroxy compounds, especially cellulosic fibres. When these compounds are heated, they soften, lose their water of hydration and then form a glassy coating around the cellulosic fibres. When the temperature is reached at which extensive decomposition

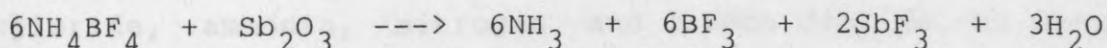
occurs, the coating of residual boron oxide reacts with the hydroxyl groups of the cellulose to liberate additional water. This action causes the polymer to swell, forming an intumescent coating on the surface, which insulates the bulk of the polymer from the heat source (Little 1947).

Zinc borate, commonly used to reduce the flammability of PVC, acts both in the gas and condensed phases. The hydrogen chloride generated by the decomposition of PVC reacts with the zinc borate as follows:



The non-volatile zinc compounds and meta-boric acid promote char formation, thereby reducing the amounts of volatile products and the boron trichloride and water dilute the flame (Kirk-Othmer 1980).

Ammonium fluoborate is another flame retardant used in combination with antimony trioxide. The following mechanism has been proposed (Finn 1979):



The ammonia, boron trifluoride and water released into the gas phase cool the flame and at the same time dilute the gaseous fuel generated on decomposition of the polymer. The flame-inhibiting reactions of antimony trihalides have been

discussed earlier in this Section.

As mentioned in Section 1.4.2.1., intumescent and non-intumescent fire retardants can also be used to confer some degree of flame retardancy on organic polymers. The mechanism of formation of an intumescent coating (a protective layer of foamed char) involves several inter-related stages and to achieve it, several components are needed, each having a specific function. They include a carbonific compound, a spumific compound and a resin binder.

The function of a carbonific compound is to produce a large amount of carbonaceous residue, usually as a result of dehydration by a strong inorganic acid, such as sulphuric, boric and phosphoric acid. However, compounds that decompose to generate the corresponding acid to dehydrate the carbonific compound are also used and these include ammonium phosphate, melamine phosphate and zinc borate. An effective carbonific compound must possess high carbon and hydroxyl content and examples are pentaerythritol, sugars and various polyols. The function of a spumific compound is to produce large quantities of non-flammable gases, such as hydrogen chloride, ammonia, nitrogen and carbon dioxide, on decomposition. These gases cause the char to swell or "bubble", producing a thick insulating coating. Commonly used spumific compounds include melamine, dicyandiamide, guanidine and urea. Finally, if the intumescent flame retardant is to be applied as a coating instead of being incorporated into the

polymer as a blend, it should include a resin binder which can incorporate all the other components. This would ensure the production of a continuous and uniform structure which would eventually form a skin over the foam, preventing the trapped gases from escaping. Efforts must be made to ensure that the binder does not harden or crosslink with age and does not decompose to give flammable products. Thermoplastic binders such as vinyl polymers are more practical than thermosetting binders because they melt at reasonably low temperatures.

Intumescent coatings are used mostly to protect cellulosic substrates, such as wood and fibreboard. Recently, there has been considerable interest in the use of intumescent coatings on thermoplastics such as PAN (Ballistreri et al. 1983a) and polypropylene (Halpern et al. 1984). It is important to note that the precise compositions of commercially available intumescent coatings are secrets and very limited information regarding their mode of action is available in the literature.

Non-intumescent coatings are also used to protect flammable organic polymers. The polymers used most extensively for such coatings are halogenated alkyd resins and for low-gloss, opaque coatings, hydrated alumina and calcium carbonate fillers incorporated into alkyd resins are sometimes used (Lyons 1970a).

1.4.3. Modes of Action of Smoke Suppressants.

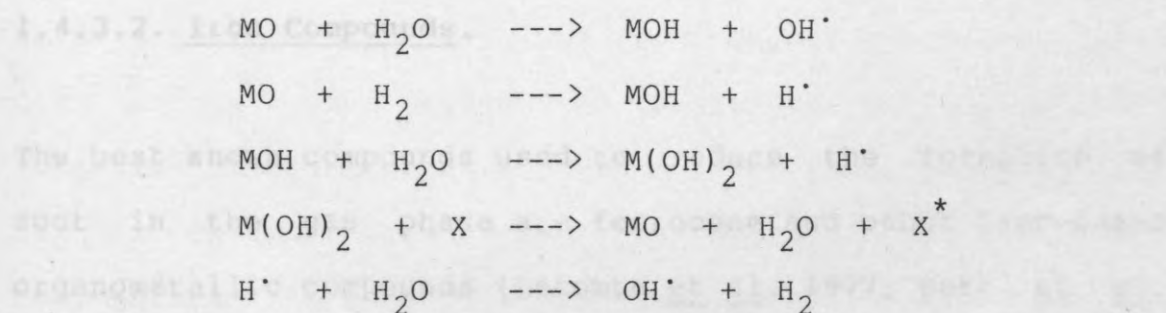
1.4.3.1. Introduction.

It is well known that halogen-containing additives enhance the formation of smoke from organic polymers. For example, when brominated additives are used, hydrogen bromide liberated during combustion reacts with and destroys flame-propagating species such as hydroxyl radicals. As a result, these highly reactive species are no longer available for oxidation of incipient carbon particles and other polymer breakdown products. Further pyrolysis of these latter compounds therefore tends to occur at the expense of oxidation and this eventually leads to the formation of larger quantities of the carbon-rich solids which constitute smoke. Antimony trioxide - halogen systems, which also generally act in the gas phase, increase quite markedly the formation of smoke from polymers into which they are incorporated. Similarly, additives such as boric acid and phosphates promote smoke formation because they are good inhibitors for the oxidation of carbonaceous materials (Rakszawski & Parker 1964).

As mentioned earlier, none of the existing theories of smoke formation discussed in Section 1.3.1.2. is entirely convincing, and to date, there is relatively little

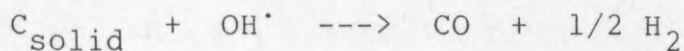
information concerning the chemical and physical mechanisms of suppression of smoke from polymers.

The very early work on smoke suppressants was focussed on additives for reducing particulate emissions from burner fuels. Shayeson (1967) found that certain organometallic additives containing barium, manganese and iron could completely eliminate smoke from the burning of aviation fuels, but compounds containing lead and boron were ineffective. In heating oils, organometallic compounds containing copper, cobalt, manganese, iron and nickel were found to be useful smoke suppressants (Vaerman 1964). The effectiveness of additives varies with the type of fuel. A general mechanism of soot suppression by metal compounds has been proposed (Cotton, Friswell & Jenkins 1971; Cotton & Jenkins 1971):



In this, the oxides or hydroxides of the metal catalyse the decomposition of molecular hydrogen and water vapour in the gas phase producing hydroxyl radicals which will oxidise the

soot particles to carbon monoxide:

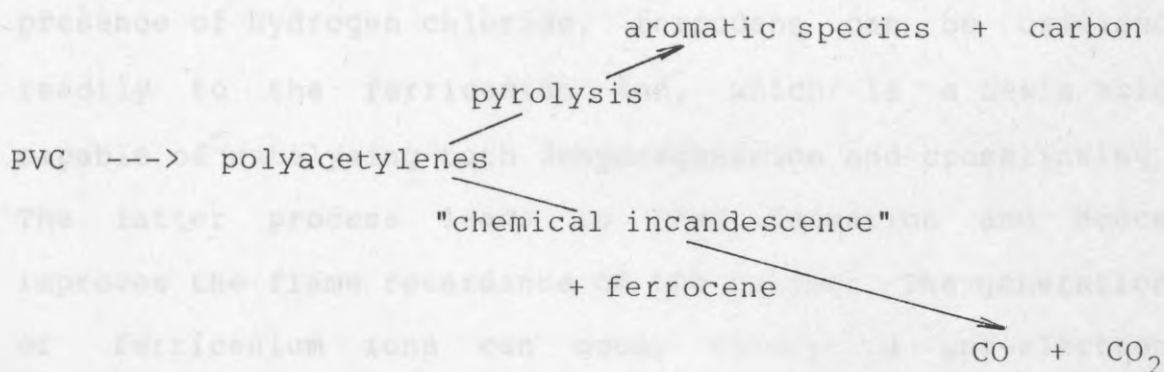


Other mechanisms have also been postulated in which carbon is oxidised directly by reaction with metal oxides or in which ionic intermediates or precursors of soot are neutralised by metal species (Addecott & Nutt 1969). Since the combustion of polymers involves a variety of processes occurring in several phases, inhibition of smoke formation can, in principle, occur not only in the gas phase but also in the condensed phase. Indeed, some smoke suppressants are known to function in the condensed phase by promoting char formation and altering the type or distribution of volatile pyrolysates. They will be discussed in the following Sections.

1.4.3.2. Iron Compounds.

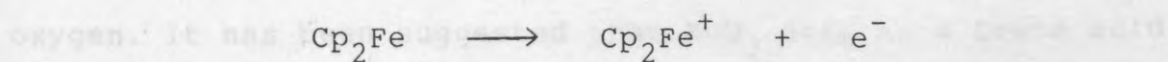
The best known compounds used to reduce the formation of soot in the gas phase are ferrocene and other iron-based organometallic compounds (Lecomte et al. 1977; Bert et al. 1978; Deets & Lee 1979; Descamps et al. 1980; Ballistreri et al. 1981, 1982). When used in PVC, the mode of action of ferrocene and compounds of other metals such as vanadium (V_2O_5) and copper (CuO) is apparently to provide an

alternative route for the reaction: for example, for ferrocene (Descamps et al. 1980):

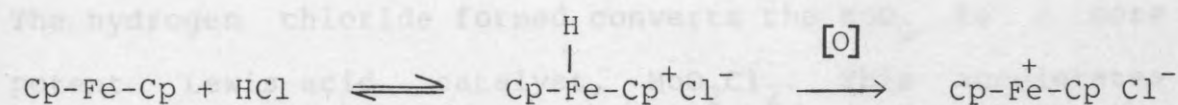


During combustion of the polymer, ferrocene volatilises and burns to form a fine "mist" of ferric oxide particles which then catalyse the oxidation of soot particles to carbon oxides, decreasing the amount of carbon available for soot formation. Recent studies suggest that, whatever the state of the iron compounds, ferrous and ferric chlorides formed during the dehydrochlorination of PVC are precursors to the formation of ferric oxide. The iron chloride intermediates can modify the degradation processes and favour the formation of light tars instead of heavy tars. In fact, the iron compounds cause smoke to be formed at a lower temperature than for pure PVC but, as ferric oxide is formed, smoke production begins to level off and then decreases. Hence, the greater the ability of the iron additives to give chlorides through reaction with hydrogen chloride and further transformation to ferric oxide, the greater is the effectiveness of the additive in reducing

smoke formation (Michel et al. 1983). Other evidence shows that ferrocene can be active in the condensed phase during the combustion of PVC (Lawson 1976). Apparently, in the presence of hydrogen chloride, ferrocene can be oxidised readily to the ferricenium ion, which is a Lewis acid capable of catalysing both dehydrogenation and crosslinking. The latter process leads to char formation and hence improves the flame retardance of the polymer. The generation of ferricenium ions can occur through a one-electron oxidation (Rosenblum 1965):



or through the sequence:



It has also been shown that, when organometallic compounds like ferrocene or benzoyl ferrocene are incorporated into styrene-based polymers, smoke formation decreases with increasing amounts of metal volatilised (Deets & Lee 1979). However, when chlorinated flame retardants are incorporated into styrene-based polymers, smoke formation increases with the amount of metal lost.

1.4.3.3. Molybdenum Compounds.

After ferrocene, molybdenum trioxide is the second most commonly used compound for reducing smoke production from PVC. It is also used, to a smaller extent, in unsaturated polyester resins and polyolefins. Moore et al. (1978) found that MoO_3 , alone or with Sb_2O_3 , decreases the amount of smoke and increases the amount of char in PVC, indicating that MoO_3 acts in the condensed phase. Further evidence was obtained when combustion studies using nitrous oxide as the gaseous oxidant gave similar results to those obtained with oxygen. It has been suggested that MoO_3 acts as a Lewis acid capable of increasing the rate of dehydrochlorination by accelerating heterolysis of the C-Cl bond (Lum 1979; Starnes & Edelson 1979; Edelson et al. 1982; Westcott et al. 1985). The hydrogen chloride formed converts the MoO_3 to a more potent Lewis-acid catalyst, MoO_2Cl_2 . This accelerates crosslinking and the isomerisation of cis, trans-polyenes to trans-polyenes which do not cyclise to benzene, thus inhibiting smoke formation. However, Lattimer and Kroenke (1981) expressed doubts on the Lewis-acid mechanism and suggested that MoO_3 , like other transition metal smoke suppressants, promotes early crosslinking of PVC chains during thermal degradation via a mechanism of reductive coupling. In effect, the smoke suppressants act as coupling agents by joining together allylic or alkyl chain segments during thermal decomposition of PVC. More recently, studies

have shown that Lewis-acid effects are certainly more important and that the reductive coupling reactions appear to make minor contributions to the overall smoke-inhibiting process (Lattimer et al. 1984).

1.4.3.4. Other Metal Compounds.

When zinc borate ($2\text{ZnO} \cdot 3\text{B}_2\text{O}_3 \cdot 3.5\text{H}_2\text{O}$) was used in conjunction with aluminium oxide trihydrate in PVC, strong synergism was observed between these two smoke suppressants (Shen & Sprague 1982). Although no precise mechanism has yet been established, it has been suggested that some of the zinc remains in the condensed phase, catalysing dehydrochlorination and crosslinking to suppress smoke formation while the volatilised zinc species probably contribute to flame retardancy.

There are numerous reports of other metal compounds (containing, for example, Al, Fe, Mg, Mo and Sn) showing smoke-suppressant properties in polymers. Various different effects have been observed when these compounds are used in a wide range of polymer systems and these have been reviewed by various authors (e.g. Lawson & Kay 1975; Kroenke 1981; Lawson 1982).

1.4.3.5. Fillers.

In general, the use of fillers is probably the best way of decreasing smoke formation as well as the flammability of organic polymers. "Inert" fillers can act as heat sinks to decrease the mass burning rate and as diluents to reduce the amount of combustible substrate. Examples of fillers are calcium carbonate, clays and carbon black. Besides acting as heat sinks, "active" fillers like aluminium oxide trihydrate and magnesium hydroxide can release water into the combustion zone which acts as a gaseous diluent for the combustible gaseous products. Hydrated alumina is by far the most widely used filler. However, in the absence of other flame retardant additives, this compound has to be incorporated into organic polymers in large concentrations in order to exert a useful flame-retardant and smoke-suppressant effect. Its presence inevitably affects the physical and mechanical properties of polymers, so that it is not used to any appreciable extent in the manufacture of fibres.

2. EXPERIMENTAL.

2.1. Materials.

2.1.1. Polymers.

Poly(vinyl chloride) (PVC) (Korylon), in powdered form, was supplied by Imperial Chemical Industries Limited (I.C.I.) and polystyrene (PS) (Caripon), in pellet form, was provided by Shell U.K. Limited. High-density polyethylene (HDPE) (Solvay - HD BATES 5 1000), in the form of pellets, was supplied by Produits Chimiques de la Rhénane. Poly(methyl methacrylate) (PMMA) (Lucite 100), in the form of pellets, was supplied by I.C.I.

EXPERIMENTAL

2.1.2. Additives.

2.1.2.1. Phosphorus Compounds.

Red phosphorus (71), containing 99.9% phosphorus and 0.1% carbon, was supplied by Hoechst U.K. Limited. Triphenyl phosphite (TPP) and tritolyl phosphite (TTP) were supplied by Hoechst U.K. Limited respectively.

2. EXPERIMENTAL.

2.1. Materials.

2.1.1. Polymers.

Poly(vinyl chloride) (PVC) (Corvic), in powdered form, was supplied by Imperial Chemical Industries Limited (I.C.I.) and polystyrene (PS) (Carinex), in pelleted form, was provided by Shell U.K. Limited. High-density polyethylene (HDPE) (Solvay - HD ELTEX B 4002), in the form of pellets, was supplied by Produits Chimiques Ugine Kuhlmann. Poly(methyl methacrylate) (PMMA) (Diakon acrylic) was supplied by I.C.I.

2.1.2. Additives.

2.1.2.1. Phosphorus Compounds.

Red phosphorus (P), containing 98.6% phosphorus and a small concentration of di-2-ethylhexylphthalate (Exolit 405), was supplied by Hoechst U.K. Limited. Triethyl phosphate (TEP) and tritolyl phosphate (TTP) were Aldrich and BDH products respectively.

2.1.2.2. Halogen Compound.

Decabromobiphenyl (DBB) (Adine 102) was supplied by Produits Chimiques Uguine Kuhlmann.

2.1.2.3. Nitrogen Compounds.

Melamine (MEL) was provided by I.C.I., and urea, guanidine carbonate (GC), barbituric acid (BA) and benzotriazole (BEN) were Aldrich products.

2.1.3. Other Additives.

Di-isooctyl phthalate (DIOP) (BDH) was used as a plasticiser for PVC; lead dibasic phosphite (Rhone-Poulenc-Stavinor PR 12) and lead dibasic stearate (Rhone-Poulenc-Stavinor DB 30) were used as stabilisers and glycerol monostearate (BDH) as a lubricant for polyethylene. Stearic acid (BDH) was used as lubricant for polystyrene and poly(methyl methacrylate).

2.1.4. Gases.

Oxygen, oxygen-free nitrogen and air were obtained from the British Oxygen Company and used without further purification for flammability measurements, thermoanalytical studies, and infrared studies of pyrolysis products.

2.2. Preparation of Polymer-Additive Samples.

2.2.1. Milling Procedure.

The machine used was a Ruth Schwabenthan two-roll mill with electrically-heated stainless steel rollers, 150 mm in diameter and rotating at 20 rpm. The rollers were heated at different temperatures, depending on the polymer and flame-retardant additives. For experiments involving PVC and HDPE, pre-weighed quantities of polymer (normally 100g) and additives were first physically blended and then added to the mill. The mixtures were fused and fluxed until a sheet had been formed on the heated roller. During the milling, the sheet was frequently cut and folded towards the centre of the roll until a homogeneous crepe was formed. The time to achieve this was normally 10-20 min.

A similar procedure was followed with PS and PMMA but the polymer and lubricant (stearic acid in both cases) were first fused to form a sheet and then the flame-retardant additives were slowly added in small doses. After each addition, the sheet was cut and folded towards the centre of the roll. This exercise was repeated until all the additives had been incorporated into the polymer and had become uniformly dispersed.

2.2.2. Compression Moulding.

This involves the use of a hot and a cold press. The hot press is an electrically-operated and electrically-heated hydraulic press, capable of attaining temperatures up to 230°C at a pressure of 5.5×10^3 kPa. The cold press is a water-cooled, hand-operated "fly-press".

Before the resulting homogeneous crepe was moulded, it was sandwiched between two "Melinex" sheets. This prevents the material from sticking to the mould and avoids contamination from previously processed materials. The sheets were then placed on top of the mould, of dimensions 3 mm x 152 mm x 152 mm, which in turn was sandwiched between two steel plates. The moulding involved treating the sample for 5 min at atmospheric pressure in a pre-heated hydraulic press and compressing it for a further 5 min at 5.5×10^3 kPa, after which the mould was removed from the hot press and introduced into a hand-operated, water-cooled press. The sheet was removed after it had cooled to room temperature.

Table 2.1 shows the different conditions used for preparing the various polymer samples.

Table 2.1

Details of preparation of different polymer-additive systems.

Polymer	Flame-retardant additive (max total loading of 30 wt %)	Other additives	Temperature (°C)		
			Front roller	Back roller	Hydraulic press
PVC	P, DBB, MEL	DIOP (40 phr)	105	100	160
PVC	P, DBB, UREA	DIOP (40 phr)	105	100	130
PVC	TEP, DBB, MEL	DIOP (40 phr)	105	100	140
PVC	P, DBB, GC	DIOP (40 phr)	105	100	140
PVC	P, DBB, BA	DIOP (40 phr)	105	100	140
PVC	P, DBB, BEN	DIOP (40 phr)	100	95	100
PS	P, DBB, MEL	Stearic acid (2 phr)	170	165	170
PS	P, DBB, UREA	Stearic acid (2 phr)	125	120	130
PS	TTP, DBB, MEL	Stearic acid (2 phr)	170	160	160
PS	P, DBB, GC	Stearic acid (2 phr)	170	160	180
PS	P, DBB, BA	Stearic acid (2 phr)	170	165	180
PS	P, DBB, BEN	Stearic acid (2 phr)	105	100	100
PMMA	P, DBB, MEL	Stearic acid (2 phr)	185	180	200
PMMA	P, DBB, BA	Stearic acid (2 phr)	185	180	200
HDPE	P, DBB, MEL	Lead dibasic phosphite (1.0 phr) Lead dibasic stearate (0.2 phr) Glycerol monostearate (0.5 phr) As above	160	155	210
HDPE	P, DBB, BA		160	155	200

2.3. Apparatus and Procedure.

2.3.1. Measurement of Flammability.

2.3.1.1. The Limiting Oxygen Index Apparatus.

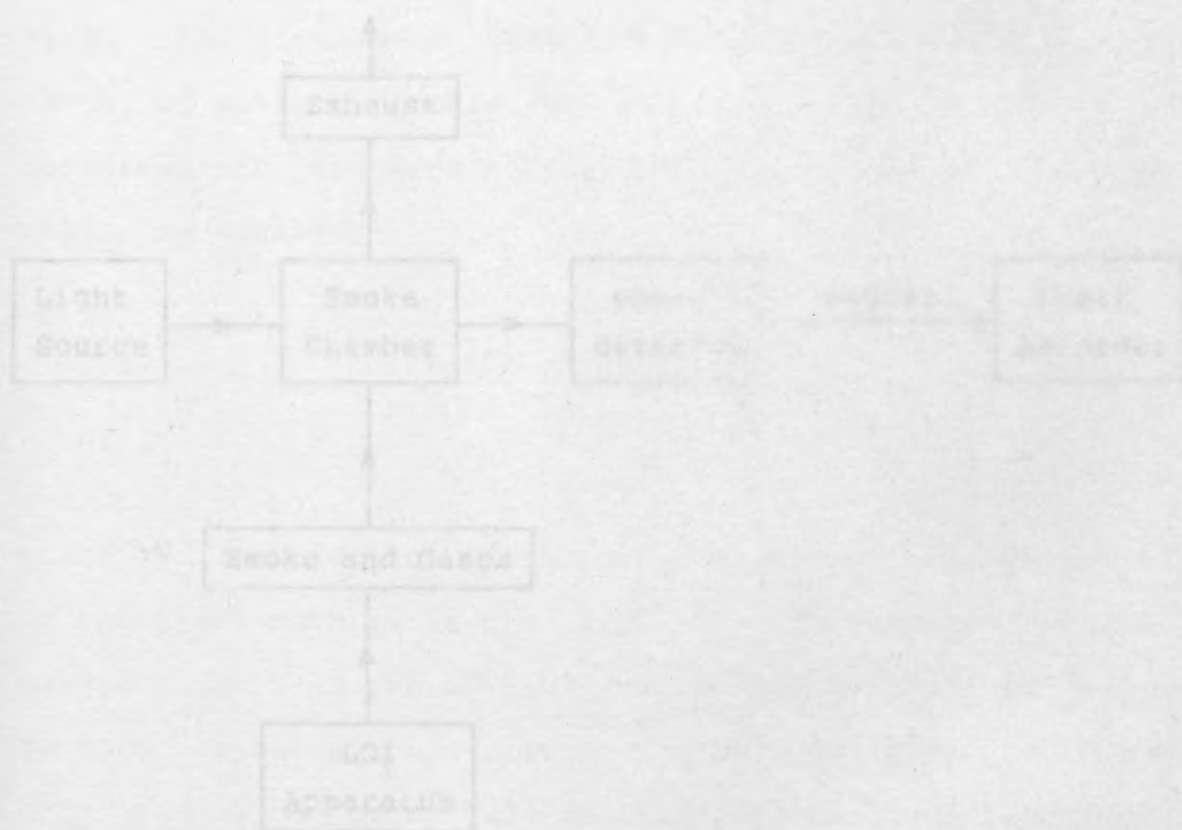
Limiting Oxygen Indices (LOI) were determined by means of a Stanton Redcroft apparatus designed to meet ASTM D2863 flammability requirements. The test method and apparatus have already been described in Section 1.2.2.6. and details of the test apparatus and its layout are shown in Figs. 1.16 and 1.17.

2.3.1.2. Determination of Limiting Oxygen Indices.

Samples of polymeric material, length 75-150 mm, width 6 ± 0.5 mm and thickness 3 ± 0.25 mm, were held vertically at the centre of the test column with a standard sample holder. The gases were used, with no prior treatment, at a cylinder outlet pressure of 170 kPa.

The tip of the specimen was ignited for 20 s (or until a stable flame was attained) with a standard ignition source (a tube with an orifice of diameter 1-3 mm, from which a 20-40 mm long gas flame was obtained). The flow rates of oxygen and nitrogen were adjusted to achieve a particular concentration of oxygen and a total gas flow rate of 18

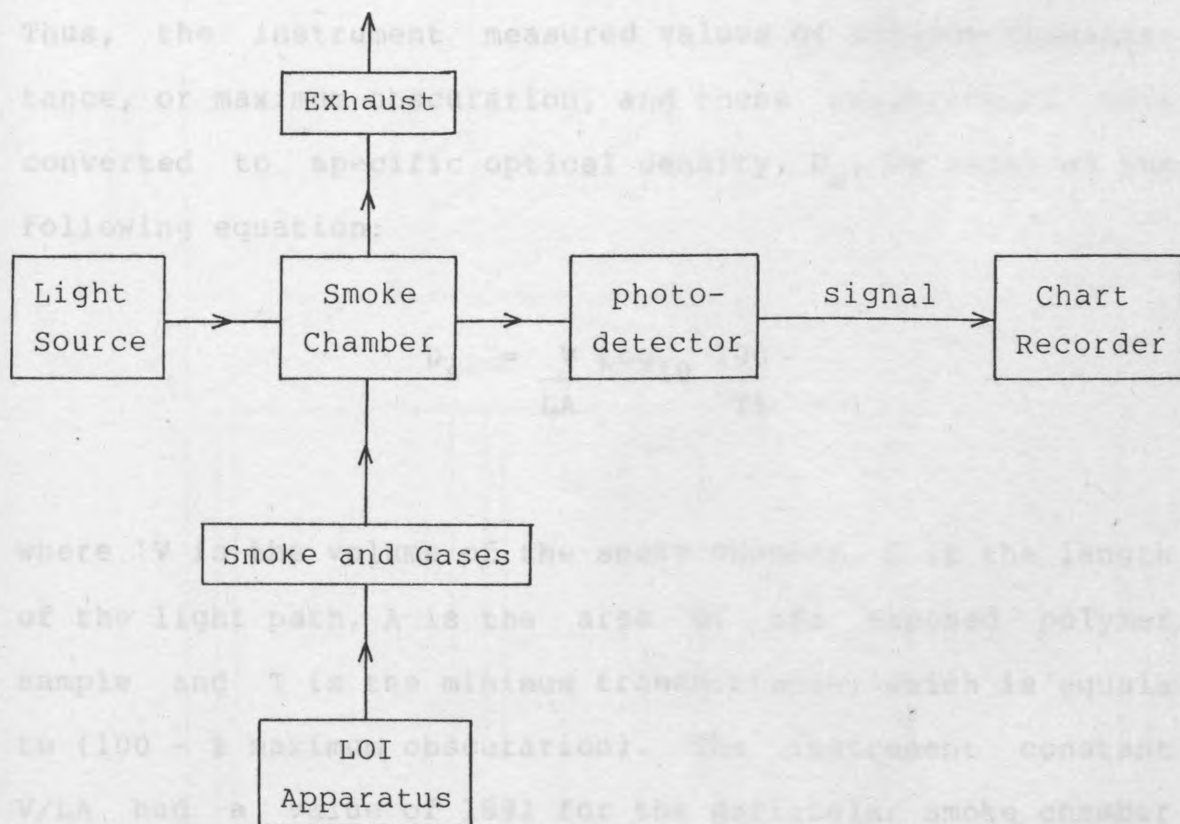
litres min^{-1} . These were maintained for at least 30 s prior to ignition, to ensure that the atmosphere is stabilised at that concentration of oxygen. After ignition, if the polymeric material burned for more than 3 min, the oxygen concentration was gradually reduced and, if the specimen was extinguished in less than 3 min, the oxygen concentration was increased. This procedure was repeated until an oxygen concentration was reached at which extinction occurred 3 min after ignition. The percentage of oxygen in which a candle of polymer burned for a period of 3 min was recorded as the LOI. The system is shown below:



2.3.2. Measurement of Smoke.

2.3.2.1. The Smoke Chamber.

The amount of smoke generated was determined from measurements based on light obscuration, in a dynamic smoke chamber. The system consisted essentially of an oxygen index apparatus and a smoke chamber coupled to a chart recorder. The smoke chamber was located above the LOI apparatus from which the gases and smoke flowed. A schematic representation of the system is shown below:



The smoke chamber consisted of a metal cabinet, of dimensions 62 cm high, 61 cm deep and 123 cm wide, with a sliding glass window (Fig.2.1). At the top of the chamber was an extraction flue, operated by an electric fan which discharged the smoke and product gases out into the exhaust tube.

The photometric system consisted of a high-intensity light source on the left of the chamber, which shone onto a photocell across it. When the smoke chamber was in operation, the intensity of light reaching the photocell was plotted by a chart recorder as percentage transmittance. Thus, the instrument measured values of minimum transmittance, or maximum obscuration, and these measurements were converted to specific optical density, D_s , by means of the following equation:

$$D_s = \frac{V}{LA} \log_{10} \frac{100}{T\%}$$

where V is the volume of the smoke chamber, L is the length of the light path, A is the area of the exposed polymer sample and T is the minimum transmittance, which is equals to (100 - % maximum obscuration). The instrument constant V/LA had a value of 1891 for the particular smoke chamber concerned.

Figure 2.1

The smoke chamber.

Prior to carrying out a test, the smoke chamber was calibrated on and the chart recorder was calibrated so that a linear transmittance when the light source was at the top and the photo-cell at the bottom.

respectively. Samples of polymer were cut into rectangular pieces 25 mm, width 5 ± 0.5 , thickness 2.5 ± 0.5 mm.

vertically in the oxygen chamber. The oxygen chamber was calibrated so that the samples could be placed in the chamber and the oxygen concentration could be measured.

of ignition, the oxygen concentration was measured. The value of the oxygen concentration was recorded. The oxygen concentration was measured at the top and the photo-cell at the bottom.

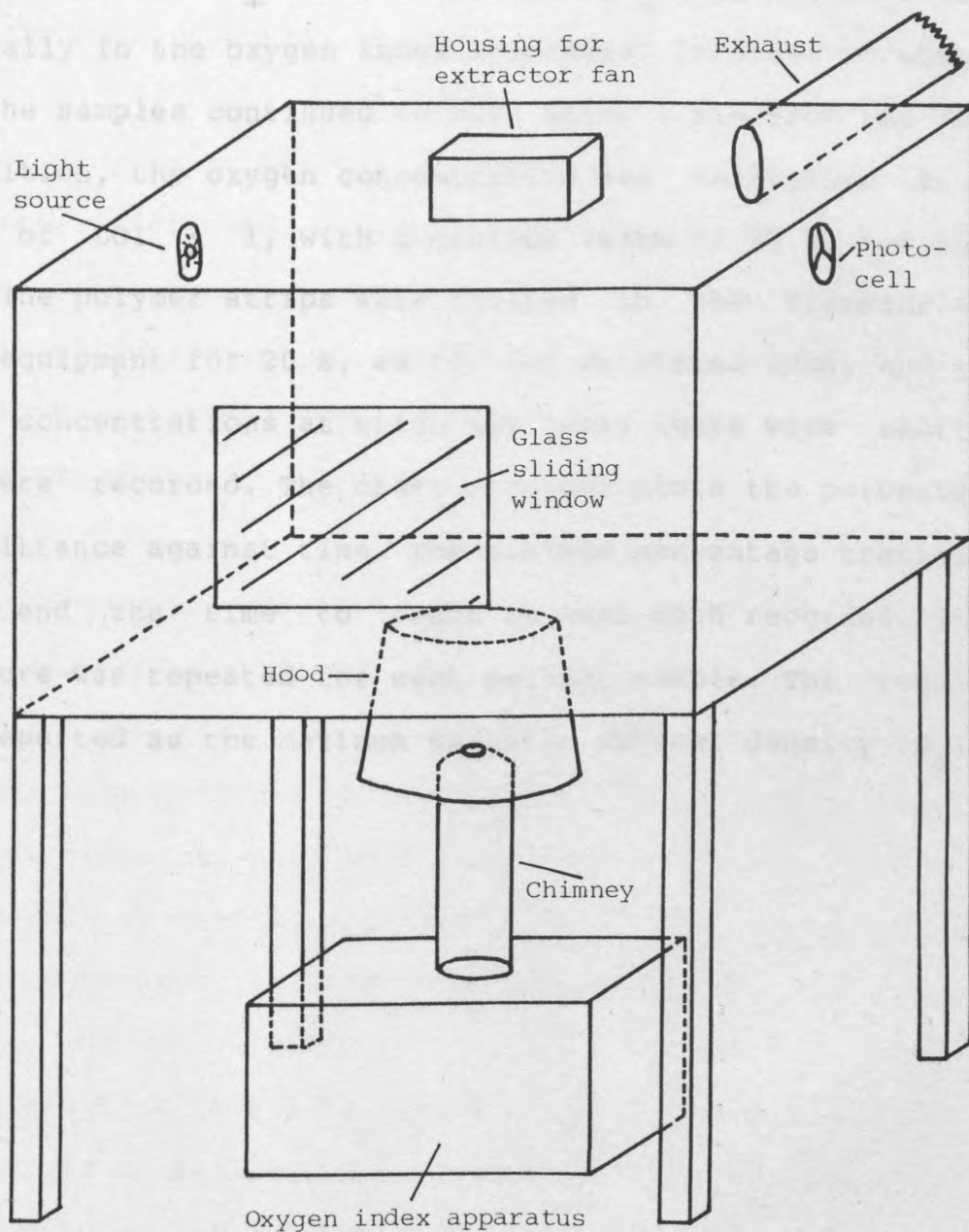
test equipment for 2 s, as shown in Figure 2.1. The oxygen concentration was measured at the top and the photo-cell at the bottom.

oxygen concentration was measured. The value of the oxygen concentration was recorded. The oxygen concentration was measured at the top and the photo-cell at the bottom.

transmittance again. The value of the transmittance was recorded. The transmittance was measured at the top and the photo-cell at the bottom.

procedure was repeated. The value of the transmittance was recorded. The transmittance was measured at the top and the photo-cell at the bottom.

were plotted as the rate of smoke production. The rate of smoke production was measured at the top and the photo-cell at the bottom.



2.3.2.2. Measurement of Extent of Smoke Formation.

Prior to carrying out a test, the light source was switched on and the chart recorder was calibrated to read 0 and 100% transmittance when the light was "off" and "on" respectively. Samples of polymeric material, of length 150 ± 25 mm, width 6 ± 0.5 , thickness 3 ± 0.25 mm, were held vertically in the oxygen index apparatus. In order to ensure that the samples continued to burn after 3 min from the time of ignition, the oxygen concentration was maintained at a value of $\text{LOI} \pm 1$, with a minimum value of 20.9, for each test. The polymer strips were ignited in the flammability test equipment for 20 s, as for LOI determinations, and the oxygen concentrations at which the smoke tests were carried out were recorded. The chart recorder plots the percentage transmittance against time. The minimum percentage transmittance and the time to reach it were both recorded. This procedure was repeated for each polymer sample. The results were reported as the maximum specific optical density (D_s).

2.3.3. Statistical Treatment of Data.

The flammability and smoke density results for the systems with mixed additives are represented in the form of triangular diagrams. These are constructed, using the City University Honeywell mainframe computer system, by fitting the LOI and D_s values determined for the systems concerned by a polynomial function of the composition coordinates.

The programme was set to read an introductory set of statements, followed by the observed values of the oxygen index or smoke density, as a function of composition. The composition variables are scaled to a triangular grid, with selected compositions forming the vertices, so as to include most 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 regression analysis procedure, 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.

Polynomials of orders 1 to 4 were tried and the coefficients were defined as follows. Y_i represents the calculated LOI for polynomial of order i and x_1 , x_2 and x_3 are the

composition coordinates of any point expressed on the triangular coordinate system, derived from the selected vertices. (They are thus transformations of the original composition coordinates).

First order polynomial (linear):

$$y_1 = \sum_{j=1}^3 a_j x_j$$

Second order (quadratic):

$$y_2 = y_1 + a_4 x_1 x_2 + a_5 x_1 x_3 + a_6 x_2 x_3$$

Third order (reduced cubic):

$$y_{3r} = y_2 + a_7 x_1 x_2 x_3$$

Third order (full cubic):

$$y_3 = y_{3r} + a_8 x_1 x_2 (x_1 - x_2) + a_9 x_1 x_3 (x_1 - x_3) + a_{10} x_2 x_3 (x_2 - x_3)$$

Fourth order (quartic):

$$\begin{aligned} y_4 = y_3 &+ a_{11} x_1 x_2 (x_1^2 + x_2^2 - 3x_1 x_2) + a_{12} x_1 x_3 (x_1^2 + x_3^2 - 3x_1 x_3) \\ &+ a_{13} x_2 x_3 (x_2^2 + x_3^2 - 3x_2 x_3) + a_{14} x_1^2 x_2 x_3 + a_{15} x_1 x_2^2 x_3 \\ &+ a_{16} x_1 x_2 x_3^2 \end{aligned}$$

The quality of fit was assessed from the value of the root mean square difference between calculated and observed LOI values (σ), from the multiple regression correlation coefficient (RCC) and by the examination of the individual differences between calculated and observed LOI values. A sequential F-test calculation was used to assess the significance of the last added variables. The results presented in each case are for the lowest order giving a satisfactory fit. The contour plots obtained allow the effect of additives on the response to be seen more clearly and may reveal details not immediately apparent from the data.

A similar calculation was carried out for smoke density values except that a weighted least-squares method was used since the experimental uncertainty in smoke density was found to be proportional to the smoke density value.

For quantitative assessment of flame retardance by additives or combinations of additives, the "overall effectiveness coefficients" and "overall synergism coefficients" introduced by Baldry (1985) were used. These coefficients (and their uncertainties) are calculated from the least-squares coefficients and represent the average contribution to the LOI of the system attributable to each additive or combination of additives over a specific composition range (in this work, the range was 0 to 30 wt % additive loading). Thus,

for a single additive i , present in weight fraction x_i , the increase in LOI is $k_i x_i$ due to that additive; for two additives i and j , weight fractions x_i and x_j , the increase in LOI due to synergism is $k_{ij} x_i x_j$, where k_i is the coefficient for effectiveness of additive i and k_{ij} is the coefficient for synergism between i and j . Thus, for a system containing 10 wt % of each of two additives, a synergism coefficient of 100 is equivalent to an increase of LOI of $100 \times 0.1 \times 0.1 = 1$ unit. Similarly, for a system containing 10 wt % of each of three additives, a synergism coefficient of 1000 is equivalent to an increase in LOI of $1000 \times 0.1 \times 0.1 \times 0.1 = 1$ unit.

2.3.4. Thermoanalytical Measurements.

2.3.4.1. The Thermobalance.

Thermoanalytical studies of the degradation and oxidation of the polymers and of the extent of interaction between various additives were made using a Mettler "Thermoanalyser 2" thermobalance, interfaced to an Apple II microcomputer via a U-Microcomputers model U-A/D interface, with other hardware and software developed in the Department of Chemistry at the City University. This 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 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: 0-10 mg, 0-100 mg and 0-1000 mg. A weight expansion unit provides greater accuracy

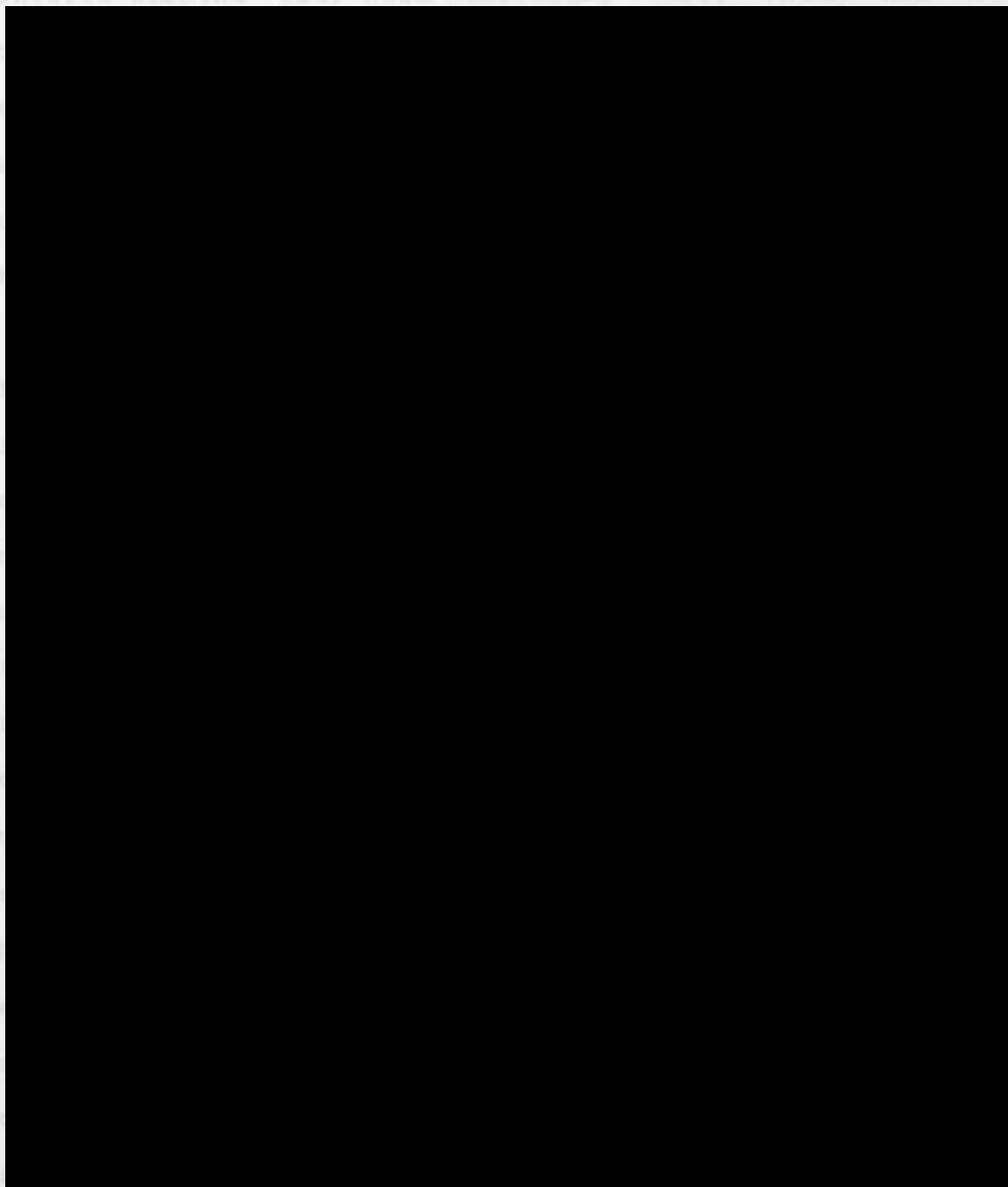
by electronic amplification of the weight signal by a factor of ten. An accuracy of $\pm 0.2\%$ of the range can be attained for all three ranges of sample mass.

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 $\pm 0.4\%$ in the differential thermogravimetry (DTG) range. Temperature measurements are carried out by means of a Pt/10% Rh - Pt thermocouple. The hot junction is located underneath and in contact with the crucible. Temperatures can be measured with an accuracy of $\pm 2.5^\circ$ at 100°C and $\pm 2.0^\circ$ at 500°C . The DTA unit has six ranges: 20, 50, 100, 200, 500 and $1000 \mu\text{V}$. An accuracy of $\pm 0.2\%$ over the range can be attained for all six ranges. The A/D conversion uses an instrumentation amplifier with a maximum linearity error of $\pm 0.2\%$ and a 12-bit A/D converter with maximum non-linearity 1-bit ($\pm 0.024\%$ full-scale).

The furnace tube is of quartz and is surrounded by a reflecting shield. The heating element consists of a non-inductively wound Kanthal wire filament inside a bifilar quartz spiral (Fig. 2.2). The furnace may be heated from 25 to 1025°C under computer control at a heating rate of up to a maximum of $\text{ca. } 500^\circ/\text{min}$ (linear up to $100^\circ/\text{min}$).

Figure 2.2

Bifilar quartz spiral furnace.

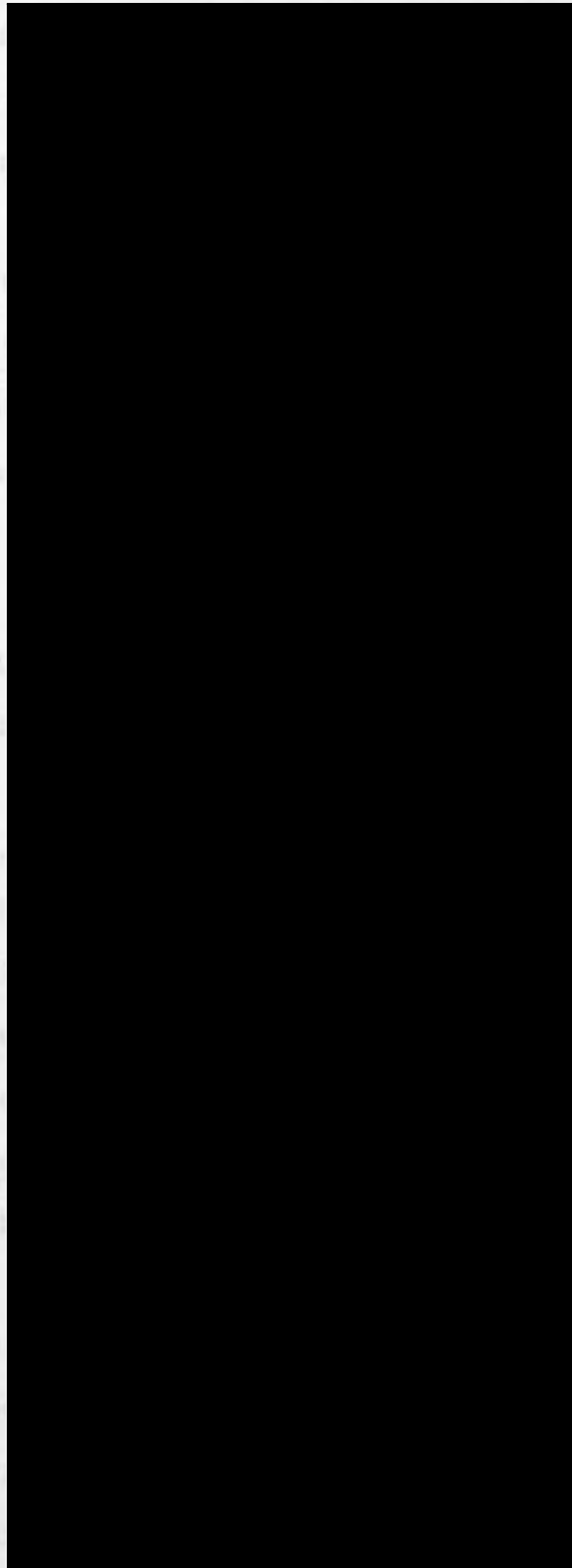


Sample holder geometry and composition are of great importance in thermal analysis. Two matched flat-bottomed platinum crucibles were used. These were 8 mm in diameter and had a short straight wall rising vertically from the bottom of the crucible. The crucibles were supported on a sintered alumina four-hole capillary tube, which had a cross-piece 270 mm from the end, bearing two short alumina pegs, 11 mm apart (Fig. 2.3). 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.

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 gases leaving the furnace can be passed through a gas analyser. 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 chart to a high degree of accuracy, this is impaired by base-line drifts caused by defects inherent in the instrument design.

Figure 2.3

Crucible holder.



The base-line drift in the weight channel is caused by buoyancy effects due to 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% in a sample of 9 mg weight. From 100 to 1000°C the base-line rises approximately linearly at ca. 0.03 mg/100°.

Base-line drift also occurs on the DTA channel, which leads to errors in calculation 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 accurately 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 was used.

A 12-channel, 6-point dot recorder simultaneously traces in different coloured inks, the temperature curve, the two weight traces (normal and expanded), the differential of the weight trace and the DTA trace. The dot intervals of the

tracings were chosen, so that each curve, according to its gradient, had the optimum point density. When these points are later joined up, a series of curves and lines are obtained. Block schematic diagrams of the balance mechanism and of the recording and electric systems are shown in Figs. 2.4 and 2.5 respectively.

2.3.4.2. Mettler Computer Interface System.

Interface hardware : Fig. 2.6 shows a schematic diagram of the Mettler computer interface system, viz. an Apple II microcomputer with twin disc drives, interfaced through a U-Microcomputers model U-A/D interface, consisting of a digital board plugged into one of the Apple expansion slots and connected to an A/D converter unit. The digital board has two 6522 VIAs; one is used for timing and the other for digital output. The A/D converter 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, 1 V or 10 V (under software control) for maximum output. The converter is an AD574 i.e. a 12-bit device with a conversion time of 25 μ s.

Analog inputs are taken from the Mettler amplifier outputs, where they are scaled to 10 mV for full-scale deflection on the chart recorder. Weight and temperatures are amplified

Figure 2.4

Block schematic diagram of the balance mechanism.

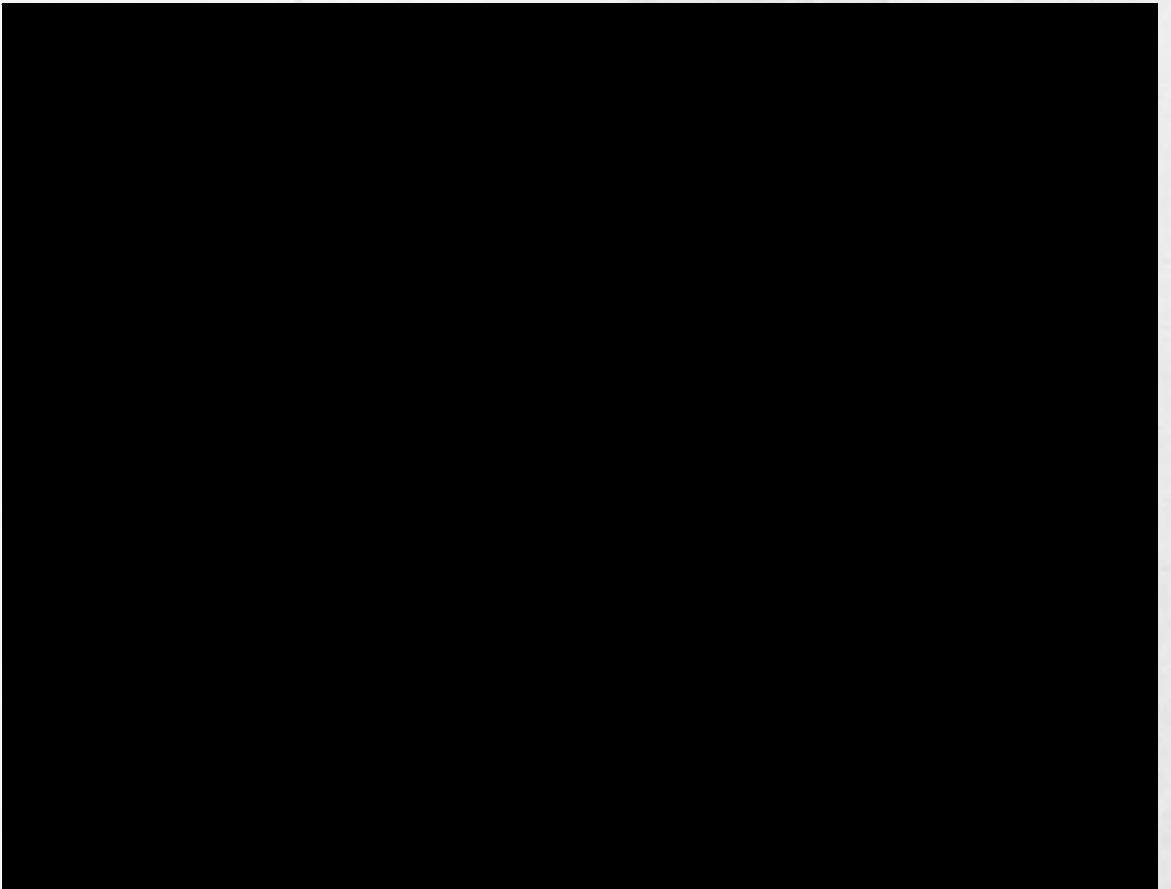


Figure 2.5

Schematic diagram of the Mettler Thermoanalyser.

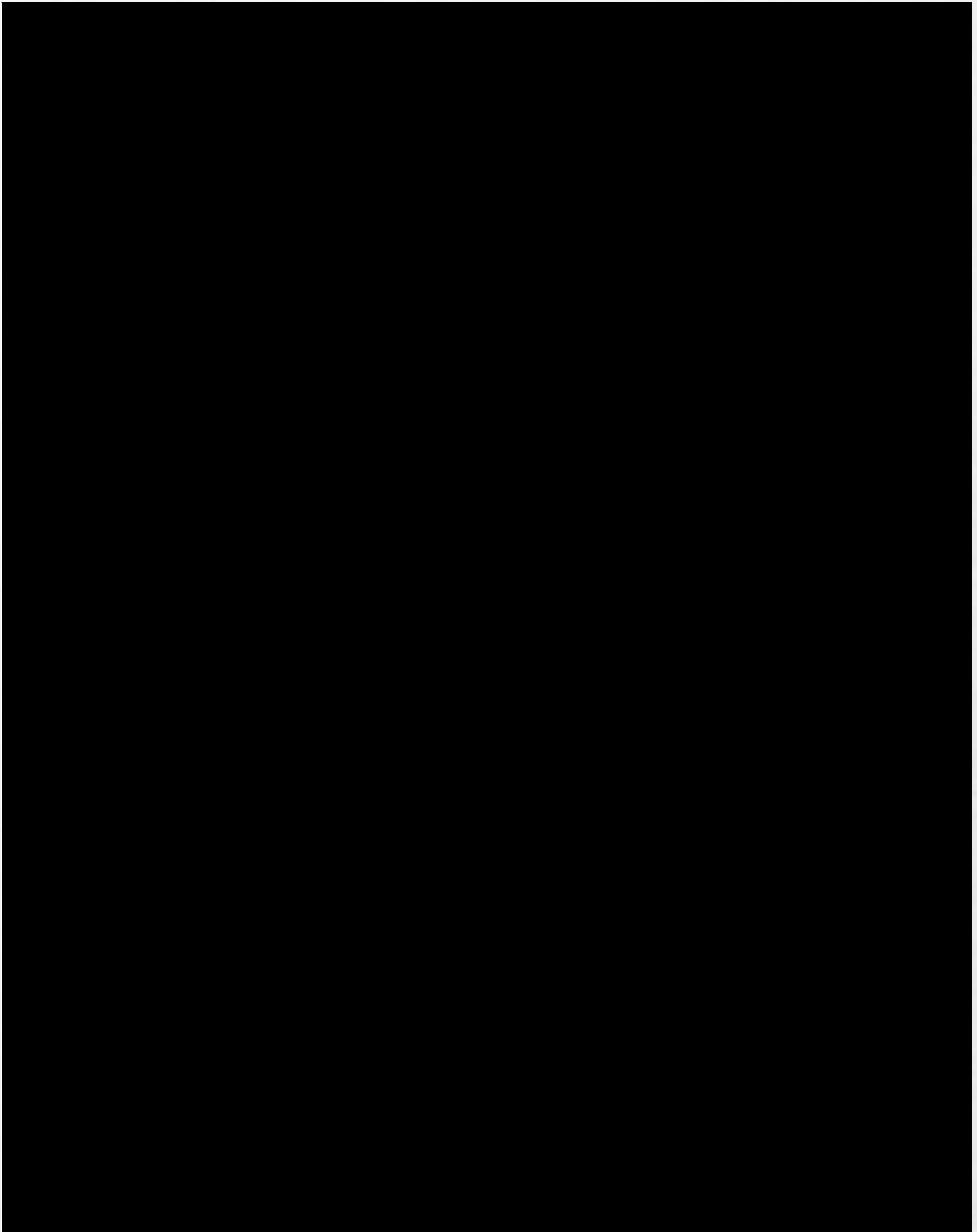
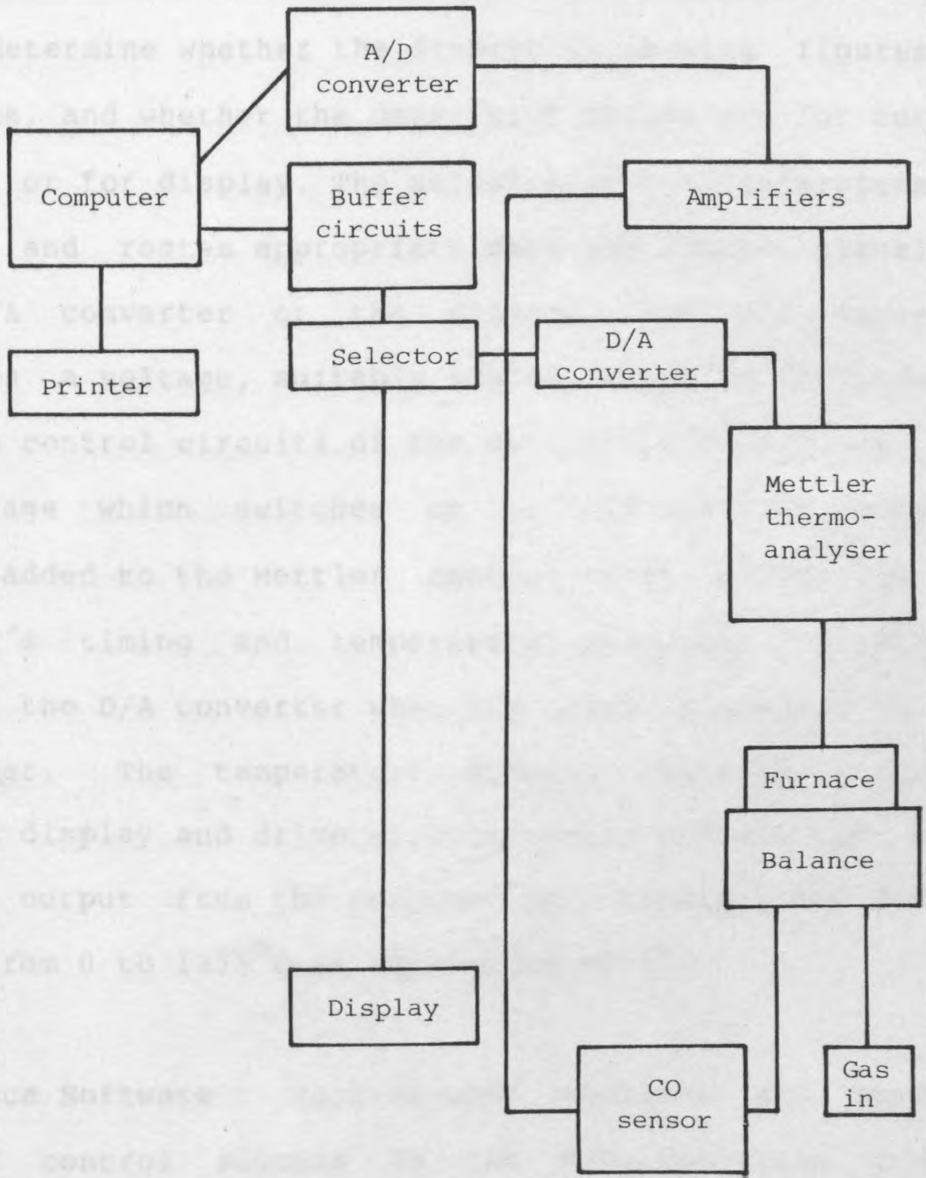


Figure 2.6

Schematic diagram of the Mettler computer interface system.



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, by 0.5.

Digital outputs from the computer are used for furnace control and to display the approximate temperature. The computer sends alternately control codes and data; control codes determine 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 thermobalance, 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 programme circuits and connect the D/A converter when the power is applied to the converter. The temperature display contains a liquid crystal display and drive circuits which convert the 8-bit binary output from the computer to a 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 thermobalance. Programme (ii) produces a file of calibration data which are used by programme (iii) to convert digital input to numerical data. Programme (iii) samples data continuously and writes data (selected by criteria chosen by the user) to one or more data discs.

Further programmes deal with the data stored on discs: (i) a plotting programme produces suitably scaled plots of any pair of data items; (ii) a printing programme produces a complete listing of the data stored in a particular disc file, and (iii) a tape punching programme produces a paper tape containing selected data from the run; this may be read and stored by a main-frame computer for detailed kinetic analysis and plotting.

2.3.4.3. Procedure for Thermal Analysis.

After the recorder had been switched on, the air flow rate was set at $60 \text{ cm}^3 \text{ min}^{-1}$. Small strips of polymer samples, cut from the centre of a standard plate, were spread evenly over the crucible surface. A sample weight of 8-10 mg was normally used. The range shift on the DTG panel was set on manual and a sensitivity of 5 mg min^{-1} per full scale deflection was used throughout. The range used for differential analysis was 200 μV , and the range for temperature readings was 10 mV; the heating rate used throughout was 5° min^{-1} . The results of thermogravimetric and DTA runs were printed on a 25 cm wide chart of a 6-channel chart recorder and numerical data were collected by the computer system.

2.3.4.4. Microanalysis.

Polymer-additive samples before and after various stages of thermal decomposition were analysed for C, H, N, O, P and Cl by the microanalysis service of this Department. The heating of the sample was carried out on the thermoanalyser, using the procedure for thermal analysis described in Section 2.3.4.3, except that a larger sample weight, 100 mg, was used. The runs were stopped at specific stages of degradation or oxidation and the residues were analysed.

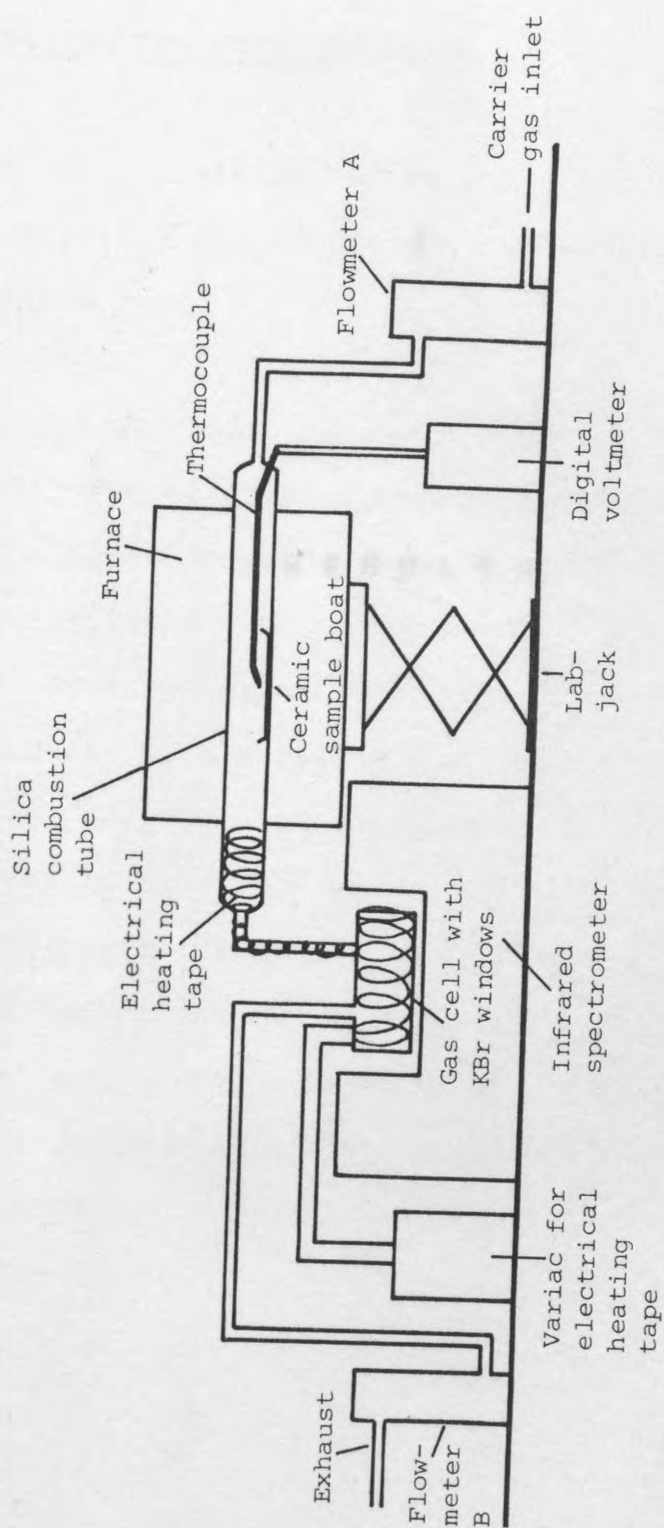
2.3.5. Infrared Analysis.

The gaseous products from the combustion of some polymer-additive samples were analysed by infrared spectrometry. The apparatus is shown in Fig. 2.7.

A ceramic boat containing approximately 1 g of sample was placed in a silica tube, 400 mm long and 25 mm in diameter, which was then heated at a rate of about $6^{\circ} \text{ min}^{-1}$ in a horizontal tube furnace, capable of reaching temperatures of up to 700°C . The temperature of the sample was measured continuously using a chromel-alumel thermocouple, which was in contact with the sample. The thermocouple was connected to a digital millivoltmeter and to a chart recorder. The gaseous products were swept continuously through an infrared gas cell, fitted with sodium chloride windows, with air or nitrogen at 100 ml min^{-1} . Infrared spectra were recorded every 5 min using a Perkin-Elmer Model 257 grating spectrometer. To prevent condensation of the products, the exposed ends of the silica tube and the tubing leading to the cell were heated by means of electrical heating tape.

Figure 2.7

Apparatus for infrared spectroscopic measurements.



3. RESULTS

3.1. Flammability and Smoke-formation Measurements.

3.1.1. Values for Pure Polymers.

Values of the limiting oxygen index (LOI) and the maximum smoke density (MSD) for the various pure polymers studied are given in Table 3.1.

R E S U L T S

Unplasticized PVC has LOI values between 25 and 27 (Table 3.1) but with PVC plasticized with aromatic compounds, a flammable aromatic compound (LOI 19.5) was used. The value of plasticized PVC was 19.5, which is a significant amount of smoke is produced. The polymer burns very easily and burns with a thick black smoke. There is considerable melting and dripping of the polymer. The methacrylate is about the same as the PVC polymer, but due to its high oxygen content, it produces very little smoke. Like polystyrene, it burns with a thick black smoke readily in air with a lot of dripping. However, it burns with a thick black smoke and produces levels of smoke.

3. RESULTS.

3.1. Flammability and Smoke-formation Measurements.

3.1.1. Values for Pure Polymers.

Values of the limiting oxygen index (LOI) and the maximum smoke density (D_s) for the various pure polymers studied are given in Table 3.1.

Unplasticised PVC has LOI values between 45 and 49 (Table 1.3) but with PVC plasticised with di-isooctyl phthalate, a flammable aromatic compound, the LOI falls to ca. 25. The D_s value of plasticised PVC indicates that quite a significant amount of smoke is produced. Polystyrene ignites much more easily and burns with a yellow and sooty flame. There is considerable melting and dripping. The LOI of poly(methyl methacrylate) is about the same as that of polystyrene. Due to its high oxygen content, it produces only low levels of smoke. Like polystyrene, high-density polyethylene burns readily in air with considerable melting and dripping. However, it burns with a blue flame and produces fairly low levels of smoke.

3.1.2. Effects of Additives on the Flammability and Smoke-Producing Tendency of the Polymers.

Table 3.1

3.1.1. LOI and maximum smoke density values of pure polymers.

The two main substrates used in this study were polystyrene and poly(vinyl chloride). The bulk of the work was carried out with mixtures of substrate and large different additives, one containing phosphorus, one nitrogen and one bromine. The phosphorus additives were triethyl phosphite, triethyl phosphite and triethyl phosphite.

Polymer	LOI	D _s
Poly(vinyl chloride)	25.2	569
Polystyrene	17.5	646
Poly(methyl methacrylate)	17.7	97
High-density polyethylene	18.3	97

As mentioned above, the effect of the additives on the above, the effect of the additives on the phosphorus and nitrogen additives was studied. The results are represented in the form of triangles in all binary and ternary systems, the maximum values are for each additive at 10 wt. %, and only one triangle was used to represent the results for each system investigated at the 5 wt. % level. For binary systems, the compositions were spread over the composition ranges bounded by 50 wt. % of substrate, and 50 wt. % of additive and 10 wt. % of each

3.1.2. Effects of Additives on the Flammability and Smoke-Producing Tendency of the Polymers.

3.1.2.1. Introduction.

The two main substrates used in this study were polystyrene and poly(vinyl chloride). The bulk of the work was carried out with mixtures of substrate and three different additives, one containing phosphorus, one nitrogen and one bromine. The phosphorus additives were red phosphorus, triethyl phosphate and tritolyl phosphate; the nitrogen additives were melamine, urea and guanidine carbonate, and the bromine additive was decabromobiphenyl. In addition to the above, the effect of the ternary system : red phosphorus, melamine and DBB, was studied in poly(methyl methacrylate) and in high-density polyethylene.

As mentioned in Section 2.3.3., the flammability and smoke density results for the various systems with mixed additives are represented in the form of triangular diagrams. In all binary and ternary systems, the maximum loading was the same for each additive at 30 wt %, so that only equilateral triangles were used to represent the results. For each system studied, between 35 and 45 compositions were used. For binary systems, the compositions were spread over the composition ranges bounded by the points 100 wt % of substrate, and 70 wt % of substrate and 30 wt % of each

additive. For ternary systems, a constant total additive loading of 30 wt % was used, with each vertex being 70 wt % of substrate and 30 wt % of one of the additives.

For ease of interpretation and comparison of one triangular diagram with another, the intervals of the contour lines in all triangular diagrams is the same. Thus, the intervals in the flammability and smoke-formation plots are 0.5 LOI unit and 200 D_s units respectively.

Quantitative assessment of the effects of additives on the flammability of, and smoke formation from, PVC, PS, PMMA and HDPE are shown in Tables 3.2 and 3.3.

3.1.2.2. Poly(vinyl chloride).

P/DBB/MEL : Fig. 3.1 shows the triangular diagrams for the flammability of, and smoke production from, PVC containing P, DBB and MEL. The diagrams show that red phosphorus on its own enhances both the flammability and smoke-forming tendency of PVC. In fact, at a loading of 30 wt % P, the LOI is about 3 units lower than that of the polymer on its own. In general, the LOI increased whereas the D_s decreased with increasing Br/P ratio. Thus, the "effectiveness coefficients" of flame retardance and smoke formation of DBB are 25 ± 2 and 1580 ± 580 , which is equivalent to increasing the LOI by 7.5 units and D_s by 470 units respectively (Tables

Table 3.2

Quantitative assessment of the flame-retardant effects of additives on PVC, PS, PMMA and HDPE.

Additive system	Coefficient order	R.M.S. diff.	"Effectiveness Coefficient"						
			P	Br	N	P-Br	P-N	Br-N	P-Br-N
Poly(vinyl chloride)									
P/DBB/MEL	full cubic	0.77	-9 ± 2	25 ± 2	10 ± 2	-3 ± 30	100 ± 32	31 ± 33	1077 ± 563
DBB/MEL	linear	0.43	-	26 ± 1	13 ± 1	-	-	-	-
P/DBB/UREA	full cubic	0.83	-14 ± 2	28 ± 2	4 ± 2	-24 ± 31	136 ± 32	-105 ± 30	270 ± 616
P/DBB/GC	full cubic	0.89	-11 ± 3	25 ± 3	22 ± 2	15 ± 34	171 ± 33	-61 ± 35	492 ± 624
TEP/DBB/MEL	quadratic	0.41	3 ± 1	26 ± 1	10 ± 1	-23 ± 12	-11 ± 13	-24 ± 13	-
Polystyrene									
P/DBB/MEL	full cubic	0.49	16 ± 1	27 ± 1	8 ± 1	12 ± 17	168 ± 27	-35 ± 19	428 ± 362
P/MEL	red. cubic	0.59	19 ± 3	-	9 ± 3	-	248 ± 25	-	-
DBB/MEL	full cubic	0.58	-	32 ± 4	14 ± 4	-	-	-83 ± 25	-
P/DBB/UREA	full cubic	0.54	16 ± 2	26 ± 1	7 ± 2	22 ± 19	158 ± 21	3 ± 22	-488 ± 374
P/UREA	full cubic	0.39	22 ± 2	-	10 ± 2	-	202 ± 15	-	-
P/DBB/GC	quartic	0.63	15 ± 2	27 ± 2	10 ± 2	27 ± 29	171 ± 29	49 ± 29	209 ± 479
TTP/DBB/MEL	quadratic	0.43	20 ± 1	26 ± 1	12 ± 1	34 ± 14	-59 ± 14	-55 ± 13	-
Poly(methyl methacrylate)									
P/DBB/MEL	red. cubic	0.44	20 ± 1	11 ± 1	14 ± 1	103 ± 17	93 ± 17	-11 ± 17	823 ± 316
High-density polyethylene									
P/DBB/MEL	full cubic	0.51	5 ± 1	17 ± 1	11 ± 1	74 ± 19	157 ± 20	-24 ± 20	-1060 ± 356

Table 3.3

Quantitative assessment of the effects of additives
on smoke formation from PVC, PS, PMMA and HDPE.

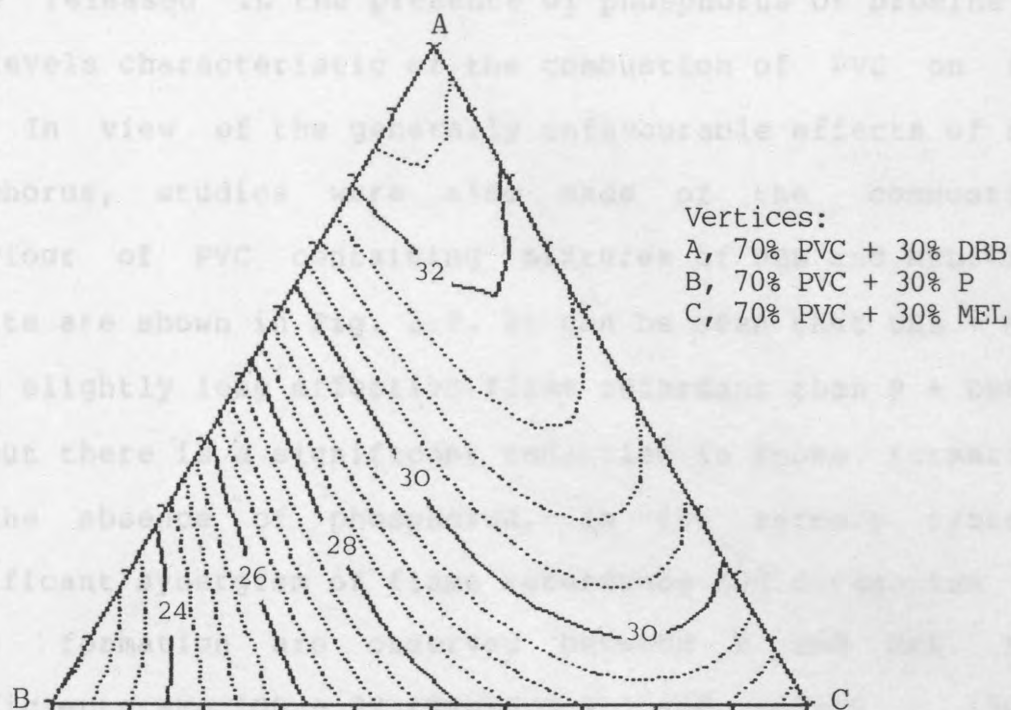
Additive system	Coefficient order	R.M.S. diff.	"Effectiveness Coefficient"			
			P	Br	N	
Poly(vinyl chloride)						
P/DBB/MEL	full cubic	192	10710 ± 1670	1580 ± 580	-650 ± 240	
DBB/MEL	full cubic	148	-	1920 ± 600	-1370 ± 480	
TEP/DBB/MEL	full cubic	187	2600 ± 620	2490 ± 580	-760 ± 210	
Polystyrene						
P/DBB/MEL	quadratic	184	3870 ± 790	1520 ± 310	-1130 ± 170	
P/MEL	red. cubic	223	640 ± 820	-	-1070 ± 710	
DBB/MEL	quadratic	129	-	2110 ± 480	630 ± 410	
P/DBB/UREA	red. cubic	168	1920 ± 420	1550 ± 300	-1940 ± 100	
P/UREA	full cubic	146	770 ± 610	-	-780 ± 560	
TTP/DBB/MEL	full cubic	185	-710 ± 240	1890 ± 480	-990 ± 180	
Poly(methyl methacrylate)						
P/DBB/MEL	quadratic	127	15250 ± 630	1740 ± 220	-50 ± 40	
High-density polyethylene						
P/DBB/MEL	full cubic	64	3040 ± 210	2030 ± 140	-190 ± 10	

Table 3.3
(contd.)

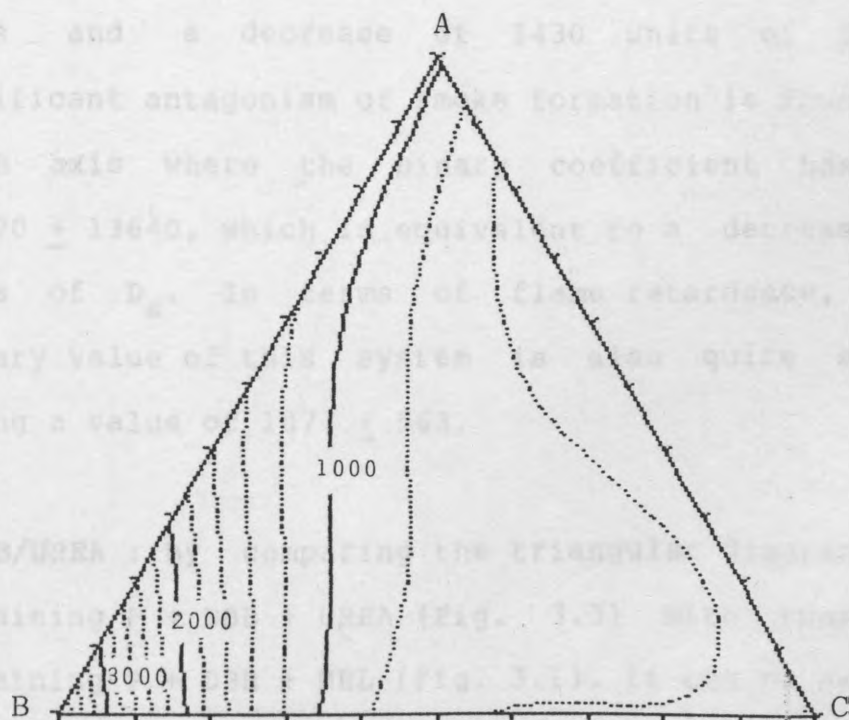
Additive system	"Effectiveness Coefficient"			
	P-Br	P-N	Br-N	P-Br-N
Poly(vinyl chloride)				
P/DBB/MEL	-45970 ± 13640	-63510 ± 13030	-12280 ± 5480	238890 ± 128070
DBB/MEL	-	-	-19840 ± 3980	-
TEP/DBB/MEL	44640 ± 9890	-3950 ± 5630	-21030 ± 5260	-277170 ± 126050
Polystyrene				
P/DBB/MEL	-26870 ± 6390	19340 ± 7620	1360 ± 4090	-
P/MEL	-	27640 ± 7700	-	-
DBB/MEL	-	-	8940 ± 3280	-
P/DBB/UREA	-11320 ± 5560	14460 ± 3940	-3610 ± 3460	-338460 ± 68940
P/UREA	-	23470 ± 4600	-	-
TTP/DBB/MEL	-8880 ± 5180	7760 ± 3170	1570 ± 5150	52700 ± 90500
Poly(methyl methacrylate)				
P/DBB/MEL	-66430 ± 4890	-55390 ± 2930	1260 ± 1440	-
High-density polyethylene				
P/DBB/MEL	-5410 ± 2230	-16080 ± 1550	2920 ± 1250	84110 ± 17920

Figure 3.1

The effects of red phosphorus, decabromobiphenyl and melamine on the (a) LOI and (b) Ds values of PVC.



(a)



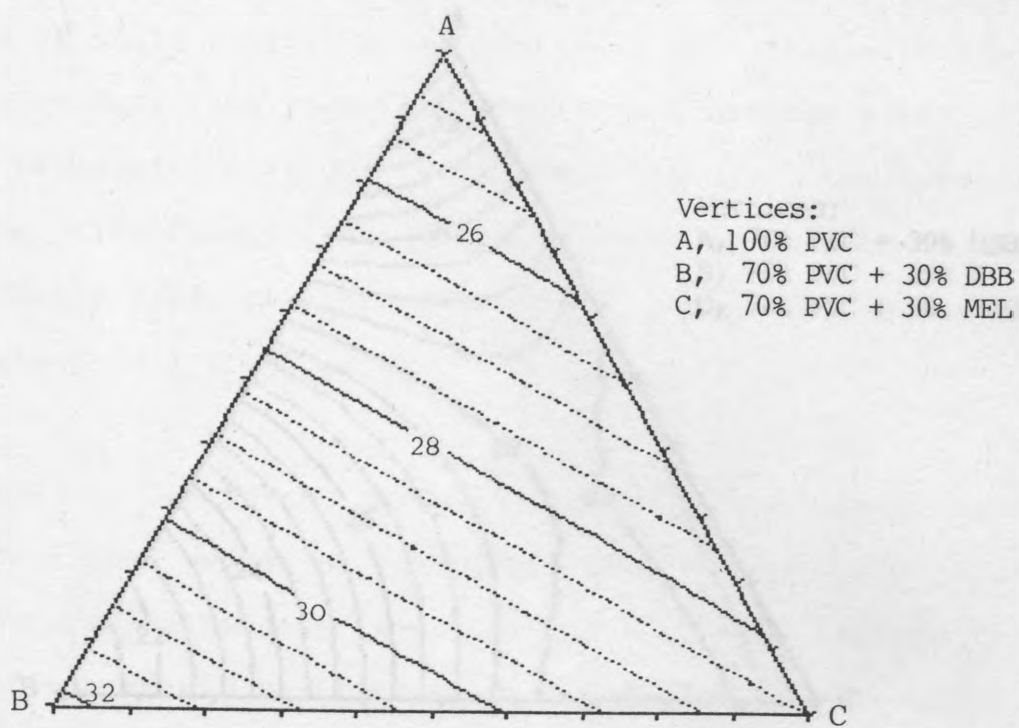
(b)

3.2 and 3.3). Melamine, while having little effect on flammability, tended to decrease the very large amounts of smoke released in the presence of phosphorus or bromine to the levels characteristic of the combustion of PVC on its own. In view of the generally unfavourable effects of red phosphorus, studies were also made of the combustion behaviour of PVC containing mixtures of DBB and MEL. The results are shown in Fig. 3.2. It can be seen that DBB + MEL is a slightly less effective flame retardant than P + DBB + MEL but there is a significant reduction in smoke formation in the absence of phosphorus. In the ternary system, significant synergism of flame retardance and antagonism of smoke formation are observed between P and MEL, the coefficients are 100 ± 32 (Table 3.2) and -63510 ± 13030 (Table 3.3) respectively. In other words, the presence of phosphorus and melamine gave rise to an increase of 2.3 LOI units and a decrease of 1430 units of D_s . Further significant antagonism of smoke formation is found along the P-DBB axis where the binary coefficient has a value of -45970 ± 13640 , which is equivalent to a decrease of 1030 units of D_s . In terms of flame retardance, the overall ternary value of this system is also quite significant, having a value of 1077 ± 563 .

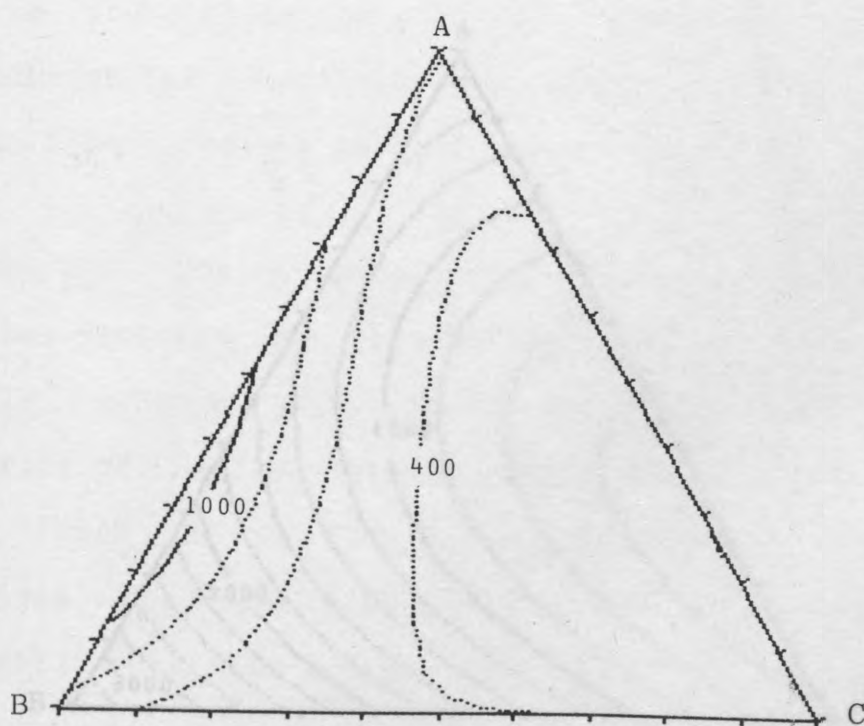
P/DBB/UREA : By comparing the triangular diagrams for PVC containing P + DBB + UREA (Fig. 3.3) with those for PVC containing P + DBB + MEL (Fig. 3.1), it can be seen that the

Figure 3.2

The effects of decabromobiphenyl and melamine
on the (a) LOI and (b) Ds values of PVC.



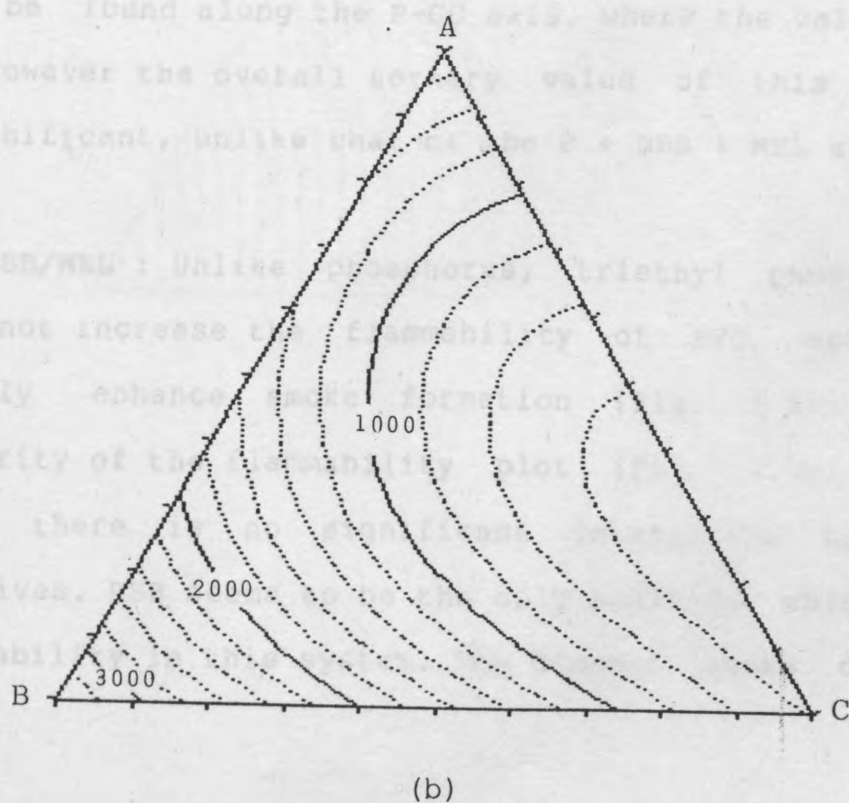
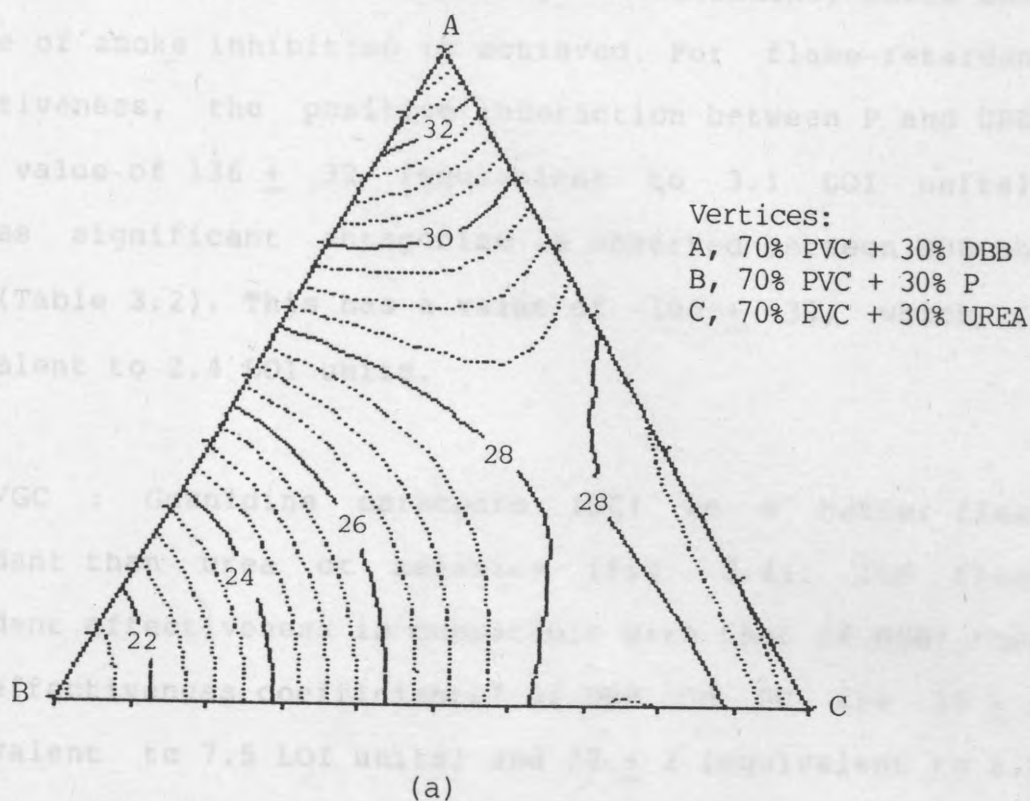
(a)



(b)

Figure 3.3

The effects of red phosphorus, decabromobiphenyl and urea on the (a) LOI and (b) Ds values of PVC.



overall flammability and smoke formation values are quite similar. Here too, the flammability is low at high loadings of DBB. Urea behaves similarly to melamine, where some degree of smoke inhibition is achieved. For flame-retardant effectiveness, the positive interaction between P and UREA has a value of 136 ± 32 (equivalent to 3.1 LOI units), whereas significant antagonism is observed between DBB and UREA (Table 3.2). This has a value of -105 ± 30 , which is equivalent to 2.4 LOI units.

P/DBB/GC : Guanidine carbonate (GC) is a better flame retardant than urea or melamine (Fig. 3.4). Its flame retardant effectiveness is comparable with that of DBB; thus the "effectiveness coefficients" of DBB and GC are 25 ± 3 (equivalent to 7.5 LOI units) and 22 ± 2 (equivalent to 6.6 LOI units) respectively (Table 3.2). A positive interaction can be found along the P-GC axis, where the value is 171 ± 33 . However the overall ternary value of this system is insignificant, unlike that of the P + DBB + MEL system.

TEP/DBB/MEL : Unlike phosphorus, triethyl phosphate (TEP) does not increase the flammability of PVC, nor does it greatly enhance smoke formation (Fig. 3.5). The near linearity of the flammability plot (Fig. 3.5a) indicates that there is no significant interaction between the additives. DBB seems to be the only additive which reduces flammability in this system. The highest smoke density is

Figure 3.4

The effects of red phosphorus, decabromobiphenyl and guanidine carbonate on the LOI values of PVC.

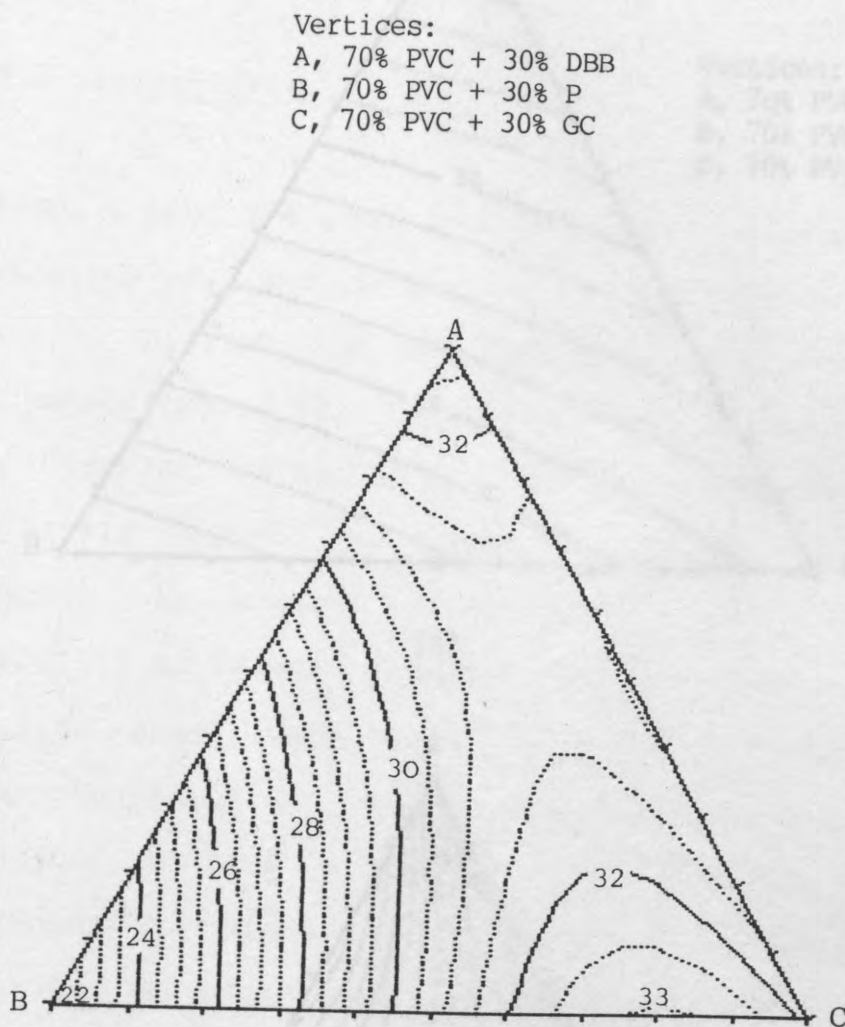
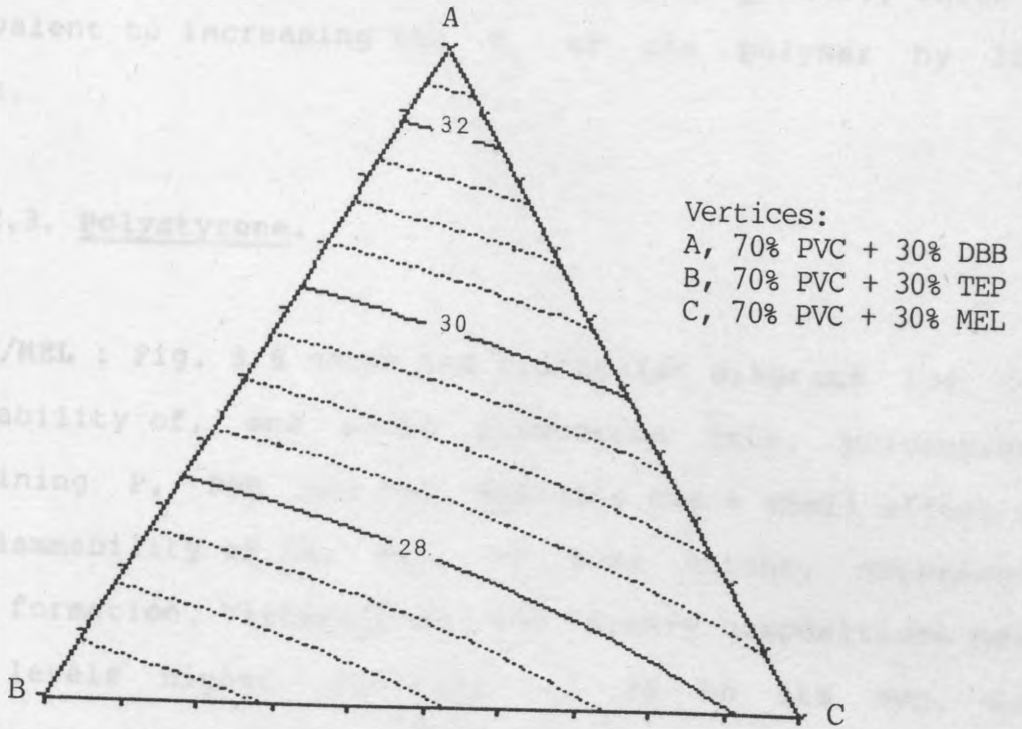
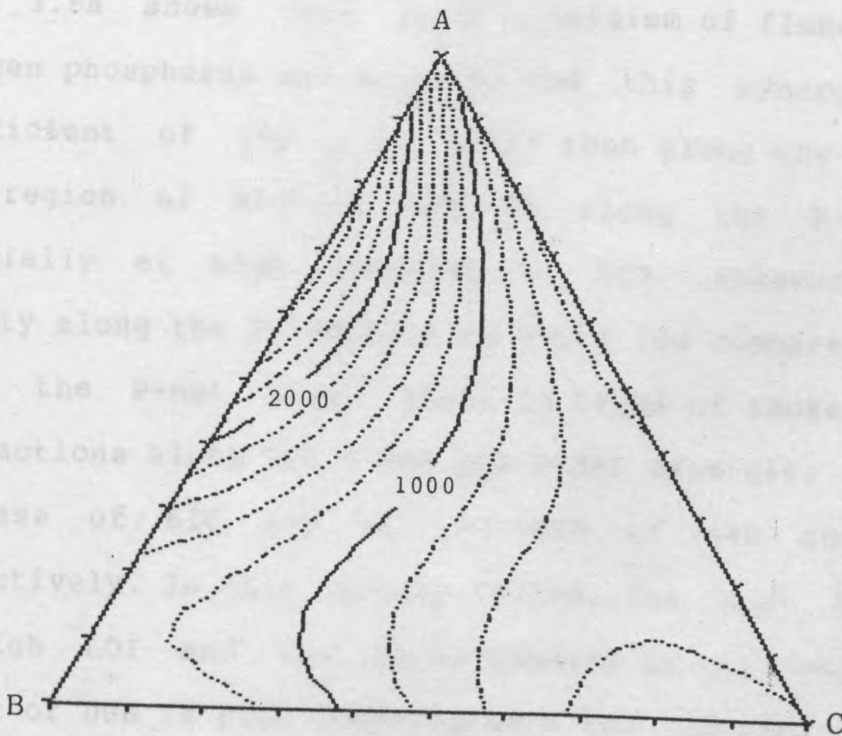


Figure 3.5

The effects of triethyl phosphate, decabromobiphenyl and melamine on the (a) LOI and (b) Ds values of PVC.



(a)



(b)

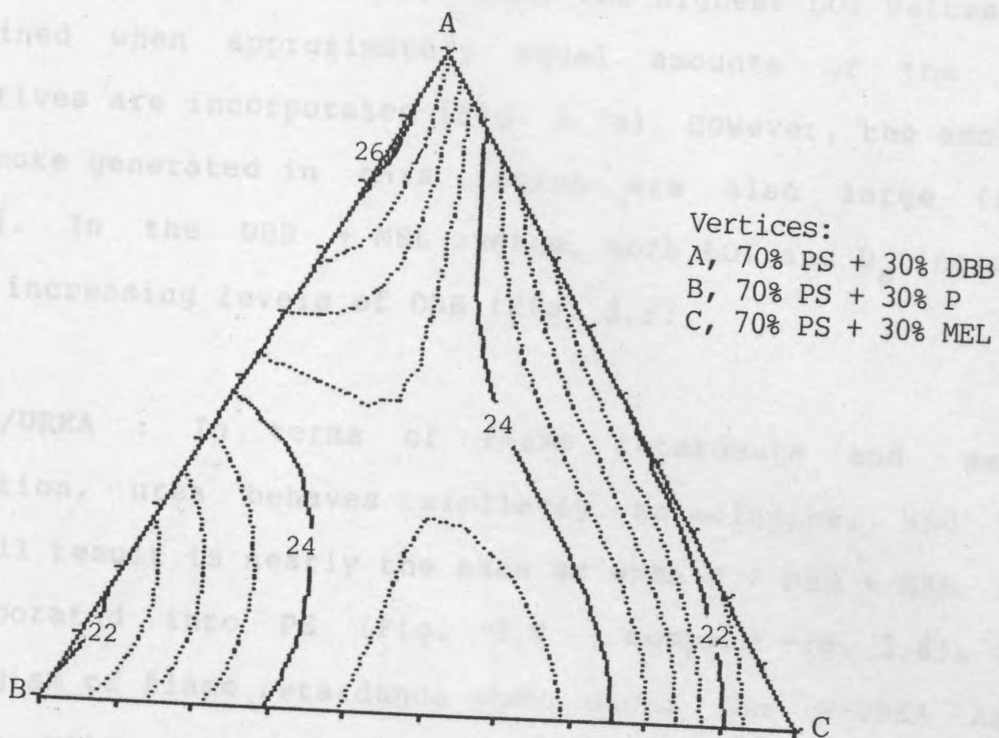
found along the TEP-DBB axis (Fig. 3.5b). In terms of smoke formation, the interaction along the TEP-DBB axis is synergistic, having a value of 44640 ± 9890 , which is equivalent to increasing the D_s of the polymer by 1000 units.

3.1.2.3. Polystyrene.

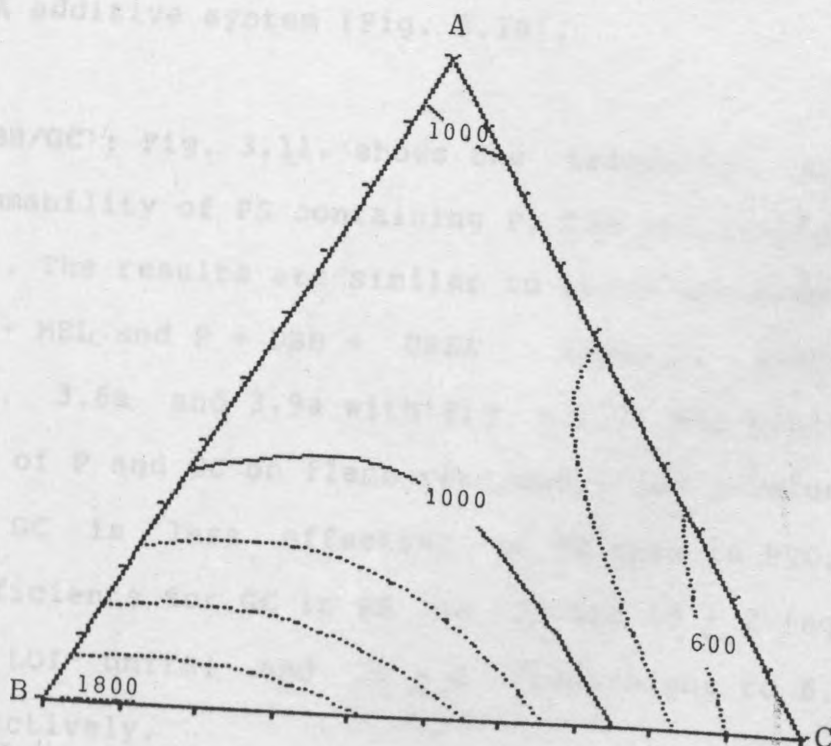
P/DBB/MEL : Fig. 3.6 shows the triangular diagrams for the flammability of, and smoke production from, polystyrene containing P, DBB and MEL. Melamine has a small effect on the flammability of PS, but, to some extent, suppresses smoke formation. Virtually all the ternary compositions have smoke levels higher than that of PS on its own. Red phosphorus has a small favourable effect in decreasing the flammability of PS but greatly enhances smoke formation. Fig. 3.6a shows very clear synergism of flame retardance between phosphorus and melamine and this synergism has a coefficient of 168 ± 27 . Other than along the P-MEL axis, the region of highest LOI is along the P-DBB axis, especially at high loadings of DBB. However the smoke density along the P-DBB axis is quite low compared with that along the P-MEL axis. Thus, in terms of smoke formation, interactions along the P-DBB and P-MEL axes give rise to a decrease of 610 and an increase of 440 units of D_s respectively. In this ternary system, the best combination of high LOI and low smoke density is obtained where the amount of DBB is high compared with the amounts of P and

Figure 3.6

The effects of red phosphorus, decabromobiphenyl and melamine on the (a) LOI and (b) Ds values of PS.



(a)



(b)

MEL. Results obtained for binary mixtures of P + MEL (Fig. 3.7) and DBB + MEL (Fig. 3.8) confirm the above observation. In a system containing P + MEL, the highest LOI values are obtained when approximately equal amounts of the two additives are incorporated (Fig. 3.7a). However, the amounts of smoke generated in this region are also large (Fig. 3.7b). In the DBB + MEL system, both LOI and D_s increase with increasing levels of DBB (Fig. 3.8).

P/DBB/UREA : In terms of flame retardance and smoke formation, urea behaves similarly to melamine, and the overall result is nearly the same as when P + DBB + MEL are incorporated into PS (Fig. 3.9 ; compare Fig. 3.6). The synergism of flame retardance shown along the P-UREA axis has a value of 158 ± 21 and this positive interaction is also apparent in the triangular diagrams for the binary P + UREA additive system (Fig. 3.10).

P/DBB/GC : Fig. 3.11 shows the triangular diagram for the flammability of PS containing P, DBB and guanidine carbonate (GC). The results are similar to those obtained with the P + DBB + MEL and P + DBB + UREA additive systems (compare Figs. 3.6a and 3.9a with Fig. 3.11). The positive interaction of P and GC on flame retardance has a value of 171 ± 29 . GC is less effective in PS than in PVC. Indeed, the coefficients for GC in PS and PVC are 10 ± 2 (equivalent to 3.0 LOI units) and 22 ± 2 (equivalent to 6.6 LOI units) respectively.

Figure 3.7

The effects of red phosphorus and melamine
on the (a) LOI and (b) Ds values of PS.

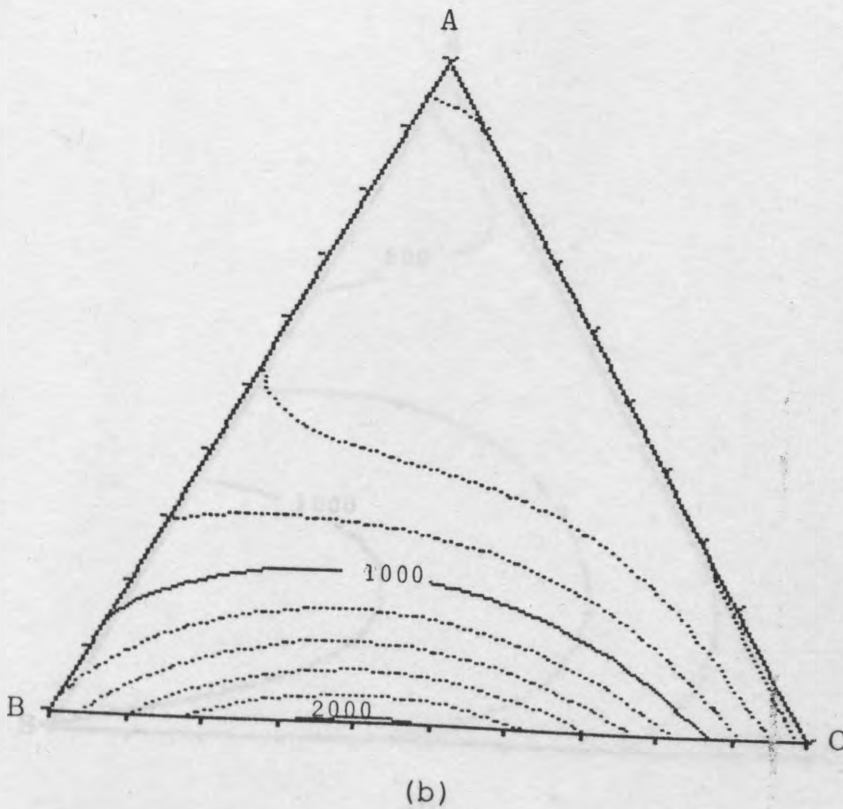
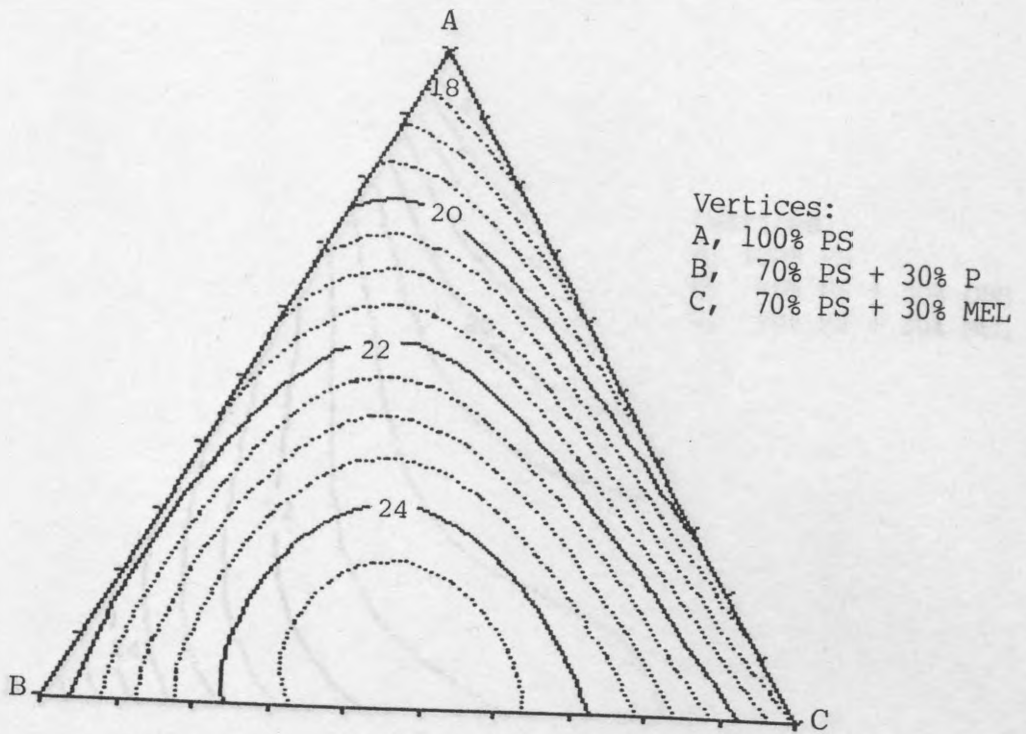
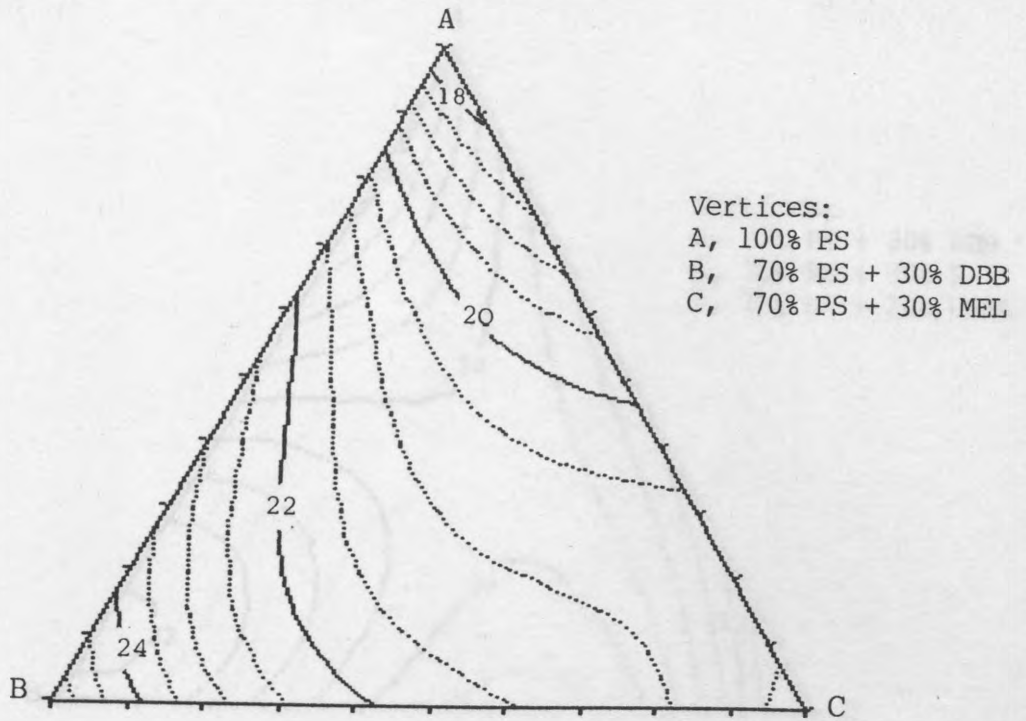
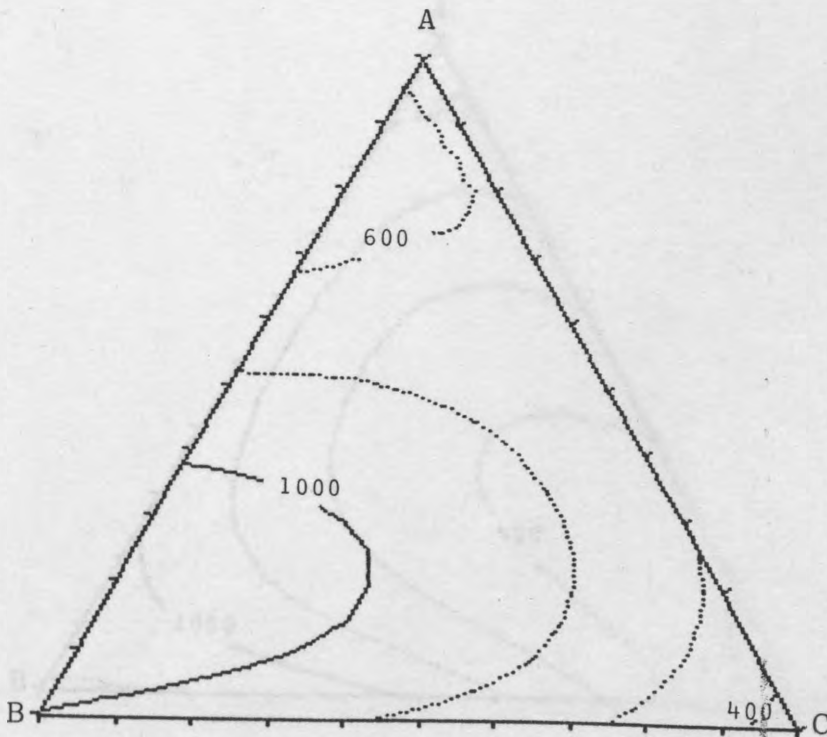


Figure 3.8

The effects of decabromobiphenyl and melamine
on the (a) LOI and (b) Ds values of PS.



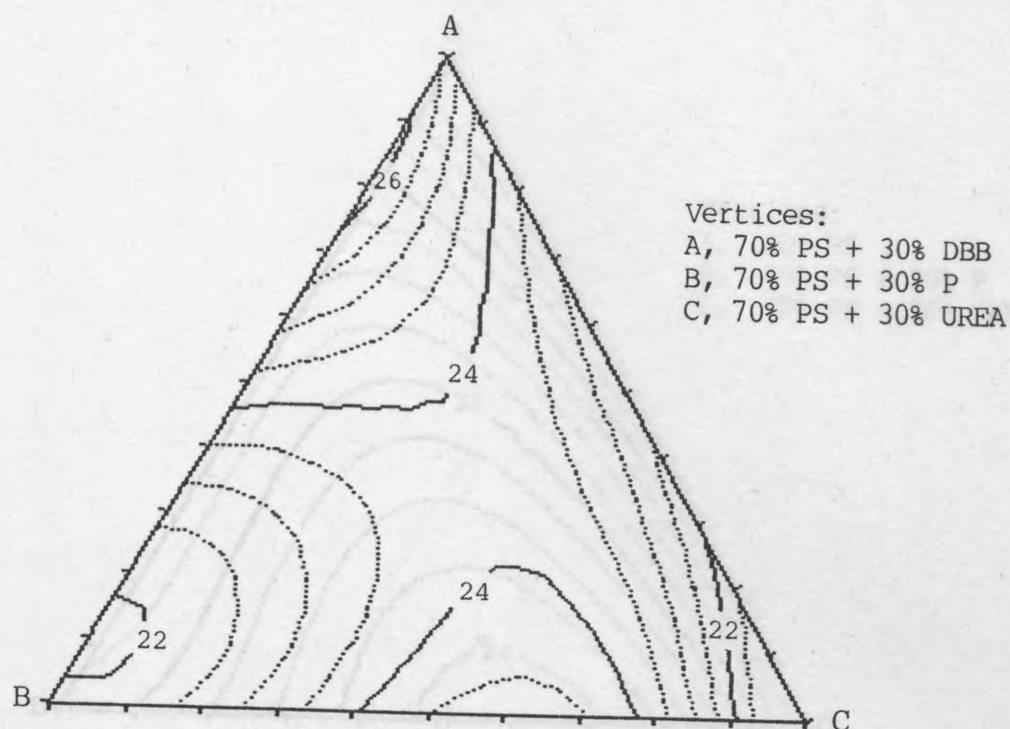
(a)



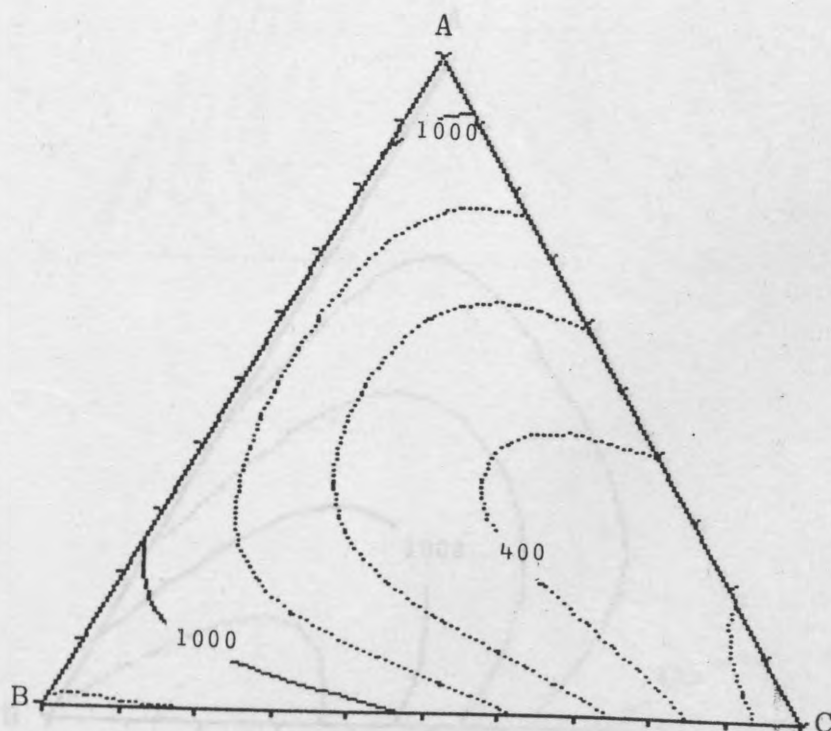
(b)

Figure 3.9

The effects of red phosphorus, decabromobiphenyl and urea on the (a) LOI and (b) Ds values of PS.



(a)



(b)

Figure 3.10

The effects of red phosphorus and urea
on the (a) LOI and (b) Ds values of PS.

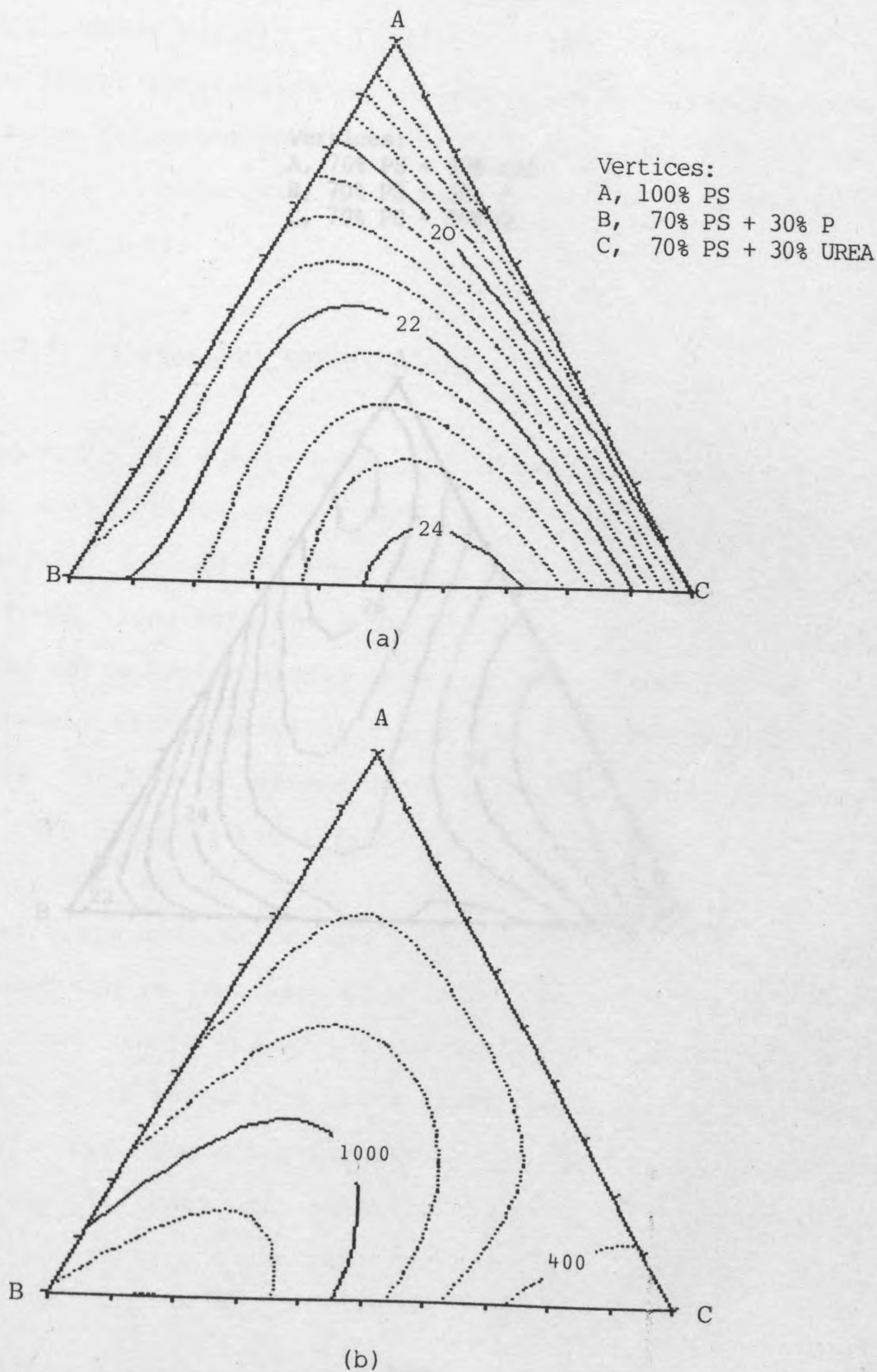


Figure 3.11

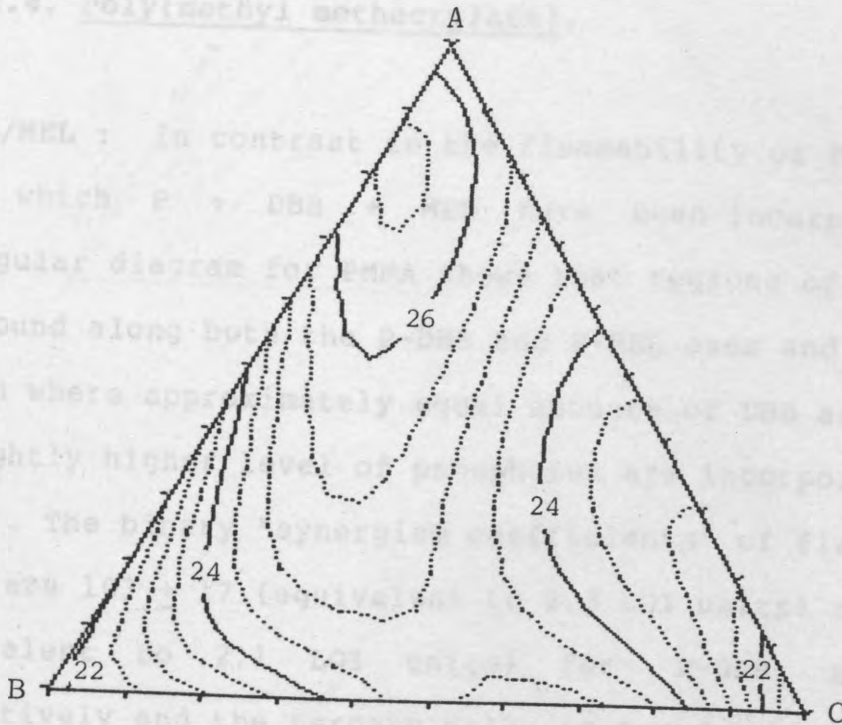
The effects of red phosphorus, decabromobiphenyl and guanidine carbonate on the LOI values of PS.

Vertices:

A, 70% PS + 30% DBB

B, 70% PS + 30% P

C, 70% PS + 30% GC



TTP/DBB/MEL : Tritolyl phosphate (TTP) shows some effectiveness as a flame retardant, especially in combination with a high level of DBB (Fig. 3.12a) and, in its presence, the overall smoke density is relatively low (Fig. 3.12b). No significant interaction of the additives on flame retardance or smoke formation of the polymer is observed. TTP is more effective in reducing the flammability of PS than TEP is in PVC (Fig. 3.5).

3.1.2.4. Poly(methyl methacrylate).

P/DBB/MEL : In contrast to the flammability of PVC and PS into which P + DBB + MEL have been incorporated, the triangular diagram for PMMA shows that regions of high LOI are found along both the P-DBB and P-MEL axes and around the region where approximately equal amounts of DBB and MEL and a slightly higher level of phosphorus are incorporated (Fig. 3.13a). The binary "synergism coefficients" of flame retardance are 103 ± 17 (equivalent to 2.3 LOI units) and 93 ± 17 (equivalent to 2.1 LOI units) for P-DBB and P-MEL respectively and the ternary value is found to be 823 ± 316 . Although DBB is less effective in decreasing flammability in PMMA than in PS and PVC, it nevertheless gives a LOI value of 21.0 which is about 3 units higher than the LOI of PMMA on its own. The effectiveness of red phosphorus as a flame retardant in PMMA is slightly higher than in PS. The coefficients for P are 20 ± 1 (equivalent to 6.0 LOI units)

Figure 3.12

The effects of tritolyl phosphate, decabromobiphenyl and melamine on the (a) LOI and (b) Ds values of PS.

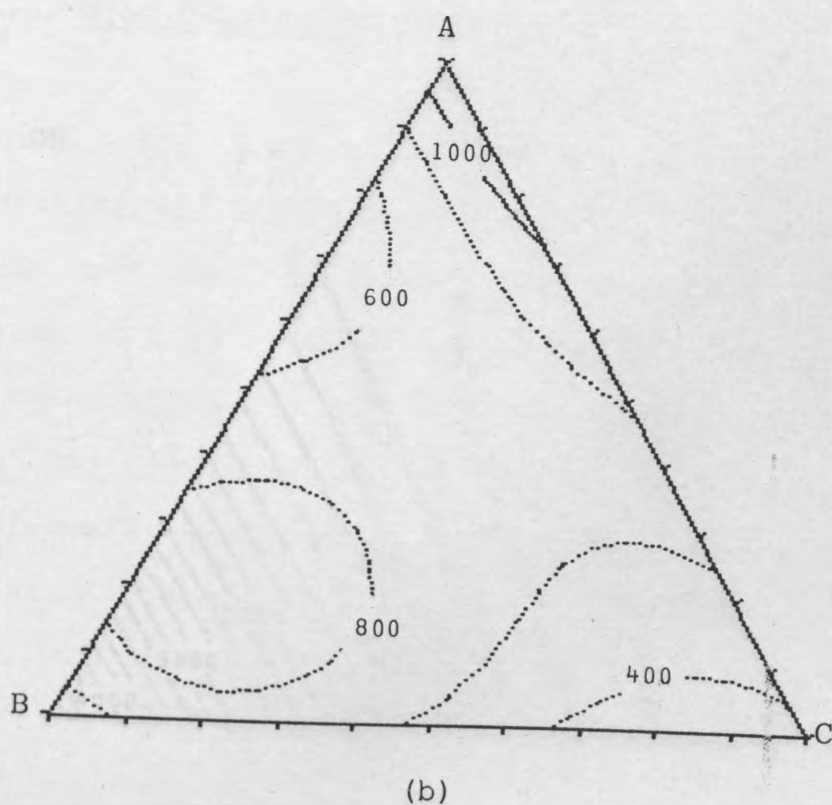
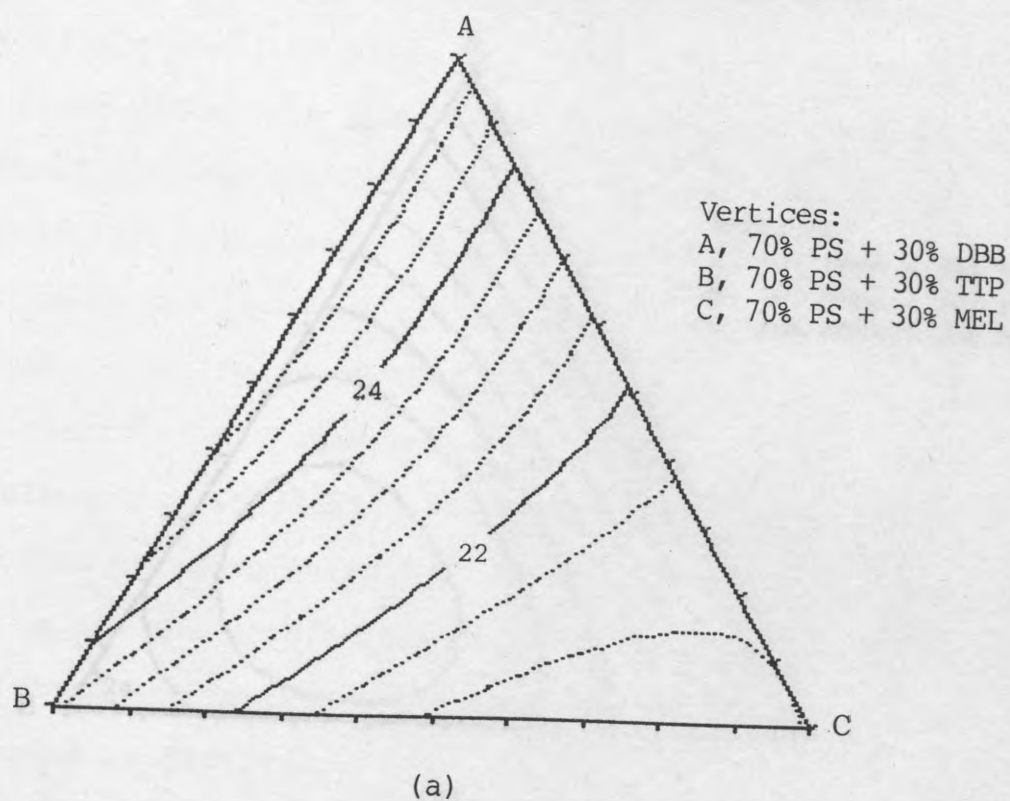
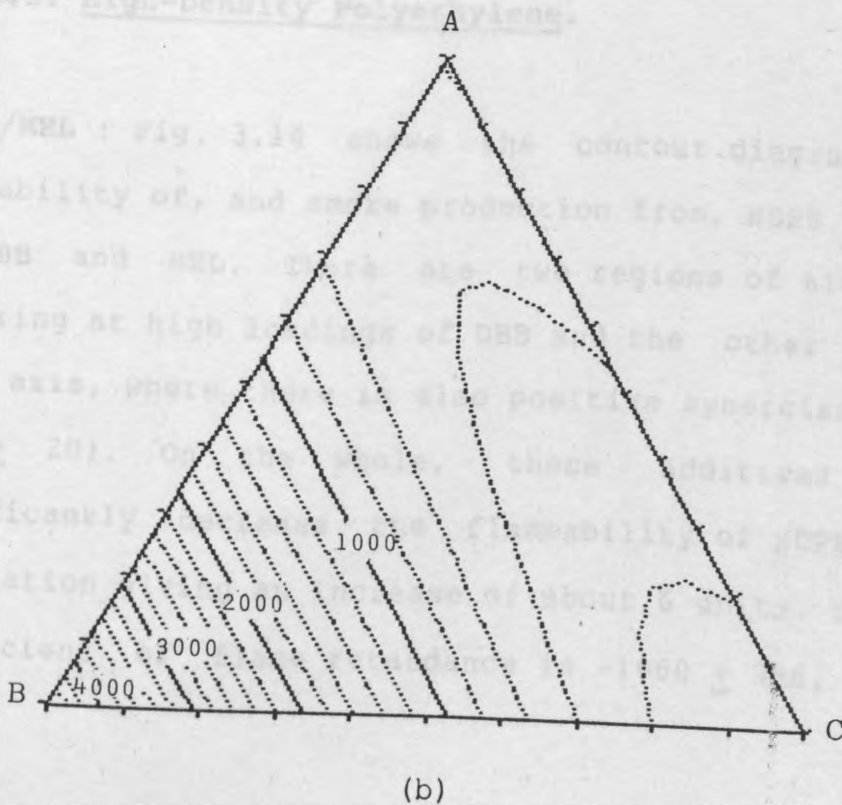
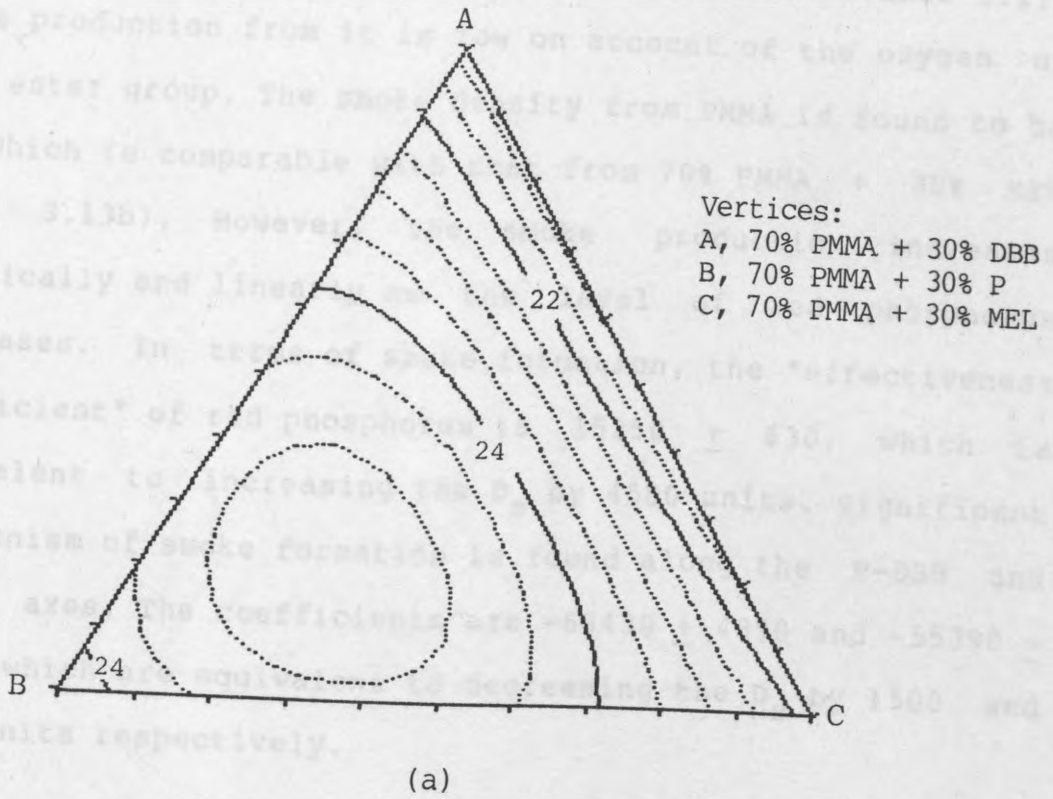


Figure 3.13

The effects of red phosphorus, decabromobiphenyl and melamine on the (a) LOI and (b) Ds values of PMMA.



in PMMA and 16 ± 1 (equivalent to 4.8 LOI units) in PS.

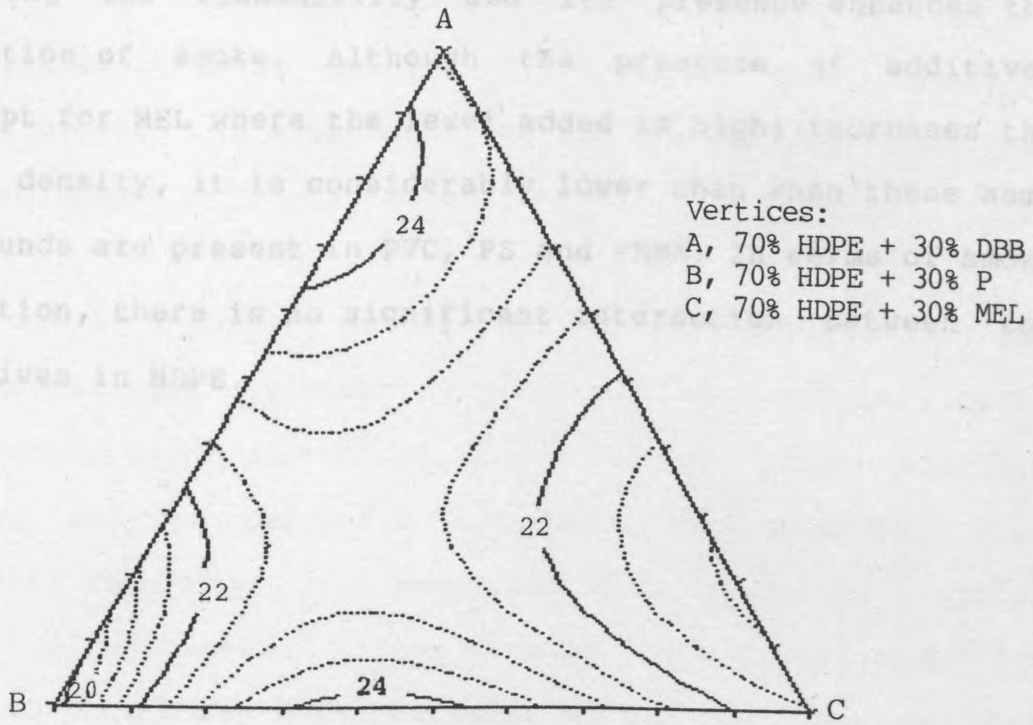
Although PMMA on its own is highly flammable (Table 3.1), smoke production from it is low on account of the oxygen of the ester group. The smoke density from PMMA is found to be 97, which is comparable with that from 70% PMMA + 30% MEL (Fig. 3.13b). However, the smoke production increases drastically and linearly as the level of red phosphorus increases. In terms of smoke formation, the "effectiveness coefficient" of red phosphorus is 15250 ± 630 , which is equivalent to increasing the D_s by 4580 units. Significant antagonism of smoke formation is found along the P-DBB and P-MEL axes. The coefficients are -66430 ± 4890 and -55390 ± 2930 , which are equivalent to decreasing the D_s by 1500 and 1250 units respectively.

3.1.2.5. High-Density Polyethylene.

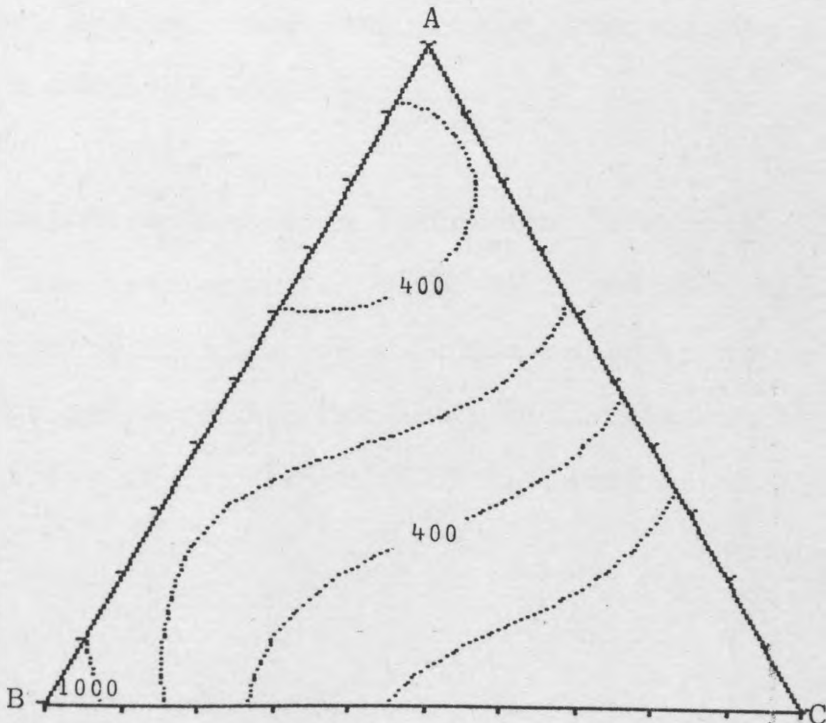
P/DBB/MEL : Fig. 3.14 shows the contour diagrams for the flammability of, and smoke production from, HDPE containing P, DBB and MEL. There are two regions of high LOI, one appearing at high loadings of DBB and the other along the P-MEL axis, where there is also positive synergism (value of 157 ± 20). On the whole, these additives do not significantly decrease the flammability of HDPE, the best combination giving an increase of about 6 units. The ternary coefficient of flame retardance is -1060 ± 356 , indicating

Figure 3.14

The effects of red phosphorus, decabromobiphenyl and melamine on the (a) LOI and (b) Ds values of HDPE.



(a)



(b)

that the additives in HDPE behave antagonistically. Red phosphorus incorporated into HDPE is not effective in reducing the flammability and its presence enhances the formation of smoke. Although the presence of additives (except for MEL where the level added is high) increases the smoke density, it is considerably lower than when these same compounds are present in PVC, PS and PMMA. In terms of smoke formation, there is no significant interaction between the additives in HDPE.

Experiments were carried out at a single level additive loading and the values for "synergistic effectiveness" were estimated from Figs. 3.12 and 3.13. The values of "synergistic effectiveness" of the pairs of the nitrogen compounds with red phosphorus were calculated by the least-squares regression analysis procedure and therefore took into consideration the contribution of these additives to the LOI of the system over the whole composition range of 0 to 30 wt % additive loading.

The phosphorus-guanidine carbonate "synergistic effectiveness" is greatest in both PVC and PS. The phosphorus-barbituric acid additive system appears to be effective in all four polymers but the phosphorus-urea system appears to be effective in PS and HDPE but not in PVC and PMMA.

3.1.3. A Comparison of the Effects of Phosphorus and a Nitrogen Compound on the Flammability of Polymers.

The results given in Section 3.1.2. show that synergism exists between red phosphorus and all the nitrogen compounds studied (Figs. 3.15 - 3.19).

Table 3.4 is a summary of the results. For mixtures of red phosphorus with barbituric acid and with benzotriazole, experiments were carried out at a single total additive loading and the values for "synergistic effectiveness" were estimated from Figs. 3.18 and 3.19. The values of "synergistic effectiveness" of the rest of the nitrogen compounds with red phosphorus were calculated by the least-squares regression analysis procedure and therefore took into consideration the contribution of these additives to the LOI of the system over the whole composition range of 0 to 30 wt % additive loading.

The phosphorus-guanidine carbonate "synergistic effectiveness" is greatest in both PVC and PS. The phosphorus-barbituric acid additive system appears to be effective in all four polymers but the phosphorus-melamine system appears to be effective in PS and HDPE but less so in PVC and PMMA.

Figure 3.15

Interaction between phosphorus and melamine
in the flame retardance of PVC, PS, PMMA and HDPE.

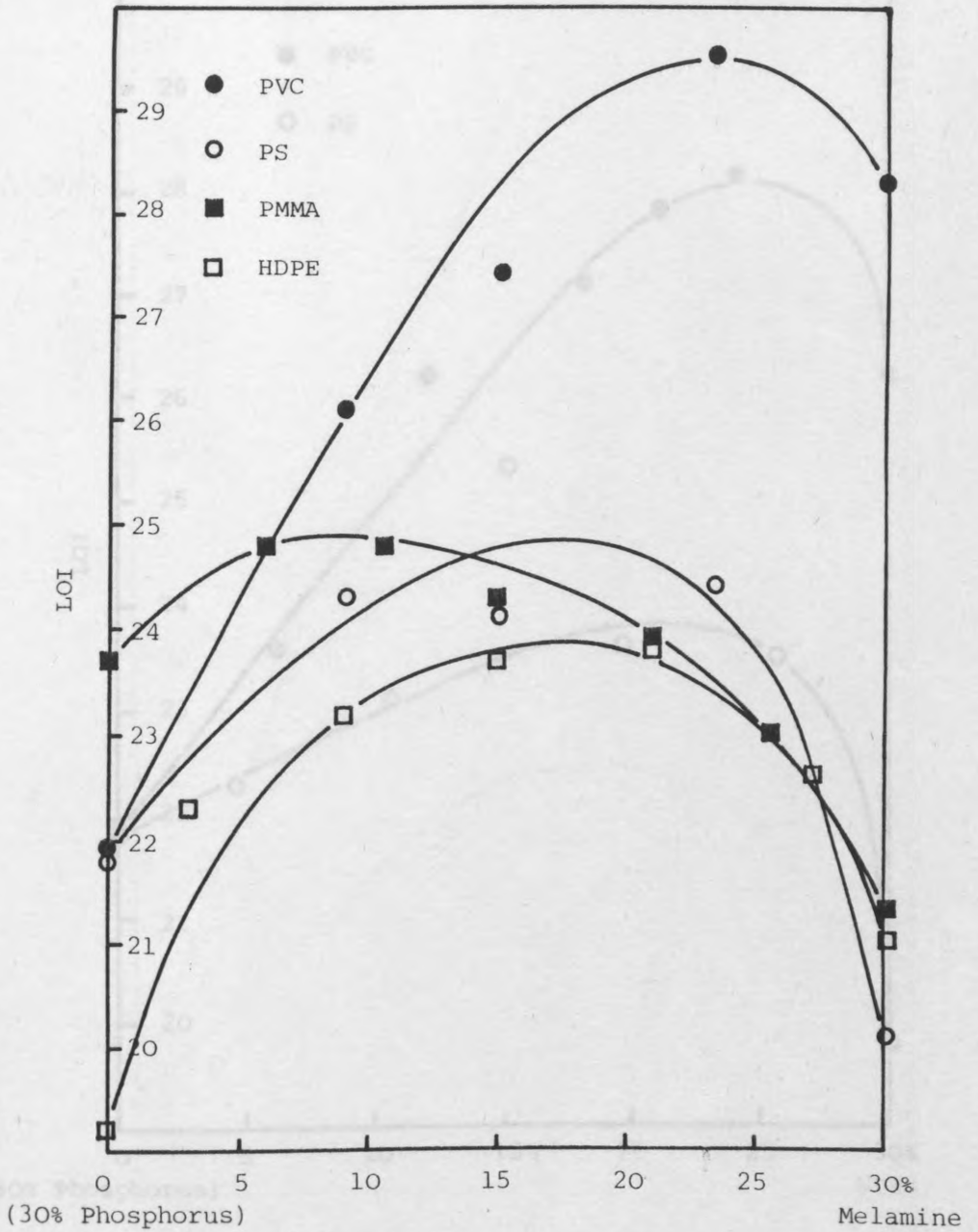


Figure 3.16

Interaction between phosphorus and urea
in the flame retardance of PVC and PS.

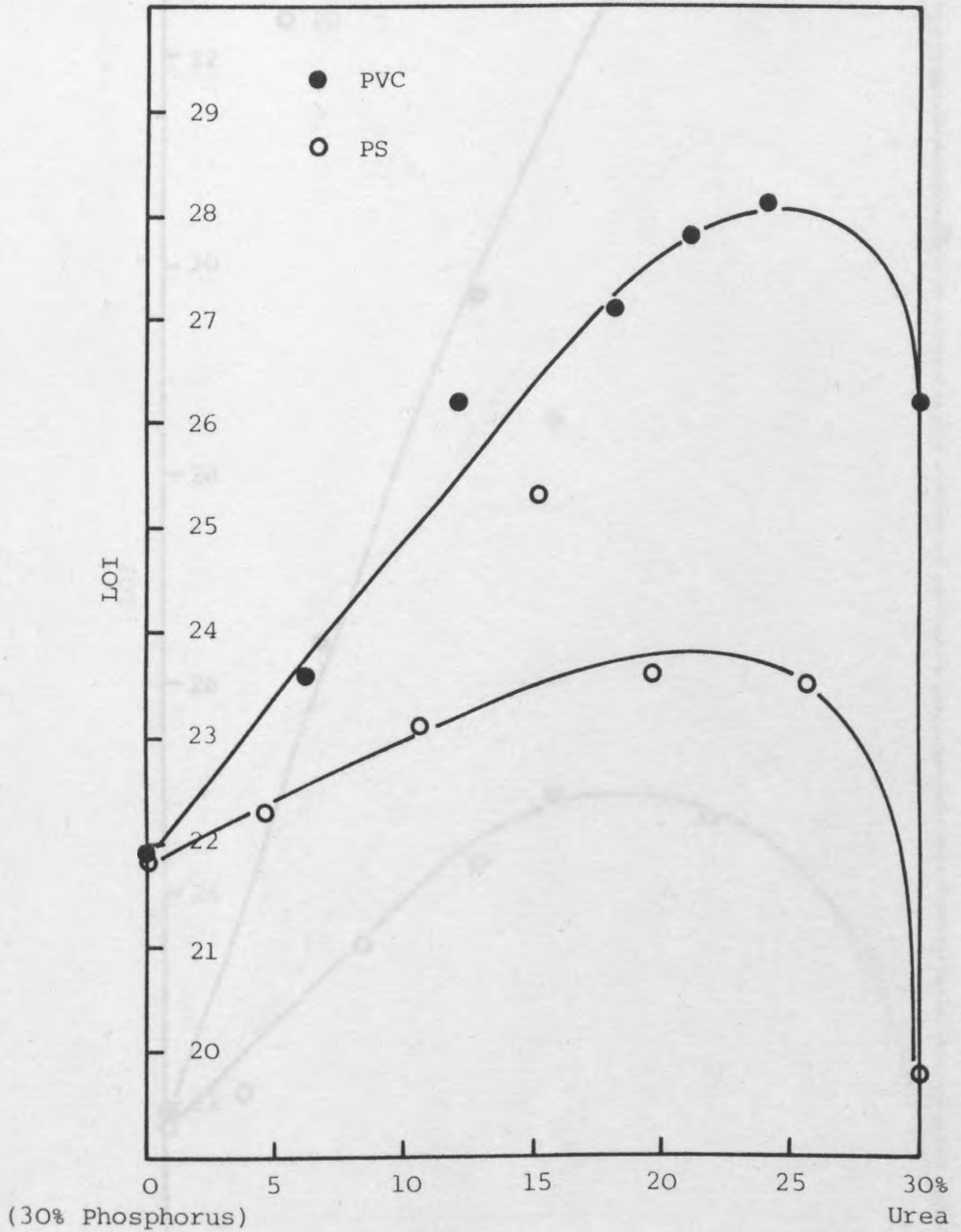


Figure 3.17

Interaction between phosphorus and guanidine carbonate
in the flame retardance of PVC and PS.

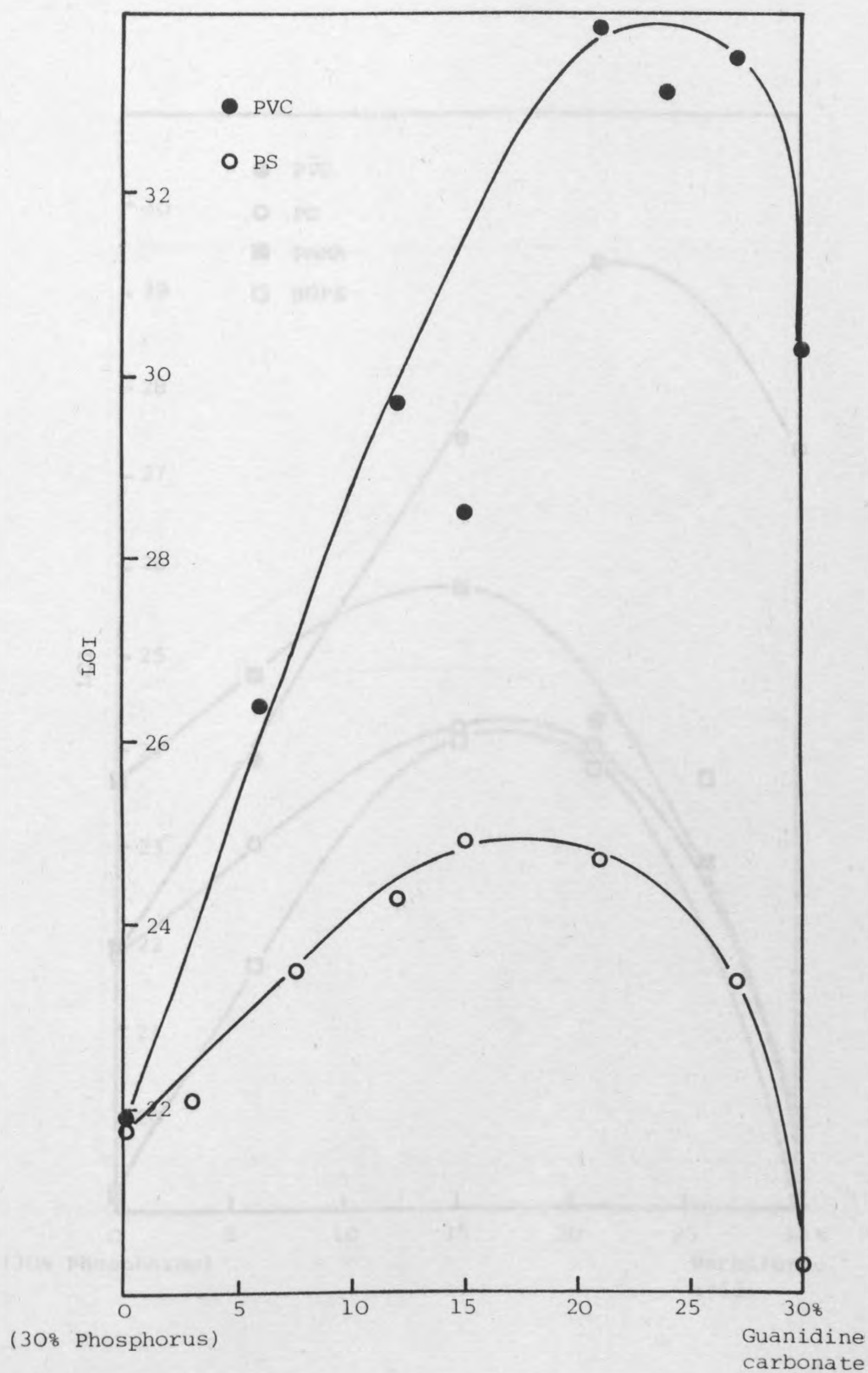


Figure 3.18

Interaction between phosphorus and barbituric acid
in the flame retardance of PVC, PS, PMMA and HDPE.

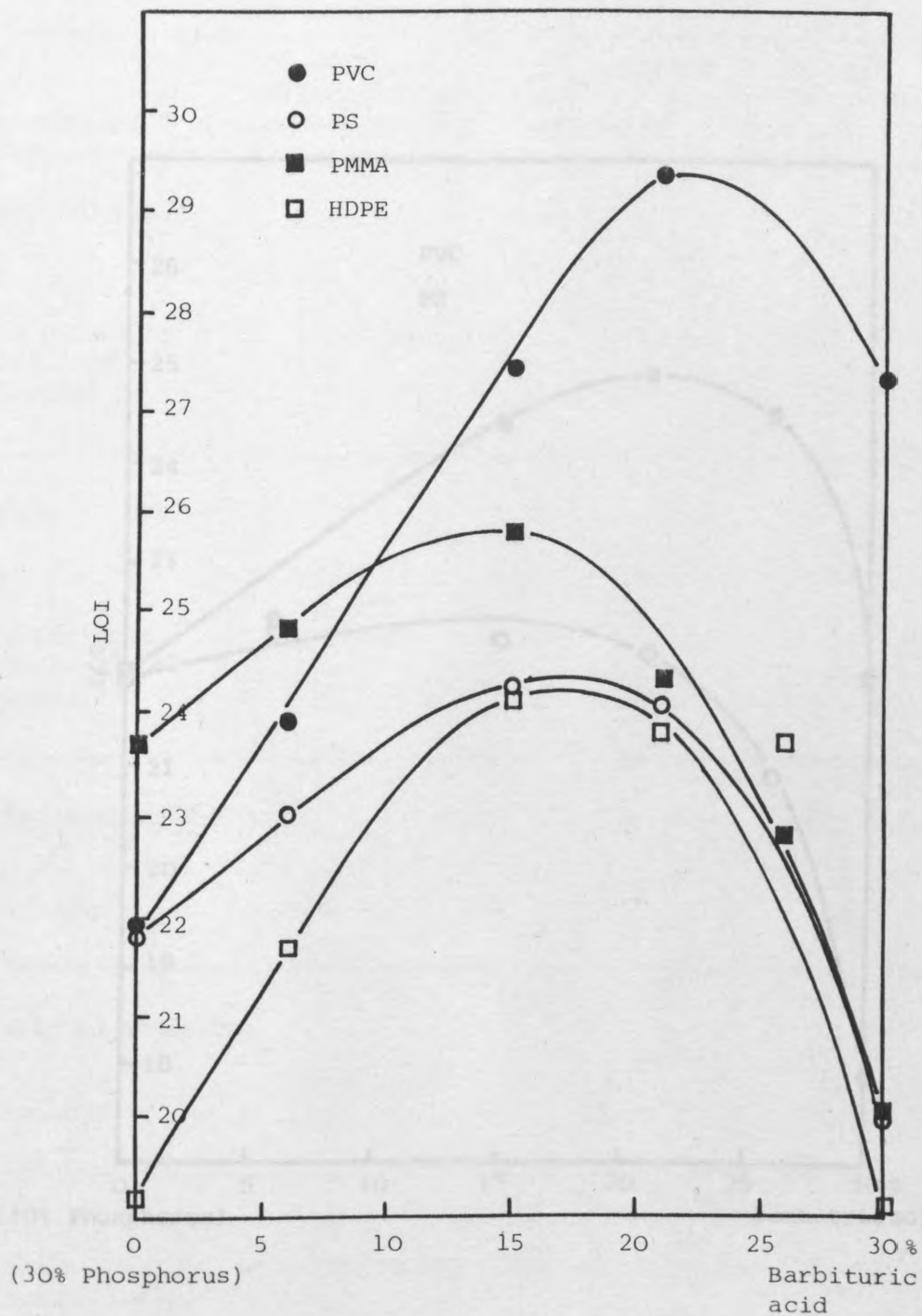


Figure 3.19

Interaction between phosphorus and benzotriazole
in the flame retardance of PVC and PS.

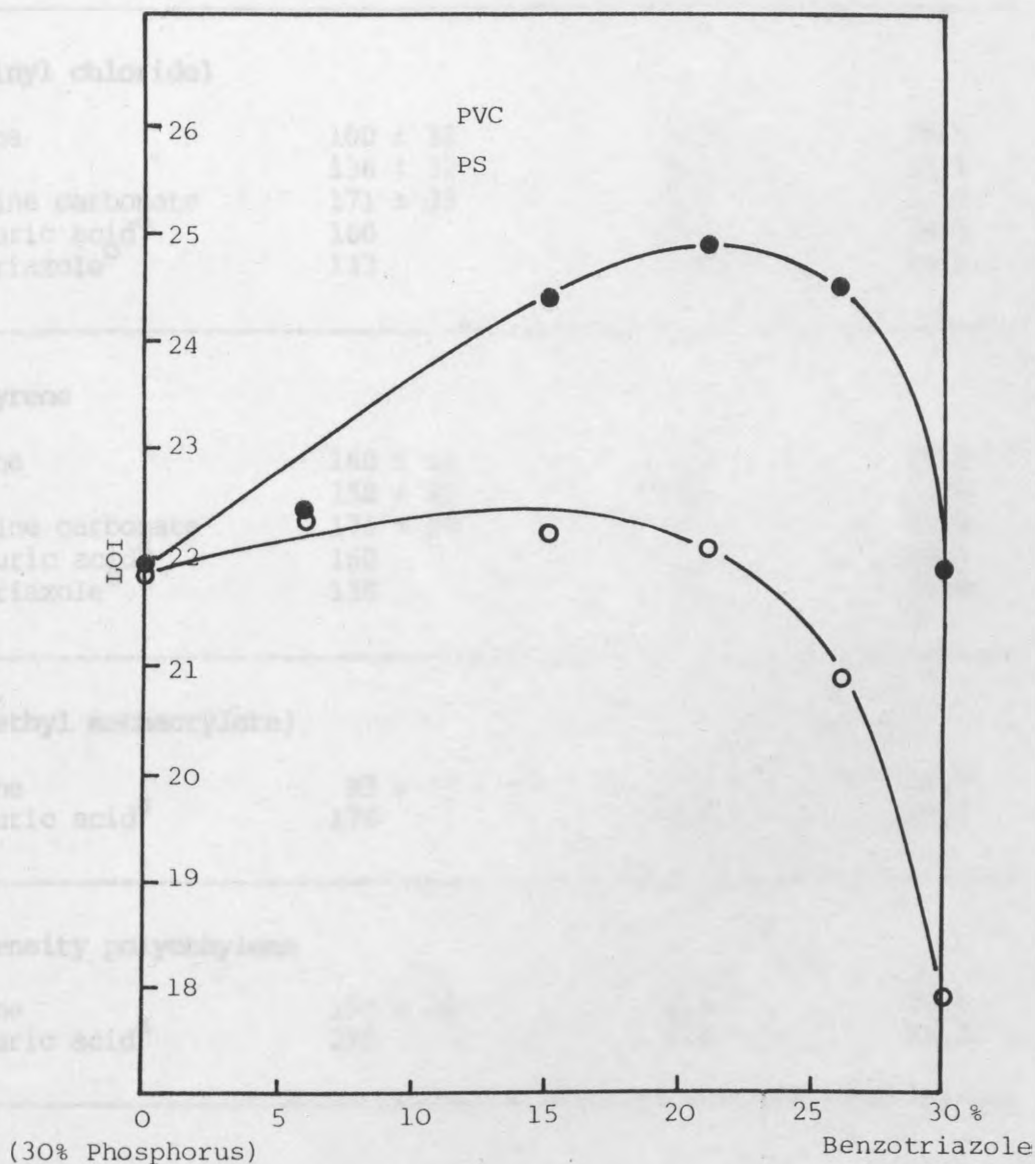


Table 3.4

Values of "synergistic effectiveness" of
red phosphorus and different nitrogen compounds.

Nitrogen compound	"Synergistic effectiveness" of P & N cpd	LOI increase due to synergism	Max LOI at optimum ratio
Poly(vinyl chloride)			
Melamine	100 ± 32	2.3	29.5
Urea	136 ± 32	3.1	28.1
Guanidine carbonate	171 ± 33	3.8	33.8
Barbituric acid ^a	160	3.6	29.3
Benzotriazole ^b	133	3.0	24.9
Polystyrene			
Melamine	168 ± 20	3.8	24.8
Urea	158 ± 21	3.6	23.8
Guanidine carbonate	171 ± 29	3.8	24.9
Barbituric acid ^a	160	3.6	24.3
Benzotriazole ^b	138	3.1	22.4
Poly(methyl methacrylate)			
Melamine	93 ± 17	2.1	24.9
Barbituric acid ^a	178	4.0	25.7
High-density polyethylene			
Melamine	157 ± 20	3.5	23.8
Barbituric acid ^a	222	5.0	24.2

a & b : These results were estimated from Figs. 3.18 and 3.19 respectively.

3.1.4. Summary of Flammability and Smoke-Formation Results.

Table 3.5 summarises the effects of the additives investigated on the LOI and D_s values of the various polymers. Phosphorus increases the flammability of PVC but decreases that of all the other polymers. It is particularly effective as a flame retardant for PS and PMMA. However it also drastically increases the formation of smoke from all polymers.

DBB decreases the flammability of all the polymers, increasing the LOI of the base polymers by between 3 and 8 units. Although DBB increases the smoke density of all the polymers, the levels of smoke produced are considerably lower than when phosphorus is incorporated in the samples. Both melamine and urea decrease the flammability of all the polymers tested to a small extent but are more effective in reducing the amounts of smoke produced. Of the five nitrogen-containing compounds used in PVC, benzotriazole is the only compound that has an adverse effect on its flammability.

The results obtained with ternary systems containing phosphorus, DBB and a nitrogen-containing compound show that high LOI values are found at high loadings of DBB, except with PMMA where the lowest flammability is found with high loadings of phosphorus and low loadings of DBB and

Table 3.5

Summary of the effects of additives on the LOI and Δs of PVC, PS, PMMA and HDPE.

Additives (at 30 wt. % loading)			PVC		PS		PMMA		HDPE	
Compound	N content (%)	Mol. wt.	$a_{\Delta LOI}$	$a_{\Delta DS}$	$a_{\Delta LOI}$	$a_{\Delta DS}$	$a_{\Delta LOI}$	$a_{\Delta DS}$	$a_{\Delta LOI}$	$a_{\Delta DS}$
Phosphorus	-	31	-2.7	3210	4.8	1160	6.0	4580	1.5	910
DBB	-	943	7.5	470	8.1	460	3.3	520	5.1	610
Melamine	67	126	3.0	-200	2.4	-340	4.2	20	3.3	-60
Urea	47	60	1.2	-190	2.1	-580	-	-	-	-
Guanidine carbonate	47	180	6.6	-	3.0	-	-	-	-	-
Barbituric acid	22	128	2.1	-	2.4	-	2.3	-	0.8	-
Benzotriazole	35	119	-3.3	-	0.1	-	-	-	-	-
Triethyl phosphate	-	182	0.9	780	-	-	-	-	-	-
Tritolyl phosphate	-	368	-	-	6.0	-210	-	-	-	-

a : The change in LOI and Δs due to the additives are calculated from the "effectiveness coefficients" (Tables 3.2 and 3.3), except for barbituric acid and benzotriazole where the change in LOI is calculated from direct LOI measurements.

melamine. Furthermore, in PVC containing P, DBB and GC, a second region of high LOI is found at high loadings of GC.

3.2.1. Degradation of PVC and PVC-additive mixtures.

When phosphorus is replaced by organic phosphates, it is found that TTP increases the LOI and decreases the D_s of PS, whereas TEP has a small effect in reducing the flammability but substantially increases smoke formation for PVC.

In all the systems tested, synergism of flame retardance (equivalent to LOI values of between 2 to 5 units) is found between phosphorus and nitrogen-containing compounds. Synergism (equivalent to 2 LOI units) is also found in PMMA and HDPE between phosphorus and DBB. Antagonism is found between DBB and urea (equivalent to 2 LOI units), and DBB and GC (equivalent to 1 unit) in PVC.

In terms of smoke formation, significant interactions are found along the P-DBB axis of PVC, PS and PMMA containing P + DBB + MEL. The antagonism is equivalent to decreasing the D_s values by 610 to 1500 units.

The nitrogen content or molecular weights of the compounds do not appear to have a simple relationship to their effects on the flammability of PVC and PS.

3.2. Simultaneous Thermoanalytical Measurements.

3.2.1. Degradation of PVC and PVC-additive Mixtures.

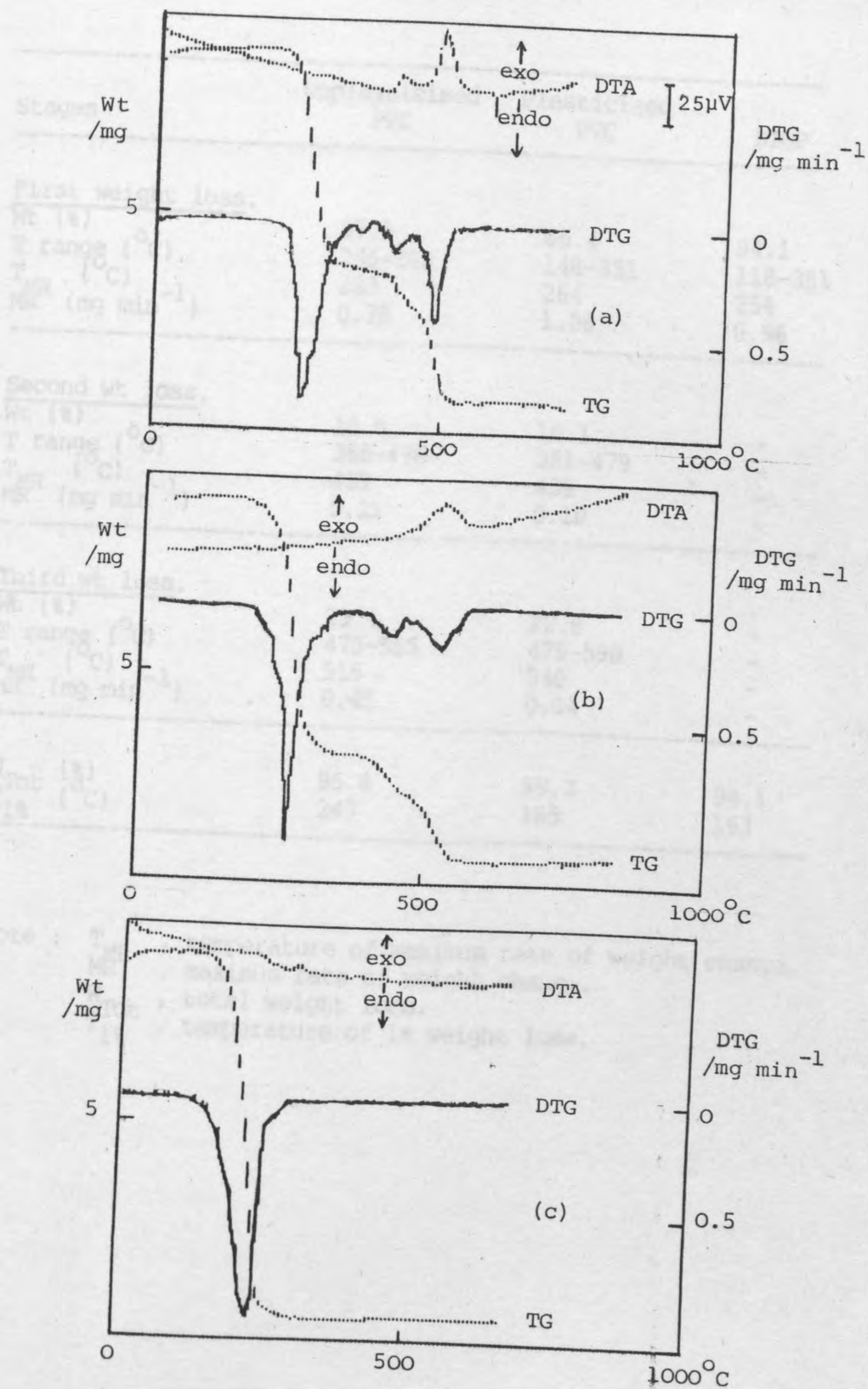
3.2.1.1. PVC.

Figs. 3.20a and b show the DTG, TG and DTA curves for plasticised PVC, containing 40 p.h.r. of di-isooctyl phthalate (DIOP) and for unplasticised PVC. Both sets of curves are quite similar. The first and main breakdown stage of PVC corresponds to dehydrochlorination and occurs between 150 and 350°C (Table 3.6). Thermal analysis of DIOP shows that it too is lost in the same temperature range (Fig. 3.20c and Table 3.6). The simultaneous loss of DIOP during dehydrochlorination of the polymer is supported by the 66.4% weight loss observed, compared with the theoretical value of 70.0%.

The second weight loss of 10% occurring between 350 and 480°C corresponds to the loss of aliphatic and aromatic hydrocarbons. The carbon burn-off stage is observed between 480 and 600°C, with an accompanying weight loss of about 23%.

Figure 3.20

Thermal analysis curves for (a) plasticised and (b) unplasticised PVC and (c) di-isooctyl phthalate.



3.2.1.2. PVC + P/PBS/MEL Table 3.6

Simultaneous thermal analysis of plasticised and unplasticised PVC and di-isooctyl phthalate.

Stages	Unplasticised PVC	Plasticised PVC	DIOP
First weight loss.			
Wt (%)	57.5	66.4	94.1
T range (°C)	206-368	148-351	118-381
T _{MR} (°C)	283	264	254
MR (mg min ⁻¹)	0.78	1.06	0.96
Second wt loss.			
Wt (%)	10.6	10.1	-
T range (°C)	368-478	351-479	-
T _{MR} (°C)	439	439	-
MR (mg min ⁻¹)	0.21	0.10	-
Third wt loss.			
Wt (%)	23.4	22.8	-
T range (°C)	478-555	479-598	-
T _{MR} (°C)	515	540	-
MR (mg min ⁻¹)	0.45	0.14	-
W _{Tot} (%)	95.8	99.3	94.1
T _{1%} (°C)	243	185	163

Note : T_{MR} , temperature of maximum rate of weight change.
 MR , maximum rate of weight change.
 W_{Tot} , total weight loss.
 T_{1%} , temperature of 1% weight loss.

3.2.1.2. PVC + P/DBB/MEL.

Table 3.7 and 3.8 show thermoanalytical data for the main weight loss and weight gain stages during the heating of red phosphorus, decabromobiphenyl and melamine and of PVC containing various combinations of these additives.

Red phosphorus, when heated on its own, first exhibits a weight gain of 31% between 180 and 420°C (Table 3.7). This is undoubtedly attributable to its oxidation in air to phosphorus oxides. The next stage, between 420 and 430°C is very exothermic and involves a very rapid loss of weight of about 70%. The last weight-loss stage occurs between 430 and 590°C. However, it is found that the relatively large weight gain by P on its own is almost completely absent when it is incorporated into PVC, but the highly exothermic rapid weight-loss stage is still observed in all PVC samples containing P (Figs. 3.21 - 3.22).

At maximum loadings of DBB and of melamine, the loss of additives appears to coincide with the first two decomposition stages of PVC (Table 3.7). Melamine appears to lower the temperature at which dehydrochlorination of PVC occurs but the loss of aromatic hydrocarbons occurs at a lower temperature with DBB present, and at a higher temperature with melamine.

Table 3.7

Simultaneous thermal analysis of red phosphorus,
decabromobiphenyl and melamine on their own and with PVC.

PVC (%)	-	-	-	70	70	70
P (%)	100	-	-	30	-	-
DBB (%)	-	100	-	-	30	-
MEL (%)	-	-	100	-	-	30
<u>First wt loss.</u>						
Wt (%)	-	-	94.9	49.5	48.8	49.0
T range (°C)	-	-	221-353	158-341	170-334	173-416
T _{MR} (°C)	-	-	240	283	281	252
MR (mg min ⁻¹)	-	-	1.57	0.75	0.86	0.63
<u>Second wt loss.</u>						
Wt (%)	-	94.4	-	-	19.5	-
T range (°C)	-	295-443	-	-	334-463	-
T _{MR} (°C)	-	420	-	-	360	-
MR (mg min ⁻¹)	-	2.25	-	-	0.12	-
<u>First wt gain.</u>						
Wt (%)	30.7	-	-	0.9	-	-
T range (°C)	178-422	-	-	341-432	-	-
<u>Third wt loss.</u>						
Wt (%)	69.3	-	-	5.3	-	15.4
T range (°C)	422-426	-	-	432-435	-	416-507
T _{MR} (°C)	422	-	-	432	-	461
MR (mg min ⁻¹)	18.43	-	-	1.84	-	0.14
DTA (μV)	298	-	-	125	-	-
<u>Second wt gain.</u>						
Wt (%)	-	-	-	1.6	-	-
T range (°C)	-	-	-	435-445	-	-
T _{MR} (°C)	-	-	-	437	-	-
MR (mg min ⁻¹)	-	-	-	0.15	-	-
<u>Fourth wt loss.</u>						
Wt (%)	36.3	-	-	42.1	24.4	27.7
T range (°C)	426-586	-	-	445-764	463-555	507-602
T _{MR} (°C)	503	-	-	513	531	592
MR (mg min ⁻¹)	0.14	-	-	0.29	0.29	0.56
W _{Tot} (%)	74.9	94.4	94.9	94.4	92.7	92.1
T _{1%} (°C)	-	-	-	187	211	208

Note : T_{MR} , temperature of maximum rate of weight change.
 MR , maximum rate of weight change.
 DTA , differential thermal analysis.
 W_{Tot} , total weight loss.
 T_{1%} , temperature of 1% weight loss.

Table 3.8

Simultaneous thermal analysis of PVC + P/DBB/MEL additive mixtures.

PVC (%)	70	70	70	70
P (%)	15	15	-	10
DBB (%)	15	-	15	10
MEL (%)	-	15	15	10
First wt loss.				
Wt (%)	50.0	47.8	56.5	51.5
T range (°C)	153-360	133-341	152-403	138-385
T _{MR} (°C)	281	247	255	254
MR (mg min ⁻¹)	0.78	0.63	0.68	0.63
Second wt loss.				
Wt (%)	9.2	5.7	-	8.0
T range (°C)	360-457	341-441	-	385-483
T _{MR} (°C)	393	368	-	426
MR (mg min ⁻¹)	0.12	0.10	-	0.07
Third wt loss.				
Wt (%)	1.2	2.6	13.3	-
T range (°C)	457-467	441-443	403-500	-
T _{MR} (°C)	459	441	468	-
MR (mg min ⁻¹)	0.72	0.92	0.12	-
DTA (μV)	202	184	-	-
First wt gain.				
Wt (%)	-	0.4	-	0.2
T range (°C)	-	443-447	-	483-495
T _{MR} (°C)	-	447	-	-
MR (mg min ⁻¹)	-	0.05	-	-
Fourth wt loss.				
Wt (%)	13.2	18.2	-	8.8
T range (°C)	467-543	447-527	-	495-499
T _{MR} (°C)	507	497	-	499
MR (mg min ⁻¹)	0.12	0.12	-	4.50
Fifth wt loss.				
Wt (%)	18.5	20.3	21.8	19.7
T range (°C)	543-751	527-720	500-641	499-762
T _{MR} (°C)	592	573	571	621
MR (mg min ⁻¹)	0.11	0.11	0.17	0.08
W _{Tot} (%)	92.1	94.2	91.6	87.8
T _{1%} (°C)	187	173	191	182

Note : T_{MR} , temperature of maximum rate of weight change.
 MR , maximum rate of weight change.
 DTA , differential thermal analysis.
 W_{Tot} , total weight loss.
 T_{1%} , temperature of 1% weight loss.

Figure 3.21

Thermal analysis curves for
(a) 70%PVC + 30%P and (b) 70%PVC + 15%P + 15%DBB.

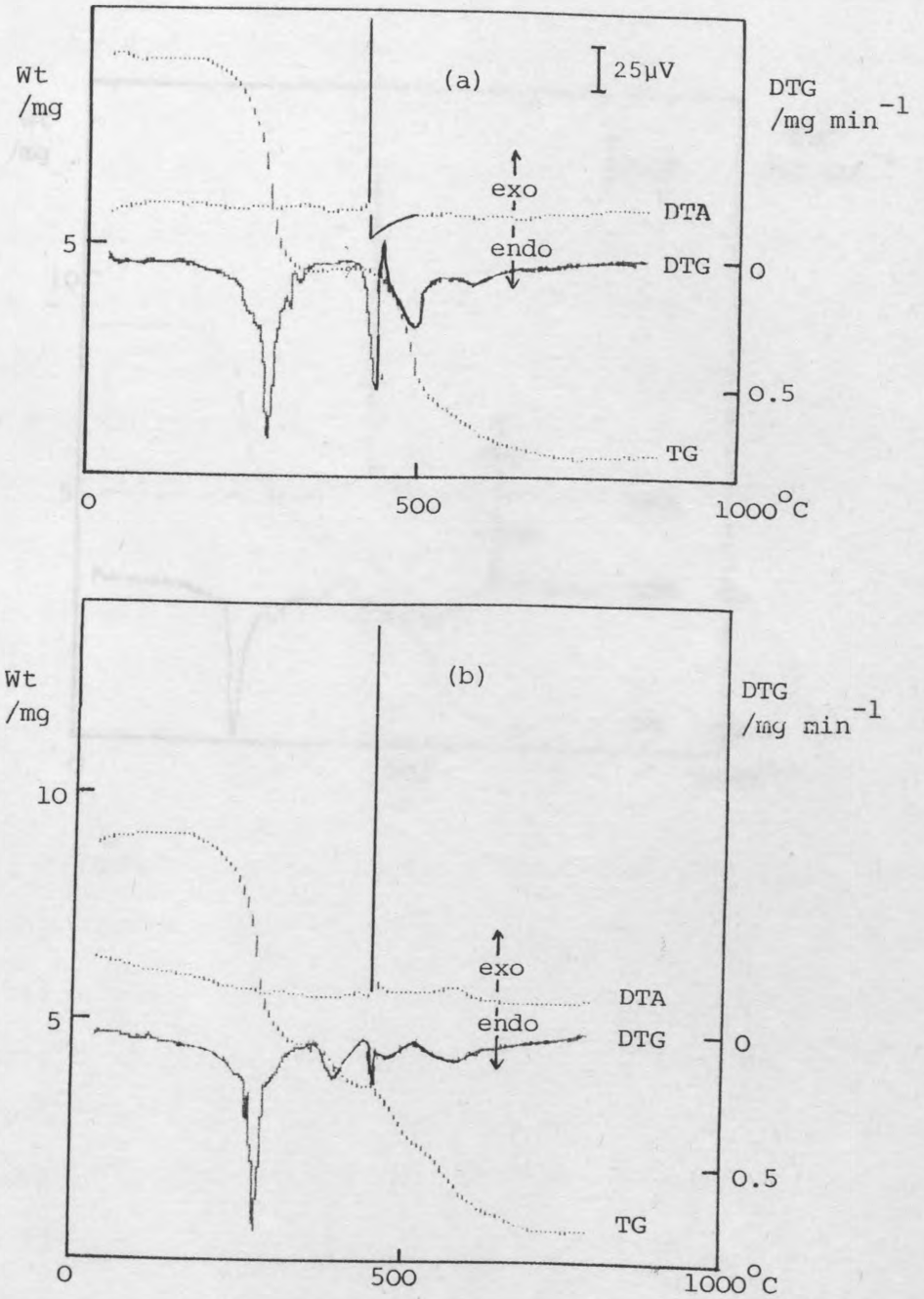
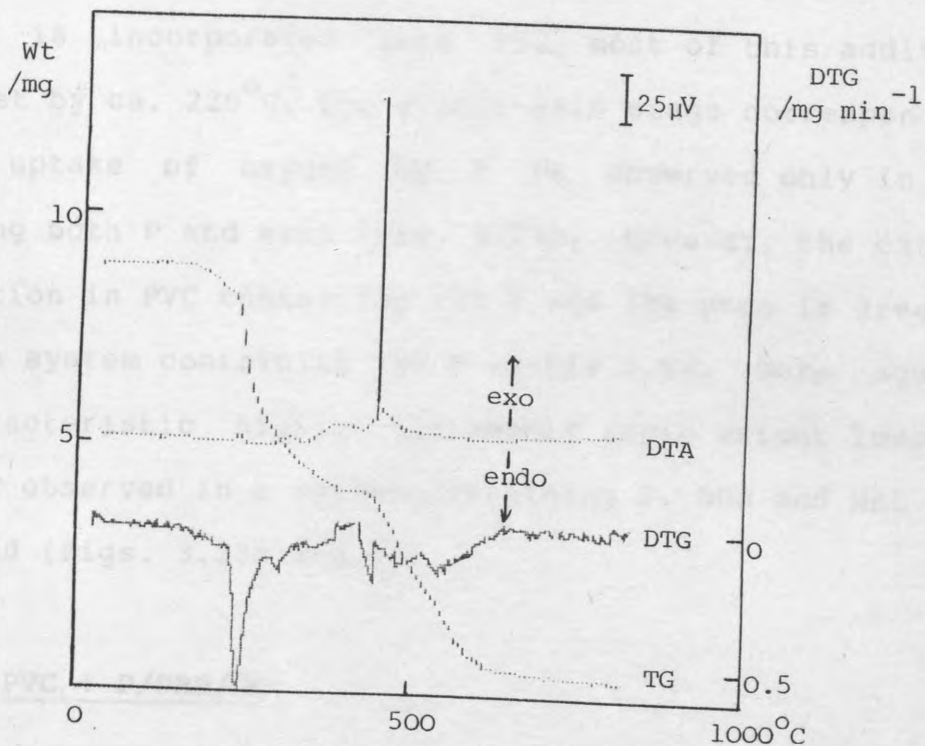


Figure 3.22

Thermal analysis curves for 70%PVC + 15%P + 15%MEL.



3.2.1.3. PVC + P/DBB/UREA.

It can be seen from Table 3.9 that, when urea is heated by itself, about half of it is lost by ca. 230°C . Urea has very little effect on the dehydrochlorination stage of PVC (Fig. 3.23a) but the breakdown pattern of the urea is different when it is incorporated into PVC, most of this additive being lost by ca. 220°C . The weight-gain stage corresponding to the uptake of oxygen by P is observed only in PVC containing both P and urea (Fig. 3.23b). However, the extent of oxidation in PVC containing 12% P and 18% urea is greater than in a system containing 30% P (Table 3.9). Here again, the characteristic highly exothermic rapid weight loss at ca. 430°C observed in a system containing P, DBB and MEL is also found (Figs. 3.23b and c).

3.2.1.4. PVC + P/DBB/GC.

Guanidine carbonate on its own starts to decompose at about 180°C and by 250°C , about half of it is lost (Table 3.10 and Fig. 3.24a). In the presence of GC, the dehydrochlorination of PVC appears to occur at lower temperatures and in two stages (compare Fig. 3.24b with 3.24c); the first being found between 130 and 200°C and the main weight loss between 200 and 300°C . The oxidation of P is observed in both samples containing P (Figs. 3.25a and b).

Table 3.9

Simultaneous thermal analysis of
urea and PVC + P/DBB/UREA additive mixtures.

PVC (%)	-	70	70	70	70
P (%)	-	-	12	-	10
DBB (%)	-	-	-	12	10
UREA (%)	100	30	18	18	10
<u>First wt loss.</u>					
Wt (%)	59.0	28.7	15.5	14.0	9.2
T range (°C)	138-231	96-217	102-191	118-201	107-196
T _{MR} (°C)	224	168	155	168	168
MR (mg min ⁻¹)	0.76	0.28	0.15	0.17	0.11
<u>Second wt loss.</u>					
Wt (%)	5.5	47.9	47.9	50.9	47.9
T range (°C)	231-260	217-389	191-350	201-354	196-338
T _{MR} (°C)	249	242	249	247	246
MR (mg min ⁻¹)	0.19	0.71	0.49	0.70	0.54
<u>First wt gain.</u>					
Wt (%)	-	-	0.5	-	-
T range (°C)	-	-	350-410	-	-
<u>Third wt loss.</u>					
Wt (%)	27.8	5.4	1.4	-	6.0
T range (°C)	260-445	389-466	410-445	-	338-457
T _{MR} (°C)	354	439	-	-	417
MR (mg min ⁻¹)	0.56	0.06	0.02	-	0.06
DTA (μV)	-	-	146	-	140
<u>Second wt gain.</u>					
Wt (%)	-	-	4.0	-	-
T range (°C)	-	-	433-451	-	-
T _{MR} (°C)	-	-	445	-	-
MR (mg min ⁻¹)	-	-	1.48	-	-
<u>Fourth wt loss.</u>					
Wt (%)	-	13.8	15.3	27.2	8.5
T range (°C)	-	466-569	451-573	354-580	457-553
T _{MR} (°C)	-	508	494	526	490
MR (mg min ⁻¹)	-	0.13	0.12	0.19	0.08
<u>Fifth wt loss.</u>					
Wt (%)	-	-	13.7	-	20.0
T range (°C)	-	-	573-765	-	553-758
T _{MR} (°C)	-	-	625	-	613
MR (mg min ⁻¹)	-	-	0.10	-	0.14
W _{Tot} (%)	92.3	95.8	89.3	92.1	91.6
T _{1%} (°C)	-	138	133	140	133

Note : T_{MR} , temperature of maximum rate of weight change.
 MR , maximum rate of weight change.
 DTA , differential thermal analysis.
 W_{Tot} , total weight loss.
 T_{1%} , temperature of 1% weight loss.

Figure 3.23

Thermal analysis curves for (a) 70%PVC + 30%UREA,
(b) 70%PVC + 12%P + 18%UREA and (c) 70%PVC + 10%P + 10%DBB + 10%UREA.

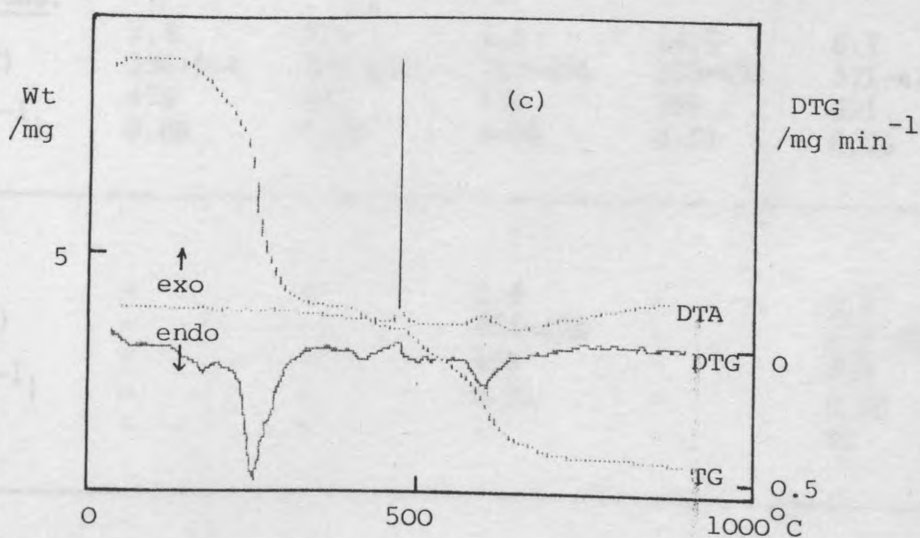
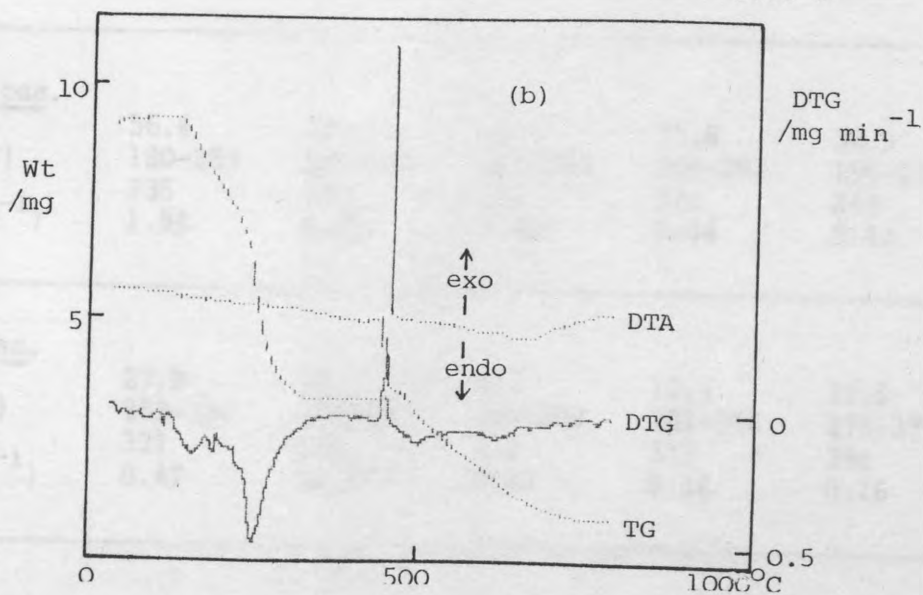
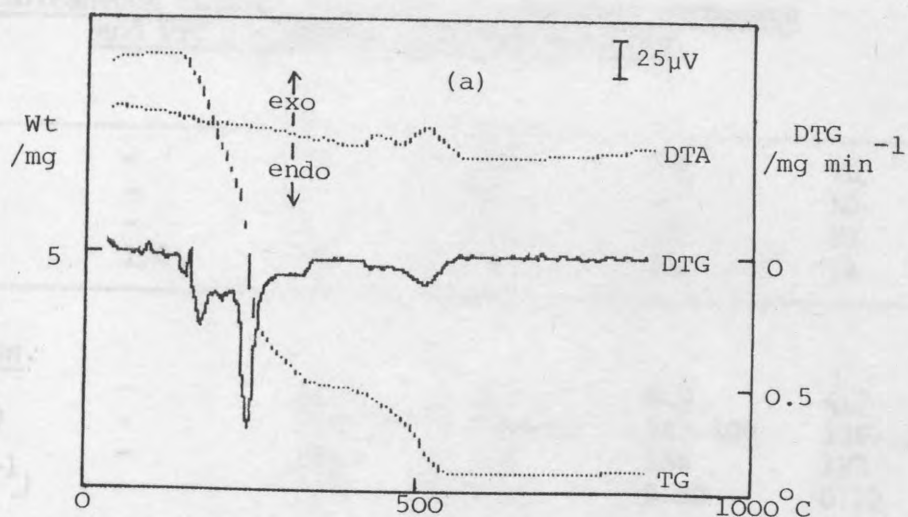


Table 3.10

Simultaneous thermal analysis of guanidine carbonate
and PVC + P/DBB/GC additive mixtures.

PVC (%)	-	70	70	70	70
P (%)	-	-	15	-	10
DBB (%)	-	-	-	15	10
GC (%)	100	30	15	15	10
First wt loss.					
Wt (%)	-	13.5	6.7	6.9	4.7
T range (°C)	-	133-196	135-201	145-200	138-196
T _{MR} (°C)	-	181	188	186	187
MR (mg min ⁻¹)	-	0.34	0.16	0.20	0.12
Second wt loss.					
Wt (%)	56.4	28.7	37.9	35.8	36.9
T range (°C)	180-253	196-263	201-300	200-281	196-278
T _{MR} (°C)	235	219	241	232	244
MR (mg min ⁻¹)	1.94	0.35	0.38	0.44	0.43
Third wt loss.					
Wt (%)	27.9	18.3	9.2	12.4	12.8
T range (°C)	253-336	263-395	300-389	281-358	278-371
T _{MR} (°C)	321	290	322	313	296
MR (mg min ⁻¹)	0.47	0.14	0.13	0.18	0.16
Fourth wt loss.					
Wt (%)	9.4	9.6	2.1	14.6	6.7
T range (°C)	336-564	395-500	389-454	358-492	371-478
T _{MR} (°C)	455	441	436	399	421
MR (mg min ⁻¹)	0.08	0.08	0.06	0.12	0.08
Wt gain.					
Wt (%)	-	-	1.4	-	2.1
T range (°C)	-	-	454-498	-	478-482
T _{MR} (°C)	-	-	498	-	480
MR (mg min ⁻¹)	-	-	0.05	-	0.58
DTA (μV)	-	-	-	-	50

Table 3.10
(contd.)

PVC (%)	-	70	70	70	70
P (%)	-	-	15	-	10
DBB (%)	-	-	-	15	10
GC (%)	100	30	15	15	10
Fifth wt loss.					
Wt (%)	-	-	10.0	-	10.3
T range (°C)	-	-	498-573	-	482-557
T _{MR} (°C)	-	-	526	-	524
MR (mg min ⁻¹)	-	-	0.36	-	0.16
DTA (μV)	-	-	144	-	-
Sixth wt loss.					
Wt (%)	-	21.8	20.9	22.8	19.6
T range (°C)	-	500-648	573-773	492-644	557-728
T _{MR} (°C)	-	569	657	555	638
MR (mg min ⁻¹)	-	0.26	0.22	0.36	0.21
DTA (μV)	-	28	11	23	23
W _{Tot} (%)	93.7	91.9	85.4	92.5	88.9
T _{1%} (°C)	-	157	172	147	172

Note : T_{MR} , temperature of maximum rate of weight change.
 MR , maximum rate of weight change.
 DTA , differential thermal analysis.
 W_{Tot} , total weight loss.
 T_{1%} , temperature of 1% weight loss.

Figure 3.24

Thermal analysis curves for (a) guanidine carbonate, (b) plasticised PVC and (c) 70%PVC + 30%GC.

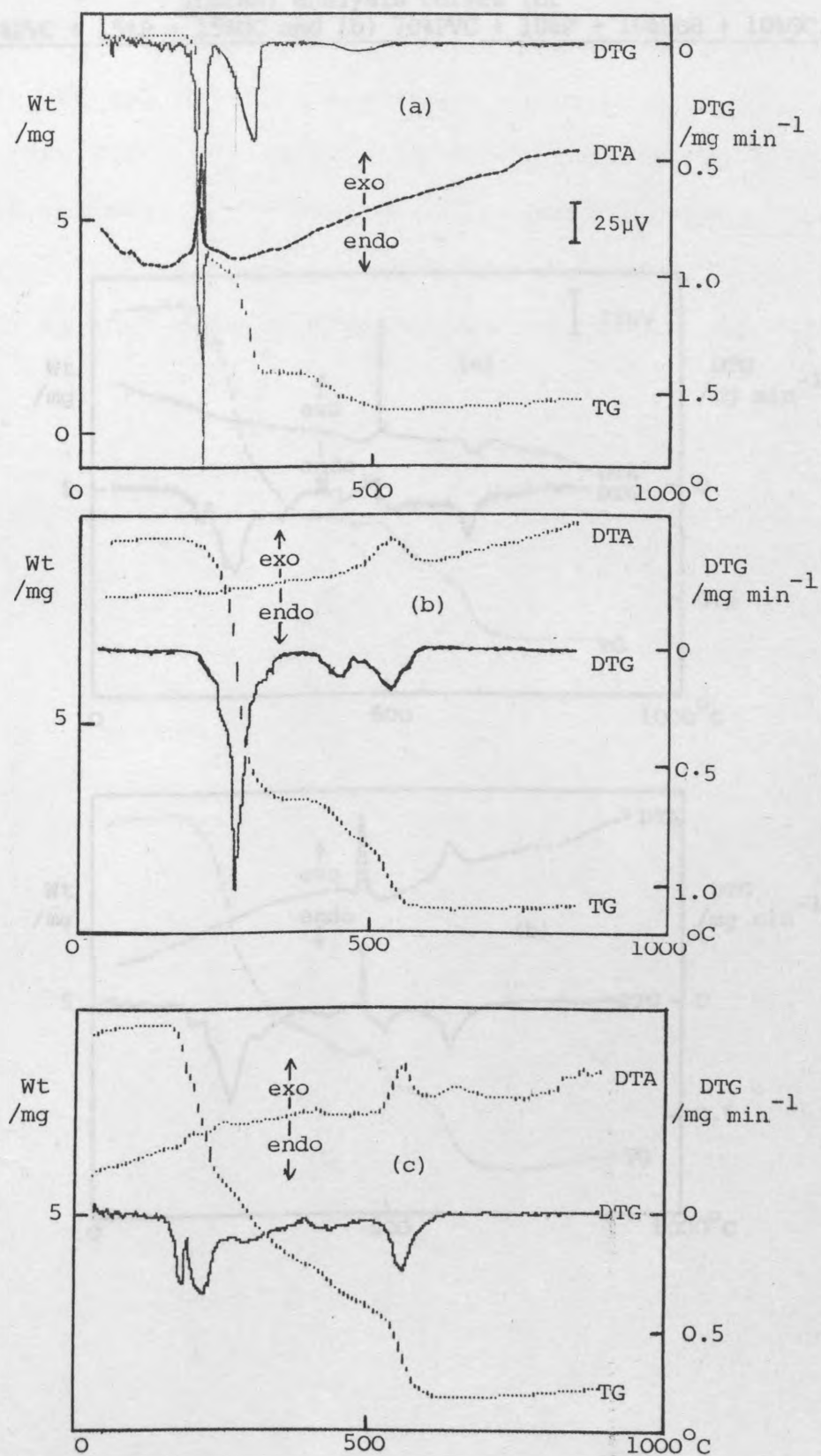
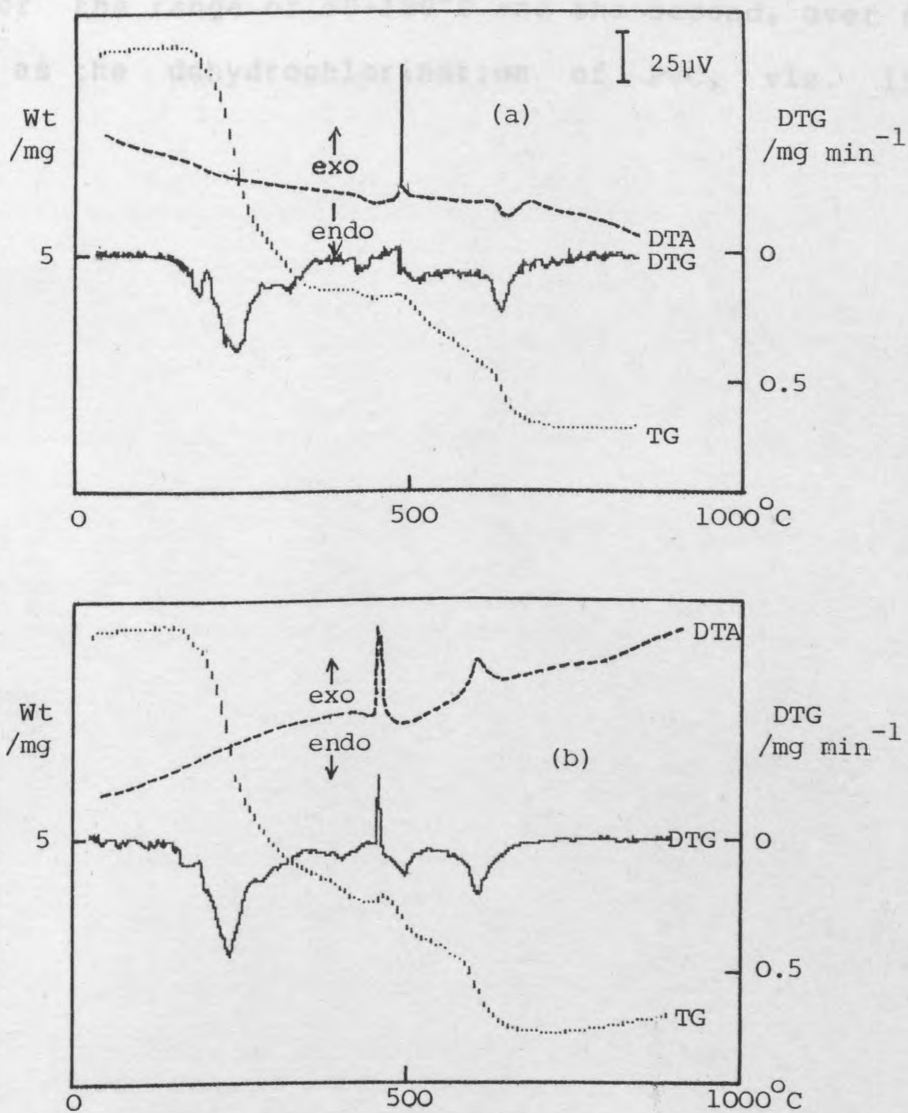


Figure 3.25

Thermal analysis curves for
(a) 70%PVC + 15%P + 15%GC and (b) 70%PVC + 10%P + 10%DBB + 10%GC.

phosphate, DBB and melamine are shown in Table 3.13. In the presence of PVC, the appearance of exothermic peaks is observed instead of one when it is heated on its own. The first loss occurs over the range 200-300°C, and the second over the range 400-500°C.



3.2.1.5. PVC + TEP/DBB/MEL.

The thermoanalytical results for PVC containing triethyl phosphate, DBB and melamine are shown in Table 3.11. In the presence of PVC, TEP appears to volatilise in two stages, instead of one when it is heated on its own. The first loss occurs over the range of 50-180°C and the second, over the same range as the dehydrochlorination of PVC, viz. 150-410°C.

First wt. loss.

wt (%)
T range (°C)
T_{max} (°C)
MR (mg min⁻¹)

Second wt. loss.

wt (%)
T range (°C)
T_{max} (°C)
MR (mg min⁻¹)

Third wt. loss.

wt (%)
T range (°C)
T_{max} (°C)
MR (mg min⁻¹)

W_{residue} (%)
T_{max} (°C)
MR (mg min⁻¹)

Notes: 1. T_{max} = temperature of maximum rate of weight loss.
MR = maximum rate of weight loss.
DIA = differential thermal analysis.
W_{residue} = weight of residue left after heating.
T₁₀ = temperature at which 10% weight loss has occurred.

Table 3.11

Simultaneous thermal analysis of triethyl phosphate
and PVC + TEP/DBB/MEL additive mixtures.

PVC (%)	-	70	70	70	70
TEP (%)	100	30	15	15	10
DBB (%)	-	-	15	-	10
MEL (%)	-	-	-	15	10
<u>First wt loss.</u>					
Wt (%)	95.0	6.6	2.3	3.9	2.2
T range (°C)	25-148	56-163	65-148	65-172	85-160
T _{MR} (°C)	123	112	123	112	133
MR (mg min ⁻¹)	1.62	0.07	0.04	0.04	0.04
<u>Second wt loss.</u>					
Wt (%)	-	62.2	60.6	60.3	58.5
T range (°C)	-	163-386	148-363	172-404	160-409
T _{MR} (°C)	-	264	277	258	269
MR (mg min ⁻¹)	-	0.89	0.69	0.76	0.71
<u>Third wt loss.</u>					
Wt (%)	-	7.6	9.3	7.3	11.0
T range (°C)	-	386-486	363-470	404-490	409-494
T _{MR} (°C)	-	437	439	457	439
MR (mg min ⁻¹)	-	0.08	0.09	0.07	0.10
<u>Fourth wt loss.</u>					
Wt (%)	-	15.0	20.2	19.5	20.3
T range (°C)	-	486-600	470-592	490-665	494-659
T _{MR} (°C)	-	533	533	565	553
MR (mg min ⁻¹)	-	0.13	0.17	0.13	0.17
W _{Tot} (%)	95.0	91.4	92.4	91.0	92.0
T _{1%} (°C)	-	85	112	99	120

Note : T_{MR} , temperature of maximum rate of weight change.
 MR , maximum rate of weight change.
 DTA , differential thermal analysis.
 W_{Tot} , total weight loss.
 T_{1%} , temperature of 1% weight loss.

3.2.2. Degradation of PS and PS-additive Mixtures.

3.2.2.1. PS.

Thermoanalytical studies of PS show that more than 90% of the sample is volatilised before 430°C and that the breakdown of polymer actually begins at ca. 160°C (Table 3.12 and Fig. 3.26a). The second weight loss of 5% occurs in the range of $430-710^{\circ}\text{C}$ and corresponds to the carbon burn-off stage.

3.2.2.2. PS + P/DBB/MEL.

In contrast to the behaviour of PVC containing 30% P, thermal analysis of all PS samples containing P show that there is extensive oxidation of the P (Table 3.12 and Figs. 3.26b,c and 3.27a,b). However, a highly exothermic weight loss similar to those observed in the PVC samples containing P is detected only in PS containing 30% P (Fig. 3.27b). The PS breakdown is affected by P in PS + 30% P, less PS being lost in the first stage and more in the carbon burn-off stage than when PS is heated alone. Both DBB and melamine volatilise during the main decomposition stage of PS and appear to have little effect on the decomposition of PS.

Simultaneous thermal analysis of PS and PS + P/DBB/MEL additive mixtures.

PS (%)	100	70	70	70	70	70	70
P (%)	-	30	-	-	-	15	70
DBB (%)	-	-	30	-	-	15	10
MEL (%)	-	-	-	30	-	15	10

Wt (%)	93.1	50.9	90.7	86.1	71.1	74.4	84.8	79.4
T range ($^{\circ}\text{C}$)	166-430	174-414	172-404	182-406	187-404	133-418	191-404	152-399
T _{MR} ($^{\circ}\text{C}$)	392	412	375	383	379	370	392	391
MR (mg min ⁻¹)	0.92	1.74	1.01	0.83	0.71	0.44	1.47	1.08
DTA (μV)	-32	221	10	14	31	26	15	26

Wt (%)	8.0	-	-	-	9.8	11.0	-	8.2
T range ($^{\circ}\text{C}$)	414-437	-	-	-	404-483	418-483	-	399-468
T _{MR} ($^{\circ}\text{C}$)	414	-	-	-	406	467	-	411
MR (mg min ⁻¹)	0.97	-	-	-	0.14	0.10	-	0.13

Wt (%)	4.7	46.3	6.0	7.2	30.6	30.3	9.3	21.5
T range ($^{\circ}\text{C}$)	430-712	437-727	404-571	406-619	483-720	483-698	404-695	468-743
T _{MR} ($^{\circ}\text{C}$)	507	521	517	519	539	531	533	551
MR (mg min ⁻¹)	0.04	0.33	0.06	0.06	0.30	0.26	0.06	0.18

W _{Tot} (%)	97.8	89.2	96.7	93.3	92.5	93.7	94.1	92.7
T _{1%} ($^{\circ}\text{C}$)	234	261	243	234	252	211	246	223

Note : T_{MR} , temperature of maximum rate of weight change.
 MR , maximum rate of weight change.
 DTA , differential thermal analysis.
 W_{Tot} , total weight loss.
 $T_{1\%}^{Tot}$, temperature of 1% weight loss.

Figure 3.26

Thermal analysis curves for (a) 100%PS,
(b) 70%PS + 15%P + 15%DBB and (c) 70%PS + 15%P + 15%MEL.

(a) 70%PS + 15%P + 15%DBB (b) 70%PS + 15%P + 15%MEL

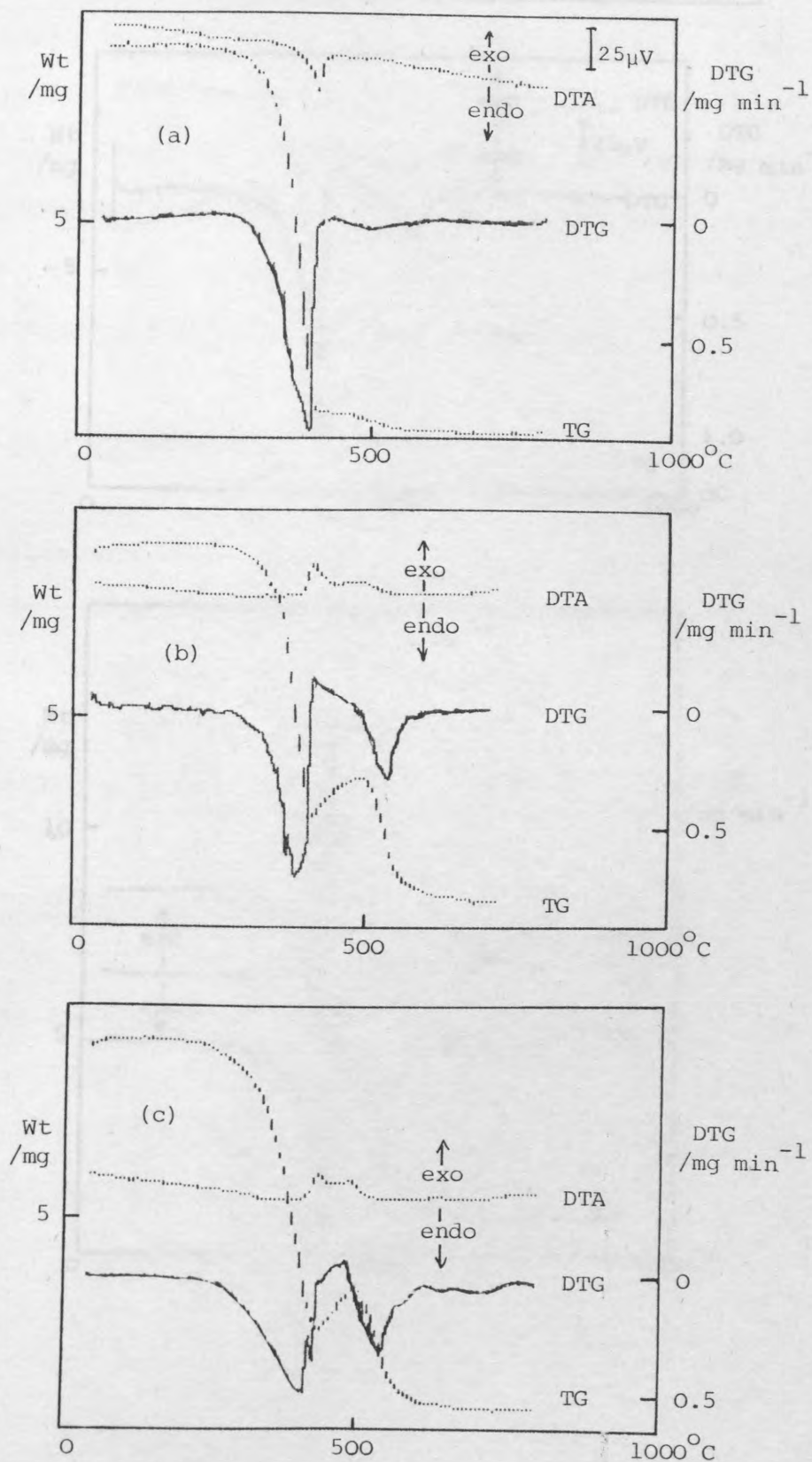
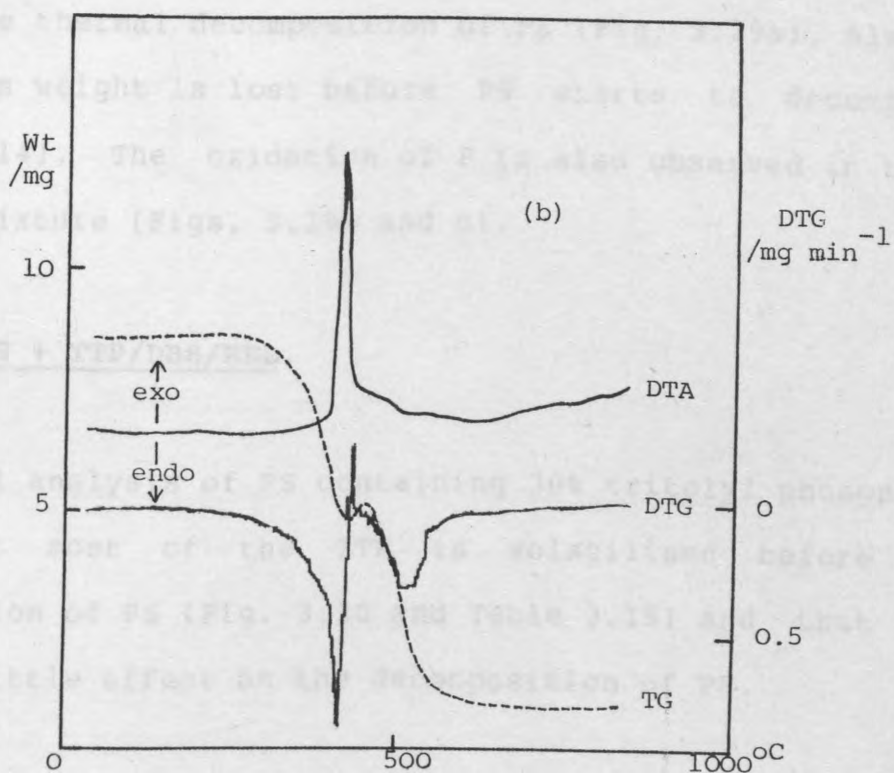
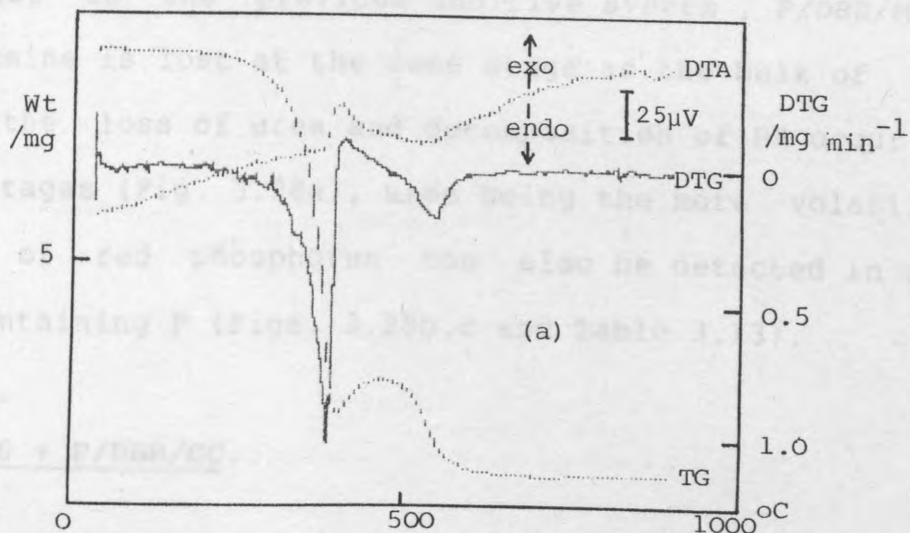


Figure 3.27

Thermal analysis curves for
(a) 70%PS + 10%P + 10%DBB + 10%MEL and (b) 70%PS + 30%P.



3.2.2.3. PS + P/DBB/UREA.

In contrast to the previous additive system, P/DBB/MEL, where melamine is lost at the same stage as the bulk of the polymer, the loss of urea and decomposition of PS occur in separate stages (Fig. 3.28a), urea being the more volatile. Oxidation of red phosphorus can also be detected in all samples containing P (Figs. 3.28b,c and Table 3.13).

3.2.2.4. PS + P/DBB/GC.

Like melamine and urea, guanidine carbonate does not seem to affect the thermal decomposition of PS (Fig. 3.29a). Almost half of its weight is lost before PS starts to decompose (Table 3.14). The oxidation of P is also observed in this additive mixture (Figs. 3.29b and c).

3.2.2.5. PS + TTP/DBB/MEL.

The thermal analysis of PS containing 30% tritolyl phosphate shows that most of the TTP is volatilised before the decomposition of PS (Fig. 3.30 and Table 3.15) and that it thus has little effect on the decomposition of PS.

Figure 3.28

Thermal analysis curves for (a) 70%PS + 30%UREA,
(b) 70%PS + 15%P + 15%UREA and (c) 70%PS + 10%P + 10%DBB + 10%UREA.

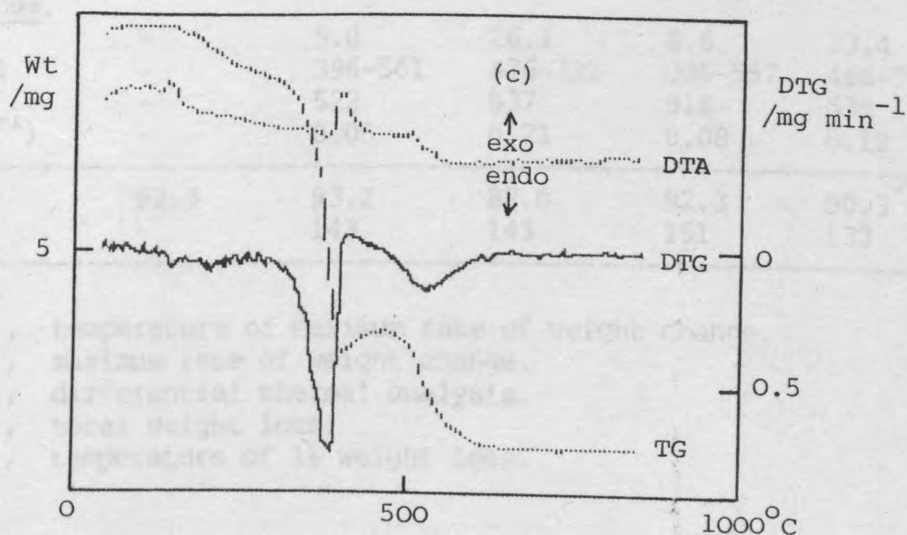
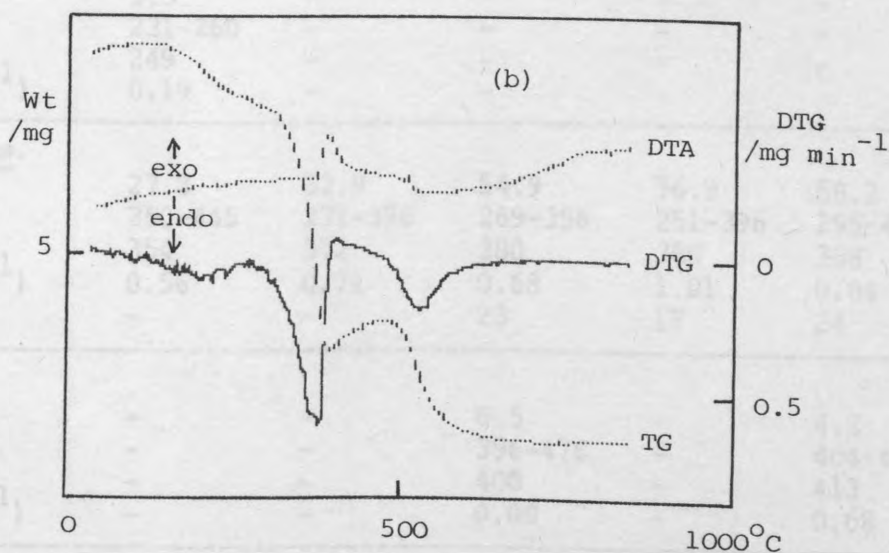
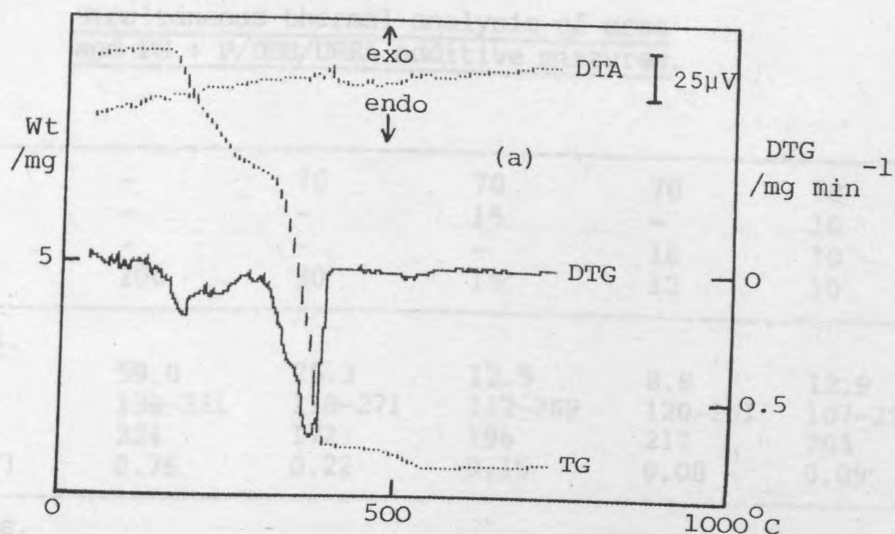


Table 3.13

Simultaneous thermal analysis of urea
and PS + P/DBB/UREA additive mixtures.

PS (%)	-	70	70	70	70
P (%)	-	-	15	-	10
DBB (%)	-	-	-	18	10
UREA (%)	100	30	15	12	10
<u>First wt loss.</u>					
Wt (%)	59.0	25.3	12.5	8.8	12.9
T range (°C)	138-231	118-271	112-269	120-251	107-295
T _{MR} (°C)	224	172	196	217	203
MR (mg min ⁻¹)	0.76	0.22	0.15	0.08	0.09
<u>Second wt loss.</u>					
Wt (%)	5.5	-	-	-	-
T range (°C)	231-260	-	-	-	-
T _{MR} (°C)	249	-	-	-	-
MR (mg min ⁻¹)	0.19	-	-	-	-
<u>Third wt loss.</u>					
Wt (%)	27.8	62.9	54.9	76.9	58.2
T range (°C)	260-445	271-396	269-396	251-396	295-404
T _{MR} (°C)	354	372	380	380	388
MR (mg min ⁻¹)	0.56	0.71	0.68	1.01	0.84
DTA (μV)	-	-	23	17	24
<u>Wt gain.</u>					
Wt (%)	-	-	6.5	-	4.2
T range (°C)	-	-	396-476	-	404-466
T _{MR} (°C)	-	-	400	-	413
MR (mg min ⁻¹)	-	-	0.09	-	0.08
<u>Fourth wt loss.</u>					
Wt (%)	-	5.0	26.1	6.6	23.4
T range (°C)	-	396-561	476-721	396-557	466-706
T _{MR} (°C)	-	522	537	518	535
MR (mg min ⁻¹)	-	0.05	0.21	0.08	0.18
W _{Tot} (%)	92.3	93.2	87.0	92.3	90.3
T _{1%} (°C)	-	143	143	151	133

Note : T_{MR} , temperature of maximum rate of weight change.
 MR , maximum rate of weight change.
 DTA , differential thermal analysis.
 W_{Tot} , total weight loss.
 T_{1%} , temperature of 1% weight loss.

Figure 3.29

Thermal analysis curves for (a) 70%PS + 30%GC, (b) 70%PS + 15%P + 15%GC and (c) 70%PS + 10%P + 10%DBB + 10%GC.

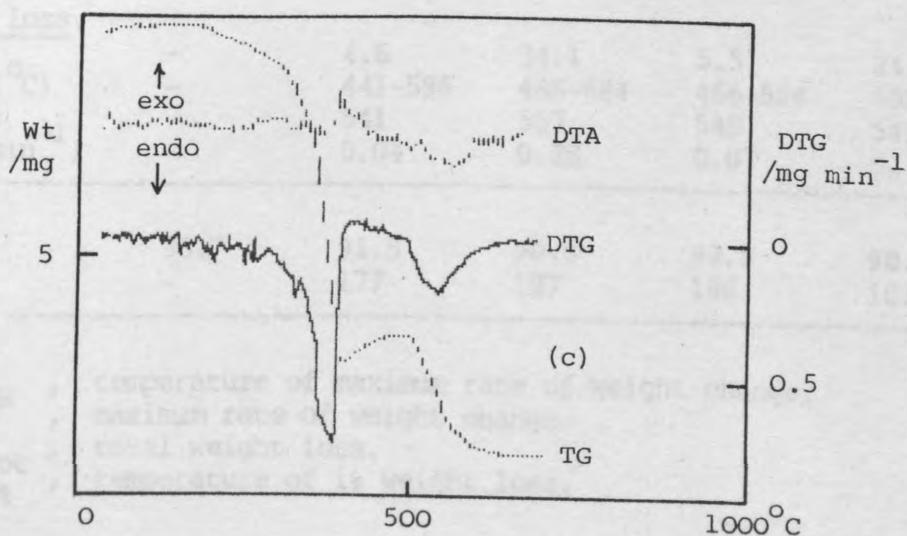
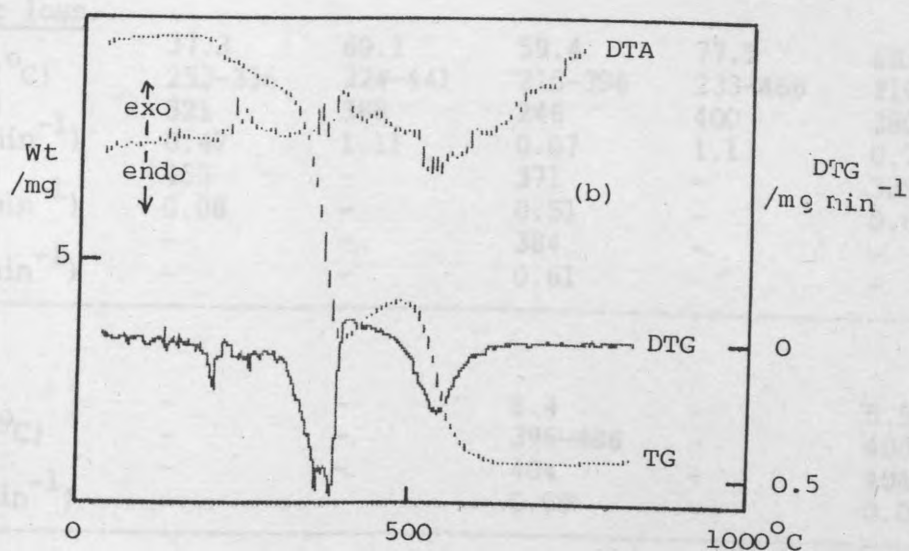
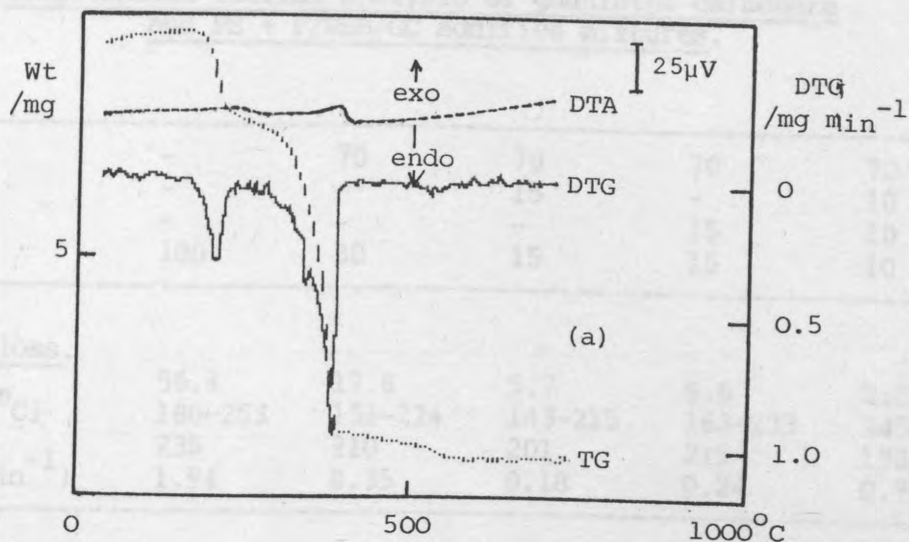


Table 3.14

Simultaneous thermal analysis of guanidine carbonate
and PS + P/DBB/GC additive mixtures.

PS (%)	-	70	70	70	70
P (%)	-	-	15	-	10
DBB (%)	-	-	-	15	10
GC (%)	100	30	15	15	10

<u>First wt loss.</u>					
Wt (%)	56.4	17.8	5.7	9.5	2.8
T range (°C)	180-253	151-224	143-215	163-233	145-210
T _{MR} (°C)	235	210	201	215	198
MR (mg min ⁻¹)	1.94	0.35	0.18	0.24	0.71

<u>Second wt loss.</u>					
Wt (%)	37.3	69.1	59.4	77.5	68.5
T range (°C)	253-336	224-441	215-396	233-466	210-400
T _{MR1} (°C)	321	388	246	400	380
MR (mg min ⁻¹)	0.47	1.11	0.07	1.13	0.78
T _{MR2} (°C)	455	-	371	-	389
MR (mg min ⁻¹)	0.08	-	0.51	-	0.83
T _{MR3} (°C)	-	-	384	-	-
MR (mg min ⁻¹)	-	-	0.61	-	-

<u>Wt gain.</u>					
Wt (%)	-	-	8.4	-	5.5
T range (°C)	-	-	396-486	-	400-492
T _{MR} (°C)	-	-	404	-	404
MR (mg min ⁻¹)	-	-	0.09	-	0.06

<u>Third wt loss.</u>					
Wt (%)	-	4.6	34.1	5.5	24.5
T range (°C)	-	441-596	486-684	466-584	492-680
T _{MR} (°C)	-	541	557	545	549
MR (mg min ⁻¹)	-	0.04	0.28	0.07	0.24

W _{Tot} (%)	93.7	91.5	90.8	92.5	90.3
T _{1%} (°C)	-	177	187	196	187

Note : T_{MR} , temperature of maximum rate of weight change.
 MR , maximum rate of weight change.
 W_{Tot} , total weight loss.
 T_{1%} , temperature of 1% weight loss.

Figure 3.30

Thermal analysis curves for 70%PS + 30%TTP.

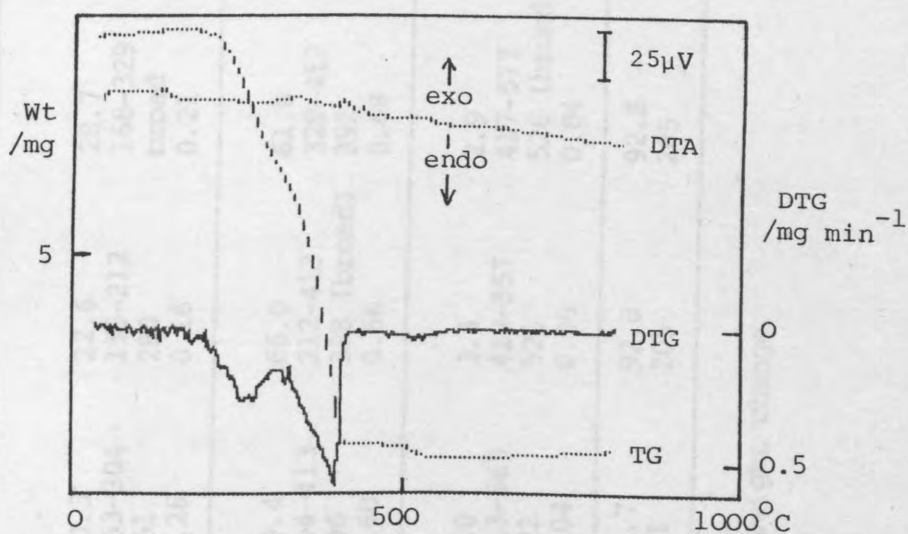


Table 3.15

Simultaneous thermal analysis of PS,
tritolyl phosphate and PS + TTP/DBB/MEL additive mixtures.

PS (%)	100	-	70	70	70	70
TTP (%)	-	100	30	15	15	10
DBB (%)	-	-	-	15	-	10
MEL (%)	-	-	-	-	15	10
First wt loss.						
Wt (%)	-	92.2	30.3	22.6	28.7	17.6
T range (°C)	-	148-375	163-304	158-212	168-329	158-304
T _{MR} (°C)	-	282	251	280	broad	broad
MR (mg min ⁻¹)	-	1.31	0.26	0.16	0.21	0.16
Second wt loss.						
Wt (%)	93.1	-	59.4	66.0	61.0	70.2
T range (°C)	166-430	-	304-413	212-413	329-417	304-413
T _{MR} (°C)	392	-	396	388 (broad)	392	396
MR (mg min ⁻¹)	0.92	-	0.60	0.66	0.68	1.00
Third wt loss.						
Wt (%)	4.7	-	3.0	3.4	2.9	4.3
T range (°C)	430-712	-	413-565	413-557	417-577	413-565
T _{MR} (°C)	507	-	522	526	526 (broad)	530
MR (mg min ⁻¹)	0.04	-	0.04	0.06	0.04	0.06
W _{Tot} (%)	97.8	92.2	92.7	92.0	92.6	92.1
T _{1%} (°C)	234	-	201	205	205	205

Note : T_{MR} , temperature of maximum rate of weight change.
 MR , maximum rate of weight change.
 W_{Tot} , total weight loss.
 T_{1%} , temperature of 1% weight loss.

Table 3.16
3.2.3. Degradation of PMMA and PMMA-additive Mixtures.

3.2.3.1. PMMA.

PMMA decomposes completely between 260 and 420°C (Table 3.16 and Fig. 3.31a).

3.2.3.2. PMMA + P/DBB/MEL.

The oxidation of P is observed in all samples containing P but the highly exothermic stage found in some other systems containing P is not observed (Figs. 3.31b, c and 3.32a, b). The presence of melamine and P appears to cause PMMA to decompose in two stages (Table 3.16, Figs. 3.31c and 3.32b). DBB seems to volatilise after PMMA.

Table 3.16

Simultaneous thermal analysis of PMMA
and PMMA + P/DBB/MEL additive mixtures.

PMMA (%)	100	70	70	70	70	70	70
P (%)	-	30	-	15	-	15	10
DBB (%)	-	-	30	-	15	-	10
MEL (%)	-	-	-	15	15	15	10

First wt loss.							
Wt (%)	93.7	44.5	67.8	36.9	54.2	44.1	15.7
T range (°C)	260-413	280-383	196-346	187-314	296-368	172-324	196-319
T _{MR} (°C)	316	373	293	293	359	broad	299
MR (mg min ⁻¹)	3.54	1.02	0.84	0.61	0.83	0.28	0.27
DTA (μV)	-32	63	-	-	21	0.55	-

Second wt loss.							
Wt (%)	-	15.0 (s)	28.0	56.2	23.7 (s)	49.9 (s)	64.0
T range (°C)	-	383-396	346-415	314-413	368-400	324-417	319-406
T _{MR} (°C)	-	398	367	359	390	375	380
MR (mg min ⁻¹)	-	0.91	0.52	0.55	0.50	0.97	0.80

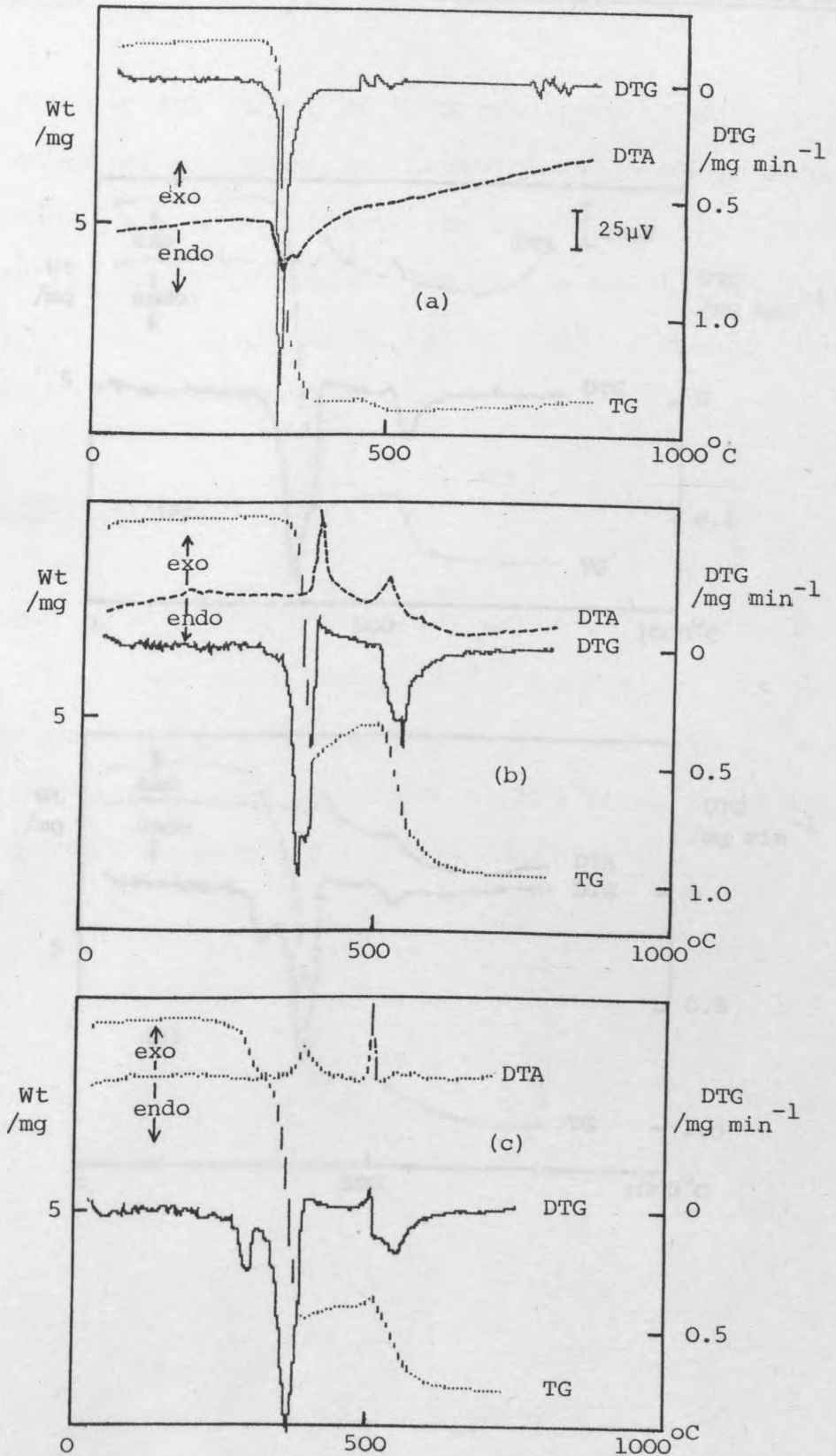
Wt gain.							
Wt (%)	-	9.5	-	-	5.3	-	2.0
T range (°C)	-	396-510	-	-	400-526	-	406-502
T _{MR} (°C)	-	400	-	-	broad	-	409
MR (mg min ⁻¹)	-	0.14	-	-	0.06	0.17	0.04

(contd.)

Note : T_{MR}^{MR} , temperature of maximum rate of weight change.
 T_{MR} , maximum rate of weight change.
 DTA , differential thermal analysis.
 W_{Tot} , total weight loss.
 $T_{1\%}$, temperature of 1% weight loss.
 S , shoulder.

Figure 3.31

Thermal analysis curves for (a) 100%PMMA,
(b) 70%PMMA + 30%P and (c) 70%PMMA + 15%P + 10%MEL.

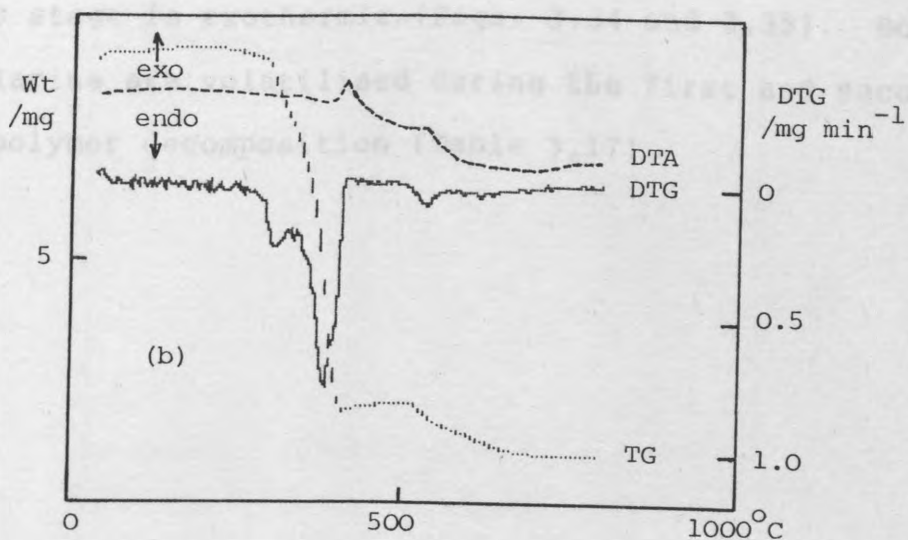
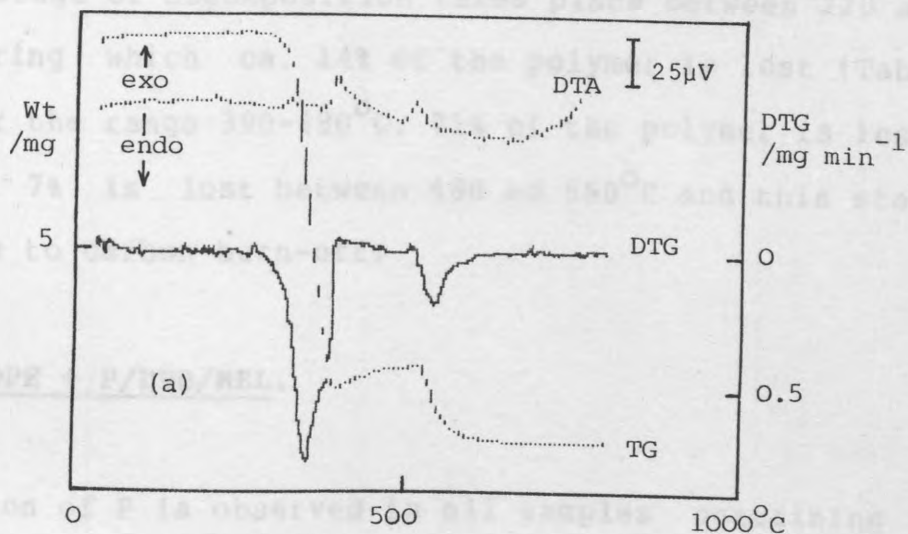


3.2.4. Degradation of HMPA and PMA-additive mixtures.

Figure 3.32

Thermal analysis curves for

(a) 70%PMMA + 15%P + 15%DBB and (b) 70%PMMA + 10%P + 10%DBB + 10%MEL.



3.2.4. Degradation of HDPE and HDPE-additive Mixtures.

3.2.4.1. HDPE.

The TG, DTG and DTA curves of HDPE are shown in Fig. 3.33. The first stage of decomposition takes place between 220 and 390°C, during which ca. 14% of the polymer is lost (Table 3.17). Over the range 390-480°C, 71% of the polymer is lost. A further 7% is lost between 480 and 580°C and this stage corresponds to carbon burn-off.

3.2.4.2. HDPE + P/DBB/MEL.

The oxidation of P is observed in all samples containing P (Figs. 3.34b, 3.35a, b and Table 3.17). Generally, the main weight-loss stage is exothermic (Figs. 3.34 and 3.35). Both DBB and melamine are volatilised during the first and second stages of polymer decomposition (Table 3.17).

Figure 3.33
Thermal analysis curves for 100%HDPE.

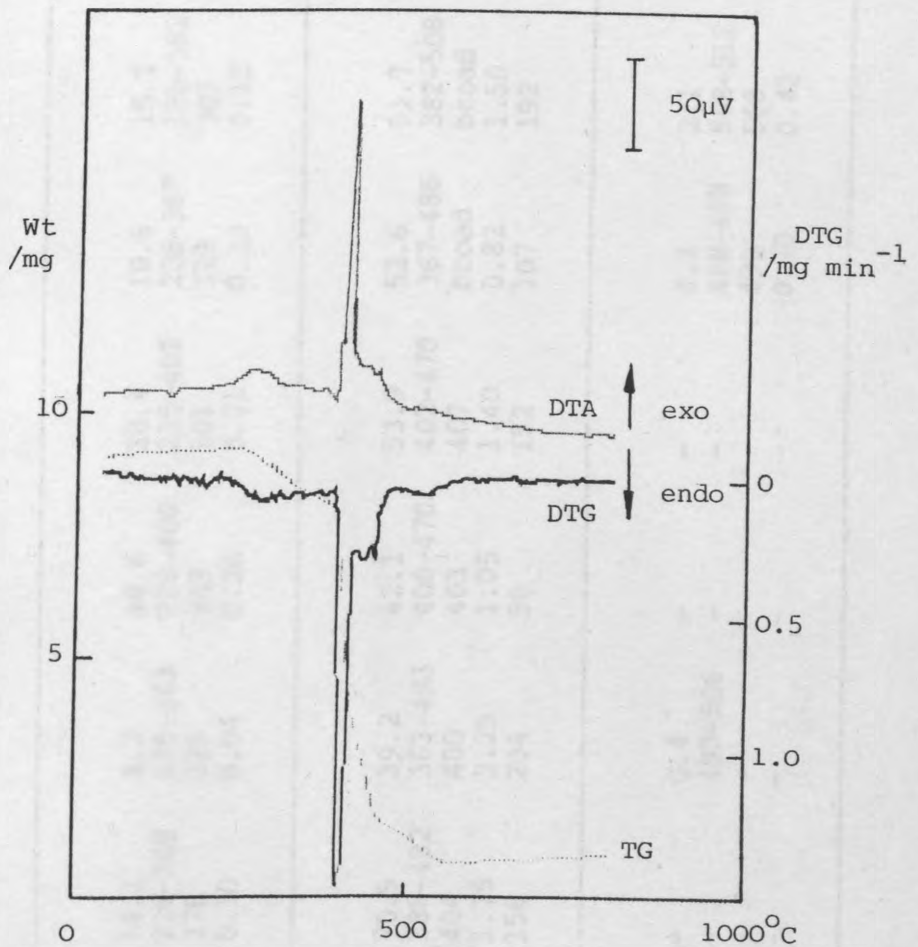


Table 3.17

Simultaneous thermal analysis of HDPE
and HDPE + P/DBB/MEL additive mixtures.

HDPE (%)	100	70	70	70	70	70	70
P (%)	-	30	-	-	15	-	10
DBB (%)	-	-	30	-	15	15	10
MEL (%)	-	-	-	30	-	15	10
First wt loss.							
Wt (%)	14.2	3.3	40.6	28.4	10.8	15.2	16.4
T range (°C)	226-388	245-363	228-400	215-402	228-367	188-382	212-367
T _{MR} (°C)	278	325	349	301	329	307	319
MR (mg min ⁻¹)	0.10	0.04	0.26	0.21	0.13	0.12	0.12
Second wt loss.							
Wt (%)	70.9	39.2	42.1	53.9	52.6	51.7	50.0
T range (°C)	388-482	363-493	400-470	402-470	367-486	382-508	367-494
T _{MR} (°C)	404	400	403	407	broad	broad	490
MR (mg min ⁻¹)	1.75	3.25	1.05	1.40	0.82	1.50	1.32
DTA (μV)	156	204	50	152	107	192	84
Wt gain.							
Wt (%)	-	0.4	-	-	4.2	2.1	0.9
T range (°C)	-	493-506	-	-	486-498	508-512	494-502
T _{MR} (°C)	-	-	-	-	490	508	496
MR (mg min ⁻¹)	-	-	-	-	0.70	0.42	0.10

Table 3.17
(contd.)

Third wt loss.										
Wt (%)	7.0	41.4	10.5	9.7	27.0	21.0	12.9	22.2		
T range (°C)	482-577	506-813	470-545	470-535	498-805	512-752	480-594	502-784		
T _{MR} (°C)	522	573	522	482	569	563	516	553		
MR (mg min ⁻¹)	0.09	0.28	0.14	0.12	0.21	0.13	0.17	0.11		
W _{Tot} (%)	92.1	83.5	93.2	92.0	86.2	85.8	94.9	87.7		
T _{1%} (°C)	255	299	273	242	269	237	241	237		

Note : T_{MR} , temperature of maximum rate of weight change.
 MR , maximum rate of weight change.
 DTA , differential thermal analysis.
 W_{Tot} , total weight loss.
 T_{1%} , temperature of 1% weight loss.

Figure 3.34

Thermal analysis curves for

(a) 70%HDPE + 30%P and (b) 70%HDPE + 15%P + 15%DBB.

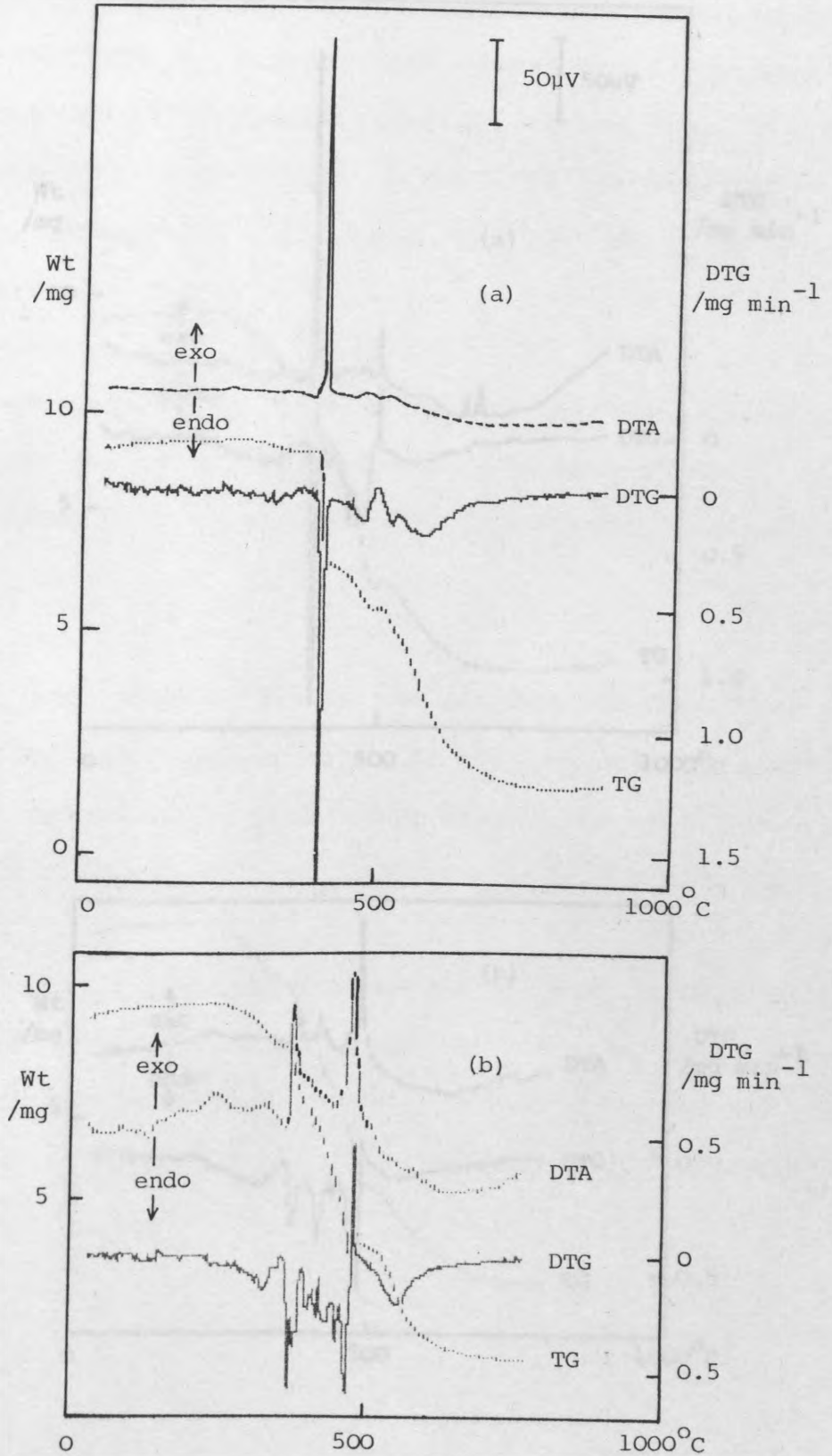
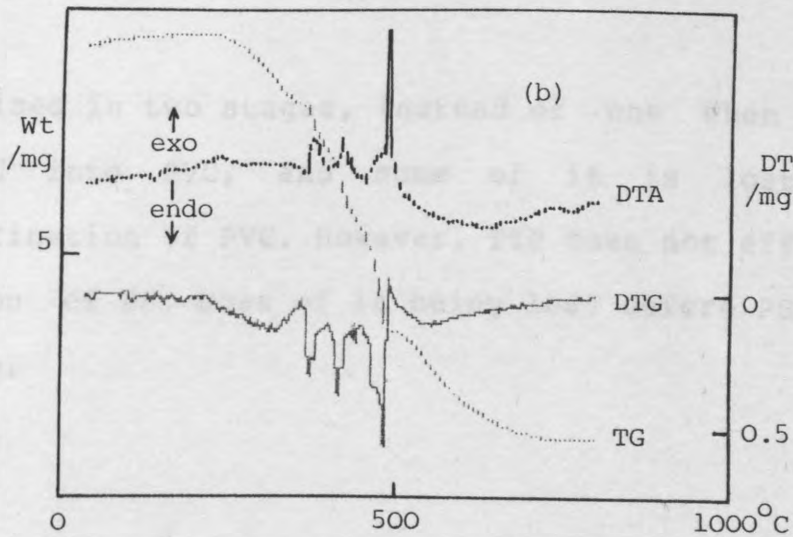
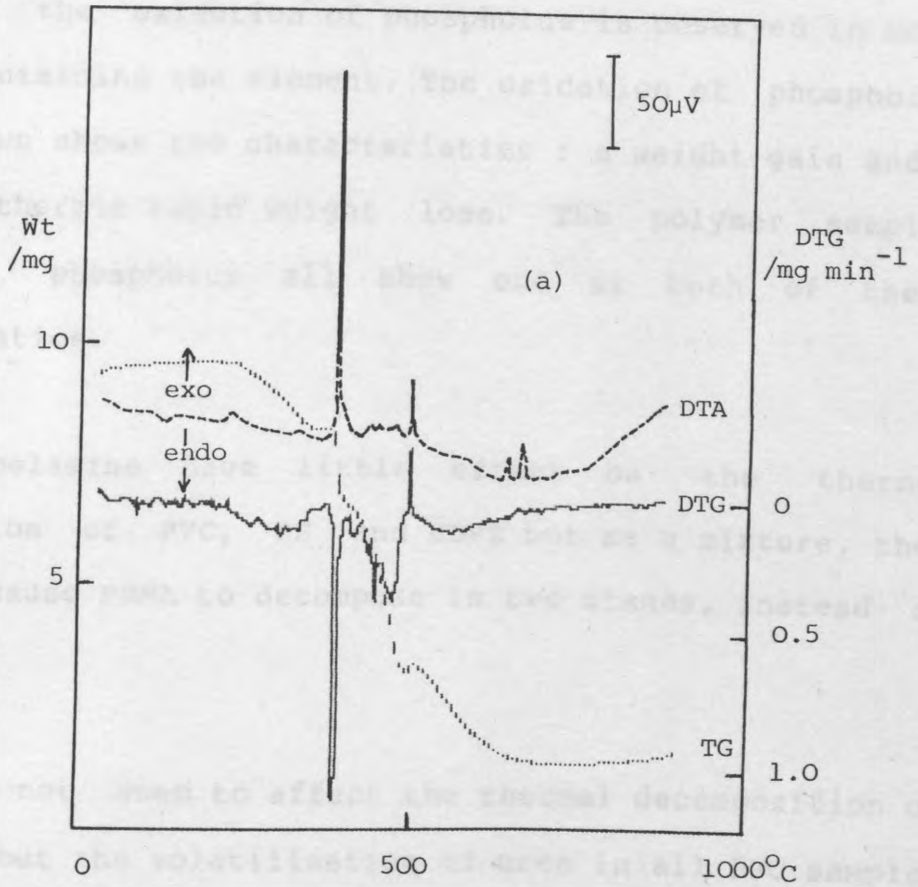


Figure 3.35

Thermal analysis curves for

(a) 70%HDPE + 15%P + 15%MEL and (b) 70%HDPE + 10%P + 10%DBB + 10%MEL.



3.2.5. Summary of Simultaneous Thermal Analysis Results.

Generally, the oxidation of phosphorus is observed in most samples containing the element. The oxidation of phosphorus on its own shows two characteristics : a weight gain and a highly exothermic rapid weight loss. The polymer samples containing phosphorus all show one or both of these characteristics.

DBB and melamine have little effect on the thermal decomposition of PVC, PS and HDPE but as a mixture, they appear to cause PMMA to decompose in two stages, instead of one.

Urea does not seem to affect the thermal decomposition of PVC and PS but the volatilisation of urea in all PVC samples occurs at temperatures lower than when it is heated on its own. This is observed only in PS containing 30% of urea.

TEP volatilises in two stages, instead of one when it is incorporated into PVC, and some of it is lost during dehydrochlorination of PVC. However, TTP does not affect the decomposition of PS, most of it being lost before PS starts to decompose.

3.3. Microanalytical Measurements.

3.3.1. Microanalysis of Polymers Containing Phosphorus alone.

Table 3.18 shows the results of microanalysis of polymer samples containing 30 wt % phosphorus, before and after various stages of heat treatment. In all cases, hardly any phosphorus is volatilised before the weight-gain stage and the bulk of the weight loss, between 34 to 36% of the original phosphorus, occurs during oxidation. With PVC, virtually all the chlorine is lost before any phosphorus is converted to volatile species.

The percentage weight gain of oxygen after oxidation, unlike that of phosphorus, varies widely from polymer to polymer : 420%, 670%, 260% and 160% in PVC, PS, PMMA and HDPE respectively. By the end of the weight-gain stage, the amounts of oxygen detected in the samples exceed that of phosphorus. The ratios of O_2/P in PVC, PS, PMMA and HDPE are 1.2, 2.0, 1.5 and 1.7 respectively.

With PVC, the percentage of carbon lost at the end of oxidation is smaller than with the other polymers.

Table 3.18

Microanalysis of polymer + red phosphorus
mixtures before and after being heated in air.

Sample	C		H		Cl		O		P		% Residue remaining
	wt %	mg	wt %	mg	wt %	mg	wt %	mg	wt %	mg	
70% PVC + 30% P											
Before heating	34.8	3.48	4.5	0.45	30.2	3.02	1.9	0.19	28.6	2.86	-
Theoretical value	34.0	3.40	4.4	0.44	28.4	2.84	3.3	0.33	30.0	3.00	-
Before wt gain	31.7	1.62	2.5	0.13	2.7	0.14	10.2	0.52	52.9	2.71	51.2
After wt gain	24.9	1.48	3.0	0.18	4.4	0.26	36.4	2.16	31.3	1.86	59.4
70% PS + 30% P											
Before heating	62.7	6.27	5.7	0.57	-	-	4.0	0.40	27.6	2.76	-
Theoretical value	64.6	6.46	5.4	0.54	-	-	-	-	30.0	3.00	-
Before wt gain	28.1	1.39	2.3	0.11	-	-	10.9	0.54	58.7	2.91	49.5
After wt gain	16.0	1.07	3.4	0.23	-	-	53.6	3.59	27.0	1.81	66.9
70% PMMA + 30% P											
Before heating	41.9	4.19	4.9	0.49	-	-	26.0	2.60	27.2	2.72	-
Theoretical value	42.0	4.20	5.6	0.56	-	-	22.4	2.24	30.0	3.00	-
Before wt gain	18.5	0.81	2.4	0.11	-	-	22.1	0.97	57.0	2.50	43.9
After wt gain	8.8	0.43	3.7	0.18	-	-	51.8	2.52	35.7	1.74	48.6
70% HDPE + 30% P											
Before heating	61.2	6.12	10.5	1.05	-	-	0.9	0.09	27.4	2.74	-
Theoretical value	60.0	6.00	10.0	1.00	-	-	-	-	30.0	3.00	-
Before wt gain	23.1	1.42	4.7	0.29	-	-	30.8	1.90	41.4	2.55	61.6
After wt gain	16.5	0.98	3.8	0.22	-	-	50.1	2.96	29.6	1.75	59.1

3.3.2. Microanalysis of Polymers Containing Phosphorus and Melamine.

Before the weight-gain stage, scarcely any phosphorus is lost from any of the polymers except HDPE, where more than 50% is lost (Table 3.19). In the presence of melamine, the amounts of phosphorus lost after oxidation differed widely from polymer to polymer, ranging from 17% in PVC, 22% in PS and 29% in PMMA to 51% in HDPE. It therefore appears that melamine affects the loss or oxidation of phosphorus in the polymer samples. Here again, almost all the chlorine in PVC is lost before the phosphorus volatilises.

In PS, PMMA and HDPE, at least 70% of the nitrogen is lost before and a further 20% is lost after oxidation. Thus, it appears that PVC retains nitrogen better than the other polymers. In addition, the percentage of carbon remaining in PVC samples before and after oxidation is higher than in the other polymers.

At the end of the oxidation stage, the ratios of O_2/P in PVC, PS, PMMA and HDPE are 2, 1.2, 1.6 and 2.3 respectively.

Table 3.19

Microanalysis of polymer + red phosphorus
+ melamine mixtures before and after being heated in air.

Sample	C		H		N		Cl		O		P		% Residue remaining
	wt %	mg	wt %	mg	wt %	mg	wt %	mg	wt %	mg	wt %	mg	
70% PVC + 15% P + 15% MEL													
Before heating	38.4	3.84	5.0	0.50	9.3	0.93	30.0	3.00	3.0	0.30	14.3	1.43	-
Theoretical value	38.3	3.83	5.1	0.51	10.0	1.00	28.4	2.84	3.3	0.33	15.0	1.50	-
Before wt gain	40.1	2.04	3.5	0.18	14.1	0.72	4.9	0.25	9.9	0.50	27.5	1.40	50.9
After wt gain	24.9	1.42	3.1	0.18	7.7	0.44	1.3	0.07	42.0	2.39	21.0	1.19	56.9
70% PS + 15% P + 15% MEL													
Before heating	68.6	6.86	6.7	0.67	9.4	0.94	-	-	-	-	15.3	1.53	-
Theoretical value	68.9	6.89	6.1	0.61	10.0	1.00	-	-	-	-	15.0	1.50	-
Before wt gain	34.3	1.03	2.4	0.07	7.4	0.22	-	-	11.6	0.35	44.3	1.33	30.0
After wt gain	18.4	0.68	3.1	0.12	7.0	0.26	-	-	39.3	1.45	32.2	1.19	37.0
70% PMMA + 15% P + 15% MEL													
Before heating	47.0	4.70	6.5	0.65	9.8	0.98	-	-	22.8	2.28	13.9	1.39	-
Theoretical value	46.3	4.63	6.3	0.63	10.0	1.00	-	-	22.4	2.24	15.0	1.50	-
Before wt gain	26.0	0.94	2.7	0.10	2.3	0.08	-	-	31.3	1.14	37.7	1.37	36.3
After wt gain	18.6	0.63	2.8	0.09	2.2	0.08	-	-	47.1	1.60	29.3	0.99	33.9
70% HDPE + 15% P + 15% MEL													
Before heating	63.4	6.34	11.0	1.10	8.9	0.89	-	-	1.7	0.17	15.0	1.50	-
Theoretical value	64.3	6.43	10.7	1.07	10.0	1.00	-	-	-	-	15.0	1.50	-
Before wt gain	29.5	0.78	2.8	0.07	9.1	0.24	-	-	27.7	0.73	30.9	0.82	26.4
After wt gain	15.4	0.48	3.5	0.11	3.4	0.11	-	-	54.2	1.70	23.5	0.73	31.3

3.4. Infrared Spectroscopic Measurements.

3.4.1. PVC-additive Systems.

The gas-phase spectra of 70%PVC + 30%P show that HCl is given off above 250°C and this is accompanied by the evolution of CO , CO_2 and CH_4 ; these latter compounds are probably formed from the plasticiser, DIOP. The spectra also show that from 440°C onwards, strong, broad peaks at 950, 1030 and 1250 cm^{-1} are observed (Fig. 3.36). These peaks can be assigned to the P-O and P=O stretches of some phosphorus oxides. In fact, the P-O and P=O peaks of phosphoric acid absorb in this region (Fig. 3.37), so that it can be inferred that phosphoric acid is formed by the absorption of water by P_2O_5 , which is given off during combustion of the sample. The amounts of CH_4 given off from 70%PVC + 30%P appear to be higher than from plasticised PVC.

For 70%PVC + 15%P + 15%MEL, HCl is again detected above 250°C but the amount formed appears to be smaller than from 70%PVC + 30%P. CO , CO_2 and CH_4 start to be evolved above 300°C . Trace amounts of ammonia are detected between 480 and 515°C . From 305°C onwards, peaks between 1180 and 1215 cm^{-1} are observed and above 480°C , three broad peaks at 930, 1070 and 1250 cm^{-1} are also observed (Fig. 3.38). This indicates that oxidised phosphorus species are produced.

Figure 3.36

Infrared spectrum of pyrolysis products from 70%PVC + 30%P
between 440 and 490°C.

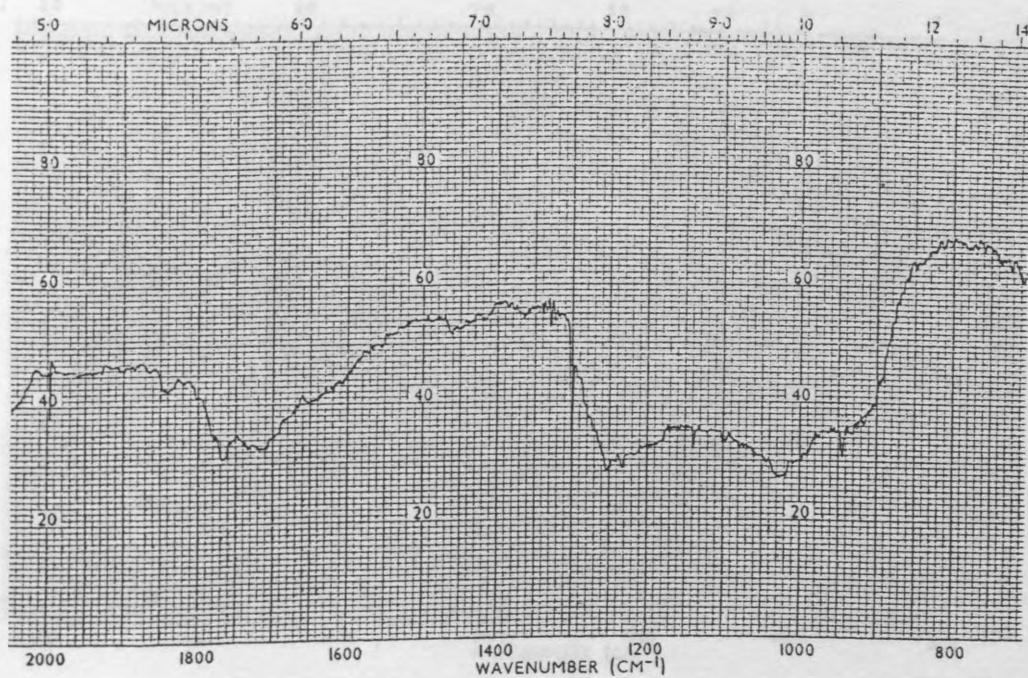


Figure 3.37

Infrared spectrum of pyridyl

Figure 3.37

Infrared spectrum of phosphoric acid.

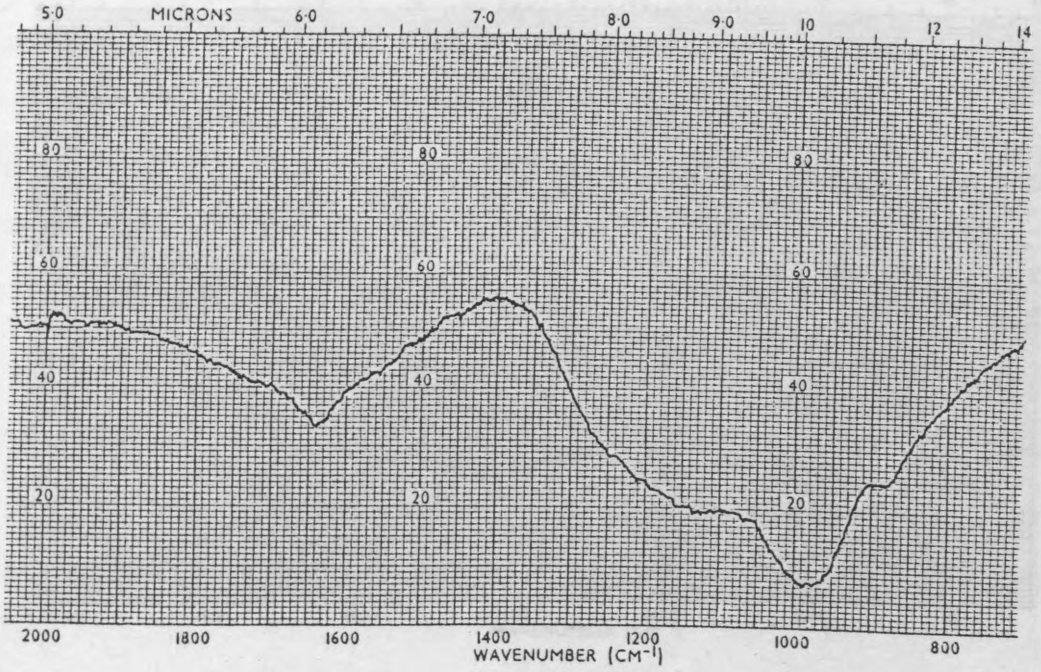
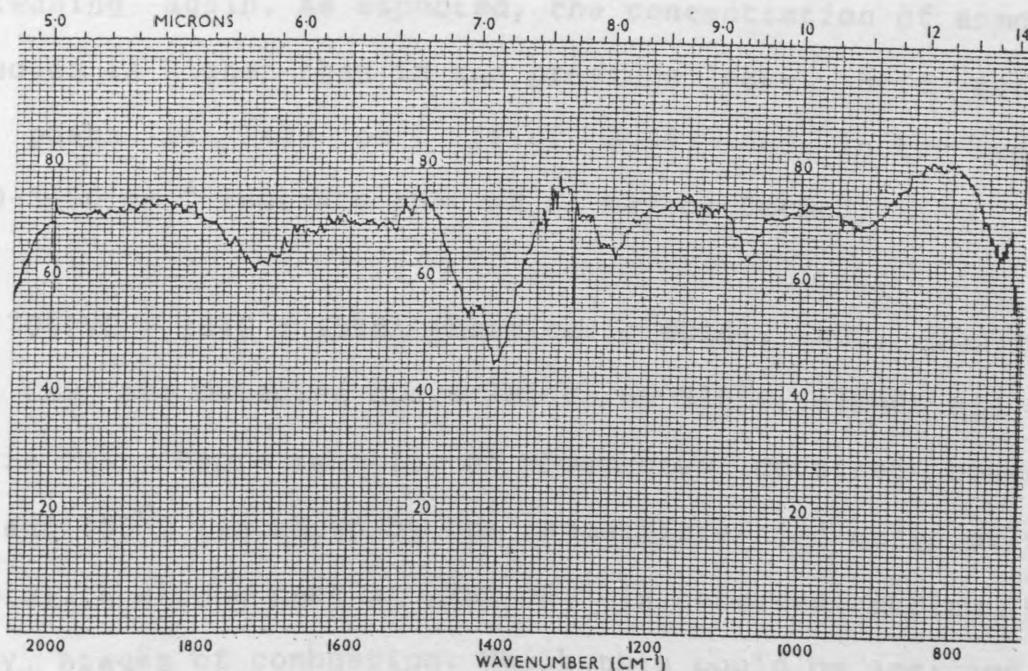


Figure 3.38

Infrared spectrum of pyrolysis products from 70%PVC + 15%P + 15%MEL
is probably formed between 520 and 535°C.



Peaks at 1400 (Fig. 3.38) and 3120 cm^{-1} indicate that NH_4Cl is probably formed from HCl and NH_3 .

In 70%PVC + 30%MEL, HCl , CO , CO_2 and CH_4 are evolved from 280°C onwards, and ammonia is detected above 435°C (Fig. 3.39), the amount increasing rapidly up to 575°C and then decreasing again. As expected, the concentration of ammonia detected is higher than in the previous case. Here again, the peaks at 1410 cm^{-1} (Fig. 3.39) and in the region $3300\text{--}3450\text{ cm}^{-1}$ indicate that NH_4Cl may be formed.

For 70%PVC + 15%P + 15%BA (barbituric acid), HCl , CO , CO_2 and CH_4 are detected above 285°C . By 510°C , almost all the HCl is lost. Rapid ignition of phosphorus occurred between 415 and 485°C (as shown by the temperature-time curve of the sample). A strong peak at 1260 cm^{-1} is observed during the early stages of combustion. While this could be assigned to the C-O stretches of DIOP, it is still observed after other peaks associated with the plasticiser have disappeared (by 540°C). This peak may therefore be due to some oxidised phosphorus species (Fig. 3.40). The spectra also show that barbituric acid decomposes within the temperature range $395\text{--}455^\circ\text{C}$. Ammonia is not detected.

The spectra of 70%PVC + 15%P + 15%DBB show that large amounts of CO and CO_2 are evolved from 510°C onwards. HCl and CH_4 are detected above 310°C . Trace amounts of HBr are

Figure 3.39

Infrared spectra of pyrolysis products from 70%PVC + 30%MEL
between (a) 435 and 470°C and (b) 470 and 500°C.

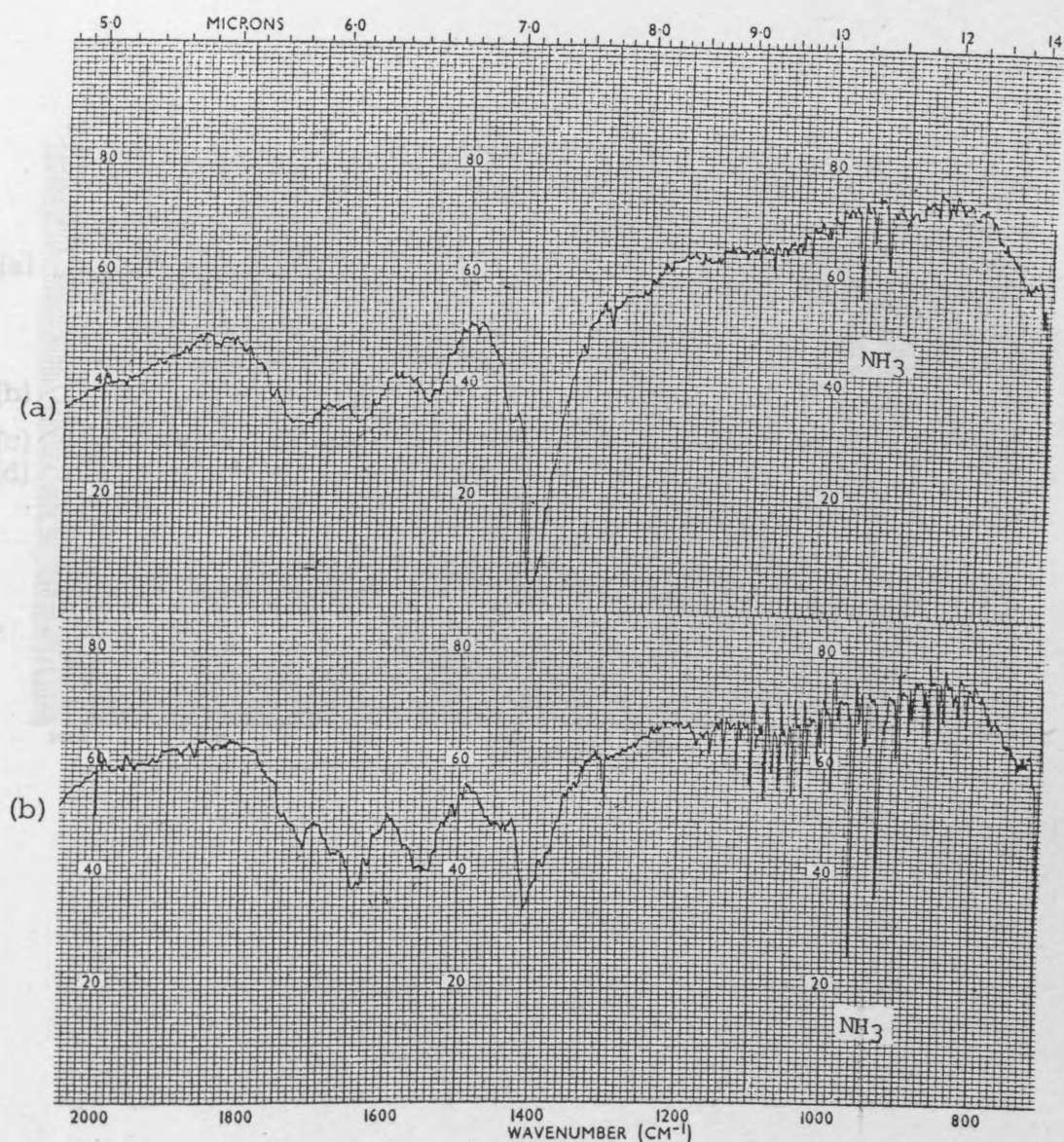
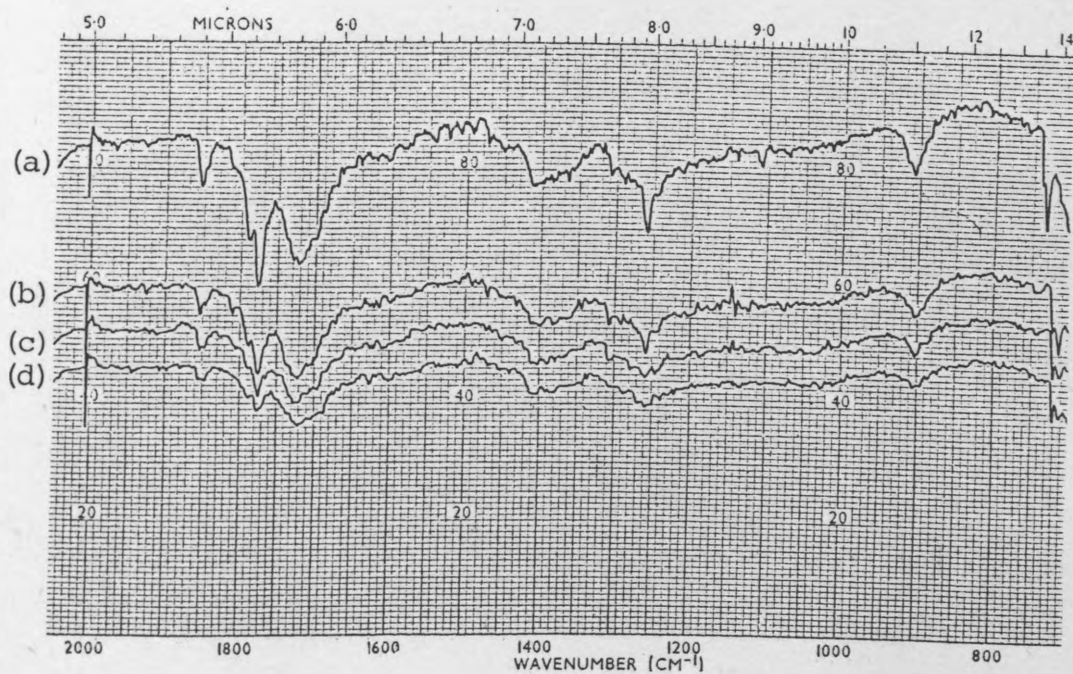


Figure 3.40

Infrared spectra of pyrolysis products from 70%PVC + 15%P + 15%BA
between (a) 490 and 510°C, (b) 510 and 540°C, (c) 540 and 560°C
and (d) 560 and 580°C.



also detected in the temperature ranges 460-495°C (Fig. 3.41) and 510-535°C. Weak absorption peaks at 1250 and 1050 cm^{-1} are only seen between 500 and 510°C (Fig. 3.42).

Trace amounts of HBr are also seen in the spectra of 70%PVC + 30%DBB, starting from 460-575°C.

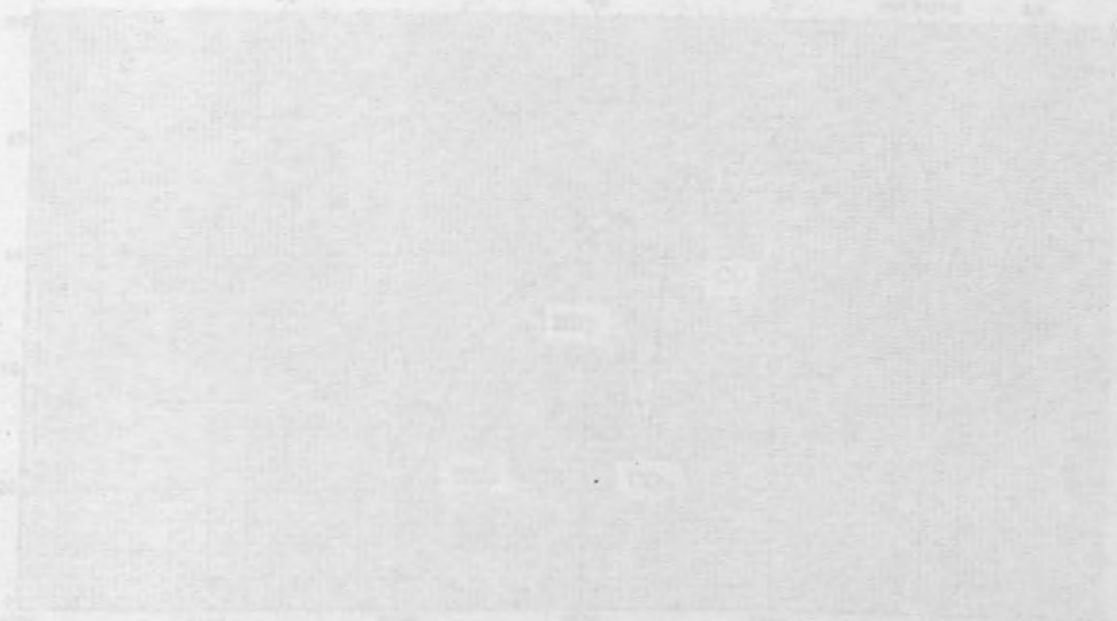
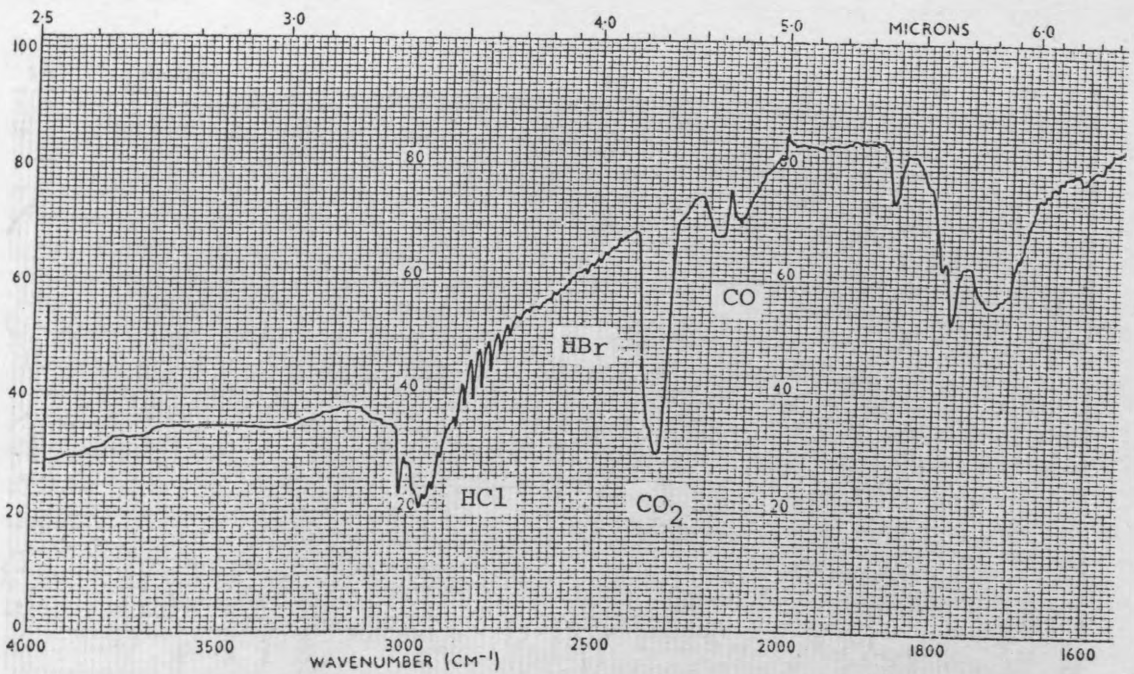


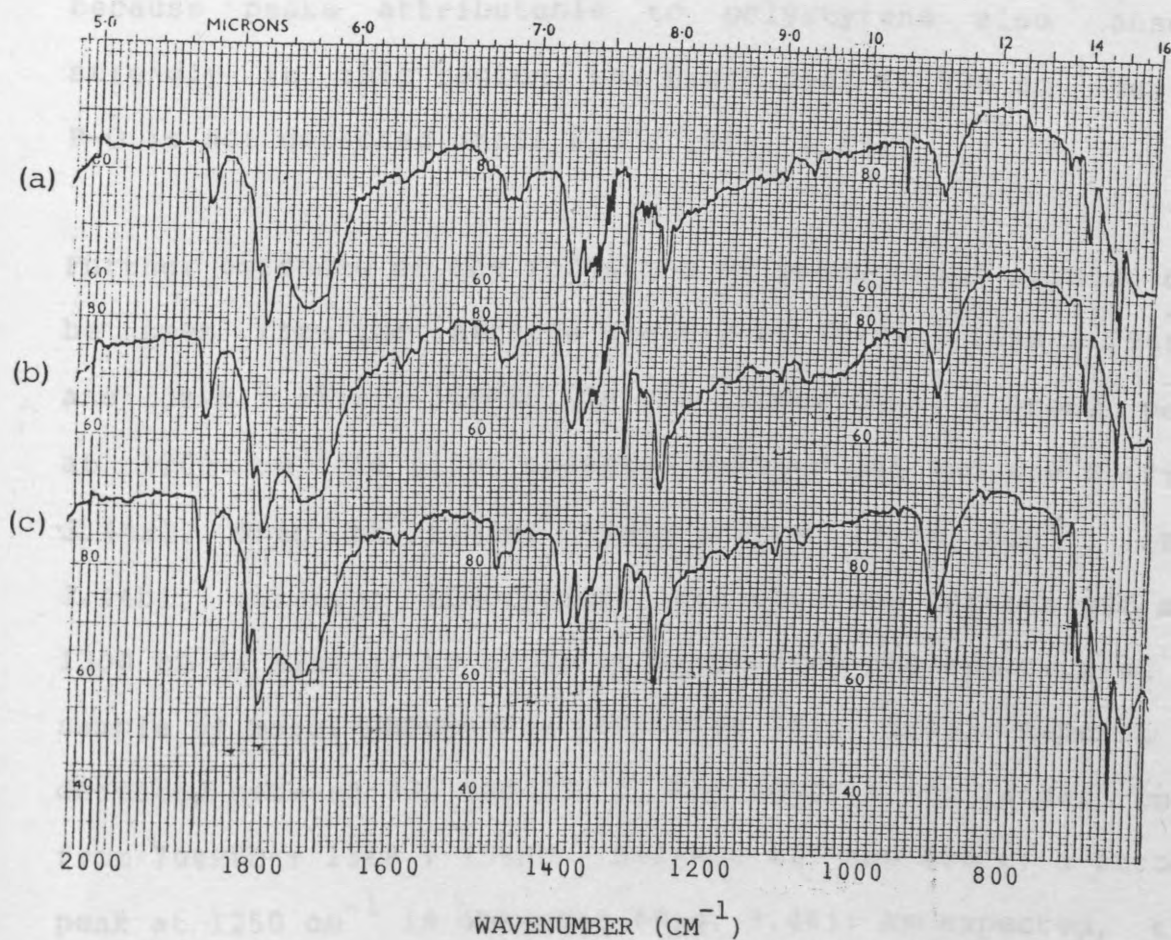
Figure 3.41

Infrared spectrum of pyrolysis products from 70%PVC + 15%P + 15%DBB
between 460 and 495°C.



3.4.2. PS-additive system Figure 3.42

Infrared spectra of pyrolysis products from 70%PVC + 15%P + 15%DBB between (a) 460 and 495°C, (b) 500 and 510°C and (c) 510 and 535°C.



3.4.2. PS-additive Systems.

The infrared spectra of 70%PS + 30%P show that the polymer starts to decompose above 250°C and that this reaction is accompanied by the evolution of CO and CO₂. Broad peaks at 1030 and 1200 cm⁻¹, assigned to the P-O and P=O stretches of phosphorus oxides, are detected from 435°C onwards and because peaks attributable to polystyrene also absorb strongly in this region, the broad peak at 930 cm⁻¹ due to P-O is not detected until 625°C (Fig. 3.43).

Further evidence of the formation of phosphorus oxides can be seen from the infrared spectra of 70%PS + 15%P + 15%DBB and 70%PS + 15%P + 15%MEL. In the former case, a broad peak at 1200 cm⁻¹ is first observed between 355 and 410°C (Fig. 3.44a). Then at higher temperatures (from 625°C) (Fig. 3.44b), stronger absorptions are observed between 900 and 1300 cm⁻¹, similar to those observed from the spectrum of a sample of moist phosphorus pentoxide (Fig. 3.45). Ammonia is detected between 335 and 430°C; the amounts are larger than from 70%PVC + 15%P + 15%MEL. Between 435 and 480°C, a strong peak at 1250 cm⁻¹ is observed (Fig. 3.46). As expected, the concentration of ammonia found in 70%PS + 30%MEL is higher than from 70%PS + 15%P + 15%MEL (ammonia given off from 320 to 560°C). No HBr is detected from either 70%PS + 30%DBB or 70%PS + 15%P + 15%DBB, unlike the result obtained for PVC and DBB mixtures, where trace amounts of HBr were seen. A

Figure 3.43

Infrared spectra of pyrolysis products from 70%PS + 30% P
between (a) 435 and 475°C, (b) 600 and 615°C and (c) 625 and 635°C.

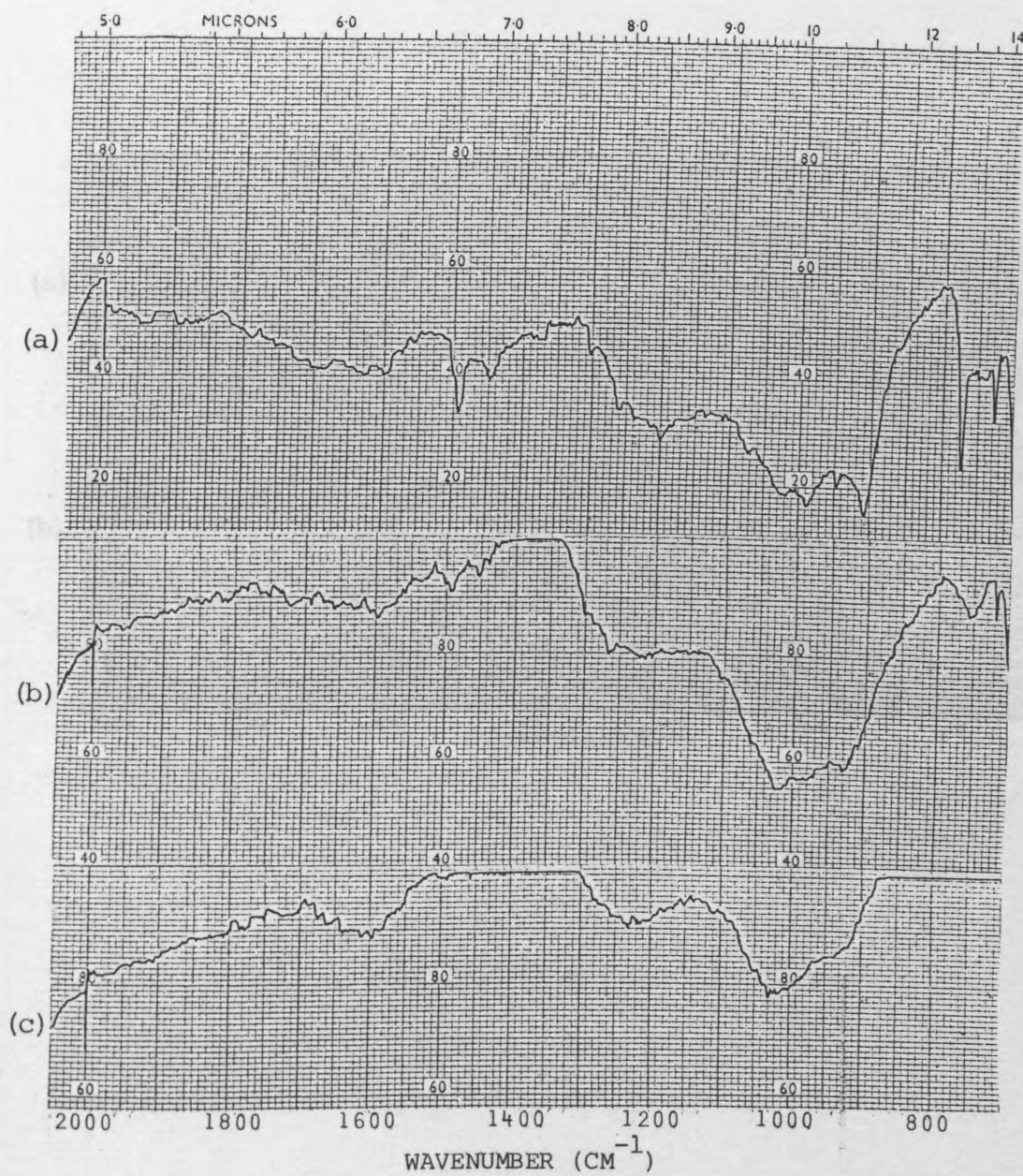


Figure 3.44

Infrared spectra of pyrolysis products from 70%PS + 15%P + 15%DBB
between (a) 355 and 410°C and (b) 625 and 635°C.

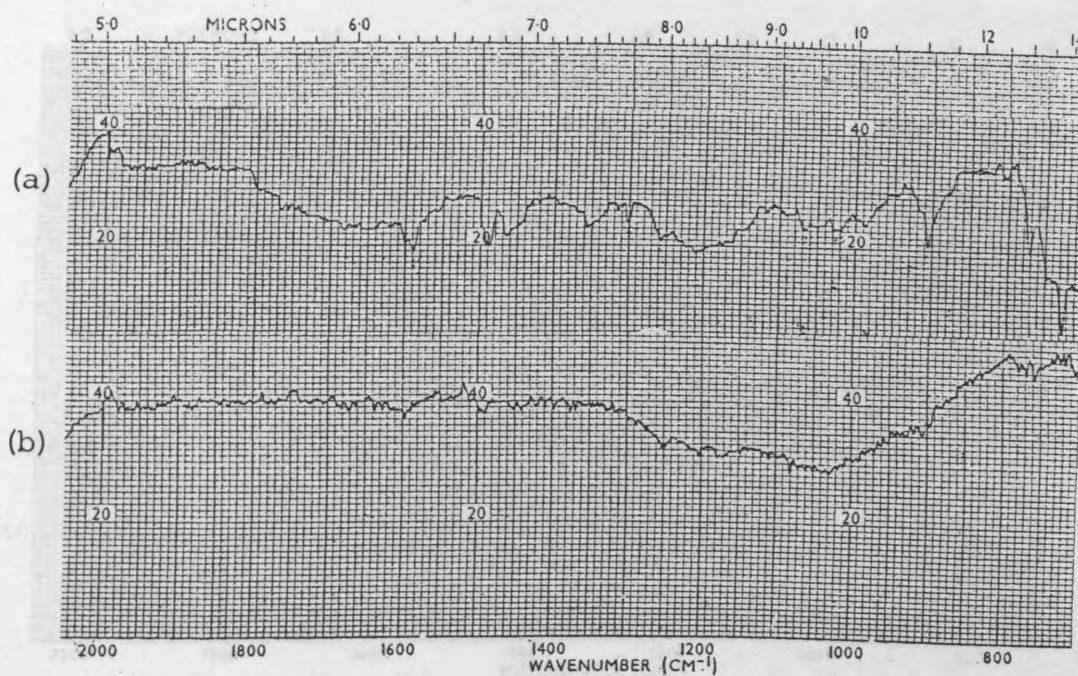


Figure 3.45

Infrared spectrum of pyrolysis products from a sample of moist P_2O_5 (as a thin film).

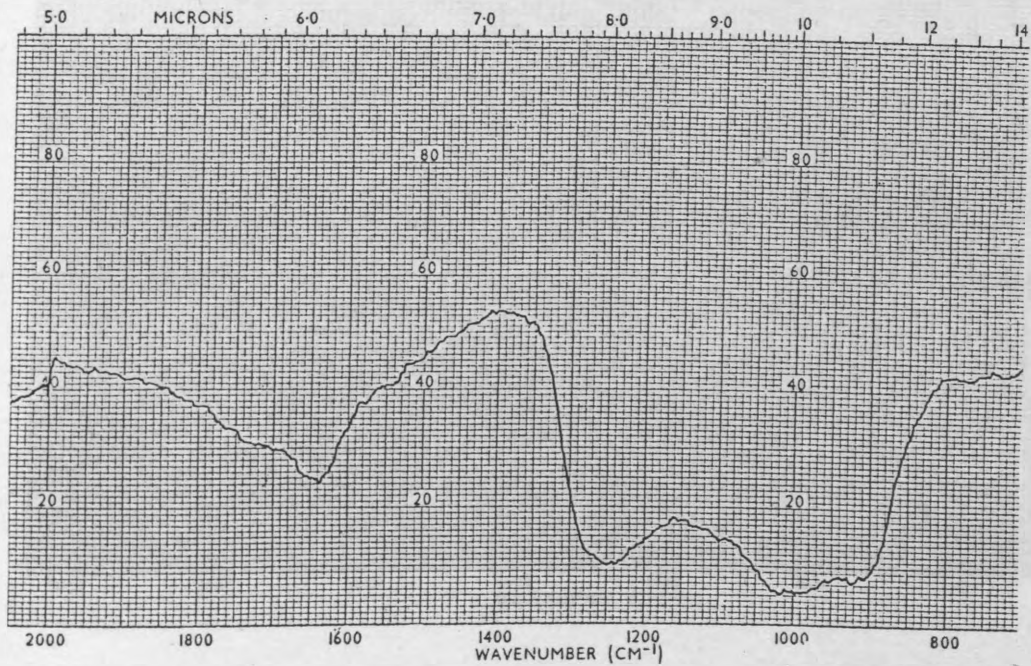
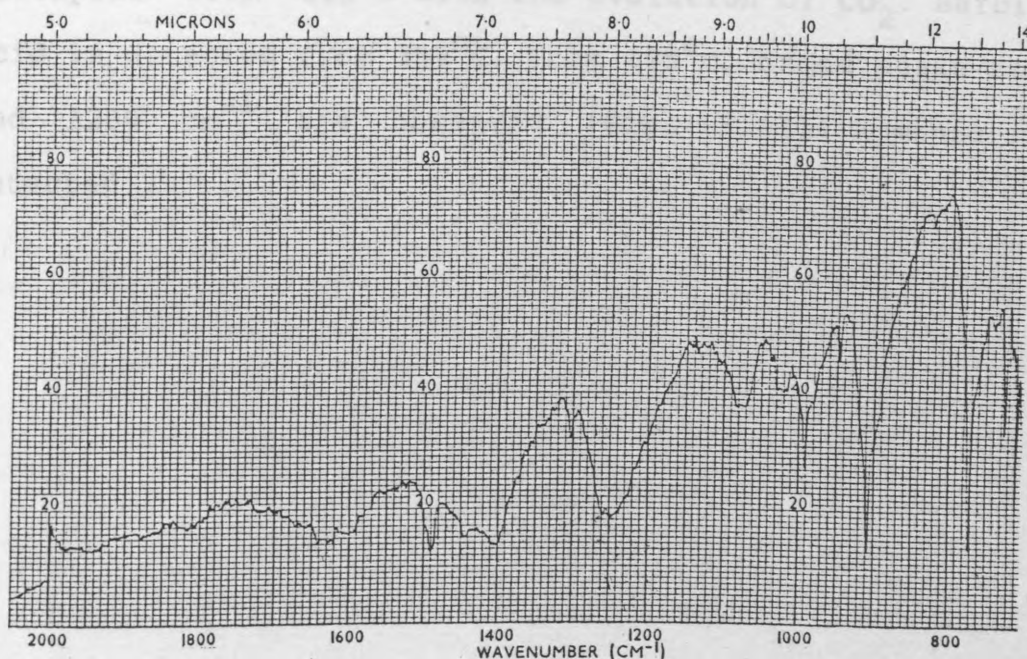


Figure 3.46

Infrared spectrum of pyrolysis products from 70%PS + 15%P + 15%MEL
between 435 and 480°C.



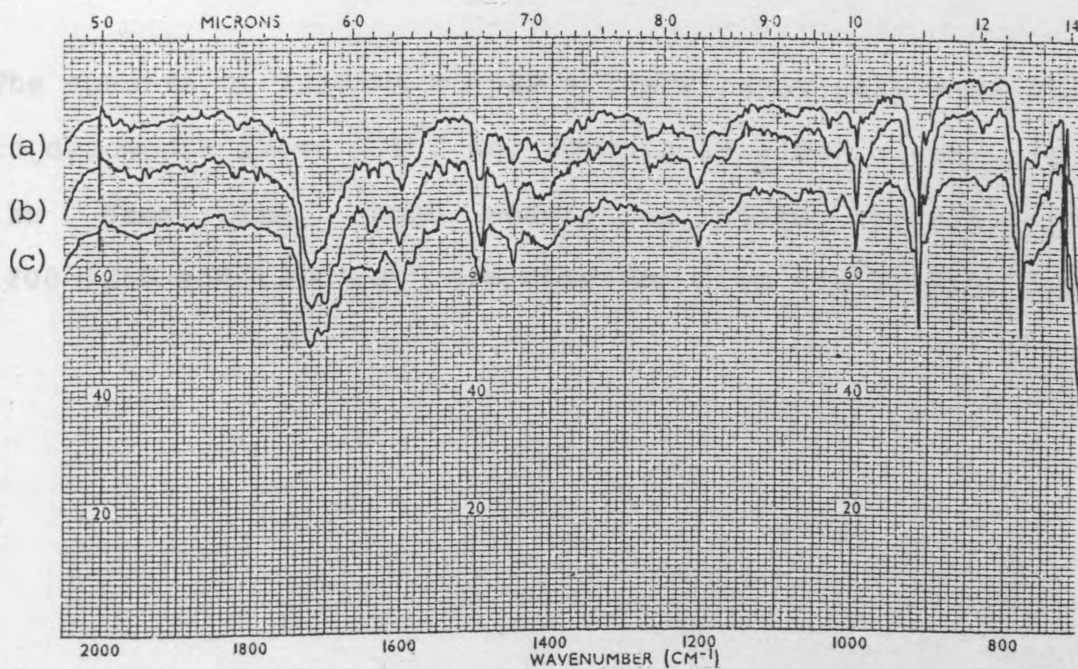
possible reason for this discrepancy could be the evaporation of DBB before ignition of the sample, which is plausible in view of the relatively low heating rate used in these experiments.

The spectra of 70%PS + 15%P + 15%BA show that PS starts to decompose from 235°C with the evolution of CO₂. Barbituric acid is detected from 355°C. From 495°C, broad peaks at 1000 and 1200 cm⁻¹ are observed (Fig. 3.47). Ammonia is not detected.



3.4.3. PMA-additive Figure 3.47

Infrared spectra of pyrolysis products from 70%PS + 15%P + 15%BA between (a) 455 and 490°C, (b) 495 and 510°C and (c) 515 and 535°C.



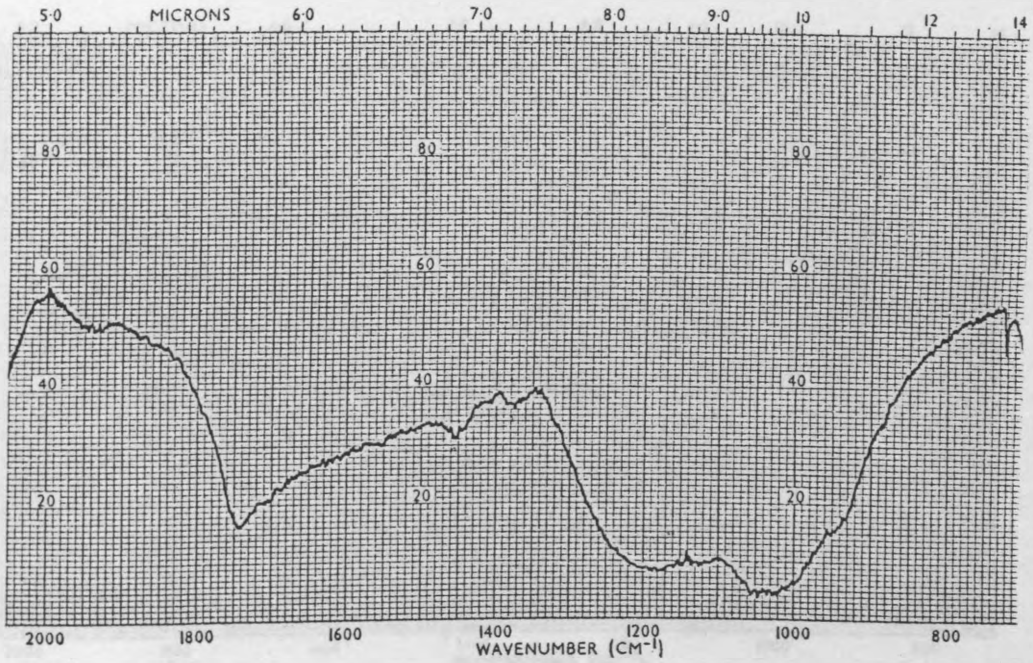
3.4.3. PMMA-additive Systems.

The infrared spectra of 70%PMMA + 30%P show that PMMA starts to decompose from 125°C. CO and CO₂ are evolved during decomposition. By 520°C, almost all the polymer is lost and two broad peaks at 1030 and 1200 cm⁻¹ and a shoulder at 950 cm⁻¹ are observed (Fig. 3.48).

The spectra of 70%PMMA + 15%P + 15%MEL show that PMMA starts to decompose above 270°C and ammonia is also given off at the same time. Broad absorption peaks at 935, 1065, 1200-1250 and 1280 cm⁻¹ are observed from 465°C (Fig. 3.49).

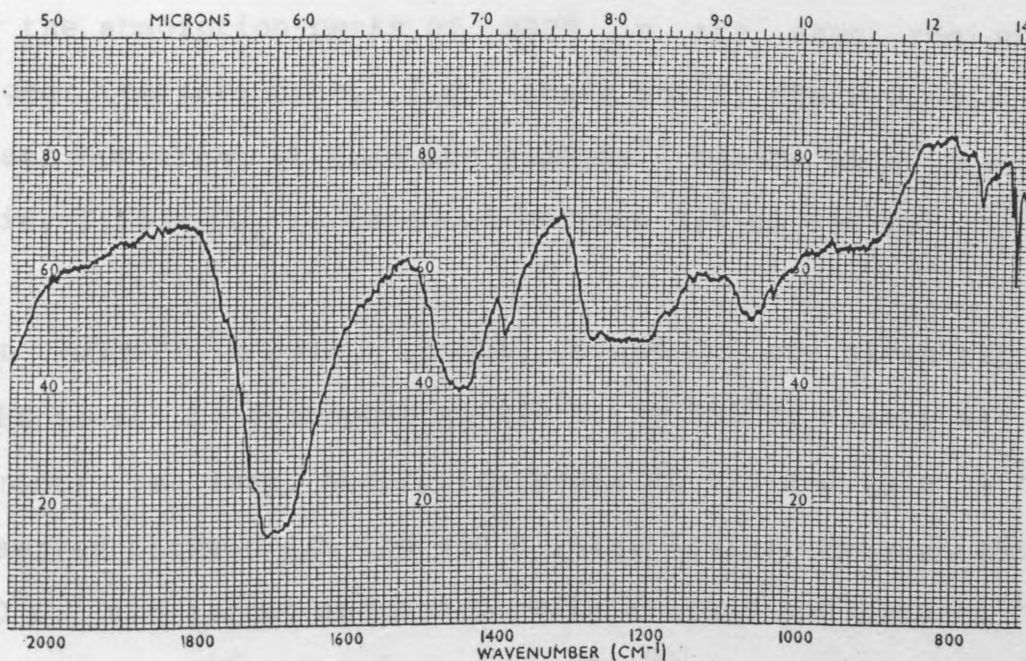
Figure 3.48

Infrared spectrum of pyrolysis products from 70%PMMA + 30%P
between 520 and 535°C.



3.4.4. NDPZ-additive Figure 3.49

Infrared spectrum of pyrolysis products from 70%PMMA + 15%P + 15%MEL
between 465 and 495°C.



3.4.4. HDPE-additive Systems.

The infrared spectra of 70%HDPE + 30%P show that HDPE starts to decompose above 275°C and that the reaction is accompanied by the evolution of CO and CO₂. Above 510°C, broad peaks at 1000 and 1200 cm⁻¹ start appearing. These peaks are not observed earlier, probably due to the presence of the absorption peaks of HDPE in the same region. At higher temperatures, i.e. above 530°C, the P-O absorption peaks appearing at 1010 and 1160 cm⁻¹ become more prominent (Fig. 3.50). CH₄ is detected between 385 to 595°C.

For 70%HDPE + 15%P + 15%MEL, CO and CO₂ are given off when HDPE starts to decompose at 230°C. By 505°C, almost all the ammonia is lost. Absorption peaks at 920 and 1070 cm⁻¹ are observed between 425 and 450°C (Fig. 3.51a). Between 455 and 490°C, two strong and broad peaks at 1080 and 1250 cm⁻¹ are also observed (Fig. 3.51b). From 505°C onwards, strong peaks at 920, 1060, 1160 cm⁻¹ are observed (Fig. 3.51c). CH₄ is detected from 385 to 505°C.

Figure 3.50

Infrared spectrum of pyrolysis products from 70%HDPE + 30%P
between 530 and 540°C.

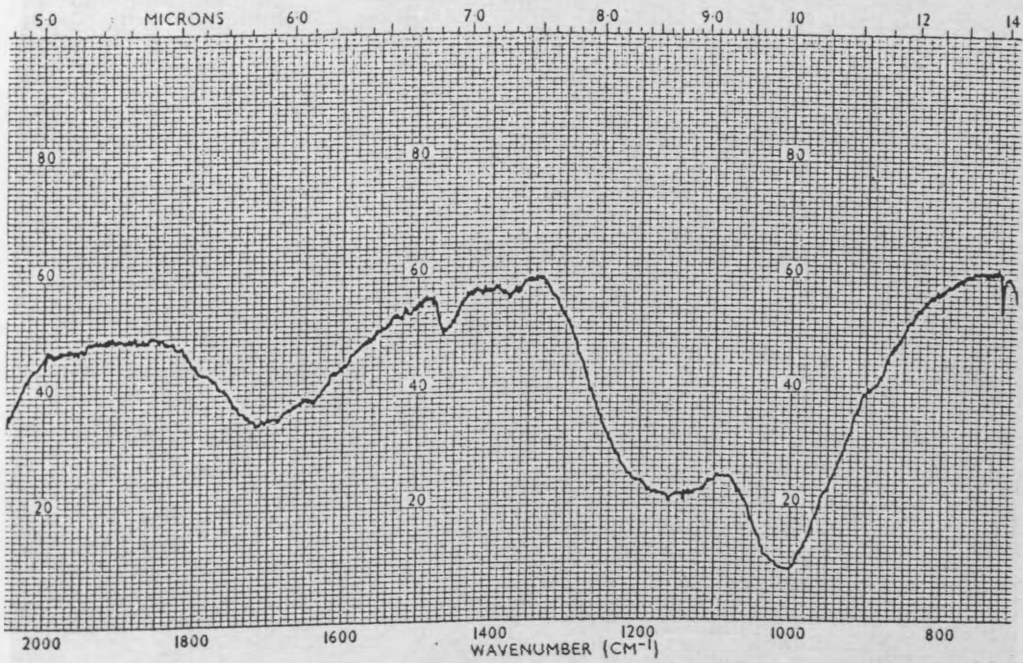
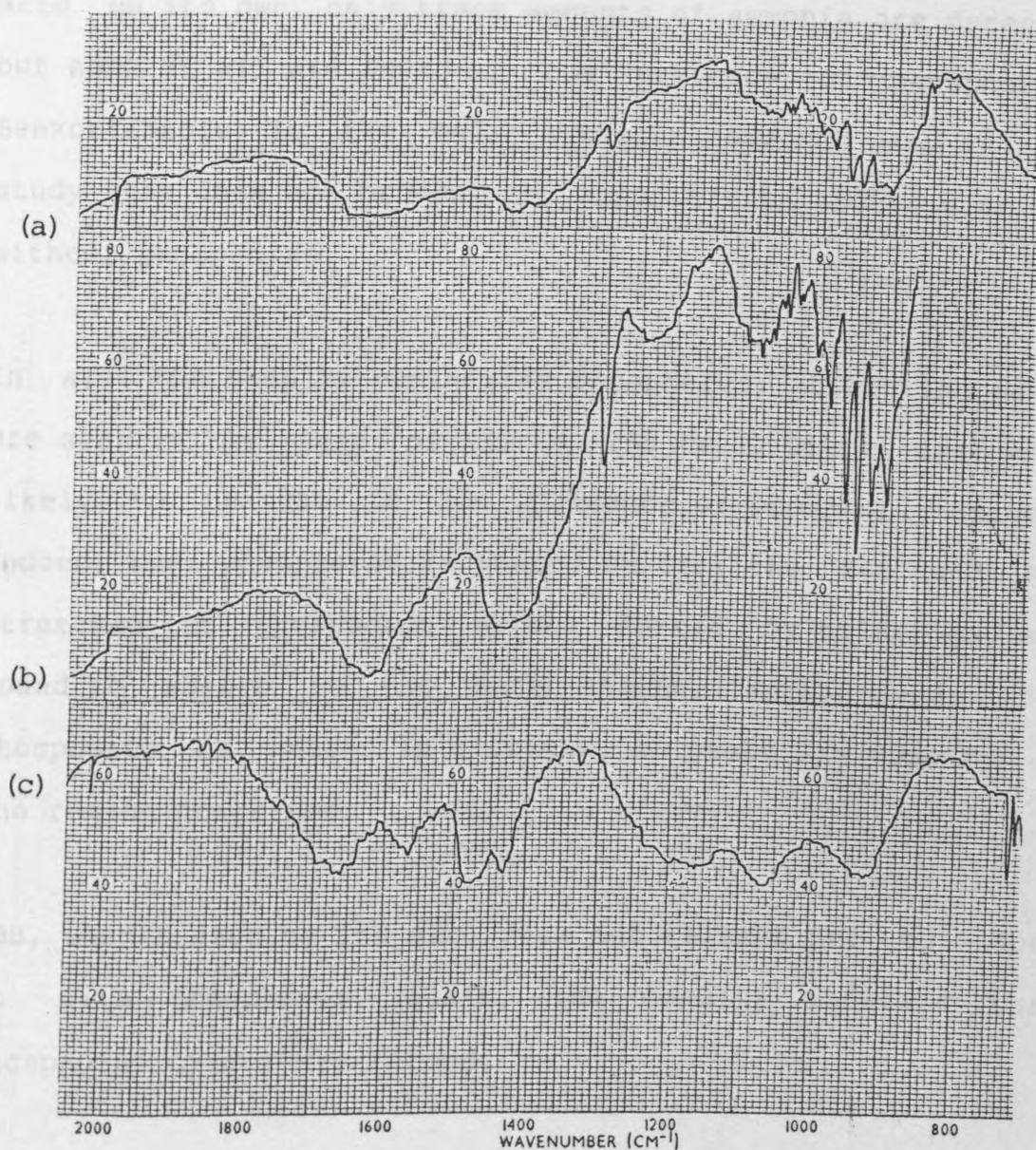


Figure 3.51

Infrared spectra of pyrolysis products from 70%HDPE + 15%P + 15%MEL
between (a) 425 and 455°C, (b) 455 and 490°C and (c) 505 and 520°C.



3.4.5. Additives On Their Own.

Table 3.20 shows the results of infrared analysis of the additives on their own. Melamine, urea and guanidine carbonate give off large amounts of ammonia when heated alone and also when phosphorus is present. From barbituric acid on its own, only trace amounts of ammonia are detected but none at all are found in the presence of phosphorus. Benzotriazole is the only nitrogen compound used in this study that does not produce any ammonia when heated with or without phosphorus.

In all the samples containing phosphorus, absorption peaks are seen in the region of 930 to 1390 cm^{-1} . These are most likely to be due to the presence of phosphorus oxides. Indeed, when phosphorus is heated in air, the P-O and P=O stretches of phosphorus oxides formed by oxidation, are found to absorb in the same region. Furthermore, when phosphorus is heated in nitrogen, no peaks are observed in the region concerned.

DBB, when heated on its own, does not release HBr but does so with phosphorus. Again, the results indicate that phosphorus oxides are formed.

The temperature-time curves of all the samples containing phosphorus show a rapid rise in temperature between 420 and 500°C. This is almost certainly due to the ignition of phosphorus.

Table 3.20

Results of infrared analysis of additives on their own.

Compound	NH ₃		P-O	
	Amount	Tr (°C)	Absorption peaks (cm ⁻¹)	Tr (°C)
P (in N ₂)	-	-	-	-
P (in air)	-	-	980 s; 1010 s; 1390 s	365-415
Residue from air	-	-	930 b,s; 1210 b,s	(analysed as thin film)
oxidation of P (above)				
Melamine	large	335-385	-	-
Melamine + P	large	260-315	950-1030 b,s; 1335-1355 b,s	460-540
Urea	large	175-235	-	-
Urea + P	large	165-230	980 b,s; 1360 s	445-510
Guanidine carbonate	large	170-240	-	-
Guanidine carbonate + P	large	215-275	1025 m	500-515
Barbituric acid	trace	420-455	-	-
Barbituric acid + P	-	-	1030 b,m; 1300 b,m	420-480
Benzotriazole	-	-	-	-
Benzotriazole + P	-	-	950 s; 1025 s; 1380 s	445-485
Compound	HBr		P-O	
	Amount	Tr (°C)	Absorption peaks (cm ⁻¹)	Tr (°C)
DBB	-	-	-	-
P + DBB	medium	400-450	1030 s; 1200 b,s	495-525

Note : Tr is the temperature range at which the peaks were first observed.
b, m, & s are broad, medium and strong respectively.

3.4.6. Summary of Infrared Analysis.

Methane is detected in all PVC and HDPE samples and not in any PS or PMMA samples. Trace amounts of HBr are observed in the PVC samples containing DBB but none is detected in the PS samples.

In all samples containing phosphorus, absorption peaks appear in the region between 900 and 1280 cm^{-1} and are generally evident around the temperature at which phosphorus ignites. These peaks can be assigned to the P-O and P=O stretches of oxidised phosphorus species.

DISCUSSION

4. DISCUSSION.

4.1. Combustion Behaviour of PVC.

When PVC is heated, it undergoes degradation by dehydrochlorination reaction (1,2,3,4,5), forming conjugated polyenes. Subsequently, these polyenes can cross-link via Diels-Alder cycloaddition:

4

DISCUSSION



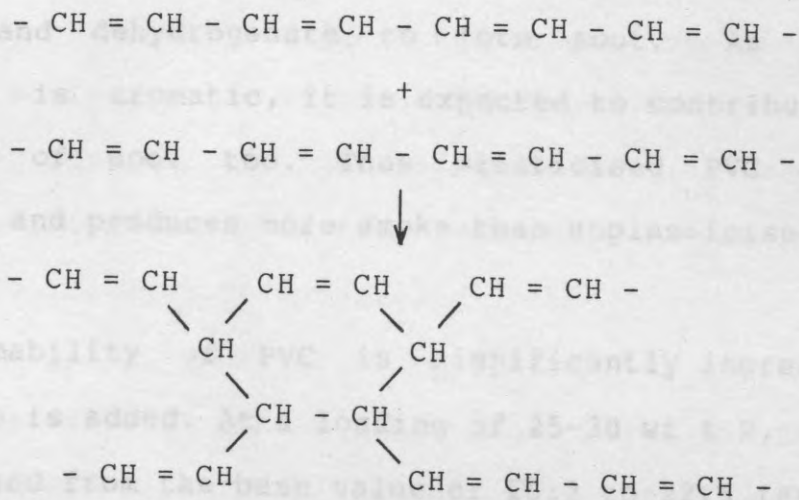
The polyenes can also form aromatic pyrolyses, such as benzene, via intramolecular cyclization and intermolecular abstraction of a hydrogen atom:



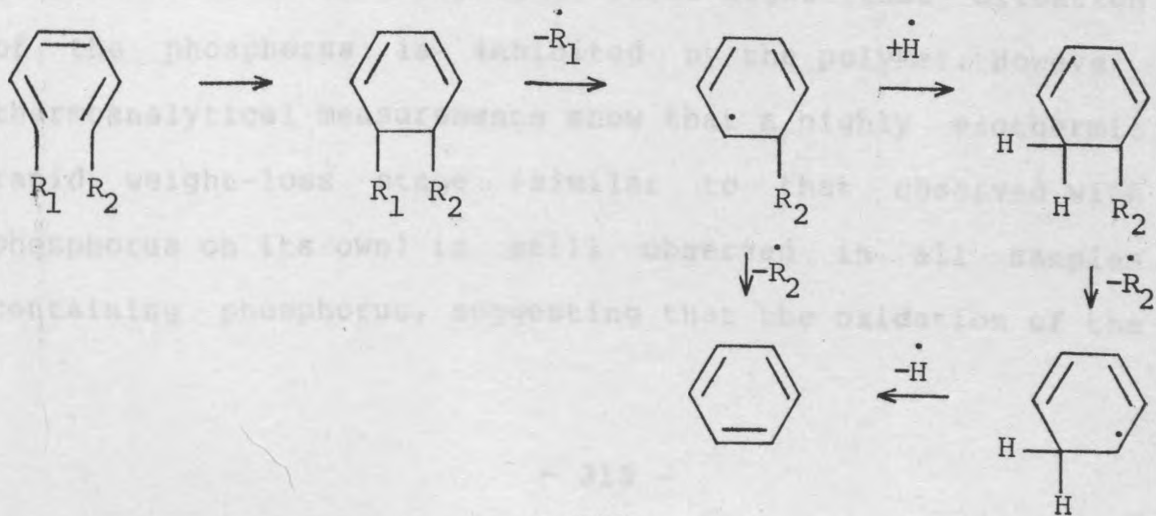
4. DISCUSSION.

4.1. Combustion Behaviour of PVC.

When PVC is heated, it undergoes degradation by dehydrochlorination (Section 1.3.2.1.), forming conjugated polyenes. Subsequently, these polyenes can crosslink via Diels-Alder cycloaddition:



The polyenes can also form aromatic pyrolyzates, such as benzene, via intramolecular cyclisation and intermolecular abstraction of a hydrogen atom:



Unplasticised PVC does not burn readily and has LOI values between 45 and 49 but, when a plasticiser is incorporated into the polymer, it burns quite readily. In this study, all PVC samples have incorporated 40 p.h.r. of di-isooctyl phthalate (DIOP) and the LOI of plasticised PVC is 25.2. On pyrolysis, the plasticiser decomposes to give octenes and phthalic anhydride (O'Mara 1970). The octenes formed are a source of fuel for the combustion processes and, on further pyrolysis, they break down to form smaller fragments which cyclise and dehydrogenate to form soot. As phthalic anhydride is aromatic, it is expected to contribute to the formation of soot too. Thus plasticised PVC is more flammable and produces more smoke than unplasticised PVC.

The flammability of PVC is significantly increased when phosphorus is added. At a loading of 25-30 wt % P, the LOI is decreased from the base value of 25.2 to 22.5 (Fig. 3.1). When red phosphorus is heated on its own, oxidation starts to occur at about 180°C, resulting in a gain in weight of at least 30%. But when phosphorus is incorporated into PVC, with or without other additives, relatively small weight gains are observed, implying at first sight that oxidation of the phosphorus is inhibited by the polymer. However, thermoanalytical measurements show that a highly exothermic rapid weight-loss stage (similar to that observed with phosphorus on its own) is still observed in all samples containing phosphorus, suggesting that the oxidation of the

element in the condensed phase does occur in the presence of PVC and other additives. The rather small weight gain is due to the fact that the oxidation of phosphorus is constantly competing with the volatilisation of oxidised phosphorus species, such as P_2O_5 , and with the loss of aromatics from PVC. Indeed, microanalytical measurements show that at least 30% of the phosphorus is lost during oxidation, although there is a very small loss before oxidation commences. Further evidence for the uninhibited oxidation of phosphorus is shown by the fact that the third weight-loss stage of 70% PVC + 30% P mixtures is sandwiched between two small weight-gain stages (Table 3.7). Infrared spectra of all PVC samples containing phosphorus show the presence of P-O and P=O bonds (Figs. 3.36, 3.38, 3.40 and 3.42).

So far, the evidence shows that the oxidised phosphorus species formed are unable to decrease the flammability of PVC. Phosphorus does not appear to affect the temperature at which PVC decomposes but the high exothermicity observed in all samples containing phosphorus could undoubtedly contribute to a further rise in the temperature of the combustion zone, thereby increasing the rate of polymer decomposition. This in turn would enhance the flammability of PVC.

The large amounts of smoke produced by PVC containing

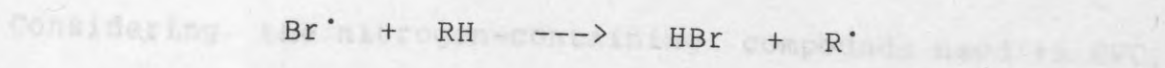
phosphorus is probably due to the unavailability of oxygen caused by the oxidation of phosphorus. Thus, further pyrolysis of incipient carbonaceous particles and other decomposition products would therefore occur at the expense of oxidation, leading to the formation of smoke.

Triethyl phosphate has very little effect on the flammability of PVC. Thermoanalytical studies show that the organic phosphate does not affect the decomposition of the polymer; neither the temperature nor the weight loss is altered. However, the additive itself is stabilised by the polymer, the bulk of which is volatilised at higher temperatures, coinciding with the dehydrochlorination of PVC. The non-flammable hydrogen chloride, that is released, is likely to serve as a diluent in the combustion zone and the volatilisation of triethyl phosphate over the same temperature range is not expected to decrease further the flammability to any significant extent.

The amount of smoke produced by PVC containing triethyl phosphate is considerably lower than when red phosphorus is present (Table 3.5). The phosphorus in triethyl phosphate is already present in an oxidised form so that, unlike red phosphorus which undergoes rapid oxidation when heated, it does not consume oxygen as readily. Thus, in the absence of red phosphorus, oxygen is more readily available to oxidise carbonaceous particles, formed from the decomposition of the

polymer, thereby decreasing the amounts of smoke formed.

The accepted mechanism of action of decabromobiphenyl involves its breakdown to bromine atoms which then react with the fuel to generate hydrogen bromide:

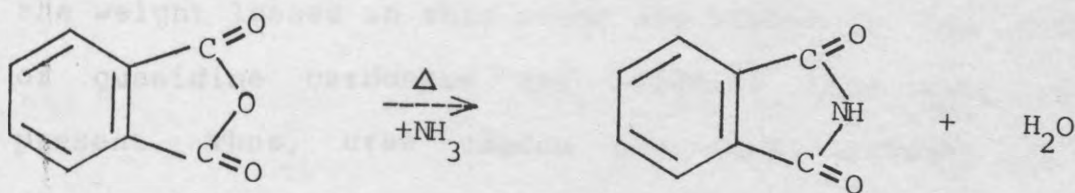


The HBr then reacts with $\text{H} \cdot$ atoms and $\text{OH} \cdot$ radicals which are responsible for the propagation of combustion. In fact, decabromobiphenyl is found to be effective in decreasing the flammability of PVC (Table 3.5). Thermoanalytical measurements also show that decabromobiphenyl lowers the temperature at which aliphatic and aromatic hydrocarbons (second weight-loss stage) are lost, implying that decabromobiphenyl acts in the condensed phase by decreasing the thermal stability of the polymer. This would increase the flammability so that the observed flame retardance demonstrates the importance and efficiency of the gas-phase mechanism.

Halogen-containing additives are known to enhance smoke formation from organic polymers. The hydrogen halide produced during combustion reacts with and destroys flame-propagating species, such as hydroxyl radicals. Thus these radicals are no longer available to oxidise the decomposition products. Eventually, larger quantities of

carbon-rich solids are formed, thereby increasing the amounts of smoke produced. Indeed, decabromobiphenyl is found to increase the amounts of smoke produced from PVC. The increase in smoke also supports the above flame-retardant mechanism.

Considering the nitrogen-containing compounds used in PVC, melamine, urea and guanidine carbonate produce large amounts of ammonia when heated; barbituric acid yields only trace amounts and benzotriazole gives none at all. The lower and upper limits of flammability of ammonia in air are 15.5 and 27.0 (Weast 1974). Thus, although ammonia is flammable, it is flammable over only a small range and the amounts produced when these ammonia-producing compounds are present are likely to be outside this range. Ammonia can nevertheless act as a diluent and lower the temperature of the gaseous products, thereby decreasing the flammability of the polymer (Chamberlain 1978). As mentioned previously, the plasticiser, DIOP, decomposes to give octenes and phthalic anhydride (O'Mara 1970). The latter compound reacts with ammonia to form phthalimide:



It is not known whether this has any significant effect on the combustion processes involved. However, this reaction involves the replacement of ammonia (flammable) by water (non-flammable), so that the flammability of the polymer is expected to be decreased to some extent. Guanidine carbonate is particularly effective in decreasing the flammability of PVC. Thermoanalytical measurements show that guanidine carbonate causes hydrogen chloride to be evolved at a lower temperature (Table 4.1) and, since hydrogen chloride is non-flammable, it would serve as a diluent early on in the combustion process. At higher temperatures, ammonia released from guanidine carbonate further dilutes the gaseous decomposition products. Hydrogen chloride and ammonia are released in four distinct stages over the temperature range 130-500°C. When melamine is present, these two compounds are released in two stages, between 170 and 510°C (Table 4.1). When guanidine carbonate is present, the residence times of the diluents in the combustion zone are longer, making them more effective in decreasing the flammability of the polymer. When urea is present, the temperature of maximum carbon burn-off is 30° lower than in plasticised PVC on its own, whereas it is 30° and 50° higher in the presence of guanidine carbonate and melamine respectively. Furthermore, the weight losses in this stage are higher in the presence of guanidine carbonate and melamine than when urea is present. Thus, urea causes the final stages of PVC decomposition to occur at lower temperatures and increases

Table 4.1

Simultaneous thermal analysis of
plasticised PVC and PVC + nitrogen compounds.

PVC (%)	100	70	70	70
MEL (%)	-	30	-	-
UREA (%)	-	-	30	-
GC (%)	-	-	-	30
First wt loss.				
Wt (%)	-	-	28.7	13.5
T range (°C)	-	-	96-217	133-196
T _{MR} (°C)	-	-	168	181
Second wt loss.				
Wt (%)	-	-	47.9	28.7
T range (°C)	-	-	217-389	196-263
T _{MR} (°C)	-	-	242	219
Third wt loss.				
Wt (%)	66.4	49.0	-	18.3
T range (°C)	148-351	173-416	-	263-395
T _{MR} (°C)	264	252	-	290
Fourth wt loss.				
Wt (%)	10.1	15.4	5.4	9.6
T range (°C)	351-479	416-507	389-466	395-500
T _{MR} (°C)	439	461	439	441
Fifth wt loss.				
Wt (%)	22.8	27.7	13.8	21.8
T range (°C)	479-598	507-602	466-569	500-648
T _{MR} (°C)	540	592	508	569
W _{Tot} (%)	99.3	92.1	95.8	91.9
T _{1%} (°C)	185	208	138	157

Note : T_{MR} , temperature of maximum rate of weight change.
W_{Tot} , total weight loss.
T_{1%} , temperature of 1% weight loss.

the amounts of the polymer lost in the earlier stages. In addition, most of the urea is volatilised before the polymer decomposes. Thus, urea is a less effective flame retardant than melamine and guanidine carbonate.

Red phosphorus is found to be particularly effective as a flame retardant. Generally, the amount of smoke generated from a polymer can be decreased by incorporating compounds that decompose to form non-combustible gases. Thus, it is not surprising that both melamine and urea do in fact decrease the amounts of smoke produced from PVC.

The maximum rate occurs at about 300°C (Table 1.12). However, when phosphorus is incorporated into the polymer, it degrades at a higher rate and at higher temperatures suggesting that the activation energy of the reaction is increased. In addition, less of the polymer is lost in the main weight-loss stage and more is lost in the carbon burn-off stage. Thus, although phosphorus causes the rate of decomposition to increase, it nevertheless has a stabilising effect on the polymer.

Extensive oxidation of phosphorus is observed in all samples containing phosphorus but the high exothermicity that is observed with the combustion of phosphorus on its own is only found in the sample of PE containing 10 wt % P. The exothermicity of the reaction is sufficiently high to raise the temperature of the sample by 50°C, which explains the increased rate of weight loss of the polymer when phosphorus is present. Microanalytical measurements show that

4.2. Combustion Behaviour of PS, PMMA and HDPE.

4.2.1. Effects of Phosphorus.

Red phosphorus is found to be particularly effective as a flame retardant for PS. PS on its own degrades to form mainly monomer, together with dimers and trimers (Section 1.3.2.2.) and thermoanalytical measurements show that more than 90% of the polymer is lost in one stage, over the temperature range 160-430°C. The maximum rate occurs at about 390°C (Table 3.12). However, when phosphorus is incorporated into the polymer, PS degrades at a higher rate and at higher temperatures suggesting that the activation energy of the reaction is increased. In addition, less of the polymer is lost in the main weight-loss stage and more is lost in the carbon burn-off stage. Thus, although phosphorus causes the rate of decomposition to increase, it nevertheless has some stabilising effect on the polymer.

Extensive oxidation of phosphorus is observed in all samples containing phosphorus but the high exothermicity that is observed with the combustion of phosphorus on its own is only found in the sample of PS containing 30 wt % P. The exothermicity of the reaction is sufficiently high to raise the temperature of the sample by 50°, which explains the increased rate of weight loss of the polymer when phosphorus is present. Microanalytical measurements show that

phosphorus is lost mainly during oxidation and it is reasonable to assume that the oxidised phosphorus species, such as P_2O_5 , are at least partly volatilised as they are formed. The formation of oxidised phosphorus species is confirmed by infrared spectroscopy (Figs. 3.43, 3.44, 3.46 and 3.47). It is unlikely that these oxidised phosphorus species are wholly responsible for inhibiting flame reactions, since a large proportion of the polymer is lost before oxidation takes place. It is more likely that phosphorus acts in the condensed phase by causing less of the polymer to volatilise during the early stages of decomposition. A possible mechanism involves phosphoric acids, formed from oxidised phosphorus species, attacking the aromatic nucleus of the polymer, thereby forming species that are less volatile. Furthermore, PS samples containing phosphorus readily undergo melting and dripping when subjected to a flame. In the extreme case, this would lead to the removal of the flame front from the bulk of the polymer or, in the less extreme case, melting and dripping can remove heat that may otherwise be fed back to the unburnt polymer. This phenomenon is not apparent from thermoanalytical measurements.

Fenimore and Jones (1964) have shown that the gas-phase mechanism of polymer combustion is dependent on the nature of the oxidant. Thus, a flame retardant which acts in the gas phase when oxygen is the oxidant would be less effective

when the oxidant is changed to nitrous oxide. If a condensed-phase mechanism prevails, then the change of oxidant would not alter the effectiveness of the flame retardant. However, the above cannot be true if the effective flame retardants are oxidised species, the formation of which is also sensitive to the oxidant. Since the present work includes the use of phosphorus which may be a flame retardant of this type, flammability measurements involving a change of oxidant were not carried out.

The extensive oxidation of phosphorus shows that the decomposition products of PS will have to compete with phosphorus for oxygen. In the absence of oxygen, smoke tends to be formed. Thus, it is not surprising that phosphorus enhances smoke formation from PS.

Phosphorus is found to be effective in decreasing the flammability of PMMA as well as of PS. PMMA on its own undergoes depolymerisation, resulting in a loss of at least 90% of its weight (Table 3.16). In the presence of phosphorus, PMMA is found to decompose in two stages, both of which occur before the oxidation of phosphorus (Table 3.16). Here again, both thermoanalytical and microanalytical measurements show that the oxidised phosphorus species are volatilised almost as soon as they are formed and that only small amounts of phosphorus are lost before oxidation commences. These findings suggest that the oxidised

phosphorus species formed are unlikely to inhibit flame reactions. Red phosphorus is more likely to exert its influence in the condensed phase. Indeed, thermal analysis shows that the rate at which PMMA decomposes is greatly reduced when phosphorus (and other additives) are present (Table 3.16). In effect, the production of volatile species, which are a source of fuel for the propagation of flame, is decreased. Furthermore, the temperature at which the polymer decomposes is increased when phosphorus is present. It has been reported that red phosphorus retards the decomposition of PMMA to volatile fragments by reaction with the methyl-ester functional group of the polymer to form phosphonium cations (Brown et al. 1981). These cations have been suggested to retard flames by functioning as free-radical traps (Granzow & Savides 1978). Other studies have shown that phosphoric acids or phosphoric acid-forming compounds alter the thermal degradation of PMMA and that reduction in flammability results largely from changes in the condensed-phase reactions at high temperatures that increase char formation (Gruntfest & Young 1961). Indeed, some char is formed when PMMA samples containing phosphorus are burned in air. The amount formed is small, so that char formation is only partly responsible for decreasing the flammability of PMMA. Unfortunately, the amount of char formed cannot be calculated from the thermal analysis as oxidised phosphorus species are also volatilised in about the same temperature range as the carbon burn-off stage (Table 3.16). The

formation of char suggests that perhaps crosslinking is involved. This is supported by the more complex breakdown of the polymer in the presence of phosphorus.

Phosphorus enhances the production of smoke from PMMA. Thus, it would appear that phosphorus not only lowers the rate of depolymerisation but also causes formation of larger fragments which can then cyclise and dehydrogenate, resulting in the formation of smoke particles. In summary, phosphorus decreases the flammability of PMMA by increasing the thermal stability of the polymer and hence reducing the rate of production of combustible gaseous species. Another factor that may affect the flammability is the absence of the highly exothermic rapid weight-loss stage that is observed during the combustion of phosphorus on its own. The depolymerisation of PMMA on its own is slightly endothermic.

Phosphorus is not particularly effective as a flame retardant for HDPE. Both thermal analysis and microanalysis of HDPE containing 30 wt % P indicate that oxidised phosphorus species are volatilised as they are formed. In fact, phosphorus affects the breakdown of HDPE in such a way that the rate of volatilisation of the polymer before oxidation is higher but the amount of polymer lost is smaller than when HDPE is degraded on its own. Indeed, microanalysis of HDPE containing 15 wt % P and 15 wt % MEL shows that the proportions of carbon and hydrogen lost

before oxidation are higher than in HDPE containing 30 wt % P. In other words, the greater the proportion of phosphorus present, the lower the proportion of polymer lost. The improved thermal stability of HDPE in the presence of phosphorus was also observed by Peters (1979). Brauman (1977) has reported that the mode of action of some inorganic phosphate flame retardants in hydrocarbon polymers consists in the formation of residual phosphoric acids, which accumulate during burning, as a protective coating that physically restricts fuel volatilisation and excludes oxygen from the flame front. Since red phosphorus in HDPE undergoes oxidation to form phosphoric acid derivatives, it may well function in the condensed phase by limiting the generation of fuel.

The increase in smoke production from HDPE containing phosphorus indicates that larger decomposition fragments are formed which subsequently cyclise and dehydrogenate to form soot. The formation of such fragments may be due to the scavenging of oxygen by phosphorus so that the hydrocarbons produced by polymer decomposition are not oxidised as they would normally be in the combustion of HDPE.

4.2.2. Effects of Decabromobiphenyl.

As mentioned earlier, brominated flame retardants are believed to act largely in the gas phase by abstracting hydrogen atoms from the fuel to form hydrogen bromide which then reacts with the atoms and radicals ($H^\cdot$, $O^{\cdot\cdot}$ and $OH^\cdot$) responsible for flame propagation. Thus, when decabromobiphenyl is incorporated into PS, PMMA and HDPE, some degree of flame inhibition is achieved. As expected, its effect in PMMA is less marked than in the other polymers. In PMMA, the number of hydrogen atoms attached to the carbon backbone which are available for abstraction by the bromine atom is smaller than in the other polymers. Moreover, thermal analysis indicates that decabromobiphenyl is more thermally stable than PMMA (Table 3.16); the bulk of the polymer is depolymerised before decabromobiphenyl is volatilised. When it is incorporated into PS, decabromobiphenyl volatilises over the same temperature range as the polymer. Thus it is not surprising that decabromobiphenyl is effective in PS. Furthermore, decabromobiphenyl encourages melting and dripping of PS, thereby causing some heat that would otherwise be fed back to the burning polymer to be removed. Decabromobiphenyl appears to increase the amount of HDPE lost and the temperature at which it is first lost (by about 70°C) (Table 3.17). Nevertheless, the bromine compound is volatilised during the second weight-loss stage for HDPE, where it can still interfere with the gaseous products.

4.2.3. Effects of Melamine, Urea and Guanidine Carbonate.

The extent to which melamine affects the flammability of PS, PMMA and HDPE is similar to that observed with PVC. The thermal stabilities and breakdown patterns of these polymers are different; melamine volatilises during the main weight-loss stage for PS but before that for HDPE. When incorporated into PMMA, it causes the polymer to decompose in two stages instead of one. Yet the flammability of these polymers is decreased to nearly the same extent in each case, which strongly suggests that, although melamine affects the polymer breakdown in the condensed phase, the main contribution to flame retardance comes from effects in the gas phase. Since large volumes of ammonia are released when melamine is heated, the gas may serve as a diluent for combustible gaseous fuel mixtures. The release of the diluent gas not only decreases flammability but also reduces the tendency of these polymers to form smoke. At first glance, melamine may not appear to be effective in suppressing the formation of smoke from PMMA and HDPE but it must be noted that these polymers produce negligible amounts of smoke when heated on their own (Table 3.1).

Flammability tests were also made on PS containing other nitrogen compounds. When urea is present, most of it is volatilised before PS decomposes, whereas guanidine carbonate decomposes in two stages, the latter stage

coinciding with the decomposition of PS. Both these compounds behave similarly to melamine in that they are volatilised during different stages of polymer decomposition and yet both have some effect in decreasing the flammability of PS, probably by releasing ammonia as in the case of melamine. However, flammability tests carried out on PS samples containing barbituric acid and benzotriazole show that, although barbituric acid liberates only trace amounts of ammonia on heating, it nevertheless decreases the flammability of PS to the same extent as melamine, urea and guanidine carbonate, all of which liberate large amounts of ammonia on decomposition. On the other hand, benzotriazole, which does not break down to yield ammonia, has no significant effect on the flammability of PS. Thus, the release of ammonia is not the only factor that influences the flammability of the polymer. Since there is no simple correlation between the nitrogen contents of the compounds and their effects on the flammability of the polymers, it can be deduced that the chemical nature of these compounds is important. Smoke measurements carried out on PS containing urea show that urea decreases the formation of smoke from PS.

4.2.4. Effects of Tritolyl Phosphate.

Tritolyl phosphate is also effective in decreasing the flammability of PS. Thermoanalytical studies show that the bulk of the organic phosphate is lost before PS decomposes, suggesting that its effectiveness is due largely to gas-phase mechanisms. As discussed in Section 1.4.2.2., some phosphates act mainly by a physical mechanism, in which oxygen is excluded from the combustion zone by the formation of a dense blanket of vapour over the flame (Martin & Price 1968; Benbow & Cullis 1972, 1973). Tritolyl phosphate has also been found to confer some degree of flame retardance on PMMA, PE and polymethylene (Fenimore & Jones 1966). It may well function by this type of mechanism too. Tritolyl phosphate has an additional mode of action in that, when it is incorporated into PS, it tends to enhance melting and dripping, especially at high loadings.

4.3. Interaction of Additives.

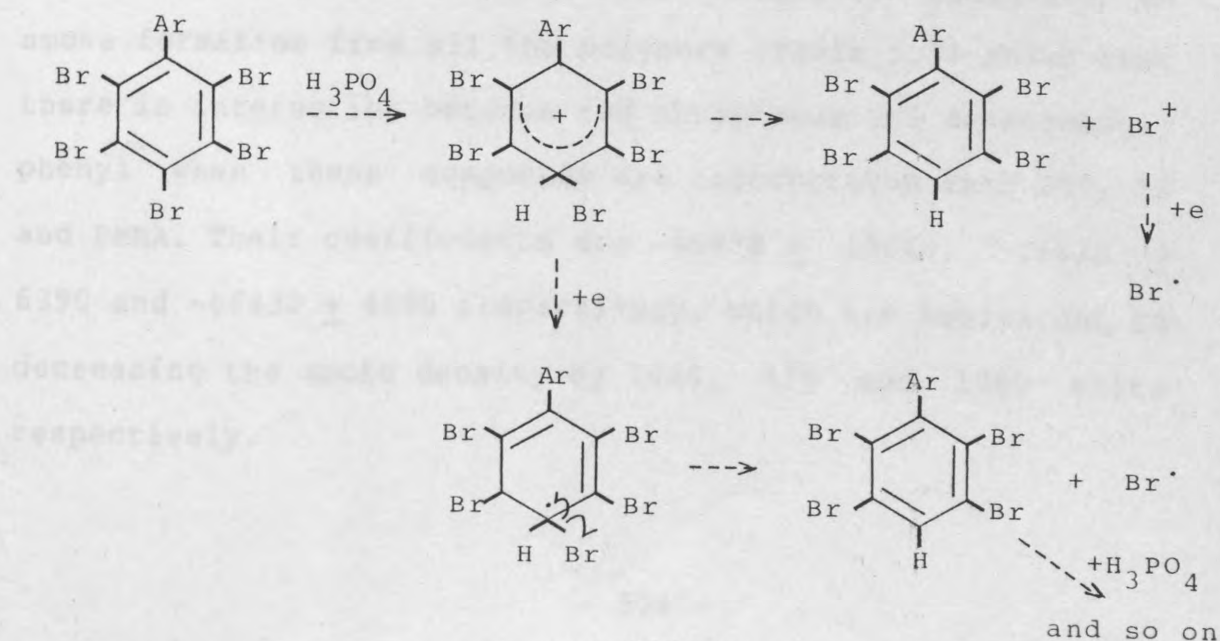
4.3.1. Phosphorus - Halogen Interaction.

Up to date, there is still considerable disagreement about the existence of synergistic effects of phosphorus and halogens as flame retardants in polymers (Section 1.4.2.3.). In fact, Weil (1975) questions its existence, suggesting that such effects are more likely to be due to additivity or to the inherent non-linearity of the system. However, in this study, the interaction of additives in a polymeric system is determined by means of "effectiveness coefficients" which are calculated in a such a way as to exclude non-linear effects of individual additives. These coefficients represent the average contribution to the LOI or D_s of the polymeric-additive system of each additive or combination of additives over a specific composition range and are calculated from the least-squares coefficients of the lowest order that gives the most satisfactory fit. Thus, this method of analysis can reflect any real synergism or antagonism in a polymer-additive system.

The quantitative assessment of the flame-retardant effects of additives on PVC, PS, PMMA and HDPE (Table 3.2) shows that there is positive interaction between red phosphorus and decabromobiphenyl when these compounds are incorporated into PMMA and HDPE. These coefficients are found to be 103 ± 17 and 74 ± 19 in these two polymers respectively. In other

words, for PMMA and HDPE, the interaction of 15 wt % P and 15 wt % DBB is equivalent to an increase of LOI of 2.3 and 1.7 units respectively.

As mentioned previously, the oxidation of phosphorus is observed in all polymer samples containing phosphorus (Sections 4.1 and 4.2.1.) and in the presence of water the oxidation products will form phosphoric acids. Aromatic systems are susceptible to attack by such strong acids. Thus, decabromobiphenyl which is aromatic, can undergo reactions involving protonation. The protonated aromatic system can undergo further reaction, either by expelling a Br^+ ion which then abstracts an electron from species present in the decomposing polymer to form a bromine atom, or by undergoing reduction first before expelling a bromine atom. In either case, the bromine atom can then proceed to abstract a hydrogen atom from the fuel to form hydrogen bromide, a species that is known to be responsible for flame inhibition:



Thus, when phosphorus and decabromobiphenyl are both present, this mechanism provides a more facile source of bromine atoms and hydrogen bromide than when decabromobiphenyl is present in the polymer on its own.

No significant interaction between phosphorus and decabromobiphenyl is found in either PVC or PS. PVC breaks down by eliminating hydrogen chloride and produces a vast array of aliphatic hydrocarbons and aromatic hydrocarbons (mainly benzene). PS breaks down to form largely monomer, dimers and trimers etc. Thus, unlike PMMA and HDPE, which contain saturated aliphatic main chains, PVC and PS decompose to give mainly alkyl aromatics which are more reactive to protonation or attack by acids than brominated aromatic systems. Thus, fewer bromine atoms are expected to be produced from PVC and PS containing phosphorus and decabromobiphenyl, which means that phosphorus-halogen synergism should not occur to any appreciable extent.

The quantitative assessment of the effects of additives on smoke formation from all the polymers (Table 3.3) shows that there is interaction between red phosphorus and decabromobiphenyl when these compounds are incorporated into PVC, PS and PMMA. Their coefficients are -45970 ± 13640 , -26870 ± 6390 and -66430 ± 4890 respectively, which are equivalent to decreasing the smoke density by 1030, 610 and 1500 units respectively.

As mentioned previously, the large amounts of smoke produced by the polymers containing phosphorus may be due to the scavenging of oxygen by phosphorus to form oxidised species, while decabromobiphenyl increases smoke by consuming radicals which are formed by the reaction of fuel species with oxygen (Sections 4.1 and 4.2.1). Thus, competition is set up between phosphorus and the fuel for oxygen, so that fewer reactive radicals will be available to react with decabromobiphenyl. The extent to which phosphorus causes smoke to be produced is different in different polymers. Phosphorus drastically increases the smoke densities of PVC and PMMA but has less effect in PS and HDPE and, although decabromobiphenyl causes smoke formation from all the polymers, it does not affect them as dramatically as phosphorus does. Thus, when these two compounds are incorporated into the polymers, the competition for oxygen inevitably alters the extent to which smoke is formed from them. It is not surprising then that the antagonism of smoke formation between phosphorus and decabromobiphenyl is found to be significant in PVC and PMMA and less so in PS and HDPE because phosphorus on its own causes extremely large amounts of smoke to be formed from PVC and PMMA.

4.3.2. Phosphorus - Nitrogen Interaction.

Synergistic effects of phosphorus and nitrogen compounds as flame retardants have been reported in cellulosic materials and their mechanisms are fairly well established (Section 1.4.2.4.). Although such effects have also been reported to appear in polymers other than cellulose, no acceptable mechanism has yet been proposed in these cases (Weil 1975). As mentioned in Section 4.3.1., such effects as have been observed have been attributed to additivity or to non-linearity. Nevertheless, the results of this study strongly suggest that phosphorus-nitrogen synergism does exist (Table 3.4). In fact, the synergism is also observed in PVC, where phosphorus on its own has an antagonistic effect (Table 3.5). The "synergistic effectiveness" values obtained for the systems in this study range from 100 to 222. In other words, the LOI increase due to this synergistic effect range from 2.3 to 5.0 units. The consistency of the results suggests that the formation of ammonia from the nitrogen-containing compounds is unlikely to be a contributory factor to the synergism observed; barbituric acid releases only trace amounts of ammonia when subjected to heat and yet it reacts with phosphorus in almost all the polymers investigated to give "synergistic effectiveness" values higher than those for melamine, which releases ammonia readily when heated. Furthermore, benzotriazole, which does not yield ammonia at all, gives a value

equivalent to an LOI increase of 3.0 units. By comparing the "synergistic effectiveness" of melamine and phosphorus with that of barbituric acid and phosphorus, it can be seen that barbituric acid is more effective in all polymers except PS, where it is marginally less effective than melamine (Table 3.4). The molecular weights of melamine and barbituric acid are quite similar but the nitrogen content of melamine (67%) is three times that of barbituric acid (22%) (Table 3.5). Furthermore, a comparison of the "synergistic effectiveness" of guanidine carbonate and urea shows that guanidine carbonate is marginally more effective than urea in PVC and PS. Guanidine carbonate and urea have the same nitrogen content but the molecular weight of guanidine carbonate is three times that of urea. Thus, there does not appear to be any correlation between either nitrogen content or molecular weight of the additives and the flammability of the resulting system.

Synergism between phosphorus and nitrogen has been observed in polyurethanes and a condensed-phase mechanism has been proposed, whereby the phosphorus compound decomposes to give acidic products that catalyse the formation of char; this, in turn, can insulate the remainder of the polymer from the thermal effects of flame (Piechota 1965; Papa & Proops 1972). However, evidence of this nature is not easily obtainable from thermoanalytical studies in the present work, since oxidised phosphorus species also volatilise in

the same temperature range as the carbon burn-off stage of the polymers. Furthermore, some phosphorus is lost earlier, i.e. before the carbon burn-off stage, and some involatile phosphate residue is also formed, so that it is difficult to estimate how much of the weight loss during the carbon burn-off stage is actually due to phosphorus. Nevertheless, comparison of the weight losses during the carbon burn-off stage of the polymers containing phosphorus and decabromobiphenyl with those lost from polymers containing phosphorus and nitrogen compounds shows no systematic differences (Table 4.2). Yet some degree of interaction is observed between phosphorus and decabromobiphenyl in PMMA and HDPE but not in PVC or PS. Furthermore, the increase in the temperature of the carbon burn-off stage of the different polymers caused by the combined addition of phosphorus and nitrogen-containing compounds does not appear to be consistent (Table 4.2). Thus, although phosphorus may act in the condensed phase in some of the polymers studied here, it may not react synergistically with the nitrogen-containing compounds to increase char formation from the polymers. Microanalytical studies of all the polymers (except PVC) containing 15 wt % P and 15 wt % MEL show that the bulk of the nitrogen-containing compound is lost before oxidation of phosphorus can take place. In other words, the nitrogen compound is generally volatilised before phosphorus is lost from the polymer matrix. Thus, it would appear that the synergism is due largely to gas-phase mechanisms rather than

Table 4.2

Details of the carbon burn-off stage of PVC, PS, PMMA and HDPE.

Carbon burn-off stage	Polymer on its own	P+DBB	P+MEL	DBB+MEL	P+UREA	DBB+UREA	P+GC	DBB+GC	TEP/ TTP+DBB	TEP/ TTP+MEL
Poly(vinyl chloride)										
Wt loss (%)	22.8	18.5	20.3	21.8	13.7	27.2	20.9	22.8	20.2	19.5
T range (°C)	479-598	543-751	527-720	500-641	573-765	354-580	573-773	492-644	470-592	490-665
T max rate (°C)	540	592	573	571	625	526	657	555	533	565
Polystyrene										
Wt loss (%)	4.7	30.6	30.3	9.3	26.1	6.6	34.1	5.5	3.4	2.9
T range (°C)	430-712	483-720	483-698	404-695	476-721	396-557	486-684	466-584	413-557	417-577
T max rate (°C)	507	539	531	533	537	518	557	545	526	526
Poly(methyl methacrylate)										
Wt loss (%)	-	16.6	22.6	-	-	-	-	-	-	-
T range (°C)	-	526-745	522-740	-	-	-	-	-	-	-
T max rate (°C)	-	553	565	-	-	-	-	-	-	-
High-density polyethylene										
Wt loss (%)	7.0	27.0	21.0	12.9	-	-	-	-	-	-
T range (°C)	482-577	498-805	512-752	480-594	-	-	-	-	-	-
T max rate (°C)	522	569	563	516	-	-	-	-	-	-

Note : T range is the temperature range;

T max rate is the temperature at maximum rate of weight change.

condensed-phase ones.

Phosphorus nitride can be prepared from the elements under the influence of an electric discharge and by reacting active nitrogen with phosphine gas. Emission spectrometric analysis of phosphorus nitride prepared by the latter method shows the presence of phosphorus nitride radicals (Sutton et al. 1978; Hood & Niemczyk 1986). The phosphorus nitride radical has also been identified by mass-spectrometric analysis of flame species when flame retardants such as trimethyl phosphate and triphenyl phosphine oxide are added to a hydrogen/oxygen/nitrogen flame (Hastie 1973c; Hastie & McBee 1975). Thus, even in the absence of nitrogen compounds, phosphorus nitride species are formed in flames, albeit in small quantities. Other species that have been identified in the same experiments are $\text{PO}^\bullet$, $\text{HPO}_2^\bullet$, $\text{PO}_2^\bullet$, P_2 and HPO . Although the species produced in the most significant amounts is $\text{PO}^\bullet$, the other species can nevertheless exert their influence by catalysing the recombination of and hence destroying flame-propagating species. The results of this study suggest that the phosphorus nitride species may be important in the gas-phase reactions of polymers containing phosphorus and nitrogen-containing additives. The diatomic molecule, PN , has an analogous structure to nitrogen, N_2 , but unlike nitrogen, phosphorus nitride is thermodynamically unstable at temperatures below 1800°C (Huffman et al. 1954). It tends to polymerise by reducing

its bond order so that attack by the flame-propagating species is likely to occur. Another species likely to be formed from phosphorus and nitrogen-containing compounds is phosphoryl nitride, OPN. It is a thermal decomposition product of phosphoramidate (Steger & Mildner 1964) and the OPN radical is also likely to be unstable at flame temperatures. Phosphoryl nitride tends to polymerise at temperatures between 450 and 500°C and is involatile up to 750°C (Wetroff 1937). Thus, it would appear that the phosphorus-nitrogen synergism is due to gas-phase flame inhibition by species, such as PN and OPN, which are unstable at flame temperatures and so capable of reacting with the flame-propagating species.

Interaction of phosphorus and nitrogen compounds as smoke suppressants is only found in PVC and PMMA containing phosphorus and melamine, in contrast to their effects as flame retardants, where synergism is observed in all cases. As mentioned previously, melamine releases ammonia which can serve as a diluent in the combustion zone, thereby decreasing flammability and thus smoke formation. Since phosphorus is exceptionally effective in causing smoke to be formed from PVC and PMMA, it is not surprising to observe some degree of antagonism in smoke formation when melamine, a smoke suppressant, is present together with phosphorus.

Table 3.2 shows that there is no significant interaction

between the organic phosphates (triethyl and tritolyl phosphates) and melamine as flame retardants. This is not surprising because the phosphorus is already present in an oxidised form, and therefore less likely to react with the nitrogen-containing additive to form reduced species such as phosphorus nitride.

No significant interaction can be found between the organic phosphates and melamine as smoke suppressants.

4.3.3. Halogen - Nitrogen Interaction.

No synergism is detected between decabromobiphenyl and the nitrogen-containing additives as flame retardants in PVC, PS, PMMA or HDPE. However, some degree of antagonism is observed between decabromobiphenyl and urea, and to a lesser extent, between decabromobiphenyl and guanidine carbonate when they are incorporated into PVC. The effect is equivalent to -2.4 LOI units for the DBB-UREA interaction and -1.4 LOI units for that of DBB-GC. The origin of these effects is not known. No significant interaction between decabromobiphenyl and the various nitrogen-containing additives can be detected from the thermoanalytical measurements (Tables 3.7 - 3.17).

No significant binary interaction of the additives, as smoke suppressants is observed.

No significant ternary interactions of the additives as smoke suppressants are observed.

4.3.4. Phosphorus - Halogen - Nitrogen Interaction.

Generally, the ternary interactions of the additives as flame retardants are less marked than the binary interactions. However, significant ternary interactions of the additives are observed in PVC and in HDPE containing decabromobiphenyl, phosphorus and melamine. The "effectiveness coefficients" are 1077 ± 563 (synergistic) and -1060 ± 356 (antagonistic) respectively, and both are equivalent to 1.1 LOI units. The effects are quite small and coupled with the complexity of the systems studied (in each case three different additives are used, so that complications can arise from thermoanalytical measurements), it is difficult to be sure what causes these effects. However, the antagonistic effects seen in HDPE may be due to the reaction of basic melamine and acidic phosphorus species formed by oxidation. This reaction would inevitably lower the availability of the acid, which may be responsible for inhibiting flame reactions. In the case of PVC, the release of hydrogen chloride would ensure the availability of phosphoric acids to act as flame retardants.

No significant ternary interactions of the additives as smoke suppressants are observed.

4.4. Conclusion.

Red phosphorus is particularly effective in reducing the flammability of PS and PMMA but not that of PVC and HDPE. Results from this study suggest that phosphorus affects flammability mainly by condensed-phase mechanisms, viz. by enhancing melting and dripping (as in PS and HDPE), or by promoting char formation (as in PMMA), or by stabilising the polymer (as in PS, PMMA and HDPE). However, red phosphorus greatly enhances the formation of smoke from all the polymers, probably by scavenging oxygen, which would otherwise be available to oxidise carbon particles to carbon oxides. Thus, although red phosphorus is effective as a flame retardant for PS and PMMA, its use is limited due to its adverse effect on smoke formation. Furthermore, its application will be limited to those systems where the colour of the finished product is not important. Further disadvantages are that red phosphorus is toxic and flammable, so that great care has to be taken when handling it.

Generally, decabromobiphenyl is effective in decreasing flammability in all the polymers studied in the present work. Results from thermoanalytical measurements show that this compound affects the thermal breakdown of the polymers. Thus, decabromobiphenyl exerts its influence not only in the gas phase but also in the condensed phase. Although deca-

bromobiphenyl enhances the formation of smoke from all these polymers, the increase is lower than that caused by red phosphorus.

Melamine, urea, guanidine carbonate and barbituric acid have some effect in decreasing the flammability of all the polymers studied. Tests on samples containing benzotriazole show that, although ammonia, released from the above-mentioned compounds, can influence flammability, other factors, such as the chemical nature of these compounds, are important. Tests on samples containing the various nitrogen compounds also show that there is no simple correlation between the nitrogen contents of the compounds and their effects on the flammability of the polymers.

Quantitative assessment of the flame-retardant effects of additives on the polymers shows that there is positive interaction between red phosphorus and decabromobiphenyl in PMMA and HDPE. No significant interaction is detected between decabromobiphenyl and the nitrogen compounds in the polymers except for the decabromobiphenyl-urea and decabromobiphenyl-guanidine carbonate additive systems in PVC. One interesting finding is the synergistic effects of phosphorus and nitrogen compounds observed in all the polymers studied in the present work. The consistency of the results suggests that the formation of ammonia from the nitrogen compounds is unlikely to be wholly responsible for

the observed synergism. As mentioned previously, the chemical nature of these compounds may be important. There is reason to believe that phosphorus nitride and phosphoryl nitride species may be partly responsible for the synergistic interactions observed. Generally, the ternary interactions of the additives as flame retardants are less significant than the binary interactions.

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