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A Thesis

entitled

Inorganic Sulphur Oxyacid Salts as Flame Retardants for Cotton

submitted by

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for the Degree of Doctor of Philosophy

at The City University

LONDON

October 1985

Department of Chemistry

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Acknowledgments

I would like to thank all those very kind people who have helped me in their various ways to bring this thesis to fruition.

In particular I am greatly indebted to Professor C.F. Cullis, who is my Supervisor in London, who has guided and assisted me in the compilation of my work with the utmost care and consideration for which I am eternally grateful. I would also like to express my heartfelt thanks to Professor S.E. Morsi, who is my supervisor at UNARC for his faith and confidence in me and for permitting me to come to London on two occasions to pursue my studies here.

For their supervision and guidance I would like to express my gratitude to [redacted] and [redacted] [redacted] for all their help and advice while I have been in London. I would also like to express my gratitude to Dr. S.H. Kandil, for his advice and supervision at UNARC.

In the Combustion Laboratory in London my thanks go to [redacted] [redacted] for his willingness to render help and assistance at all times. I would also like to thank [redacted] [redacted] [redacted] for her patience in undertaking the typing of this thesis.

Finally, I would like to thank The British Council without whose valuable financial support this work could not have been undertaken and in particular their representative: [redacted] [redacted] in Egypt and [redacted] in London.

The City University,

LONDON.

October 1985.

Abstract

This thesis describes studies of the action of a number of sulphur oxyacid salts as flame retardants for cellulose (cotton) and of the sulphur-bromine synergism observed when inorganic sulphates and related compounds are used in conjunction with an organic bromine compound, decabromobiphenyl oxide (DBBO).

In the Introduction, a general description is given of the phenomena of combustion, flame and fire with special reference to the processes involved in the burning of organic polymers and its inhibition. An account is given of the properties and of the importance as textile fibre of cotton, which was the form of cellulose used in the present investigation; and a review is included of previous work on the thermal decomposition and combustion of cellulose and of mechanisms involved in its flame retardance.

The Experimental section describes the techniques used to prepare the cotton samples and to determine their flammability by means of the limiting oxygen index method. A description is given too of the computer method used to fit polynomial functions to the observed data for cotton-additive systems and to plot these functions in the form of triangular diagrams. Measurements of flammability were complemented by studies of the thermoanalytical behaviour of untreated cotton and of numerous treated cotton samples. In some cases, determinations were made of the amounts of carbon monoxide liberated during breakdown of the various cottons and of the elemental composition of solid residues remaining after various stages of decomposition.

In the Results section, the flammability measurements and thermoanalytical and microanalytical behaviour are recorded for all the cotton-sulphur oxyacid salt systems in the absence and presence of DBBO. It is shown that some of the systems used are very efficient flame retardants and attention has been concentrated mainly on the four best sulphur compounds in this respect, viz. aluminium sulphate, zinc sulphate, ammonium sulphamate and ammonium sulphate.

In the Discussion section, some mechanisms are first proposed to account for the flame-retardant effects of the various sulphur oxyacid salts in terms largely of their differing abilities to cause dehydration of the cellulose to form carbon. The order of flame-retardant efficiency of the corresponding sulphur oxyacid salt-DBBO systems is somewhat different and explanations are advanced to account for the differences observed. It is clear that, with some of the system studied, both condensed-phase and gas-phase mechanisms may be involved.

1. Introduction

1.1 Combustion, flames and fire

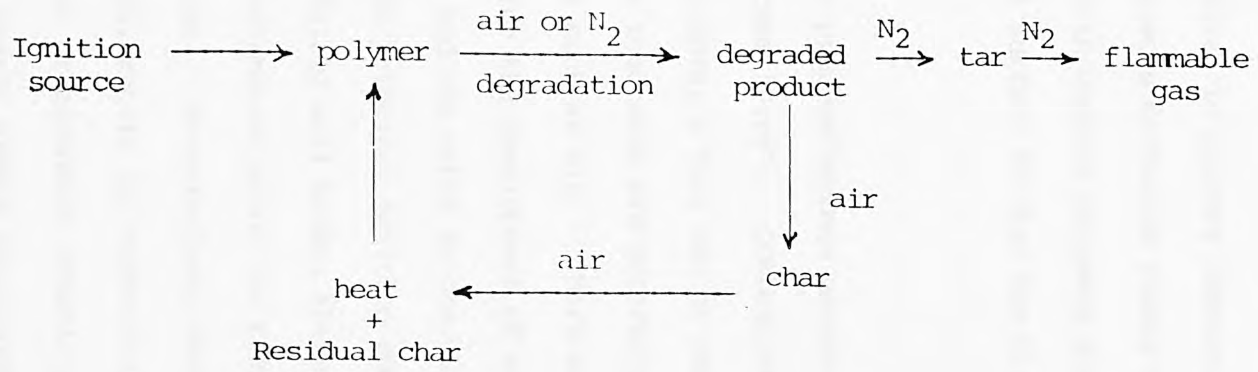
1.1 Combustion, flames and fire

Combustion is the name given to overall exothermic reactions, usually of an oxidative character, which have the ability to propagate throughout the phase concerned. Various types of combustion behaviour can be observed. Sometimes the materials undergoing combustion simply react smoothly and isothermally with the oxidant in which case we speak of 'slow combustion'. Under more severe conditions, there may be substantial changes in temperature in different parts of the system. Flaming combustion is accompanied by the production of visible flames as gases present ignite and burn freely. Non-flaming combustion, which is a term used to cover both smouldering and glowing combustion, propagates by a "front" or "wave" involving the gaseous oxidation of the pyrolysis products of the material concerned. Glowing combustion is generally accompanied by pale flames due to the burning of carbon to form carbon oxides. However smouldering combustion is generally self-sustaining although it may require assistance from an energy source if the thermal conductivity of the material is very low (Einhorn 1971). Smouldering combustion usually occurs when solid materials with high surface to weight ratios are either isolated from an appropriate heat sink or, if in contact with it, are of a certain minimum thickness (Friedman 1977). One

of the most important findings is that, although a minimum thickness of material is needed for combustion to occur, the flow of air across the surface considerably reduces the minimum thickness needed in still air. A general model for smouldering combustion is shown in Fig. 1.1.
After ignition the first stage is pyrolysis. The resulting decomposed polymer will not smoulder unless sufficient oxygen is present. However in the presence of an adequate supply of oxidant the initially degraded products will undergo charring and, if the heat flux is sufficiently high, the hot char will propagate smouldering combustion back to the polymer.
Smouldering is generally accompanied by production of smoke due to pyrolysis at or near the surface. Since the smoke is combustible, a transition to flaming combustion may occur.

In flaming combustion, as the name implies, combustion is accompanied by clearly visible flames. Flames are highly exothermic combustion reactions, generally associated with the emission of light and the production of high temperatures in which both the fuel and the oxidant are present in the gas phase. However the term 'flame' cannot be defined very precisely because certain expected features are sometimes lacking.

Fig. 1.1 General scheme for smouldering combustion



eventually to collapse or blow-off of the flame. In general, however, the flames involved in polymer combustion have much greater similarity to gaseous diffusion flames than to premixed flames, although with certain polymers air may be in contact with the polymer surface so that the flame is at least partly premixed.

When the combustion process becomes uncontrolled, it is often described by the term 'fire'. Combustion processes usually involve two reactants, a fuel and an oxidant, and in the case of a fire these reactants are generally a condensed phase fuel and gaseous oxidant such as air. There are at least two essential requirements for the development of any fire. One is a source of ignition and the other is one or more flammable materials. Although the principal ignition sources responsible for starting fires are fairly well known, there is still relatively little statistical information about the precise types of materials involved in fire. Nevertheless, most of the flammable components of residential, public and commercial buildings consist largely of either natural or synthetic organic polymers; and such materials are therefore nearly always implicated in, if not directly responsible for, fires in urban areas. In about a quarter of fires, a textile fabric of some kind is believed to be the material first ignited. Since natural cellulosic fibres, such as cotton, still represent an overwhelming large proportion of the

Thus flames of hydrogen burning in dust-free air are virtually non-luminous and mixtures of certain organic compounds and oxygen emit light at fairly low temperatures ("cool flames"). When gaseous fuels burn in a gaseous oxidant, flames of two basic but extreme types may be produced. The flame reactions may be controlled either by the rate of the chemical reactions concerned or by physical mixing process such as diffusion or flow. In general, flames which are kinetically controlled (premixed flames) have the fuel, oxidant, and products uniformly distributed in the gas phase; gaseous explosions are a typical example. When there are sizeable gradients of chemical species and temperatures with the reactants diffusing into the flame zone and products and heat diffusing out, the combustion is diffusion-controlled (diffusion flames). In practice, however, many flame are intermediate between the two extreme types. Premixed flames have been the subject of much more detailed scientific investigation than diffusion flames because they can give information about a number of fundamental properties of the gaseous mixture, such as burning velocity, flame temperature, and the chemical reactions occurring. The burning velocity is the rate at which the flame front travels in a direction normal to its surface into the adjacent unburnt gas and relative to the rate of movement of the unburnt mixture

Diffusion flames may be homogeneous with all the reactants in the gas phase or they may be heterogeneous as with solid or liquid fuels burning in oxidizing gaseous atmospheres. Most flames of commercial importance are not premixed flames for safety reasons but are instead diffusion flames. In spite of the economic importance of diffusion flames relatively few fundamental studies have been made of them. The rate of chemi- cal reaction is normally much higher than the rate of inter- diffusion of the fuel and oxidant which thus controls the velo- city of the flame reaction, and there is normally a steady change in gas composition as the flame is traversed. Thus the study of diffusion flames is difficult and yields few important parameters. The position with diffusion flames may be further complicated by thermal decomposition of the fuel prior to its contact with the oxidant.

Flames associated with burning organic polymers are invariably stationary flames, as opposed to propagating or exploding flames, which may be observed in purely gaseous systems. In contrast to the situation existing with flames of gaseous fuels, in which the fuel is supplied to the flame front at an arbitrary rate, a burning polymer generates its own fuel at a rate which must satisfy the equilibrium condition for maintenance of the burning process. Because fuel generation in the condensed phase is inevitably coupled with fuel consumption in the gas phase, the rates of these processes must be in equilibrium in order to maintain a steady state of combustion. Acceleration or deceleration of either process will tend to lead to disequilibrium and hence material used for textiles, it is very important to develop effective treatments which will render such natural fabrics flame-resistant. Table 1.1 represents fires in the United Kingdom in which a textile was the first material ignited.

Table 1.1 Fires in the U.K. in which a textile was the first material ignited

	Bedding	Upholstery	Curt- and blinds	Floor coverings	Clothing on person	Clothing not on person	Other furnishings and fittings
No. fires (1960)	2084	2048	796	1064	–	–	–
No. fires (1964)	3575	2106	715	1064	–	–	–
No. fires (1969)	4980	2522	874	1282	–	–	–
No. fires (1973)	5520	3194	856	1118	310	2478	212
No. fires (1976)	5365	2625	739	1114	–	–	–
No. fatal injuries (1973)	144	110	4	18	134	22	8
No. non-fatal injuries (1973)	520	398	34	100	152	150	32

After PD 2777, BSI 1977, and Christian 1979.

1.2 The general principles of polymer combustion and its inhibition

1.2 The general principles of polymer combustion and its inhibition

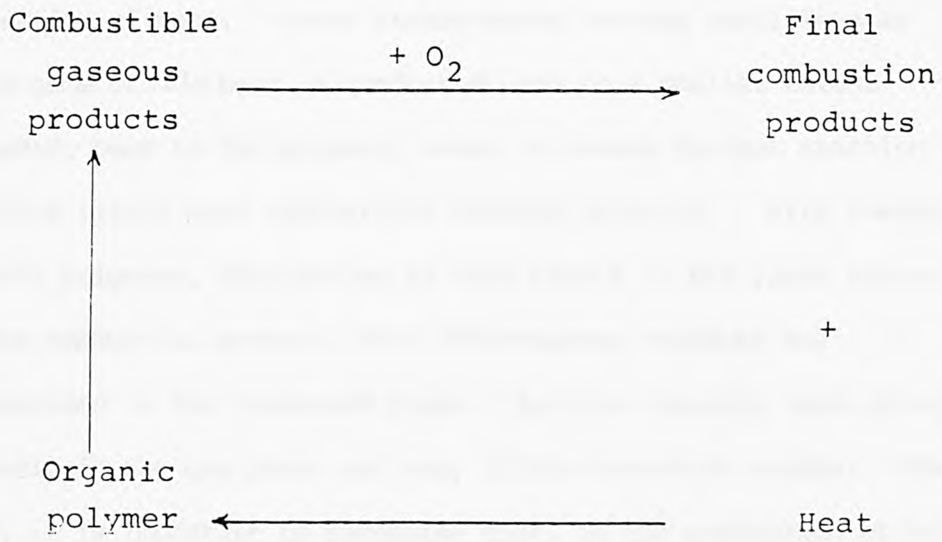
1.2.1 Introduction

A burning polymer constitutes a highly complex combustion system. Chemical reaction may take place in three interdependent regions, i.e. within the condensed phase, at the interface between the condensed phase and the gas phase, and in the gas phase.

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

During the burning of organic polymers two extreme types of behaviour may be observed. The difference between them is shown by a comparison of the behaviour during combustion of certain thermoplastic hydrocarbon polymers with that of some thermosetting polymers and cellulosic compounds such as cotton. Thus, with thermoplastics, thermal or oxidative decomposition leads to the formation of large amounts of volatile products which subsequently burn in the gas phase above the polymers. On the other hand, with many thermosetting resins and cellulosic materials, the initial reaction involved in combustion is the splitting off of water or other generally non-combustible fragments to form a loose carbonaceous matrix (Shafizadeh 1975). However, oxygen or other oxidants are always needed for the complete combustion of these materials which react directly with the oxidant, the surface oxidation often being accompanied by glowing or smouldering combustion. The burning of these polymers therefore tends to take place largely in the condensed phase and to involve extensive direct chemical interaction between the gaseous oxidant and the surface of the polymer (Moussa, Toong and Garris 1977; McCarter 1977). Despite the existence of these two extreme types of behaviour, most polymers behave in an intermediate fashion and indeed in some cases the burning mechanism changes as combustion proceeds. The sustained burning of many thermoplastic polymers can be envisaged as taking place in several quite distinct stages (Fig. 1.2).

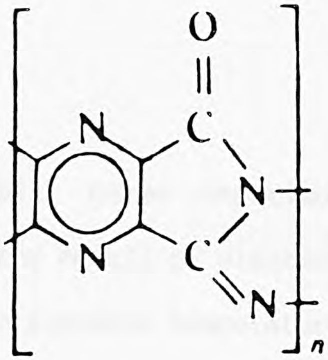
Fig. 1.2 Separate stages involved in polymer combustion



The polymer first reacts in the condensed phase to give gaseous products which are usually combustible. These products then enter the flame zone above the burning polymer. Here they undergo combustion only in the gas phase and this leads to the formation of the final products (usually carbon dioxide and water) and the liberation of heat. Under steady-state burning conditions, at least some of this heat is conducted, and to a smaller extent radiated, back to the polymer, where it causes further reaction and thus yields more combustible gaseous products. With thermoplastic polymers, smouldering is rare except in the later stages of the combustion process, when carbonaceous residues may be oxidized in the condensed phase. Ignition usually takes place entirely in the gas phase and very little oxidation occurs. However, it is important to recognise that, in the combustion of many thermoplastic polymers, the situation is considerably more complicated than this and the separate stages identified are not normally as clear cut as the above outline suggests. Non-flaming combustion of other polymers can be similarly represented in terms of separate stages.

1.2.2 Mechanisms of polymer decomposition

Organic polymers when heated under vacuum or in inert atmospheres decompose to give varying amounts of volatile products and solid residues. The thermal stability of an organic polymer is generally expressed in terms of the temperature at which the polymer starts to decompose (Korshak 1977). In general, only about 1 per cent of the bonds in the polymer backbone need to rupture in order to produce catastrophic changes in mechanical properties. The thermal stability depends on the unit structure making up the polymer and in particular on the weakest bonds present in this structure. C-C bonds are more resistant to homolytic fission than any other bonds between identical atoms (except H-H bonds which are not relevant to organic polymers). C-H, C-O, C-F and C-B bonds are stronger than C-C bonds but if any other element replaces carbon the bond is weakened. Other general features are that aromaticity strengthens C-C bonds by about 60 kJ mol and that the presence of electronegative atoms (other than fluorine) weakens them. This explains the increase in thermal stability which occurs when aromatic groups or fluorine atoms are introduced into polymers. The presence of hydrogen contributes to the formation of "weak" bonds, and polymers which contain no hydrogen at all, such as:



are very stable (Marvel 1973).

In order to assess the thermal stability of polymers properly, it is generally necessary to apply somewhat arbitrary qualitative and quantitative methods (Reich and Levi 1967). For example, with polymers which volatilise completely below 900 K, the relative stability can be estimated by heating them under the same experimental conditions and comparing either the amounts vaporised after a given time or the temperatures at which a given percentage of the initial weight of the polymer has been lost (Wright 1961; Madorsky 1961).

Thermomechanical properties have also been used to compare the thermal stability of polymers. One method is based on the postulate that a polymer remains useful if it retains 50 per cent of its mechanical strength after it has suffered a 10 per cent weight loss (Eirich and Mark 1961). Other comparisons have been made on the basis of changes in the moduli of elasticity when polymers are maintained at a given elevated temperature (Kanavest and Batalava 1961).

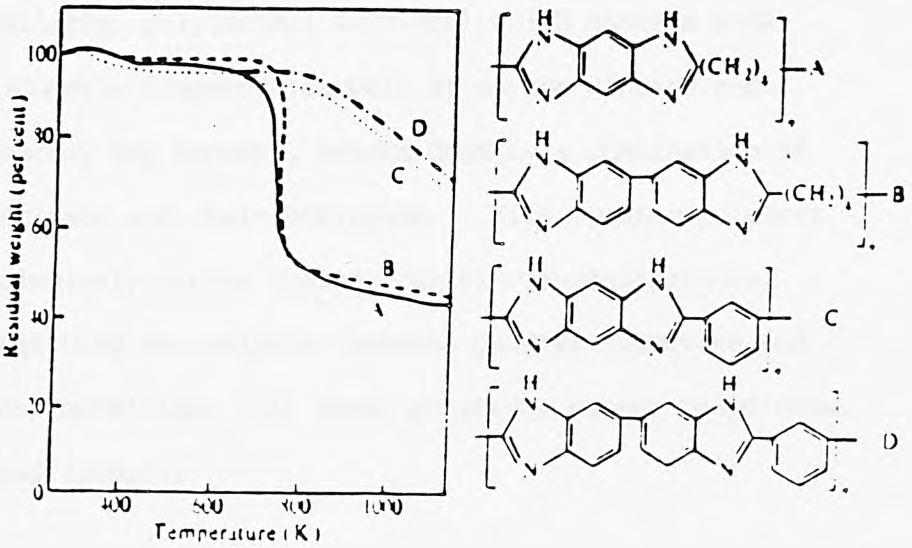
Most quantitative estimates of the thermal stability of polymers are however derived from TGA measurements. In some cases simple visual observation of TGA curves enables valuable qualitative deductions to be made. Thus, in the thermal decomposition of polybenzimidazoles (Marvel 1964), the replacement of an alkyl group by a phenyl group raises the initial decomposition temperature from 700 to 800 K and completely alters the mechanism of decomposition (Fig. 1.3). Various semi-quantitative thermal stability indices have also been devised (Doyle 1961). Furthermore, the lifetime of a polymer under isothermal conditions, which can be used as a quantitative measure of thermal stability (Reich and Levi 1963) can be deduced from TGA data by means of the expression:

$$\log t_i = (E/2.303\ RT) + \text{constant}$$

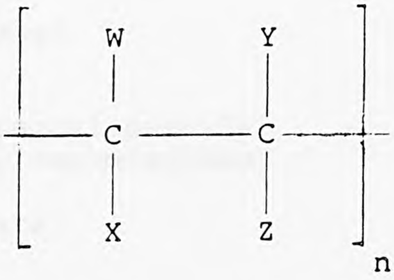
where t_i is the isothermal ageing time and T is the absolute thermogravimetric analysis temperature corresponding to the equivalent ageing time t_i.

Fig. 1.3 TGA curves for some polybenzimidazoles in nitrogen

——, A; ———, B; ...... C; -.-.-.-.-.-, D.



In the thermal decomposition of organic polymers, four general mechanisms can be identified (Wall 1972), and these are shown in Table 1.2. While some polymers undergo reactions which fall almost exclusively into one of the four classes shown, others exhibit mixed behaviour. For example, polystyrene, which yields up to 50 per cent of monomer together with some oligomeric fragments, decomposes by a mixture of random-chain and end-chain scisson. Similarly, poly(methyl acrylate),which gives a wide variety of oligomeric fragments as well as carbon dioxide and methanol but hardly any monomer, breaks down by a combination of random-chain scisson and chain-stripping. With organic polymers containing exclusively carbon chains, certain generalizations can be made regarding the relation between polymer structure and mechanism of decomposition. All these polymers, except polydienes, have the general formula:



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

Yields of monomer obtained when some vinyl polymers decompose are given in Table 1.3. from which several behaviour patterns can be discerned. When neither W nor X are hydrogen atoms but Y and Z are, yields of monomer are very high. When X is replaced by

Table 1.2 General mechanisms of thermal decomposition of organic polymers

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

---

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

Table 1.3 Yields of monomer from the thermal decomposition of polymers of general formula $(CWX — CYZ)_n$

Polymer	W	X	Y	Z	Monomer yield (wt.%)	Decom-position mechanism
PMMA	H	H	CH_3	CO_2CH_3	91-98	E
poly(α-methylstyrene)	H	H	CH_3	C_6H_5	95	E
polymethacrylonitrile	H	H	CH_3	CN	90	E
poly(α-deuterostyrene)	H	H	D	C_6H_5	70	E
polystyrene	H	H	H	C_6H_5	42-45	E/R
poly(m-methylstyrene)	H	H	H	C_7H_8	44	E/R
poly(β-deuterostyrene)	H	D	H	C_6H_5	42	E/R
polyisobutene	H	H	CH_3	CH_3	18-25	E/R
polyethylene	H	H	H	H	0.03	R
polypropylene	H	H	H	CH_3	0.17	R
poly(vinyl chloride)	H	H	H	Cl	0-0.07	S
poly(vinyl alcohol)	H	H	H	OH	-	S
polyacrylonitrile	H	H	H	CN	5	C

E, end-chain scission; R, random-chain scission; S, chain-stripping; C, cross-linking.

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

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

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

This leads to the formation of monomer as the principal, if not the exclusive, product. The presence or otherwise of hydrogen in the β-position (Y or Z) has a considerably smaller effect than in the α-position, as shown by the relative yields of monomer formed from poly(α-methylstyrene) and poly (β-methylsytrene) (Table 1.3). If the availability of hydrogen atoms were the only important factor governing the decomposition behaviour of this polymer, monomer yields would be expected to be either very small, as with polyethylene and polypropylene, or very large as with poly(methyl methacrylate) but not moderately large as with polystyrene and polyisobutene.

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

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

Little work has been done on the mechanism of the cross-linking reactions leading to char formation. Here the polymer structures are usually complicated and the reactions occurring in the solid phase are not readily accessible to normal chemical techniques of investigation.

1.2.3 Inhibition of polymer combustion

1.2.3.1 General

It has already been pointed out that the burning of an organic polymer is a very complex process involving a number of inter-related and interdependent stages. It is thus possible, at least in principle, to decrease the overall rate of polymer combustion by interfering with one or more of these constituent stages. (Fig. 1.2). This is nearly always achieved by the use of additives which may affect the various stages of the burning process in a number of different ways, although other methods can occasionally be used to control the rates of these stages and hence alter the flammability of the polymer.

The simplest way conceptually of preventing polymer combustion is of course to design the polymer so that it is thermally very stable. Its initial breakdown will be effectively prevented and the whole combustion process will never be able to be initiated with that polymer. The thermally stable polymers which have been developed in recent years for special applications are not, however, easy to process and do not possess many of the other performance characteristics needed for wide acceptance. Furthermore, they are very expensive to produce. This approach provides no help in imparting flame retardance to the organic polymers currently being produced at an annual rate of millions of tons. Indeed it is doubtful whether these relatively new high-temperature polymers will ever acquire sufficient versatility in processing and performance to be able to displace to a significant extent the present high-tonnage polymers.

The additives which are widely used in practice to inhibit the combustion of the commoner synthetic organic polymers are generally incorporated throughout the polymeric materials concerned, although they can also be coated on the external surface of the polymer to form a suitable protective barrier. Additives may be, broadly speaking, of two broad types. The methods of manufacture of existing flammable polymers can be modified by replacement of one or more of the unsubstituted reactant monomers normally used by a substituted mononer containing heteroelements known to confer some degree of flame retardance. The substituted monomers are then known as reactive flame retardants and the hetereoelements become an integral part of the resulting polymer structure. Compounds containing such elements can also be introduced into the monomers during the polymerization process in such a way that they chemically alter occasional structural units in the polymer in the same way as a co-monomer. Such additives also constitute reactive flame retardants. Alternatively, compounds, again containing elements with known flame-retardant properties, can be intimately mixed, as they are, with existing polymers in order to make them less susceptible to combustion. In this case, the compounds do not react chemically with the polymers and are known as additive flame retardants. Various types of radiation can be used to incorporate additive flame retardants into organic polymers, particularly textiles (Garris 1972; Liepins, Surles, Morosoff, Stannett 1978; Liepins, Stannett, Surles and Morosoff and Day 1978; Harris, Keating and Coynes 1980). Radiation processing is claimed to be more economical than conventional methods of incorporation; its use reduces flammability hazards (as no solvents are involved) as well as toxicological hazards. Few commercial methods based on radiation processing for the production of flame-retarded polymers are, however, yet in use. From the manufacturing point of view, the introduction of additive flame retardants undoubtedly constitutes the simplest way of making an organic polymer less flammable, because the additives can be incorporated during the final stages of production of the finished materials. Some of the otherwise desirable additive flame retardants have, however, poor compatibility with the polymers into which they needed to be incorporated. Furthermore, many of these compounds are appreciably volatile or subject to hydrolysis, so that their flame-retardant action may decrease with time. Reactive flame retardants need, however, to be incorporated at a much earlier stage of manufacture but once introduced become a permanent part of the polymer structure. However, in the case of natural polymers, it is of course necessary to use additive flame retardants. Combinations of flame retardants are often used which are said to have synergistic or antagonistic effects. Synergism is a larger-than-additive effect, whereas antagonism is a smaller-than-additive effect. The use of the term additive is generally based on the assumption that the effects of flame retardants vary linearly with their concentrations. This is not, however, usually the case (Weil 1975). Several combinations of flame retardants have therefore been misleadingly termed synergistic, when the other flame retardant simply has a beneficial effect. Sometimes a hetereoelement already present in the polymer backbone may interact with a flame retardant and thus exhibit synergism or antagonism.

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

Additives can act by a variety of mechanisms for both flaming and non-flaming combustion. It is difficult, however, to attribute uneqivocally to a particular additive or class of additives a single mode of action. Many, if not most, flame retardants appear to be capable of functioning simultaneously by several different mechanisms, often depending on the nature of the organic polymer.

1.2.3.2 Inhibition of flaming combustion

It has already been pointed out that the sustained burning of polymers may, for simplicity, be envisaged as involving three fairly distinct stages (Fig. 1.2). The polymer is first converted into combustible gaseous products, these products then burn in the surrounding oxidant-containing atmosphere, and finally at least some of the resulting heat of combustion is transferred back to the solid or molten polymer, thereby causing the formation of a continuous steady supply of breakdown products. In principle, flame retardance can thus be conferred by preventing or at least retarding sufficiently any one or more of these stages.

The most obvious stage which can be affected by an additive is the initial thermal decomposition of the polymer to give combustible gaseous products. In other words, the flame retardant may alter the breakdown of the polymer in such a way that either the nature or the rate of evolution of the gaseous decomposition products is changed. In consequence, when these products mix with the oxidant the composition of the resulting mixture may no longer lie within the flammable range. There are, however, several different ways in which the breakdown of the solid polymer can be affected.

Clearly in some cases a flame retardant acts simply by chemical termination in the condensed phase of the free-radical chains by which thermal decomposition of the polymer takes place. A completely different mode of action is that exerted by apparently inert solids incorporated into polymers. Such materials, which are generally known as fillers, tend when present in considerable quantities both to act as heat sinks as a result of their heat capacity and to conduct heat away by virtue of their thermal conductivity. They may thus prevent polymers from reaching temperatures at which they undergo significant breakdown to yield combustible gaseous products. The temperature is of course kept down even more effectively if compounds are used which decompose endothermically. Another quite distinct method of imparting flame retardance is to arrange that the surface of the polymer is, or becomes, covered with a non-flammable protective coating. This will help to insulate the flammable polymer from the source of heat and thus prevent the formation, or at any rate the escape into the gas phase, of the combustible breakdown products; it may also exclude the gaseous oxidant (normally air or oxygen) from the surface of the polymer. Certain compounds which may be initially incorporated into or simply coated on an organic polymer either decompose or react with other materials in the condensed phase at high temperatures to give a protective barrier in which the gaseous products of polymer decomposition are trapped as they are formed. An intumescent coating is then said to have formed on the polymer surface. Alternatively, direct application of a non-flammable layer on the surface of the polymer yields a non-intumescent coating.

The other stage in the burning of an organic polymer which can clearly be inhibited by additives is the combustion of the gaseous products of polymer decomposition or, in other words, the flame reactions. Here again there are several rather distinct possible modes of action. For example, a flame retardant may cause a reactive gaseous compound to be released into the combustion zone, where it enters chemically into the flame reactions and reduces the flame speed, generally as a result of the replacement of highly active free radicals by less reactive ones. In other cases, the additive may cause the evolution during combustion of the polymer of a "mist" of small particles which interfere with flame propagation by acting as "third bodies" to catalyse free-radical recombination and hence chain termination. Another possible mechanism of flame inhibition is for the additive to release, on decomposition, relatively large amounts of an inert gas which change the composition and perhaps also the temperature of the gaseous products of polymer decomposition, so that the resulting mixture with the surrounding gaseous oxidant is no longer capable of flame propagation. In some systems, when the polymer burns, the flame-retardant additive appears to be released chemically unchanged and in the form of a heavy vapour which effectively "smothers" the flame by interfering with the normal interchange of combustible gaseous polymer decomposition products and combustion air or oxygen.

However, it is sometimes possible to inhibit combustion by interfering with the normal transfer of the heat of combustion back to the polymer. Thus, for example, certain additives may promote depolymerization and hence, as a result of the lowering of the molecular weight of the polymer, facilitate melting. As the burning melt drips away from the bulk of the polymer, it carries with it a substantial proportion of the heat which would otherwise be used to bring about decomposition of the polymer to volatile products and hence feed the flame.

Thus in principle ready melting decreases flammability, although in practice droplets of burning polymer may help a fire to spread to other combustible materials. Another method of delaying, if not 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 and thus remove much of the associated heat with them from the combustion zone. This mechanism of action, known as ablation (D'Alelio 1971; Wilby 1973) is, in a sense, the parallel in the solid phase of melting and dripping in the liquid phase. A surface char layer is frequently formed which isolates the bulk of the polymeric material from the high temperature environment. This charry layer remains attached to the substrate for at least a short period while a degradation zone is formed underneath it. It is in this zone that the organic polymer undergoes melting, vaporization, oxidation or pyrolysis. The ablative performance of any polymeric material is influenced not only by its composition and structure (e.g. higher hydrogen, nitrogen and oxygen contents of the polymer increase

1.2.3.3 Inhibition of non-flaming combustion

The smouldering combustion and the closely related phenomenon of glowing combustion occur principally with polymeric materials of high surface area which break down during combustion to form a residual carbonaceous char. Although it is not possible in practice to identify separate well-defined stages in the non-flaming combustion of organic polymers, the first stage conceptually is thermal or oxidative breakdown to form only relatively small proportions of volatile products and a solid char. The second stage consists of the ignition and burning of this char. Under conditions of smouldering, ignition of the carbonaceous residue may occur at temperatures well below the ignition temperature of the volatile products (Brown and Wall 1958). Thus the first material to ignite is the char and the volatile products often do not burn, either because there is no local ignition source of sufficient intensity or because their rate of production is so low that the gaseous mixture formed is too lean.

In principle, then, it is possible to inhibit non-flaming 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 must act in the condensed phase. The possible mechanisms are clearly the same as those which apply in the case of flaming combustion; chemical inhibitors, inert fillers, and protective coatings are all able to slow down or even prevent completely 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. Studies of the combustion of substantially pure carbons (Walker, Shellef and Anderson 1968) show that almost every impurity exhibits either a promoting or an inhibiting effect under appropriate experimental conditions.

1.3 Cotton: its history, properties and importance as a textile fibre

1.3 Cotton: its history, properties and importance as a textile fibre

1.3.1 History

There is good reason to believe that cotton existed in Egypt as early as 12000 BC. Its use in cloth in 3000 BC was indicated by archaeological findings and recorded evidence exists of its cultivation in India as far back as 700 BC. In the fifth century BC, Herodotus wrote of trees growing wild in India bearing wool of a softness and beauty equivalent to that of the sheep; clothes made from this tree were described as garments of extraordinary perfection. It seems that Alexander the Great introduced Indian cotton into Egypt in the 4th century BC, and from there it spread to Greece, Italy and Spain. In about 700 AD, China began growing cotton as a decorative plant. Cotton was of little importance in European commerce until the sixteenth and seventeenth centuries. The invention of the spinning jenny, the flying shuttle, the spinning frame and the cotton gin greatly enhanced the manufacture of cotton textiles. Following these developments the cotton industry flourished, and control of the industry shifted principally to England and to the United States. During the nineteenth century, cultivation of cotton increased, so that it displaced wool as the world's major textile fabric. Indeed cotton became an important agricultural product, a principal form of wealth and international trade, and one of the most important raw materials in the Industrial Revolution. During the present century, the cultivation of cotton has been mechanised, the varieties available have been increased and agricultural practices have been improved.

1.3.2 Cultivation and growth

Cotton is the most important vegetable fibre used in spinning. The cotton plant is a herbaceous shrub having a normal height of 1-2 m. The most favourable growing conditions for cotton include a warm climate (mean temperature of 17-27°C), where fairly moist and loamy, rather rich, soil is an important factor; seed planted in dry soil produces fine and strong, but short, fibres of irregular lengths and shapes. Under normal climatic conditions, cotton seeds germinate in 7-10 days. After one more day the cotton boll begins to grow rapidly if the flower has been fertilized. The mature boll opens 45-90 days after flowering, depending on variety and environmental conditions. Within the boll are 3-5 divisions called locks, each of which normally has 7-9 seeds that are covered both with lint and with fibres. These fibres form a short, shrubby undergrowth beneath the lint hairs on the seeds. Each seed contains at least 10,000 fibres in each boll.

The cotton fibre is a single cell that originates in the epidermis of the seed coat at about the time the flower opens. As the boll matures, the fibre grows until it attains its maximum length, which averages about two thousand five hundred times its width. In 17-25 days after the flower opens, when the boll is half mature, the fibre attains virtually its full length, at which time it begins to deposit layers of cellulose on the inside of the thin casing, or primary wall. The pattern of deposition is such that one layer of cellulose is formed each day in a centripetal manner until the mature fibre has developed a thick secondary wall of cellulose, from the primary wall to the lumen or central canal. The fibre now consists of three main parts: primary wall, secondary wall, and lumen. At the end of the growing period when the boll bursts open, the fibres dry out and collapse, forming shrivelled, twisted and flattened tubes.

1.3.3 Production

The bale is the unit of cotton production, but the weight of a bale varies appreciably from one country to another. For convenience of comparison, the crop statistics of various countries are frequently converted into units of 478 lb net weight of cotton. Because cotton is an agricultural crop, there are pronounced fluctuations in yield per acre in all countries, according to the prevailing growth conditions and the

Table 1.4 World production and consumption of cotton (tonnes)

(a) Production	Year		
Area	1968	1973	1978
North America	2.23	3.68	3.82
South America	1.53	1.04	1.04
Western Europe	116.873	198.77	200.94
Eastern Europe and the U.S.S.R	2.06	2.496	2.749
Asia and Australia	3.98	5.07	5.22
Africa	1.036	1.27	1.12
Total:-	10.364	13.76	14.15
(b) Consumption			
Total:-	9.471	13.105	11.452

incidence of pests and diseases. Moreover, political and economic changes may result in intermittent restrictions on the size of the acreage planted, or on the choice of seed variety. Moreover there are sizeable fluctuations from year to year in the amount of cotton produced in various countries.

For more than one hundred and fifty years, cotton has maintained undisputed leadership in its use as a textile fibre. Indeed, its production accounts for more than one half of the total world production of fibres, and for more than 65% of the fibres which are used in the world textile industry. Table 1.4 shows the world production as well as the consumption of cotton; the apparent overproduction in recent years can probably be ascribed to the increased impact of synthetic fibres. At present, the chief cotton-growing countries of the world are the Union of Soviet Socialist Republics (22%), the People's Republic of China (19%), the United States (11%), India (9%), Pakistan (4%) and Egypt (3%).

1.3.4 Physical properties

Length is the most important parameter of the cotton fibre. This usually varies from less than 2.5 cm for short staple types to more than 2.9 cm for long staple types. Short staple varieties tend to be coarser, whereas the longer staple varieties are fine, silky and soft. Diameter of the fibre is an inherited characteristic that can be greatly influenced by soil and weather. The shape ranges from circular to elliptical to linear in most varieties. Fineness is a measure of the size, diameter, density and weight per unit length. The strength of the cotton fibre is attributed to the cellulose it contains and, in particular, to the molecular chain length and orientation of the cellulose. The cotton fibre, which is trapped for a short length at the tip, is twisted frequently along its entire length, with the direction of twist reversing occasionally. These twists are referred to as convolutions and it is believed that they are important in spinning, because they contribute to the natural interlocking of fibres in a yarn.

Staple length is one of the most important characteristics of raw cotton and to a large extent determines the commercial value of cotton. The longer staple length cottons yield yarns of greater length than shorter staple length cottons.

Finer yarns can also be spun from the longer staple length cottons. Maturity of cotton fibre is a measure of the development of its secondary cell walls. Poorly developed walls result when the agricultural conditions are such as to encourage attack of the plant by diseases or pests. Immature fibres are weaker and less rigid than mature fibres. During mechanical organization of immature fibres into yarns and fabrics, these properties result in much breakage and in the formation of tangles or small balls of fibres known as reps.

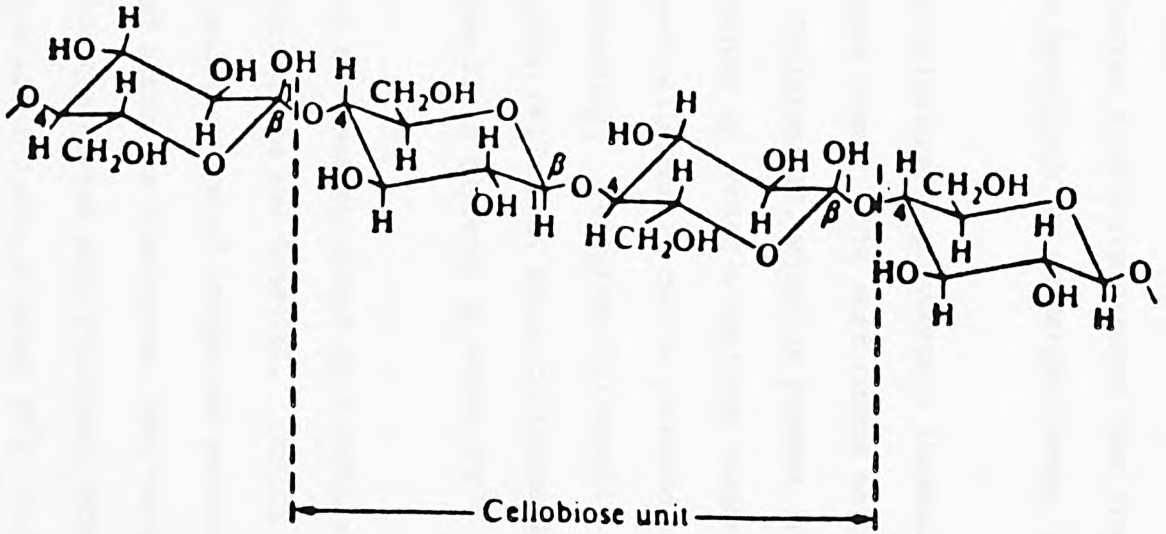
The elastic properties of cotton fibres are determined by measuring the amount of energy expended on extension of the fibre under selected conditions and then recovered on relaxation of the fibre under the same conditions. The dimensional recovery of the fibre following the extension and relaxation of the fibre also provides useful information.

1.3.5 Chemical reactions involved in the treatment of natural cotton

Although the cotton fibre, on being dried, loses its round shape and much of its water, some moisture is tenaciously retained in it. This moisture can be expressed either as *moisture regain*, which is the amount of moisture as a percentage of that in an oven-dry sample, or less commonly as *moisture content*, which is the amount of moisture as a percentage of the original sample weight. Under ordinary atmospheric conditions, the chemical properties of cotton are essentially those of the cellulose contained therein. The molecular chains of cotton cellulose, like other forms of cellulose, consist of anhydroglucose units joined by 1-4 linkages. These linkages are characteristic of the cotton cellulose, which is a polysaccharide (Fig. 1.4). The empirical formula of cellulose is $(C_6H_{10}O_5)$. The value of n, the degree of polymerization, for cotton cellulose can be as high as 4,000 to 5,000, giving molecular weights of up to 8×10^5. Owing to the polymeric nature of cotton, molecular weights determined by different methods may give different values.

A measure of the average chain length can be obtained by measuring the fluidity of a solution of cotton. Many solvents may be used for this purpose, the most common one being copper (II)

Fig. 1.4 Structure of cellulose



ethylenediamine hydroxide. Low fluidities indicate a high molecular weight, whereas fluidities greater than that of untreated cotton indicate hydrolytic or oxidative damage to the cellulose.

Cotton cellulose is polymorphic inasmuch as it crystallizes in different forms. The most common natural structure is cellulose I. Cellulose II, which is present in mercerized cotton, can be obtained by adding a swelling reagent to cellulose I. Cellulose III and cellulose IV can be produced synthetically and do not occur naturally. Cellulose III results from removal of ammonia from cotton cellulose, while cellulose IV is obtained on heating cellulose II in glycerol at about 200°C.

Most of the uses of cotton as a textile material require some modification of the raw material. One of the earliest processes for the modification of cotton was mercerization, the process being named after its discoverer, John Mercer. The process involves treating the cotton with relatively strong (25%) caustic soda solution for about 2 min at about 35°C, followed by washing with water at about 50°C. Any remaining sodium hydroxide is then neutralized by a weak acetic acid solution and the cotton is washed again with water at about 35°C. Mercerization is performed under conditions where the cotton fabric is not allowed to shrink in length or in width. This produces cotton fabrics with improved lustre and dyeability, and to a lesser extent, improved strength. More recently, relatively cool sodium hydroxide solution has been substituted by a hotter solution that is allowed to cool while the cotton remains immersed in it. This increases the efficiency of the mercerization process. If the fabric is allowed to shrink during the application of the caustic soda solution, a product is formed which has increased strength; this has certain specialised applications.

Effects similar to those produced by mercerization are obtained by treatment of cotton fabrics with ammonia. Improvements in lustre and strength are similar to those produced by sodium hydroxide, but the dyeability is not improved in this case. The chemical difference between the two methods is that sodium hydroxide solution converts cellulose I to cellulose II, while ammonia converts it to cellulose III.

Bleaching is one of the most important processes for giving the cotton fabric a white colour. The process is oxidative in nature, the aim of the treatment being (1) to convert the coloured impurities to soluble ones that can be removed by washing and (2) to decrease the absorption of light by the cotton. The substances which discolour cotton are usually more sensitive to oxidation than is celluose itself. However, the oxidative treatments must be carefully carried out in order to minimise damage to the fabric. The bleaching agents used include sodium hypochlorite and hydrogen peroxide, which are known to increase the whiteness of the fabric. The control of the pH and the concentration and temperature of the oxidizing agents are important factors governing bleaching activity. Optical bleaches may also be applied after the main bleaching and this gives the fabrics a uniform light reflectance and increased whiteness.

The hydroxyl groups in the 2, 3 and 6 positions of the anhydroglucose unit are very reactive and provide sites at which cotton cellulose can be modified to give changes in certain properties. The two most important modifications involve esterification and etherication of the cotton cellulose hydroxyl groups. Of the three most important esters, viz. cellulose sulphate, cellulose nitrate and cellulose phosphate, only the sulphate is soluble in water. A recent addition to possible reactive dyestuffs for cotton is a type of phosphonic acid or phosphoric acid dye, which phosphorylates the cellulose (Graham and Suratt 1979). A large class of cellulose-reactive dyestuffs become attached to cellulose as a result of an alkali-catalyzed esterification by the chlorotriazine moiety of the dyestuff.

Cellulose-OH + Cl-dyestuff → cellulose- O - dyestuff + HCl

One of the most important modifications of cotton cellulose occurs through etherification to produce durable-press, shrink-resistant and smooth-drying properties, involving the cross-linking of adjacent cellulose chains through amidomethyl ether linkages. Most reagents for cross-linking cotton proceed through either Lewis acid or Bronsted acid catalysis (Pierce and Renhardt 1976) by a carbonium ion mechanism. The effects are to increase resilience as well as smooth-drying and shape-holding properties, which are all important to cotton textiles. The amount of moisture present in the fibre at the time of etherification influences both the response of the microstructure of the etherified fibre to swelling and solvation and certain physical properties of the cotton product (Reeves and Perkins 1960).

Based-catalyzed reactions of cotton cellulose with mono or diepoxides to form cellulose ethers produce fabrics with increased resilience. Monoepoxides bring about a great improvement in resilience. Etherification of cellulose by ethyleneimine produces special properties in the cotton with the end product dependent on the attached group. Some degree of waterproofing can be obtained as a result of etherification; a typical example is the product formed by reaction of stearamidomethylpyridinium chloride with the cellulose. Polyfluorinated polymers were found to make cotton oil-repellent. Another interesting reaction of cotton cellulose occurs when the material is subjected to high-energy radiation. Depolymerization of the cellulose occurs with some carbonyl formation, carboxyl formation and chain cleavage. Accompanying these chemical changes there is a corresponding increase in solubility in water and alkali and a decrease in fibre strength. Irradiation with γ-rays causes the cotton to possess base ion-exchange properties. However, the use of light in the near ultra-violet region of the spectrum causes formation of free radicals and mild oxidative degradation of the cotton.

1.4 The decomposition and combustion of cellulose and mechanisms for its flame retardance

1.4 The decomposition and combustion of cellulose and mechanisms for its flame retardance

The thermal decomposition of cellulose produces at least 70-80 volatile products, the two most important being laevoglucosan (one of the monomers) and water. Each generally accounts for about 20 wt% of the total products (Tsuchiya and Sumi 1970), although over 50 wt% can be obtained during the decomposition of very pure cellulose. There is also a high proportion of char and of tar in the products but the other monomer, 6-anhydro-D glucofuranose, is the only other simple organic compound formed in significant quantities (ca. 2 wt%). The yields of all products, even laevoglucosan, vary markedly with different types of cellulose as well as with the purity of a given type of cellulose. In this connection, pure cellulose does not smoulder on its own but impurities, which are generally present, can cause smouldering combustion.

The pyrolysis conditions may also affect the product distribution. Rapid heating yields less char but more tar and flammable gases than slow heating. The nature of the gaseous products formed by thermal decomposition is not appreciably affected by the presence of oxygen in the gas phase (Schwenker and Beck 1963).

There have been several reviews of the thermal decomposition of cellulose (Brown and Wall 1958; Broido and Kilzer 1963; Shafizadeh 1968; Kilzer 1971; Alger 1972; Cerny and Stanek 1977) and these suggest various mechanisms at temperatures above 550 K (Fig.1.5). The first is an intermolecular reaction which results in dehydration through cross-linking. The second, which occurs concurrently with dehydration, is an unzipping reaction involving scission of C-O bonds as a result of which depolymerization is propagated through the cellulose molecule and laevoglucosan is formed by rearrangement of the severed glucosan units. The third is a decomposition of the dehydrated product (dehydrocellulose) to form char and volatile organic compounds. Laevoglucosan can undergo further reaction and will then form lower molecular weight volatile compounds; carbon monoxide eventually becomes the predominant product (Cullis, Hirschler, Townsend and Visanuvimol 1983). It has been postulated that random scission of C-O bonds accounts for both the depolymerization and the formation of smaller product molecules (water, carbon monoxide, carbon dioxide and hydrogen). Below 550 K, the rates of dehydration and cross-linking are comparable with that of depolymerization but above this temperature unzipping predominates.

Thus, although it is an over simplification of the position, it can be assumed that cellulose decomposes by essentially two different routes (Fig. 1.6). One involves depolymerization to

Fig. 1.5 Mechanism of decomposition of cellulose

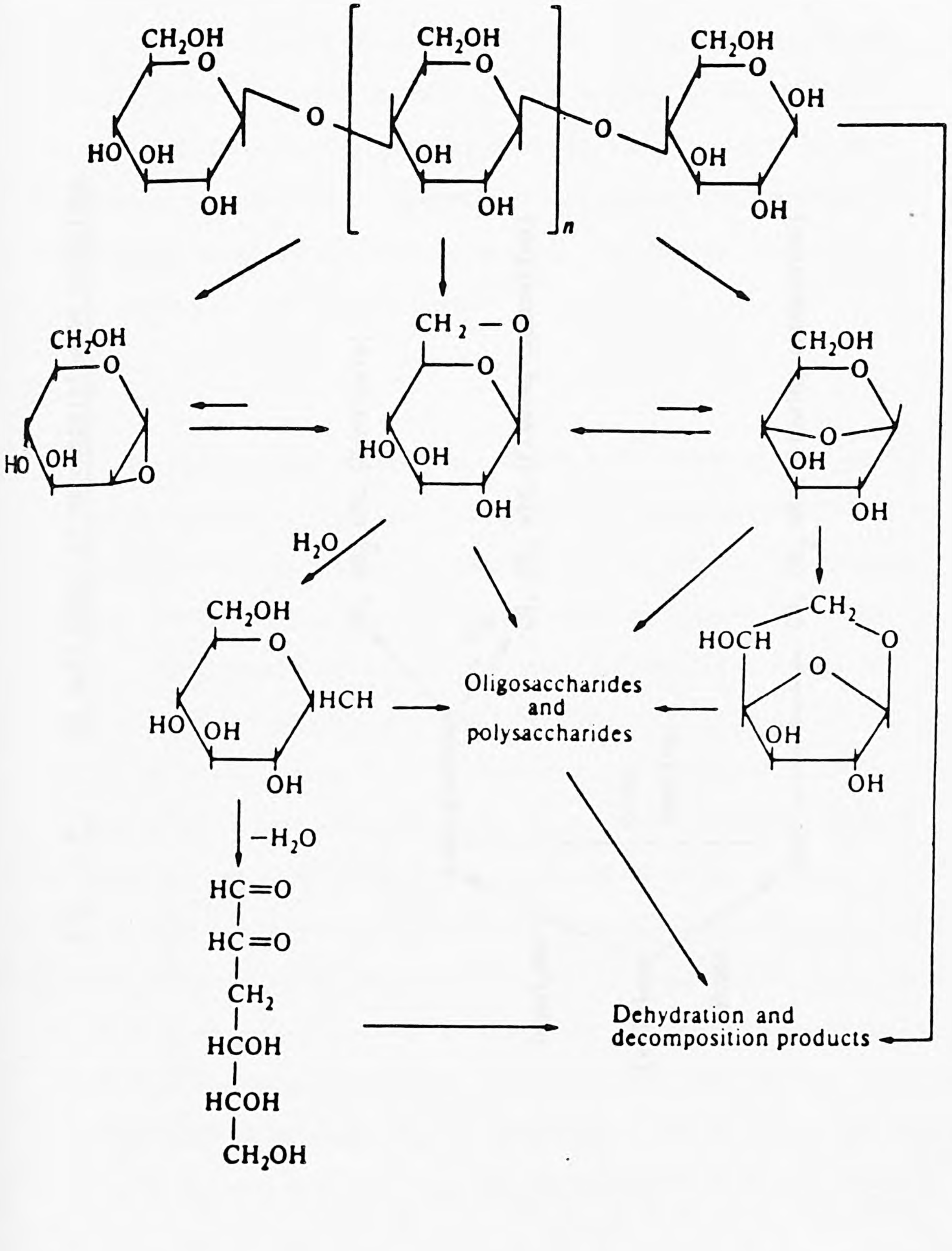
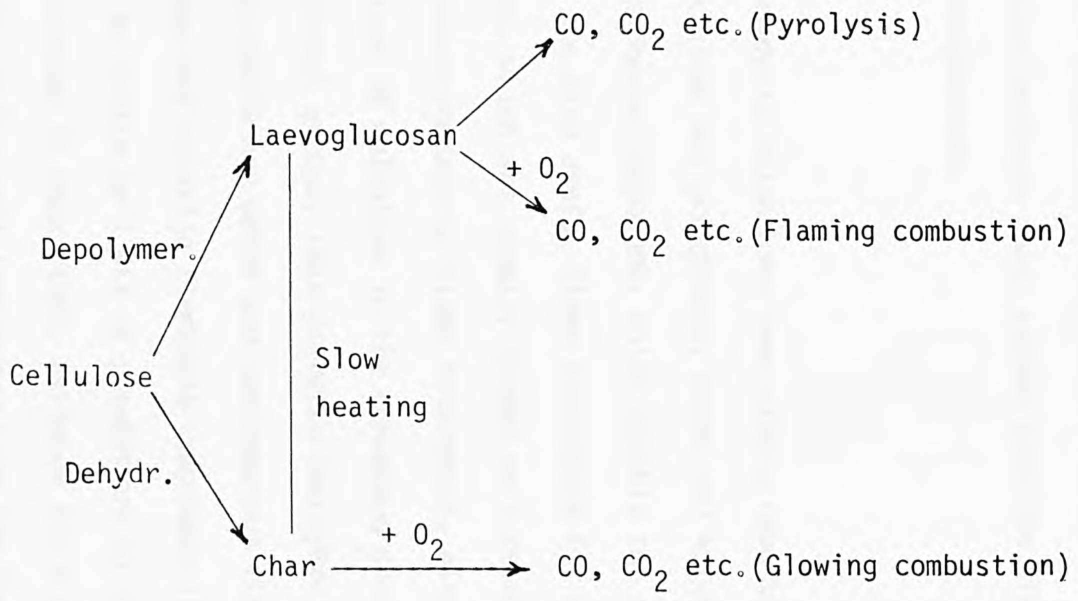


Fig. 1.6 Two main modes of decomposition of cellulose



yield laevoglucosan, which in turn, breaks down to give flammable gaseous products. The other is a chain-stripping reaction, in which the substituents on the carbon chain, mainly hydroxyl groups, are eliminated as water, and the residue becomes an unsaturated char, which reacts with oxygen to give smouldering or glowing combustion. The ideal flame retardant should promote decomposition by the second mechanism which produces char, rather than the first one, which produces laevoglucosan.

In practice the elements which have been widely used to confer flame retardance on cellulose are phosphorus, boron and sulphur. Inorganic and organic phosphorus compounds, which inhibit the combustion of thermoplastics, are also useful flame retardants for cellulose. Phosphorus acids, which are usually formed as a result of the oxidation of phosphorus-containing flame retardants, alter the mechanism of decomposition of cellulose in the condensed phase by phosphorylating the hydroxyl groups; this prevents depolymerization so that the principal products are water and carbonaceous char rather than laevoglucosan and volatile flammable compounds (Lyons 1970). Indeed, the addition of as little as 1 wt% of phosphorus to cellulose can cause a several-fold increase in char yield. Evidence for a mechanism involving phosphorylation of the cellulose comes from the fact that, in the condensed phase, virtually all phosphorus compounds which are capable of being oxidised to acidic species, are effective flame retardants.

Furthermore phosphorus compounds decrease the heat of combustion of cellulose as well as the rate of heat release.

In summary, then, although cellulose undergoes decomposition by at least two competing routes, as shown in Fig. 1.7, the dehydration route, to yield carbon and water generally, proceeds only slowly in the absence of catalysts. In the presence of an additive such as phosphoric acid, however, this reaction becomes the predominant one, replacing the fuel-producing reaction.

Combinations of phosphoric acid and various nitrogen bases, such as urea, guanidine and dicyandiamide, are more effective flame retardants for cotton than are the separate components. Further evidence for phosphorus-nitrogen synergism is provided by the experimental finding that the minimum amount of phosphorus required to confer flame retardance on cotton decreases with increasing amounts of nitrogen present (Fig. 1.8). Similar conclusions have been reached from studies of the effects of different fixed amounts of nitrogen compounds on the variation with phosphorus content of the limiting oxygen index of cotton (Willard and Wondra 1970).

Fig.1.7 Decomposition of cellulose by two competing pathways

Fig. 1.7 Decomposition of cellulose by two competing pathways

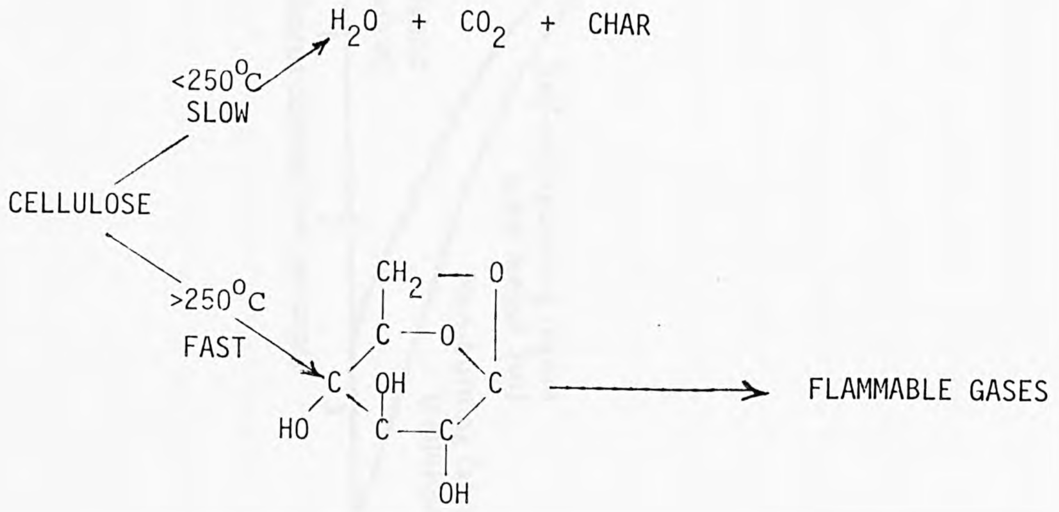
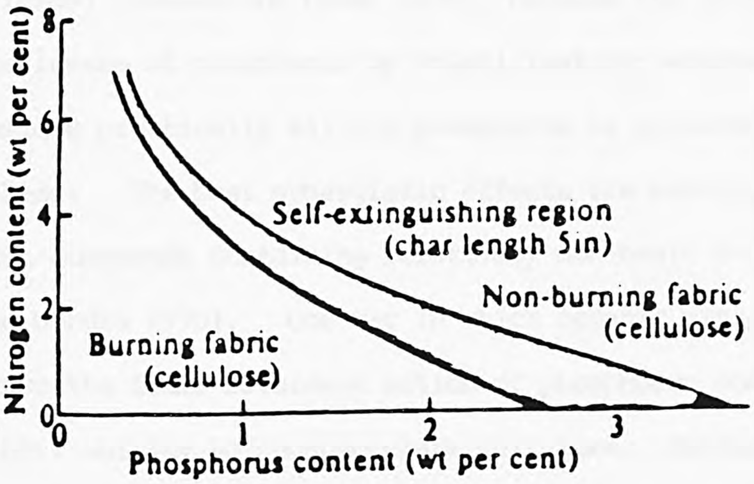


Fig. 1.8 Effect of nitrogen on the minimun amount of phosphorus needed to render cotton flame retardant. (Tesoro 1970)



However, in general, the flame-retardant effect of nitrogen depends in a complex way on its structural environment. Thus, the limiting oxygen index of phosphorus-containing polymers can be increased, unchanged, or even decreased by increasing nitrogen content. Thus polyacrylonitrile has an unfavourable effect on the flame retardancy of cotton treated with tetrakis (hydroxymethyl) phosphonium hydroxide (THPOH) (Reeves and Drake 1970), because the nitrile groups induce large losses of phosphorus by volatilisation; whereas with amines or amides practically all the phosphorus is retained in the condensed phase. The best synergistic effects are usually found with nitrogen compounds containing relatively non-basic N-H groups (Willard and Wondra 1970). One way in which organic nitrogen compounds improve the flame retardant action of phosphorus compounds is by enhancing their ability to phosphorylate cellulose. Certainly some nitrogen compounds catalyse the thermal condensation of phosphoric acid to poly(phosphoric acids) (Shen, Stahlheber and Dyroff 1969), which are better phosphorylating agents for cellulose. Amino groups also enable carbohydrates to decompose at lower temperatures to give carbon and water. It thus seems that certain nitrogen compounds promote the phosphorylation of cotton by phosphorus-containing flame-retardants and there is no evidence to support of the suggestion that nitrogen oxides are formed and catalyse char formation. However another advantage of the incorporation of nitrogen is the improvement which it gives to the durability of the flame-retardant finish as a result of its ability to attach the phosphorus firmly to the cotton fabric. Nitrogen oxides may also inhibit the flame reactions by acting as free radical traps in the gas phase.

Borate treatments were among the first to be extensively applied to cotton and soon afterwards to wool. The theory was advanced that the cellulosic fibre in cotton becomes coated with an impenetrable glassy skin which excludes oxygen and thus prevents combustion (Gay-Lussac 1821). This has been the basis of most subsequent explanations of the action of inorganic borates. Boric acid and its hydrated salts, in contrast to the anhydrous borates, have low melting points and thermal decomposition takes place according to:

$$2H_3BO_3 \xrightarrow[-H_2O]{400-470\ K} \underset{\substack{\text{meta-}\\ \text{boric}\\ \text{acid}}}{2HBO_2} \xrightarrow[-H_2O]{533-543\ K} \underset{\substack{\text{boric}\\ \text{oxide}}}{B_2O_3}$$

Boric oxide softens to a glass at 600 K but above 775 K it becomes sufficiently fluid to flow. Borax when heated in air dissolves in its water of hydration and swells to a frothy mass; it then loses water and finally fuses to a clear melt. The mixture of boric acid and borax on evaporation of the hydrated water leaves a glassy dustless layer which adheres uniformly to cellulosic fibres. Thus when polymers containing boric acid and borax are heated to temperatures at which extensive decomposition starts to occur, dehydration takes place. The liberated water vapour makes the polymer swell and an intumescent coating is formed on the surface which insulates the bulk of the polymer from the heat source. The formation of an intumescent coating cannot however be the only mode of action of boron-containing salts because otherwise they would be effective flame retardants for many other polymers. The boric acid-borax system also enhances char formation in cellulosic polymers as a result of chemical interaction between the boron compounds and the exposed hydroxyl groups, followed by loss of water. This produces cross-linking which leads to the formation of carbon rather than oxides of carbon and also inhibits the formation of laevoglucosan. The char was found to contain 90% of the boron. The greater effectiveness of hydrated borates as compared with that of the anhydrous compounds is probably ascribable both to the endothermicity of the dehydration processes and to the dilution of the gaseous breakdown products by the water vapour released.

In summary, three principal modes of action can be ascribed to boron-containing additives:

(a) Inorganic glassy deposits may be formed within or at the surface of the solid phase; these may act as intumescent coatings which can be removed either chemically or physically.

(b) With cellulose and other hydroxylated polymers boric oxide forms borate esters in the condensed phase. This promotes the formation of char at the expense of flammable gaseous products such as laevoglucosan.

(c) Boric acid can release into the gas phase water vapour, which removes the heat required for further dehydration and at the same time dilutes the gaseous fuel released on decomposition of the polymer.

Compounds containing sulphur, particularly metal sulphates (such as alum, Plaster of Paris and copperas) are among the oldest flame retardants for organic polymers. They were originally used mainly for treating wood but in the eighteenth century mixtures containing alum were recommended also for decreasing the flammability of textiles and of paper pulp (Wyld, 1735). Although the use of alum and other metal sulphates as flame retardants has now been largely abandoned, ammonium sulphate, first introduced for flame proofing flannelette (Perkin 1913), is still widely used as a flame retardant for other cellulosic materials. Ammonium sulphate resembles certain other ammonium salts (e.g. phosphates and phosphonates) in esterifying hydroxyl groups in cellulose and, in addition, liberating large volumes of gaseous ammonia, which is probably primarily responsible for the flame-retardant effect observed.

In view, however, of the well-known flame-retardant action of many metal compounds (Cullis 1981), it was considered of interest to carry out a new investigation of the effect of some metal (and other inorganic) sulphur oxyacid salts as flame retardants for cellulose. Since it has been claimed that there is an "internal synergistic effect" between sulphur and bromine (Jolles 1967), studies were also made of the way in which an added organic bromine compound affects the flame-retardant action of some metal sulphates.

2. Experimental

2. Experimental

2.1 Materials

2.1.1 Polymer

Cellulose, in the form of both mercerized and unmercerised Egyptian cotton cloth, was kindly provided by Bide Company Limited. The mercerized cotton was prepared by the Kier-boil method using 1.5 wt% sodium hydroxide solution at a temperature of $70\ ^{\circ}\mathrm{C}$ and a pressure of 530 kPa. Wave characteristics: weight, 192 gm m^{-2}; warp threads, 3 gm cm^{-1}; weft threads 26 cm^{-1}.

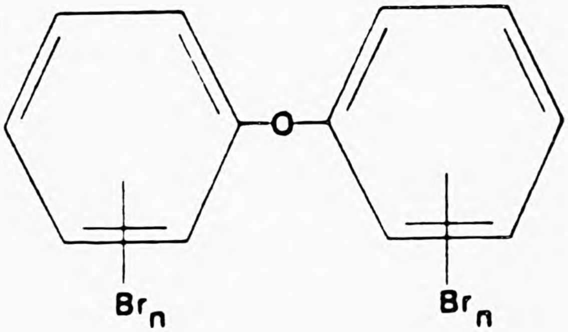
2.1.2 Additives

2.1.2.1 Inorganic sulphur oxyacid salts

Aluminium sulphate ($Al_2(SO_4)_3.16H_2O$), ammonium sulphate ($(NH_4)_2SO_4$), ammonium sulphamate ($(NH_4)(NH_2SO_3)$), cobalt (II) sulphate ($CoSO_4.7H_2O$), copper (II) sulphate ($CuSO_4.5H_2O$), potassium sulphate (K_2SO_4), magnesium sulphate ($MgSO_4.7H_2O$), iron (II) sulphate ($FeSO_4$), zinc sulphate ($ZnSO_4.7H_2O$) and sodium sulphite (Na_2SO_3) were all good-quality commercial samples and were used without further purification.

2.1.2.2 Organic compounds

Decabromobiphenyl oxide (Saytex 102E)



DBBO

was kindly provided by Saytech, Inc. and poly(vinyl chloride) (Corvic) was supplied by courtesy of Imperial Chemical Industries Limited.

2.1.3 Gases

Oxygen, oxygen-free nitrogen and air were obtained from the British Oxygen Company in London and from Cupper Industries in Alexandria and were used without further purification.

2.1.4 Sample preparation

The inorganic salts were incorporated into the cotton by putting weighed samples of the cotton cloth (ca. 30 gm) through aqueous solutions of the salts using a manually-operated wringer. Solutions containing initially about 20 wt% and about 5 wt% were used in the first instance; but solutions of other concentrations were later used in the case of the salts showing the greatest flame-retardant effect. Before treatment the cotton was kept overnight in a controlled atmosphere of constant humidity (saturated sodium chloride solution). After treatment the cotton was dried in an oven at about 343 K for 7 hours to ensure minimum migration of the salts after the impregnation procedure and to evaporate excess water. Subsequently the dried, treated samples were again kept overnight in the same controlled-humidity atmosphere.

The amounts of the various salts incorporated were determined gravimetrically by difference, and frequent control measurements of the cation concentrations in the extracted solutions were made by atomic absorption spectroscopy.

In view of the low solubility of decambromobiphenyl oxide, this compound and poly(vinyl chloride) in a 3:1 weight ratio were applied directly to the treated cotton cloth. The polymer was needed as an adhesive and application involved the use of pressure by means of a heavy warm iron, covered with a removeable perforated polytetrafluoroethylene sleeve to prevent adhesion of the additive to the iron itself.

2.2 Apparatus and procedure

2.2.1 The limiting oxygen index apparatus

Flammability was measured using Stanton Redcroft limiting oxygen-index equipment, designed to meet ASTM D2843 specifications. The lay-out is shown schematically in Fig. 2.1 and in detail in Fig. 2.2. The right-hand side of the equipment houses the gas line. Two gas inlets at the rear of the instrument lead to two filters fitted with numerical controls. This enables the needle valves to be set very precisely. An ON-OFF lever is situated adjacent to each control needle valve in each gas line. The two separate pipes merge at a mixing chamber to give a homogeneous combined gas flow. The main portion (ca. 99.5%) passes directly to the principal indicating flowmeter, which is calibrated to read from 0-25 dm^3 min^{-1} for air. From the flowmeter the gas passes directly to the mesh at the base of the test column. The small by-pass flow (ca. 0.5% of the total) goes to a paramagnetic oxygen analyser which produces a digital read-out of the percentage of oxygen in the gas mixture.

The instrument was connected up to cylinders of oxygen and nitrogen via a two-stage regulator, and supply pressures of 25 p.s.i. were employed in order to achieve the required flow rates during the test.

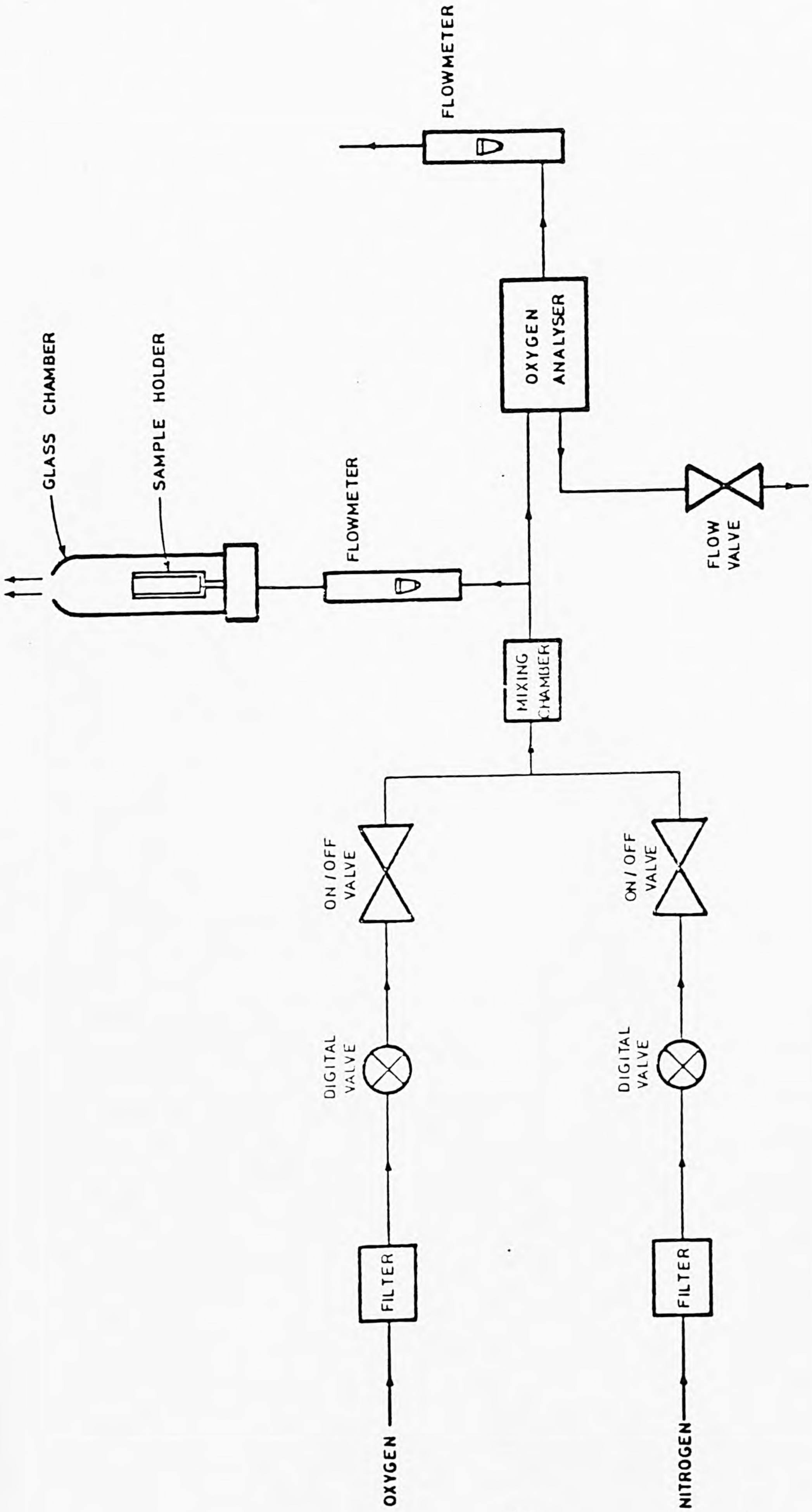

OXYGEN
FILTER
DIGITAL VALVE
ON/OFF VALVE
NITROGEN
FILTER
DIGITAL VALVE
ON/OFF VALVE
MIXING CHAMBER
FLOWMETER
SAMPLE HOLDER
GLASS CHAMBER
OXYGEN ANALYSER
FLOW VALVE
FLOWMETER

Fig. 2.2 (p. 89)
Limiting oxygen index apparatus
has been removed for
copyright reasons

The test column on the limiting oxygen index equipment is a heat-resistant glass tube of 75 mm minimum internal diameter and 450 mm minimum height, which rests in a casing designed with special entry ports so that the entering gas gives a laminar flow up the column (see Fig. 2.3). At the base of the column is a perforated metal screen designed to catch any fragments or burning droplets formed during combustion of the polymer samples. The standard sample holder is situated at the centre of the column. The burner is a 150 mm long copper tube attached to a natural gas supply; a standard 25 mm flame was used to ignite the samples.

2.2.2. Measurement of limiting oxygen index

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

Fig. 2.3 (p. 91)
Limiting oxygen index apparatus for
non-self supporting polymer material
has been removed for copyright reasons

concentration of oxygen was increased until a candle-like flame was obtained and that oxygen concentration was taken as the LOI value for that sample.

2.2.3 The computer programme

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

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

Polynomials of order 1-4 were tried and the coefficients were defined as below. 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:

$$Y_1 = \sum_{J=1}^{3} a_J x_J$$

Second order:

$$Y_2 = Y_1 + a_4 X_1 X_2 + a_5 X_1 X_3 + a_6 X_2 X_3$$

Third order (reduced):

$$Y_{3r} = Y_2 + a_7 X_1 X_2 X_3$$

Third order (full):

$$Y_3 = Y_{3r} + a_8 X_1 X_2 (X_1 - X_2) + a_9 X_3 X_1 (X_3 - X_1) + +a_{10} X_2 X_3 (X_2 - X_3)$$

Fourth order:

$$Y_4 = Y_3 + a_{11} X_1 X_2 (X_1^2 + X_2^2 - 3X_1 X_2) + a_{12} X_1 X_3 (X_1^2 + X_3^2 - 3X_1 X_3) + a_{13} X_2 X_3 (X_2^2 + X_3^2 - 3X_2 X_3) + a_{14} X_1 X_2^2 X_3 + a_{15} X_1 X_2 X_3^2$$

The quality of the fit was assessed by the value of the root mean square difference between calculated and observed LOI values (σ) by the multiple regression correlation coefficient (RCC), by the examination of the individual difference between calculated and observed LOI values, and by a sequential F-test to assess the significance of the most recently introduced items.

Data input

1 Name of composition variables

2 " " " "

3. " " " "

4. Title of calculation

5. Control variable

Min LOI, step size, input selector, output selector

$$\text{where step size} = \frac{\text{Max LOI} - \text{Min LOI}}{10}$$

Input selector = 1

Output selector = 3

6. - 6th line cavc, h, C sub.

cavc = index for average coefficent calculation
= 0 (no calculation)
= 1 (calculate for 2 additives)
b = additive loading for coefficient calculation
c sub + if cavc = 2, this is the substrate response (LOI)
if cavc = 3, this is the change in additive loading over which incremental calculation is carried out

7.	LOI	comparison variable 1	comparison variable 2	comparison variable 3
n ←	-1	0.0	0.0	0.0
n+1 ←		composition coordinates of vertices		
n+2 ←		" " " "		
n+3 ←		" " " "		

To run

← CONV * = Frogdata : S

← JRN runfrog

← SUNMB XXXXt

← JSTS XXXXt

← JOUT XXXXt

Function ← Activity 02

Function ← Direct online

Triangular diagrams were plotted using the computer for:-

(1) Cotton - aluminium sulphate - DBBO

X (1) - 100% cotton
0% aluminium sulphate
0% DBBO

X (2) - 70% cotton
30% aluminium sulphate
0% DBBO

X (3) - 70% cotton
0% aluminium sulphate
30% DBBO

(2) Cotton - ammonium sulphamate - DBBO

X (1) - 100% cotton
0% ammonium sulphamate
0% DBBO

X (2) - 70% cotton
30% ammonium sulphamate
0% DBBO

X (3) - 70% cotton
0% ammonium sulphamate
30% DBBO

(3) Cotton - ammonium sulphate - DBBO

X (1) - 100% cotton
0% ammonium sulphate
0% DBBO

X (2) - 70% cotton
30% ammonium sulphate
0% DBBO

X (3) - 70% cotton
0% ammonium sulphate
30% DBBO

(4) Cotton - zinc sulphate - DBBO

X (1) - 100% cotton
0% zinc sulphate
0% DBBO

X (2) - 70% cotton
30% zinc sulphate
0% DBBO

X (3) - 70% cotton
0% zinc sulphate
30% DBBO

2.2.4 The thermobalance

Thermoanalytical studies of the degradation and oxidation of the cellulose and of the extent of interaction between it and the various additives were made using a Mettler "Thermoanalyser 2" thermobalance interfaced to an Apple II microcomputer via a U-microcomputer U-A/D interface, with other hardware and software developed in the Department. 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 the photodiode current is amplified and passed through a coil attached to the balance beam which produces the restoring force. The current in the coil is used to measure the sample mass. The balance allows taring of samples of up to 15.99 g and has three sensitivity ranges, 0-1000 mg, 0-100 mg and 0-10 mg respectively. A weight expansion unit provides greater accuracy by electronic amplification of the weight signal by a factor of ten. An accuracy of ±0.2% of the range can be attained for all three ranges of sample mass.

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

Temperature measurements are carried out by means of a Pt/10%Rh 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 V. An accuracy of ±0.2% over the range can be attained for all six ranges. The analog/digital conversion uses an instrumentation amplifier with linearity error 0.2% and a 12-bit A/D converter with maximum non-linearity 1 bit (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. 2.4). The furnace may be heated from 25 to 1025°C under computer control at a heating rate up to a maximum of ca. 500°/min (linear up to 100°/min).

Sample holder geometry and composition are of great importance in thermal analysis. Two matched flat-bottomed Pt/10%Rh crucibles were used; these were 8 mm in diameter and had a short straight wall rising vertically from the bottom of the crucible. The crucibles were supported on a sintered four-hole capillary tube which had a cross-piece 270 mm from the end, bearing two short alumina pegs, 11 mm apart. Special metal bands, which have no influence on the accuracy of weighing, were used to connect the thermocouple leads from the crucible holder to the fixed balance housing (Fig. 2.5).

The flow of gas through the furnace is controlled by a pressure-regulating valve and the flow rate is metered by a "rotameter". The passage of gas between the balance housing and the reaction area is shielded by a metal baffle which rests in a socket on top of the balance housing when the crucible holder is in position. This prevents any substance which may fall from the crucible from entering and contaminating the balance housing. The gas leaving the furnace can be passed through a gas analyser; in the present work a City Technology CO sensor was used, and the response of this is also read by the computer.

Fig. 2.4 Bifilar quartz spiral furnace

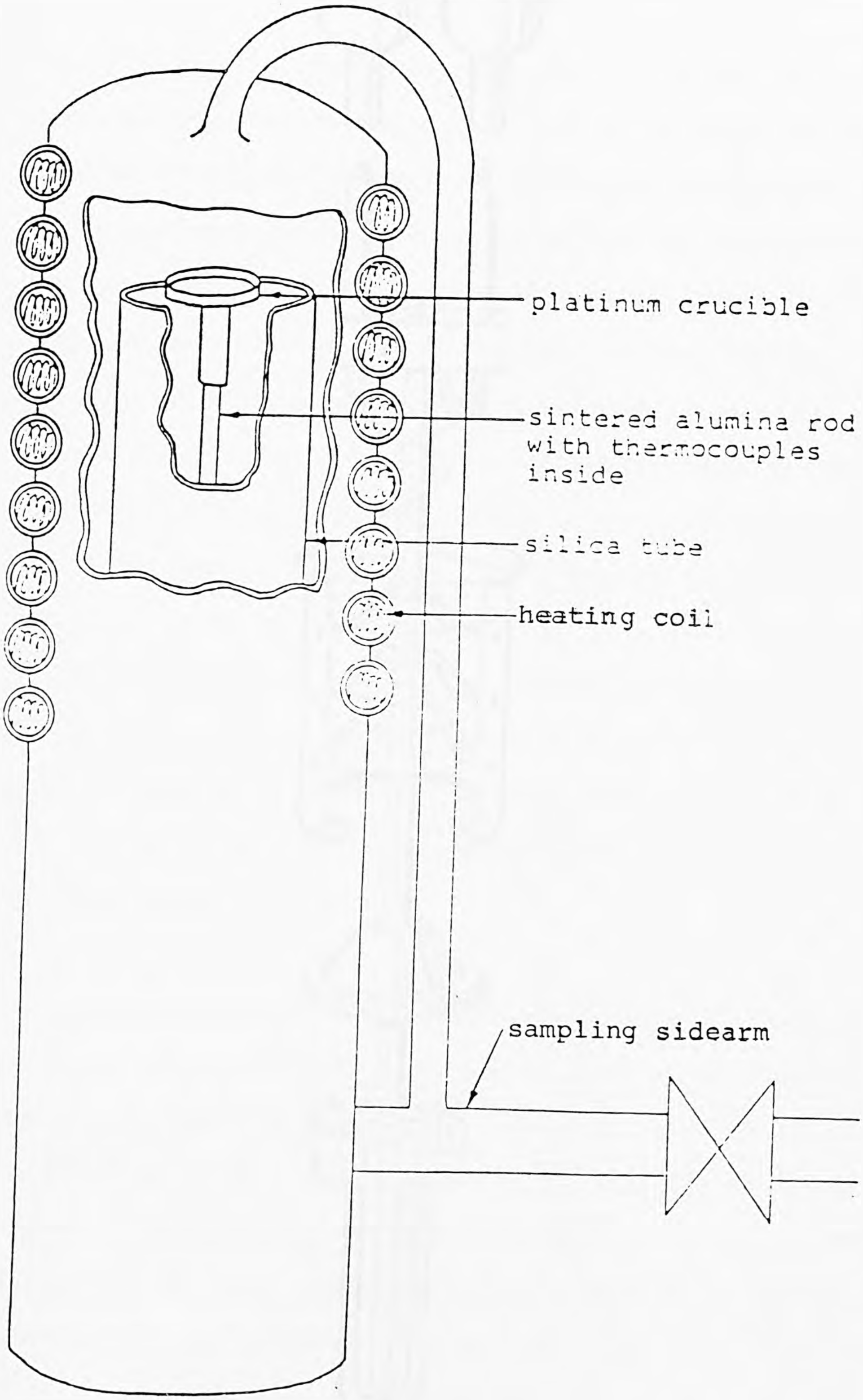


Fig. 2.5 (p. 103)
Crucible holder for DTA
has been removed for
copyright reasons

The limits of error stated in this Section for the various channels other than the temperature channel are lower than those which can be obtained on most other commercial thermobalances. However, although the data points can be read off the recorder chart to a high degree of accuracy, this is impaired by base-line drifts caused by defects inherent in the instrument design. The base-line drift in the weight channel is caused by buoyancy effects due to the heating. In some other commercial thermobalances this has been overcome by use of two matched furnaces, one for each arm of the balance, and by symmetrical design of the balance. In the Mettler "Thermoanalyser 2" thermobalance, most of the base-line drift finishes by the time the sample reaches 75-100°C. The extent of this drift can be as high as 0.15 mg, which corresponds to 1.66% 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 calculations of the peak areas of thermal changes. Because the sample is supported on a long rod inside the furnace, it is impossible to align the crucible with the axis of the furnace. As a result there is a difference in temperature between the sample and reference crucibles, which causes the base-line drift. High heating rates increase the effect significantly.

Base-line drift in DTA would be reduced if a furnace with a more even temperature distribution were used.

A 12-channel, 6-point dot recorder simultaneously traces in different coloured inks, the temperature curve, the two weight traces (natural 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. 2.6 and 2.7 respectively.

2.2.4.1 Mettler computer interface system

Interface hardware: (Fig. 2.8) shows a schematic diagram of the Mettler computer interface system viz. an Apple II microcomputer with twin disc drives, interfaced through a U-Microcomputers U-A/D interface, consisting of a digital board, plugged into one of the Apple expansion slots, connected to an A/D converter unit. The digital board has two 6522 VIA; one is used for timing and the second is used for digital output. The A/D computer board has been modified by adding filtering and by changing the input resistors to give a symmetrical input configuration. The A/D converter unit has eight input channels with a sensitivity

Fig. 2.6 Block schematic diagram of the balance mechanism

[redacted]

Fig. 2.7 Block schematic diagram of the balance mechanism and the recording and electric systems

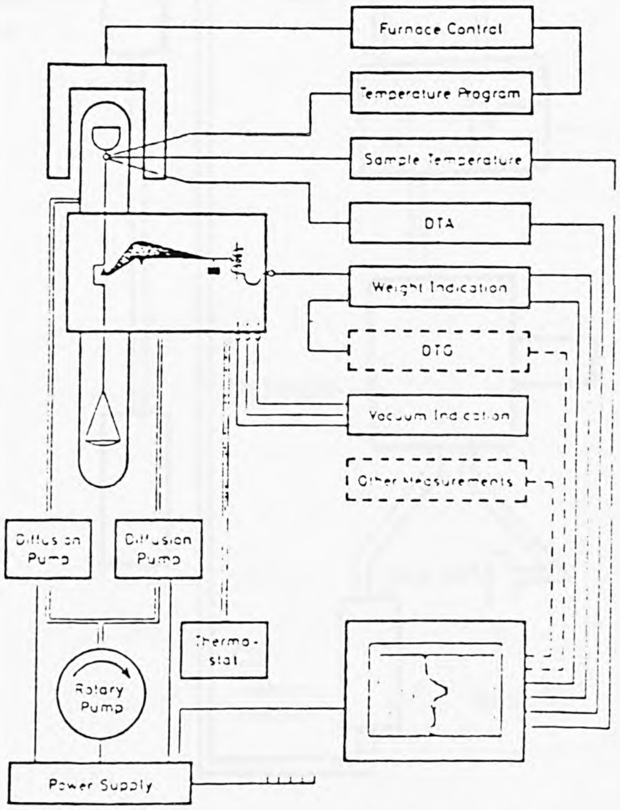
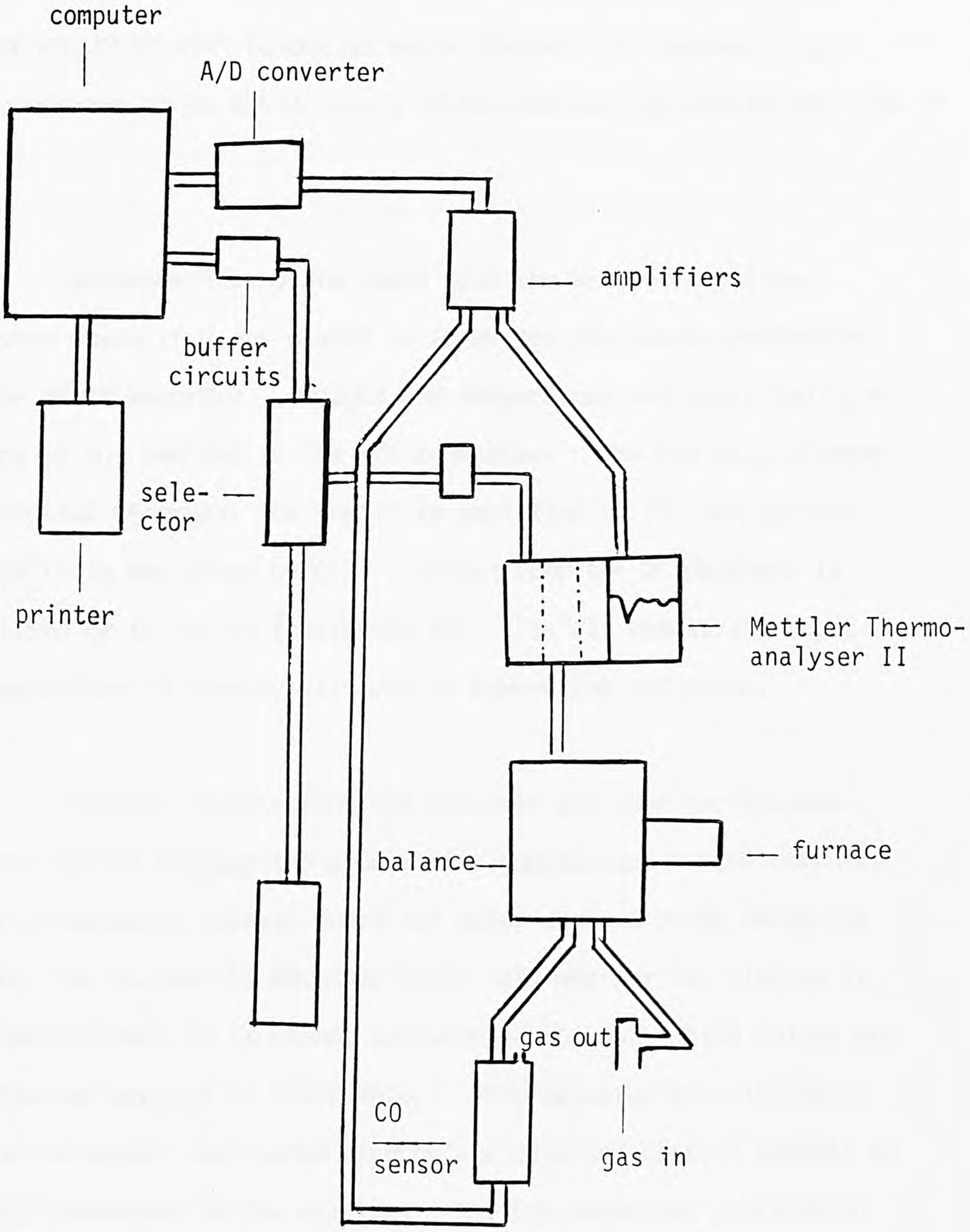


Fig.2.8 Schematic diagram of Mettler Computer interface system



of 100 mV, 1V or 10V (under software control) for maximum output. The converter is an AD574 i.e. a 12-bit device with conversion time of 25μs.

Analogue 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 temperature are amplified by a factor of 10, and fed to the A/D converter. The DTA output feeds two digital channels; for one it is amplified by 25, and for the second it is amplified by 0.5. Output from the CO detector is amplified by 10 or 100 [currently 10]. In all cases, the input to the amplifier is heavily filtered to remove hum and noise.

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 furnace is switched on or off, whether the display is showing figures or is blank, and whether the data which follow are for furnace control or for display. The selector circuit interprets the codes, and routes appropriate data and control signals to the D/A converter or the display. The D/A converter provides a voltage, suitably scaled, which is fed into the furnace control circuits of the Mettler, and a voltage which switches on or off the furnace power. Relays added to the Mettler control unit disconnect the Mettler timing and temperature programme circuits and connect the D/A converter when 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 bcd scaled from 0 to 1275°C in increments of 5°.

2.2.4.2 Software

General scheme: 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 programes: (i) real-time graphical display of input data, for initial setting up, (ii) reading and averaging data provided by standard input conditions, for calibration purposes, and (iii) control and data collection during normal running of the Mettler. Program (ii) produces a file of calibration data which are used by program (iii) to convert digital input to numerical data. Program (iii) samples data continuously and writes selected data (selected by criteria chosen by the user) to one or more data discs.

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

2.2.5 Procedure for thermoanalysis

After the recorder had been switched on, the air flow rate was set at 60 $cm^3\ min^{-1}$ for a sample weight of 8-10 mg. Small strips of cotton fabric were cut from the centre of the whole sample and placed in the crucible. The range shift on the DTG panel was set on manual and a sensitivity of 5mg min^{-1} per full scale deflection was used throughout. The range used for differential thermal analysis was 200μV, while for temperature readings it was 10mV; the heating rate used throughout was $5^{\circ}\ min^{-1}$.

The results of thermogravimetric and differential thermal analysis runs were printed on a 25 cm-wide chart of a six-channel chart recorder.

DTA is often referred to as an "operator-sensitive" technique and indeed differences in procedure, instrument design and sample properties can account for discrepancies observed between different experiments.

2.2.6 Carbon monoxide sensors

A carbon monoxide sensor was obtained from City Technology Limited. This is an electrochemical sensor of the fuel cell type, designed to be maintenance-free and stable over long periods of time. The sensor uses capillary diffusion barrier technology. This results in a low temperature coefficient and a direct response to concentration (volume %) which is virtually unaffected by pressure. The use of electrodes based on fuel cell technology gives a high reserve of activity which makes for long-term stability. Carbon monoxide diffusing to the sensing electrode (anode) reacts according to the equation:

$$CO + H_2O = CO_2 + 2H^+ + 2e^-$$

At the other electrode (cathode) the reaction is:

$$\tfrac{1}{2}O_2 + 2H^+ + 2e^- = H_2O$$

The oxygen required is automatically supplied from the ambient air by controlled diffusion.

The gases liberated on thermal decomposition of the polymer were collected through a furnace specially designed for use with the thermobalance; they were then allowed to pass through the sensor giving a signal corresponding to the amount of carbon monoxide, which is amplified and recorded as ppm of carbon monoxide as a function of the temperature given by the controlled temperature programme.

2.2.7 Microanalytical measurements

Elemental microanalysis was carried out by [redacted] in the Department of Chemistry at The City University, London. Samples for microanalysis were obtained by interrupting the thermal decomposition at temperatures corresponding to the maximum rate of weight loss for the second and third stage.

3. Results

3.1 General

3. General

3.1.1 Flammability measurements

The LOI values determined for the systems with mixtures of additives were fitted by a polynomial function of the composition co-ordinates of the form introduced by Scheffe (1958). A linear transformation of the composition coordinates (Kurotori 1966) was used to enable limited ranges of composition to be studied conveniently and accurately. Although any three different compositions can be used as vertices of a triangular diagram representing composition, only equilateral triangles have been used in this work so as to facilitate visual interpretation of the results. In order to determine the most reliable plots of LOI versus composition and to assess the accuracy of the fit, a longer number of compositions (>40) were studied for each of the four systems, viz. cotton-aluminium sulphate-DBBO, cotton-zinc sulphate-DBBO, cotton-ammonium sulphamate-DBBO and cotton-ammonium sulphate-DBBO. These compositions were spread uniformly over the ranges bounded roughly by the points A: 100 wt% cotton; B: 70 wt% cotton, 30 wt% inorganic salt and C: 70 wt% cotton, 30 wt% DBBO. This region was found, experimentally, to contain all the highest levels of flame retardance up to total additive loadings of 30 wt%. Coefficients of the polynomials were calculated by a least-squares regression analysis procedure. Polynomials of orders 1-4 were tested and the coefficients were defined as below, where y_i represents the calculated LOI for polynomial order i and x_1, x_2 and x_3 are the compositions at the vertices of all the equilateral triangles chosen.

First order polynomial:

$$Y_1 = \sum_{J=1}^{3} a_J x_J$$

Second order:

$$Y_2 = Y_1 + a_4 X_1 X_2 + a_5 X_1 X_3 + a_6 X_2 X_3$$

Third order (reduced):

$$Y_{3r} = Y_2 + a_7 X_1 X_2 X_3$$

Third order (full):

$$Y_3 = Y_{3r} + a_8 X_1 X_2 (X_1 - X_2) + a_9 X_3 X_1 (X_3 - X_1) + + a_{10} X_2 X_3 (X_2 - X_3)$$

Fourth order:

$$Y_4 = Y_3 + a_{11} X_1 X_2 (X_1^2 + X_2^2 - 3X_1 X_2) + a_{12} X_1 X_3 (X_1^2 + X_3^2 - 3X_1 X_3) + a_{13} X_2 X_3 (X_2^2 + X_3^2 - 3X_2 X_3) + a_{14} X_1 X_2^2 X_3 + a_{15} X_1 X_2 X_3^2$$

The quality of the fit was assessed by the value of the root mean square difference between calculated and observed LOI values (σ), by the multiple regression correlation coefficient (RCC), by the sequential F-test for extra variables added, and by examination of the individual differences between the calculated and observed LOI values.

The LOI values, in terms of composition, were represented as a map, for 9-10 equidistant LOI values calculated from the best-fit polynomial and plotted as contour lines of constant LOI. The correlation coefficient should approach 1.0 for a perfect fit, (it is zero if there is no correlation between LOI and the polynomial of the compositions) and for the representation of experimental data to be adequate, should be comparable with the uncertainty in LOI, which can be estimated as ±1 LOI unit. Thus, from these diagrams, the compositions at which the maximum LOI values occur can be obtained. That is to say, the diagrams give useful qualitative information about the systems as well as quantitative information such as the amounts which each component contributes to the flammability which can be found more precisely by examination of the average coefficients over the range X2 or X3 = 0-0.3 for each component. The degree of synergism over this range is represented in the Tables in the following sections by the abbreviation "syn".

3.1.2 The effect of DBBO on its own on the flammability of the cotton fabric

Table 3.1 shows the effect of decabromobiphenyl oxide on the flammability of the cotton. The results show that this compound has relatively little influence on its own, even at loadings as high as 27 wt%, the increase in the LOI being only about 6 LOI units compared with the untreated fabric (LOI, 18.1).

3.1.3 Simultaneous thermal analysis of cotton fabric

Fig. 3.1 shows the DTG and TG curves for the untreated cotton and Table 3.2 gives some characteristic features of the various stages. Pure cotton breaks down in three stages: (i) a very fast main decomposition at 500-600 K representing over 70% weight loss; (ii) a very slow stage up to 720 K; and (iii) a short carbon burn-off stage (CBO) accounting for just over 10% of the original weight of the sample.

3.1.4 Simultaneous thermal analysis of cotton treated with DBBO

Fig. 3.2 shows the DTG and TG curves for a sample treated with DBBO alone and Table 3.3 gives the characteristic features of the various stages. It is quite clear from Fig. 3.2 that the

Table 3.1 **The effect of DBBO on the flammability of cotton**

DBBO (wt%)	LOI
7.11	18.85
10.9	19.7
14.5	19.9
16.29	20.7
23.61	23.2
27.1	24.1

Table 3.2 Thermoanalytical results for untreated cotton

Initial weight (mg)					
Total weight lost (mg/%)	93.5				
T_0 (°C/K)					
$T_{1\%}$ (°C/K)					
Gain Stage					
Wt gain (mg/%)					
DTG_{max} (mg min^{-1}/% min^{-1})					
T (DTG_{max}) (°C/K)					
DTA_{max} (μV/μV mg^{-1})					
T (DTA_{max}) (°C/K)					
T range (°C/K)					
First Loss					
Wt loss (mg/%)					
DTG_{max} (mg min^{-1}/% min^{-1})					
T (DTG_{max}) (°C/K)					
DTA_{max} (μV/μV mg^{-1})					
T (DTA_{max}) (°C/K)					
T range (°C/K)					
Second Loss					
Wt loss (mg/%)	71.8				
DTG_{max} (mg min^{-1}/% min^{-1})	25.0				
T (DTG_{max}) (°C/K)	335				
DTA_{max} (μV/μV mg^{-1})					
T (DTA_{max}) (°C/K)					
T range (°C/K)	225-365				
Third Loss					
Wt loss (mg/%)	10.5				
DTG_{max} (mg min^{-1}/% min^{-1})	0.2				
T (DTG_{max}) (°C/K)	402				
DTA_{max} (μV/μV mg^{-1})					
T (DTA_{max}) (°C/K)					
T range (°C/K)	365-445				
Fourth Loss					
Wt loss (mg/%)	11.2				
DTG_{max} (mg min^{-1}/% min^{-1})	2.0				
T (DTG_{max}) (°C/K)	477				
DTA_{max} (μV/μV mg^{-1})					
T (DTA_{max}) (°C/K)					
T range (°C/K)	455-490				
LOI	18.1				
D_s					

Table 3.3 Thermoanalytical results for cotton + 14.5 wt% DBBO

Initial weight (mg)				
Total weight lost (mg/%)	93.4			
T_0 (°C/K)				
$T_{1\%}$ (°C/K)				
Gain Stage				
Wt gain (mg/%)				
DTG_{max} (mg min^{-1}/% min^{-1})				
T (DTG_{max}) (°C/K)				
DTA_{max} (μV/μV mg^{-1})				
T (DTA_{max}) (°C/K)				
T range (°C/K)				
First Loss				
Wt loss (mg/%)				
DTG_{max} (mg min^{-1}/% min^{-1})				
T (DTG_{max}) (°C/K)				
DTA_{max} (μV/μV mg^{-1})				
T (DTA_{max}) (°C/K)				
T range (°C/K)				
Second Loss				
Wt loss (mg/%)	69.3			
DTG_{max} (mg min^{-1}/% min^{-1})	17.9			
T (DTG_{max}) (°C/K)	325			
DTA_{max} (μV/μV mg^{-1})				
T (DTA_{max}) (°C/K)				
T range (°C/K)	250–360			
Third Loss				
Wt loss (mg/%)	10.9			
DTG_{max} (mg min^{-1}/% min^{-1})	0.3			
T (DTG_{max}) (°C/K)	430			
DTA_{max} (μV/μV mg^{-1})				
T (DTA_{max}) (°C/K)				
T range (°C/K)	360–440			
Carbon burn off				
Wt loss (mg/%)	13.1			
DTG_{max} (mg min^{-1}/% min^{-1})	1.5			
T (DTG_{max}) (°C/K)	455			
DTA_{max} (μV/μV mg^{-1})				
T (DTA_{max}) (°C/K)				
T range (°C/K)	440–505			
LOI	19.9			
D_s				

Fig. 3.1 Thermogravimetric analysis curves for untreated cotton

TG,―――――― DTG, - - - - - - - - -

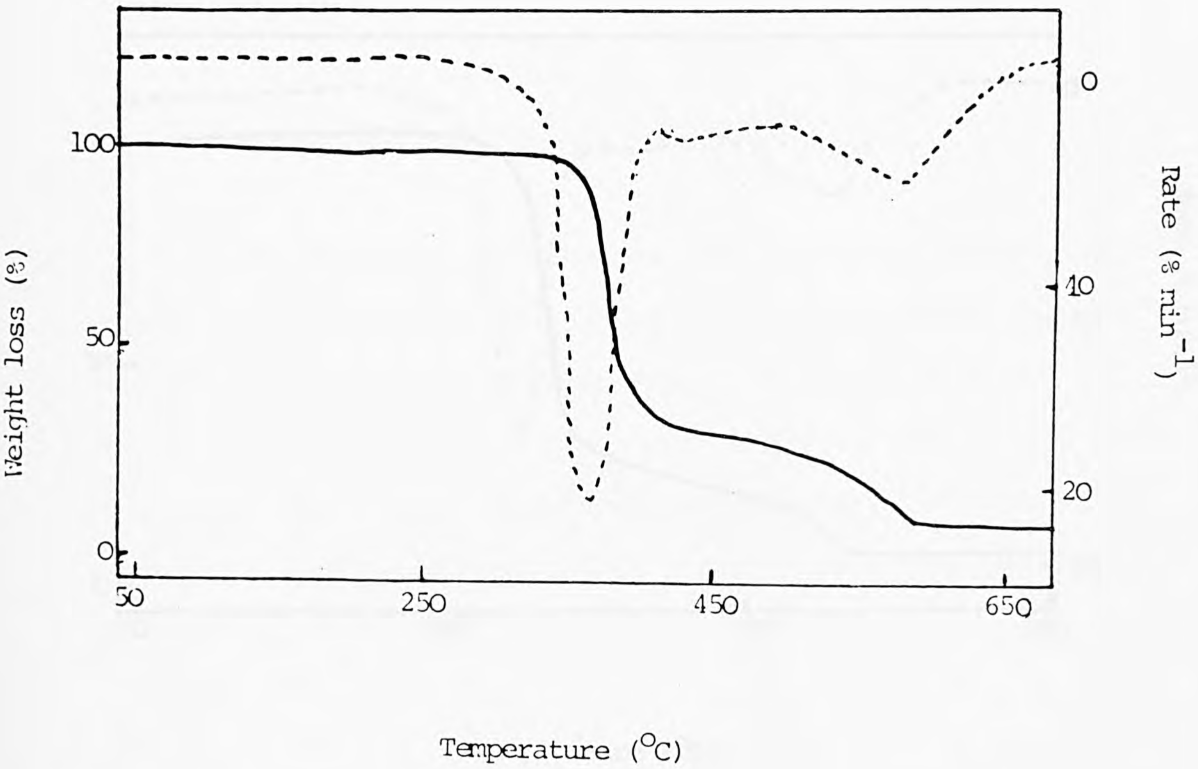
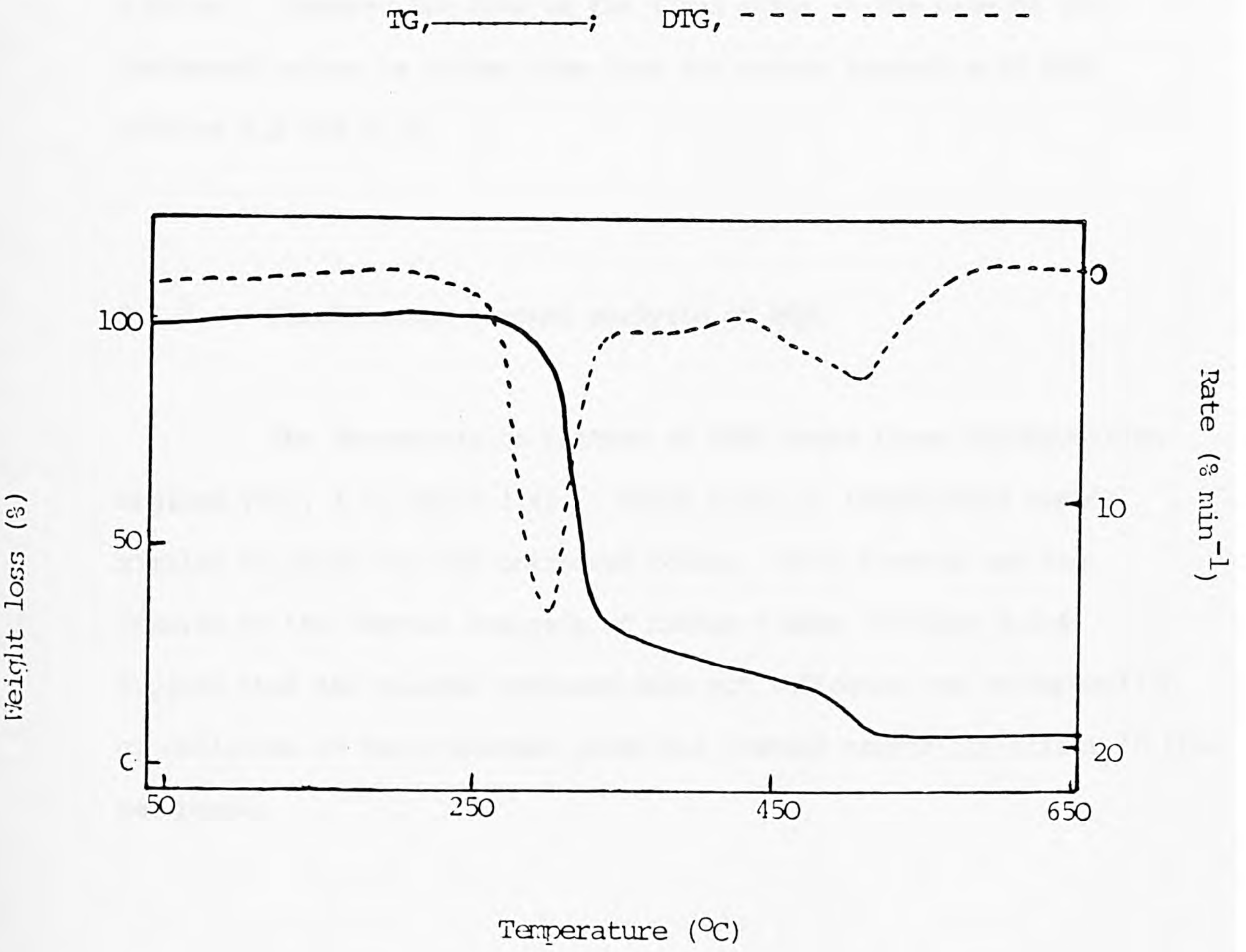


Fig. 3.2 Thermogravimetric analysis curves for cotton treated with 14.5 wt% DBBO



decomposition pattern of the sample is very similar to that of pure cotton and that the extents and the rates of weight loss are similar. However the rate of the final stage in the case of the untreated cotton is higher than that for cotton treated with DBBO (Tables 3.2 and 3.3).

3.1.5 Simultaneous thermal analysis of DBBO

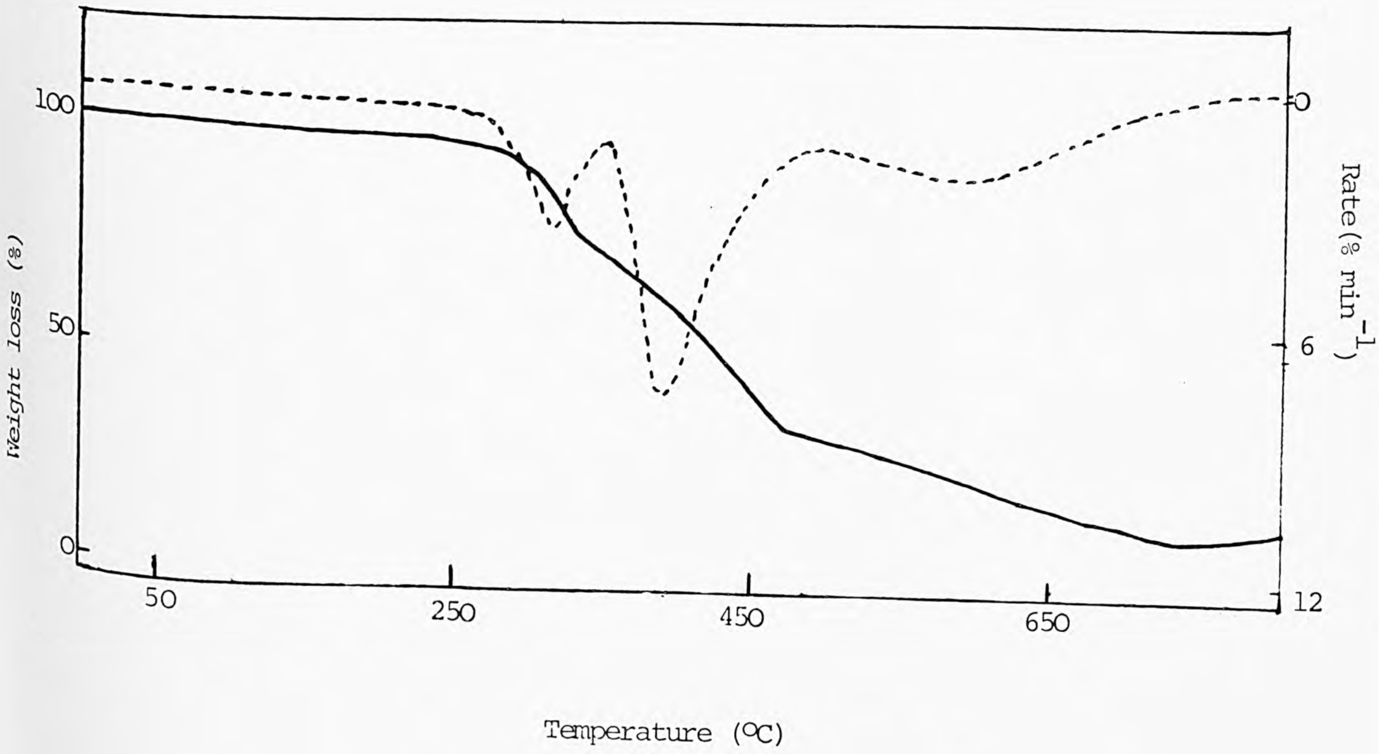
The decomposition pattern of DBBO shows three decomposition regions (Fig. 3.3, Table 3.4). These occur in temperature ranges similar to those for the untreated cotton. This finding and the results of the thermal analysis of cotton + DBBO (Section 3.1.4) suggest that the halogen compound does not influence the decomposition of cellulose in the condensed phase but instead exerts its effect in the gas phase.

Table 3.4 Thermoanalytical results for a 3:1 DBBO-PVC mixture

Initial weight (mg)	8.606				
Total weight lost (mg/%)	93.00				
T_D (°C/K)					
$T_{1\%}$ (°C/K)					
Gain Stage					
Wt gain (mg/%)					
DTG_{max} (mg min^{-1}/% min^{-1})					
T (DTG_{max}) (°C/K)					
DTA_{max} (µV/µV mg^{-1})					
T (DTA_{max}) (°C/K)					
T range (°C/K)					
First Loss					
Wt loss (mg/%)					
DTG_{max} (mg min^{-1}/% min^{-1})					
T (DTG_{max}) (°C/K)					
DTA_{max} (µV/µV mg^{-1})					
T (DTA_{max}) (°C/K)					
T range (°C/K)					
Second Loss					
Wt loss (mg/%)	21.87				
DTG_{max} (mg min^{-1}/% min^{-1})	3.47				
T (DTG_{max}) (°C/K)	315				
DTA_{max} (µV/µV mg^{-1})					
T (DTA_{max}) (°C/K)					
T range (°C/K)	240–330				
Third Loss					
Wt loss (mg/%)	52.43				
DTG_{max} (mg min^{-1}/% min^{-1})	6.395				
T (DTG_{max}) (°C/K)	390				
DTA_{max} (µV/µV mg^{-1})					
T (DTA_{max}) (°C/K)					
T range (°C/K)	330–465				
Fourth Loss					
Wt loss (mg/%)	18.70				
DTG_{max} (mg min^{-1}/% min^{-1})	1.74				
T (DTG_{max}) (°C/K)	550				
DTA_{max} (µV/µV mg^{-1})					
T (DTA_{max}) (°C/K)					
T range (°C/K)	465–700				
LOI					
O_s					

Fig. 3.3 Thermogravimetric analysis curves for 3:1 DBBO-pvc mixture

TG, ————; DTG, - - - - - - - - - - - -



3.2 The effect of aluminium sulphate-DBBO mixtures on the flammability of cotton fabric

3.2 The effect of aluminium sulphate-DBBO mixtures on the flammability of cotton fabric

3.2.1 The effect of aluminium sulphate on its own on the flammability of cotton fabric

Table 3.5 shows the effect of aluminium sulphate (which contains 16 molecules of water of hydration) on the LOI of the fabric. It is clear that aluminium sulphate is a good flame retardant for cotton fabric; for example at a loading of ca. 7 wt% the value of the LOI is 27.4 and at a loading of about 24 wt% it is 45. The data in Table 3.5 show a slight decrease in effectiveness per unit concentration of the additive as the loading is increased.

3.2.2 The combined effect of aluminium sulphate and DBBO on the flammability of cotton fabric

Measurements were made of the LOI of cotton-aluminium sulphate-DBBO ternary systems with over 45 different compositions spread over the range bounded by the points A: 100 wt% cotton; B: 70 wt% cotton; 30 wt% aluminium sulphate and C: 70 wt% cotton; 30 wt% DBBO (Table 3.6). In all the diagrams the statistical analysis shows that better values of the regression correlation coefficient are produced as the order of the polynomial is increased (Table 3.7). Thus, for the first order polynomial the value is 0.823 and increases to 0.993 for the fourth order. The root mean square difference between the calculated and observed LOI values is comparable with the uncertainty in the LOI, which is ± 1 unit, and

Table 3.5 The effect of aluminium sulphate on the LOI value of cotton

Al (wt%)	LOI
2.84	22.8
7.52	27.4
9.91	31.0
11.56	33.4
14.08	36.22
17.39	39.4
18.55	40.7
24.25	45.0

Table 3.6 The effect of a mixture of aluminium sulphate and DBBO on the flammability of cotton

Al (wt%)	DBBO (wt%)	LOI
4.87	20.15	40.4
5.26	19.75	40.7
22.92	5.33	45.95
19.35	7.80	46.2
15.72	15.72	47.1

much improvement in the value of is observed as the order of the polynomial increases. Thus the value decreases from 4.158 for the first order polynomial to 1.466 for the full cubic to 0.927 for the fourth order polynomial.

Table 3.7 also shows the average coefficients over the range of X2 or X3 = 0-0.3 as well as the degree of synergism between the two additives. These values show that the aluminium sulphate contributes the largest amount towards the reduction of the flammability of the fabric. This observation is best represented by the quartic function. The full cubic shows a rapidly increasing LOI as the aluminium sulphate vertex is approached, whereas the observed LOI values give no indication of this.

A sequential F-test also shows that fourth order polynomial coefficients are needed (Table 3.7). A degree of synergism of about 895 with an uncertainty of 54.5 was obtained for the best- fit quartic model. The results in Fig.3.4 suggest that, with 70 wt% cotton present, the maximum LOI is obtained with 3.5 wt% of DBBO and 26.4 wt% of aluminium sulphate i.e. at an atomic ratio of Br:Al of 0.484 which is much less than the stoichiometric ratio in aluminium bromide (3.0). The addition of small amounts of the brominated compound in the presence of large amounts of aluminium sulphate does not seem to affect the LOI significantly. With 24 wt% of aluminium sulphate alone, the LOI value is about 45, whereas at 23 wt% of alumuminium sulphate at 5.3 wt% of DBBO the LOI value is 46 and at 20.2 wt% of DBBO and only

Table 3.7 Regression correlation coefficients (RCC), root mean square errors (σ), F-test ratios, average coefficients and synergism values as a function of the order of the polynomials for cotton-aluminium sulphate-DBBO systems

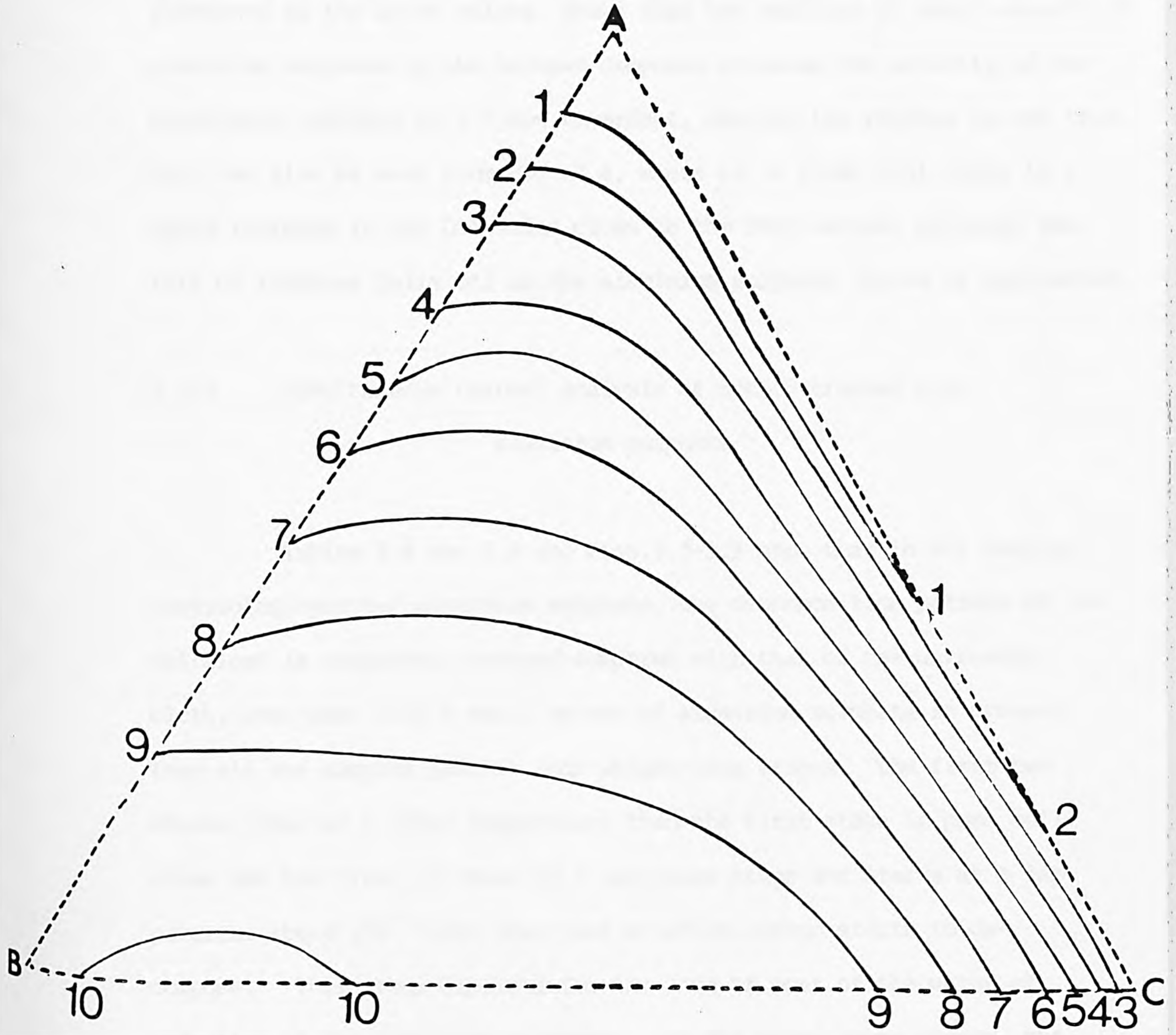
order	RCC	σ	F-test ratio		* average coefficients synergism	
1	0.823	4.158	62.2685	≠Al	117.846	D. 8.69
				DBBO	49.791	D. 10.58
				+syn	0	D. 0
2	0.947	2.366	28.8401	Al	127.957	D. 10.20
				DBBO	46.003	D. 9.83
				syn	649.05	D. 78.77
3r	0.964	1.980	16.8333	Al	109.870	D. 9.47
				DBBO	27.059	D. 9.440
				syn	723.59	D. 68.4
3	0.981	1.466	10.8849	Al	123.370	D. 7.87
				DBBO	29.205	D. 7.88
				syn	741.055	D. 56.25
4	0.993	0.927	10.8865	Al	115.119	D. 5.749
				DBBO	18.456	D. 5.612
				syn	895.496	D. 54.48

*average coefficients over range of X2 or X3 = 0-0.3

+ syn = synergism

≠ Al = aluminium sulphate

Fig. 3.4 Triangular diagram showing variation of LOI with composition for cotton-aluminium sulphate-DBBO systems



LOI values: (0) 18.10; (1) 21.00; (2) 23.90; (3) 26.80; (4) 29.70; (5) 32.60; (6) 35.50; (7) 38.40; (8) 41.30; (9) 44.20; (10) 47.10.

4.9 wt% of aluminium sulphate the LOI value is 40.4. However, as mentioned previously, DBBO by itself has little effect on the LOI and reference to the above values shows that the addition of small amounts of aluminium sulphate to the halogen compound enhances the activity of the brominated compound as a flame retardant, whereas the reverse is not true. This can also be seen from Fig. 3.4, where it is clear that there is a rapid increase in the LOI value close to the DBBO vertex, although the rate of increase falls off as the aluminium sulphate vertex is approached.

3.2.3 Simultaneous thermal analysis of cotton treated with aluminium sulphate

Tables 3.8 and 3.9 and Figs.3.5-3.9 show that in all samples containing hydrated aluminium sulphate, the decomposition pattern of the cellulose is completely changed compared with that of the untreated cloth, even when only a small amount of aluminium sulphate is present. Thus all the samples exhibit four weight-loss stages. The first two stages occur at a lower temperature than the first stage in pure cellulose and the first of these is a very slow stage and starts at a temperature about 170^{o} lower than that at which cotton starts to decompose. This stage accounts for the loss of most of the water of hydration of the aluminium sulphate. In the other three stages, the extents and rates of weight loss are similar to one another, but the

Table 3.8 Thermoanalytical results for cotton + aluminium sulphate

wt% Al	2.84		7.52		11.56
Initial weight (mg)					
Total weight lost (mg/%)	92.6		92.3		90.2
T_0 (°C/K)					
$T_{1\%}$ (°C/K)					
Gain Stage					
Wt gain (mg/%)					
DTG_{max} (mg min^{-1}/% min^{-1})					
T (DTG_{max}) (°C/K)					
DTA_{max} (μV/μV mg^{-1})					
T (DTA_{max}) (°C/K)					
T range (°C/K)					
First Loss					
Wt loss (mg/%)	1.3		2.0		3.7
DTG_{max} (mg min^{-1}/% min^{-1})					
T (DTG_{max}) (°C/K)					
DTA_{max} (μV/μV mg^{-1})					
T (DTA_{max}) (°C/K)					
T range (°C/K)	50–160		50–140		50–165
Second Loss					
Wt loss (mg/%)	37.0		33.9		32.0
DTG_{max} (mg min^{-1}/% min^{-1})	4.8		4.7		4.4
T (DTG_{max}) (°C/K)	247		240		228
DTA_{max} (μV/μV mg^{-1})					
T (DTA_{max}) (°C/K)					
T range (°C/K)	160–290		140–265		165–260
Third Loss					
Wt loss (mg/%)	23.6		26.1		25.9
DTG_{max} (mg min^{-1}/% min^{-1})	1.3		2.2		2.1
T (DTG_{max}) (°C/K)	305		306		308
DTA_{max} (μV/μV mg^{-1})					
T (DTA_{max}) (°C/K)					
T range (°C/K)	290–365		265–370		260–360
Fourth Loss					
Wt loss (mg/%)	30.7		30.3		28.7
DTG_{max} (mg min^{-1}/% min^{-1})	1.6		2.7		2.5
T (DTG_{max}) (°C/K)	441		443		437
DTA_{max} (μV/μV mg^{-1})					
T (DTA_{max}) (°C/K)					
T range (°C/K)	365–475		370–485		360–485
LOI	22.8		27.4		33.4
D_s					

Table 3.9 Thermoanalysis results for cotton + aluminium sulphate

wt% Al	14.08		17.39	
Initial weight (mg)				
Total weight lost (mg/%)	89.1		84.9	
T_0 (°C/K)				
$T_{1\%}$ (°C/K)				
<u>Gain Stage</u>				
Wt gain (mg/%)				
DTG_{max} (mg min^{-1}/% min^{-1})				
T (DTG_{max}) (°C/K)				
DTA_{max} (µV/µV mg^{-1})				
T (DTA_{max}) (°C/K)				
T range (°C/K)				
<u>First Loss</u>				
Wt loss (mg/%)	3.6		6.1	
DTG_{max} (mg min^{-1}/% min^{-1})	0.3			
T (DTG_{max}) (°C/K)	80			
DTA_{max} (µV/µV mg^{-1})				
T (DTA_{max}) (°C/K)				
T range (°C/K)	50–130		50–165	
<u>Second Loss</u>				
Wt loss (mg/%)	31.9		28.9	
DTG_{max} (mg min^{-1}/% min^{-1})	4.5		5.0	
T (DTG_{max}) (°C/K)	227		243	
DTA_{max} (µV/µV mg^{-1})				
T (DTA_{max}) (°C/K)				
T range (°C/K)	130–255		165–265	
<u>Third Loss</u>				
Wt loss (mg/%)	25.9		21.9	
DTG_{max} (mg min^{-1}/% min^{-1})	1.8		2.5	
T (DTG_{max}) (°C/K)	307		313	
DTA_{max} (µV/µV mg^{-1})				
T (DTA_{max}) (°C/K)				
T range (°C/K)	225–360		265–375	
<u>Fourth Loss</u>				
Wt loss (mg/%)	29.3		28.0	
DTG_{max} (mg min^{-1}/% min^{-1})	2.3		3.1	
T (DTG_{max}) (°C/K)	443		453	
DTA_{max} (V/ V mg^{-1})				
T (DTA_{max}) (°C/K)				
T range (°C/K)	360–475		375–505	
LOI	26.20		39.40	
D_s				

Fig. 3.5. Thermogravimetric analysis curves for cotton treated with 2.84 wt% aluminium sulphate

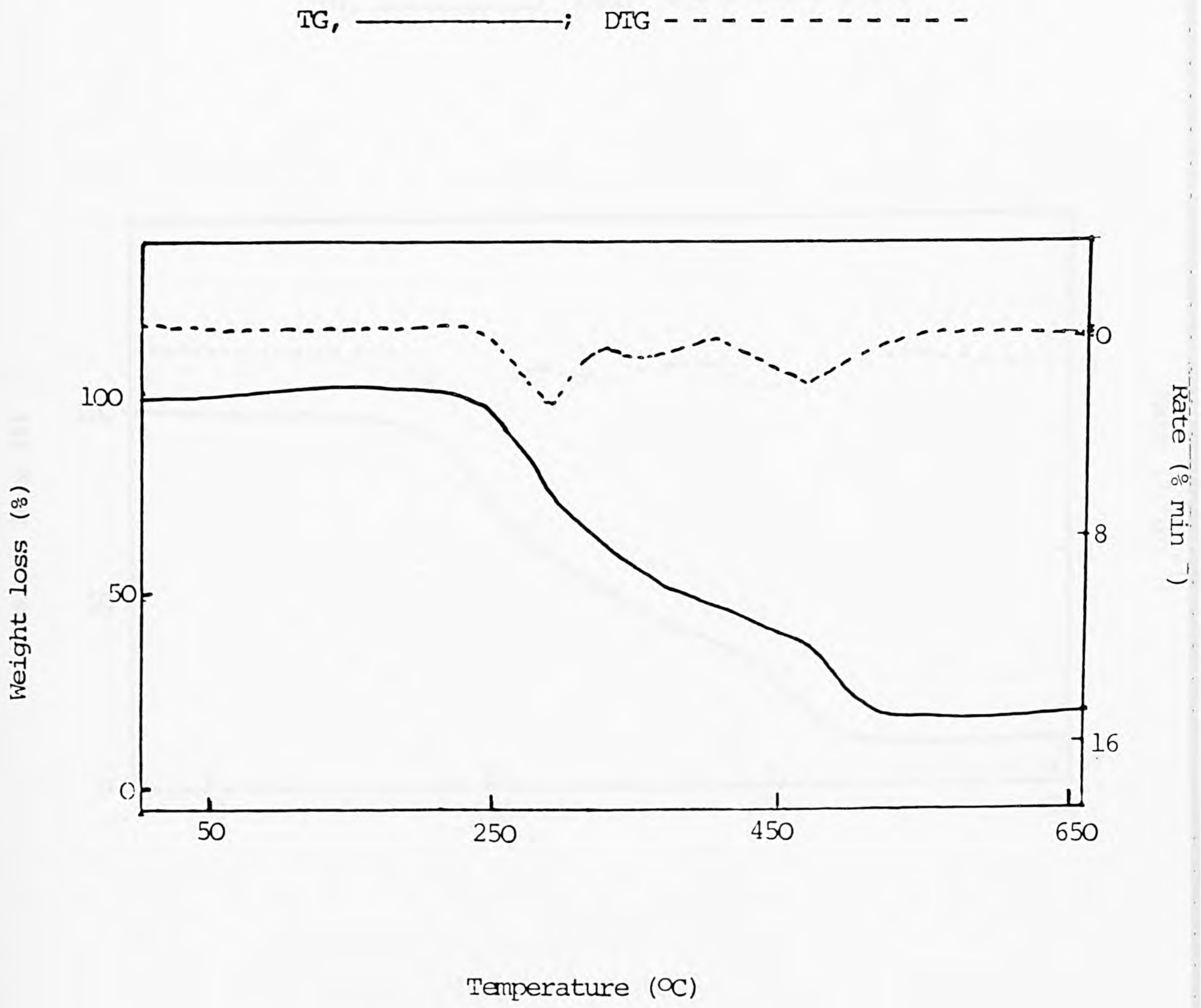


Fig. 3.6. Thermogravimetric analysis curves for cotton treated with 7.52 wt% aluminium sulphate

TG, ————; DTG, - - - - - - - - - -

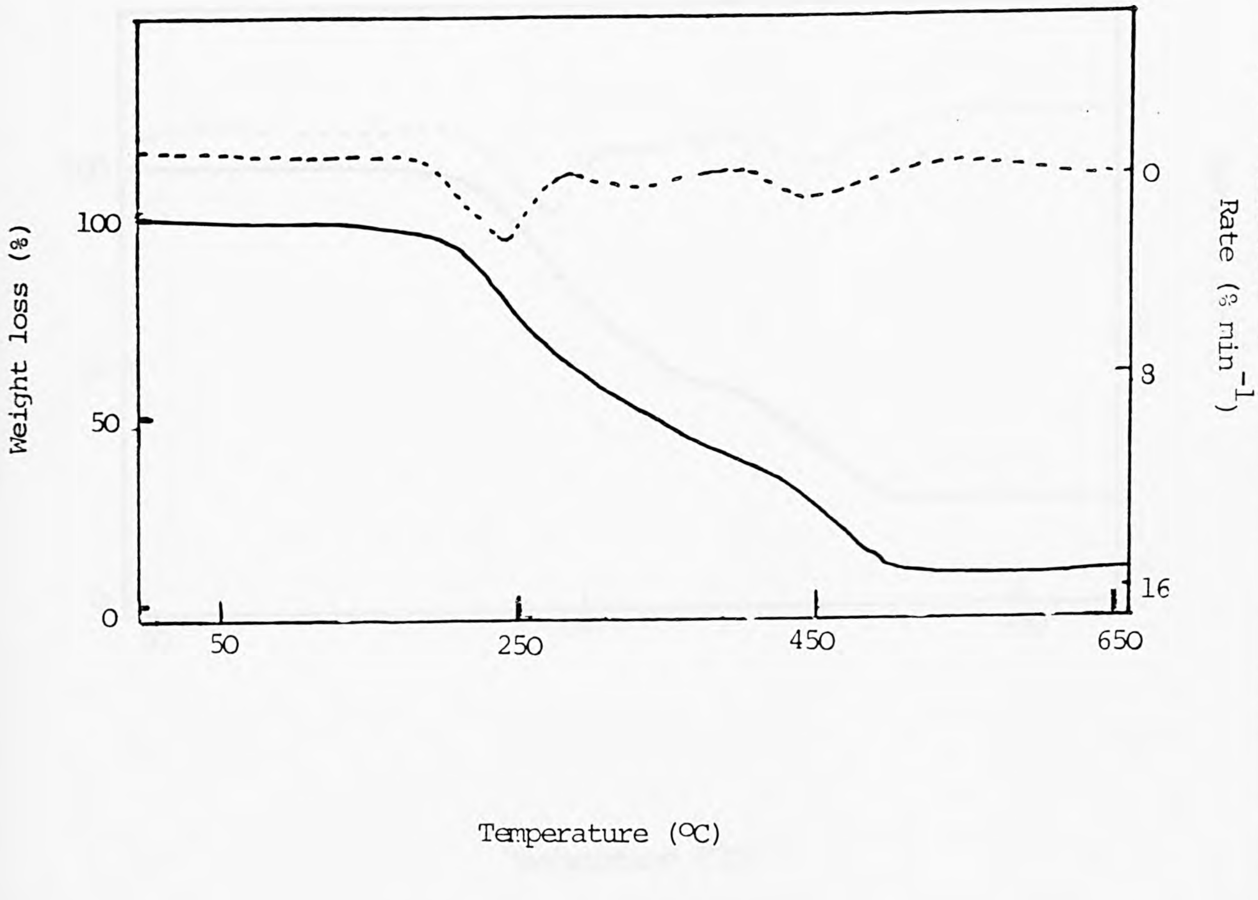


Fig. 3.7. Thermogravimetric analysis curves for cotton treated with 11.56 wt% aluminium sulphate

TG, ———————; DTG - - - - - - - - - -

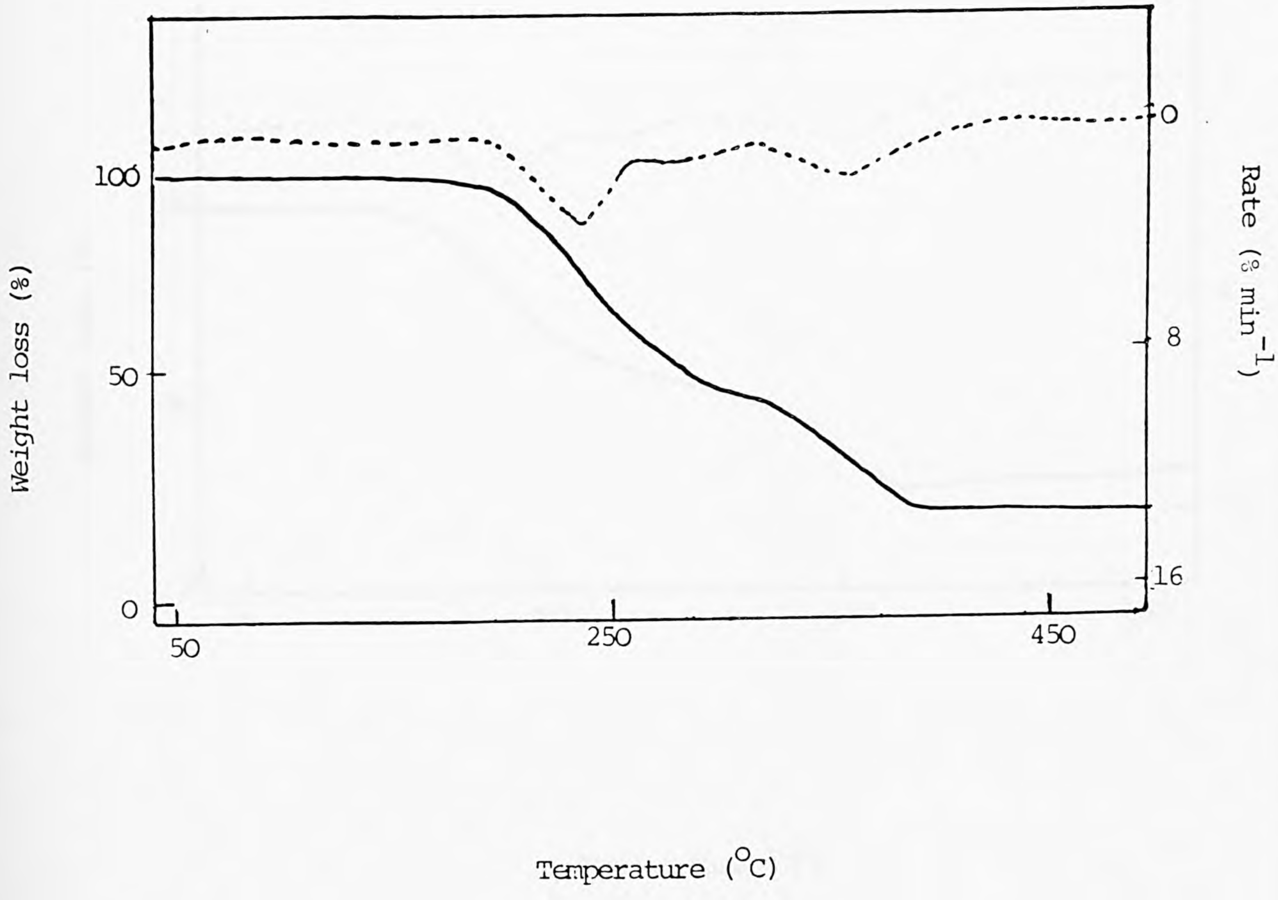


Fig. 3.8. Thermogravimetric analysis curves for cotton treated with 14.08 wt% aluminium sulphate

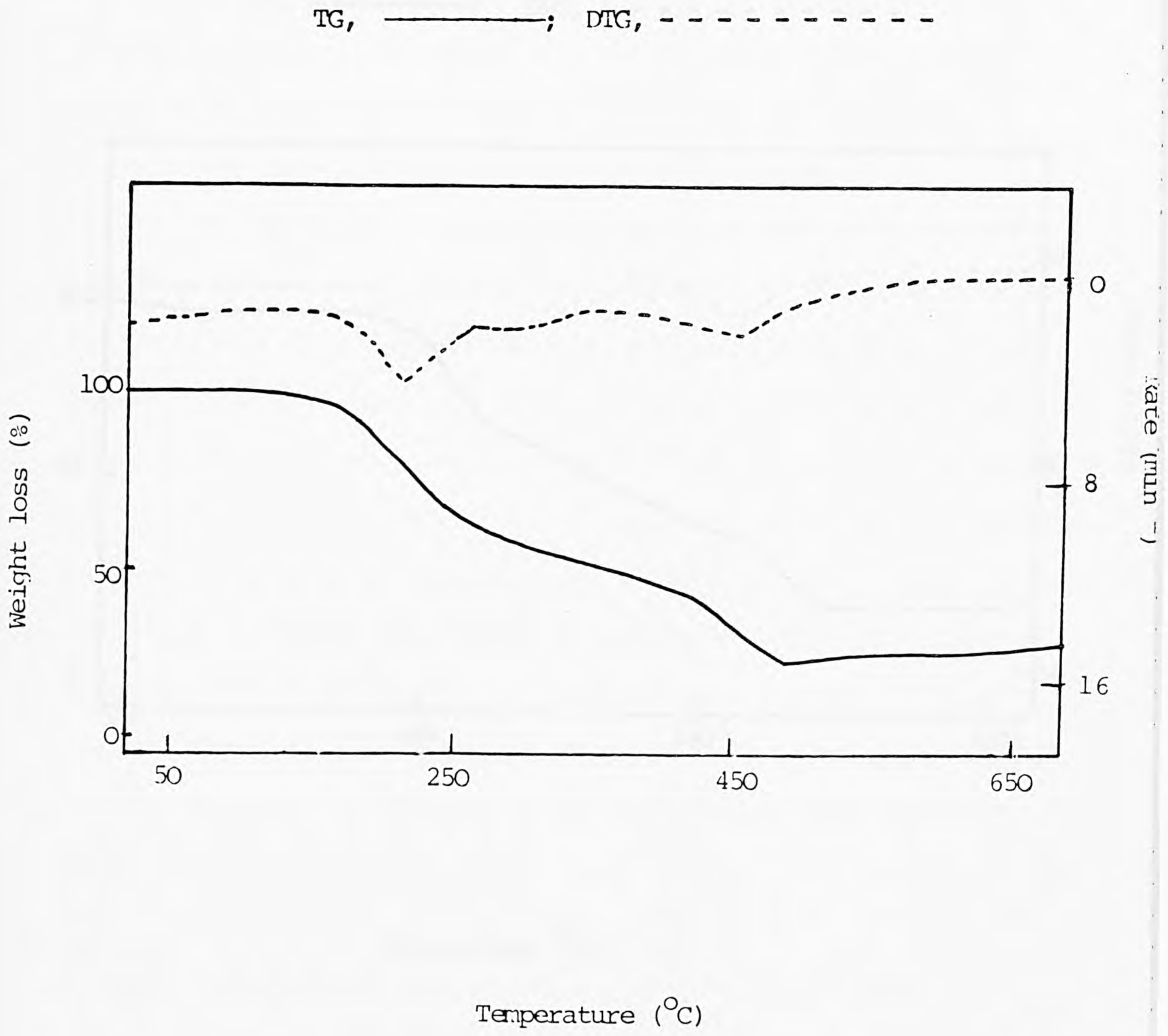
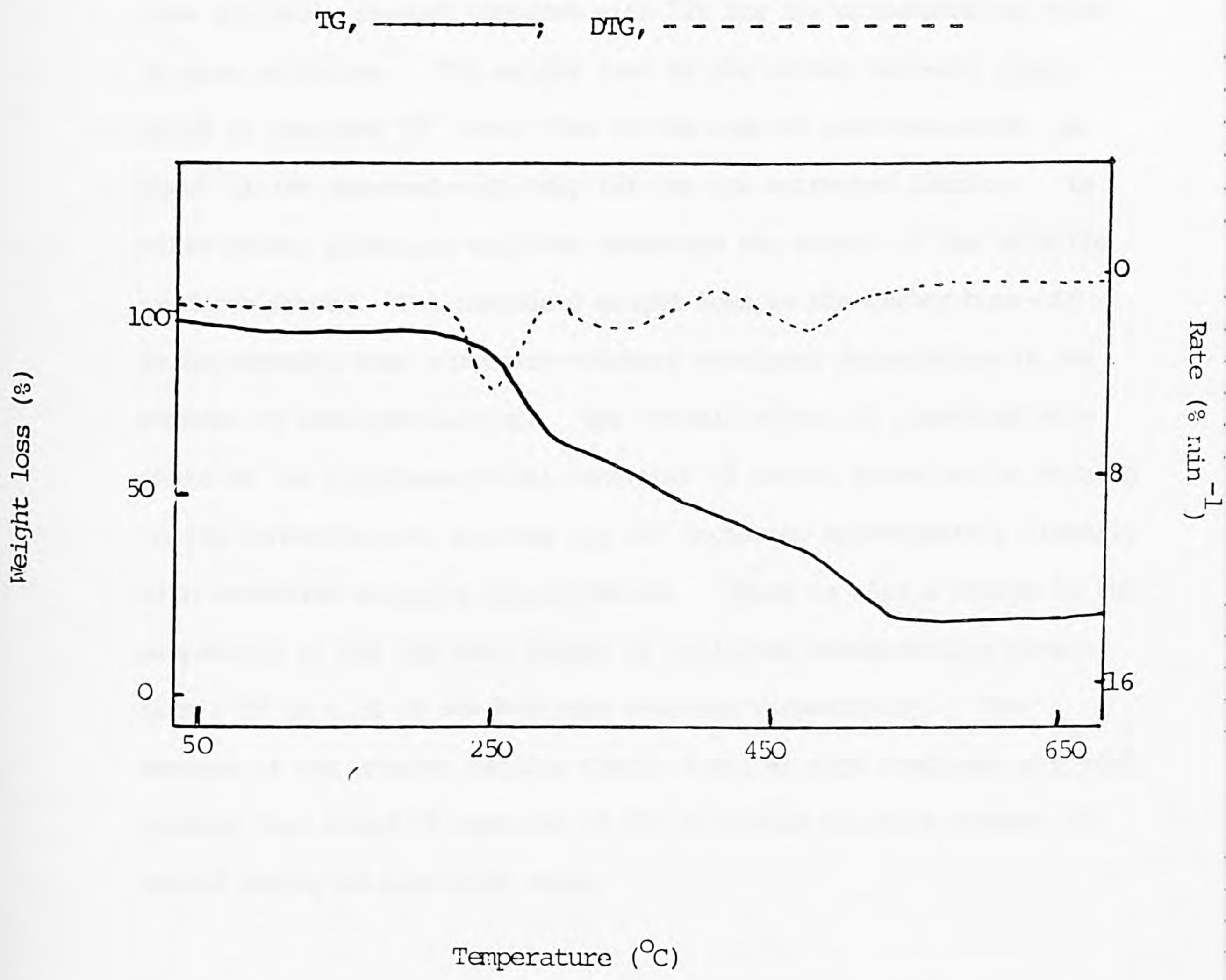


Fig. 3.9 Thermogravimetric analysis curves for cotton treated with 17.39 wt% aluminium sulphate



first of these stages is more rapid than the other two. The total weight loss of the second and third stages is about 60% of the cellulose initially present compared with 72% for the corresponding stage in pure cellulose. The weight loss at the carbon burn-off stage, which is observed 32° lower than in the case of pure cellulose, is about 31-34% compared with only 11% for the untreated fabrics. In other words, aluminium sulphate decreases the amount of the volatile products formed. The increased weight loss at the carbon burn-off stage suggests that aluminium sulphate catalyses dehydration at the expense of depolymerization. The overall effect of aluminium sulphate on the thermoanalytical behaviour of cotton seems not be related to its concentration, whereas the LOI increases approximately linearly with aluminium sulphate concentration. There is also a change in the proportion of the two main stages of cellulose decomposition ranging from 1.57 to 1.32 at low and high loadings respectively. The amounts of the unburnt residue (Table 3.9), at high loadings, are much greater than would be expected if the aluminium sulphate present remained simply as aluminium oxide.

3.2.4 Simultaneous thermal analysis of cotton treated with aluminium sulphate-DBBO mixtures

Table 3.10 and Figs.3.10 and 3.11 show that the addition of the bromine compound to samples treated with aluminium sulphate results in

Table 3.10 Thermoanalytical results for cotton + aluminium sulphate + DBBO

wt% Al.	14.23		12.39	
wt% DBBO	6.69		14.01	
Initial weight (mg)				
Total weight lost (mg/%)	95.2		89.30	
T_0 (°C/K)				
$T_{1\%}$ (°C/K)				
Gain Stage				
Wt gain (mg/%)				
DTG_{max} (mg min^{-1}/% min^{-1})				
T (DTG_{max}) (°C/K)				
DTA_{max} (μV/μV mg^{-1})				
T (DTA_{max}) (°C/K)				
T range (°C/K)				
First Loss				
Wt loss (mg/%)	2.1		1.9	
DTG_{max} (mg min^{-1}/% min^{-1})	0.1		0.1	
T (DTG_{max}) (°C/K)	87		98	
DTA_{max} (μV/μV mg^{-1})				
T (DTA_{max}) (°C/K)				
T range (°C/K)	35-130		50-140	
Second Loss				
Wt loss (mg/%)	26.9		30.1	
DTG_{max} (mg min^{-1}/% min^{-1})	3.8		3.5	
T (DTG_{max}) (°C/K)	228		224	
DTA_{max} (μV/μV mg^{-1})				
T (DTA_{max}) (°C/K)				
T range (°C/K)	130-250		140-250	
Third Loss				
Wt loss (mg/%)	34.8		36.5	
DTG_{max} (mg min^{-1}/% min^{-1})	2.8		3.0	
T (DTG_{max}) (°C/K)	347		341	
DTA_{max} (μV/μV mg^{-1})				
T (DTA_{max}) (°C/K)				
T range (°C/K)	250-365		250-360	
Fourth Loss				
Wt loss (mg/%)	25.6		26.7	
DTG_{max} (mg min^{-1}/% min^{-1})	1.5		1.3	
T (DTG_{max}) (°C/K)	436		440	
DTA_{max} (V/ V mg^{-1})				
T (DTA_{max}) (°C/K)				
T range (°C/K)	365-495		360-495	
LOI	42.8		43.0	
O_s				

Fig. 3.10 Thermogravimetric analysis curves for cotton treated with 14.23 wt% aluminium sulphate and 6.69 wt% DBBO

TG, ——————; DTG - - - - - - - - -

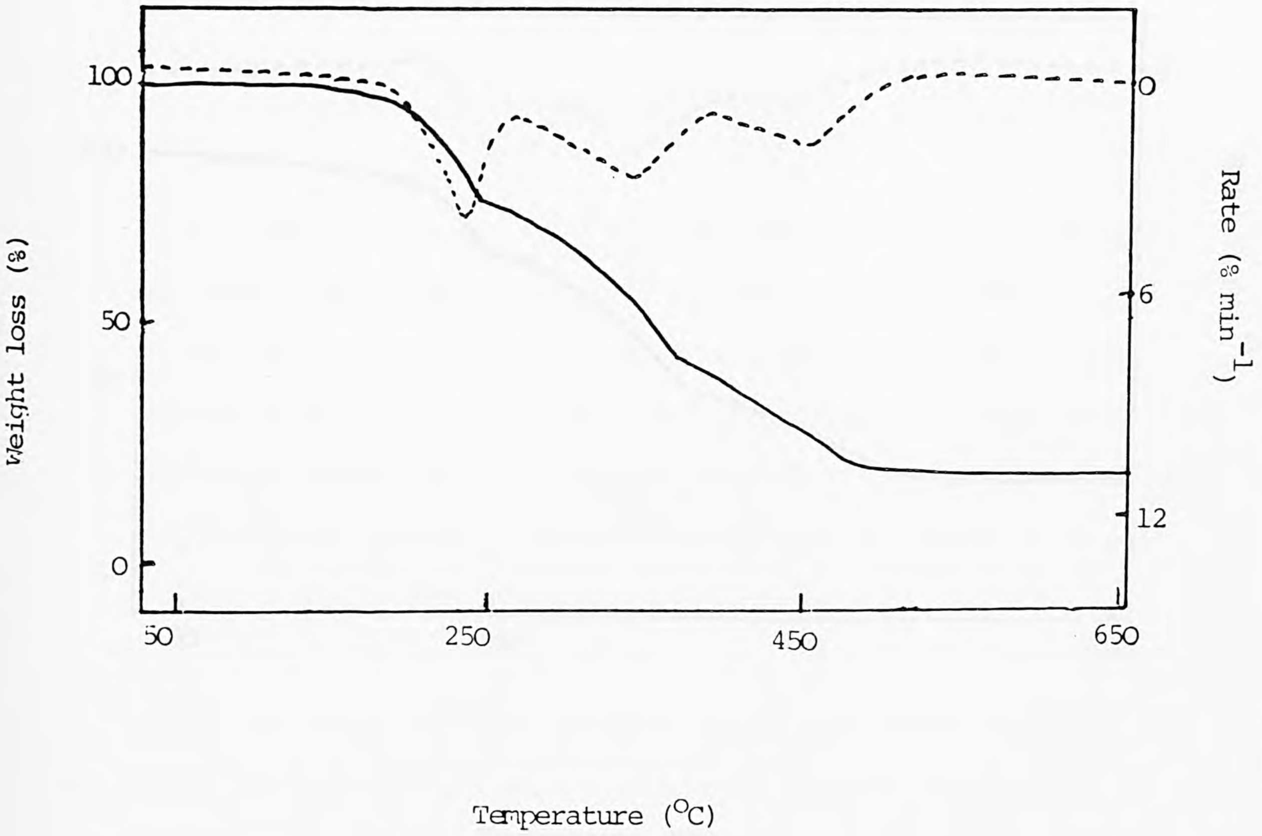
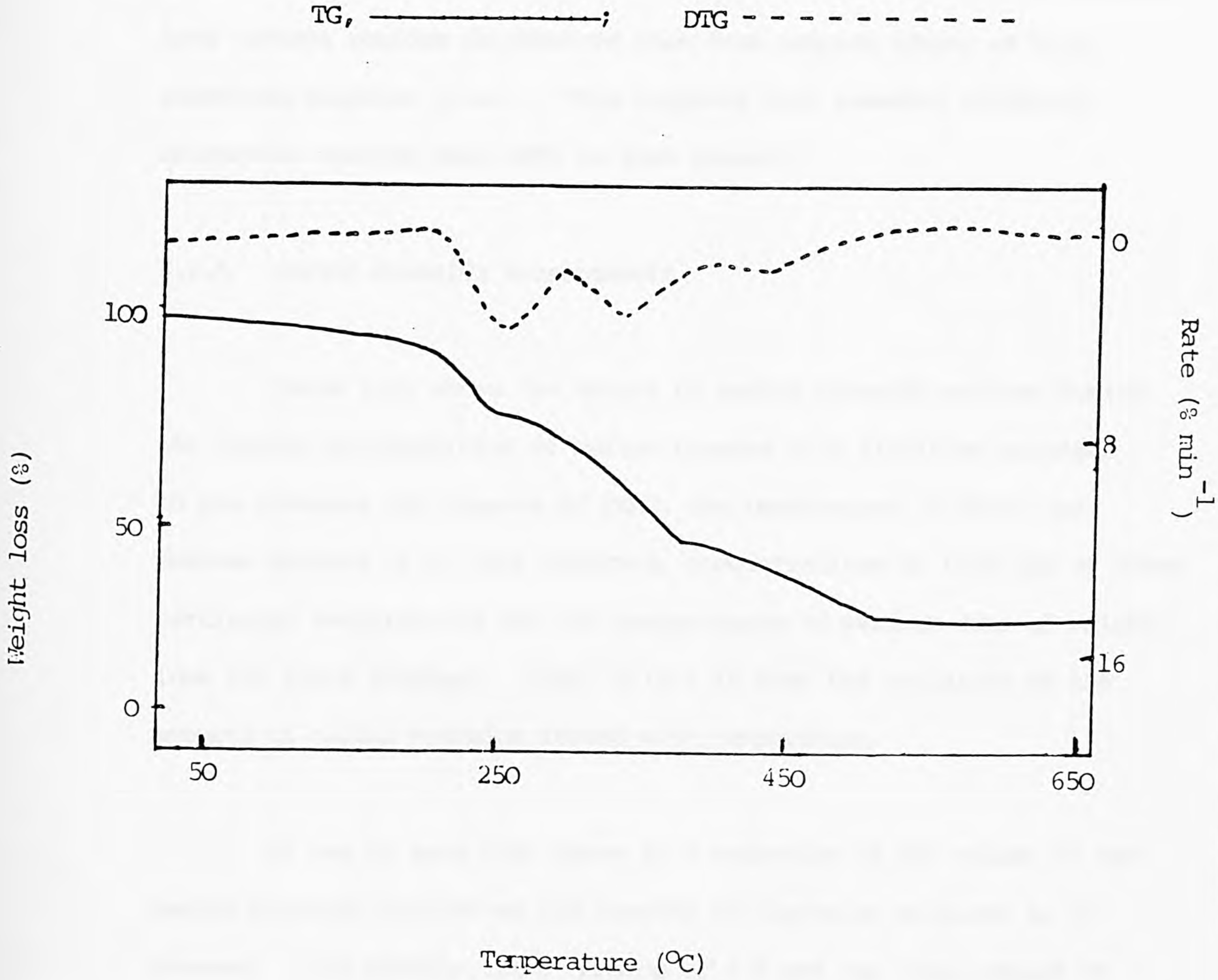


Fig. 3.11 Thermogravimetric analysis curves for cotton treated with 12.39 wt% aluminium sulphate and 14.01 wt% DBBO



effects similar to those found when cotton is treated with aluminiumn sulphate alone. However the ratio of the two main weight loss peaks is now 0.77 and the carbon burn-off weight is about 32%. Furthermore, less unburnt residue is obtained than from samples treat- ed with aluminium sulphate alone. This suggests that somewhat different mechanisms operate when DBBO is also present.

3.2.5 Carbon monoxide measurements

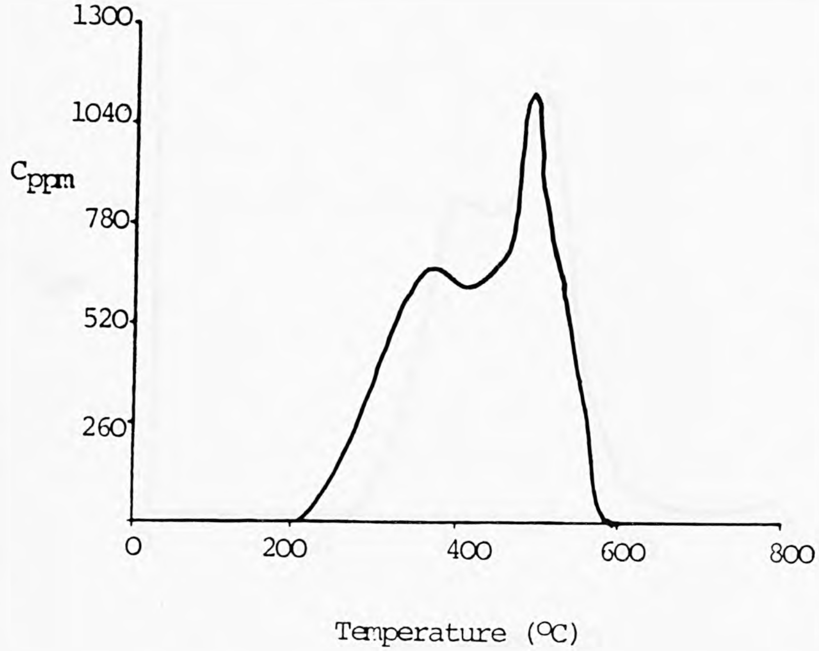
Table 3.11 shows the amount of carbon monoxide evolved during the thermal decomposition of cotton treated with aluminium sulphate in the presence and absence of DBBO, the temperature at which the maximum amounts of CO were observed, concentrations of this gas at these particular temperatures and the temperatures of maximum rate of weight loss for these samples. Figs. 3.12-3.14 show the variation of the amounts of carbon monoxide formed with temperature.

It can be seen that there is a reduction in the volume of the carbon monoxide evolved as the loading of aluminium sulphate is increased. For example, at a loading of 7.5 wt% the total amount of the gas is 0.91 ml, whereas at a higher loading of Ca 11.6 wt% the volume is decreased to 0.76 ml. The temperature at which the carbon monoxide peaks were obtained are about 40° higher than those at which the third and the fourth DTG maxima occur. The addition of the bromine compound increases the total amount of carbon monoxide

Table 3.11 The variation of carbon monoxide concentration with additives composition

wt% salt	wt% DBBO	$V_{co/ml}$	maximum concentration (ppm)	$T(CO_{max})$	maximum concentration (ppm)	$T(CO_{max})$	T max rate		
							2nd	3rd	4th
7.52	-	0.910	590	350	1261.3	475	247	305	441
11.56	-	0.757	650	364	878	470	240	306	443
14.23	6.69	1.315	-	-	1382	490	226	347	436

Fig. 3.12 The variation of carbon monoxide concentration with temperature for cotton treated with 7.52 wt% aluminium sulphate



The total volume of carbon monoxide evolved during the thermal decomposition of cotton treated with 7.52 wt% aluminium sulphate

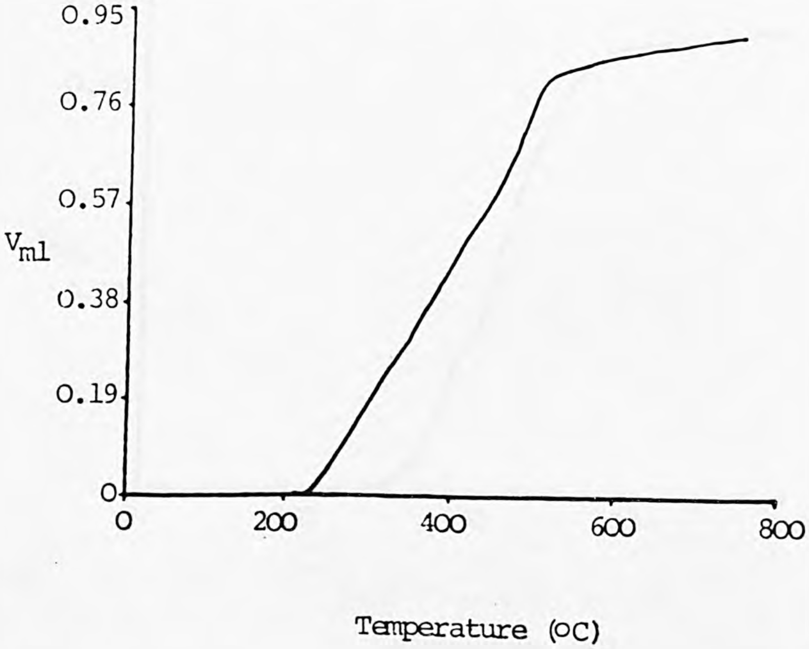
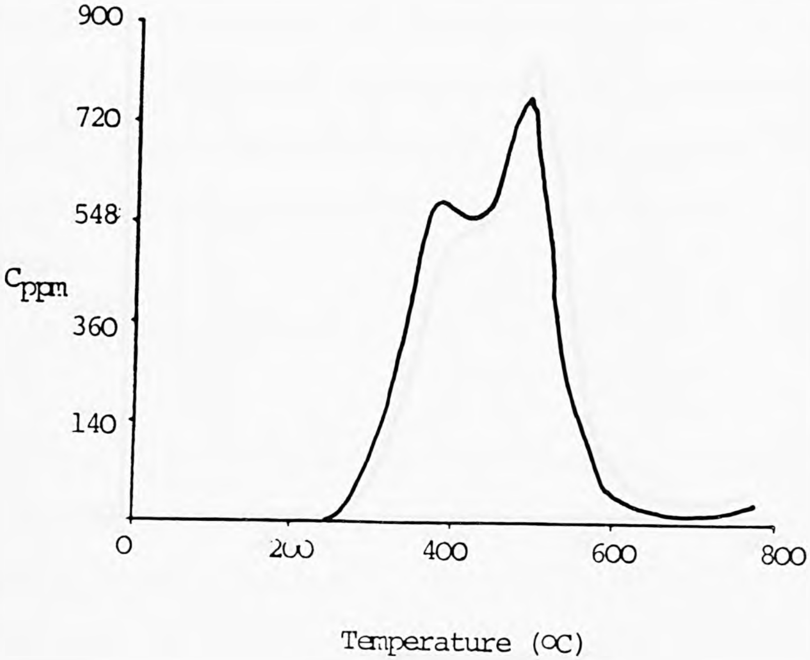


Fig. 3.13 The variation of carbon monoxide concentration with temperature for cotton treated with 11.50 wt% aluminium sulphate



The total volume of carbon monoxide evolved during the thermal decomposition of cotton treated with 11.5 wt% aluminium sulphate

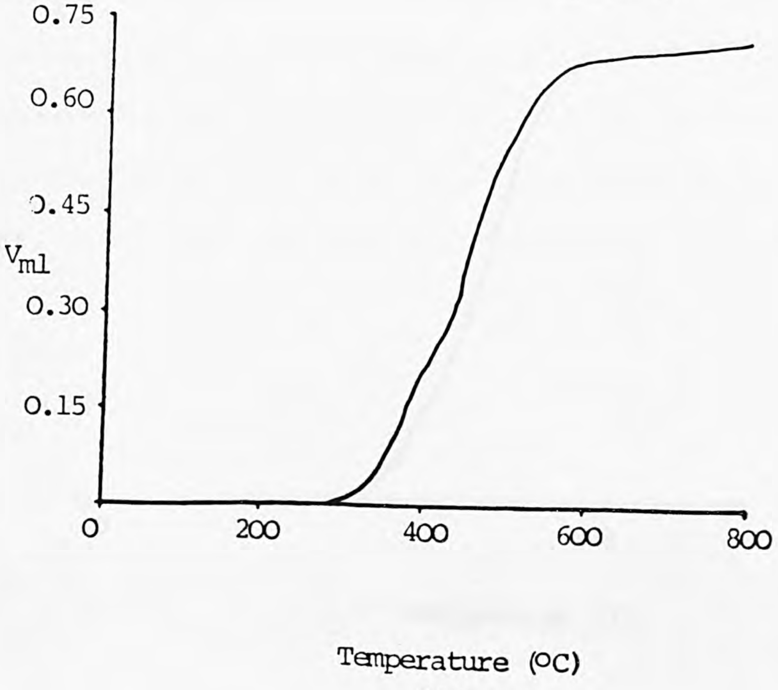
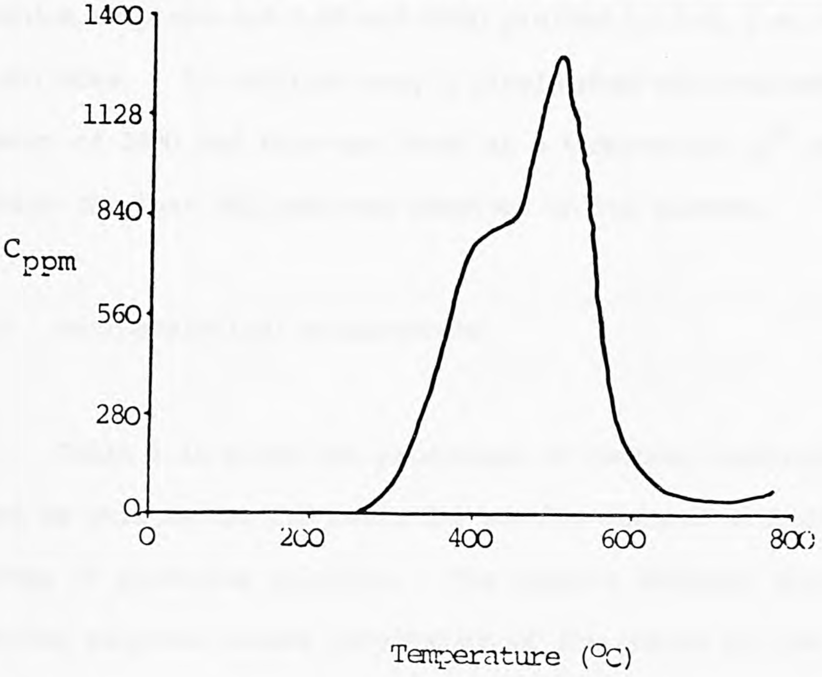
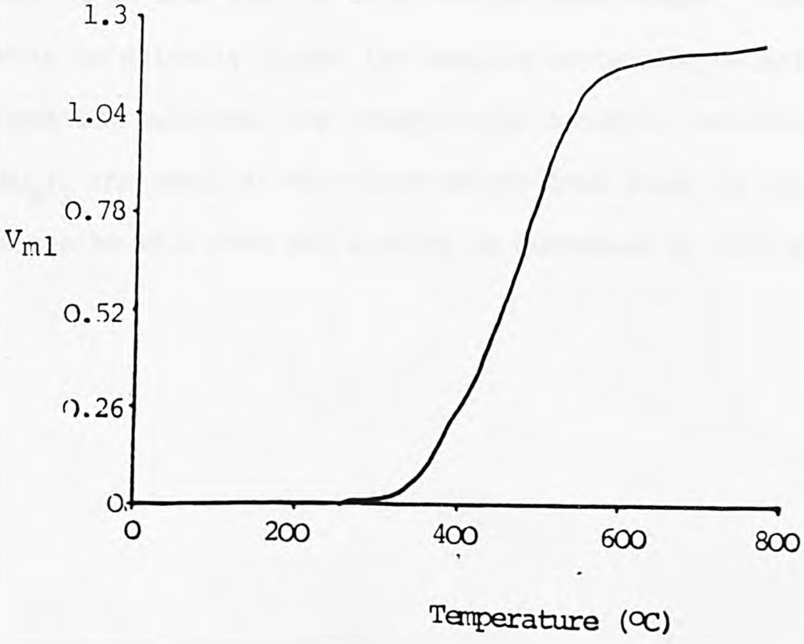


Fig. 3.14 The variation of carbon monoxide concentration with temperatures for cotton treated with 14.2 wt% aluminium sulphate and 6.7 wt% DBBO



The total volume of carbon monoxide evolved during the thermal decomposition of cotton treated with 14.20 wt% aluminium sulphate and 6.7 wt% DBBO



formed. For example a sample treated with about 11.5 wt% of the $Al_2(SO_4)_3$ gave 0.76 ml whereas one treated with 14.2 wt% aluminium sulphate and 6.69 wt% DBBO yielded 1.31 ml i.e. about 0.6 mol more. In addition only a single peak was obtained in the presence of DBBO and this was found at a temperature 50° above that at which the last DTG peak was observed in its absence.

3.2.6 Microanalytical measurements

Table 3.12 gives the percentage of carbon, hydrogen and oxygen as well as the C:H ratio for samples treated with different loadings of aluminium sulphate. The results indicate that the aluminium sulphate causes dehydration of the cotton so that the C/H ratio is much higher than in the case of pure cellulose. Furthermore the extent of dehydration is much greater in the third weight loss stage. For example the C:H ratio was found to be about 12.7 at the temperature of the maximum rate for the second weight loss stage, whereas it is 18.9 for the third weight loss stage. The C/H ratio was found to be slightly higher for samples containing relatively low loadings of aluminium sulphate; for example with a sample containing 17.39 wt% $Al_2(SO_4)_3$ the ratio at the third weight loss stage is 18.9 but increases to 19.1 when the loading is decreased to 7.52 wt%.

Table 3.12 Microanalysis measurements for samples treated with aluminium sulphamate

wt% salt	weight loss stage	%C	%H	%O	C:H
7.5	2nd	58.369	4.303	37.328	13.564
	3rd	60.260	3.155	36.585	19.099
17.4	2nd	55.33	4.361	40.300	12.687
	3rd	57.84	3.058	39.461	18.914

3.3 The effect of zinc sulphate-DBBO mixtures on the flammability of cotton fabric

3.3 The effect of zinc sulphate-DBBO mixtures on the flammability of cotton fabric

3.3.1 The effect of zinc sulphate on its own on the flammability of cotton fabric

Table 3.13 gives the LOI values for some cotton samples containing zinc sulphate together with the percentage weight of this inorganic salt. It is clear that there is an increase in the LOI values as the loading of the salt increases, although this increase is not as great as those caused by the addition of other sulphur compounds such as aluminium sulphate (Section 3.2). Thus a LOI value of 21.2 is obtained on addition of about 5 wt% of zinc sulphate and at a loading of about 21.6 wt% the LOI reaches 29.4, i.e. 11 LOI units above that for untreated cotton. It can also be seen from Fig.3.15 that there is a steady increase in the LOI values until a loading of about 10 wt% zinc sulphate is reached and then the value increases more rapidly as the concentration of the salt is increased.

3.3.2 The combined effect of zinc sulphate and DBBO on the flammability of cotton fabric

The results in Table 3.14 indicate that decabromobiphenyl oxide, when added to cellulose pretreated with zinc sulphate, greatly increases the flame retardant activity of this inorganic salt.

Table 3.13 The effect of zinc sulphate on the LOI value of cotton

Zn (wt%)	LOI
5.64	21.2
9.90	21.7
14.06	27.1
15.52	27.2
21.65	29.4

Fig. 3.15 The effect of zinc sulphate on the flammability of cotton fabric

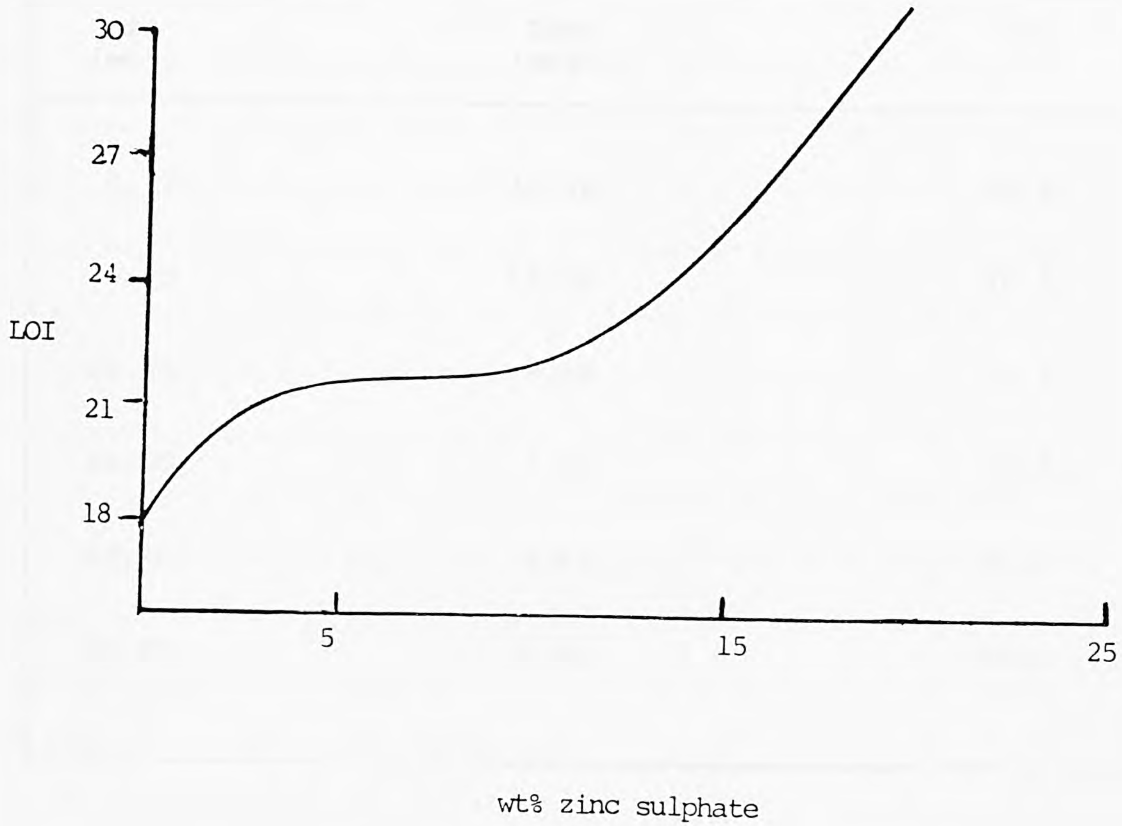


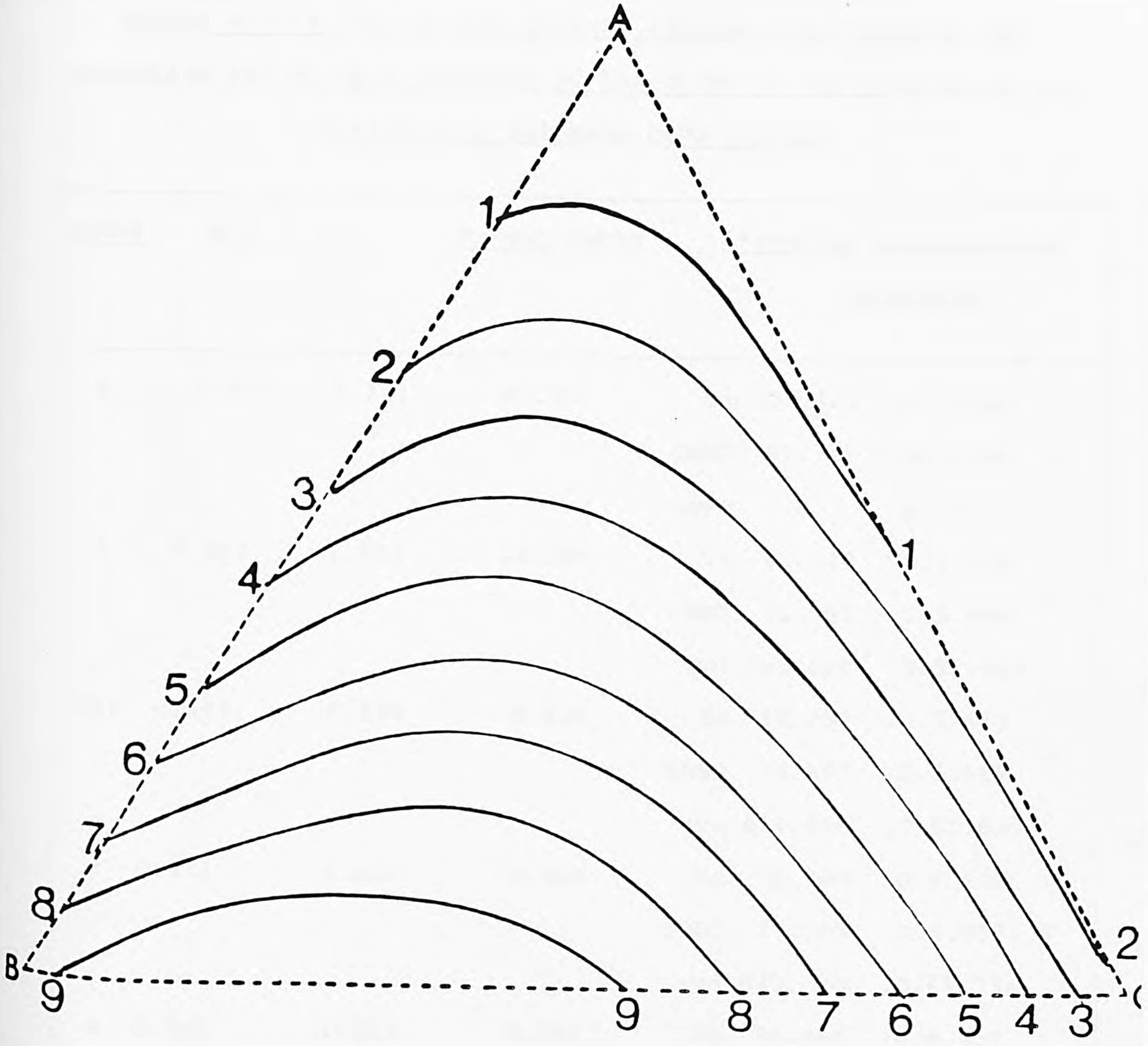
Table 3.14 The effect of a mixture of zinc sulphate and DBBO on the flammability of cotton

Zn (wt%)	DBBO (wt%)	LOI
5.37	13.48	29.9
9.79	14.80	36.4
15.60	9.38	38.9
20.00	7.81	43.9
20.80	4.65	40.2
21.70	5.90	40.0

Thus for example a system containing 21.6 wt% of zinc sulphate has a LOI of 29.4 (Table 3.14), whereas a system containing a mixture of 21.7 wt% of zinc sulphate and about 6 wt% of the brominated compound has a LOI of 40.0 i.e. the addition of only a small amount of the brominated compound causes an increase in the LOI value of about 11 units over that of a sample containing the above amount of zinc sulphate alone. However, as mentioned before, the decabromobiphenyl oxide has little effect on its own in increasing the LOI value of the fabric. Fig.3.16 is a map of the LOI values for a reduced cubic polynomial in terms of composition for up to 9 equidistant LOI values; these are plotted as contour lines of constant LOI for the system bounded by the vertices: A: 100% cotton, B: 70% cotton, 30% zinc sulphate; and C: 70% cotton, 30% DBBO. Table 3.15 gives the parameters of all the fitting routines. These include the average coefficients over the range X2 or X3 = 0–0.3, the degree of synergism between the two additives, RCC values, σ values and the F-test ratio. The reduced cubic polynomial is found to give the best fit with a correlation coefficient close to the optimum value of 1.0 and a value for σ of 1.32; this latter value is comparable with the uncertainty value which is estimated at ±1 LOI unit and thus provides a good representation of the experimental data.

Little improvement occurred on using the full cubic model as

Fig. 3.16 Triangular diagram showing variation of LOI with composition for cotton-zinc-sulphate-DBBO system



LOI values: (0) 18.10; (1) 20.68; (2) 23.26; (3) 25.84; (4) 28.42; (5) 31.00; (6) 33.58; (7) 36.16 (8) 38.74; (9) 41.32

Table 3.15 Regression correlation coefficients (RCC) root mean square errors (σ), F-test ratios, average coefficients and synergism values as a function of the order of the polynomial for cotton-zinc sulphate-DBBO systems

order	RCC		F-test ratio		*average coefficients synergism	
1	0.827	3.214	65.761	Zn	107.424	.D.7.706
				DBBO	61.719	.D.7.956
				+syn	0	.D. 0
2	0.967	1.451	54.384	Zn	62.840	.D.5.928
				DBBO	21.993	.D.5.620
				syn	595.606	.D.55.039
3r	0.973	1.324	8.626	Zn	58.208	.D.5.635
				DBBO	14.897	.D.5.669
				syn	614.466	.D.50.639
3	0.979	1.228	2.994	Zn	58.369	.D.6.525
				DBBO	19.013	.D.5.852
				syn	643.020	.D.68.786
4	0.980	1.303	0.241	Zn	59.465	.D.8.553
				DBBO	18.013	.D.6.508
				syn	546.183	.D.193.690

* average coefficients over a range of X2 or X3=0-0.3

\+ syn = synergism

≠ Zn = zinc sulphate

shown in Table 3.15. It is clear from Fig 3.16 that, for a mixture of the two components, the values of the LOI increase rapidly close to the DBBO-cotton axis and then gradually level off. A broad maximum of LOI values is obtained when some DBBO is replaced by zinc sulphate. Thus, for example, at a total additive loading of about 27 wt% the LOI increases rapidly as the concentration of the zinc sulphate increases until the weight ratio of Br/Zn becomes equal to 1.5. At this point the LOI remains essentially constant up to a weight ratio of 0.25 and the maximum LOI values are obtained at an atomic ratio of Br/Zn of 0.834 which is less than the stoichiometric ratio for this system.

3.3.3 Simultaneous thermal analysis of cotton treated with zinc sulphate

Figs. 3.17-3.19 show some TG and DTG curves for samples treated with zinc sulphate and Table 3.16 presents some characteristic features of the various stages. With all the samples into which zinc sulphate is impregnated, decomposition occurs over a wide range of temperature in contrast to the behaviour observed with pure cellulose. The treated samples exhibited four weight loss stages. The first accounts for the loss of water by hydration from the salt and the second and third stages both occur at temperatures lower than that at which cellulose itself begins to decompose.

Table 3.16 Thermoanalytical results for cotton + zinc sulphate

wt% zinc sulphate	7.64	15.52	21.65
Initial weight (mg)	8.100	8.200	9.098
Total weight lost (mg/%)	82.80	86.5	77.84
T_0 (°C/K)			
$T_{1\%}$ (°C/K)			
Gain Stage			
Wt gain (mg/%)			
DTG_{max} (mg min^{-1}/% min^{-1})			
T (DTG_{max}) (°C/K)			
DTA_{max} (μV/μV mg^{-1})			
T (DTA_{max}) (°C/K)			
T range (°C/K)			
First Loss			
Wt loss (mg/%)	2.790	6.536	8.452
DTG_{max} (mg min^{-1}/% min^{-1})	0.98	1.25	2.20
T (DTG_{max}) (°C/K)	75	55	60
DTA_{max} (μV/μV mg^{-1})			
T (DTA_{max}) (°C/K)			
T range (°C/K)	50–210	45–195	45–205
Second Loss			
Wt loss (mg/%)	36.71	33.62	29.99
DTG_{max} (mg min^{-1}/% min^{-1})	6.12	7.01	6.60
T (DTG_{max}) (°C/K)	270	265	250
DTA_{max} (μV/μV mg^{-1})			
T (DTA_{max}) (°C/K)			
T range (°C/K)	210–295	195–290	205–290
Third Loss			
Wt loss (mg/%)	20.75	37.80	34.07
DTG_{max} (mg min^{-1}/% min^{-1})	2.60	1.80	1.60
T (DTG_{max}) (°C/K)	320	315	310
DTA_{max} (μV/μV mg^{-1})			
T (DTA_{max}) (°C/K)			
T range (°C/K)	295–365	290–445	290–425
Fourth Loss			
Wt loss (mg/%)	22.54	8.53	5.342
DTG_{max} (mg min^{-1}/% min^{-1})	2.60	1.2	1.1
T (DTG_{max}) (°C/K)	410	470	465
DTA_{max} (V/ V mg^{-1})			
T (DTA_{max}) (°C/K)			
T range (°C/K)	365–510	445–515	425–505
LOI	21.4	27.2	29.4
D_s			

Fig. 3.17. Thermogravimetric analysis curves for cotton treated with 7.64 wt% zinc sulphate

TG, ————————; DTG, - - - - - - - - - - - - - -

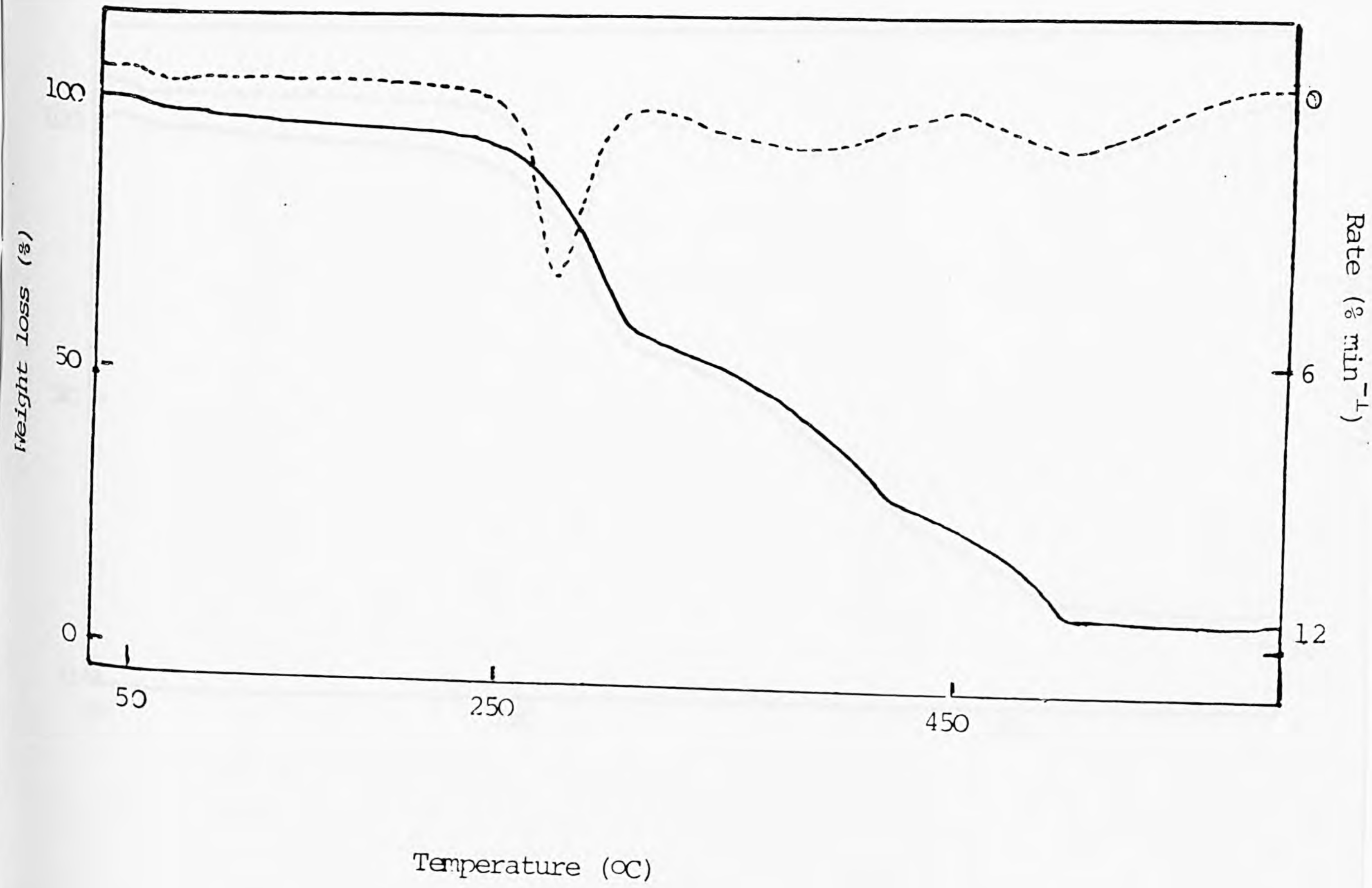


Fig. 3.18. Thermogravimetric analysis curves for cotton treated with 15.52 wt% zinc sulphate

TG, ——————; DTG, - - - - - - - - - - - -

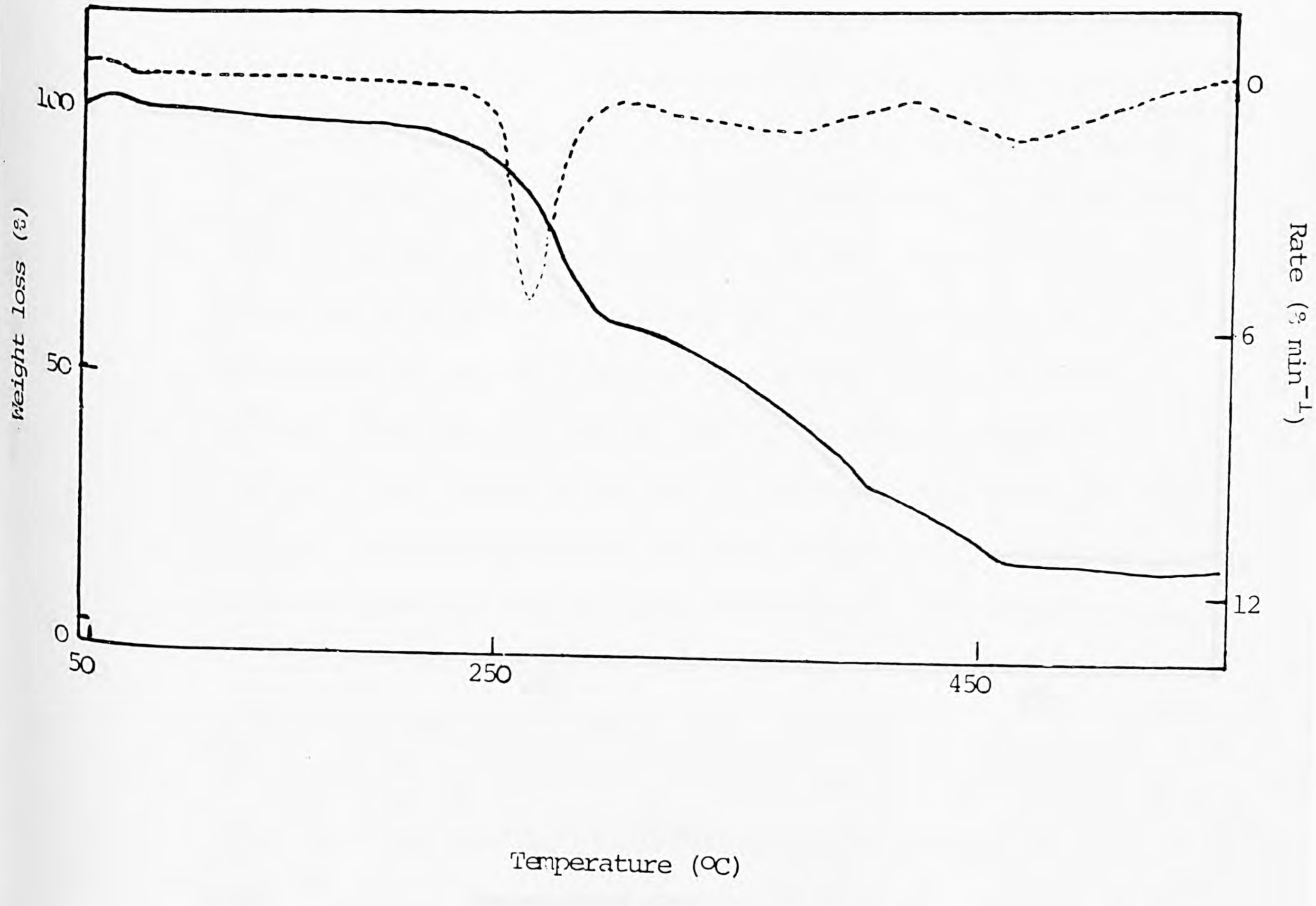
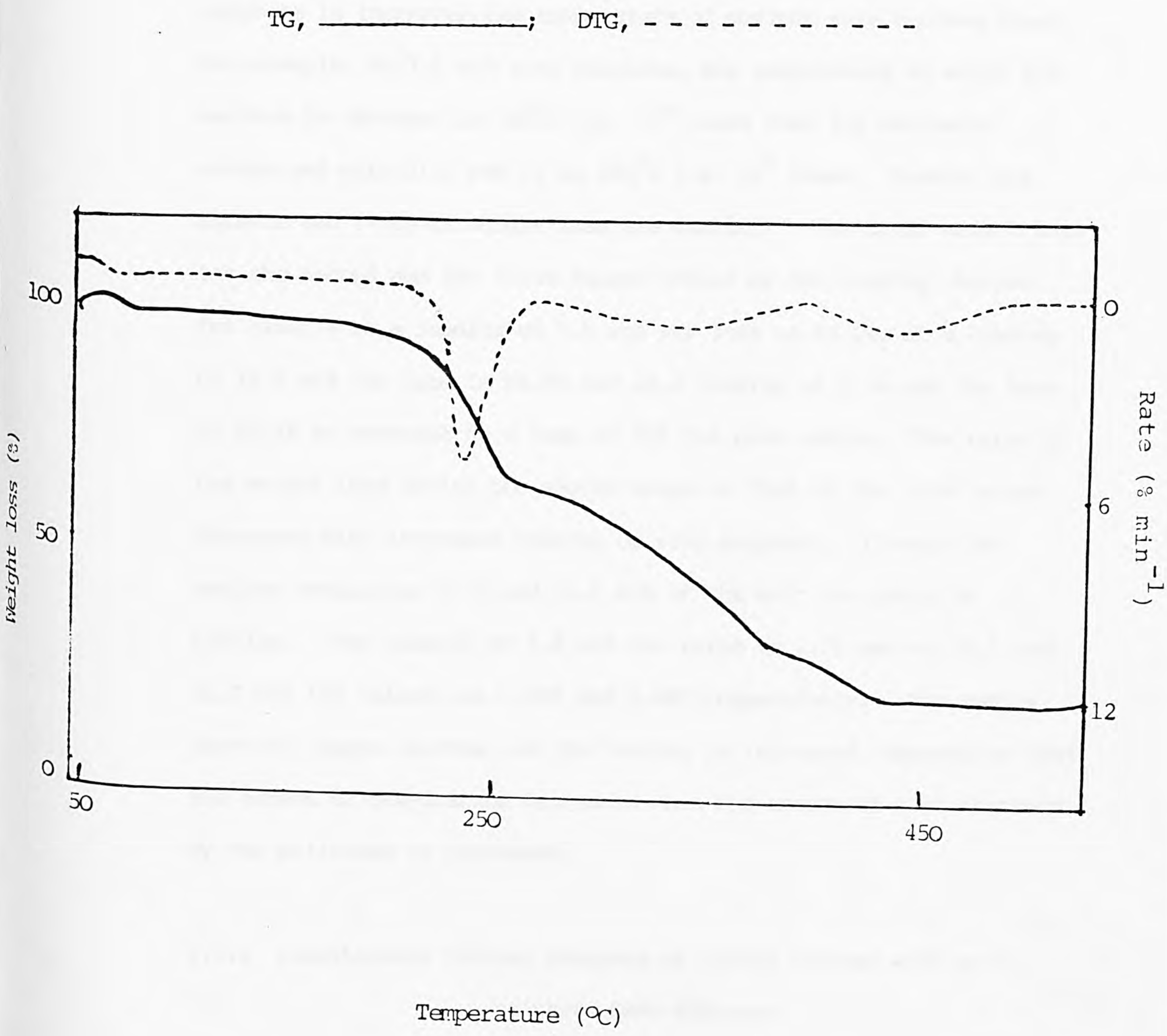


Fig. 3.19 Thermogravimetric analysis curves for cotton treated with 21.65 wt% zinc sulphate



However, the temperature of the third stage is not much lower than that for cellulose on its own but when the loading of zinc sulphate is increased the temperature of maximum rate becomes lower. For example, at 7.6 wt% zinc sulphate, the temperature at which the maximum is obtained is 320°C i.e. 15° lower than for untreated cotton and with 21.6 wt% it is 310°C i.e. 25° lower. However the extents and rates of weight loss are similar. The total weight loss for the second and the third stages varies as the loading changes. For example at a loading of 7.6 wt% the loss is 62.2%, at a loading of 15.5 wt% the loss is 84.5% and at a loading of 21.6 wt% the loss is 80.4% in contrast to a loss of 72% for pure cotton. The ratio of the weight loss during the second stage to that of the third stage decreases with increased loading of zinc sulphate, although for samples containing 15.5 and 21.6 wt% of the salt the ratio is similar. For example at 7.6 wt% the ratio is 1.76 and at 15.5 and 21.7 wt% the values are 0.889 and 0.880 respectively. The carbon burn-off stages decrease as the loading is increased, suggesting that the extent of dehydration decreases when the amount of salt absorbed by the cellulose is increased.

3.3.4 Simultaneous thermal analysis of cotton treated with zinc sulphate-DBBO mixtures

The addition of decabromobiphenyl oxide to samples pretreated with zinc sulphate (Table 3.17 and Figs. 3.20 and 3.21) caused an increase in the ratio of the second and third weight loss stages,

Table 3.17 Thermoanalytical results for cotton + zinc sulphate + DBBO

wt% zinc sulphate	21.70		14.21		
wt% DBBO	5.96		14.86		
Initial weight (mg)	8.080		9.192		
Total weight lost (mg/%)	74.50		76.9		
T_0 (°C/K)					
$T_{1\%}$ (°C/K)					
Gain Stage					
Wt gain (mg/%)					
DTG_{max} (mg min^{-1}/% min^{-1})					
T (DTG_{max}) (°C/K)					
DTA_{max} (μV/μV mg^{-1})					
T (DTA_{max}) (°C/K)					
T range (°C/K)					
First Loss					
Wt loss (mg/%)	3.24		4.51		
DTG_{max} (mg min^{-1}/% min^{-1})	2.4		1.26		
T (DTG_{max}) (°C/K)	60		60		
DTA_{max} (μV/μV mg^{-1})					
T (DTA_{max}) (°C/K)					
T range (°C/K)	50–215		50–205		
Second Loss					
Wt loss (mg/%)	29.04		29.12		
DTG_{max} (mg min^{-1}/% min^{-1})	6.1		6.52		
T (DTG_{max}) (°C/K)	270		270		
DTA_{max} (μV/μV mg^{-1})					
T (DTA_{max}) (°C/K)					
T range (°C/K)	215–290		205–290		
Third Loss					
Wt loss (mg/%)	21.84		25.38		
DTG_{max} (mg min^{-1}/% min^{-1})	3.1		2.44		
T (DTG_{max}) (°C/K)	330		335		
DTA_{max} (μV/μV mg^{-1})					
T (DTA_{max}) (°C/K)					
T range (°C/K)	290–360		290–360		
Fourth Loss					
Wt loss (mg/%)	23.27		17.88		
DTG_{max} (mg min^{-1}/% min^{-1})	2.4		1.6		
T (DTG_{max}) (°C/K)	415		420		
DTA_{max} (V/ V mg^{-1})					
T (DTA_{max}) (°C/K)					
T range (°C/K)	360–485		360–500		
LOI	40.0		40.5		
D_s					

Fig. 3.20. Thermogravimetric analysis curves for cotton treated with 21.70 wt% zinc sulphate and 5.96 wt% DBBO

TG, ————————, DTG, - - - - - - - - - - -

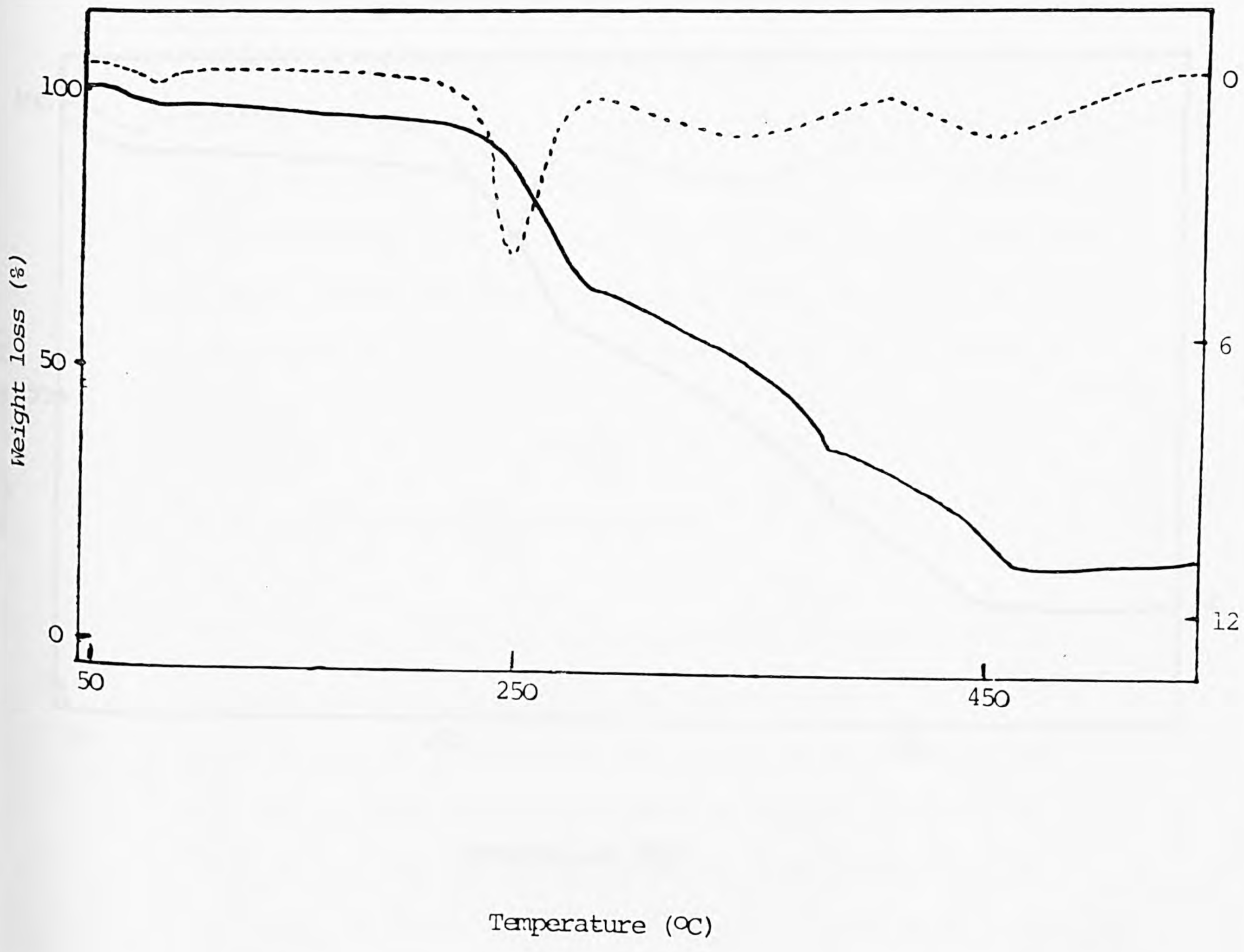
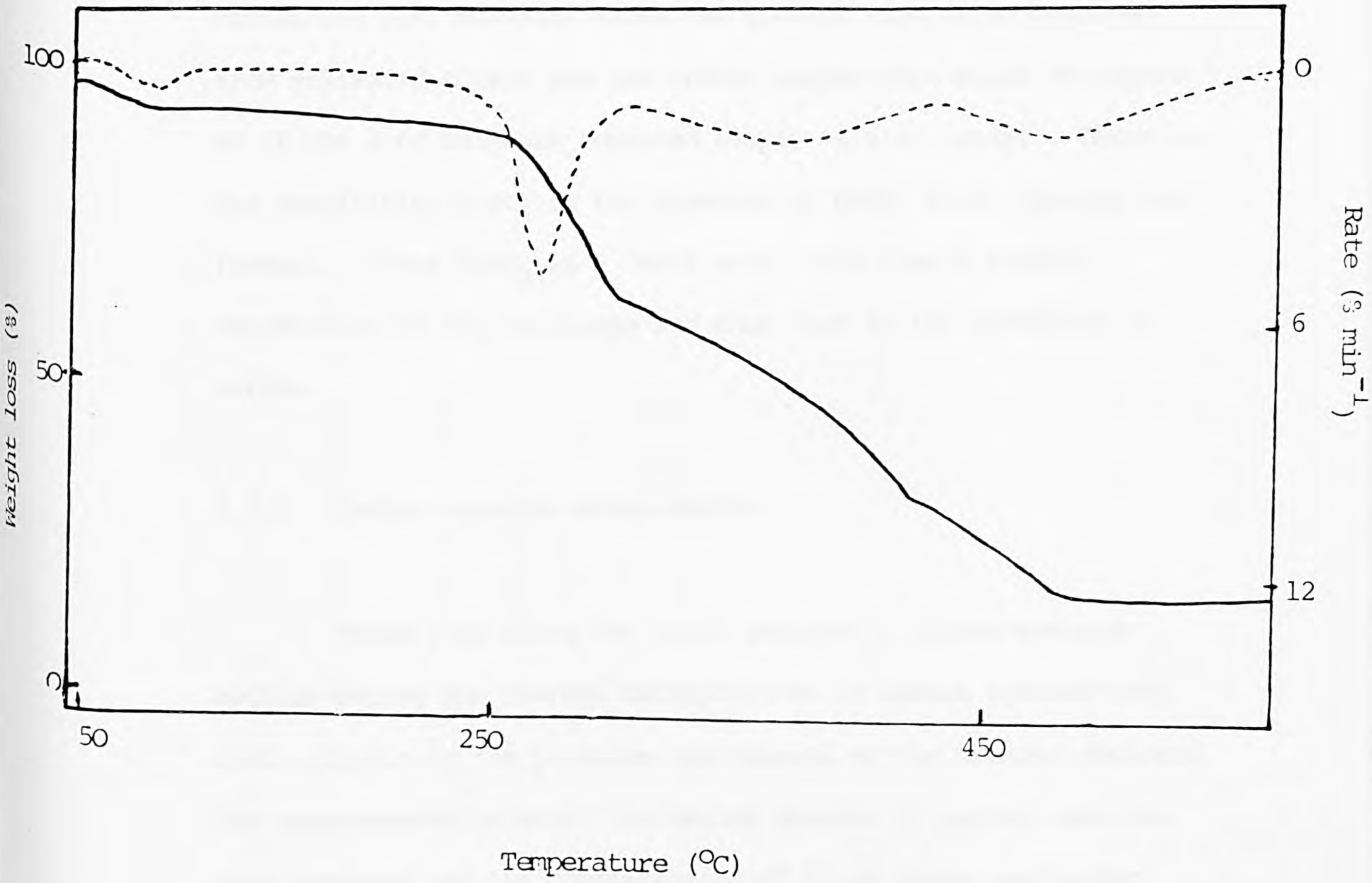


Fig. 3.21. Thermogravimetric analysis curves for cotton treated with 14.21 wt% zinc sulphate and 14.86 wt% DBBO

TG, ————————, DTG,- - - - - - - - - - - -



compared with the corresponding ratio found for cotton samples treated with 21.6 and 15.5 wt% zinc sulphate alone. Larger amounts of solid residue are obtained in the presence of the halogen compound than in its absence but the difference is considerable and may be accounted for by carbon formed from the DBBO. However the amounts of solid residue derived from samples containing zinc sulphate alone are greater than those obtained from untreated cotton and are indeed larger than would be expected if the zinc sulphate remained simply as zinc oxide. There is the possibility that, in the presence of DBBO, Zn-Br species are formed. Since $ZnBr_2$ is a Lewis acid, this should enhance dehydration of the cellulose and thus lead to the formation of carbon.

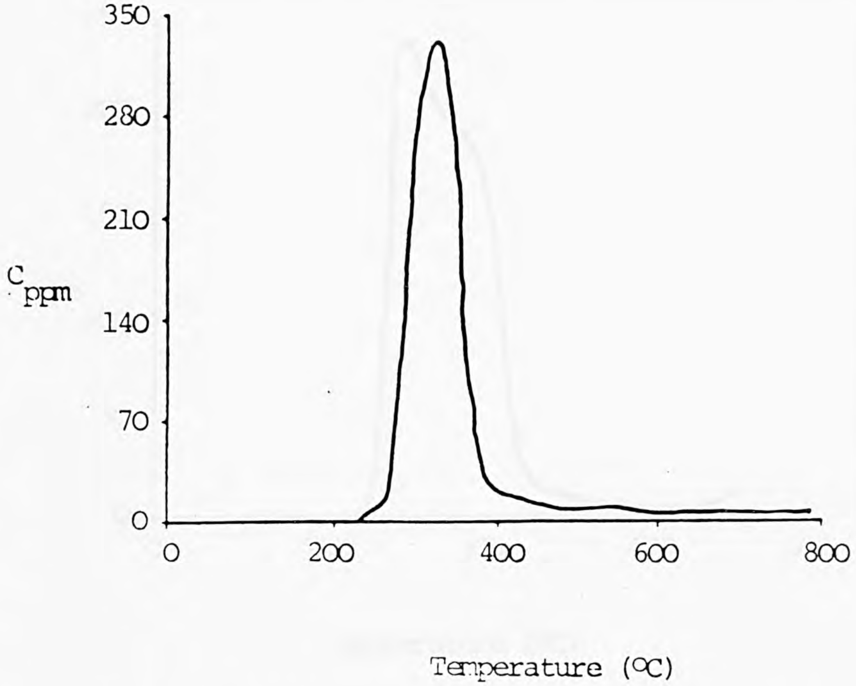
3.3.5 Carbon monoxide measurements

Table 3.18 gives the total amounts of carbon monoxide evolved during the thermal decomposition of cotton treated with zinc sulphate in the presence and absence of the bromine compound, the temperatures at which the maxima amounts of carbon monoxide were observed and the concentration of CO at these particular temperatures. It also shows the temperatures of maximum rate of weight loss for these samples. Figs. 3.22-3.25 show the variation of concentration of carbon monoxide with temperature. It is clear that the total amount of CO decreases when the concentration

Table 3.18 The variation of carbon monoxide concentration with additives composition

wt% salt	wt% DBBO	V_{co}/ml	maximum concentration (ppm)	T(CO_{max})	maximum concentration (ppm)	T(CO_{max})	$T_{max\ rate}$		
							2nd	3rd	4th
7.64	-	0.199	329	329	-	-	270	320	410
21.65	-	0.147	251	310	-	-	250	310	405
21.7	5.96	0.335	342	355	276	423	270	330	415
14.21	14.88	0.606	460	357	377	421	270	335	420

Fig. 3.22 The variation of carbon monoxide concentration with temperature for cotton treated with 7.6 wt% zinc sulphate



The total volume of carbon monoxide evolved during the thermal decomposition of cotton treated with 7.6 wt% zinc sulphate

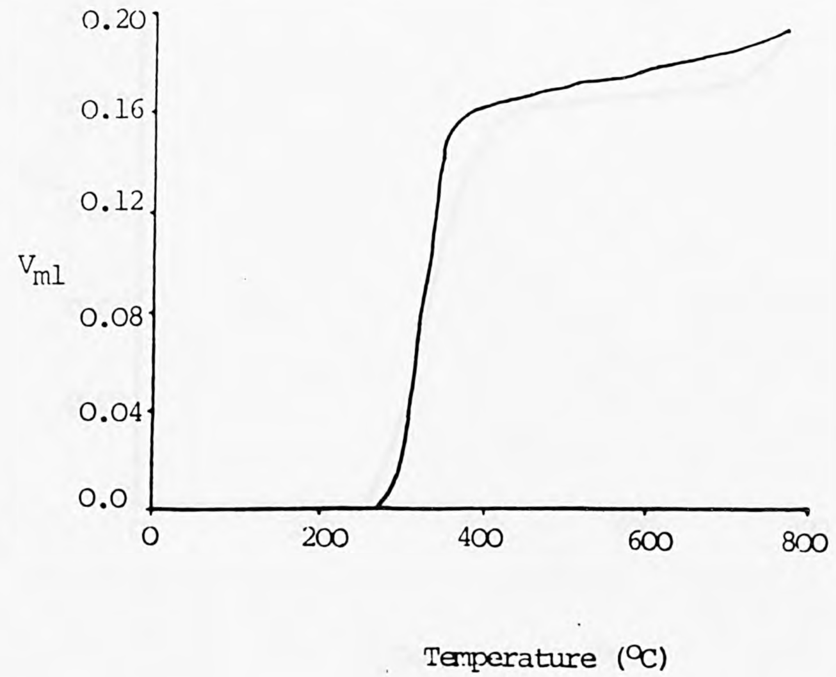
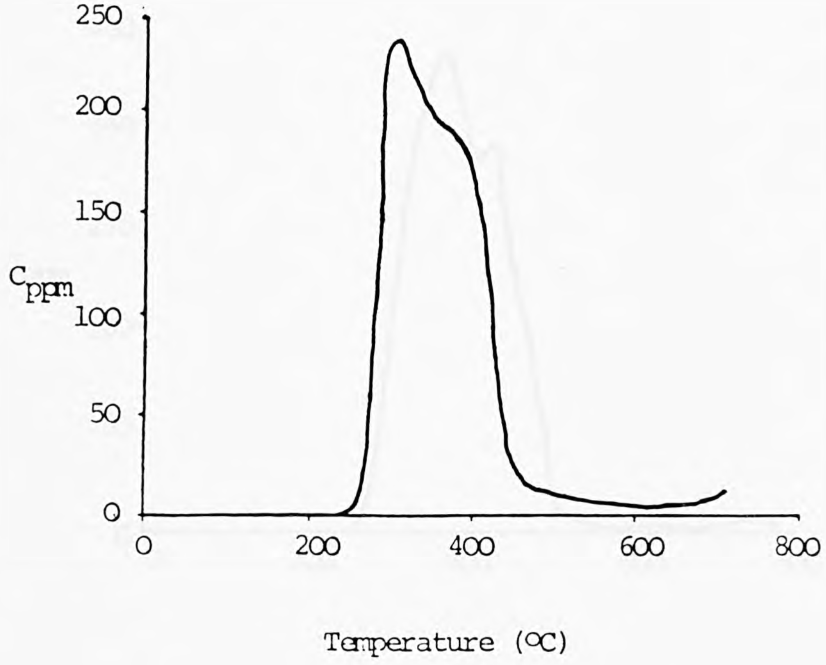


Fig. 3.23 The variation of carbon monoxide concentration with temperature for cotton treated with 21.6 wt% zinc sulphate



The total volume of carbon monoxide evolved during the thermal decomposition of cotton treated with 21.6 wt% zinc sulphate

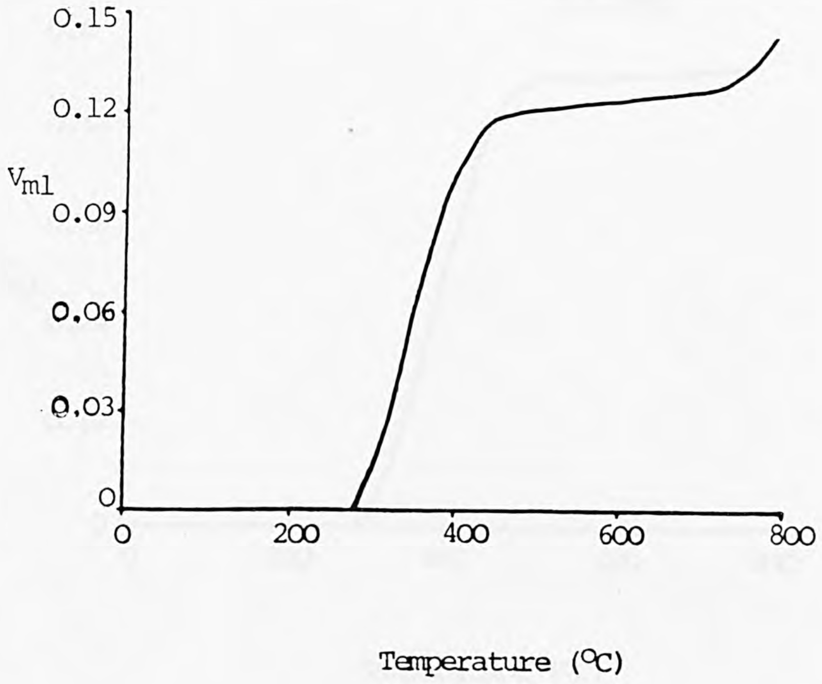
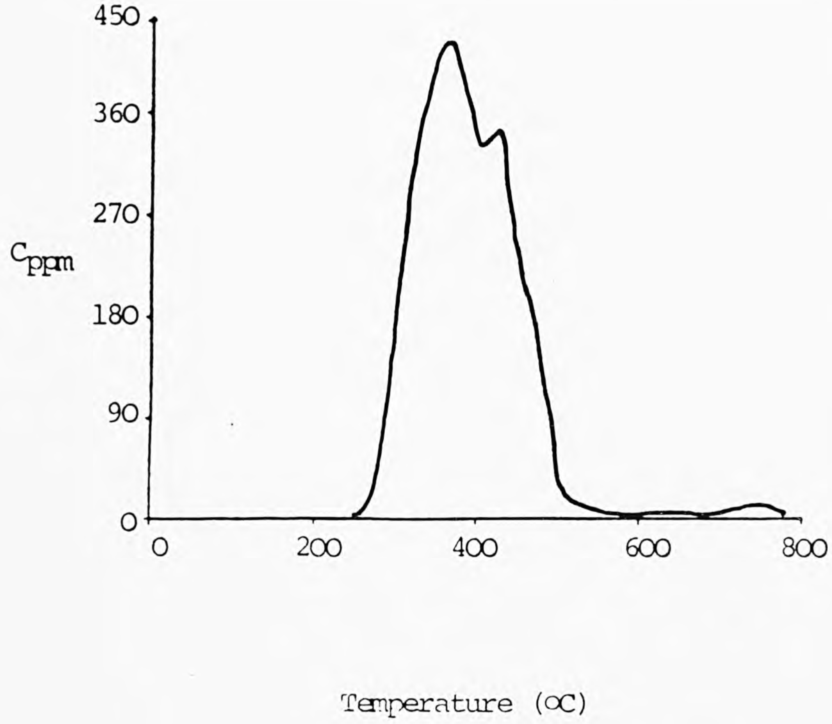


Fig. 3.24 The variation of carbon monoxide concentration with temperature for cotton treated with 14.2 wt% zinc sulphate and 14.8 wt% DBBO



The total volume of carbon monoxide evolved during the thermal decomposition of cotton treated with 14.2 wt% zinc sulphate and 14.8 wt% DBBO

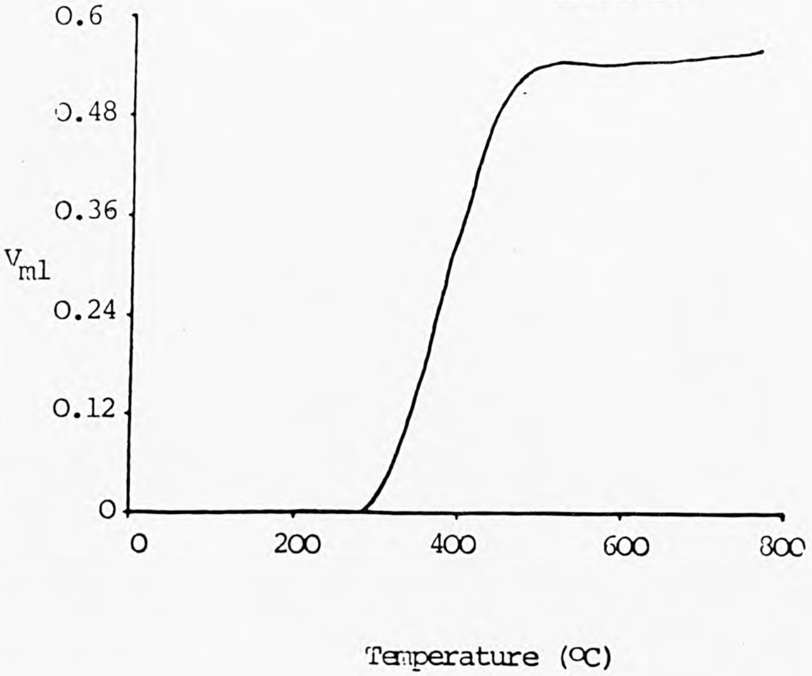
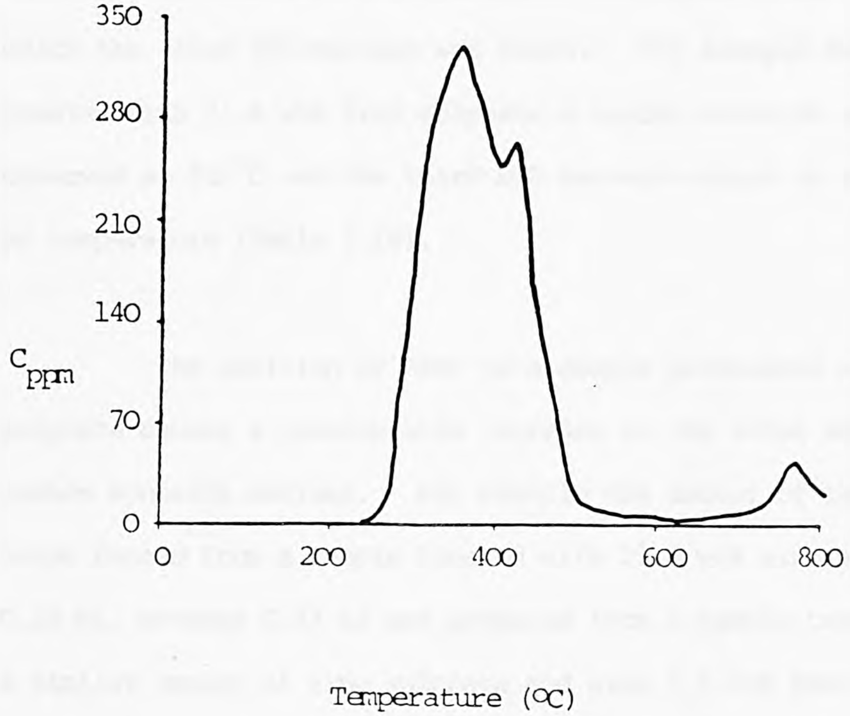
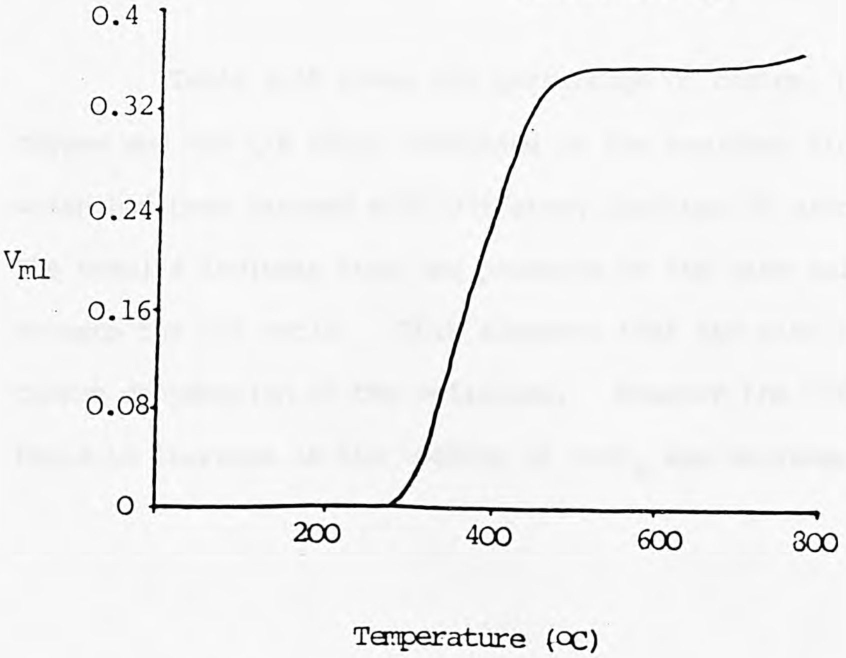


Fig. 3.25 The variation of carbon monoxide concentration with temperature for cotton treated with 21.7 wt% zinc sulphate and 5.96 wt% DBBO



Total volume of carbon monoxide evolved during the thermal decomposition of cotton treated with 21.7 wt% zinc sulphate and 5.96 wt% DBBO



of the additive is increased. One carbon monoxide maximum was obtained and occurs at a temperature corresponding to that at which the third DTG maximum was found. For example for a sample treated with 21.6 wt% zinc sulphate a carbon monoxide maximum is observed at 310°C and the third DTG maximum occurs at a similar temperature (Table 3.18).

The addition of DBBO to a sample pretreated with zinc sulphate causes a considerable increase in the total amount of carbon monoxide evolved. For example the amount of carbon monoxide formed from a sample treated with 21.6 wt% zinc sulphate is 0.19 ml, whereas 0.33 ml are produced from a sample treated with a similar amount of zinc sulphate and also 5.9 wt% DBBO. The tem- perature of the carbon monoxide peak is found to be slightly higher than the temperature of the third DTG maximum.

3.3.6 Microanalytical measurements

Table 3.19 gives the percentage of carbon, hydrogen and oxygen and the C/H ratio remaining in the residues from cottons which had been treated with different loadings of zinc sulphate. The results indicate that the presence of the zinc sulphate increases the C/H ratio. This suggests that the zinc sulphate causes dehydration of the cellulose. However the C/H ratio was found to increase as the loading of $ZnSO_4$ was decreased. Thus, for

Table 3.19 Microanalysis measurements for samples treated with zinc sulphate

wt% salt	weight loss stage	%C	%H	%O	C:H
7.0	2nd	63.542	2.912	33.546	21.814
	3rd	60.110	3.307	36.583	18.176
19.7	2nd	52.870	3.550	43.580	14.890
	3rd	58.583	3.355	38.062	17.45

example, the ratio for a cotton sample treated with 21.65 wt% zinc sulphate at the third weight loss was 17.45, whereas for a sample treated with 17.64 wt% zinc sulphate the ratio was 18.18. At high loadings (e.g. 21.6 wt%) of $ZnSO_4$, the extent of dehydration is greater in the third weight loss stage than in the second weight loss stage but at lower loadings (e.g. 7.6 wt%) of the zinc salt the reverse is true.

3.4 The effect of ammonium sulphamate-DBBO mixtures on the flammability of cotton fabric

3.4 The effect of ammonium sulphamate-DBBO mixtures on the flammability of cotton fabric

3.4.1 The effect of ammonium sulphamate on its own on the flammability of cotton fabric

Table 3.20 presents LOI values for some cotton samples treated with various concentrations of ammonium sulphamate. It is clear from the table that ammonium sulphamate on its own is a good flame retardant for cotton. At a relatively low loading of ca 4 wt% the LOI observed is 25.1 and at a loading of 25.9 wt% the LOI rises to 35.7. The plot in Fig. 3.26 shows that there is a rapid increase in the LOI values as the loading increases up to about 10 wt%, then a slower increase up to about 24 wt% followed by a further rapid increase up to a loading of 30 wt%.

3.4.2 The combined effect of ammonium sulphamate and DBBO on the flammability of cotton fabric

Table 3.21 shows the LOI values for cotton containing various loadings of both additives. Fig. 3.27 shows the LOI values, calculated from the quartic polynomial in terms of composition (47 different compositions were used) and plotted as contour lines for 10 equidistant LOI values bounded by the vertices: A: 100 wt% cotton, B: 70 wt% cotton, 30 wt% ammonium sulphamate and C: 70 wt% cotton, 30 wt% DBBO. Table 3.22 gives the parameters of all the fitting routines, the average coefficients, degrees of synergism over a

Table 3.20 The effect of ammonium sulphamate on the LOI value of cotton

ammonium sulphamate wt%	LOI
4.26	25.1
9.36	29.2
10.91	29.6
14.00	31.6
16.89	32.0
21.88	34.0
25.90	35.7
28.00	38.8

Fig. 3.26 The effect of ammonium sulphamate on the flammability of cotton fabric

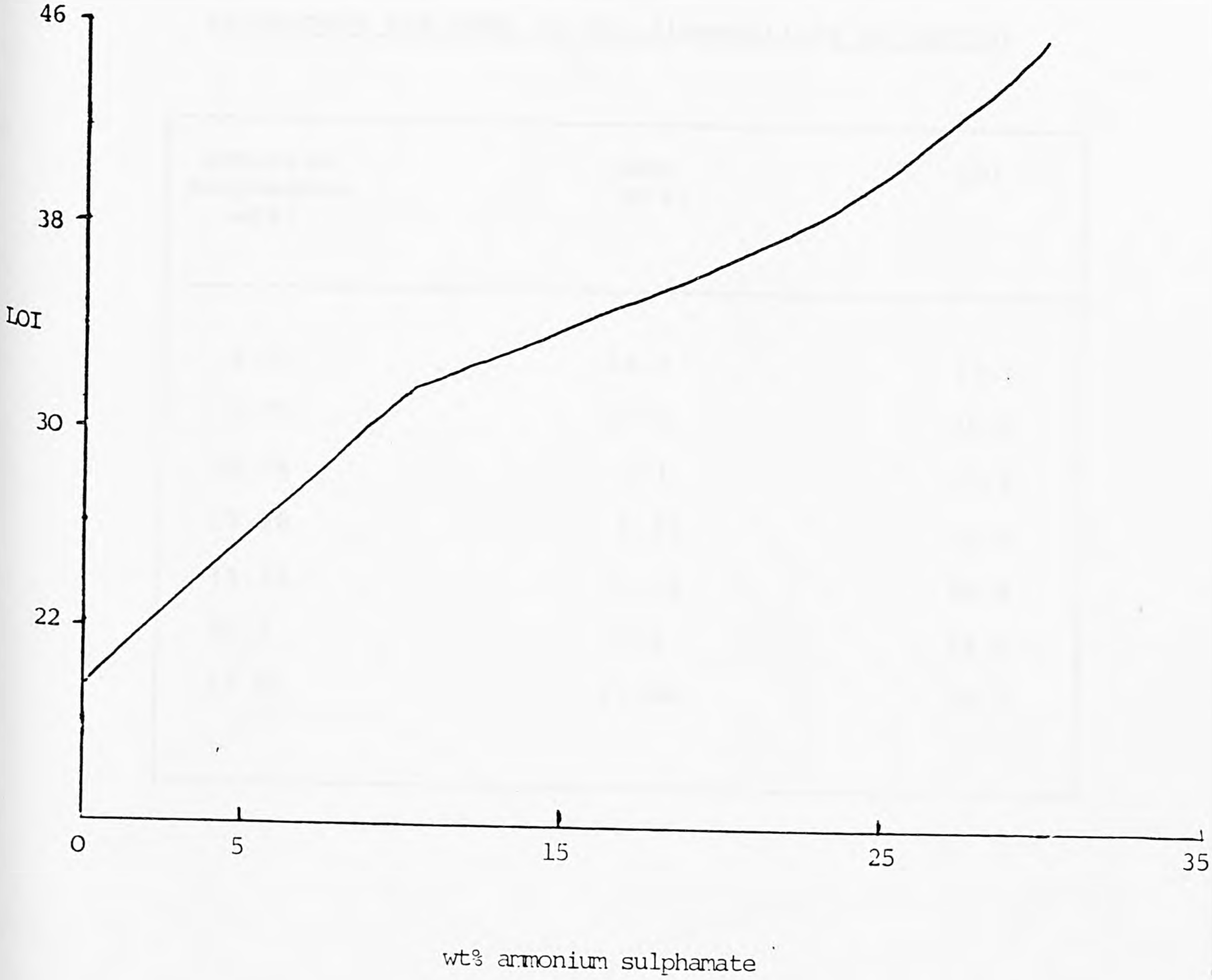
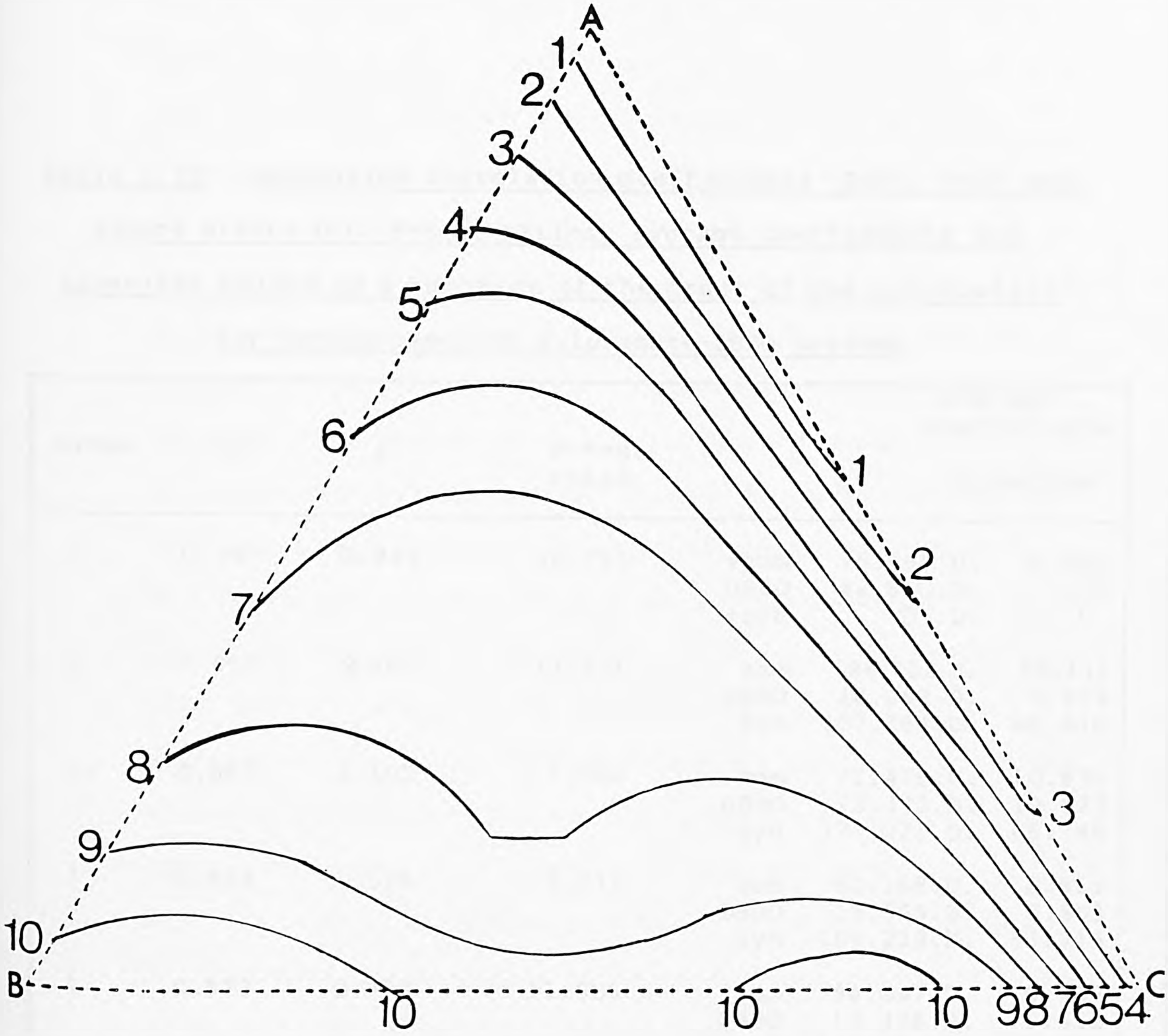


Table 3.21 The effect of a mixture of ammonium sulphamate and DBBO on the flammability of cotton

ammonium sulphamate (wt%)	DBBO (wt%)	LOI
8.95	18.3	37.3
5.70	21.8	36.0
24.76	3.4	37.6
15.98	8.49	34.2
14.14	15.05	36.8
20.4	9.6	38.6
12.60	11.40	34.7

Fig. 3.27 Triangular diagram showing variation of LOI with composition for a cotton-ammonium sulphamate-DBBO system



LOI values: (0) 18.10; (1) 20.18; (2) 22.26; (3) 24.34; (4) 26.42; (5) 28.50; (6) 30.58; (7) 32.66; (8) 34.74; (9) 36.82; (10) 38.90.

Table 3.22 Regression correlation coefficients (RCC), root mean square errors (σ), F-test ratios, average coefficients and synergism values as a function of the order of the polynomials for cotton-ammonium sulphamate-DBBO systems

order	RCC	σ	F-test ratio		average coefficients	synergism
1	0.757	2.943	46.755	≠amm	75.695.D.	6.400
				DBBO	42.880.D.	7.178
				+syn	0 .D.	0
2	0.855	2.263	11.373	amm	86.422.D.	10.333
				DBBO	38.062.D.	9.874
				syn	307.264.D.	66.410
3r	0.887	2.105	7.546	amm	72.476.D.	10.870
				DBBO	23.373.D.	10.627
				syn	377.021.D.	66.786
3	0.944	1.528	13.271	amm	90.168.D.	8.913
				DBBO	28.565.D.	8.863
				syn	369.228.D.	53.716
4	0.979	0.990	11.505	amm	84.047.D.	6.409
				DBBO	17.328.D.	6.332
				syn	570.810.D.	59.852

*average coefficients over range of X2 or X3 = 0-0.3

+ syn = synergism

≠ amm = ammonium sulphamate

range X2 or X3 = 0–0.3, regression correlation coefficients (RCC), root mean square differences (σ) and F - test ratios as a function of the order of the polynomial. It is clear from this table that there is a great improvement in the RCC and σ values as the order of the polynomial increases. The quartic model is found to provide the best fit and a good representation of the data with a correlation coefficient of 0.98, close to the optimum value of 1.0 for the perfect correlation and with a value of σ of 0.990 which is less than the uncertainty value estimated to be ±1 LOI unit. Fig. 3.27 shows that there is a rapid increase in the LOI value per unit concentration along the cotton-ammonium sulphamate axis followed by a slower increase and then again a rapid increase as the sulphamate vertix is approached. This finding was also confirmed when the LOI values were plotted against the sulphamate content as shown in Fig. 3.27. This figure also shows that, for mixtures of the two components, the LOI remains approximately constant over most of the central region of the triangle. However at high loadings of the ammonium sulphamate-DBBO mixture two maxima were observed close to both vertices as well as a minimum at weight ratio of 1:1 . Thus for example, LOI values of 34.7 and 36.8 are obtained with equal weights of the two additives and total loadings of 24 and 28 wt% respectively. However even higher LOI values are found for the same total additive loading when very different amounts of the ammonium sulphamate and DBBO are used as shown in Table 3.21.

For example at a loading of 14.14 wt% of sulphamate and 15.05 wt% of DBBO (a ratio of 1:1) the LOI value is 36.8, whereas it is in-increased to 38.6 where the mixture contains 20.4 wt% ammonium sulphamate and 9.6 wt% DBBO. The values of the average coefficients in Table 3.2.2 show that the ammonium sulphamate contributes much more than the DBBO to the observed reduction in the flammability of the fabric. The average coefficient for the ammonium sulphamate is 84.04 and that for the DBBO is 17.32 i.e. the former is about five times greater than the latter. However a higher degree of synergism was obtained when the two additives were mixed together, when a"syn" value of 570.8 was found.

3.4.3 Simultaneous thermal analysis of cotton treated with ammonium sulphamate

Figs. 3.28-3.30 show the TG and DTG curves for samples treated with ammonium sulphamate and Table 3.23 presents some of the characteristic features of the various stages. All the samples treated with ammonium sulphamate show that decomposition occurs over a wide range of temperature and all of them exhibit four weight loss stages. The second and third stages both occur at temperatures lower than that at which the cellulose itself begins to decompose. However the third stage is not much lower than that

Table 3.23 Thermoanalytical results for cotton + ammonium sulphamate

wt% ammonium sulphamate	4.26		10.91		21.88
Initial weight (mg)	8.509		9.222		9.88
Total weight lost (mg/%)	95.62		95.61		85.81
T_0 (°C/K)					
$T_{1\%}$ (°C/K)					
Gain Stage					
Wt gain (mg/%)					
DTG_{max} (mg min^{-1}/% min^{-1})					
T (DTG_{max}) (°C/K)					
DTA_{max} (μV/μV mg^{-1})					
T (DTA_{max}) (°C/K)					
T range (°C/K)					
First Loss					
Wt loss (mg/%)	2.39		3.30		4.17
DTG_{max} (mg min^{-1}/% min^{-1})					
T (DTG_{max}) (°C/K)					
DTA_{max} (μV/μV mg^{-1})					
T (DTA_{max}) (°C/K)					
T range (°C/K)	45-215				45 -215
Second Loss					
Wt loss (mg/%)	36.92		35.56		32.89
DTG_{max} (mg min^{-1}/% min^{-1})	9.40		24.39		13.25
T (DTG_{max}) (°C/K)	245		240		245
DTA_{max} (μV/μV mg^{-1})					
T (DTA_{max}) (°C/K)					
T range (°C/K)	215-285		210-275		210-280
Third Loss					
Wt loss (mg/%)	28.73		21.52		22.89
DTG_{max} (mg min^{-1}/% min^{-1})	2.35		1.626		1.38
T (DTG_{max}) (°C/K)	325		315		315
DTA_{max} (μV/μV mg^{-1})					
T (DTA_{max}) (°C/K)					
T range (°C/K)	285-415		275-390		280-410
Fourth Loss					
Wt loss (mg/%)	27.57		30.01		25.85
DTG_{max} (mg min^{-1}/% min^{-1})	2.35		1.35		1.11
T (DTG_{max}) (°C/K)	496		495		495
DTA_{max} (μV/μV mg^{-1})					
T (DTA_{max}) (°C/K)					
T range (°C/K)	415-525		390-550		410-580
LOI	25.1		29.6		34.0
O_s					

Fig. 3.28 Thermogravimetric analysis curves for cotton treated with 4.26 wt% ammonium sulphamate

TG, ——————; DTG, - - - - - - - - - -

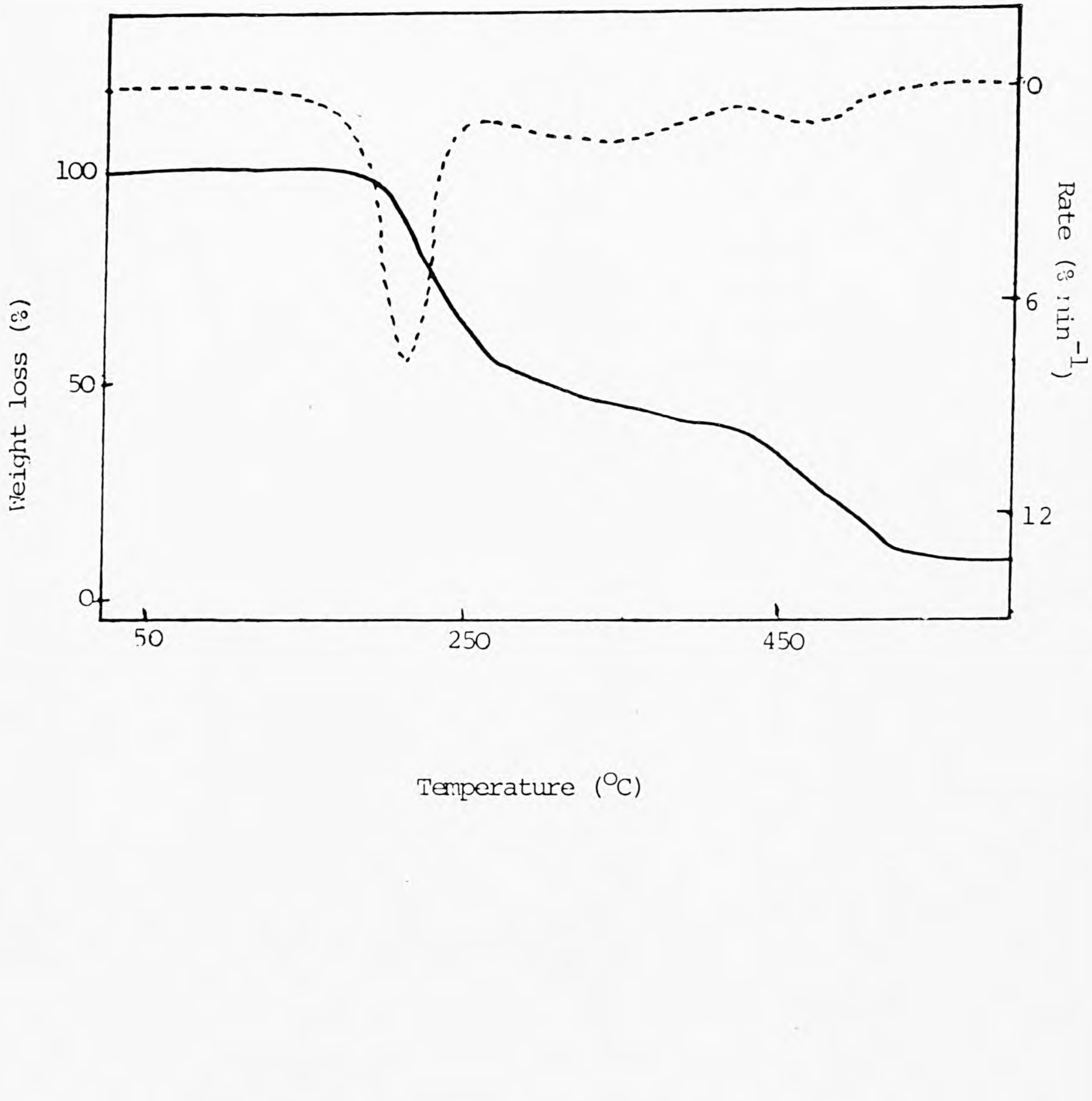


Fig. 3.29. Thermogravimetric analysis curves for cotton treated with 10.91 wt% ammonium sulphamate

TG; ———————— DTG; - - - - - - - - - - -

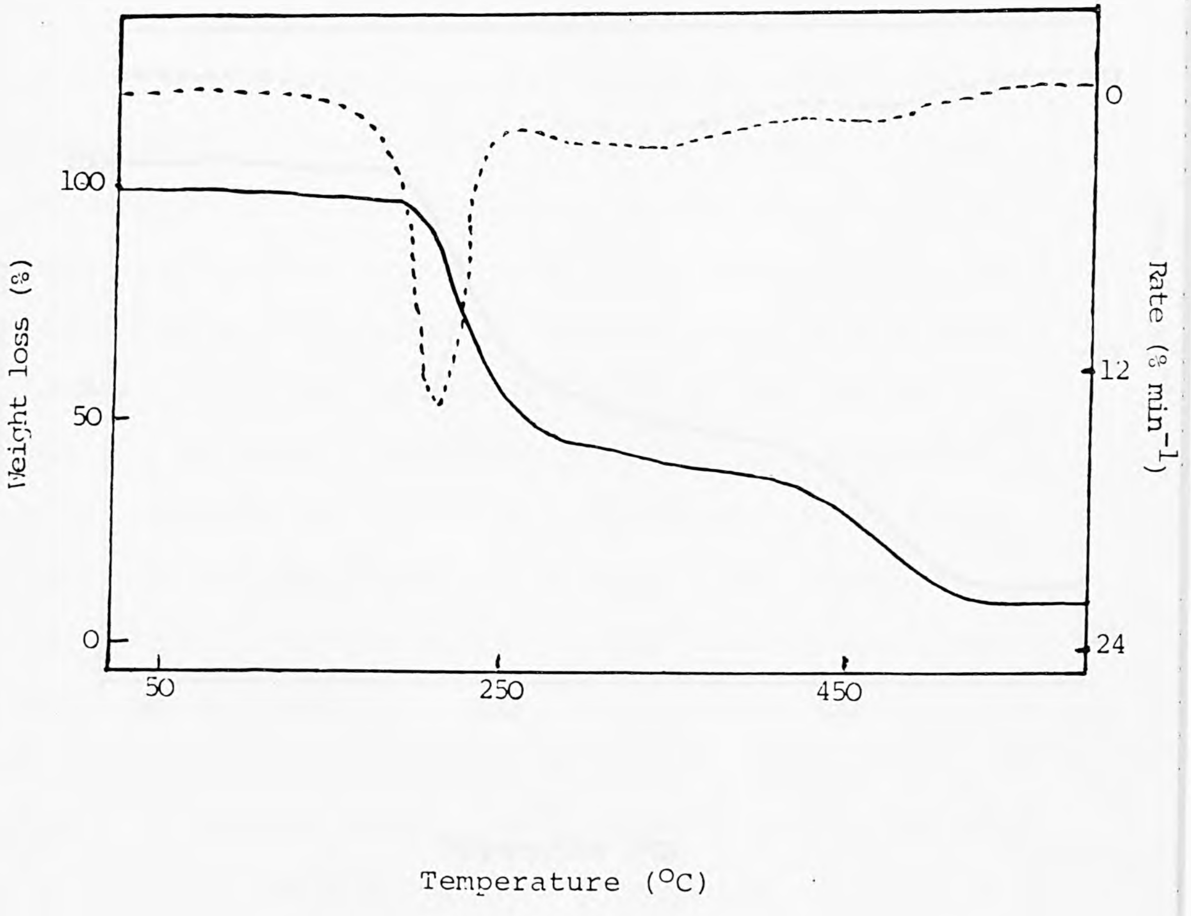
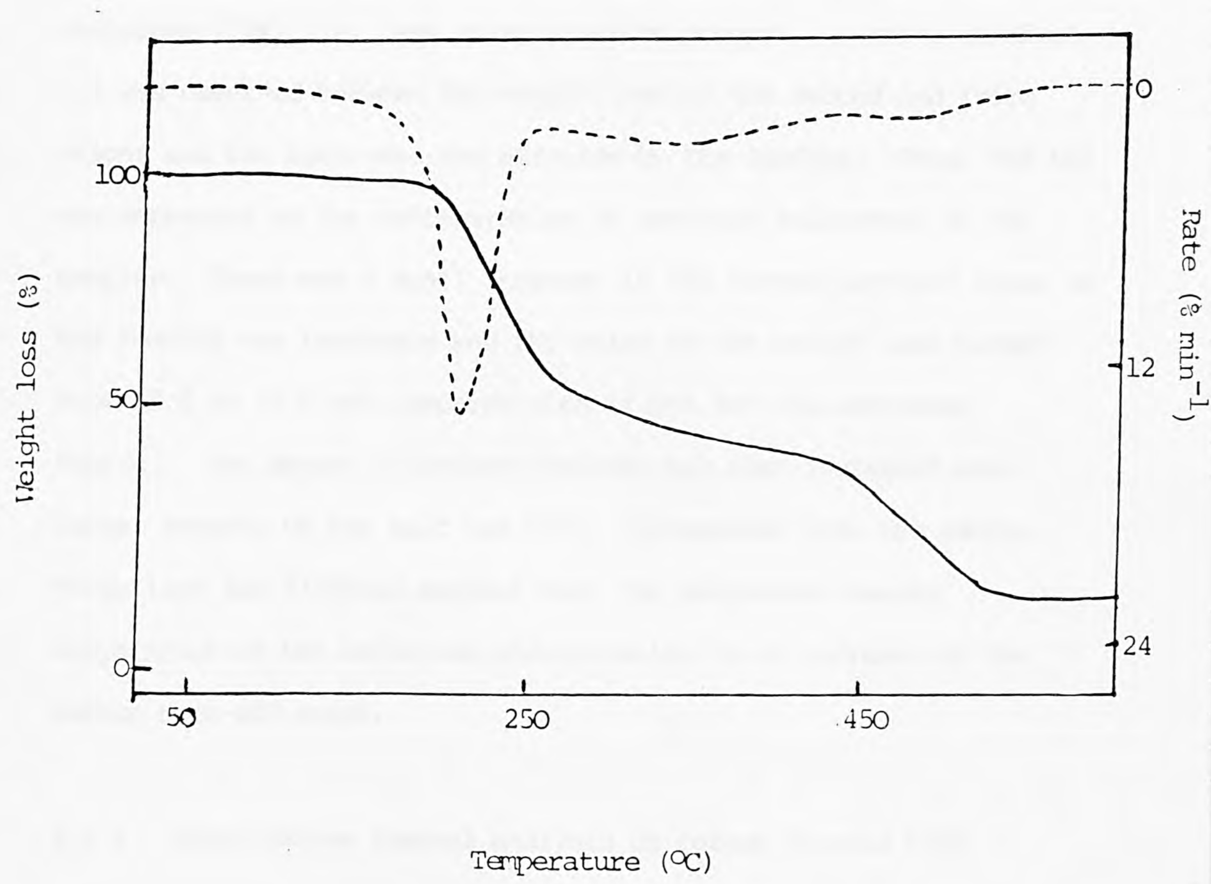


Fig. 3.30 Thermogravimetric analysis curves for cotton treated with 21.88 wt% ammonium sulphamate

TG, ——————; DTG, - - - - - - - - - - -



for untreated cotton. When the loading of ammonium sulphamate is increased, the temperature of maximum rate at this stage occurs earlier, whereas the temperature of maximum rate for the second stage is largely unaffected. The total weight loss of the cellulose initially present for these two stages (about 68 wt%) was found to be similar for all samples and lower than that observed for the pure cellulose (72%) i.e. less volatilization occurs. A ratio of about 1.3 was observed between the weight loss of the second and third stages and the ratio was not affected by the loading. Thus, the LOI was dependent on the concentration of ammonium sulphamate in the samples. There was a small increase in the carbon burn-off stage as the loading was increased and the value of the weight loss ranged from 28.8 to 33.6 wt% compared with 11 wt% for the untreated fabric. The amount of unburnt residue was also increased when larger amounts of the salt had been impregnated into the sample. These last two findings suggest that the sulphamate causes dehydration of the cellulose which results in an increase of the carbon burn-off stage.

3.4.4 Simultaneous thermal analysis of cotton treated with ammonium sulphamate-DBBO mixtures

Figs. 3.31 and 3.32 show TG and DTG curves for samples treated with the two additives together and Table 3.24 indicates the various stages of decomposition of these samples. It can be seen

Table 3.24 Thermoanalytical results for cotton + ammonium sulphamate + DBBO

wt% ammonium sulphamate	7.43		15.98	
wt% DBBO	8.80		8.439	
Initial weight (mg)	7.291		9.180	
Total weight lost (mg/%)	96.48		96.58	
T_0 (°C/K)				
$T_{1\%}$ (°C/K)				
Gain Stage				
Wt gain (mg/%)				
DTG_{max} (mg min^{-1}/% min^{-1})				
T (DTG_{max}) (°C/K)				
DTA_{max} (μV/μV mg^{-1})				
T (DTA_{max}) (°C/K)				
T range (°C/K)				
First Loss				
Wt loss (mg/%)	1.93		3.07	
DTG_{max} (mg min^{-1}/% min^{-1})				
T (DTG_{max}) (°C/K)				
DTA_{max} (μV/μV mg^{-1})				
T (DTA_{max}) (°C/K)				
T range (°C/K)	45-215		45-215	
Second Loss				
Wt loss (mg/%)	33.12		24.8	
DTG_{max} (mg min^{-1}/% min^{-1})	15.77		10.89	
T (DTG_{max}) (°C/K)	250		245	
DTA_{max} (μV/μV mg^{-1})				
T (DTA_{max}) (°C/K)				
T range (°C/K)	215-270		215-260	
Third Loss				
Wt loss (mg/%)	28.59		32.02	
DTG_{max} (mg min^{-1}/% min^{-1})	2.74		2.27	
T (DTG_{max}) (°C/K)	335		315	
DTA_{max} (μV/μV mg^{-1})				
T (DTA_{max}) (°C/K)				
T range (°C/K)	270-380		260-370	
Fourth Loss				
Wt loss (mg/%)	32.84		36.69	
DTG_{max} (mg min^{-1}/% min^{-1})	1.37		1.08	
T (DTG_{max}) (°C/K)	495		435	
DTA_{max} (V/ V mg^{-1})				
T (DTA_{max}) (°C/K)				
T range (°C/K)	380-550		370-590	
LOI	33.0		34.2	
O_s				

Fig. 3.31 Thermogravimetric analysis curves for cotton treated with 15.98 wt% ammonium sulphamate and 8.44 wt% DBBO

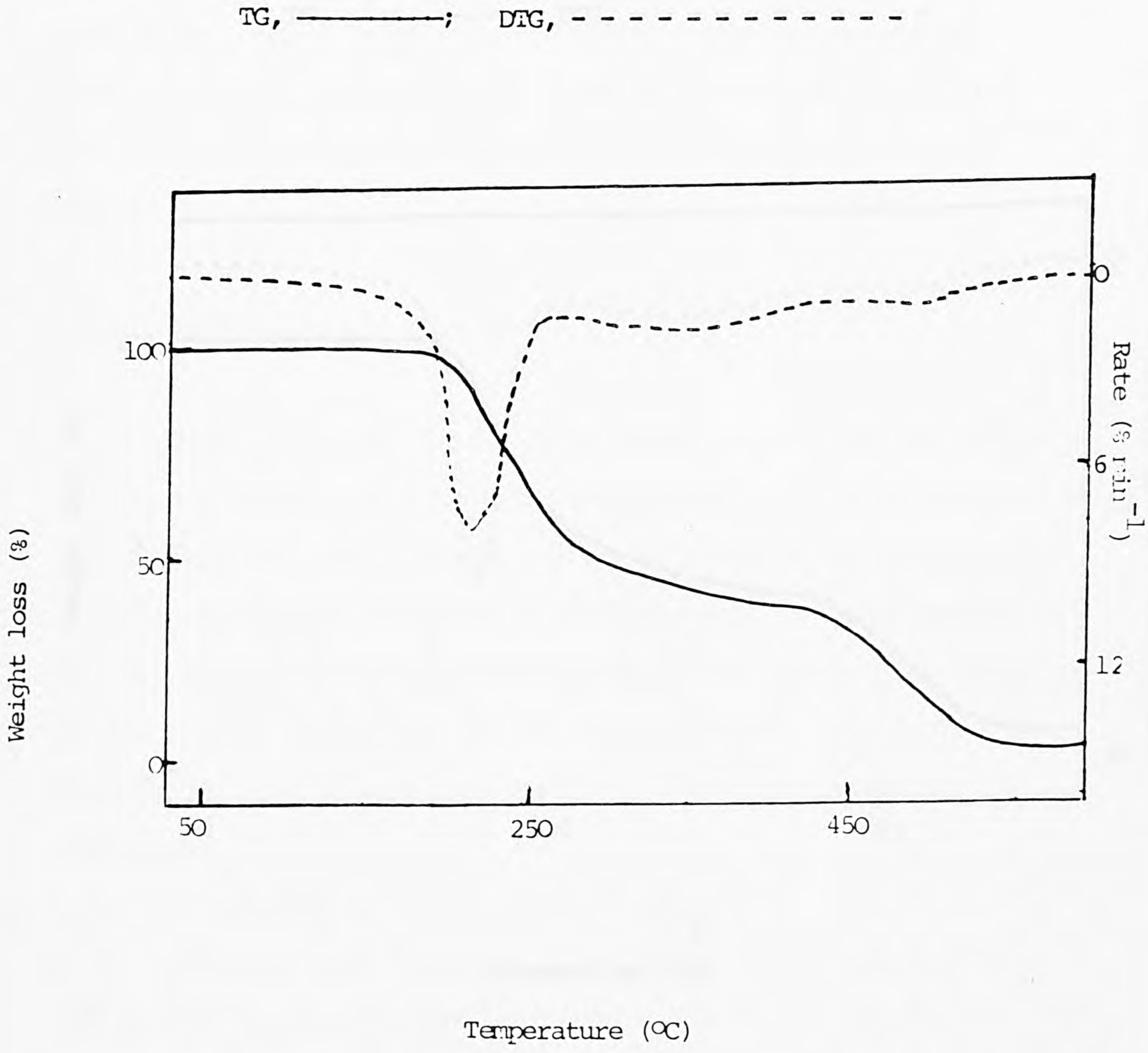
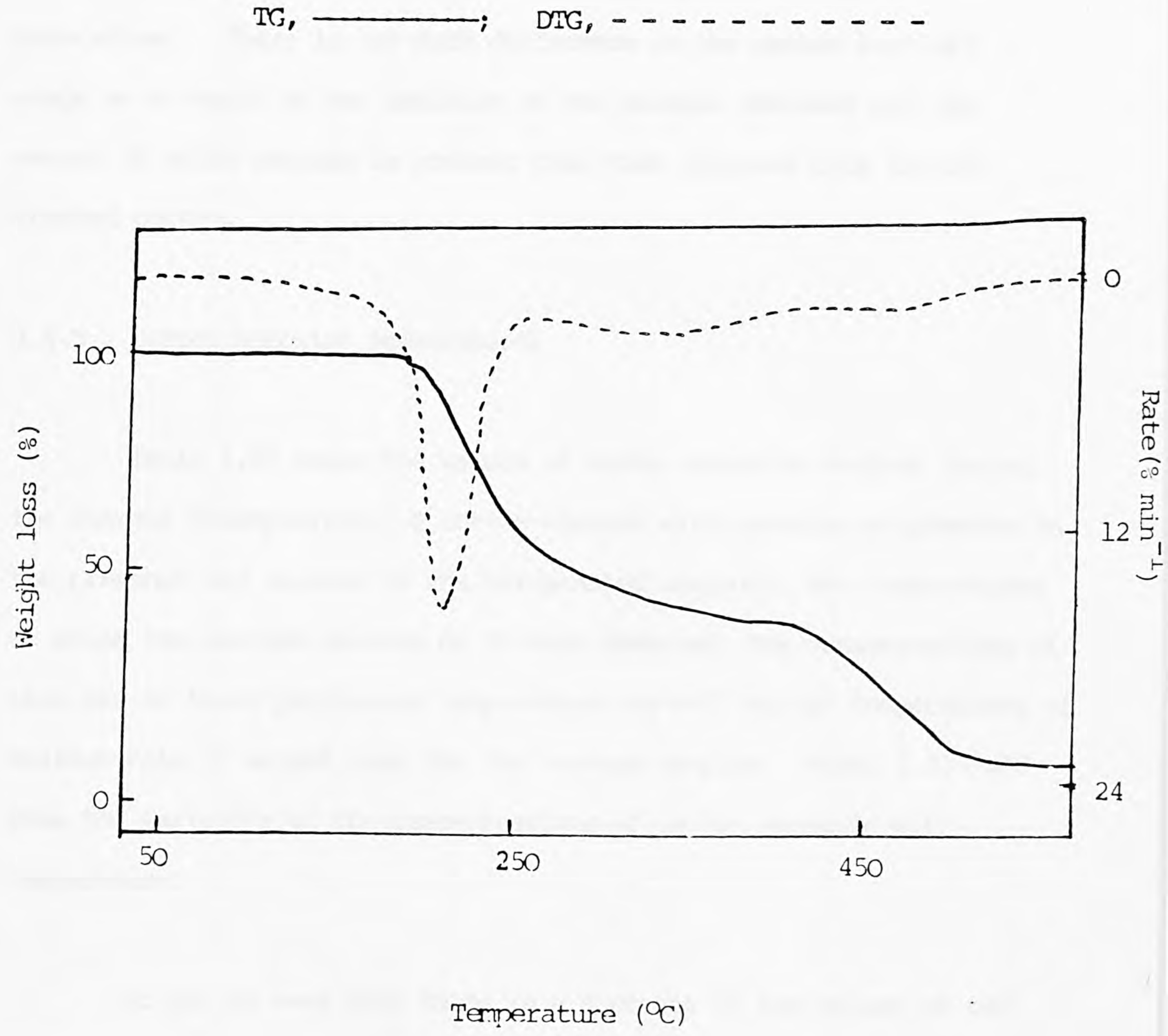


Fig. 3.32 Thermogravimetric analysis curves for cotton treated with 7.73 wt% ammonium sulphamate and 8.80 wt% DBBO



from the table that there is a small increase in the total weight loss on addition of the bromine compound but the four stages occur in temperature ranges similar to those found with ammonium sulphamate alone. There is not much difference in the carbon burn-off stage as a result of the addition of the halogen compound but the amount of solid residue is greater than that obtained from the untreated cotton.

3.4.5 Carbon monoxide measurements

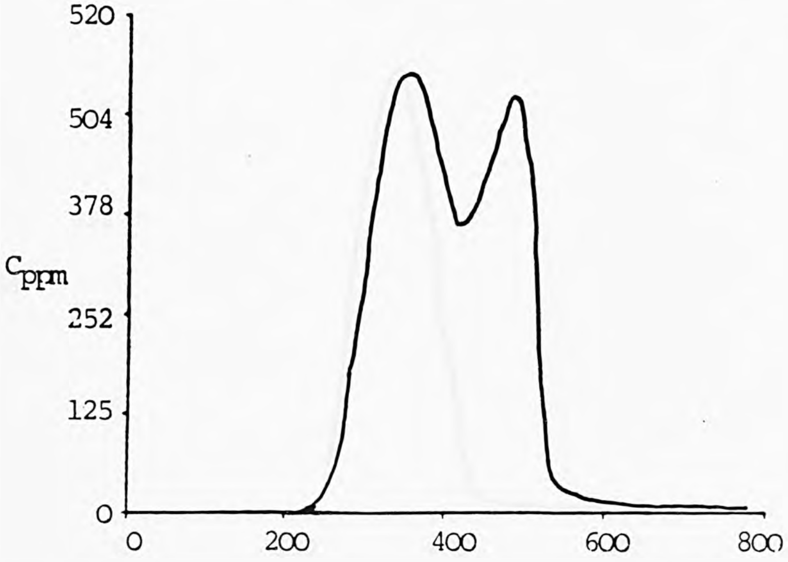
Table 3.25 shows the values of carbon monoxide evolved during the thermal decomposition of cotton treated with ammonium sulphamate in the presence and absence of the halogenated compound, the temperatures at which the maximum amounts of CO were observed, the concentrations of this gas at these particular temperatures as well as the temperatures of maximum rate of weight loss for the various samples. Figs. 3.33-3.36 show the variation of the concentrations of carbon monoxide with temperature.

It can be seen that there is a decrease in the volume of the carbon monoxide on increasing the additive loadings and two maxima were observed for a sample containing a low concentration of the ammonium sulphamate. The second peak occurred at a temperature similar to that of the fourth DTG maximum. However the first peak was obtained at a temperature 40° higher than that of the third DTG maximum. At a

Table 3. 25 The variation of carbon monoxide concentration with additive composition

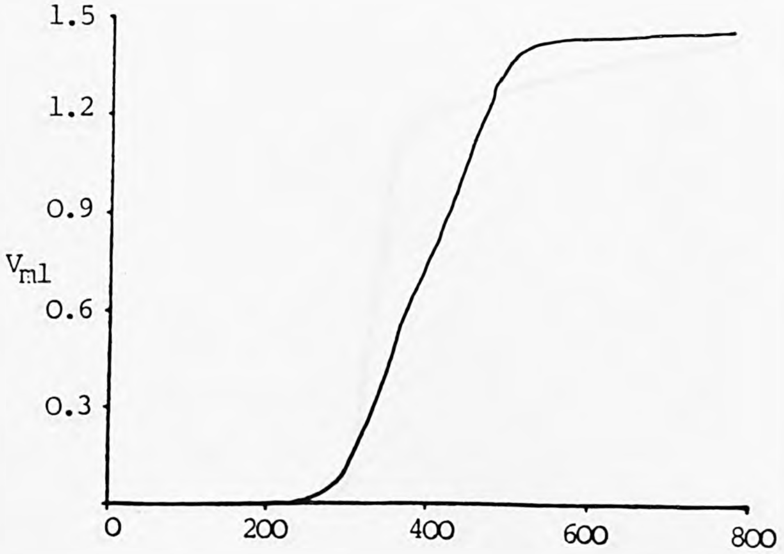
wt% salt	wt% DBBO	V_{co}/ml	maximum concentration (ppm)	T(CO_{max})	maximum concentration (ppm)	T(CO_{max})	$T_{DTG\ max}$		
							2nd	3rd	4th
4.26	-	1.11	624	361	395	490	245	325	490
21.88	-	1.064	553	360	-	-	245	315	495
7.43	8.80	1.28	581	368	500	493	250	335	495
15.9	8.4	1.29	418	364	418	405	245	315	435

Fig. 3.33 The variation of carbon monoxide concentration with temperature for cotton treated with 4.26 wt% ammonium sulphamate



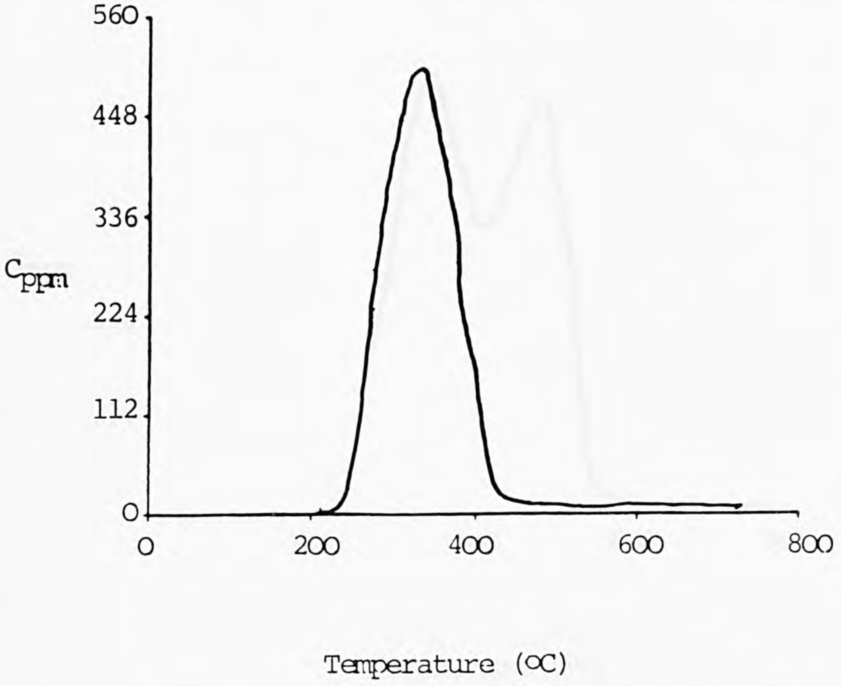
Temperature (°C)

The total volume of carbon monoxide evolved during the thermal decomposition of cotton treated with 4.26 wt% ammonium sulphamate



Temperature (°C)

Fig. 3.34 The variation of carbon monoxide concentration with temperature for cotton treated with 21.88 wt% ammonium sulphamate



The total volume of carbon monoxide evolved during the thermal decomposition of cotton treated with 21.88 wt% ammonium sulphamate

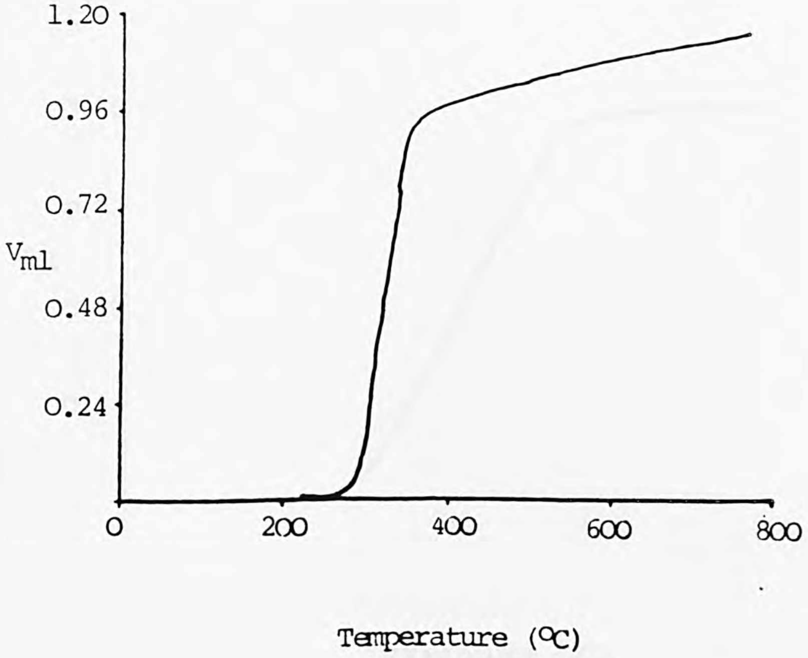
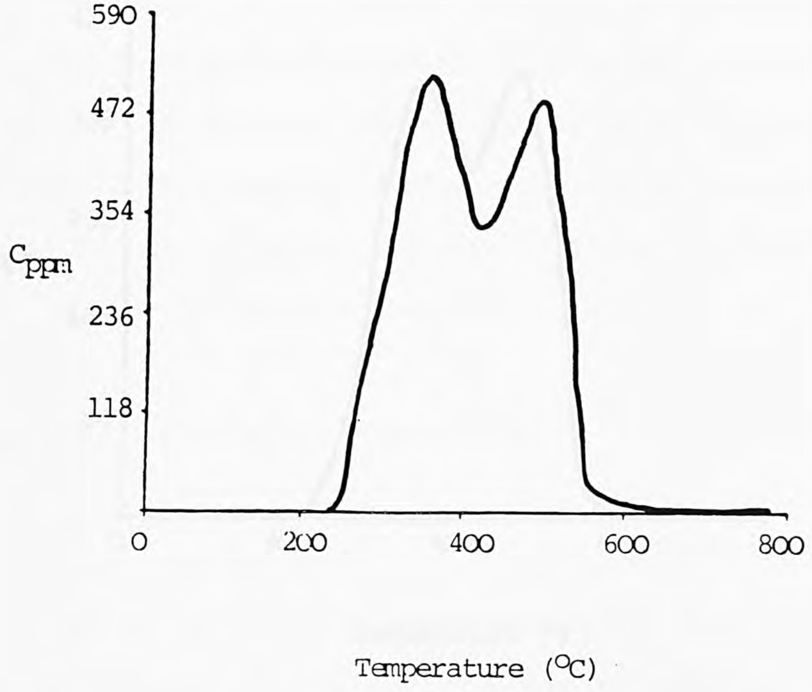


Fig. 3.35 The variation of carbon monoxide concentration With temperature for cotton treated with 7.43 wt% ammonium sulphamate and 8.80 wt% DBBO



The total volume of carbon monoxide evolved during the thermal decomposition of cotton treated with 7.43 wt% ammonium sulphamate and 8.80 wt% DBBO

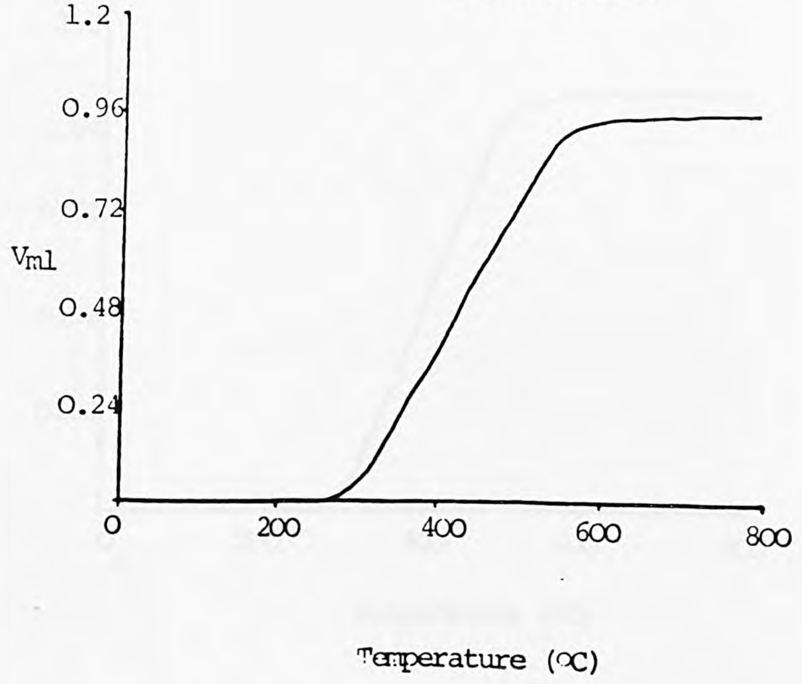
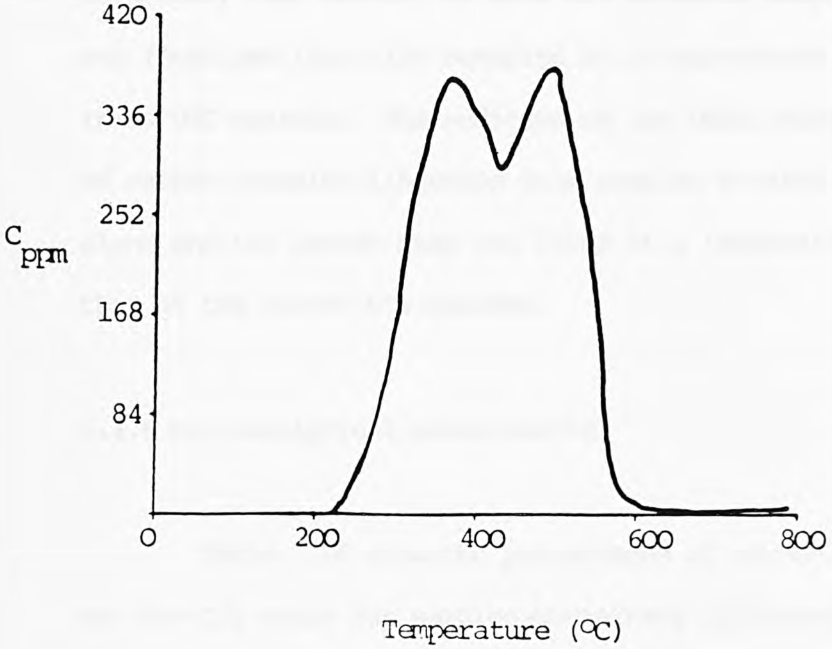
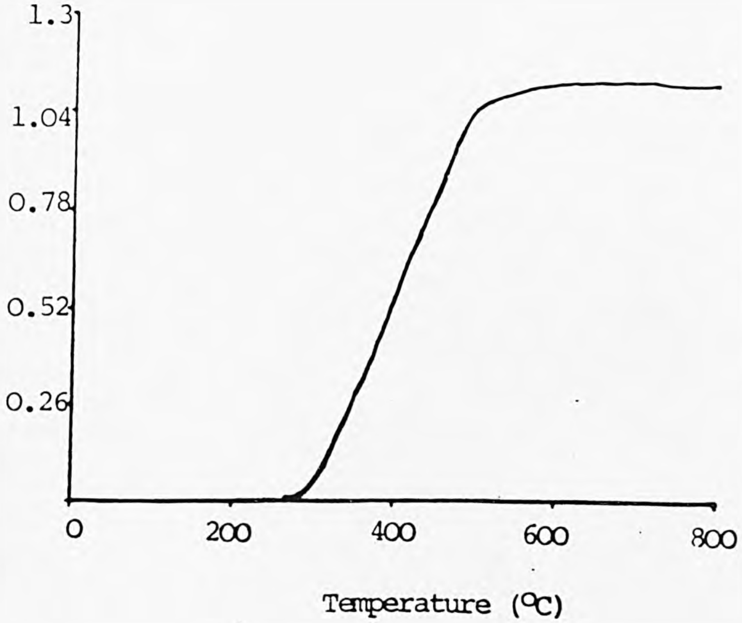


Fig. 3.36 The variation of carbon monoxide concentration with temperature for cotton treated with 15.90 wt% ammonium sulphamate and 8.40 wt% DBBO



Total volume of carbon monoxide evolved during the thermal decomposition of cotton treated with 15.90 wt% ammonium sulphamate and 8.40 wt% DBBO



relatively high loading of 21.8 wt% ammonium sulphamate, one maximum was found and this also occurred at a temperature 40° higher than the third DTG maximum. The addition of the DBBO increased the total amount of carbon monoxide liberated from samples treated with the sulphamate alone and the second peak was found at a temperature much lower than that of the fourth DTG maximum.

3.4.6 Microanalytical measurements

Table 3.26 shows the percentages of carbon, hydrogen and oxygen and the C/H ratio for samples containing different amounts of ammonium sulphamate. The results show that the extent of dehydration of the cotton increases as the temperature is raised. However a greater loading of the salt increases the C/H ratio during the second weight loss stage but decreases it for the third weight loss stage.

Table 3.26. Microanalysis measurements for samples treated with ammonium sulphamate

wt% salt	weight loss stage	%C	%H	%O	C:H
4.26	2nd	54.780	4.760	40.460	11.508
	3rd	62.130	2.210	35.660	28.113
21.88	2nd	84.740	3.790	11.770	22.358
	3rd	63.020	2.490	34.490	25.309

3.5 The effect of ammonium sulphate-DBBO mixtures on the flammability of cotton fabric

3.5 The effect of ammonium sulphate-DBBO mixtures on the flammability of cotton fabric

3.5.1 The effect of ammonium sulphate on its own on the flammability of cotton fabric

Table 3.27 gives the LOI values for some cotton samples containing ammonium sulphate together with the percentage weight of the inorganic salt. It is clear that ammonium sulphate is a good flame retardant for cotton fabric. Thus an LOI value of 31.3 is obtained on addition of about 7 wt% of the additive and at a loading of about 19 wt% the LOI was 36. However, as can be seen from Table 3.27 and Fig. 3.37, at a loading of the sulphate higher than 10 wt% there is a decrease in its effectiveness per unit concentration. Thus an increase in concentration from 3.4 to 7.1 wt% causes an increase in the LOI value of about 8 units, whereas an increase in loading from 7 to 21 wt% causes the LOI to rise by only 6.5 units.

3.5.2 The combined effect of ammonium sulphate and DBBO on the flammability of cotton fabric

The results in Table 3.28 show that the addition of DBBO to cotton pretreated with ammonium sulphate slightly increases the flame-retardant activity of the inorganic salt. Fig. 3.38 is a map of the LOI values for a quartic polynomial in terms of composition for up to 10 equidistant LOI values; these are plotted as contour lines of constant LOI, for the system bounded by the vertices: A:100% cotton; B: 70% cotton, 30% ammonium sulphate; and C: 70% cotton, 30% DBBO.

Table 3.27 The effect of ammonium sulphate on the LOI value of cotton

Ammonium sulphate (wt%)	LOI
3.38	23.9
7.10	31.3
10.20	32.4
16.97	35.2
19.05	36.1
21.30	37.8

Fig. 3.37 The effect of ammonium sulphate on the flammability of cotton fabric

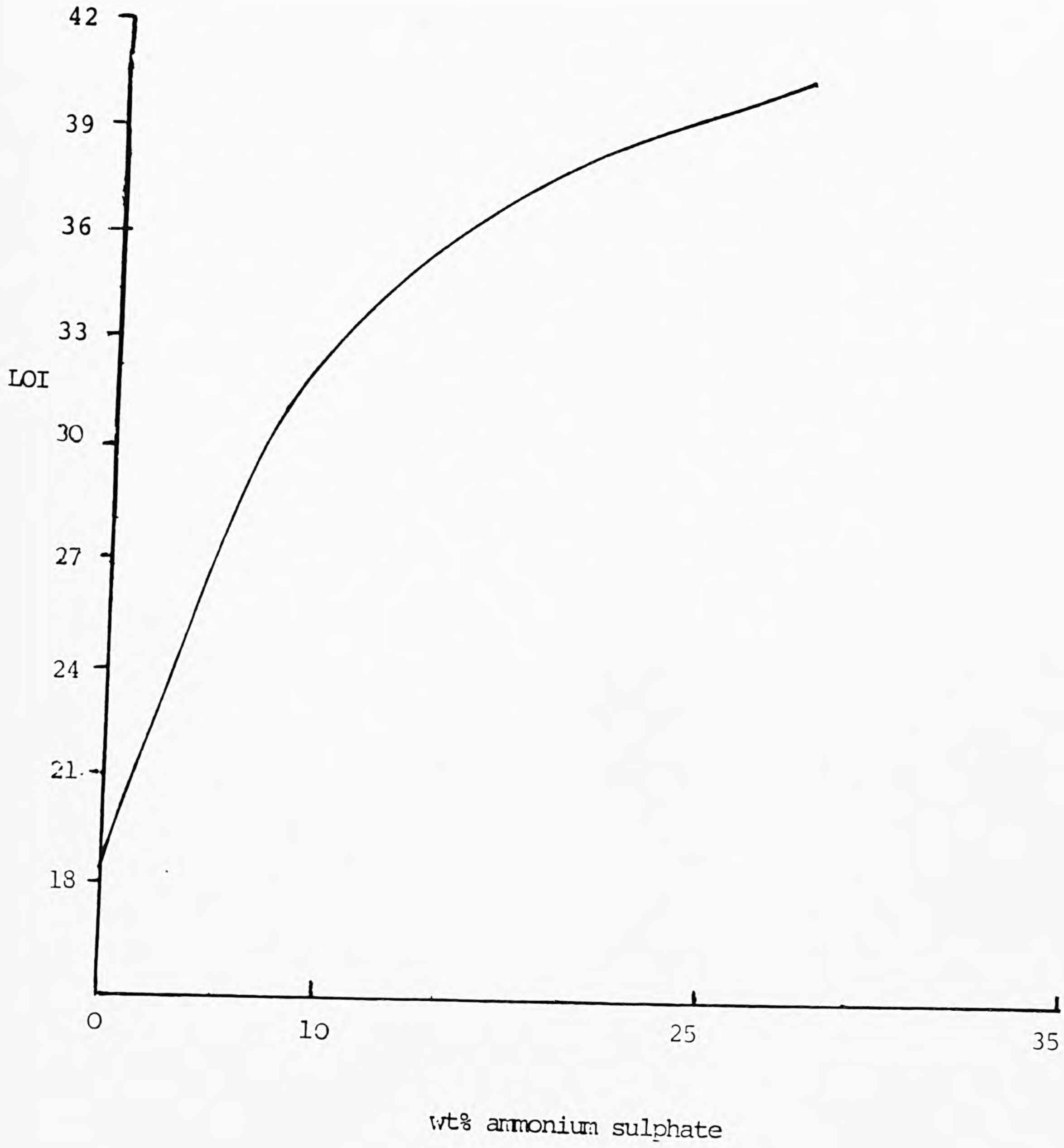
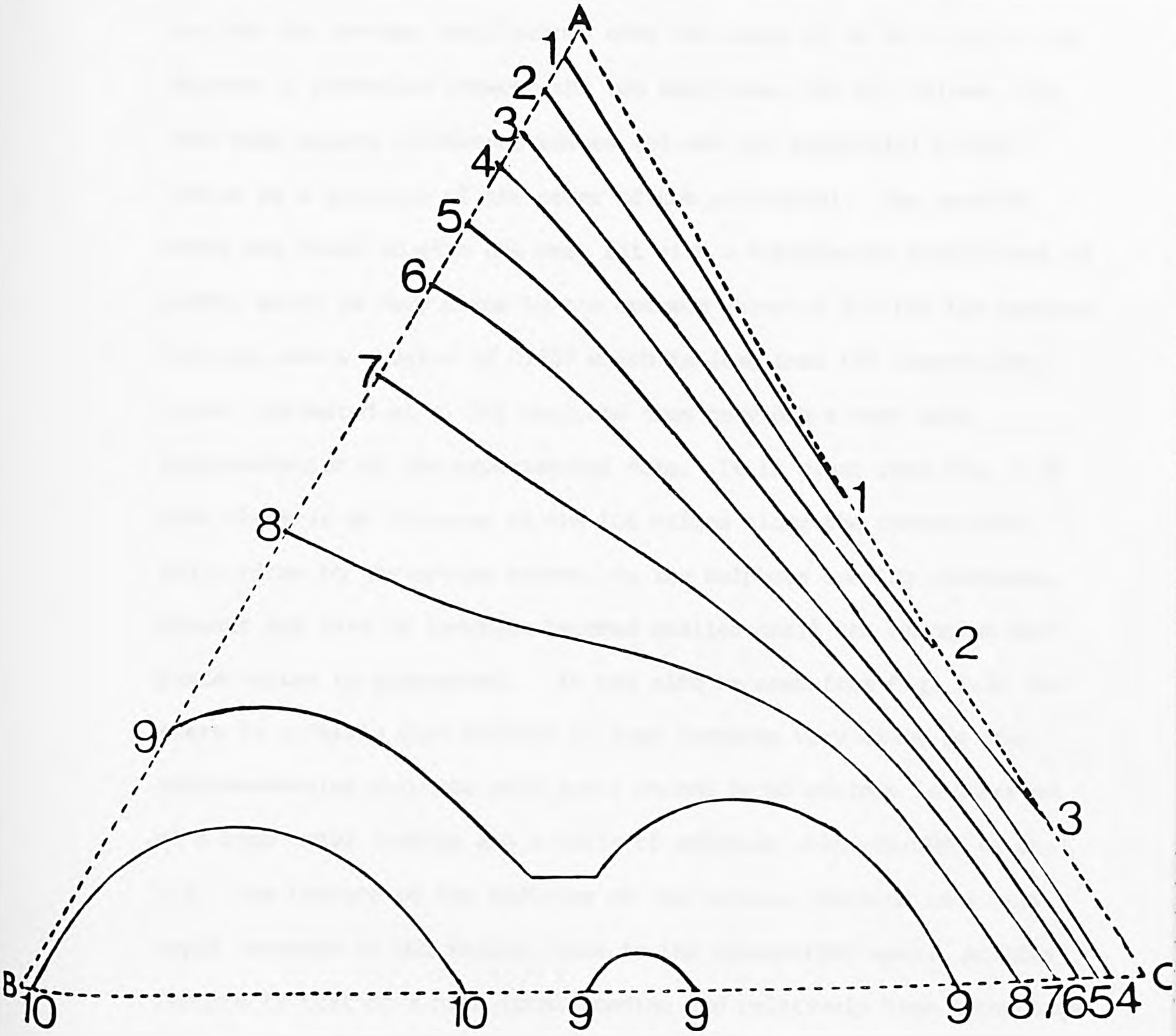


Table 3.28 The effect of a mixture of ammonium sulphate and DBBO on the flammability of cotton

Ammonium sulphate (wt%)	DBBO (wt%)	LOI
2.92	14.7	29.0
6.17	9.55	33.6
21.71	4.55	40.6
4.68	20.39	35.9
12.08	14.65	37.9
14.55	8.30	37.0

Fig. 3.38 Triangular diagram showing variation of LOI with composition for a cotton-ammonium sulphate-DBBO system



LOI values: (0) 18.10; (1) 20.24; (2) 22.38; (3) 24.52 (4) 26.66;
(5) 28.80; (6) 30.94; (7) 33.08; (8) 35.22; (9) 37.36; (10) 39.50.

Table 3.29 gives the parameters of all the fitting routines and these include the average coefficients over the range X2 or X3 = 0–0.3, the degrees of synergism between the two additives, the RCC values, the root mean square difference values (σ) and the sequential F-test ratios as a function of the order of the polynomial. The quartic model was found to give the best fit with a correlation coefficient of 0.992, which is very close to the optimum value of 1.0 for the perfect fitting, and a σ value of 0.657 which is less than the uncertainty value, estimated at ±1 LOI unit,and thus provides a very good representation of the experimental data. It is clear from Fig. 3.38 that there is an increase in the LOI values along the cotton-DBBO axis, close to the cotton vertex, as the sulphate loading increases. However the rate of increase becomes smaller until the ammonium sulphate vertex is approached. It can also be seen from Fig. 3.38 that there is a fairly flat maximum at high loadings very close to the cotton-ammonium sulphate axis and a second broad maximum is observed at a high total loading and a ratio of ammonium sulphate:DBBO of ca. 1:2. One feature of the addition of the bromine compound is a very rapid increase in LOI values close to the cotton-DBBO axis. Another feature is that at a high total loading and relatively high percentage of the bromine compound the addition of a small amount of ammonium sulphate causes a large increase in LOI values, whereas at high ratios of ammonium sulphate in the mixture the addition of the DBBO does not seem to affect the LOI values so much. Thus, for example, on fixing the loading of the bromine compound at ca. 15 wt% and varying that of ammonium

Table 3.29 Regression correlation coefficients (RCC), root mean square differences (σ), F-test ratios, average coefficients and synergism values as a function of the order of the polynomials for cotton-ammonium sulphate-DBBO systems

order	RCC	σ	F-test ratio		*average coefficient synergism	
1	0.751	3.176	42.433	≠amm	98.855.D.	8.796
				DBBO	42.810.D.	8.088
				+syn	0.2 .D.	-
2	0.901	2.073	19.861	amm	94.172.D.	9.756
				DBBO	33.711.D.	9.246
				syn	556.081.D.	83.777
3r	0.905	2.063	1.364	amm	90.659.D.	10.166
				DBBO	28.985.D.	10.053
				syn	524.440.D.	87.675
3	0.977	1.052	37.050	amm	129.198.D.	7.405
				DBBO	23.881.D.	6.240
				syn	64.655.D.	71.382
4	0.992	0.657	11.839	amm	103.074.D.	6.590
				DBBO	21.298.D.	4.254
				syn	657.818.D.	137.105

* average coefficient over a range of X2 or X3 = 0-0.3

\+ syn = synergism

≠ amm = ammonium sulphate

sulphate from 0 to 15 wt% the LOI increases from 22 to about 37 i.e. by 15 units; whereas, if the loading of ammonium sulphate is fixed also at 15 wt% and that of the bromine compound is increased to 15 wt%, the LOI increases only by about 2 units. This shows that the sulphate on its own is a good flame retardant for the cellulosic material and the area of the diagram which is most sensitive to changes in the ratio of the two additives is that close to the cotton-DBBO axis.

3.5.3 Simultaneous thermal analysis of cotton treated with ammonium sulphate

Figs. 3.39-3.41 show some TG and DTG curves for cotton treated with various amounts of ammonium sulphate and Table 3.30 gives the characteristic features of the various stages. All the samples into which ammonium sulphate is incorporated exhibit four weight loss stages. The weight loss in the first stage decreases as the loading of ammonium sulphate increases and this stage is probably due to the loss of water absorbed. The second and third stages are observed much earlier than the main decomposition stage for cellulose itself. Table 3.30 shows that the weight loss in the second stage for a sample treated with 19.1 wt% ammonium sulphate was 10% lower than for samples treated with 10.2 and 7.0 wt% of the salt; the rate of weight loss of the more heavily loaded sample is slightly lower but the maximum rate

Table 3.30 Thermoanalytical results for cotton + ammonium sulphate

wt% ammonium sulphate	19.05	10.20	7.0
Initial weight (mg)	8.980	7.84	7.640
Total weight lost (mg/%)	85.94	96.15	97.07
T_0 (°C/K)			
$T_{1\%}$ (°C/K)			
Gain Stage			
Wt gain (mg/%)			
DTG_{max} (mg min^{-1}/% min^{-1})			
T (DTG_{max}) (°C/K)			
DTA_{max} (μV/μV mg^{-1})			
T (DTA_{max}) (°C/K)			
T range (°C/K)			
First Loss			
Wt loss (mg/%)	0.278	3.31	4.93
DTG_{max} (mg min^{-1}/% min^{-1})			
T (DTG_{max}) (°C/K)			
DTA_{max} (μV/μV mg^{-1})			
T (DTA_{max}) (°C/K)			
T range (°C/K)	50.90	50.90	50.90
Second Loss			
Wt loss (mg/%)	23.66	35.58	35.45
DTG_{max} (mg min^{-1}/% min^{-1})	10.57	12.11	14.39
T (DTG_{max}) (°C/K)	250	240	240
DTA_{max} (μV/μV mg^{-1})			
T (DTA_{max}) (°C/K)			
T range (°C/K)	90–260	90–290	90–285
Third Loss			
Wt loss (mg/%)	34.97	27.29	27.22
DTG_{max} (mg min^{-1}/% min^{-1})	2.78	1.59	1.96
T (DTG_{max}) (°C/K)	275	305	300
DTA_{max} (μV/μV mg^{-1})			
T (DTA_{max}) (°C/K)			
T range (°C/K)	260–400	290–405	285–410
Fourth Loss			
Wt loss (mg/%)	27.04	29.97	29.45
DTG_{max} (mg min^{-1}/% min^{-1})	1.11	1.27	1.63
T (DTG_{max}) (°C/K)	485	500	4190
DTA_{max} (V/ V mg^{-1})			
T (DTA_{max}) (°C/K)			
T range (°C/K)	400–585	405–560	410–560
LOI			
O_3	36.1	32.4	31.3

Fig. 3.39 Thermogravimetric analysis curves for cotton treated with 7.00 wt% ammonium sulphate

TG, ——— DTG, - - - - - - -

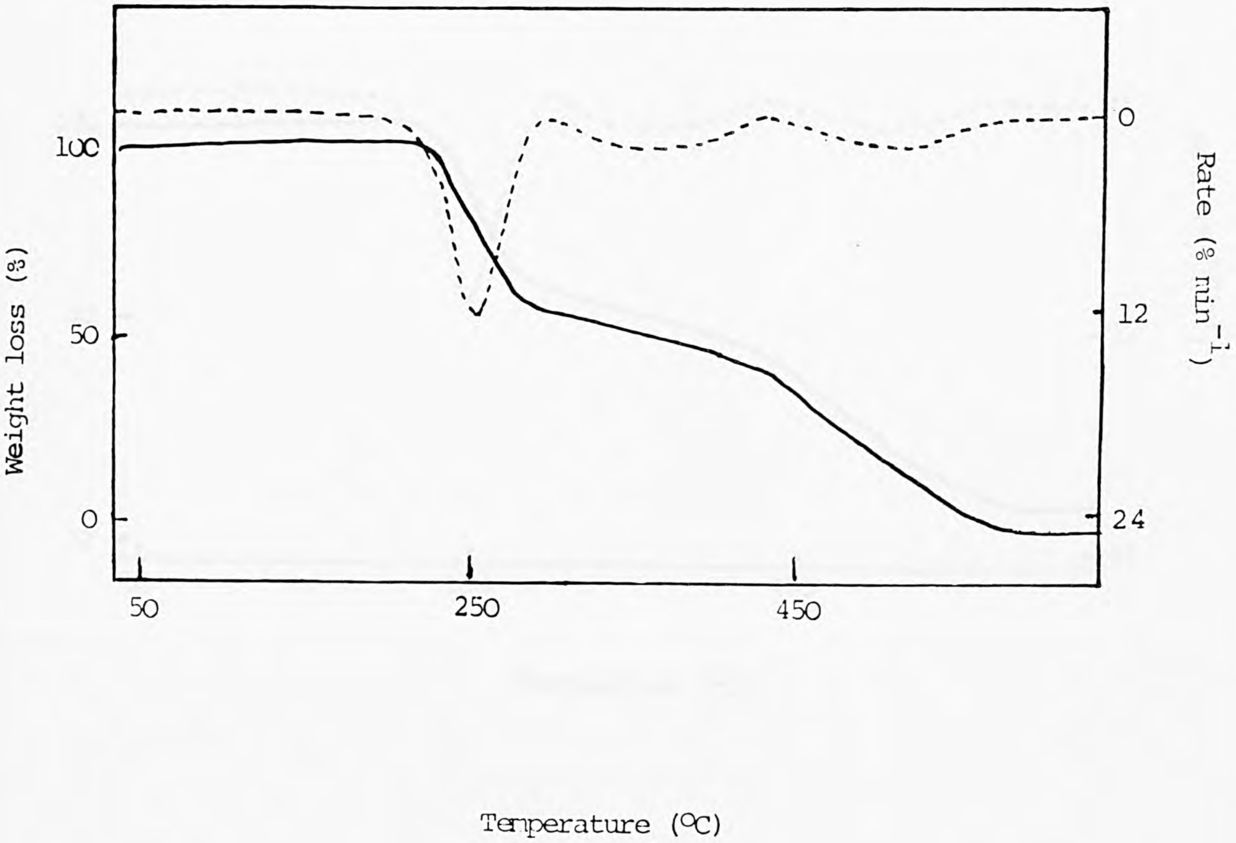


Fig. 3.40 Thermogravimetric analysis curves for cotton treated with 10.20 wt% ammonium sulphate

TG, ———— DTG, - - - - - - -

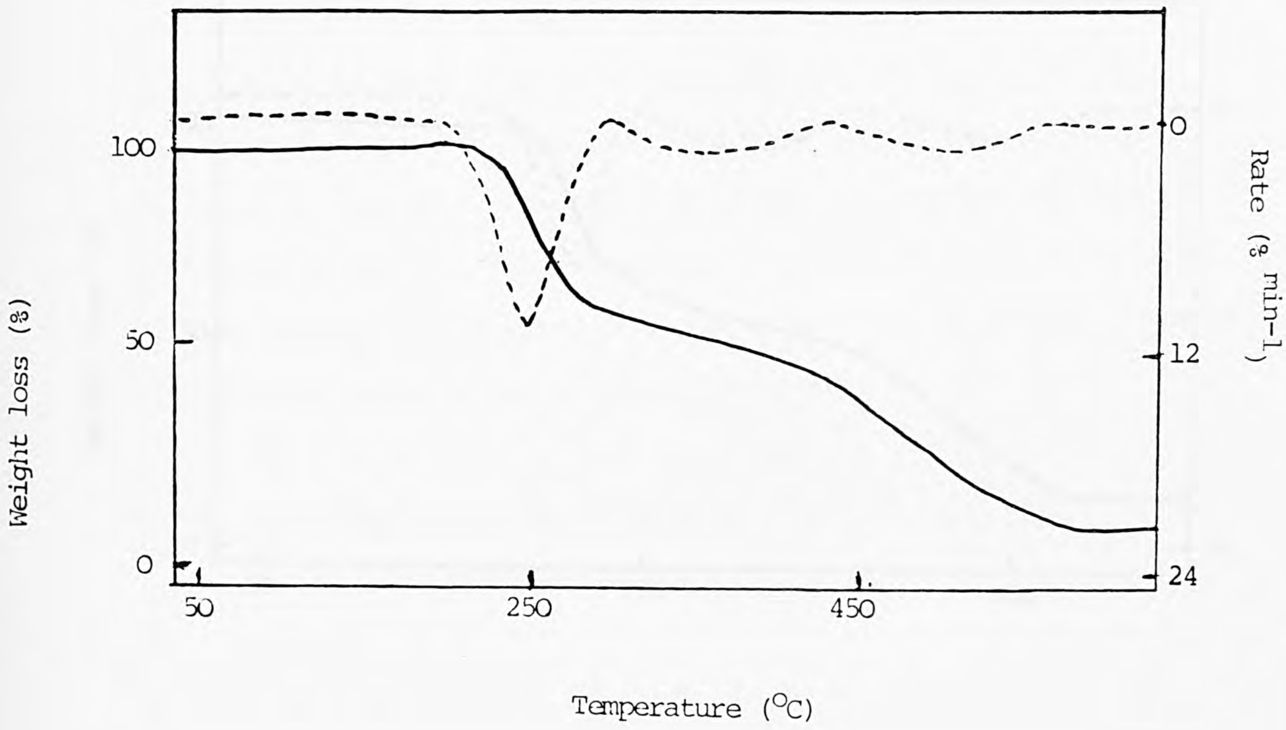
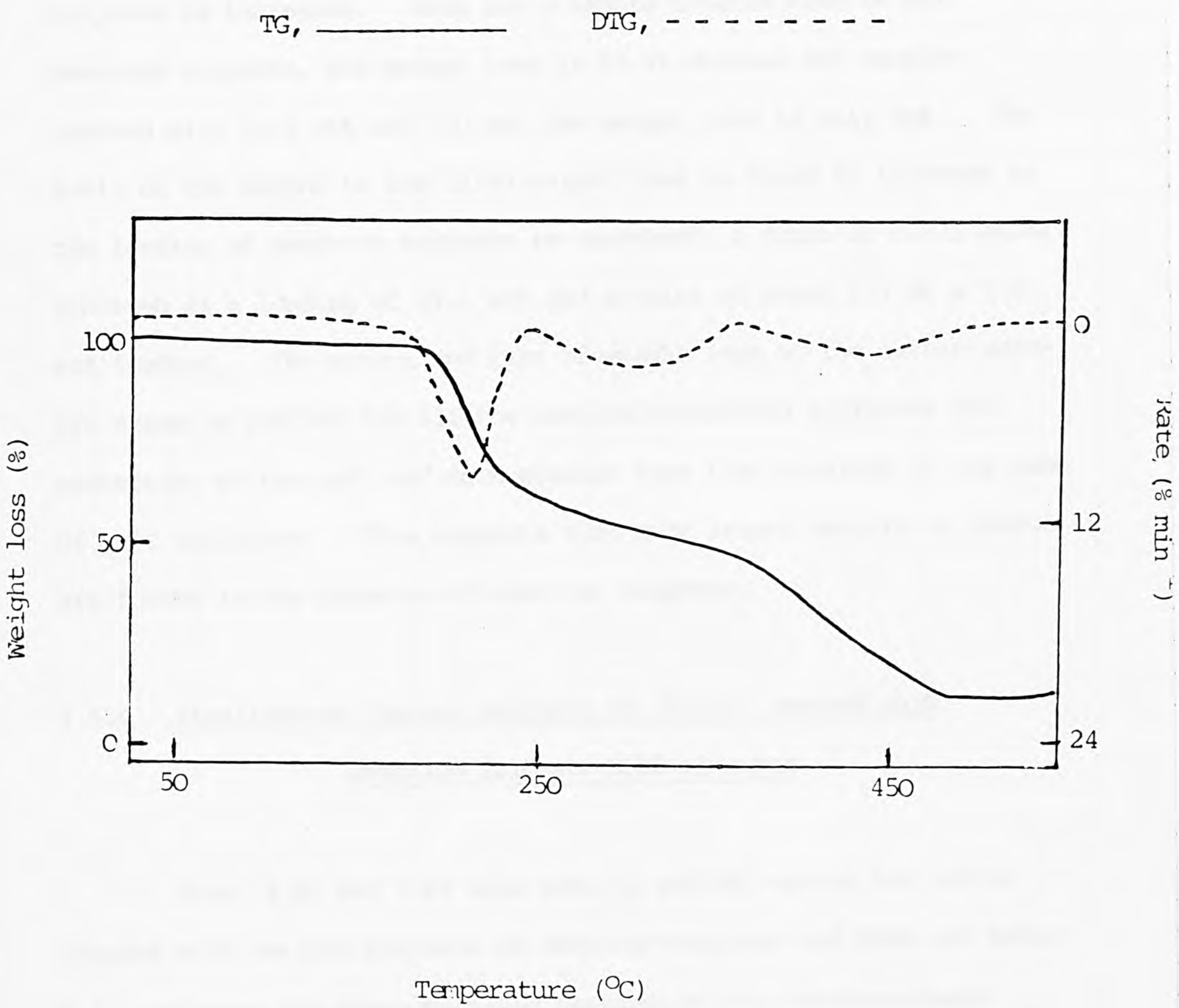


Fig. 3.41 Thermogravimetric analysis curves for sample treated with 19.05 wt% ammonium sulphate



of weight loss is observed at a slightly higher temperature. The weight loss during the third stage increases as the loading of the sulphate is increased. Thus for a sample treated with 19 wt% ammonium sulphate, the weight loss is 43.2% whereas for samples treated with 10.2 wt% and 7.0 wt% the weight loss is only 30%. The ratio of the second to the third weight loss is found to increase as the loading of ammonium sulphate is decreased, a ratio of 0.675 being achieved at a loading of 19.1 wt% and a value of about 1.3 at a 7.0 wt% loading. The extent and rate of weight loss at the carbon burn-off stage is similar for all the samples containing different concentration of the salt and much greater than that obtained in the case of pure cellulose. This suggests that much larger amounts of carbon are formed in the presence of ammonium sulphate.

3.5.4 Simultaneous thermal analysis of cotton treated with ammonium sulphate-DBBO mixtures

Figs. 3.42 and 3.43 show some TG and DTG curves for cotton treated with various mixtures of ammonium sulphate and DBBO and Table 3.31 indicates the characteristic features of the various stages. These figures and table show that all the samples treated with the mixtures exhibit four weight-loss stages. The second stage occurs as similar temperature to that obtained for samples treated with ammonium sulphate alone. However the rates of weight loss are lower. With the addition of the mixture the third stage was found

Table 3.31 Thermoanalytical results for cotton + ammonium sulphate + DBBO

wt% ammonium sulphate	14.55		12.08		
wt% DBBO	8.3		14.65		
Initial weight (mg)	7.812		8.340		
Total weight lost (mg/%)	96.521		94.35		
T_0 (°C/K)					
$T_{1\%}$ (°C/K)					
Gain Stage					
Wt gain (mg/%)					
DTG_{max} (mg min^{-1}/% min^{-1})					
T (DTG_{max}) (°C/K)					
DTA_{max} (µV/µV mg^{-1})					
T (DTA_{max}) (°C/K)					
T range (°C/K)					
First Loss					
Wt loss (mg/%)	2.841		1.90		
DTG_{max} (mg min^{-1}/% min^{-1})					
T (DTG_{max}) (°C/K)					
DTA_{max} (µV/µV mg^{-1})					
T (DTA_{max}) (°C/K)					
T range (°C/K)	50.75		50-85		
Second Loss					
Wt loss (mg/%)	33.06		36.69		
DTG_{max} (mg min^{-1}/% min^{-1})	8.96		8.393		
T (DTG_{max}) (°C/K)	240		240		
DTA_{max} (µV/µV mg^{-1})					
T (DTA_{max}) (°C/K)					
T range (°C/K)	75-255		75-260		
Third Loss					
Wt loss (mg/%)	25.04		29.365		
DTG_{max} (mg min^{-1}/% min^{-1})	3.200		3.597		
T (DTG_{max}) (°C/K)	260		265		
DTA_{max} (µV/µV mg^{-1})					
T (DTA_{max}) (°C/K)					
T range (°C/K)	255-350		260-370		
Fourth Loss					
Wt loss (mg/%)	35.58		28.29		
DTG_{max} (mg min^{-1}/% min^{-1})	1.280		1.199		
T (DTG_{max}) (°C/K)	500		500		
DTA_{max} (V/ V mg^{-1})					
T (DTA_{max}) (°C/K)					
T range (°C/K)	350-580		370-580		
LOI	37.0		37.9		
O_s					

Fig. 3.42 Thermogravimetric analysis curves for cotton treated with 14.55 wt% ammonium sulphate and 8.3 wt% DBBO

TG, ————— ; DTG, - - - - - - - - - - -

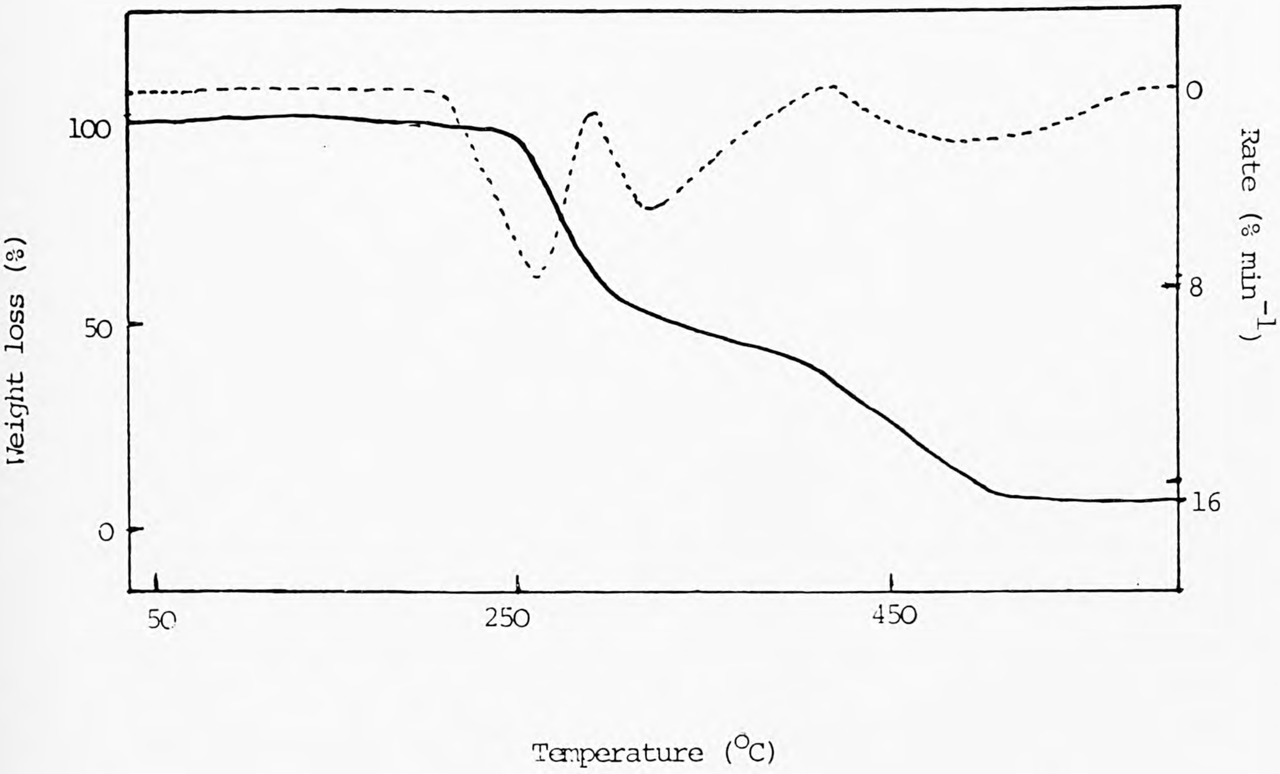
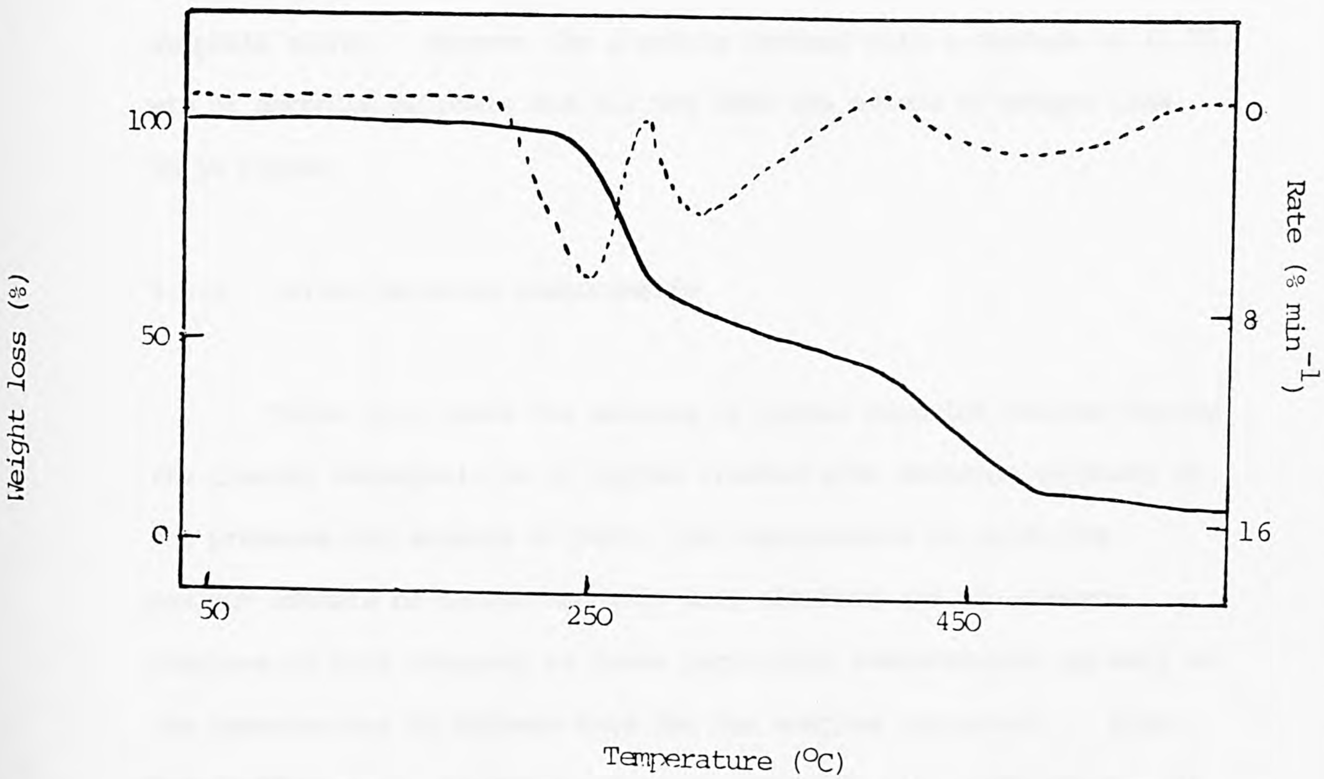


Fig. 3.43 Thermogravimetric analysis curves for cotton treated with 12.08 wt% ammonium sulphate and 14.65 wt% DBBO

TG, ———— ; DTG, - - - - - - - - - - -



at a lower temperature and showed a smaller weight loss but a higher rate compared with the third stage for samples treated with the sulphate on its own (Tables 3.30 and 3.31). The ratio of the second stage to the third stage is now 1.32 i.e. higher than that for samples treated with the inorganic salt alone. The carbon burn-off stage was found to be slightly different from that for samples treated with the sulphate alone. However for a sample treated with a mixture of 14.55 wt% of ammonium sulphate and 8.3 wt% DBBO the extent of weight loss is 5% higher.

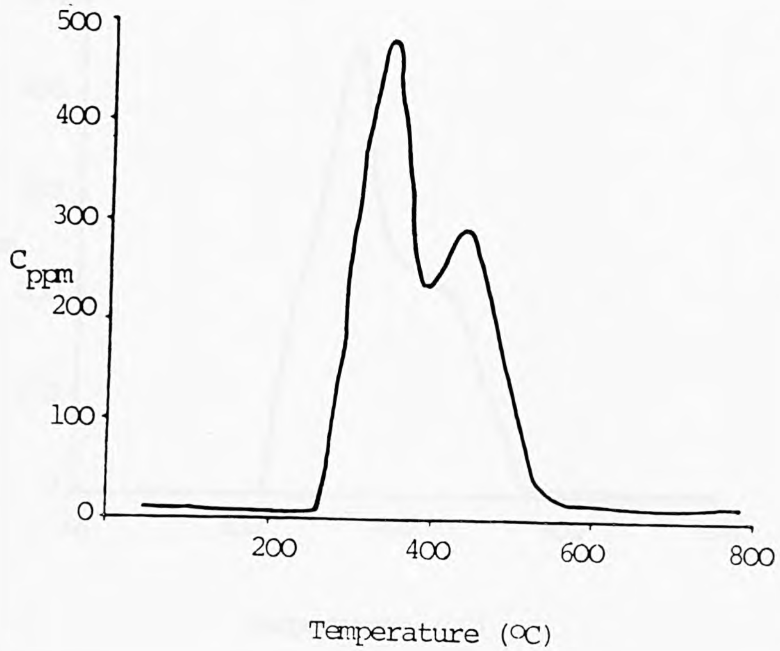
3.5.5 Carbon monoxide measurements

Table 3.32 shows the amounts of carbon monoxide evolved during the thermal decomposition of cotton treated with ammonium sulphate in the presence and absence of DBBO, the temperatures at which the maximum amounts of carbon monoxide were obtained and the concentrations of this compound at these particular temperatures, as well as the temperatures of maximum rate for the samples concerned.. Figs. 3.44-3.47 show the variation of carbon monoxide with temperature. It can be seen from this table and Figs. 3.44-3.47 that there is a slight increase in the amount of carbon monoxide evolved as the loading of the ammonium salt is increased. Two peaks were found at the higher loading, whereas only one was observed at the lower loading. The first CO peak was found to be higher than the second and third DTG maxima and much lower than the fourth maximum. However the second peak was

Table 3.32 The variation of carbon monoxide concentration with additives composition

wt% salt	wt% DBBO	V_{co}/ml	maximum concentration (ppm)	$T(CO_{max})$	maximum concentration (ppm)	$T(CO_{max})$	T_{DTG} max		
							2nd	3rd	4th
7.00	-	0.683	460	350	-	-	240	300	490
19.05	-	0.728	493	343	296	438	250	275	455
14.55	8.30	1.201	545	370	528	506	240	260	500
12.08	14.65	1.270	477	373	447	515	244	265	500

Fig. 3.44 The variation of carbon monoxide concentration with temperature for cotton treated with 19.05 wt% ammonium sulphate



The total volume of carbon monoxide evolved during the thermal decomposition of cotton treated with 19.05 wt% ammonium sulphate

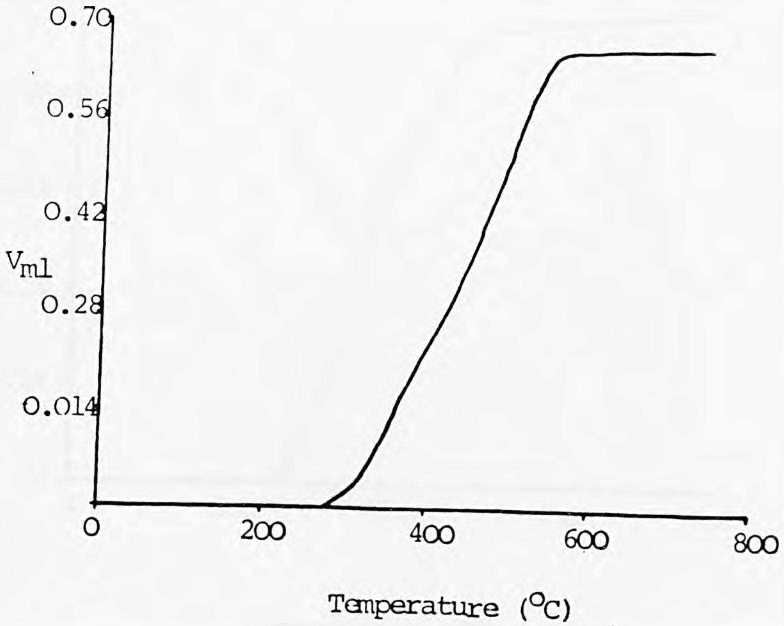
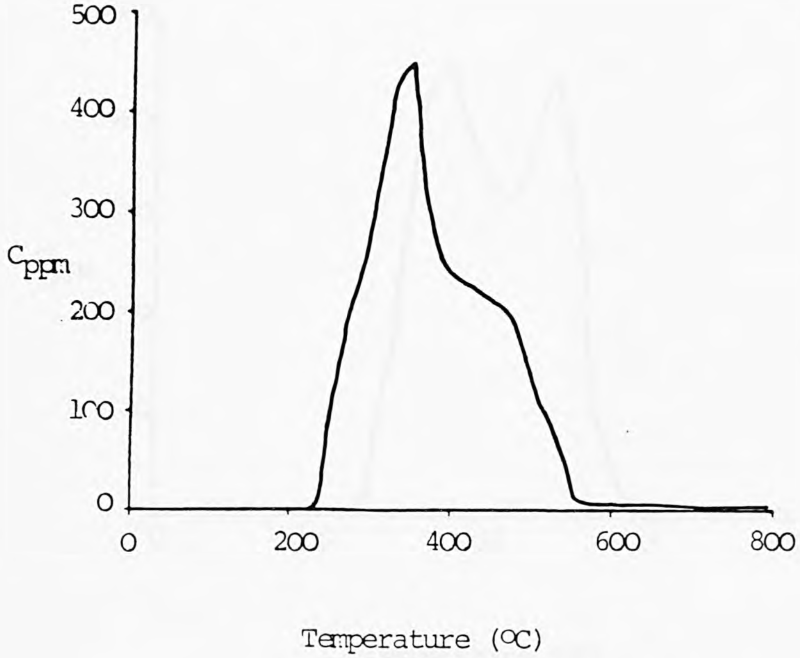


Fig. 3.45 The variation of carbon monoxide concentration with temperature for cotton treated with 7.0 wt% ammonium sulphate



The total volume of carbon monoxide evolved during the thermal decomposition of cotton treated with 7.0 wt% ammonium sulphate

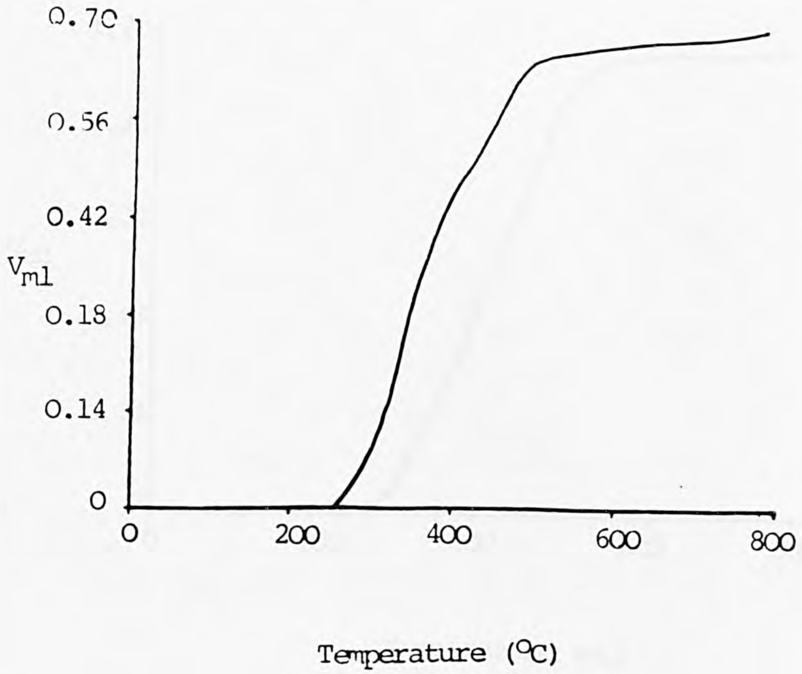
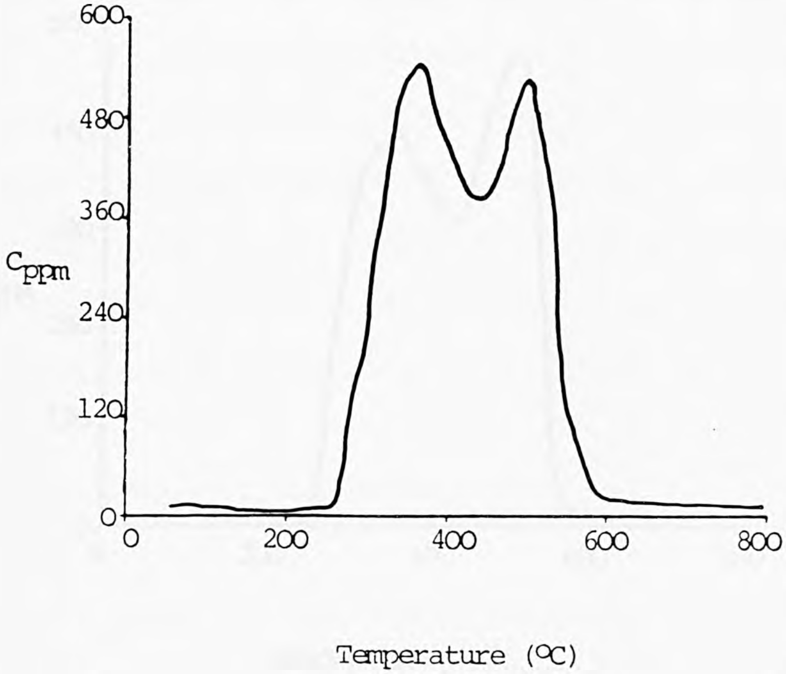


Fig. 3.46 The variation of carbon monoxide concentration with temperature for cotton treated with 14.55 wt% ammonium sulphate and 8.3 wt% DBBO



The total volume of carbon monoxide evolved during the thermal decomposition of cotton treated with 14.55 wt% ammonium sulphate and 8.3 wt% DBBO

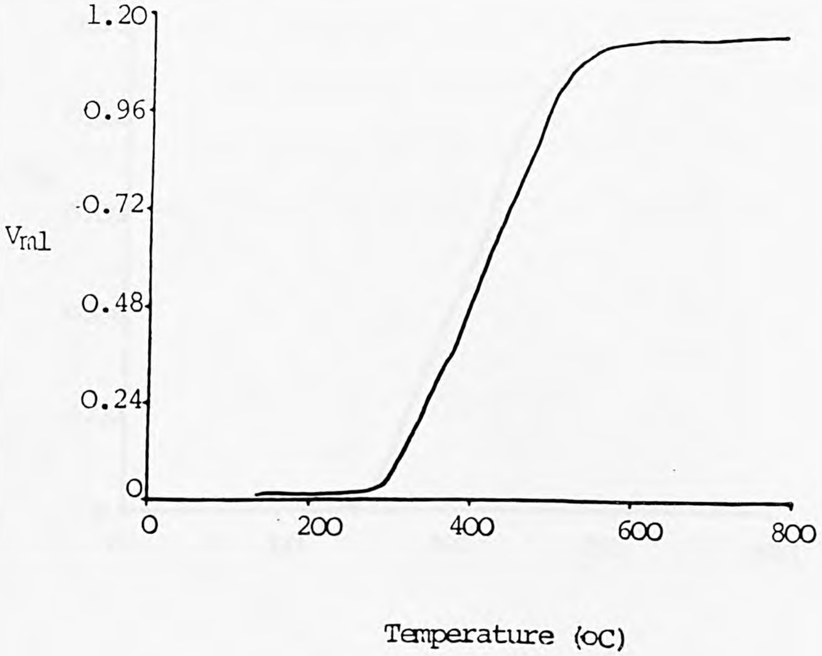
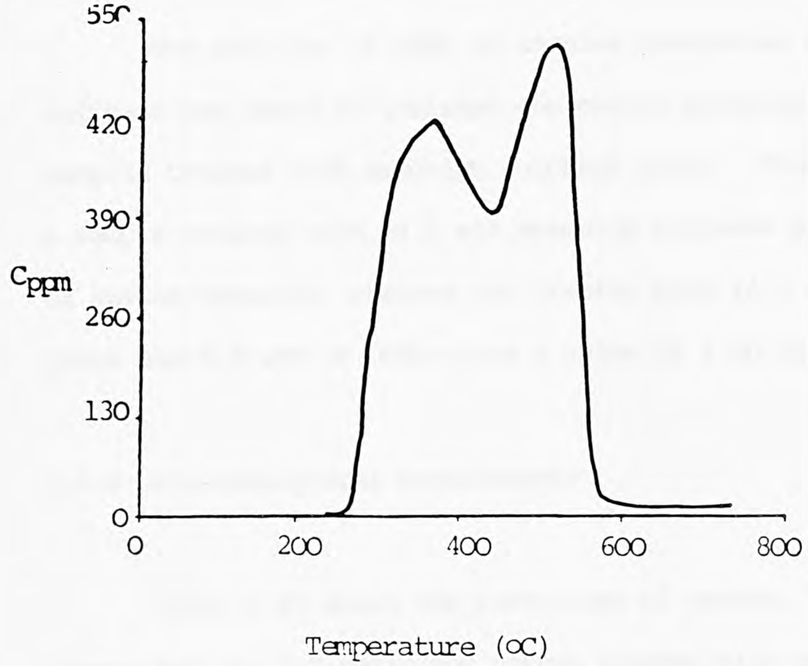
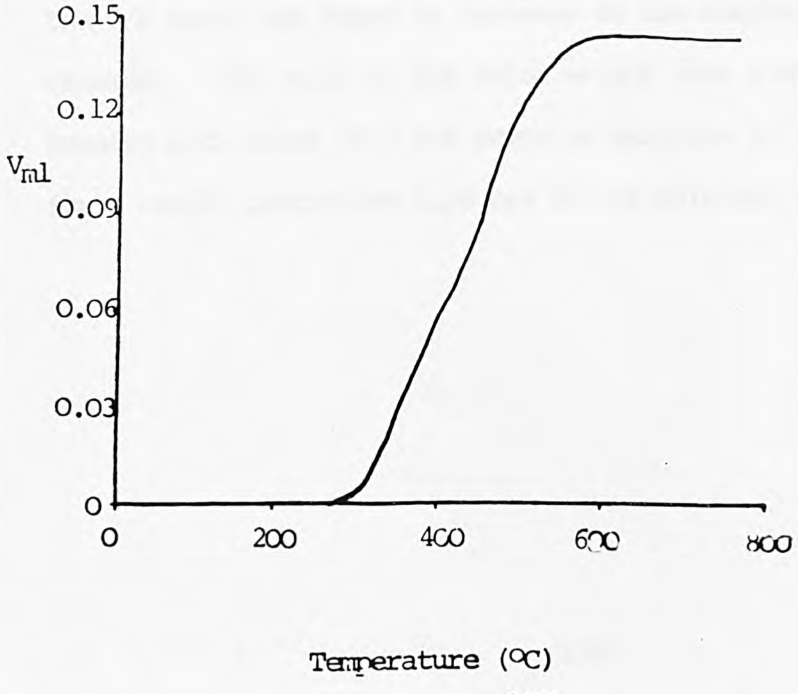


Fig. 3.47 The variation of carbon monoxide concentration with temperature for cotton treated with 12.1 wt% ammonium sulphate and 14.65 wt% DBBO



The total volume of carbon monoxide evolved during the thermal decomposition of cotton treated with 12.1 wt% ammonium sulphate and 14.65 wt% DBBO



found at a temperature 50° below the fourth DTG maximum.

The addition of DBBO to samples pretreated with ammonium sulphate was found to increase the carbon monoxide more than for samples treated with ammonium sulphate alone. Thus for example a sample treated with 19.1 wt% ammonium sulphate produces 0.73 ml of carbon monoxide, whereas one treated with 14.5 wt% of the sulphate and 8.3 wt% of DBBO gives a value of 1.20 ml.

3.5.6 Microanalytical measurements

Table 3.33 shows the percentage of carbon, hydrogen and oxygen and the C:H ratio for cotton treated with various loadings of ammonium sulphate. The results show that the treatment of cotton fabric with the sulphate causes dehydration of the cellulose and the extent of the dehydration is greater in the third weight loss stage than in the second weight loss stage. However the C/H ratio was found to increase as the sulphate loading decreased. The ratio at the third weight loss stage for a sample treated with about 19.1 wt% ammonium sulphate is 16.89, whereas for a sample containing 7.00 wt% of the sulphate it is 20.7.

Table 3.33 Microanalysis measurements for samples treated with ammonium sulphate

Wt% salt	weight loss stage	%C	%H	%C	C:H
7.0	2nd	62.02	4.453	33.52	13.927
	3rd	67.28	3.242	28.834	20.752
19.1	2nd	56.93	6.340	36.72	9.452
	3rd	72.66	4.30	23.04	16.897

3.6 The effects of other sulphur oxyacid salts on cotton

3.6 The effects of other sulphur oxyacid salts on cotton

3.6.1 Flammability measurements for samples treated with other metal sulphates

Table 3.34 gives the LOI values for samples treated with different inorganic sulphates together with the percentage weight of sulphate present. It can be seen that potassium sulphate, iron (III) sulphate and magnesium sulphate are not good flame retardants for cotton even at high loadings. For example a sample containing 17.9 wt% of potassium sulphate has an LOI value of 19.9 i.e. about 2 units higher than the untreated cotton. It can also be seen that cottons treated with copper sulphate and cobalt sulphate have higher LOI values than those treated with the other sulphates. However these figures are for flaming combustion. In fact the samples containing copper and cobalt exhibit smouldering combustion even at very low concentrations of oxygen, so that none of the sulphates in the table are effective flame retardants for the cotton fabric even when DBBO compound is added to them. A sample treated with 19.4 wt% of copper sulphate and about 5 wt% of DBBO had an LOI value of about 38 but still underwent smouldering combustion. The same situation was observed for samples treated with cobalt sulphate where the transition metal appeared to enhance smouldering of the cotton fabric.

Table 3.34 The effect of various sulphur oxyacid salts on the LOI value of cotton fabric

Salt	wt% salt	wt% DBBO	LOI
cobalt(II)	17.91	7.99	31.20
sulphate	7.31	16.82	28.40
	19.30	-	25.35
copper(II)	19.45	4.67	38.35
sulphate	7.19	16.59	40.90
	19.80	-	29.20
potassium	21.7	2.35	20.7
sulphate	8.69	18.69	22.0
	17.90	-	19.9
	9.42	-	19.6
iron(III)	14.92	8.11	27.3
sulphate	17.51	-	23.8
magnesium	10.68	19.08	27.6
sulphate	5.47	19.84	23.9
	8.24	-	18.7
	14.53	-	20.35

3.6.2 Simultaneous thermal analysis of cotton treated with different sulphates

Tables 3.35-3.38 give the characteristic features of the various decomposition stages of the cotton samples studied and Figs. 3.48-3.51 show the decomposition patterns for these salts. It can be seen that all the samples exhibit four weight loss stages. The percentage weight loss at the second stage for samples treated with cobalt sulphate is about 10% higher than for cotton treated with copper sulphate. However the percentage weight losses at the third stage are comparable. The temperatures of maximum rate for the second and the third stages for samples treated with copper sulphate are higher than for those for cobalt sulphate. The second and third weight loss stages for a sample treated with copper sulphate occurred at a lower temperature than for the main weight loss stage for pure cellulose. However the third weight loss for a sample treated with cobalt sulphate occurs above that for pure cellulose. The percentage weight loss at the carbon burn-off stage for samples treated with cobalt sulphate corresponds to about 12% of the cellulose initially present which is comparable with that for untreated cotton (11%); whereas it was smaller in the case of a cotton sample treated with copper sulphate.

Table 3.35 Thermoanalytical results for cotton + copper (II) sulphate

wt% copper (II) sulphate 19.86

Initial weight (mg)	8.239			
Total weight lost (mg/%)	81.244			
T_0 (°C/K)				
$T_{1\%}$ (°C/K)				
Gain Stage				
Wt gain (mg/%)				
DTG_{max} (mg min^{-1}/% min^{-1})				
T (DTG_{max}) (°C/K)				
DTA_{max} (μV/μV mg^{-1})				
T (DTA_{max}) (°C/K)				
T range (°C/K)				
First Loss				
Wt loss (mg/%)	2.85			
DTG_{max} (mg min^{-1}/% min^{-1})				
T (DTG_{max}) (°C/K)				
DTA_{max} (μV/μV mg^{-1})				
T (DTA_{max}) (°C/K)				
T range (°C/K)	45.190			
Second Loss				
Wt loss (mg/%)	33.35			
DTG_{max} (mg min^{-1}/% min^{-1})	4.857			
T (DTG_{max}) (°C/K)	250			
DTA_{max} (μV/μV mg^{-1})				
T (DTA_{max}) (°C/K)				
T range (°C/K)	190-170			
Third Loss				
Wt loss (mg/%)	33.15			
DTG_{max} (mg min^{-1}/% min^{-1})	12.75			
T (DTG_{max}) (°C/K)	315			
DTA_{max} (μV/μV mg^{-1})				
T (DTA_{max}) (°C/K)				
T range (°C/K)	270-340			
Fourth Loss				
Wt loss (mg/%)	6.894			
DTG_{max} (mg min^{-1}/% min^{-1})	0.910			
T (DTG_{max}) (°C/K)	410			
DTA_{max} (V/ V mg^{-1})				
T (DTA_{max}) (°C/K)				
T range (°C/K)	340-480			
LOI				
D_s	29.20			

Table 3.36 Thermoanalytical results for cotton + iron (III) sulphate

wt% iron (III) sulphate 17.51

Initial weight (mg)	8.096				
Total weight lost (mg/%)	85.118				
T_D (°C/K)					
$T_{1\%}$ (°C/K)					
Gain Stage					
Wt gain (mg/%)					
DTG_{max} (mg min^{-1}/% min^{-1})					
T (DTG_{max}) (°C/K)					
DTA_{max} (µV/µV mg^{-1})					
T (DTA_{max}) (°C/K)					
T range (°C/K)					
First Loss					
Wt loss (mg/%)	0.548				
DTG_{max} (mg min^{-1}/% min^{-1})					
T (DTG_{max}) (°C/K)					
DTA_{max} (µV/µV mg^{-1})					
T (DTA_{max}) (°C/K)					
T range (°C/K)	40.215				
Second Loss					
Wt loss (mg/%)	40.14				
DTG_{max} (mg min^{-1}/% min^{-1})	8.028				
T (DTG_{max}) (°C/K)	265				
DTA_{max} (µV/µV mg^{-1})					
T (DTA_{max}) (°C/K)					
T range (°C/K)	215-295				
Third Loss					
Wt loss (mg/%)	38.04				
DTG_{max} (mg min^{-1}/% min^{-1})	6.175				
T (DTG_{max}) (°C/K)	315				
DTA_{max} (µV/µV mg^{-1})					
T (DTA_{max}) (°C/K)					
T range (°C/K)	295-370				
Fourth Loss					
Wt loss (mg/%)	6.459				
DTG_{max} (mg min^{-1}/% min^{-1})	385				
T (DTG_{max}) (°C/K)	1.6				
DTA_{max} (V/ V mg^{-1})					
T (DTA_{max}) (°C/K)					
T range (°C/K)	370-390				
LOI	23.8				
D_s					

Table 3.37 Thermoanalytical results for cotton + potassium sulphate

wt% potassium sulphate 17.90

Initial weight (mg)	8.323				
Total weight lost (mg/%)	86.39				
T_0 (°C/K)					
$T_{1\%}$ (°C/K)					
Gain Stage					
Wt gain (mg/%)					
DTG_{max} (mg min^{-1}/% min^{-1})					
T (DTG_{max}) (°C/K)					
DTA_{max} (μV/μV mg^{-1})					
T (DTA_{max}) (°C/K)					
T range (°C/K)					
First Loss					
Wt loss (mg/%)	1.237				
DTG_{max} (mg min^{-1}/% min^{-1})					
T (DTG_{max}) (°C/K)					
DTA_{max} (μV/μV mg^{-1})					
T (DTA_{max}) (°C/K)					
T range (°C/K)	40–250				
Second Loss					
Wt loss (mg/%)	58.75				
DTG_{max} (mg min^{-1}/% min^{-1})	14.94				
T (DTG_{max}) (°C/K)	325				
DTA_{max} (μV/μV mg^{-1})					
T (DTA_{max}) (°C/K)					
T range (°C/K)	250–360				
Third Loss					
Wt loss (mg/%)	21.49				
DTG_{max} (mg min^{-1}/% min^{-1})	4.8				
T (DTG_{max}) (°C/K)	335				
DTA_{max} (μV/μV mg^{-1})					
T (DTA_{max}) (°C/K)					
T range (°C/K)	360–410				
Fourth Loss					
Wt loss (mg/%)	6.15				
DTG_{max} (mg min^{-1}/% min^{-1})	1.9				
T (DTG_{max}) (°C/K)	4.5				
DTA_{max} (μV/μV mg^{-1})					
T (DTA_{max}) (°C/K)					
T range (°C/K)	420–410				
LOI					
D_s					

Table 3.38 Thermoanalytical results for cotton + cobalt (II) sulphate

wt% cobalt (II) sulphate 19.30

Initial weight (mg)	9.099			
Total weight lost (mg/%)	89.33			
T_0 (°C/K)				
$T_{1\%}$ (°C/K)				
Gain Stage				
Wt gain (mg/%)				
DTG_{max} (mg min^{-1}/% min^{-1})				
T (DTG_{max}) (°C/K)				
DTA_{max} (μV/μV mg^{-1})				
T (DTA_{max}) (°C/K)				
T range (°C/K)				
First Loss				
Wt loss (mg/%)	7.26			
DTG_{max} (mg min^{-1}/% min^{-1})	1.64			
T (DTG_{max}) (°C/K)				
DTA_{max} (μV/μV mg^{-1})				
T (DTA_{max}) (°C/K)				
T range (°C/K)	40-210			
Second Loss				
Wt loss (mg/%)	41.59			
DTG_{max} (mg min^{-1}/% min^{-1})	8.24			
T (DTG_{max}) (°C/K)	270			
DTA_{max} (μV/μV mg^{-1})				
T (DTA_{max}) (°C/K)				
T range (°C/K)	210-295			
Third Loss				
Wt loss (mg/%)	36.76			
DTG_{max} (mg min^{-1}/% min^{-1})	2.47			
T (DTG_{max}) (°C/K)	370			
DTA_{max} (μV/μV mg^{-1})				
T (DTA_{max}) (°C/K)				
T range (°C/K)	295-380			
Fourth Loss				
Wt loss (mg/%)	10.98			
DTG_{max} (mg min^{-1}/% min^{-1})	7.69			
T (DTG_{max}) (°C/K)	395			
DTA_{max} (V/ V mg^{-1})				
T (DTA_{max}) (°C/K)				
T range (°C/K)	380-435			
LOI	25.35			
O_s				

Fig. 3.48 Thermogravimetric analysis curves for cotton treated with 19.86 wt% copper (II) sulphate

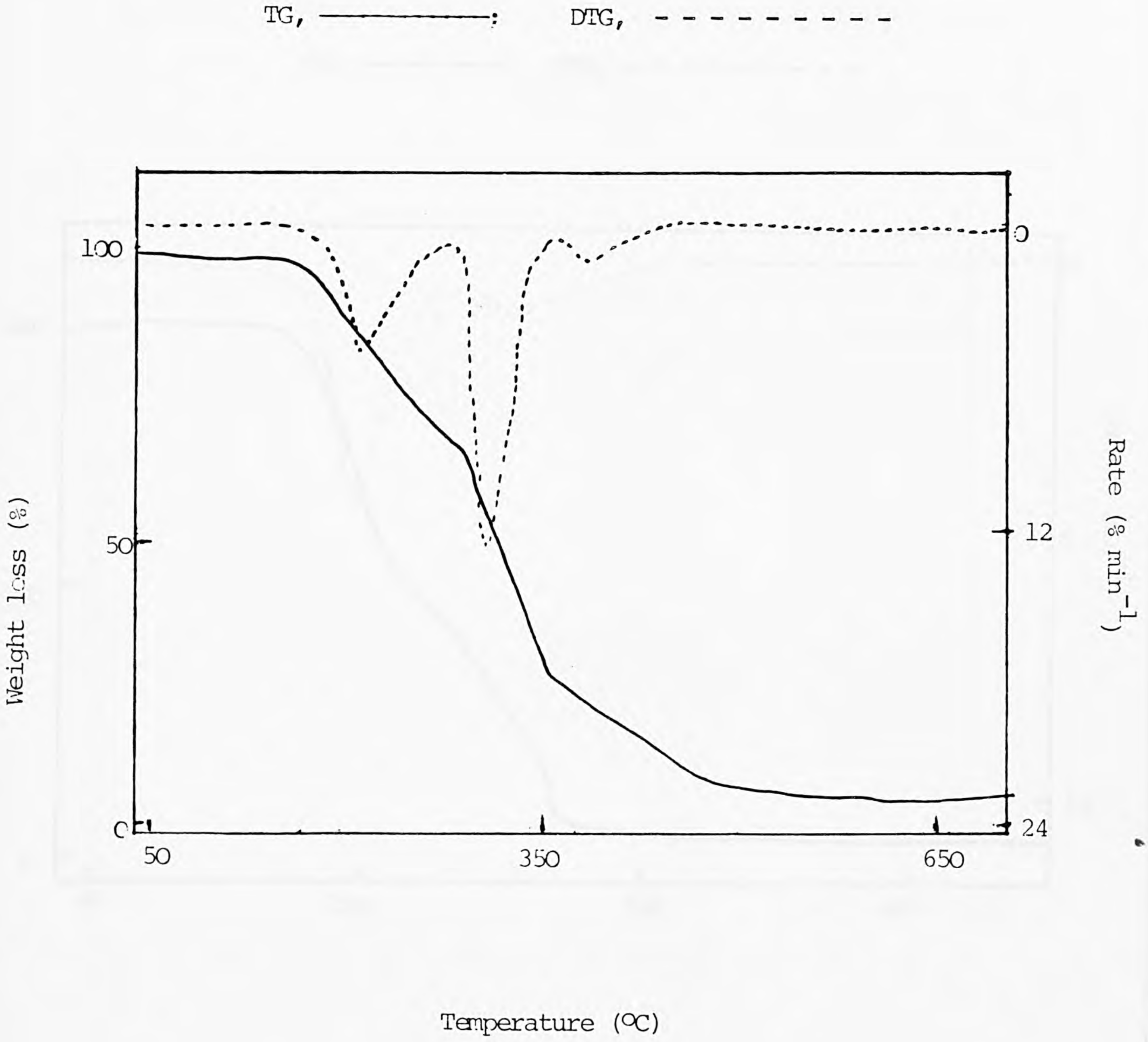


Fig. 3.49. Thermogravimetric analysis curves for cotton treated with 17.5 wt% iron (III) sulphate

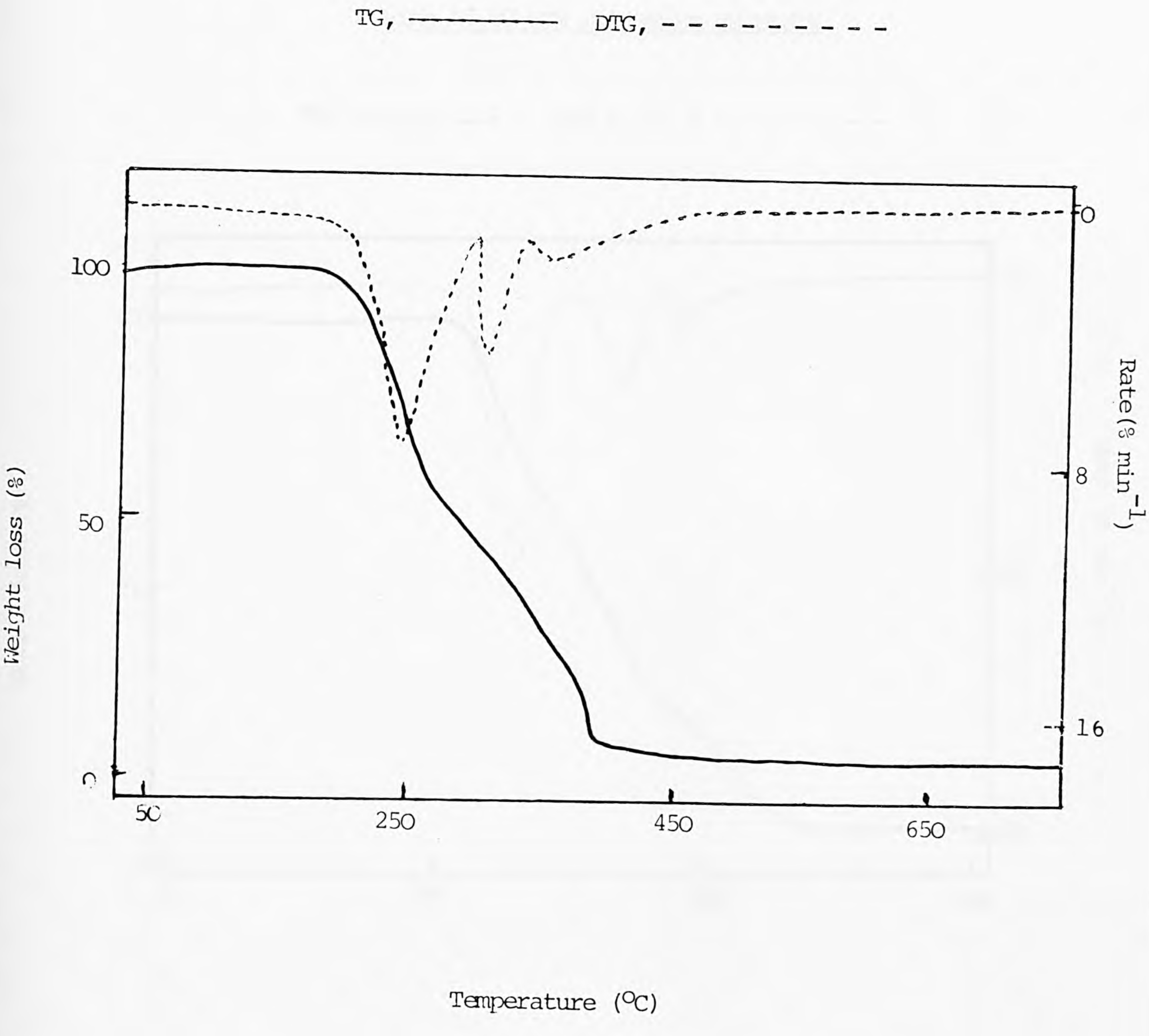


Fig. 3.50 Thermogravimetric analysis curves for cotton treated with 17.90 wt% potassium sulphate

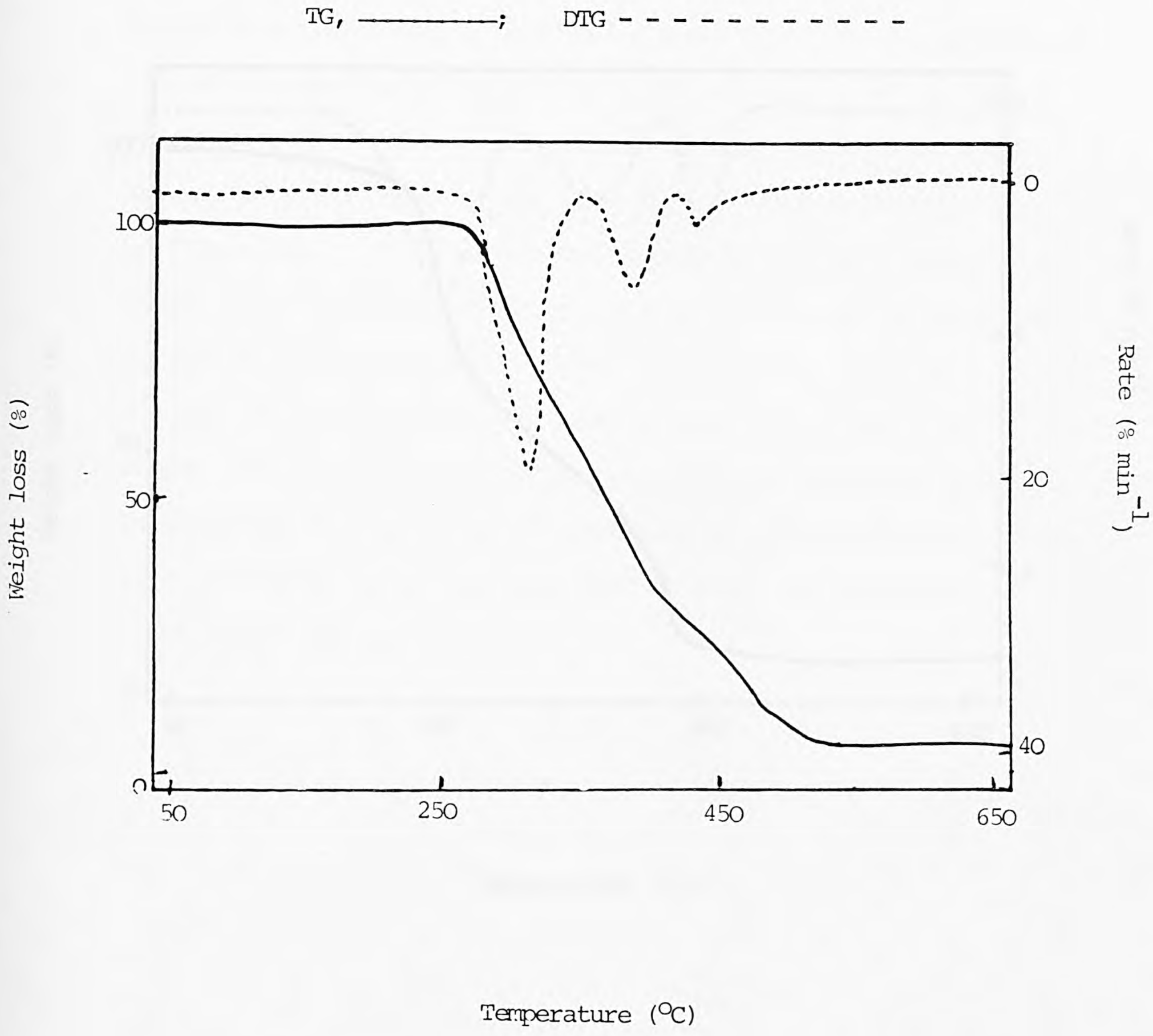
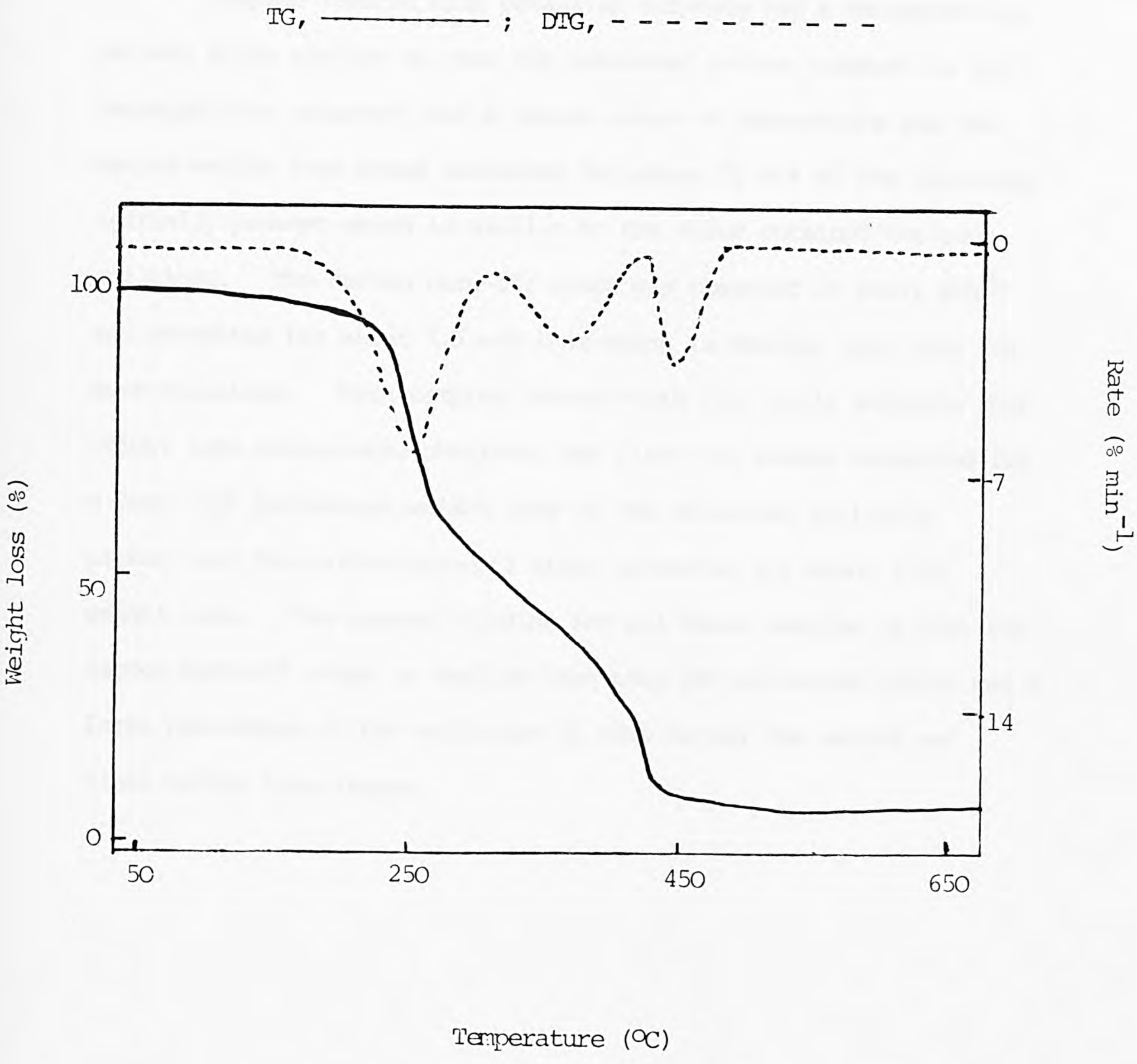


Fig. 3.51 Thermogravimetric analysis curves for cotton treated with 19.30 wt% cobalt (II) sulphate



Samples treated with potassium sulphate had a decomposition pattern quite similar to that for untreated cotton inasmuch as the decomposition occurred over a narrow range of temperature and the second weight loss stage accounted for about 72 wt% of the cellulose initially present which is similar to the value obtained for pure cellulose. The carbon burn-off stage was observed at about 405°C and accounted for about 7.5 wt% loss which is smaller than that for pure cellulose. With samples treated with iron (III) sulphate four weight loss stages were obtained; the first two stages accounted for a very high percentage weight loss of the cellulose initially present and the carbon burn-off stage accounted for about 7.9% weight loss. The general finding for all these samples is that the carbon burn-off stage is smaller than that for untreated cotton and a large percentage of the cellulose is lost during the second and final weight loss stages.

4. Discussion

4.1 Introduction

Cotton fabrics are very flammable materials, the LOI generally varying between 16 and 19 according to the weight and tightness of weave of the material. As with other organic polymers, it is possible to inhibit the combustion process by interfering with reactions taking place both in the condensed phase and in the gas phase. There are perhaps two principles which are most commonly used in order to impart some degree of flame retardance to cotton and other cellulosic materials. One is to attempt to alter the balance between the two essential alternative modes of breakdown of cellulose (Section 1.4.1); thus cellulose can either depolymerise to give monomers such as laevoglucosan and other flammable products or it can undergo dehydration to give carbon and water; the encouragement of the second process at the expense of the first will decrease the ease with which cellulose burns. The other principle is to incorporate additives which are released into the gas phase and interfere with the flame reactions. Predominant among these are compounds such as carbonates, ammonium salts and heavily hydrated salts which release into the gas phase inert gases such as carbon dioxide, ammonia and water vapour which may dilute the normally flammable gases to such an extent that they are no longer capable of flame propagation.

The present work has been concerned primarily with the effect of various sulphur oxyacid salts on the flammability of cellulose. The compounds investigated have included some ammonium salts and some quite heavily hydrated metal salts.

4.2 Relative flame-retardant effectivness of different sulphur additives on their own

The various sulphur oxyacid salts used all had some flame-retardant effect on cellulose. The relative effectiveness of the different additives is shown in Table 4.1. This shows clearly that, of the nine compounds investigated, the most effective are aluminium sulphate followed by ammonium sulphate and then ammonium sulphamate. Zinc sulphate was probably was the best of the six remaining sulphates because cobalt (II) sulphate, copper (II) sulphate and iron (III) sulphate, although giving quite high LOI values, tend to encourage smouldering combustion. Both magnesium sulphate and potassium sulphate have only a relatively small flame-retardant effect.

Table 4.2 shows the average coefficients for the contribution of the four most effective salts to the reduction of the flammability of the cotton fabric. It can be seen that aluminium sulphate gives the highest average coefficient followed by ammonium sulphate, ammonium sulphamate and finally zinc sulphate. This is the same order as is observed for the LOI values shown in Table 4.1. It might be expected that the order of effectiveness of the different sulphur

Table 4.1 The effects of various sulphur oxyacids on the flammability of cotton

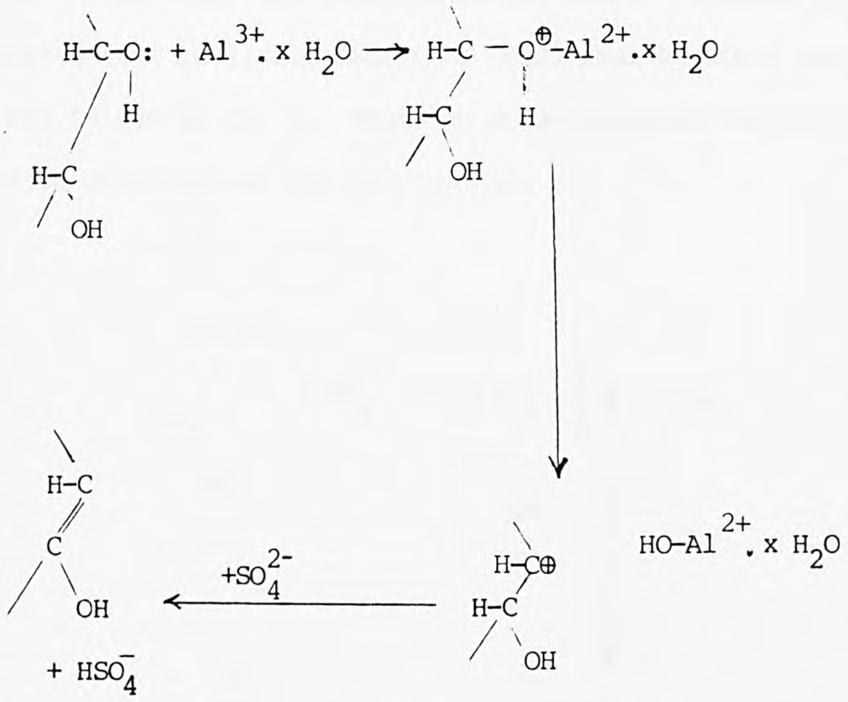
Salt	wt%	LOI
nil	-	18.1
aluminium sulphate	9.91 17.39	31.0 39.4
zinc sulphate	9.90 15.52	21.70 27.20
ammonium	10.91 16.89	29.6 32.0
ammonium sulphate	10.20 16.97	32.4 35.2
cobalt (II) sulphate	19.30	25.3
copper (II) sulphate	19.86	29.20
potassium sulphate	17.90	19.9
magnesium sulphate	14.53	20.35
iron(III) sulphate	17.51	23.8

Table 4.2 The average coefficients for the contribution of each salt in reducing the flammability of cotton

Salt	average coefficient		σ value
aluminium sulphate	115.11.D.	5.75	0.928
zinc sulphate	58.20.D.	5.63	1.324
ammonium sulphamate	84.04.D.	6.41	0.990
ammonium sulphate	103.07.D.	6.59	0.658

compounds as flame retardants would be the same as their order of efficiency in dehydrating cellulose. On this basis, aluminium sulphate and the two ammonium salts would be the best dehydrating agents. Aluminium sulphate has a small highly-charged cation. This has the ability to attack the lone pair of electrons on the OH groups of the cellulose, especially at the 6-position. If this position is blocked, the possibility of the formation of laevoglucosan will be decreased.

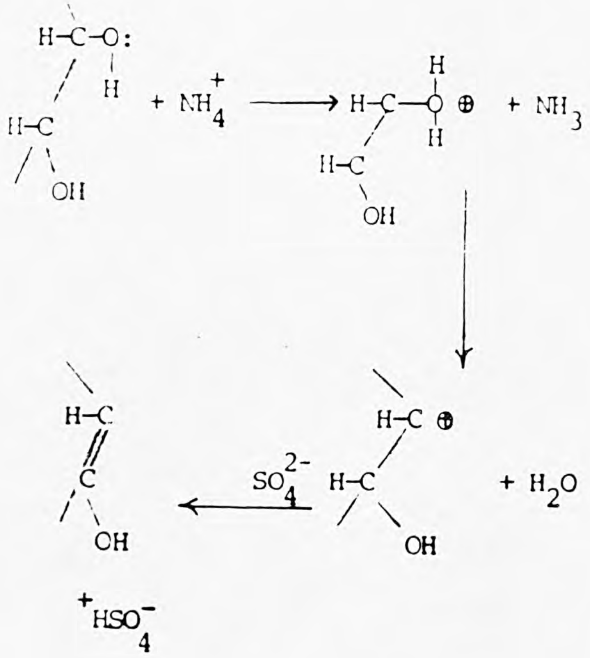
The suggested mechanism with aluminium sulphate would be:



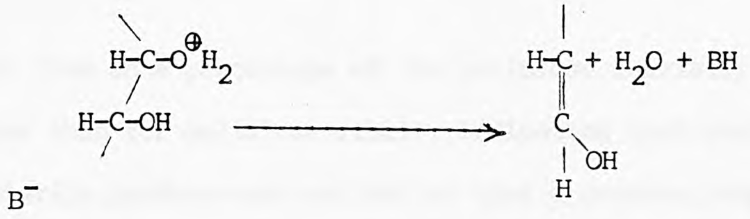
In this mechanism, the Al^{3+} ion is playing essentially the same role as a proton in the acid-catalysed dehydration of cellulose. The ammonium ion is much less polarising than aluminium, and it is unlikely to act in the same way. However the ammonium ion is in equilibrium with a proton which is a very effective dehydrating agent:

$$NH^+_{4(s)} \rightleftharpoons NH_{3(g)} + H^+$$

At ordinary temperatures this equilibrium lies well to the left (pK_a of NH_4^+ is 9.2), but since ammonia is gaseous, it has a considerably higher entropy than the ammonium ion. As the temperature increased, this entropy term will become more important, making the ammonium ion a much stronger acid. Indeed, it is estimated from published data (NBS 1952) that by 600 K the pK_a of NH_4^+ has fallen to ca. 2. Thus, an acid-catalysed dehydration reaction of cellulose may be proposed:



The difference in effectiveness between ammonium sulphate and ammonium sulphamate as flame-retardants may be attributed partly to the fact that ammonium sulphate has two ammonium ions per "molecule", whereas the sulphamate has only one. Since the molecular weights are similar, one would expect the sulphate to be twice as effective as the sulphamate (or, more accurately, the sulphate to be as effective as twice the weight of sulphamate). The coefficients for flame-retardant effectiveness (Table 4.2) and the LOI data in (Table 4.1) show that, on this basis, sulphamate is more effective than expected. Two reasons for this may be as follows: firstly, the decomposition reaction of the two salts releases three moles of diluent gas for each mole of salt in both cases, and if this is an important part of the overall flame retardant effect, it should result in the two salts having similar effect. Secondly, if the <u>elimination</u> step of the dehydration reaction of cellulose is base-catalysed, then this should proceed more readily with sulphamate, since this is the stronger base.



$B^- = SO_4^{2-}$ or $SO_3NH_2^-$

Zinc sulphate would be expected to be a less efficient dehydrating agent on account of the smaller positive charge and larger size of the zinc ion. However, apart from its ability to dehydrate cellulose as all other sulphates do, its flame retardant action might be expected to be attributable, at least in part, to the release of its water of hydration (7 mols). In accordance with this freshly dried zinc sulphate is indeed found to have considerably less flame-retardant effect than the hydrated salt. It might be expected that the water released from aluminium sulphate would be quite as effective in reducing the flammability of cotton since the percentage weight of water in the two salts is similar. With the latter salt, however, the dehydrating action appears to be so complete that the release of extra water vapour has virtually no effect.

The thermoanalytical results show that the principal salts investigated cause the decomposition of cellulose to begin at lower temperatures than the polymer on its own, to take place over a wider temperature and to exhibit four weight stages. In all cases the weight loss as a percentage of the cellulose initially present is smaller than for cellulose itself, indicating that smaller amounts of volatile products are emitted so that a greater proportion remains as residue from these cellulose breakdown stages, presumably in the form of carbonaceous char. The microanalytical results (Table 4.3) support this. Further confirmation that the additives act by enhancing dehydration comes from the observation that, for cellulose samples containing the aluminium and ammonium salts, there is a considerable increase in the extent of the carbon burn-off stage (Table 4.3). In contrast, this stage with cotton samples treated with zinc sulphate and other salts which give very low LOI values is comparable in size with that observed for untreated cotton (10%). This is consistent with the expected lower dehydrating efficiency of the latter compounds, which, as has already been shown, are not such good flame retardants.

Similarly the amounts of carbon monoxide formed from the various cotton samples decrease in line with their dehydrating and hence flame retardant effect.

Table 4.3 The percentage of carbon lost during the thermal decomposition of samples treated with sulphur oxyacid salts

Salt	wt%	carbon loss (wt%)
nil	-	11.00
aluminium sulphate	11.5	33.45
zinc sulphate	15.52	10.1
ammonium sulphamate	10.91	33.09
ammonium sulphate	10.20	33.30
cobalt (II) sulphate	19.30	12.39
potassium sulphate	17.90	7.49
copper (II) sulphate	19.86	8.51
iron(III) sulphate	17.51	6.46

4.3 Relative flame-retardant effectiveness of sulphur additive-DBBO mixtures

Halogen compounds are not very efficient flame retardants for cellulose when used on their own. Most halogen-containing additives are therefore normally used in conjunction with metal oxides or other flame retardants. The incorporation of DBBO into cotton pretreated with aluminium sulphate, zinc sulphate and the two ammonium salts used significantly increases the flame-retardant effectiveness of all the systems but affects them to different extents. Thus the order of efficiency of the inorganic salt-DBBO systems becomes:

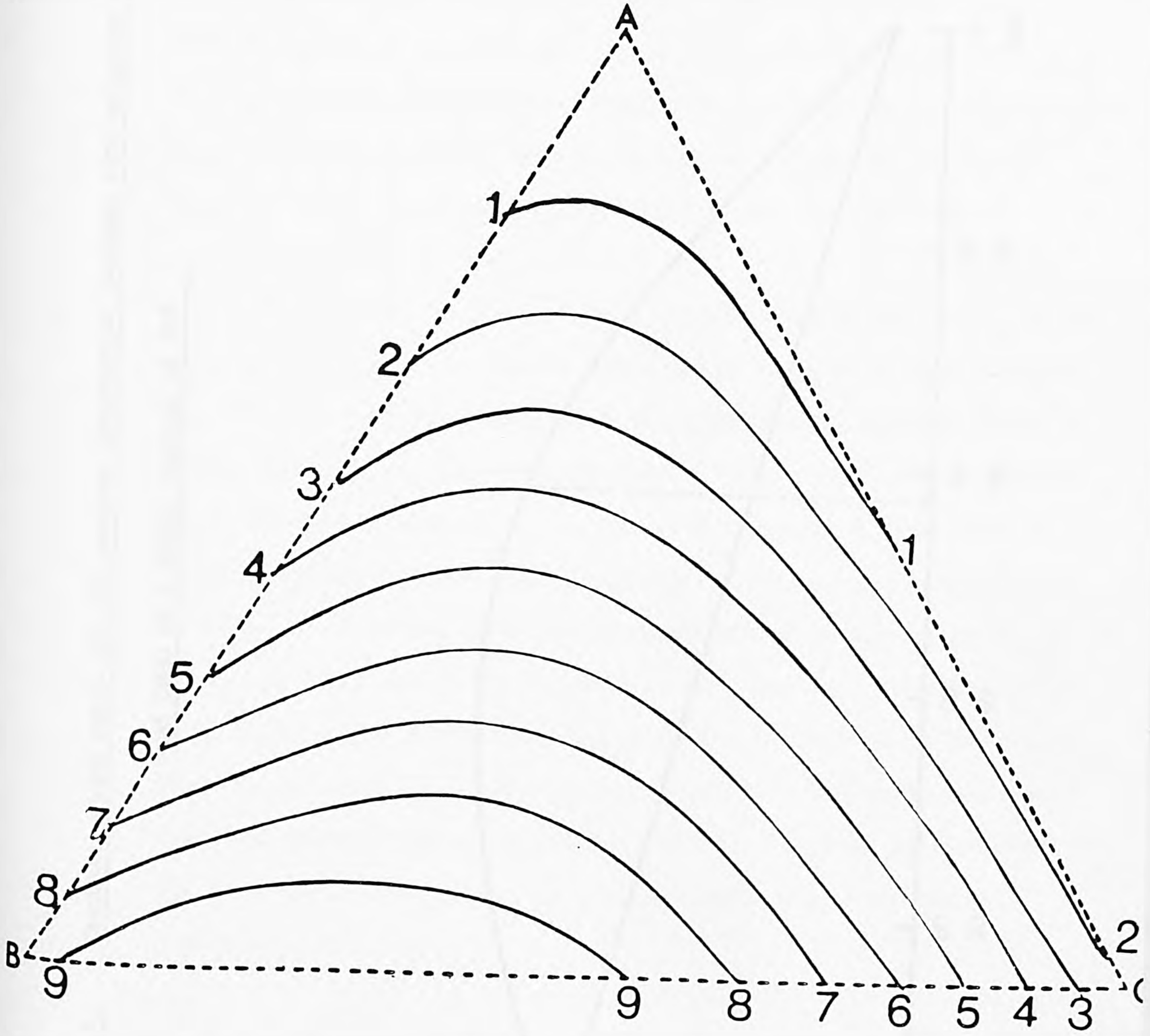
aluminium sulphate > zinc sulphate > ammonium sulphate
> ammonium sulphamate

It can be seen from Table 4.4 that the most extensive reaction between halogen compound and salt occurs with zinc sulphate and aluminium sulphate. It is clear from the triangular diagram for the zinc sulphate-DBBO system (Fig. 4.1) that the maximum LOI is obtained at an atomic ratio of Br:Zn of 0.83. However, this does not correspond to the maximum interaction between zinc sulphate and DBBO since the individual additives differ greatly in their flame retardant effectiveness as is seen in Fig. 4.2. This is a plot of the LOI against the composition of zinc sulphate-DBBO mixtures and shows that, at constant additive loading, the greatest amount of interaction takes place between

Table 4.4 LOI values for cotton treated with inorganic salts in the presence and absence of DBBO

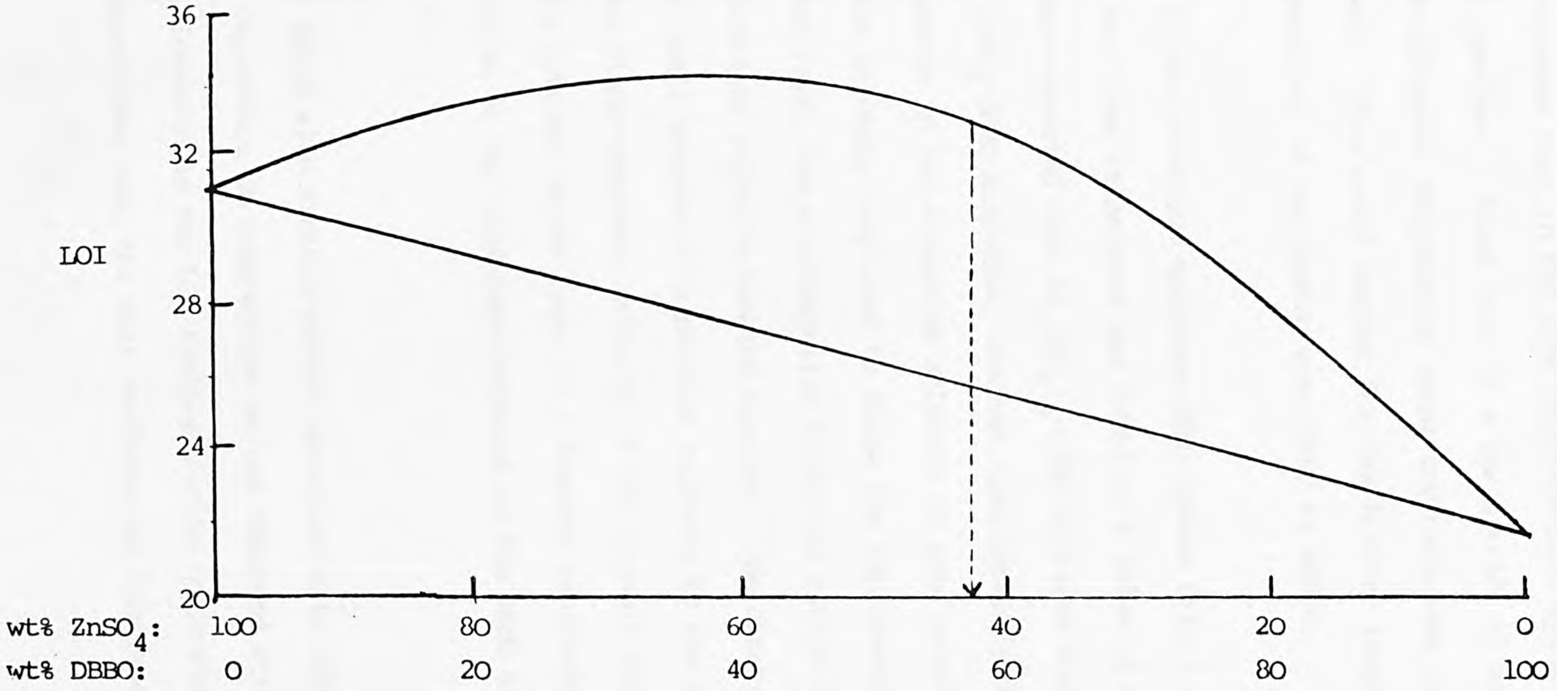
System	wt% salt	wt% DBBO	LOI
aluminium sulphate-DBBO	9.91	-	31.0
	17.39	-	39.4
	19.35	7.80	46.2
	15.77	15.72	47.1
	9.90	-	21.70
zinc sulphate-DBBO	15.52	-	27.2
	20.00	7.81	43.9
	14.21	14.86	40.5
	10.91	-	29.6
ammonium sulphamate-DBBO	16.89	-	32.0
	19.31	6.0	37.3
	14.14	15.05	36.8
	10.20	-	32.4
ammonium sulphate-DBBO	16.97	-	35.2
	19.58	5.44	40.3
	12.08	14.65	37.9
cobalt (II) sulphate	19.30	-	25.3
	17.91	7.99	31.20
copper (II) sulphate	19.86	-	29.20
	19.45	4.67	38.3
potassium sulphate	17.90	-	19.9
	21.7	2.35	20.7
magnesium sulphate	14.53	-	20.3
	5.47	19.84	23.9
iron(III) sulphate	17.51	-	23.8
	14.92	8.11	27.3

Fig. 4.1 Triangular diagram showing variation of LOI with composition for cotton-zinc sulphate-DBBO system



LOI values: (0) 18.10; (1) 20.68; (2) 23.26; (3) 25.84; (4) 28.42; (5) 31.00; (6) 33.58; (7) 36.16 (8) 38.74; (9) 41.32

Fig. 4.2. Optimum weight ratio for the maximum interaction between zinc sulphate and and DBBO at a total loading of 30%



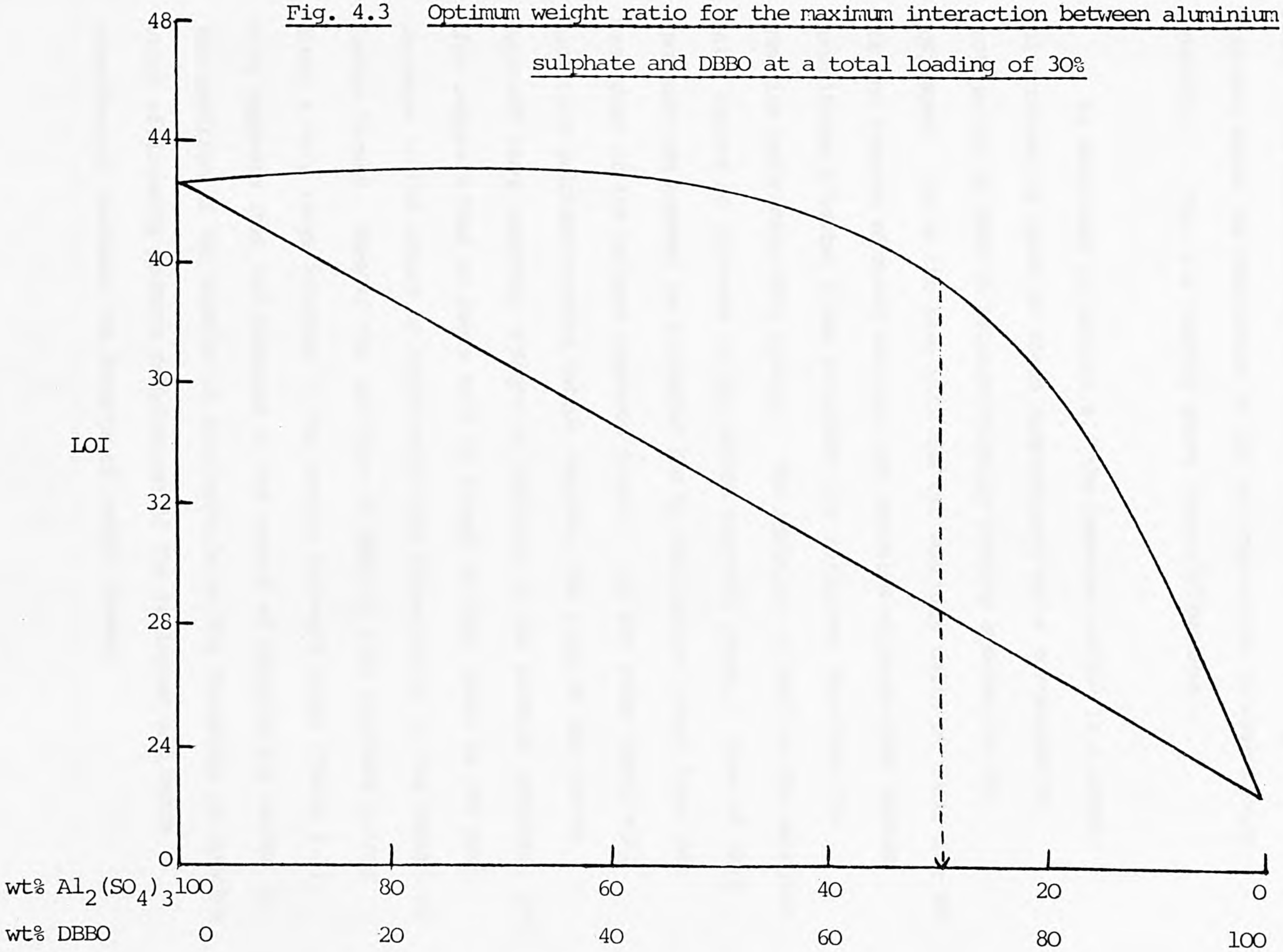
the two additives at an atomic ratio of Br to Zn of about 2.6,which is close to the stoichiometric ratio for the formation of zinc bromide(2.0).

This finding suggests that, in the zinc sulphate-DBBO system, zinc bromide is the active species. Since this is a Lewis acid, it would be expected to be a more effective dehydrating agent for cellulose than zinc sulphate is on its own. This would account for the further large decrease in the flammability of the system when DBBO is added.

In contrast, in the aluminium sulphate-DBBO system (Fig.4.3), the optimum Br/Al ratio for flame retardance was found at a value of about 11. It might have been expected that $Al_2(SO_4)_3$-DBBO mixtures would behave similarly to $ZnSO_4$-DBBO mixtures. However they probably do not do so due to the presence in the aluminium sulphate of some water of hydration which is too strongly complexed to allow its replacement by bromine. On the other hand, the electrophilic aluminium cation could attack the DBBO, liberating volatile bromine species. The observation that the addition of small amounts of aluminium sulphate to the halogen compound enhances the flame-retardant activity of the organic bromine compound, whereas the reverse is not true, is a further manifestation of the fact that the action of the aluminium sulphate on the DBBO is essentially catalytic.

The ammonium salts also exhibit marked synergism with DBBO and the LOI shows the same dependence on composition as was observed with aluminium sulphate, inasmuch as the LOI remains virtually constant over a wide range of compositions near the salt vertices but increases

Fig. 4.3 Optimum weight ratio for the maximum interaction between aluminium sulphate and DBBO at a total loading of 30%



rapidly as small amounts of the salts are added at high loadings of DBBO. This behaviour may be contrasted with that of $ZnSO_4$-DBBO mixtures where the dependence of LOI on composition is essentially parabolic. Fig. 4.4 clearly shows these differences.

As mentioned in Section 4.2 the ammonium cation is a powerful protonating agent at these temperatures and a corresponding protonation of DBBO to release volatile bromine species can be envisaged. As is the case with the two ammonium salts on their own and for the reasons advanced earlier, the ammonium sulphate-DBBO system constitutes a better flame retardant for cellulose than does the ammonium sulphamate-DBBO system. The addition of DBBO to the ammonium salts causes an increase in the carbon burn-off stage. Some of this increase can however be accounted for by the carbon formed from the breakdown of the halogen compound itself. On the other hand, with aluminium sulphate-treated cotton samples, the size of the carbon burn-off stage scarcely changes on addition of the bromine compound; and this suggests that no Lewis acid is formed so that there is not much increase in the extent of dehydration and consequently in the amount of carbon formed. However the addition of DBBO to zinc sulphate brings about a very large increase in the carbon burn-off stage (Table 4.5). This suggests that the increase in the extent of dehydration caused by the addition of the bromine is attributable to the formation of species which efficiently promote dehydration of the cellulose and hence considerably increase the amounts of carbon formed.

Fig. 4,4 The variation of the LOI with the percentages of the two additives at a total loading of 21%

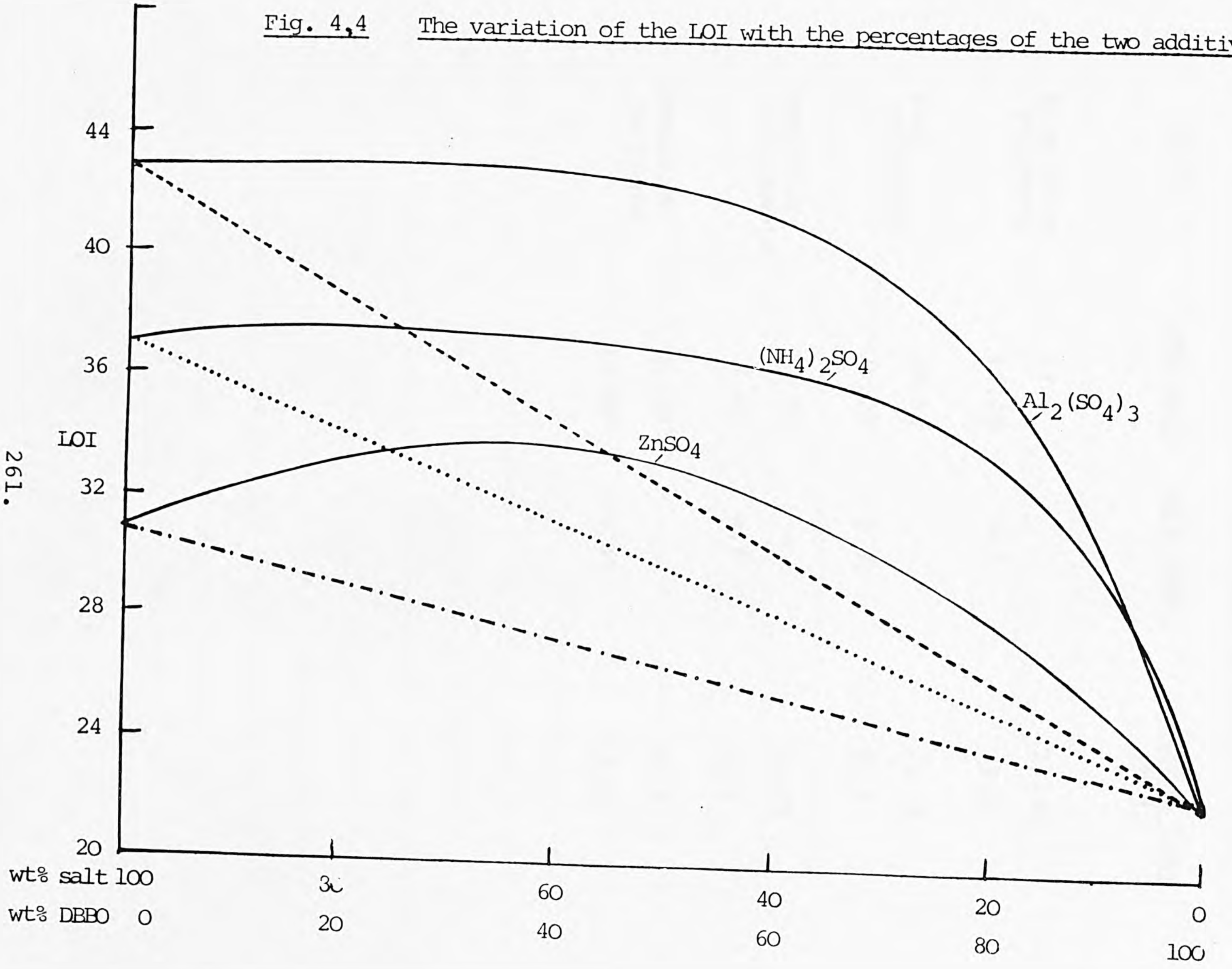


Table 4.5 The percentage of the loss of carbon in the presence and absence of DBBO

Salt	wt% salt	wt% DBBO	carbon loss (wt%)
aluminium sulphate	11.5	-	33.45
	14.23	6.7	33.8
zinc sulphate	15.52	-	32.16
	21.70	5.90	10.1
ammonium sulphamate	10.91	-	33.09
	7.43	8.8	39.2
ammonium sulphate	10.20	-	33.3
	12.08	14.65	38.61

The quantity of unburnt residue remaining after thermal analysis in the case of cotton treated with a zinc sulphate-DBBO mixture is larger than that formed from a sample treated with an aluminium sulphate-DBBO mixture and much larger than that derived from a cotton fabric containing either of the ammonium salt-DBBO mixtures. This suggests that the quantities of volatile products formed in the latter systems are greater. Indeed with aluminium sulphate-treated cottons, the yields of volatiles increase on the addition of the bromine compound, since the halogen is released into the gas phase.

All these findings suggest that the most extensive interaction of inorganic salts with DBBO occurs with zinc sulphate and rather less interaction with the other salts. This does not run parallel with the values of the synergism coefficients found for the various systems (Table 4.6), where the value for aluminium is by far the greatest. There are various reasons for this. One is that the flame-retardant efficiency of any system is a function of processes occurring both in the condensed phase and in the gas phase; whereas the extent of carbon formation depends entirely on solid phase reactions. It has already been suggested that aluminium and ammonium salts are enhancing the liberation of volatile bromine species which act in the gas phase; and there is no evidence to suggest that this occurs with zinc sulphate. The other factor is the different concentration dependence of the flame-retardant efficiences in the

Table 4.6 The average coefficients, degrees of synergism between the two additives for the range X2 or X3=0-0.3 and σ values as a function of the best-fit polynomial for each for each system studied

System	σ-value	compon-	average coefficient	synergism
aluminium sulphate-DBBO	0.928	Al	115.11.D. 5.75	895.49.D. 54.48
		DBBO	18.45.D. 5.61	
zomc sul-phate-DBBO	1.324	Zn	58.20.D. 5.6358	614.46.D. 50.64
		DBBO	14.89.D. 5.67	
ammonium sul-phamate-DBBO	0.990	Amm.	84.04.D. 6.41	570. 81.D 59.852
		DBBO	17.30.D. 6.33	
ammonium sul-phate-DBBO	0.6583	Amm.	103.07.D. 6.59	657.81.D. 137.10
		DBBO	21.29.D. 4.25	

various systems (Fig. 4.5). At the highest loading used (ca. 30%), the zinc sulphate-DBBO system has the greatest flame-retardant effect. However, below a loading of ca. 25% , this is no longer true. The order of flame-retardant effectiveness of the different salt-DBBO mixtures is thus very dependent on total loading, although the coefficients shown in Table 4.6 are averaged over the complete range of loadings used.

The addition of DBBO to samples pretreated with all the four main inorganic salts significantly increases the amount of carbon monoxide formed (Table 4.7). The yields of this gas evolved from cotton treated with $ZnSO_4$-DBBO mixtures are however smaller than those from samples impregnated with aluminium sulphate-DBBO mixtures and even smaller than for those containing the two ammonium salts. A possible explanation of this finding is that bromine atoms formed by thermal breakdown of DBBO abstract hydrogen from the cellulose or its decomposition products (RH) to generate hydrogen bromide:

$$RH + Br^{\bullet} \longrightarrow R^{\bullet} + HBr \qquad (1)$$

The hydrogen bromide formed then interacts with highly reactive free radicals, such as $H^{\bullet}$, $O^{\bullet\bullet}$ and $OH^{\bullet}$, which are responsible for flame propagation, e.g.

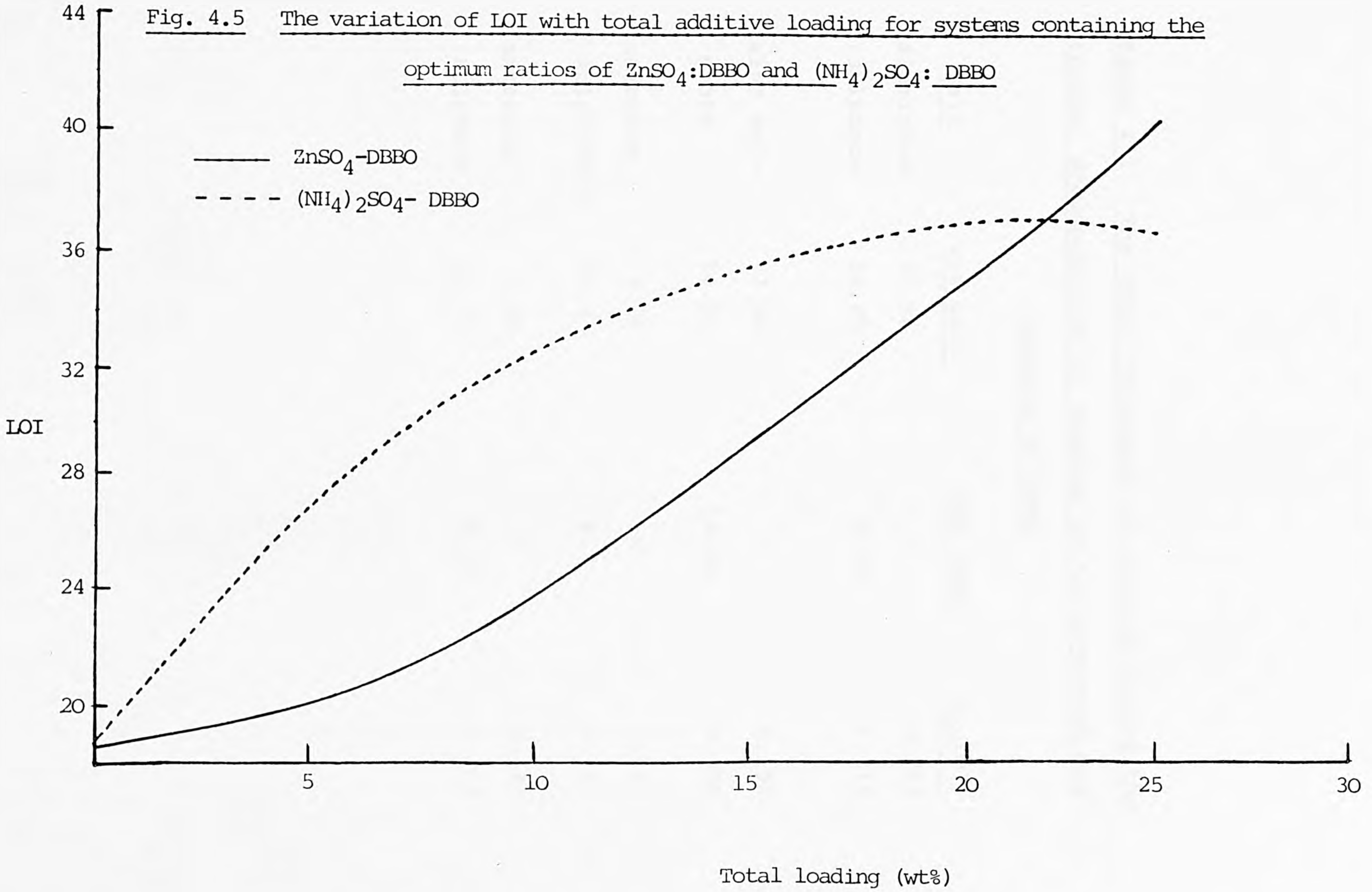


Fig. 4.5 The variation of LOI with total additive loading for systems containing the optimum ratios of $ZnSO_4$:DBBO and $(NH_4)_2SO_4$: DBBO

Table 4.7 The total volumes of CO evolved during the thermal decomposition of samples in the presence and absence of DBBO

Salt	wt% salt	wt% DBBO	V_{CO}(ml)
aluminium sulphate	11.56	-	0.757
	14.23	6.69	1.215
zinc sulphate	7.64	-	0.199
	14.21	14.86	0.606
ammonium sulphamate	4.26	-	1.11
	15.9	8.4	1.29
ammonium sulphate	7.00	-	0.683
	14.55	8.30	1.201

$$H^{\bullet} + HBr \longrightarrow H_2 + Br^{\bullet} \qquad (2)$$

$$OH^{\bullet} + HBr \longrightarrow H_2O + Br^{\bullet} \qquad (3)$$

The concentration of these active radicals is thus reduced and this inhibits the normal burning of the organic "fuel" which involves a mechanism such as:

$$H^{\bullet} + RH \longrightarrow H_2 + R^{\bullet} \qquad (4)$$

$$OH^{\bullet} + RH \longrightarrow H_2O + R^{\bullet} \qquad (5)$$

However, another mechanism which takes place during the combustion of all organic compounds is the oxidation of wet carbon monoxide to carbon dioxide. This mechanism is known to be inhibited by halogen compounds (Simmons and Wolfhard 1956; Rosser, Inami, Wise 1966; Einhorn 1971; Fristrom 1972) and this can be explained by the fact that it occurs largely as a result of the process:

$$OH^{\bullet} + CO \longrightarrow H^{\bullet} + CO_2 \qquad (6)$$

in which the hydroxyl radicals are the active species. The observed increase in the amount of carbon monoxide obtained may perhaps then be explained in terms of the decreased occurrence of reaction (6) owing to the enhanced destruction of hydroxyl radicals by hydrogen bromide. Thus, when DBBO is added to aluminium sulphate and the two ammonium salts, the yields of CO are considerably increased. This does not happen to the same extent with zinc sulphate-DBBO mixtures, because the zinc salt retains most of the bromine in the condensed phase in the form of zinc bromide. The latter species then promotes dehydration of the cellulose instead of releasing the bromine into the gas phase. With relatively little hydrogen bromide available, conversion of carbon monoxide to carbon dioxide can occur more readily.

5. Appendix

Computer program
(Appendix, p. 271-282)
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copyright reasons

6. References

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