FLAMMABILITY OF POLYMERS (INHIBITION OF FLAME REACTIONS)

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SUMMARY

All commercial plastics will burn under the right conditions. To overcome this problem incorporation of flame retardant additives and chemical modification to the polymer have been used with varying success. These measures may affect solid phase pyrolysis of the resin or the burning of volatile fragments in the gas phase. The present research was devoted to development of methods for studying the gas phase reactions in a manner applicable to burning conditions.

The performance of a range of commercial flame retardant additives was assessed in an unsaturated polyester resin system using test methods which reflect burning and ignition properties. A marked synergistic effect was noted between halogenated compounds in the presence of antimony trioxide. On heating antimony trioxide with chlorinated paraffin antimony trichloride was shown to be the chief reaction product. Weight loss experiments indicated that some mixtures should have been more effective than was observed in the early experiments. It was concluded that these test methods provided conditions of too low thermal stress and a number of resin formulations were subjected to the more severe BS.476 fire propagation test.

A diffusion flame apparatus suitable for burning model fuels was set up and a number of inhibitors were studied but practical difficulties occurred in attempting to disperse metal halides quantitatively in the flame.

An apparatus was designed for burning premixed model fuel/air flames to study materials such as metal halides. Antimony trihalides and a number of other metal halides were shown to be effective inhibitors. The particular efficiency of antimony trihalides was attributed to their ability to undergo oxidation providing solid particles which were effective in abstracting reactive flame species.

A number of techniques have been established using known technological effects, these have been used in obtaining some new information which is applicable on a broader basis.

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CHAPTER 1

THE PROBLEM

The work described in this thesis represents one half of the first stage of an investigation into the flammability of plastics materials.

More specifically the area covered involved the study of the effect of flame retardant additives on a styrene cross-linked unsaturated polyester resin with particular emphasis on additives which were active in flame inhibition.

The other half of the work (which will not be dealt with in detail in this thesis) involved the study of the effect of additives on the pyrolysis of the same cross-linked polyester system and also the identification of primary pyrolysis products from this resin.

In order to put the work described into perspective it is useful to consider the problems associated with uncontrolled fires as a whole especially those occurring in confined spaces.

1.1. The Statement of the Problem

The use of combustible materials in both structural and internal fittings, in buildings, has previously been considered acceptable. However, development of the newer synthetic polymeric materials as replacements and often in addition to these accepted materials has been viewed with considerable caution by the specifying bodies. This caution is not completely unfounded as under the right conditions all commercially important plastics materials burn. However, with careful design and use of flame retardants this should not eliminate their use in many applications.

The development of fire in buildings can be considered in three phases.

a. Ignition and growth of fire until all combustibles present are involved.

b. Burning out of all of the combustibles.

c. Gradual decay of the fire, smouldering of burnt out materials.

Ignition occurs by the transfer of heat by radiation, convection or conduction to combustible materials. If, in the case of solids the heat source is great enough to cause degradation into smaller combustible fragments such as liquids and gases then in the presence of sufficient oxidant and high enough temperature spontaneous ignition may occur. Ignition will occur more readily in the presence of an external ignition source such as a small flame. After ignition an adequate supply of heat, from the exothermic oxidation reactions occurring in the flame zone, to the unchanged material, results in a self perpetuating reaction cycle. This sequence of events is common to all combustible plastics materials, initial degradation occurring in the range 250 - 550°C.

The growth of fire now depends upon the transfer of heat from the burning component to other combustibles present. This may be achieved by:-

a. Radiation from the flames, the amount of heat radiated is dependent upon the size of the flames. To a lesser degree heat may be radiated from within the burning material.

b. By convection currents of hot gases over unchanged combustible material, this depends to a large extent on the ventilation available.

c. By conduction of heat to combustible material in contact with the flame.

Once flash over has been reached, that is the involvement of all of the combustibles, the temperature attained and the duration of this phase depends upon the nature and the amount of combustibles present.

The time from ignition to flash over is obviously important from the point of view of personnel escaping from the building, therefore, the longer this period is the greater the chance of escape. As stated previously, under the right conditions, all commercially important plastics materials burn. It therefore seems clear that once flash over has been reached any plastics present will be involved irrespective of treatment with flame retardants. Bearing this in mind it would seem necessary to see that plastics do not appreciably add to the total fuel contribution.

The function of flame retardants would therefore seem to be primarily aimed at decreasing the ease of ignition of the material and reducing the contribution of the material to spread of fire. Other points arise, however, which are equally important from an escape point of view. These are the production of smoke and toxic combustion products both of which contribute significantly to deaths in fires.

Two other factors should be considered with respect to the spread of fires involving plastics materials. These are dripping of burning materials and after glow in the char of burnt out materials. The former is mainly confined to thermoplastics materials and the latter to thermosetting resins.

The assessment of the fire hazard of plastics materials should ideally take all of these factors into account. Most of the work carried out in industry has been directed toward producing materials which satisfy various test specifications, notably the spread of flame test, paying little attention to the smoke or toxic combustion products developed. Research undertaken by the Joint Fire Research Organisation and The Rubber and Plastics Research Association is currently concerned with these apsects of the problem.

During the growth of fires in rooms variations in thermal stress occur and test methods exist which describe the performance of materials under various thermal stress conditions. Three classes of flammability tests exist ranging in size and objective from the small scale screening tests to the larger design tests, to the large scale tunnel or simulated structure tests. Little correlation is possible between results of the various classes. An important difference between the scale of test is often the heat flux produced per unit area of test piece.

Factors which contribute to this difference in heat flux are:-

a. Whether the test is open or enclosed.

b. The position of the flame front in space relative to the bulk of the unchanged material. Obviously a vertical strip of material burning downwards from the top subjects unit area of material to a much lower heat flux than the same strip burning upward from the bottom. In the latter case the convective component of hot combustion gases streaming over the material is important. Whilst in the former case heat is fed back by molecular conduction and radiation processes from the relatively small flame supported above the material.

These aspects of thermal stress may be important when assessing the effectiveness of flame retardant additives in materials. Additives which are not chemically bonded into the resin matrix are liable to migrate to the surface and leach out. Two component flame retardant systems rely on decomposition of one component to produce a species which reacts with the second component resulting in formation of the active species. (See Chapter 4). If the decomposing component is volatile below its decomposition temperature then it is feasible that under conditions which involve heating the resin below its ignition temperature this component may volatilize out of the matrix unchanged. This would result in a lower concentration of the active species formed. Thus the severity of the flammability test may in certain circumstances determine the apparent effectiveness of a system.

It is therefore apparent that in order to get an accurate picture of the performance of a material under real fire conditions, exposure to the large scale tests is required. This is expensive and an obvious requirement is the development of screening tests which yield results which may be reliably correlated to performance in real conditions.

Attempts at rendering combustible articles non-combustible by means of treatments, dates back as early as the 4th Century B.C. In 1735 an English patent was granted to J. Wyld for a flame proofing composition and in 1821 Gay Lussac studied various inorganic salts which rendered fabric non-combustible.

Since this early work a great number of patents have been granted for flame proofing compositions, which, until the early 1950's were mainly concerned with cellulosic materials i.e. wood and textiles. Some of the knowledge gained from these systems has been applied in an empirical manner over the past two decades to synthetic polymeric materials with varying degrees of success.

Flame retardance may be conferred on plastics materials in two general ways, these are loosely termed 'reactives' and 'additives'. Reactives cover those retardants which are chemically bonded into the polymer. This is achieved by substituting retardant molecules either in the main backbone of the polymer, as cross-linking agents in thermosetting materials, alternatively as side chain or ring substituents. Retardants introduced in this manner have the advantages of permanency and also that they are 'on the spot' when the polymer degrades. The main disadvantage lies in the cost of the final material. The use of reactive flame retardant compositions is increasing, particularly in the polyurethane and cross-linked polyester fields.

Flame retardant additives are extensively used in all plastics materials, the great advantage being that they may be incorporated by simple mixing processes thus rendering the cost of the final compound considerably lower than for reactives. Additives suffer from the disadvantages of migration to the surface and hence lack of permanency. It is also necessary to be careful in selecting the additive to ensure its compatibility with the base material. This is not always possible as in the case of antimony trioxide and other insoluble inorganic additives.

The three most common elements used in imparting flame retardance to plastics materials are phosphorus, chlorine and bromine. The probable modes of action of these will be developed more fully in the next chapter but let it suffice to say at present that there are two broad areas in which flame retardants may reduce the flammability of plastics materials. These are (1) The solid phase, by interference with normal pyrolysis and reducing the concentration of combustible fragments produced. (2) By upsetting gas phase reactions in the flame zone resulting in reduced feedback of energy to the unchanged material and ultimately in complete extinguishment.

This division formed the basis on which the dual approach to the problem was adopted. An attempt was made to study the effect of flame retardant additives on the pyrolysis stage and also to identify the primary thermal degradation products of a cross-linked polyester resin. This is important from the point of view of total fuel contribution to a fire. This aspect of the work will not be dealt with in detail in this thesis which was concerned with part (2) of the division.

It is clear from this brief introduction that the problems associated with the flammability of plastics materials are complex and many points need examination. While to a large degree these can be treated as separate problems they are linked together and must ultimately be considered in the context of the problem as a whole.

1.2. Approach to the Problem

It was noted in the preceding section that the broad points which need consideration are concerned with the total thermal contribution of the material, its ability to ignite and spread flame and the likelihood of production of smoke and toxic combustion products. It was also noted that other laboratories are currently studying the latter two points and it was concluded that the time available would initially be best spent on a fairly detailed investigation of one plastics material, with reference to the remaining points. The dual approach to the project was indicated in the previous section.

Styrene cross-linked unsaturated polyester resins seemed to have exceptional potential in structural applications and in the untreated condition they readily burn. For this reason a general purpose styrene crossed resin was selected for study. The additive method of incorporating retardants was chosen as this would yield directly comparable information. As a study of the mechanism of retardants was intended the resin was used in the non reinforced condition and cast specimens were tested.

The aim of the initial experiments was to provide background information about the action of a range of commercial flame retardant additives when incorporated into the standard resin. Three test methods which would yield information on the action of retardants were selected and those retardants which appeared effective by their action in the gas phase were noted. These results lead to the closer investigation of the action of moderate temperatures on some of the additives. Weight loss experiments were conducted at various temperatures between 300 - 600°C on mixtures of halogenated compounds and metal oxides as a means of following reactions. Quantitative analysis of reaction products established the active species in the organic halogenated compound/antimony trioxide system.

Selected resin formulations were tested under B.S.476 Fire Propagation Test conditions in order to compare the results obtained with the less severe smaller tests in the light of the weight loss experiment results.

One of the original objectives of the work was to identify those types of flame retardant which were active in flame inhibition and to more closely observe the nature of this inhibition. On consulting the literature, however, it was realised that the problems associated with flames and their inhibition were profound and that it was beyond the scope of a project in plastics technology to add significantly to the fundamental knowledge already available. Although the initial objectives were modified it was felt that useful information could be obtained by a less fundamental approach and equipment was set up which would be used for classifying the effect of inhibitors on premixed and diffusion flames in a semi-empirical manner. It should be emphasised that although the equipment developed was based on that used for obtaining fundamental information this was not the intention of this work but rather that they should serve as means of screening inhibitors which had appeared promising from other work.

The work carried out on flames used model fuels due to the fact that precise information was not available on the primary degradation products of cross-linked polyesters. The fuels chosen were those which appeared from preliminary identification work[47] to be important. It is hoped that when further information regarding these products becomes available the flame work will be extended to these.

Should the project be continued it would seem that a logical extension to this work would be to obtain quantitative information with regard to the concentration of inhibitor required in the gas phase to produce a given effect on the flammability test ratings. This is important in many instances from the point of view of toxicity of the inhibitor, which should also be considered in its own right.

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CHAPTER 2

LITERATURE SURVEY

A survey of the literature relating to the problem of flammability of plastics proved a difficult task. Although a great deal of work has been published little is still understood of the mechanisms of flame retardants. Much work seems to have been undertaken with a view to meeting particular test specifications and the investigation of the function of additives which achieved this result seemed to be of secondary importance.

It is not the object of this chapter to calalogue the published work on flame-proofing and flammability but rather to examine those papers which seemed to have particular relevance to the aspect of the problem to which this thesis is devoted.

For convenience, the chapter has been divided into four sections, dealing with the theories of flame inhibition, general papers on the flammability of plastics, papers relating specifically to the flammability of cross-linked polyester resins and flammability testing. In general, where published reviews exist on a topic, these are cited and only the more relevant points are selected for comment.

2.1. Flames and Flame Inhibition

The amount of research effort currently devoted to the problems associated with flames is indicated by the one hundred paper symposia sponsored bi-ennially by the Combustion Institute, most of the papers representing original research.

While it is beyond the scope of this thesis to review in detail all of this research effort an attempt has been made to select those papers which have seemed relevant to the present study and to those which represent major steps forward in the general field of flame inhibition.

It would seem a logical prerequisite of any study of flame inhibition to have a good general back ground knowledge of the processes taking place in uninhibited flames. However, except for the 'simpler' systems, such as the hydrogen/oxygen combustion reaction which is now well established[1] a complete picture of the combustion processes of even the lower hydrocarbons is still a thing of the future.

It has clearly been established that reactions occurring immediately prior to and in the flame zone involve free radicals[2] and are chain reactions. These chains are perpetuated by the regeneration of active species such as $\dot{O}$, $\dot{H}$ and $O\dot{H}$ in branching reactions which are important for the hydrogen air combustion reaction:-

$$H^{\cdot} + O_2 \longrightarrow OH^{\cdot} + O^{\cdot} \quad \ldots\ldots\ldots\ldots\ 1$$

$$OH^{\cdot} + H_2 \longrightarrow H_2O + H^{\cdot} \quad \ldots\ldots\ldots\ldots\ 2$$

$$O^{\cdot} + H_2 \longrightarrow OH^{\cdot} + H^{\cdot} \quad \ldots\ldots\ldots\ldots\ 3$$

While it is appreciated that flames involving hydrocarbons are further complicated by the presence of such species as $\dot{C}H_3$, $CH\dot{O}$ and $C\dot{O}$ radicals etc. it is reasonable to assume that branching reactions such as those in 1, 2 and 3 are again important and in addition propagation reactions such as

$$H\dot{O} + CO \longrightarrow CO_2 + H^{\cdot} \ldots\ldots\ldots\ldots\ 4$$

probably occur.

Working on this assumption it is clear that any action resulting in the decrease in concentration of the active species $O^{\bullet}$, $H^{\bullet}$, $OH^{\bullet}$ in the flame zone should result in a decrease in the chain branching reactions and ultimately cause the flame to cease propagating. All of the current theories of 'chemical' inhibition are based on the removal of active species from the reaction zone.

It is probably useful to indicate the difference between physical and chemical inhibitors. Cooling and 'blanketing' are the two main effects relied on by physical inhibitors. Large quantities of inert material with high heat capacity will upset the heat balance of the flame and will ultimately extinguish it. Alternatively if the fuel and oxidant supplies can be separated by an inert substance this will result in extinction of the flame (though this mechanism is often put forward it is a little difficult to see how it may operate in practice). Inhibitors operating by the physical mechanism are generally required in considerably higher concentrations than chemical inhibitors and for this reason research into chemical inhibition would seem to be the most rewarding.

There are two types of flames to be considered, these are the 'premixed' flame (where fuel and oxidant are mixed beforehand) and the 'diffusion' flame (where oxidant and fuel meet only at an interface and mix by diffusion processes) both of which may be encountered in a practical fire. At this stage it is convenient to consider these two types of flame, and important properties associated with them separately.

2.1.1. The Premixed Flame

Premixed flames are generally believed to be controlled by the rate of generation of heat from reactions occurring within the flame zone, the thermal diffusivity of the medium and also the molecular diffusion of the species present. No conclusive experimental evidence seems to exist regarding the relative importance of these factors.

Three of the experimentally measurable properties of premixed flames are used for assessing the relative effectiveness of inhibitors.

2.1.1.1. Flammability Limits

The majority of work undertaken has been concerned with the effect of inhibitors on these limits. The lower flammability limit of a fuel in air is the minimum concentration (by volume) of fuel in a fuel/air mixture through which a flame just propagates. Increasing the concentration of fuel above this level results in altering the characteristics of the flame (such as speed, temperature, luminosity) until the upper limit is reached. The general affect of adding inhibitors to flammable mixtures is to reduce the range of flammable mixtures. When assessing inhibitor effectiveness a property known as the peak percentage is determined. This is the lowest concentration of inhibitor in fuel which prevents flame propagation through all mixtures of fuel and oxidant.

Much discussion has arisen regarding the limits of flammability and questions have been put forward regarding their actual existence. Three solutions appear possible[2]:-

a. Limits currently measured represent asymptotic approaches to a fundamental limit.

b. A fundamental limit may exist but it corresponds to a weaker mixture than can be burned with conventional equipment.

c. No fundamental limit exists and observed limits are due to heat loss, gravitational disturbances or similar effects.

2.1.1.2. Quenching Diameter

This is a technique which has been developed comparatively recently[3]. Experimentally it involves allowing a premixed flame to propagate through a conical shaped combustion tube of carefully controlled dimensions and observing the diameter of the tube at which the flame is quenched. Inhibitors have the effect of increasing the quenching diameter. This value reflects the sensitivity of the flame, and associated reactions, to heat loss.

2.1.1.3. Burning Velocity

This property is a measure of the average reaction rate in the flame and will decrease with increasing inhibitor concentration. There are many experimental techniques for determining this value, varying in simplicity and accuracy.

a. One method utilizes equipment similar to that for determining flammability limits. The procedure involves timing the passage of flame between sensing electrodes set a pre-determined distance apart. Obviously quite sophisticated timing equipment is necessary for accurate results.

b. A simpler technique involves a bunsen burner type method. Premixed oxidant and fuel are burnt at the outlet of a burner tube which is concentrically situated inside a larger tube. Nitrogen is passed through the outer tube (in order to eliminate the possibility of a diffusion flame occurring around the premixed flame).

The average burning velocity is then defined as the ratio of volumetric gas flow to the area of visible flame surface.

c. A more precise method involving nozzle burners and using a Schlieren cone angle method (i.e. substantially measurement of the angle of the inner cone of the flame) has been developed. In such methods burning velocity is usually determined from the equation.

$$S_u = V_g \sin \theta$$

where V_g is the velocity of the unburned gas and θ is half the Schlieren cone angle.

Previously V_g has been obtained under cold flow conditions but experimental evidence now shows that unburned gas velocity is significantly affected by the combustion process. A technique has now been developed which involves the determination of V_g under flame conditions.[4]

2.1.2. The Diffusion Flame

Although most of the recent investigations have been confined to the simpler premixed flames quite a considerable number of the earlier studies were carried out on diffusion flames.

The main experimental technique is the concentric tube burner, with fuel flowing through the inner tube and oxidant through the outer. The flame is supported above the inner tube. The effect of inhibitors, both in the fuel and oxidant side of the flame have been studied and the conclusions drawn were generally similar to those from studies on premixed flames[2].

A different situation exists for inhibition of diffusion flames than for premixed flames[5]. In the latter case the reduction in rate of chemical reaction leads to a decrease in rate of heat release which in turn diminishes the velocity of flame propagation. While steady state combustion by a diffusion flame is not governed by the kinetics of reaction but by the rate of energy transport from the flame and the rates of mass transport of fuel and oxidiser to the flame front.

2.1.3. Flame Inhibition

Only those theories which concern 'chemical' inhibitors (as previously defined) will be considered.

Of the chemical inhibitors probably the most widely studied group are the organic or non ionic halides and of these the alkyl halides are the most extensively documented. It is clear from the preceding section that were it possible to inhibit the free radical reactions occurring at and immediately before the flame front then it may be possible to extinguish the flame.

Premixed flame studies on various fuel systems in air carried out by Burgoyne and Williams-Leir[6] and Coward and Jones[7] showed that methyl bromide was a considerably more effective flame inhibitor in all cases than nitrogen or cabon dioxide.

TABLE I

PEAK PERCENTAGES OF VARIOUS INHIBITORS

Combustible (in air)	Peak Percentages		
	Methyl Bromide	Nitrogen	Carbon Dioxide
Hydrogen	13.7	75	61
Carbon Monoxide	6.2	68	52
Ethylene	11.65	50	41
Methane	4.7	38	25
n-Hexane	7.05	42	29
Benzene	7.75	44	31
(after Friedman and Levy Ref. 2)			

Due to the low peak percentages of methyl bromide it was concluded that its action was chemical. This was supported by the work of Burdon, Burgoyne and Weinberg[8] who studied the combustion products of hydrogen/air and carbon monoxide/air flames containing methyl bromide, near the limit of flammability and showed that methyl bromide did not survive the flame. The bromine was found chiefly as hydrogen bromide and bromine.

Simmons and Wolfhard[9] observed that methyl bromide affects methane/air flammability limits to about the same extent as methane + $\frac{1}{2}$ Br_2 and concluded that the effective inhibitor is either atomic or molecular bromine and that methyl bromide served only as a halogen carrier.

A comprehensive study of the fire extinguishing properties of fifty six compounds was carried out by a group at Purdue University[10]. Results of this work tended to support the suggestion that the agent served mainly as a halogen carrier. Another generalisation which was drawn was that the halogens may be grouped in order of effectiveness Iodine > Bromine > Chlorine > Fluorine.

Simmons and Wolfhard[11] studied the inhibition of diffusion flames by methyl bromide which was added to both the fuel and also the oxidant sides of the flame. These results showed that the peak percentage when added to the air stream was about the same as those obtained for premixed flames but when the inhibitor was included in the fuel stream a much higher peak percentage was necessary. (approx. 10 x). The qualitative explanation offered for this was that in the reaction zone of methane/air flames stoichiometric amounts of methane and oxygen are present (about 10% methane). Assuming the inhibitor diffuses with the component to which it is added then in order to get the same amount of inhibitor to the reaction zone approximately 9x as much must be added to the fuel.

2.1.4. Published Theories of Flame Inhibition by the Alkyl Halides

An early theory by van Tiggelen[12] suggested that a reaction of the type

$$CH_3^{\bullet} + RX \longrightarrow RCH_3 + X^{\bullet} \quad \ldots\ldots\ldots\ldots\ldots\ 5$$

was responsible for inhibition of methane flames. This explanation relies on the relative ease with which the alkyl radical reacts with alkyl halides. It is suggested that this reaction is preferred to the alternative reaction of the methyl radical with more fuel, and that the halogen atoms are chemically incapable of continuing the reaction chains.

Belles[13] favoured the reaction suggested by Fryburg[14]

$$H^{\bullet} + CH_3X \longrightarrow HX + CH_3^{\bullet} \quad \ldots\ldots\ldots\ldots\ldots\ 6$$

This has the advantage in that it is a known reaction for which activation energies had been estimated for all four halides. (Reaction rates of the halides were also known to be in the order Iodide > Bromide > Chloride > Fluoride). However it has the disadvantage of generating an active radical.

Burdon, Burgoyne and Weinberg[8] measured product composition and calculated flame temperatures for near limit hydrogen/air systems containing methyl bromide, From this data they calculated the energy of activation of the chain breaking reaction, the value of 3 Kcal they obtained was of the order of magnitude which had been assigned to the reaction between $H^{\bullet}$ and CH_3Br. This would seem to support the reaction suggested by Fryburg.

It should be noted, however, that these calculations rely on very broad assumptions of reaction temperatures and rates and it is probably only fortuitous that the results obtained agreed with predicted values.

However a further study, by Fenimore and Jones[15], to test the proposal was carried out by probing flames burning on a cooled porous plate at low pressure. An independent value of the rate constant for the proposed reaction was determined and found to agree within a factor of 2 with the value deduced from flammability limits. It was concluded that the interpretations drawn by Burdon et al[8] were approximately valid but not exact.

Rosser and Wise[5] investigated the effect of halogen containing substances on the burning velocity of premixed methane/air and of ammonia/oxygen/nitrogen flames. They assume that the temperature at which significant inhibition occurs is above 1500°K and that it is necessary to consider the time available for reactions to occur at this temperature. For methane/air flames the time is estimated to be approximately 3×10^{-4} secs. These conditions are adequate for dissociation of species such as Br_2, I_2 and F_2 but not for Cl_2 it may therefore be assumed that only in the case of chlorine is there likely to be molecular species in the flame, discounting the possibility that Br_2 or I_2 are inhibitors.

Similar considerations may be applied to the halogen containing substances CH_3Br, CH_2Br_2, $CHBr_3$ and CF_3Br and it appears that CH_3Br is the least likely to be dissociated under these conditions. However, the reaction

$$CH_3Br \longrightarrow \dot{C}H_3 + \dot{B}r \quad \ldots\ldots\ldots\ldots\ldots\ldots \; 7$$

is probably catalysed by $\dot{B}r$:-

$$\dot{B}r + CH_3Br \longrightarrow Br_2 + \dot{C}H_3 \quad \ldots\ldots\ldots\ldots\ldots\ldots \; 8$$

$$Br_2 \longrightarrow 2\dot{B}r \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \; 9$$

therefore less severe conditions than those anticipated result in complete destruction of CH_3Br. It would seem likely therefore that inhibition is due to a decomposition product of CH_3Br.

CF_2Br_2 and HBr are both exceptionally stable to decomposition this probably accounts for the low inhibition efficiency of CF_2Br_2. However HBr is observed to be an effective inhibitor. The breakdown of HBr in the residence time available must be above 2000°K and also

$$2HBr \longrightarrow H_2 + Br_2 \quad \ldots\ldots\ldots\ldots\ldots \; 10$$

is kinetically unlikely, therefore it is suggested that HBr is the effective inhibiting species.

The possibility of formation of HBr from other inhibitors cannot be overlooked. A consideration of the energy changes involved indicated that hydrogen abstraction is feasible for fluorine and chlorine but less likely for bromine and iodine.

The general inhibition mechanism was proposed:-

$$H\alpha + X^{\bullet} \longrightarrow HX + \alpha \quad \ldots\ldots\ldots\ldots \; 11$$

$$\beta + HX \longrightarrow X^{\bullet} + H\beta \quad \ldots\ldots\ldots\ldots \; 12$$

where $H\alpha$ is $HC\dot{O}$, $H\dot{O}_2$ etc. and β is $O\dot{H}$, $\dot{H}$, $\dot{C}H_3$ etc. The products H β and α may be stable or free radicals of lesser importance in oxidative chain propagation. These reactions must necessarily be competitive with propagation reactions.

The high reaction temperatures tend to obliterate differences in reactivity observable at lower temperatures and the near equivalence of iodine and bromine is not surprising since neither would be expected to react with CH_4 or similar stable species at a rate comparable to the extermination rate of 12. However, both chlorine and fluorine may extract H from the fuel, resulting in reduced effectiveness of these, as this constitutes a reversal of reaction 11.

The critical factor in the proposed mechanism is therefore the strength of H-X, if too strong rates of reactions such as 12 will be reduced and abstraction of hydrogen by stable species with X atoms may be favoured over reactions of type 11. Alternatively if H-X is too weak there is a tendency for the molecule to dissociate rather than react. The effectiveness of iodine and bromine reflects their almost unique balance between strength and weakness.

Similar reductions in flame speed for the system ammonia/oxygen/nitrogen were also observed and it was concluded that the proposed inhibition mechanism was not limited to hydrocarbon/air mixtures.

The work which formed the basis of this theory was extended[16] to include (a) Determination of the maximum temperature of methane/air flames (b) Flame spectra of methane/air flames (c) Study of the quenching of such flames by solid surfaces (d) The low temperature oxidation of methane.

This work supported the general inhibition mechanism represented by equations 11 and 12 and it was further added that the mechanism may be regarded as a means of substituting $X^\bullet$ for β . However, while inhibition may originate in this substitution it results from:-

i. A reduction in the rate of transfer of activity by diffusion of species such as $O^\bullet$, $OH^\bullet$, $H^\bullet$.

ii. A reduction in the rate of the exothermic propagation reaction.

$$OH^\bullet + CO \longrightarrow CO_2 + H^\bullet \quad \ldots\ldots\ldots\ldots\ldots 4$$

iii. Also a reduction in the rate of the chain branching by reactions such as

$$H^\bullet + O_2 \longrightarrow OH^\bullet + O^\bullet \quad \ldots\ldots\ldots\ldots\ldots 1$$

The chief conclusions drawn from this work was that the high efficiency of chemical inhibitors was due to

a. A cyclic mechanism involving regeneration of active species.

b. The large values of specific reaction rates between inhibitor molecules and specific chain carriers of combustion reactions.

It was suggested that little advantage may be gained from an attempt to improve significantly on this chemical process but considerable advances may be made by studying the effect of changes of physical properties of inhibitors.

Many other investigations have been carried out since this proposed inhibition mechanism the results of most of which tended to support the theory.

Rosser et al[3] used the quenching diameter method (page 16) to study the effect of various inhibitors on methane/air, methane/NO_2, methane/NO_2/air and methane/NO premixed flames. The results of the study indicated that inhibition was extremely sensitive to the oxidant and that combustion involving NO and NO_2 was insensitive to inhibition.

It was suggested that the sensitivity of hydrocarbon/oxygen combustion was due to the occurrence of the moderately endothermic (20 Kcals) reaction.

$$H^{\bullet} + O_2 \longrightarrow HO^{\bullet} + O^{\bullet} \quad \ldots\ldots\ldots\ldots\ldots \; 1$$

Permitting low concentrations of inhibitor to compete with major species for radicals such as $OH^{\bullet}$, $O^{\bullet}$, $H^{\bullet}$, thus interupting the chain reactions involving these species.

The specific mechanism represented by 11 and 12 did not explain the observed effectiveness of PCl_3 and $POCl_3$ as flame inhibitors and no explanation was offered for this.

Recent work by Edmonson and Heap[4] on burning velocity measurements of methyl bromide inhibited methane/air flames using the accurate nozzle burner Schlieren cone angle technique, in general support the inhibition mechanism described by reactions 11 and 12. In addition they showed that (a) Addition of methyl bromide causes a shift of maximum burning velocity towards leaner conditions (b) The effectiveness of methyl bromide as an inhibitor increases as the methane content of the mixture increases (c) Successive equal additions of methyl bromide causes progressively smaller reductions in burning velocity.

Butlin and Simmons[17] studied the flammability limits of hydrogen/air/hydrogen halide mixtures over a wide range of mixture compositions and final flame temperatures by varying the oxygen content of the air. The efficiency in preventing propagation of flame was shown to decrease in the order HI > HBr > HCl. HI and HBr appeared to act as chemical inhibitors while HCl was primarily a thermal diluent. They concluded that the rich limit was controlled by competition between

$$H^{\bullet} + O_2 \longrightarrow H\dot{O} + O^{\bullet} \ldots\ldots\ldots\ldots\ldots \quad 1$$

and

$$H^{\bullet} + HBr \longrightarrow H_2 + B\dot{r} \ldots\ldots\ldots\ldots\ldots \quad 13$$

but that the lean limit is not controlled in this way. Reaction 1 is generally considered to be an important chain branching reaction in methane/air flames, therefore it was assumed that this argument applies to hydrocarbon flames also.

An investigation by Creitz[18] on the effect of inhibitors on diffusion flames observed similar occurrences to those by Simmons and Wolfhard[11]. In essence the main observation was that inhibitors added to the oxidant side of the flame were more effective than when added to the fuel. This was attributed to the failure of the inhibitor to survive the combined effects of the reducing atmosphere and pyrolysis in the pre-flame zone. The lack of effectiveness, it was concluded, was due to the necessity of having the intact molecule or its freshly released decomposition products in the flame reaction zone.

Results reported in this paper and other unpublished work indicated that those materials which were most effective inhibitors had the ability of capturing electrons. Only those which form negative ions with relatively high electron affinities such as O^- and OH^- or negative halogen ions are said to be important inhibitors.

A proposal which reconciles these observations with Rossers proposed mechanism has been reported[19].

A typical inhibitor, trifluoro bromomethane, attaches low energy free electrons by a dissociative attachment process

$$CF_3Br + e^- \longrightarrow Br^- + CF_3^{\bullet} \quad \ldots\ldots\ldots\ldots 14$$

Inhibition could occur through reaction between $O^{\bullet}$, $OH^{\bullet}$ and/or $H^{\bullet}$ with the negative ion Br^- and/or the residual radical $CF_3^{\bullet}$.

i.e. $$CF_3^{\bullet} + H^{\bullet} \longrightarrow CF_3H^* \quad \ldots\ldots\ldots\ldots\ldots\ldots 15$$

Excess energy equal to C-H bond may be lost by collision with a third body M.

$$CF_3H + M \longrightarrow CF_3H + M^* \quad \ldots\ldots\ldots\ldots 16$$

Other authors have reported the ability of residual radicals to inhibit flame reactions. Rosser et al[16] proposed that the effectiveness of bromine containing inhibitors is equivalent to the equivalent amount of bromine in methane/air flames burning at maximum speed. However comparing CF_3Br with $\frac{1}{2}Br_2$ they concluded $CF_3^{\bullet}$ must contribute to the inhibition. Fenimore and Jones[15] suggest $CH_3^{\bullet}$ radicals from either CH_4 or CH_3Br are powerful inhibitors in methane/hydrogen/air flames and suggest that $CH_3^{\bullet}$ react mostly with

$O^{\cdot}$ atoms in air or oxygen flames making $O^{\cdot}$ atoms unavailable. The Br^- may also be effective

$$H^{\cdot} + Br^- \longrightarrow HBr + e^- \quad .... \quad 17$$

The stabilizing reaction is not necessary here as excess energy is carried away by e^-.

It was concluded that it was possible that both residual radicals and negative ions contribute to the inhibition process, leaving the overall result the same as in the current mechanisms. The paper includes a number of experimental observations (by other workers) which are claimed to support this theory.

2.1.5. Inhibition by Solids in the Flame

It is a well known fact that finely divided salts such as $NaHCO_3$ can be used to prevent ignition of combustible gases or alternatively as fire extinguishers. Various studies of combustion inhibition[2] have revealed that powdered materials vary widely in their ability to inhibit combustion, that alkali metal salts are effective inhibitors and that the effectiveness of some powders is proportional to the specific surface area of the material.

Rosser et al[16] proposes that any future study of flame inhibition should include a study of heterogeneous inhibition, and that the relative importance of

a. Absorption of heat by the particle.

b. The contribution of heterogeneous reaction on the surface of solid particles which remove important radicals.

c. Influence of homogenous reactions proceeding in the vapour phase between combustion radicals and substances resulting from the vaporization of the solid particles.

A later paper by the same workers[20] described a study of the effect of finely divided metal salts on premixed flames where they suggest that the inhibition mechanism of powders probably involve a succession of steps:-

i. Heating of powder particles by hot flame gases.

ii. Evaporation of powder particles.

iii. Decomposition or reaction of evaporated material to provide metal atoms.

iv. Inhibition of the combustion process by metal atoms.

This theory however has not been supported by the work of Dewitte et al[21] or Friedman and Levy[22]. The former workers studied nitrogen diluted methane/oxygen flames and showed that the residence time of the particle in the flame is only great enough to permit a temperature increase in the particle of less than 100°C. Friedman and Levy used an opposed jet type methane/air diffusion flame for studying inhibitor effectiveness and showed that elemental potassium was far less effective than a comparable concentration of bromine. They propose a mechanism where gaseous potassium hydroxide is the effective inhibiting species probably by reaction such as:-

$$KOH + \dot{H} \longrightarrow HOH + \dot{K} \quad \ldots\ldots\ldots\ldots\ldots 18$$

$$KOH + OH^{\bullet} \longrightarrow HOH + KO^{\bullet} \quad \ldots\ldots\ldots\ldots\ldots 19$$

From the early work it was clear that there were two types of solid inhibitor these were classed as physical inhibitors and chemical inhibitors. Similarly as in the case of homogeneous inhibitors physical inhibitors are thought to be active primarily by a cooling action. Dewitte et al[21] classified the inhibitors they studied and assigned Al_2O_3, $Al_2 (SO_4)_3$, SiO_2, CuO, $MgCO_3$ as thermal or physical inhibitors and K_2SO_4, K_2CO_3, KNO_3, KCl, KBr, KI and NaCl as chemical. They suggested that the efficiency of the chemical inhibitor depended upon adsorption of radicals at the particles surface where they were ideally situated for recombination and that the efficiency was related to the ease with which free valence electrons could be made available to the colliding radical. Semenov[23] pointed out that these electrons were more easily produced by solids having polar bonds than those having more covalent bonds.

The flame inhibition effectiveness of iron pentacarbonyl and lead tetraethyl has been observed[24], although these substances themselves are flammable materials. Much work has been carried out on the use of lead tetraethyl as an anti-knock agent in petroleum combustion. This work seemed relevant to the problem in that the anti-knock mechanism is thought to proceed by reduction in concentration of active combustion species. Salooja[25] showed that the lead compounds formed during combustion, in glass apparatus, of hydrocarbons containing lead tetraethyl were chiefly orthorhombic and tetragonal polymorphs of PbO. The effectiveness of lead tetraethyl is thought to be due to this formation of PbO (PbO had previously been shown to be effective in destroying peroxides and $OH^{\bullet}$ and $HO_2^{\bullet}$ radicals).

Chamberlain and Walsh[26] showed, by the use of a Tyndall beam, that the oxidation of lead tetraethyl produced a fog and that deposits from the fog consisted of PbO. Further, tellurium diethyl, iron pentacarbonyl and nickel tetracarbonyl are all known, or strongly suspected, to have produced fogs, all of them are effective anti-knocks. It is also significant that the alkyls of bismuth, lead and thallium are anti-knocks but the alkyls of mercury are not. This is explained by the fact that at combustion temperatures mercuric oxide decomposes yielding mercury which boils providing no solid surface in the flame.

It should be emphasised that the whole subject of flames and their inhibition is extremely complex and that this survey has tended towards an over simplification in order to reconcile it with the essentially technological approach, which has been adopted in this project, to the problem of flammability of plastics.

2.2. A General Review of the Literature on the Flammability of Plastics

Many excellent reviews have been published on the problem of flammability of plastics,[27, 28, 29, 30] each dealing with the subject in a similar manner. On consulting these it is immediately apparent that few significant developments have occurred since work was first commenced on the problem. Much work has been undertaken but in essence the three most common elements used in flame retardance are still chlorine, bromine and phosphorus. Inorganic materials are used to a smaller extent, mainly in conjunction with one of the previous types of compound. The bulk of the published work is in patents, of which the majority employ a variation on one or another of these methods. Four papers[31, 32, 33, 34], have been written about the work described in this thesis, copies of which may be found inside the back cover, these will be referred to in due course.

2.2.1. The Action of Chlorine

Early formulations in polystyrene used very high percentages of chlorinated materials i.e. 50 - 60% of chlorinated naphthalenes[35], 20 - 60% of chlorinated biphenyls,[36, 37], 35 - 70% of chlorinated paraffin waxes[38]. Lower concentrations of chlorinated paraffin wax were used in cellulose acetate butyrate[39] (22 - 35%). Obviously the high concentrations of these additives largely excluded their use in commercial formulations.

Patents granted to Clayton and Heffner in the late 1930's[40] and early 1940's[41] covered the use of combinations of chlorocarbons and antimony trioxide for the flame proofing of fabrics. It was found that the effectiveness of these systems was related to the ease of liberation of hydrogen chloride from the chlorine compound and it was also shown that the use of antimony trioxide considerably reduced the concentration of chlorinated material required. This practice is now widespread. Suggestions have been made as to the mechanisms of this synergistic effect although no experimental evidence has been published in support.

Bell[42] proposes that the halogenated organic compound thermally decomposes to yield hydrogen chloride which reacts with antimony trioxide to produce antimony chloride or oxychlorides. Schmidt[28] further suggests that this antimony/chlorine compound is volatilised into the flame where it is oxidised. Energy of the system is then reduced by collision of the high energy free radicals at the oxide particle surface. This he terms the wall effect. Learmonth and Thwaite[33] have shown that the predominant reaction product between chlorinated paraffin decomposition product and antimony trioxide is antimony trichloride. Subsequent work[34] showed this to be an effective flame inhibitor and that Schmidt's suggested wall effect was probably at least partly correct.

Fenimore and Jones[43] and Fenimore and Martin[44] whilst studying the flammability of polyethylene made a number of observations with regard to the effect of chlorine and antimony trioxide systems. Fenimore and Jones who studied the burning of polyethylene in oxygen and also nitrous atmospheres showed that polyethylene containing chlorine in the absence of antimony trioxide inhibited burning in both nitrous and oxygen atmospheres, while combinations of chlorine and antimony trioxide proved effective inhibitors only in oxygen atmospheres. They concluded from this that antimony trioxide/chlorine combinations inhibited by flame poisoning while chlorine alone affected the pyrolysis process. This was supported by the work of Fenimore and Martin who showed that chlorine in the polymer was considerably more effective than when introduced into ethylene/air flames.

Work on cellulose[45] and polymethyl methacrylate[46] provided evidence that the presence of chlorine affects the pyrolysis of these materials. Investigations carried out in this laboratory[47] indicated that mixtures of halogenated organic compounds with antimony trioxide have little affect on the pyrolysis processes of unsaturated polyester resins.

Martin and Price[48], while studying the flammability of epoxy resins noted that triphenyl antimony alone was an efficient flame retardant for this material. However, previous work had shown that triphenyl antimony was not a flame retardant in polyethylene, in the absence of chlorine. From this it was concluded (without direct experimental evidence) that the feedback of heat from flames resulting from the combustion of epoxy resins was sufficient to vaporize triphenyl antimony while that from polyethylene was not.

Bell et al[49] suggests that an important consideration is the chlorine, antimony trioxide ratio while Fenimore and Martin[44] demonstrate that the amount of halogen is not critical for a given level of antimony trioxide above a certain level.

The early problems associated with chlorinated additives have now been largely overcome. These included poor weathering properties and also the plasticizing effect on many plastics materials. Bell[42] has shown that substitution of a small amount of titanium dioxide for antimony trioxide greatly improves the weathering characteristics.

Obviously, detrimental effects of the additive on the physical properties of the material will be reduced by using an additive with a higher concentration of chlorine. A British Patent[50] granted to B.A.S.F. suggests that the concentration of chlorine should not be below 40% of the weight of the additive.

Schmidt[28] points out that while chlorine substituents are cheaper, breakdown to hydrogen chloride requires considerably more energy than for the corresponding bromine compound. As a result of this hydrogen chloride tends to be produced more slowly over a wider temperature range whilst hydrogen bromide may be present in greater concentrations at a given time. On the other hand the chlorinated materials are capable of withstanding the higher processing temperatures often found in such plastics materials as ABS and polypropylene.

2.2.2. The Action of Bromine

It has frequently been reported that bromine compounds are substantially more effective than chlorine containing compounds, values of between 3 and 15 times have been quoted[52]. Jolles[53] points out that this is misleading as much depends upon the ease of liberation of the halogen from a specific compound.

TABLE II

COMPARISON OF BOND STRENGTHS OF VARIOUS CHLORINATED AND BROMINATED COMPOUNDS

X	Bond Dissociation Energies D (X-Y)	
	Y	
	-Cl Kcals	-Br Kcals
H-	103	88
CH_3-	81	68
C_2H_5-	81	67
n-C_3H_7-	82	68
$(CH_3)_2CH$-	82	68
$(CH_3)_3C$-	78	64
C_6H_5-	86	71
$C_6H_5CH_2$-	68	51
CH_2:$CHCH_2$-	58	48
C_5H_5CO-	74	57
After Jolles Ref. 53		

However there is little doubt that other things being equal bromine is more effective than chlorine. Volans[54] points out also that the activity of bromine varies with the nature of the parent molecule. In general bromine in aromatic compounds is of low activity probably due to the higher bond strength. (see Table II.)

There seems to be less published evidence to show that bromine is active in altering pyrolysis processes of the base polymer than chlorine[30]. However, a study carried out by Cullis and Smith[55] on the effect of volatile bromine on the degradation of polyethylene and also its oxidation at approximately 400°C showed that the rate of degradation of the polymer is unaffected by the presence of volatile hydrocarbons. Hydrogen bromide substantially reduced the rate of weight loss but caused considerable fragmentation of initial gaseous products. Investigation of the effect of some simple organic bromine compounds showed that they retard the degradation of polyethylene only if they degrade to hydrogen bromide.

Volans[54] carried out pyrolytic studies in air and also nitrogen on four modified polystyrenes each containing 2% bromine by weight, in different chemical forms. He concluded that the crucial factor in inhibition is the initial spurt of fuel vapour rich in hydrogen bromide which occurs under essentially anaerobic conditions causing localised rupture of the flame and ultimately a complete breakdown of the flame system. This conclusion was essentially supported by Fenimore[56] who showed that the first pyrolysis products evolved from polystyrene containing tris 2, 3 dibromopropyl phosphate were 3 - 7 times richer in bromine than the concentration of bromine in the unchanged material.

As in the case of chlorine compounds antimony trioxide has been shown to have synergistic activity. Pumpelly[57] who investigated the activity of compounds other than antimony trioxide as synergists, with hexabromobenzene, in rigid polyurethane foam showed that antimony trioxide was unique amongst those materials tested.

Martin and Price[48] who used the oxygen index method of studying the flammability of epoxy resins showed that triphenyl stibene in concentrations as low as 3 Sb atoms per 1000 C atoms was an effective inhibitor. Addition of bromine to the resin did not produce any further increase in the index until the concentration of Sb atoms was raised above 3 per 1000 C atoms. Using N_2O as oxidant it was again shown that antimony is mainly important in poisoning flame reactions. From this it was suggested that the halogen is the antimony carrier and that the effectiveness of triphenyl antimony is due to its high vapour pressure and thermal stability. Triphenyl phosphorus was an effective inhibitor both in oxygen and nitrous oxide and it was concluded that this must affect pyrolysis reactions. Addition of bromine containing compounds had an effect less than additive, and it was concluded that two separate mechanisms were taking place.

Observations made by Eichhorn[58] represented a major 'break through' in the use of bromine containing compounds as flame retardants. It was shown that the concentration of acetylene tetrabromide required for self extinguishing foamed polystyrene could be reduced from 5 phr. to 0.5.phr. by inclusion of 0.5 phr. dicumyl peroxide. Similar effects were observed with other peroxides, hydroperoxides, azo compounds, quinone imines, benzothiazole sulphenamide, disulphides and a dibenzyl compound. A number of halogen compounds with dicumyl peroxide were also investigated and it was generally shown that bromine was more effective than chlorine and that aliphatic bromine was much more effective than aromatic. A general rule was that if the halogenated compound alone showed any effectiveness then this was increased by inclusion of a free radical initiator. It was thought that the synergistic activity could be explained in one or more of the following ways:

1. The initiator decomposes and increases the rate of decomposition of the halogen compound or alternatively initiates decomposition at a lower temperature. Thermogravimetric studies showed that 90% decomposition of 1,2 dibromotetrachloroethane took place at 20°C lower in the presence of dicumyl proxide than alone.

2. The initiator, halogen compound or both interacting lowers the temperature at which oxidation of the polymer occurs. In this way it is suggested the decomposition temperatures of the halogen compound and the polymer may be better matched. It has been shown that di tert butyl peroxide appreciably lowers the vapour phase oxidation temperature of benzene and also the effectiveness of hydrogen bromide in lowering the oxidation temperature of hydrocarbons is well known.

3. The initiator thermally decomposes and accelerates the breakdown of the polymer and promotes reaction between the polymer fragments and the halogen containing material

leading to a delay in the loss of halogen. Samples of polystyrene containing acetylene tetrabromide only and also acetylene tetrabromide + dicumyl peroxide were heated in air. Samples were withdrawn at various temperatures and analysed for bromine. Appreciably greater amounts of bromine were found to be present in those samples containing dicumyl peroxide over the temperature range 150 - 300°C.

It was shown also that free radical scavengers had no effect on the self extinguishing properties of polystyrene containing only acetylene tetrabromide but had considerable effect on those containing acetylene tetrabromide with peroxy synergists. Hence a free radical mechanism was confirmed.

Ingram[59] investigated the possibility of materials other than those studied by Eichhorn as synergists in foamed polystyrene. It was shown that N-nitroso N methylaniline, N-nitrosocarbazole and N-nitroso diphenylamine were all effective but had the undesirable properties of inhibiting polymerization. NN dichloro NN diphenyl urea and NN dichlorotoluene sulphonamide were effective but of limited value because of hydrolysis by atmospheric moisture.

Fenimore[56], investigating the synergistic activity between tris 2,3 dibromopropyl phosphate and dicumyl peroxide in polystyrene rods, showed that peroxides had little effect on the evolution of bromine. This supported Hindersinn[60] who proposed that the inclusion of peroxides caused the polymer to fragment and then melt more readily causing the material to drip under the test conditions, giving a false impression of its flammability.

2.2.3. The Action of Phosphorus

The use of inorganic and organic phosphorus containing compounds as flame proofing materials has been extensive, particularly in cellulosic polymers. Organic phosphorus compounds are most commonly used in polyurethanes and cross-linked polyester resins, but also find application as flame retardant plasticisers in polyvinyl chloride.

Boyer[62] points out that there are three principal methods of incorporating an organic phosphorus compound into a plastics material.

1. Incorporating the compound as a physical additive. A number of disadvantages arise from the fact that the compound is not chemically bonded to the polymer, these include a lack of permanency. The compound is liable to leach out of the resin over a period of time. Also, a softening of the resin often results from this type of incorporation. The common esters of phosphoric acid TCP, TPP and TXP are mainly used for this type of application.

2. Inclusion as a comonomer, in this way the phosphorus becomes part of the backbone of the resin. This leads to a better protection of P-O-C linkages which are liable to be hydrolysed if not chemically incorporated[63]. Also by using this method it is possible to select the sites on the polymer network where the phosphorus is to be situated.

3. Chemically combining a phosphorus containing compound to reactive sites in a ready formed, conventional

resin. In this way phosphorus may be included without subsequent reduction in molecular weight which often results if phosphorus is present during polymerization.

The efficiency of phosphorus is enhanced if used in conjunction with a halogen which may be present in the same molecule. Some workers have reported synergistic activity between the two elements although this does not appear to be applicable to all combinations.

It is not intended to deal with the methods of incorporation of phosphorus containing compounds into polymers in detail but let it suffice to say that existing reviews cover this subject[30, 61].

It is well known that phosphorus containing compounds are excellent materials for reducing the phenomenon of after-glow in many char producing materials. After-glow is the name given to the highly exothermic solid phase oxidation of carbon.

$$2C + O_2 \longrightarrow 2CO$$

This obviously represents a hazard in that it may act as ignition source for any combustible material in the near vicinity.

Jacques[63] summarizes the activity of phosphorus compounds in flame proofing as:-

a. Providing an alternative route of lower exothermicity for the oxidation of carbon. The phosphorus compound is converted to oxides of phosphorus and phosphoric acid, these may mask the surface of carbon from the atmosphere or alternatively be reduced to lone pair phosphorus compounds simultaneously to the oxidation of carbon. This reaction occurs above the polymer surface and provides a means of rapid heat exchange between the surface and the surrounding atmosphere.

b. Phosphorus acts as a halogen carrier and the ease of hydrogen halide liberation is usually enhanced by the relative ease of thermal breakdown of the phosphorus bearing part of the compound. Additionally it may act as a catalyst in halogen atom formation at the carbon surface. The formation of activated species containing P-X bonds is envisaged indicating that phosphorus may also have an effect on the gas phase reactions.

Tang and Neil[45], while working on cellulosics, showed that phosphorus compounds lower the pyrolytic decomposition temperature and raise the yield of char. It is suggested that a similar mechanism probably occurs for synthetic polymers.

2.3. Flammability of Unsaturated Polyester Resins

Unsaturated polyester resins are prepared by a condensation reaction between a dihydric alcohol, a dibasic saturated acid and a dibasic unsaturated acid. Resulting in linear chains of the type.[64]

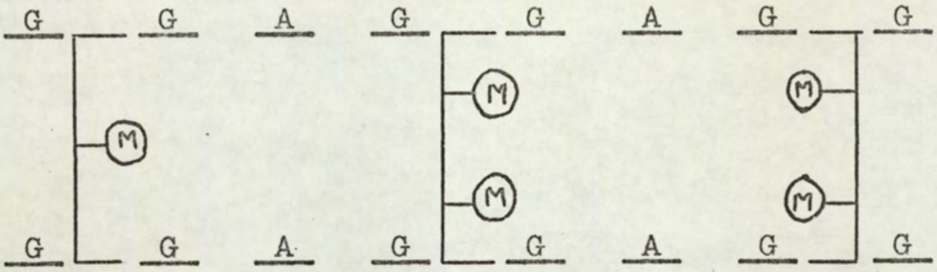
$$\underline{G}\ \underline{\underline{D}}\ \underline{G}\ \underline{A}\ \underline{G}\ \underline{\underline{D}}\ \underline{G}\ \underline{A}\ \underline{G}$$

where G is the dihydric alcohol (often 1,2 propylene glycol).

A is the dibasic acid, often phthalic acid.

$\underline{\underline{D}}$ is the dibasic unsaturated acid, often maleic acid.

Cross linking may be introduced by means of a vinyl monomer (M) usually styrene, resulting in a network such as:-



The use of glass fibre reinforced polyester resins is extensive in the road transport, building, chemical manufacturing, shipping and railway industries. Often applications arise requiring the use of a material with reduced flammability. The subject of flammability of polyester resins is adequately dealt with in four reviews.[65, 66, 67, 68].

Parkyn[65] points out that all polyester resins whether flame retarded or not are combustible at an ambient temperature of 750°C. However, in many applications a self extinguishing material (one which does not continue burning on removal of external flame) is all that is required. This property and also a reduced burning rate may be achieved in a number of ways:-

1. Incorporation of Inorganic Additives.
2. Incorporation of Organic Additives.
3. Modification of the saturated acid.
4. Modification of the unsaturated acid.
5. Modification of the glycol.
6. Modification of the monomer.

Often combinations are used.

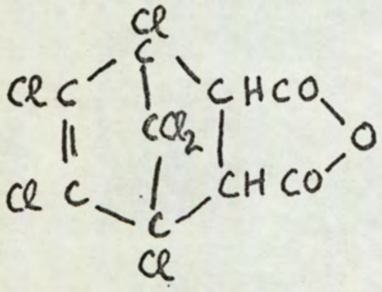
2.3.1. Inorganic Additives

In general these are only effective by diluting the amount of combustible present and they do not always have the effect of reducing flammability. For example laminates prepared using glass mat ignite more readily than cast resin of the same thickness. However borax and also alum are quite effective when used in high concentrations, chalk and silica are also used but are less effective. Alumina hydrate $Al(OH)_3$[69] used in conjunction with the conventional halogen/antimony trioxide is said to enhance the fire resistance.

The various types of organic additive almost exclusively employ halogen or phosphorus or both and the general use of these has already been dealt with (sections 2.2.1., 2.2.2., and 2.2.3.).

2.3.2. Modification of the Saturated Acid

Tetrachloro and also tetrabromo phthalic anhydride may be substituted for phthalic anhydride but the bromo compound tends not to be used commercially due to unreliable curing characteristics[65]. Het acid or hexachlorendomethylene tetrahydro phthalic acid is used quite extensively and good fire retardant properties may be achieved without additional additives



Het Anhydride

However resins prepared from this are expensive, difficult to use and tend to yellow and cloud on storage, consequently a lower chlorine content resin is prepared commercially often with additives such as chlorinated paraffin and antimony trioxide used.

2.3.3. Modification of the Unsaturated Acid

Some resins have been made with chloromaleic acid although they contain insufficient chlorine to be self extinguishing without added antimony trioxide.

2.3.4. Modification of the Glycol

This method is not widely used although a number of compounds have been reported[68] probably most of which will not find commercial application.

2.3.5. Modification of the Monomer

Jacques[63] concluded that in order to achieve a completely fire retardant composition it would be necessary to substitute at least part of the styrene, which is used as comonomer in most commercial resins. Parkyn[65] points out that good self extinguishing resins can by made by replacing all or part of the styrene with dialkyl benzene phosphonate $C_6H_5PO(OCH_2CH = CH_2)_2$. However, use of this cross linking agent tends to increase considerably the cost of the final laminate.

2,5 Dichloro styrene has been used although flammability is only slightly reduced. However this method may be useful in supplementing one or another of the methods already described. Bennet et al[70] studied a number of condensed alkyds using dibromo styrene as cross linking agent. The paper deals mainly with curing properties and physical properties of the final material but it was concluded that dibromo styrene/antimony trioxide systems achieved a degree of flame retardance comparable with commercial flame retardant resins already available.

One aspect which has not been dealt with by the review papers is the study of thermal degradation of cross linked polyesters. In fact, little work has been carried out on this subject although a large number of papers have been published, especially by Ritchie[71], regarding linear resins and associated model compounds.

There seems to be two chief techniques used in the study of thermal degradation (1) Vacuum pyrolysis and identification of products[72] (2) Thermal techniques such as differential thermal analysis (d.t.a.) and thermogravimetric analysis (t.g.a.).

2.3.6. Pyrolysis and Analysis of Products

Schmidt[73] designed an apparatus for the vacuum pyrolysis of cross linked polyesters and subsequent analysis of products by gas liquid chromatography. It was claimed that the degradation products were few and were carbon dioxide, acetaldehyde, acrolein, styrene, phthalic anhydride and a few unidentified phthalate esters in small quantities.

At 200°C carbon dioxide and unreacted styrene was given off. Just above 300°C phthalic anhydride appeared and at about 340°C all of the phthalic could be distilled out. Above 400°C phthalic anhydride, carbon dioxide and acetaldehyde were liberated rapidly, styrene also appeared, reaching a peak at 460°C. At 550°C volatile formation was completed.

Other published work appears to have been carried out with a primary objective other than product identification. Anderson and Freeman[74] identified degradation products from heating a styrene cross linked resin of phthalic, maleic, propylene glycol by means of a mass spectrometer and also infra red. A 3 gm. sample was heated, in a stream of air, at a rate of 5°C/min. from room termperature to 500°C. Over the range 200 - 300°C benzaldehyde and unsaturated hydroxy esters were detected. 300 - 400°C produced hydroxy esters and phthalic anhydride, 400 - 500°C yielded a mixture of phthalic acid and phthalic anhydride in addition to low molecular weight esters of propylene glycol. Preliminary studies[75] of other degradation products of a maleic anhydride propylene glycol, styrene crossed resin at 250°C indicated that these include crotanaldehyde, acetaldehyde, acrolein, carbon monoxide, carbon dioxide and water.

2.3.7. Thermal Analytical Techniques

Both thermogravimetric analysis and also differential thermal analysis are extremely sensitive to variations in sample size and particularly particle size of the sample[31]. For this reason it is difficult to correlate results of studies by different workers. As this aspect did not appear to have direct relevance to the present study let it suffice to cite the following references without reviewing their contents[74, 75, 76, 77, 78].

2.4. Flammability Testing

The state of flammability testing is extremely confused: many tests exist varying in sophistication from simply holding a piece of material in a bunsen flame to a full scale fire in a simulated structure. In most cases correlation of results from one test method to another is not possible. Reviews of standard flammability test methods have been published,[79, 80] but these serve only to catalogue the standard test methods in use in the U.S. and Britain. A paper by Learmonth[81] surveys generally the types of test methods available and concluded that these could be classified into three sections:-

i. Simple tests, useful for sorting purposes but not very significant.

ii. A set of more useful tests used to pick out the empirical factors involved and widely used as specification tests, effective but difficult to correlate with each other.

iii. Several tests involving small scale fires, these were informative but expensive in time and money.

Sauber and Patten[80] emphasised that two major aspects of flammability must be considered and that these were ignition and burning properties. Scott[79] took up this point and arranged his review accordingly, he listed the main specifications regarding flammability of ASTM and British standards and the following is taken from his review.

2.4.1. Ignition Tests

B.S. 476 Part 1 Section 1 1953[82]

ASTM D1929-68[83].

2.4.2. Burning Tests

(a) Screening Tests

B.S. 2782 Part 5 Misc. Methods 508A-508E[84]

B.S. 737[85]

ASTM D635[86]

ASTM D757[87]

(b) Large scale screening tests to evaluate design and material suitability for structural applications.

B.S. 476 Part 1 Section 2[88]

B.S. 476 Part 3[89]

ASTM E162[90]

ASTM E84[91]

and in addition

(c) Simulated structure tests, these are specific to a particular application and therefore are not standard methods.

In addition to these, many other methods exist which are used to a lesser extent. Fenimore and Martin[92] however have developed a small scale method which determines the oxygen demand of a burning plastic strip. The flammability of the material is assessed by a numerical index based on this. The details of this method are described more fully in the next chapter.

The surface spread of flame test is important and is used for classifying combustible wall and ceiling lining materials which are often of reinforced polyester composition. For this reason it seemed particularly relevant to discuss this method in more detail. Much development work carried out in industry is solely directed to producing a suitable material which conform to the specification of this test.

2.4.3. B.S.476 Part 1 Section 2

Six specimens each 36" x 9" and of their normal thickness are subjected to the test. The specimen is securely fixed to a suitable framework such that the face of the specimen may burn without obstruction from the supports. The framework is mounted with its longitudinal axis horizontal and brought to its test position where the face of the specimen is exposed to a source of radiant heat. The intensity of heat from the source is such that the temperature at the end of the specimen nearest to the source is 500°C and the end furthest away is 130°C. Immediately the specimen is exposed to the radiated heat a vertical 7" gas flame is applied to its hotter end for one minute.

The rate of spread of flame front for measured distances is observed along a line drawn parallel to the long axis 3" from the bottom edge of the specimen. Measurements are carried out until the flames have died out or for 10 minutes whichever is the longer. Materials are classified as follows:-

Class 1 Surface of very low flame spread, not more than $7\frac{1}{2}$".

Class 2 Surfaces of low flame spread, less than 12" in $1\frac{1}{2}$ minutes and less than 24" total spread.

Class 3 Surfaces of medium flame spread, less than 12" in 1½ minutes and less than 33" total.

Class 4 Surfaces of rapid flame spread either more than 12" per minute or more than 33" total spread.

The results of the tests on six specimens are calculated in such a way that not more than 1% of a material is likely to have a performance below the classification.

Obviously this equipment is large and sensitive to variations in construction, consequently it is quite expensive. In order to obtain consistent results, only establishments which have been licensed by the Joint Fire Research Organisation are permitted to conduct these tests.

An apparatus to be used as a preliminary to this test has been developed[93]. It is not intended that this should replace the large scale method but it does mean that if correctly applied the number of failures tested on the large scale should decrease. The preliminary test is not easy to set up, however. It requires its own room of particular dimensions with suitable provision for fume extraction etc. For this reason, again only few of these are available and it is common for those manufacturing concerns with the facilities, to carry out tests for other firms, often competitors.

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CHAPTER 3

EQUIPMENT AND PROCEDURE USED IN ASSESSING A RANGE OF COMMERCIAL FLAME RETARDANTS

Three techniques, reflecting both burning and ignition characteristics, were selected for assessing the performance of a series of commercial flame retardant additives, in a general purpose cross linked polyester resin. The objectives of this work programme were:-

a. To check that the known technological effects of the additives used applied to the resin selected.

b. To identify the types of additives which reduced flammability by their activity in the vapour phase.

c. To serve as a basis from which further work could be initiated.

3.1. Sample Preparation

The resin used was a general purpose unsaturated polyester based on phthalic and maleic anhydrides and propylene glycol in the respective molar ratios of 1:1:2.15. This was cross polymerised with 30% styrene monomer using the following procedure.

i. The solid linear resin was dissolved in styrene monomer by rotating in a Pascall ball-mill for 48 hours.

ii. Retardants were added to the resin solution and rotated in the Pascall ball-mill until good dispersion was achieved, normally about 30 minutes. The initiator (2% by weight benzoyl peroxide) was added and rotated for 10 minutes.

iii. Samples of cured resin, for testing, were prepared using a cure cycle of one hour at 70°C followed by a post cure of 24 hours at 70°C.

This cycle was arrived at by carrying out a number of cures at various times using the Vickers Pyramid Hardness Number as a simple guide to the degree of cure. A full cure was aimed at and Tables III and IV indicate that this could be achieved by using the above cycle.

TABLE III

HARDNESS NUMBERS OF ONE BATCH OF THE STANDARD RESIN CURED FOR VARIOUS TIMES

At 70°C

Cure Time (mins.)	V.P.N.
10	-
15	26.9
20	27.3
25	27.3
35	27.3
45	25.8
60	28.3
120	27.3

TABLE IV

V.P.N. VALUES FOR SIX BATCHES OF THE STANDARD RESIN PREPARED AT DIFFERENT TIMES BUT UNDER THE SAME CONDITIONS.

At 70°C

Resin Batch	P.C. 22 Hours	P.C. 38 Hours
	V.P.N.	V.P.N.
a	29.9	29.8
b	29.9	29.6
c	29.3	30.1
d	30.2	29.0
e	29.2	29.5
f	29.8	30.4

Note: Throughout this thesis standard resin refers to the cured resin using 30% by weight styrene monomer as cross linking agent, unless otherwise stated.

TABLE V

ADDITIVES USED

Trade Name	Nature of Additive	Supplier
Cereclor 70	Solid chlorinated paraffin containing 70% chlorine	Imperial Chemical Industries
" 70L	Liquid chlorinated paraffin 70% chlorine	"
" 65L	Liquid chlorinated paraffin 65% chlorine	"

Table V continued.../

Trade Name	Nature of Additive	Supplier
Cereclor S52	Liquid chlorinated paraffin 52% chlorine	Imperial Chemicals Industries
Timonox	Antimony Trioxide	Anchor Chem. Co. Ltd.
-	Bismuth Trioxide	Hopkins & Williams
-	Arsenic Trioxide	(Gen. purpose reagents)
Dechlorane 4070	Perchloropentacyclodecane 78% chlorine	Kingsley & Keith Chem. Ltd. (Hooker Chem.)
Dechlorane Plus 515	Perchloropentacyclodecane 65% chlorine	"
Firemaster T23P	tris (2,3 dibromopropyl) phosphate	"
-	tris (2,3 dichloropropyl) phosphate	Albright & Wilson Ltd.
T.T.P.	Tri tolyl phosphate	Geigy (U.K.) Ltd.
T.X.P.	Tri xylyl phosphate	Industrial Chems. Div.
Flammex 4BS	Tetra (pentabromopenoxy silane)	F. W. Berk Ltd.
" 5BT	Pentabromotoluene	"
" 5AE	Pentabromophenyl allyl ether	"
" 3AE	Tribromophenyl allyl ether	"

Table V continued.../

Trade Name	Nature of Additive	Supplier
Zinc Borate 9506	$Zn(BO_2)_2 2H_2O$	Joseph Storey Co., Ltd.
Calcium Borate 9578	$Ca(BO_2)_2 2.5H_2O$	"

A full list of the commercial flame retardant additives used is to be found in Appendix I. Appendix III gives some information on physical properties of these materials.

TABLE VI

COMPOSITION OF RESIN MIXTURES USED

Mixture No.	Resin	Additives
1	100	15 Cereclor 70
2	100	15 Antimony Trioxide
3	100	15 Cereclor 70 + 7.5 Antimony Trioxide
4	100	15 Cereclor 70L + 7.5 " "
5	100	15 Cereclor 65L + 7.5 " "
6	100	15 Cereclor S52 + 7.5 " "
7	100	15 Cereclor 70 + 15 " "
8	100	15 Dechlorane 4070 + 15 " "
9	100	15 Dechlorane Plus 515 + 15 Antimony Trioxide
10	100	15 Dechlorane Plus 515 + 7.5 " "
11	100	15 tris 2,3 Dichloropropyl phosphate + 15 Antimony trioxide
12	100	15 tris 2,3.Dichloropropyl phosphate
13	100	15 Firemaster T23P + 15 Antimony Trioxide

Table VI continued.../

Mixture No.	Resin	Additives
14	100	15 Firemaster T23P
15	100	15 Flammex 4BS + 15 Antimony Trioxide
16	100	15 Flammex 5BT + 15 " "
17	100	15 Flammex 3AE + 15 " "
18	100	15 T.T.P.
19	100	15 T.X.P.
20	100	15 T.T.P. + 15 Antimony Trioxide
21	100	15 Zinc Borate
22	100	15 Calcium Borate
23	100	15 Cereclor 70 + 7.5 Bismuth Trioxide + 7.5 Arsenic Trioxide.

Specimens were cast to the dimensions demanded by the test specifications.

3.1.1. Ignition Samples

These were blocks of dimensions $\frac{3}{4}$" x $\frac{3}{4}$" x $\frac{1}{2}$" cast into a pre-heated mould capable of producing six specimens. The mould was coated with a release agent and the top face of the specimens covered with a strip of cellophane film. On completion of the curing cycle the specimens were trimmed to a regular weight on a linishing machine. A satisfactory weight range was found to be 4.9 to 5.5. g.

3.1.2. Candle Burning Sticks

These were cast in the form of sheets in frame moulds

8 cm^2 x 3mm thickness between cellophane film backed with plate glass. On heating, the film became taut giving the resin casting a smooth finish. An initial attempt to cut test specimens from the fully cured sheet was abandoned due to loss of material through shattering. A method of cutting the material with a sharp knife when gelled but not hard proved the most satisfactory. The time taken for a sample of the material to reach this state depended upon the additive present. The optimum time for cutting the material was used to assess the effect of the additive on the curing characteristics of the resin. As flammability was the object of this study detailed attention was not paid to the effect of additives on other properties of the resin. However it was interesting to note that the additives used affected the cure of the resin in the expected manner.

TABLE VII

OPTIMUM CUTTING TIMES

Resin Mixtures No.	Time (mins.)	Resin Mixtures No.	Time (mins.)
Standard Resin	25 - 30	1	35 - 40
2	45 - 50	3	45 - 50
4	50 - 55	5	50 - 55
6	50 - 55	7	40 - 45
8	40 - 45	9	40 - 45
10	40 - 45	11	40 - 45
12	40 - 45	13	55 - 60
14	40 - 45	15	40 - 45

Table VII continued.../

Resin Mixtures No.	Time (mins.)	Resin Mixtures No.	Time (mins.)
16	35 - 40	17	45 - 50
18	50 - 55	19	60 - 65
20	45 - 50	21	35 - 40
22	35 - 40	23	40 - 45

The addition of organic materials increased the gel time as the viscosity of the added material decreased. In general the addition of inorganic compounds tended also to delay the gelling of the resin.

3.1.3. Strips for B.S.S.2782 Method 508A

A similar technique to that just described was used. The specification required specimens having dimensions of 6" x 0.5" x 0.060".

3.2. The Candle Burning Test

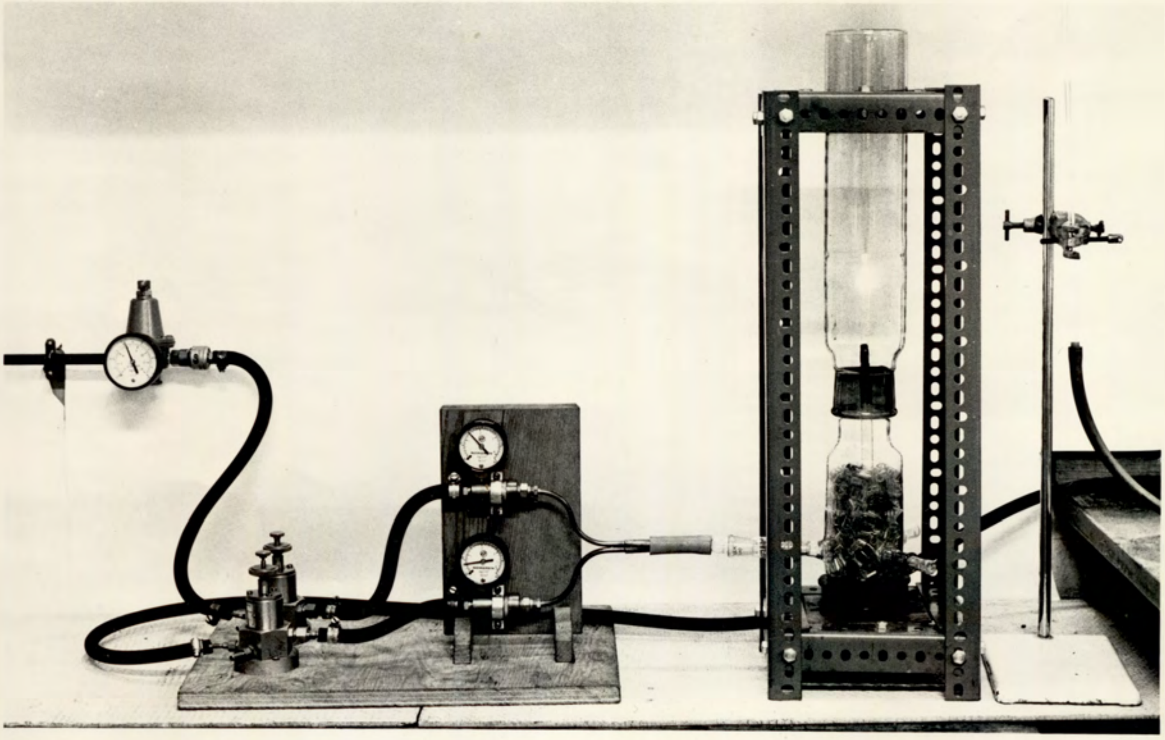
The apparatus was first devised for use with plastics by Fenimore and Martin[92]. The test procedure determines the lowest concentration of oxygen in the atmosphere supplied to the equipment which allows a test piece to completely burn. This concentration is expressed in terms of the ratio:-

$$\text{Oxygen Index } n = \frac{[O_2]}{[O_2] + [N_2]}$$

where $[O_2]$ and $[N_2]$ are the volume concentrations of oxygen and nitrogen in the atmosphere, for air n is taken to be 0.210.

FIG. I

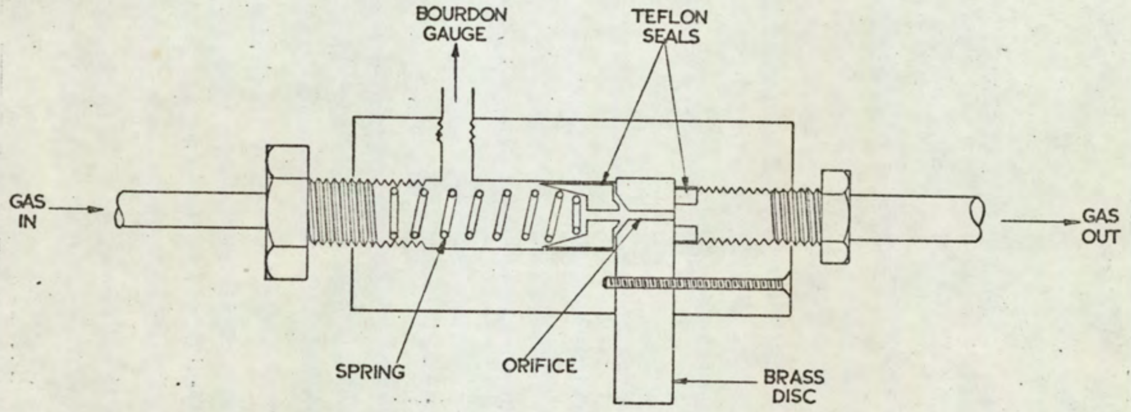
CANDLE BURNING EQUIPMENT



Essentially it consists of a vertical glass chimney 8 cm. in diameter and 60 cms. in height with facility for supporting a test piece in a vertical position, centrally inside the chimney. Atmosphere gases (air, oxygen, nitrogen) were metered using flow orifices constructed in the laboratory workshop fig. 2.

FIG. 2

DETAIL OF METERING ORIFICES



The orifices were accurately bored in a brass disc and by rotation of the disc insertion of the required orifice into the flow stream was readily achieved.

On the high pressure side of the orifice was set a Bourdon gauge, the pressure reading of which depended upon the size of the restricting orifice and the source pressure. When gas was allowed to flow into the barrel a teflon seal seated itself against the disc preventing leakage. The flow of gas into the barrel was accurately controlled by the use of precision regulators. On leaving the metering orifices the gases were mixed in a common outlet line and fed into the base of the glass chimney where further mixing was effected by passing through a layer of glass chips. Gas flow calibration curves were obtained over a wide range of gauge pressures, for each orifice, these may be found in Appendix II.

The resin strips were ignited from the top by means of a coal gas flame supported at the end of a glass tube 12" in length. For steady burning it was found necessary to ignite in an oxygen rich atmosphere, this could be reduced once a stable flame was attained. Reference to the pressure reading on the gauge and the orifice in use enabled the volume of each gas flowing through the chimney to be obtained from the calibration curves. An Elliott 803 computer was programmed to prepare tables of n values for mixtures of air/oxygen and air/nitrogen; by means of these tables equivalent oxygen indexes for varying rates of total gas flow through the chimney were readily available. The programme and tables may be found in Appendix II.

Preliminary experiments showed n values to be constant over a range of total gas flow rates through the chimney.

TABLE VIII

VALUES OF OXYGEN INDEX OF THE STANDARD RESIN FOR VARIOUS LINEAR (THROUGH THE CHIMNEY) GAS FLOW RATES

Gas Flow Rate cm/sec.	Oxygen Index
4.1	0.191
4.4	0.192
5.6	0.192
7.9	0.192
9.6	0.192
11.3	0.192
12.0	0.193
14.8	0.196

In practice, wherever possible, the value of the oxygen index was obtained for at least two different total gas flow rates within the range 4.5 - 11.0 cm./sec.

The metering equipment was not sensitive enough to obtain n values between 0.205 and 0.210 and also between 0.210 and 0.228 this was due to the very low concentration of diluent gas required to obtain these values. It was found however, that few of the materials tested fell into these categories.

Table IX (page 72) tabulates the results obtained using the three techniques but the histograms figs. 3, 4 and 5 illustrate more clearly the effect of chlorinated, brominated and phosphorus containing compounds respectively, on the oxygen index.

FIG 3.

THE EFFECT OF CHLORINATED ADDITIVES ON THE OXYGEN INDEX OF THE STANDARD RESIN

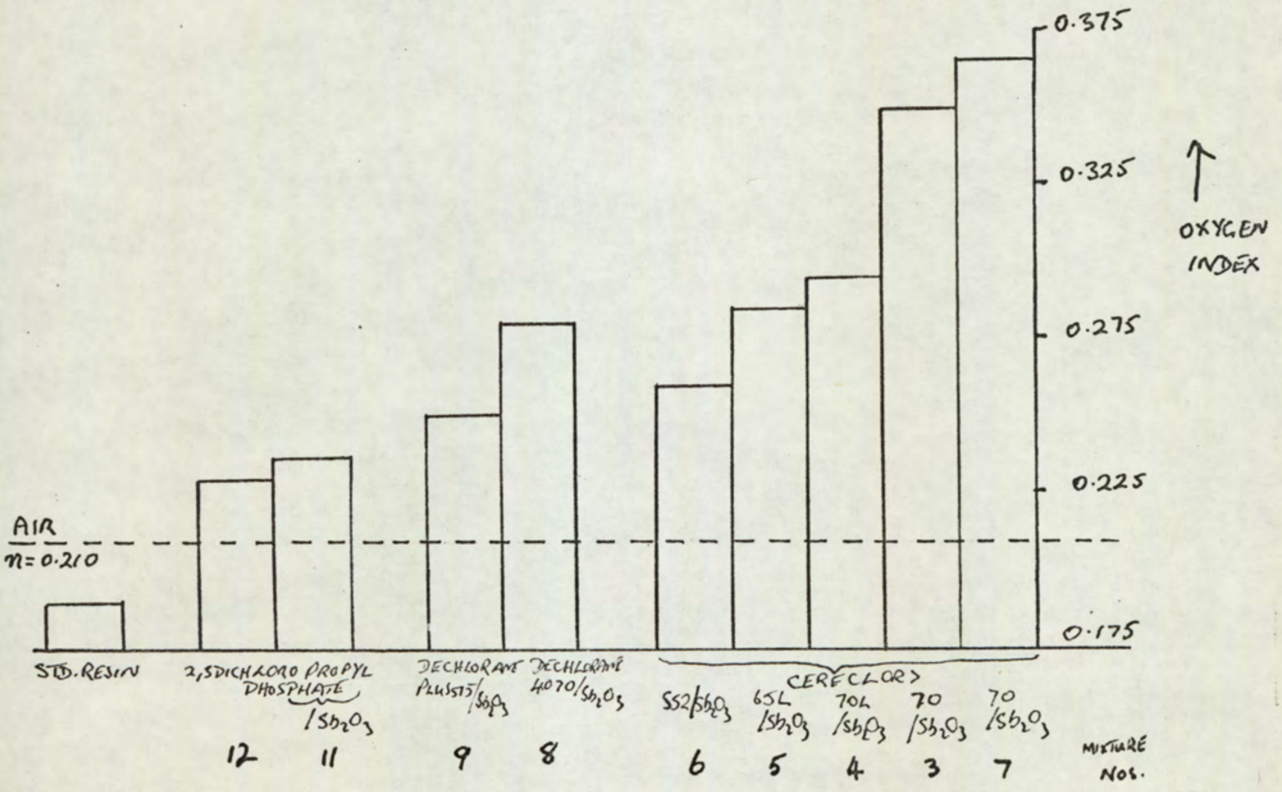


FIG. 4

THE EFFECT OF BROMINATED ADDITIVES ON THE OXYGEN INDEX OF THE STANDARD RESIN

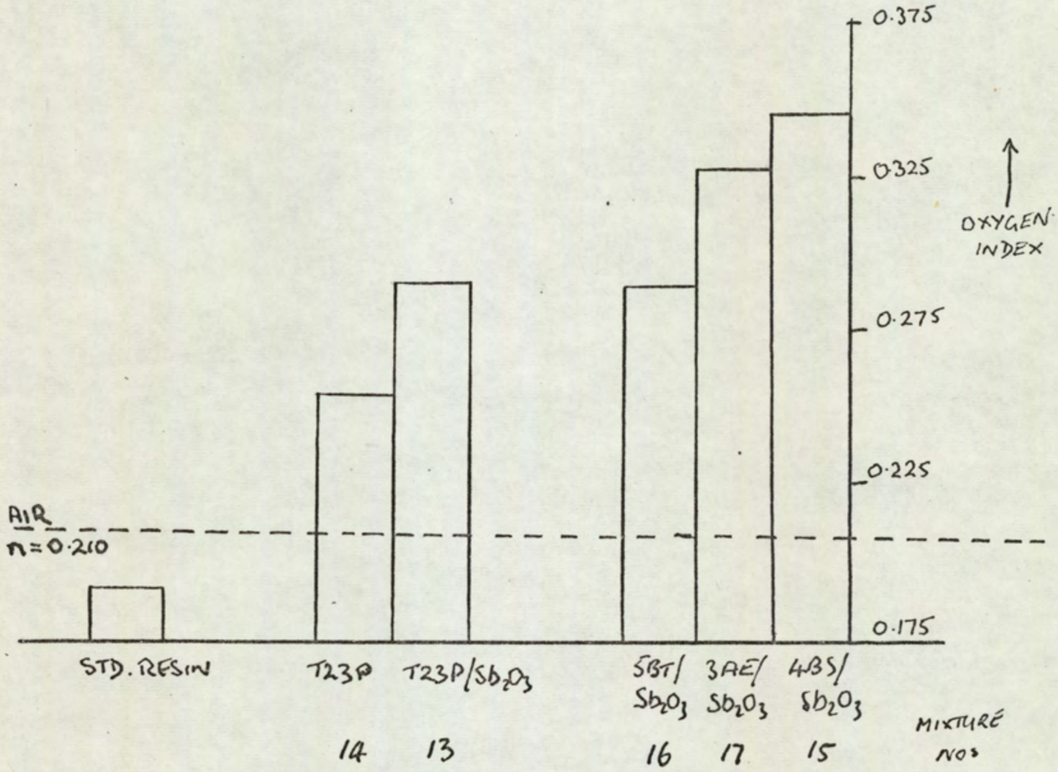
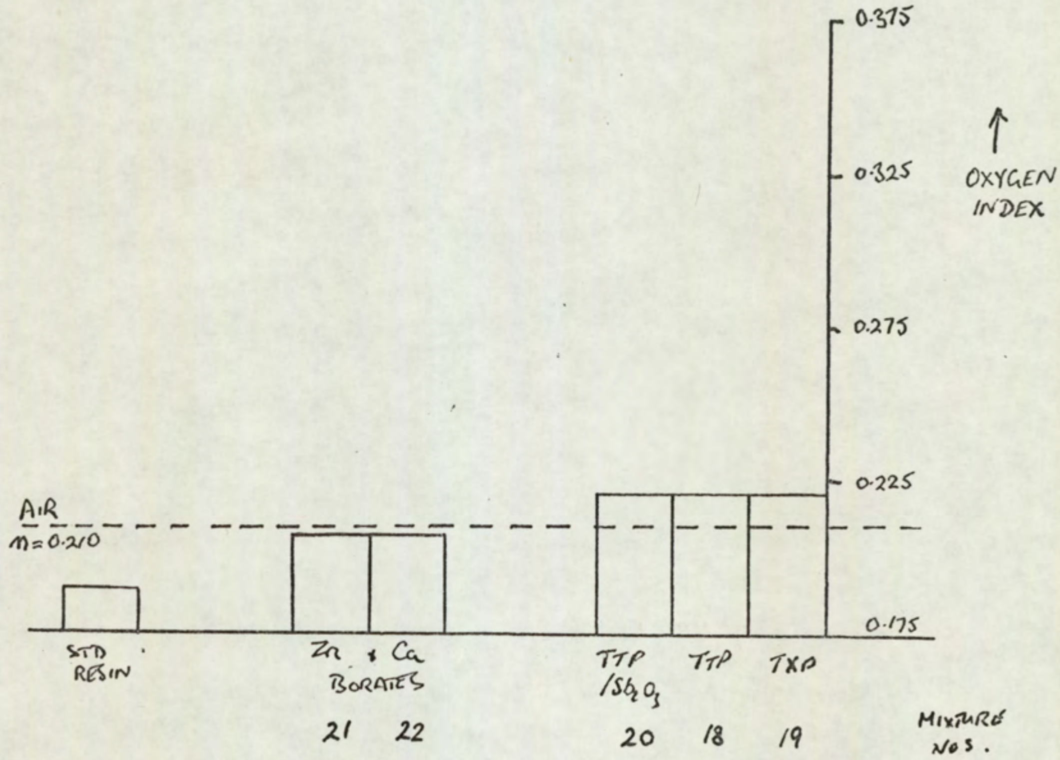


FIG. 5

THE EFFECT OF PHOSPHORUS CONTAINING ADDITIVES ON THE OXYGEN INDEX OF THE STANDARD RESIN.

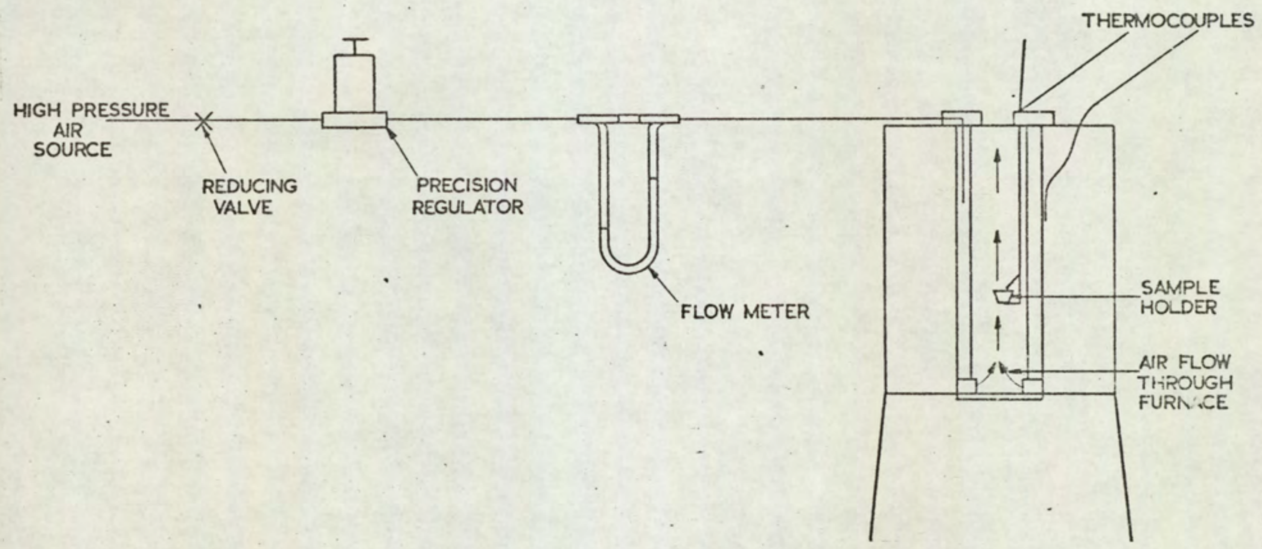


3.3. The Setchkin Ignition Test

Previous to the development of this test by Setchkin[94] methods of determining ignition temperatures of plastics probably did not, in fact, determine the lowest temperature at which ignition would occur. This method determines the lowest ambient air temperature surrounding a sample of the material for which flash or spontaneous ignition would occur. The term flash ignition describes ignition of combustibles issuing from a material by means of an external heat source, generally a flame. Spontaneous ignition, as the name suggests, is the self ignition of combustibles in the absence of an external heat source.

FIG. 6

SETCHKIN IGNITION EQUIPMENT.



Essentially it consists of a vertical tube furnace, in the centre of which a sample is sited in a crucible. Inside the furnace a coronite tube of diameter ½" less than the bore of the furnace stands on three feet. Metered air is passed down between the furnace and the tube and then circulated up through the inner tube around the sample in its path.

Temperatures are recorded at (a) Immediately above the sample surface (b) Below the sample holder (c) At the furnace coils. Temperature adjustment is made with reference to the latter thermocouple.

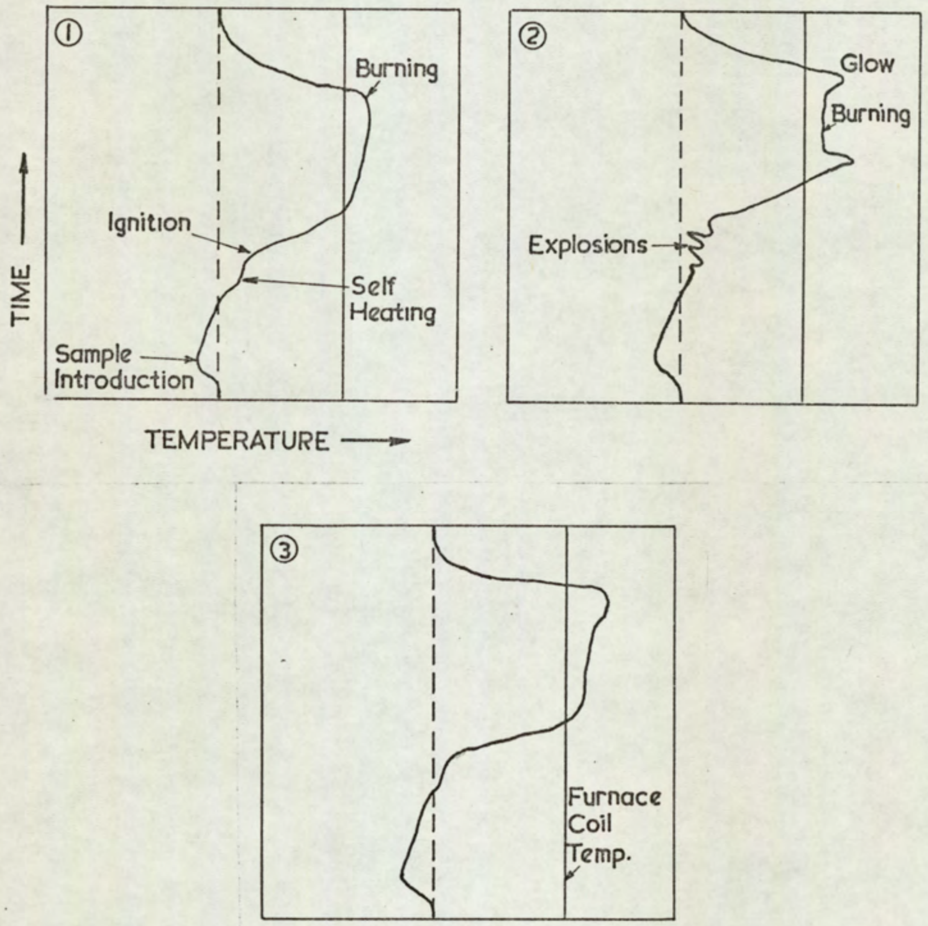
A slight modification of the procedure set out in ASTM D1929-68[83] was adopted. The specification required an approximate determination of ignition temperature by raising the furnace temperature at a rate of 500°C/hour for linear air flow rates of 5 ft./min. 10 ft./min and 15 ft./min. consecutively and observing which flow rate produced the minimum ignition temperatures. The specification required isothermal determinations to be made near the temperature and at that flow rate indicated by the previous experiments. These experiments were required to be repeated reducing the temperature until ignition failed to occur. The temperature above this was taken to be the spontaneous ignition temperature of the material.

In practice it was found that a temperature rise of 500°C/hr. was not nearly sufficient especially with resins containing flame retardants, as most of the combustible volatiles had been released before the ignition temperature had been reached. A temperature rise of 2,400°C/hr. produced ignition in every case.

Preliminary experiments on the standard resin, to determine the air flow rate which produced the lowest ignition temperature showed that a flow of 5 ft./min. through the apparatus was appropriate and this was adopted for all later experiments.

FIG. 7

TIME TEMPERATURE RECORD OF SPONTANEOUS IGNITION DETERMINATIONS



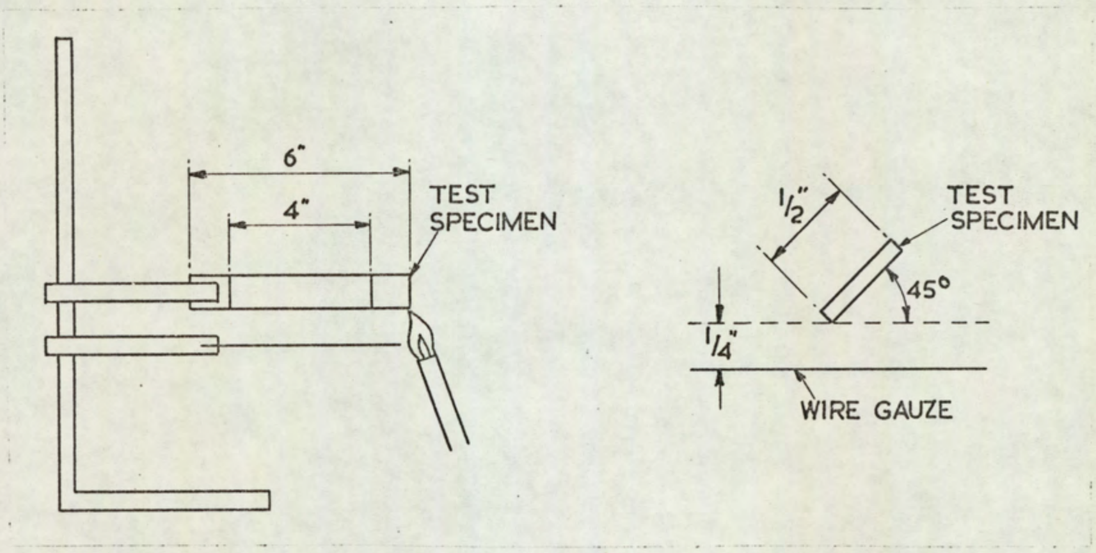
(1) Standard resin (2) Standard resin + 15 pph Cereclor 70 + 15 pph Sb_2O_3 (3) Standard resin + 15 pph TPP.

3.4. Rate of Burning Test BS.2782 Method 508A.

The tests were conducted according to the specification[84] which, briefly, required two pencil lines to be drawn on the specimen 1" and 5" from the same end and the strip to be held at an angle of 45° above a wire gauze. A coal gas flame, non luminous and $\frac{1}{2}$" in height to be held to the free end for 10 seconds and the time taken for the flame to spread between the two lines observed.

FIG. 8

BS.2782 METHOD 508A EQUIPMENT



If the flame failed to spread to the first line the material was designated self-extinguishing according to this specification. The rate of burning was then easily calculated in ins./min. Five specimens of each resin mixture were tested and the mean value was reported.

TABLE IX

OXYGEN INDEX AND OTHER DATA FOR RESIN MIXTURES

Resin No.	Oxygen Index	Ignition Temp. °C	V.P.N.	Rate of Burning in./min.
Std. Resin	0.192	459	29.7	0.83
1	0.235	483	26.2	0.72
2	0.233	466	29.6	0.58
3	0.350	480	29.8	S.E.
4	0.295	479	27.6	S.E.
5	0.287	483	21.5	S.E.
6	0.260	472	15.9	S.E.
7	0.367	506	30.9	S.E.
8	0.282	495	30.7	S.E.
9	0.286	515	38.4	S.E.
10	0.252	492	33.8	S.E.
11	0.238	506	22.1	S.E.
12	0.232	459	18.0	S.E.
13	0.295	456	32.0	S.E.
14	0.255	420	28.9	S.E.
15	0.346	481	27.5	S.E.
16	0.293	461	26.3	S.E.
17	0.328	463	10	S.E.
18	0.210 - 0.228	482	14.2	0.74
19	0.210 - 0.228	476	14.6	0.81
20	0.210 - 0.228	486	22.3	0.67
21	0.205 - 0.210	386	31.1	0.90
22	0.205 - 0.210	397	29.9	0.76
23	0.295	489	35.3	S.E.

The results quoted in this chapter will be formally discussed in Chapter 9 but it is appropriate to point out at this stage that those resin mixtures containing combinations of halogenated compound and antimony trioxide were especially active in reducing flammability in the vapour phase. On the basis of these results and other published work synergism between halogen compounds and antimony trioxide was investigated more closely and these experiments are described in the next chapter.

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CHAPTER 4

THE EFFECT OF HEAT ON MIXTURES OF HALOGEN COMPOUNDS AND METAL OXIDES

Previous work indicated that the observed synergism between antimony trioxide and halogenated organic compounds was due to the formation of a volatile antimony halogen species which was efficient in interfering with flame reactions. Working on this assumption it is reasonable to suppose that a simple guide to the effectiveness of a system could be obtained by following the weight loss of a mixture of metal oxide and organic halogen compound, over a temperature range where thermal degradation of the resin was known to occur.

4.1. Sample Preparation

Mixtures of organic halogen compound and metal oxide were 50 : 50 by weight unless otherwise stated. The powdered materials were accurately weighed and intimately ground together using an agate pestle and mortar. This method was also found satisfactory for the liquid halogen compounds. Samples containing resin were ground together with a dry ice in a bronze pestle and mortar. The sieve fraction passing through 36 mesh and retained on 100 mesh was used.

TABLE X

THE HALOGEN COMPOUNDS USED

Trade Name	Nature of Additive	Supplier
Cereclor 70	Solid chlorinated paraffin 70% Chlorine	Imperial Chemicals Industries
Cereclor 70L	Liquid chlorinated paraffin 70% Chlorine.	"
Cereclor 65L	Liquid chlorinated paraffin 65% Chlorine	"
Cereclor S52	Liquid chlorinated paraffin 52% Chlorine	"
Bromoparaffin	Bromine containing paraffin (Liquid)	" Development Product
Dechlorane 4070	Perchloropentacyclodecane 78% Chlorine	Kingsley & Keith Chemicals Ltd. (Hooker Chem.)
Flammex 5AE	Pentabromophenylallyl ether	F.W. Berk Co., Ltd.
Flammex 4BS	Tetra (pentabromophenoxy silane)	"
Flammex 5BT	Pentabromotoluene	"
-	Ammonium Chloride (NH_4Cl)	Hopkins & Williams
-	Ammonium Bromide (NH_4Br)	"

Table X continued.../

Trade Name	Nature of Additive	Supplier
Corvic P65-50	Polyvinyl chloride	Imperial Chemicals Industries

TABLE XI

THE METAL OXIDES USED
Antimony Trioxide (Sb_2O_3)
Bismuth Trioxide (Bi_2O_3)
Arsenic Trioxide (As_2O_3)
Magnesium Oxide (MgO)
Aluminium Oxide (Al_2O_3)
Stannic Oxide (SnO_2)
Zinc Oxide (ZnO)
Lead Monoxide (PbO)
Red Lead (Pb_3O_4)
Stannous Oxide (SnO)
Ferric Oxide (Fe_2O_3)
Titanium Dioxide (TiO_2)
Manganese Dioxide (MnO_2)
Ceric Oxide (CeO_2)

These were all supplied by Hopkins & Williams.

TABLE XII

THE MIXTURES USED IN THE EXPERIMENTS

a. Weight Loss Experiments

Mixture Nos.	Composition
1	Cereclor 70
2	Cereclor 70/Sb_2O_3
3	Dechlorane 4070
4	Dechlorane 4070/Sb_2O_3
5	Cereclor 70L/Sb_2O_3
6	Cereclor 65L/Sb_2O_3
7	Cereclor S52/Sb_2O_3
8	Standard Resin
9	Standard Resin containing 15 pph Cereclor 70 + 15 pph Sb_2O_3.
10	Standard Resin + 15 pph Cereclor 70 + 15 pph Sb_2O_3. (Physical mixture)
11	Flammex 5BT
12	Flammex 5BT/Sb_2O_3
13	P.V.C. Corvic P65-50
14	P.V.C. Corvic P65-50/Sb_2O_3
15	Flammex 5AE/Sb_2O_3
16	Flammex 4BS/Sb_2O_3
17	NH_4Cl/Sb_2O_3
18	NH_4Br/Sb_2O_3
19	10 parts mixture No. 18 + 1 part Dicumyl Peroxide (Dicup)
20	Cereclor 70/As_2O_3
21	Cereclor 70/Bi_2O_3

Table XII continued.../

Mixture Nos.	Composition
22	Al_2O_3/Cereclor 70
23	Cereclor 70/SnO_2
24	Cereclor 70/ZnO
25	Cereclor 70/MgO
26	Cereclor 70/PbO
27	Cereclor 70/Pb_3O_4
28	Cereclor 70/SnO
29	Flammex 4BS/As_2O_3
30	Cereclor 70/Fe_2O_3
31	Dechlorane 4070/Al_2O_3
32	Dechlorane 4070/SnO_2
33	3 parts mixture No. 31 + 1 part charcoal
34	3 parts mixture No. 22 + 1 part charcoal
35	Cereclor 70/TiO_2
36	3 parts mixture No. 35 + 1 part CeO_2
37	3 parts mixture No. 35 + 1 part MnO_2
38	4 parts mixture No. 37 + 1 part charcoal
39	4 parts mixture No. 36 + 1 part charcoal

Table XII continued.../

Mixture Nos.	Composition
40	2 parts Dechlorane 4070 + 2 parts TiO_2 + 1 part CeO_2 + 0.5 parts charcoal.
41	4 parts mixture No. 33 + 1 part CeO_2
42	10 parts mixture No. 43 + 1 part Dicumyl Peroxide
43	Bromoparaffin/Sb_2O_3

b. Hydrogen chloride and Volatile SbIII Determinations

Mixture Nos.	Composition
1	Cereclor 70
13	P.V.C. Corvic P65-50
2	Cereclor 70/Sb_2O_3

4.2. Weight Loss Experiments

Weighed specimens were heated under isothermal conditions and the percentage of the material which was volatile was followed with time.

The experiments were conducted in a stream of air passing at approximately 6 lit./min. through the Setchkin furnace (Fig. 6). Samples in 'cut-off' ignition tubes were dropped into the silica crucible which was suspended in the preheated furnace. The temperature inside the crucible was measured with a Cr/Al thermocouple. On completion of the required heating time the crucible and ignition tube were removed and a lid placed over the crucible to exclude air from the cooling sample, prior to weighing.

Throughout the following V is defined as that percentage of the original mixture which was volatile at the temperature under consideration.

KEY TO FIGURES

(h)	Mixture 1	Figs. 9, 10 and 11
(d)	Mixture 2	
(j)	Mixture 3	Figs. 12, 13 and 14
(i)	Mixture 4	
(a)	Mixture 2	Figs. 15, 16 and 17
(b)	Mixture 5	
(c)	Mixture 6	
(d)	Mixture 7	
(a)	Mixture 2	Figs. 18, 19 and 20
(e)	Mixture 10	
(f)	Mixture 9	
(g)	Mixture 8	

Fig. 9

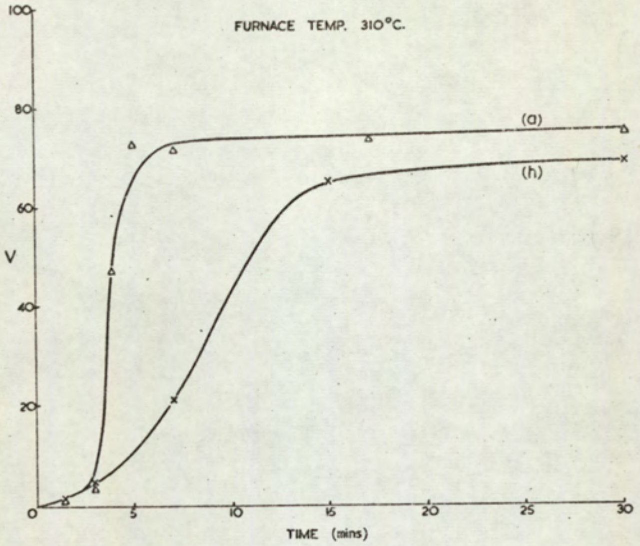


Fig. 10

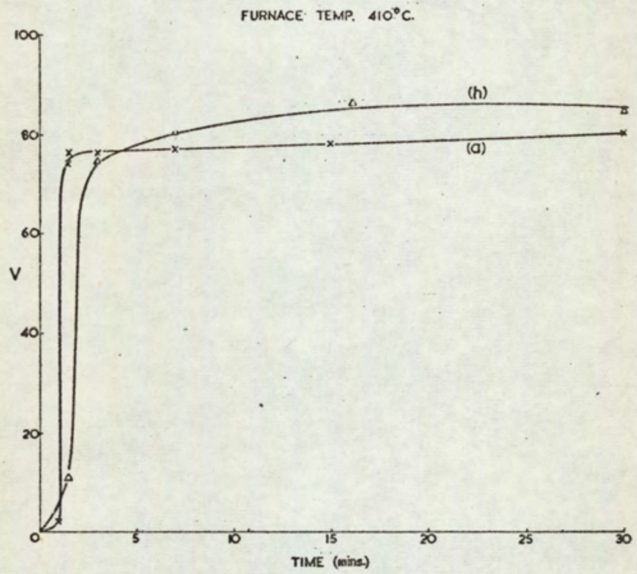
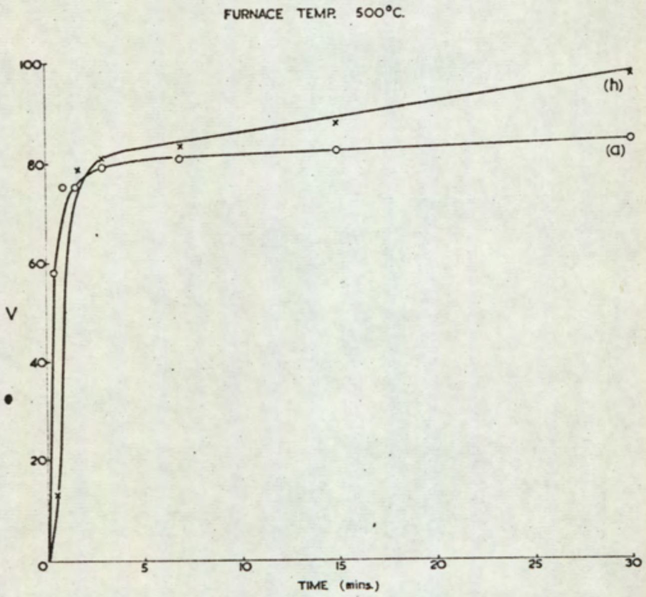


Fig. 11



Key to the Figures may be found on page 80.

Fig. 12

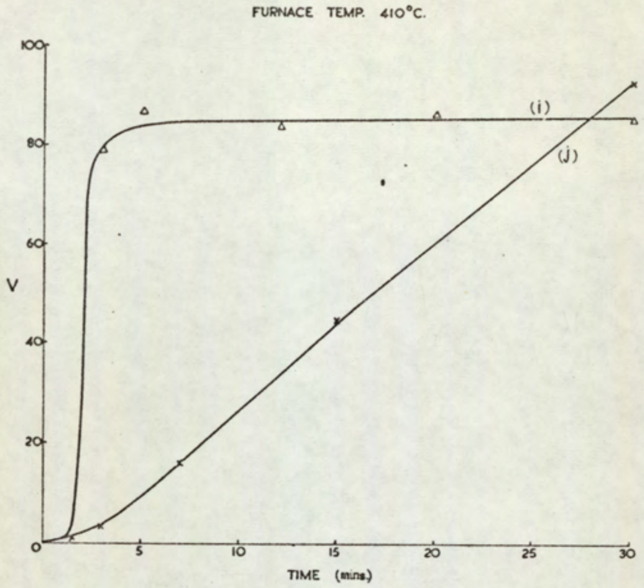


Fig. 13.

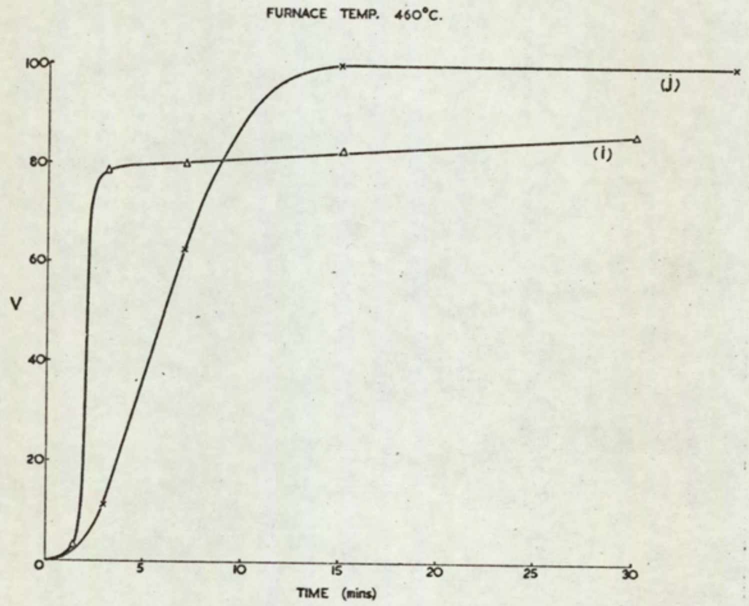
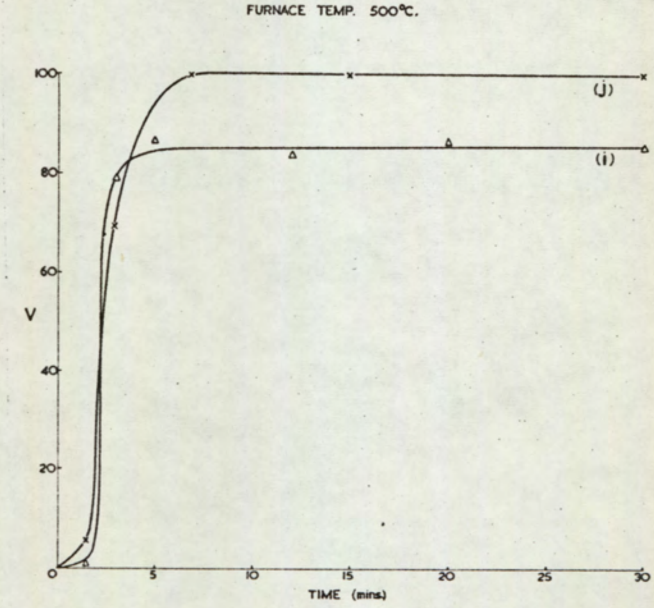


Fig. 14



Key to the figures may be found on page 80.

Fig. 15

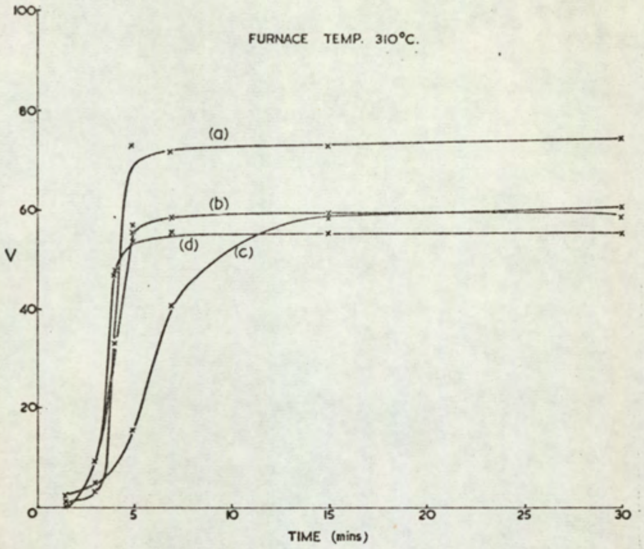


Fig. 16

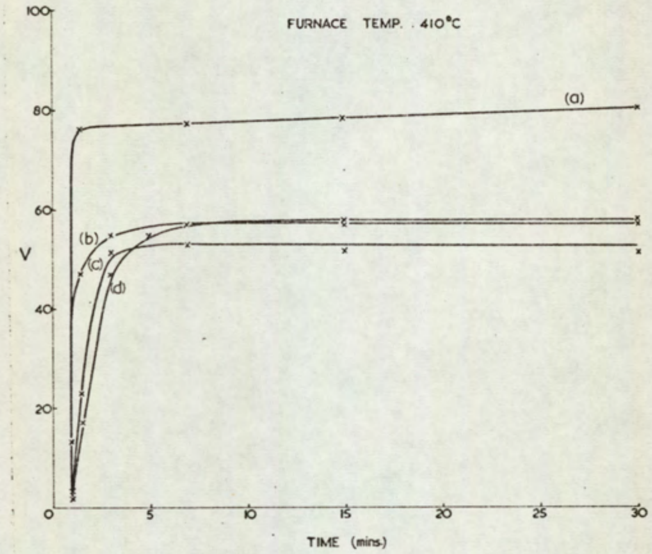
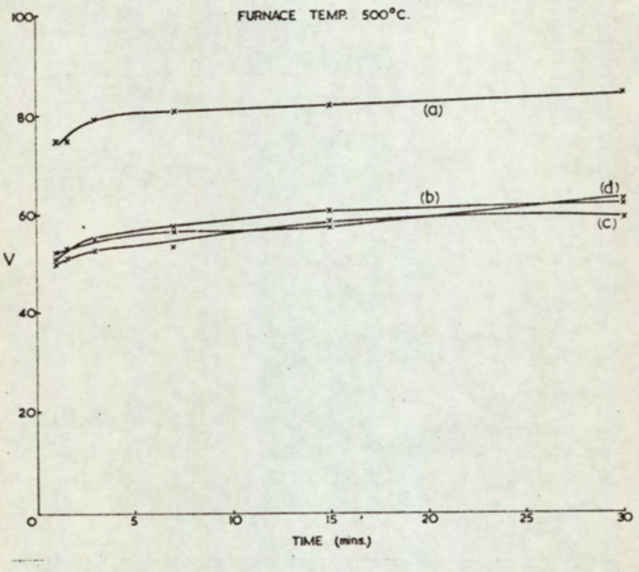


Fig. 17



Key to the Figures may be found on page 80.

Fig. 18

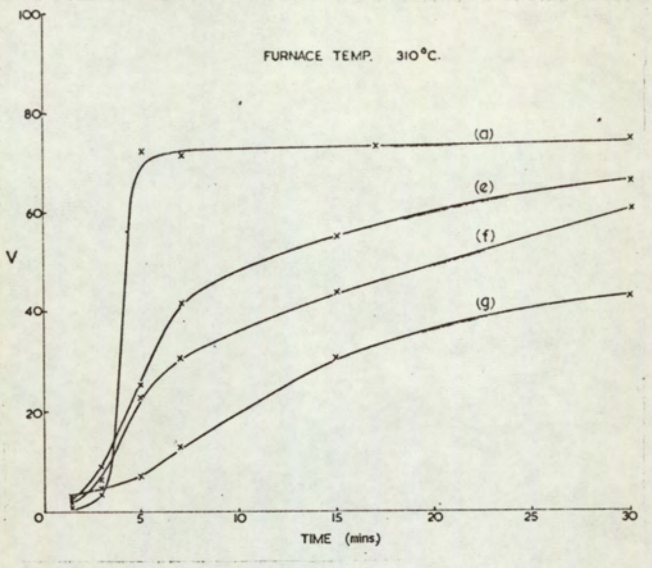


Fig. 19

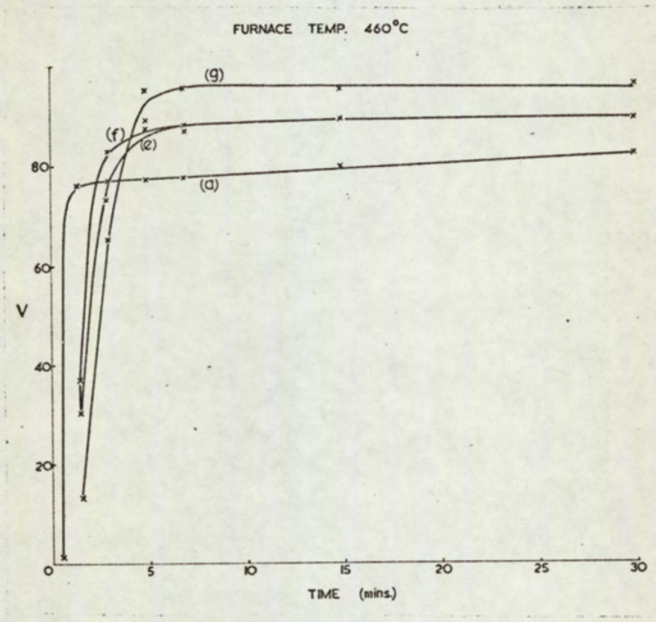
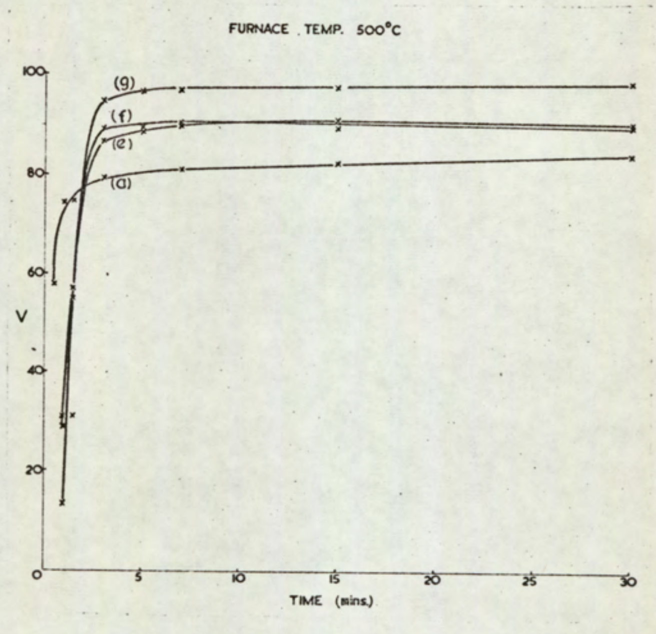


Fig. 20



Key to the Figures may be found on page 80.

FIG. 21

REACTIVITY OF Bi_2O_3, Sb_2O_3 and As_2O_3 WITH CERECLOR 70.

AT 500°C.

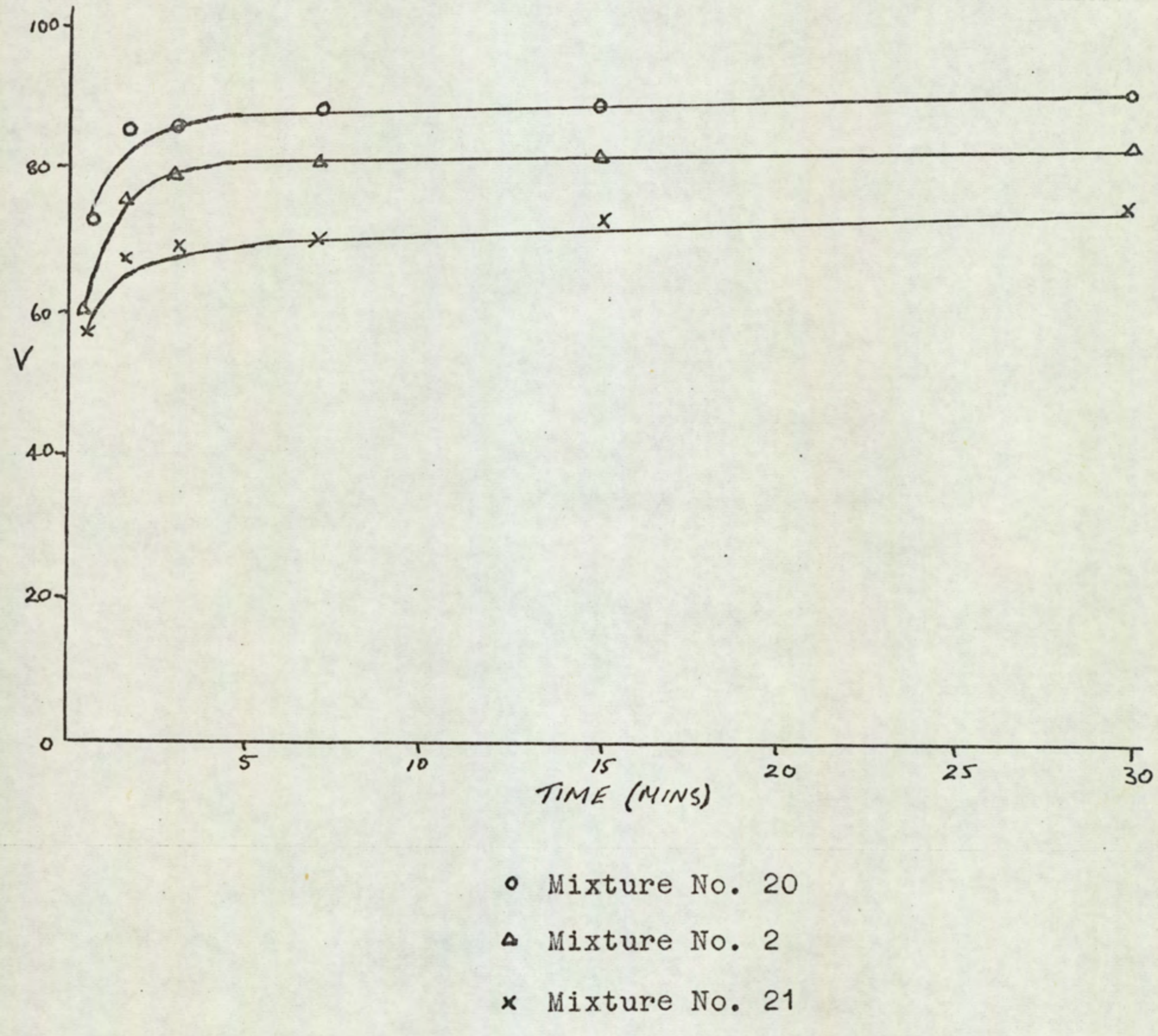


FIG. 22

THE EFFECT OF HEATING TOGETHER AMMONIUM HALIDES AND ANTIMONY TRIOXIDE AT VARIOUS TEMPERATURES.

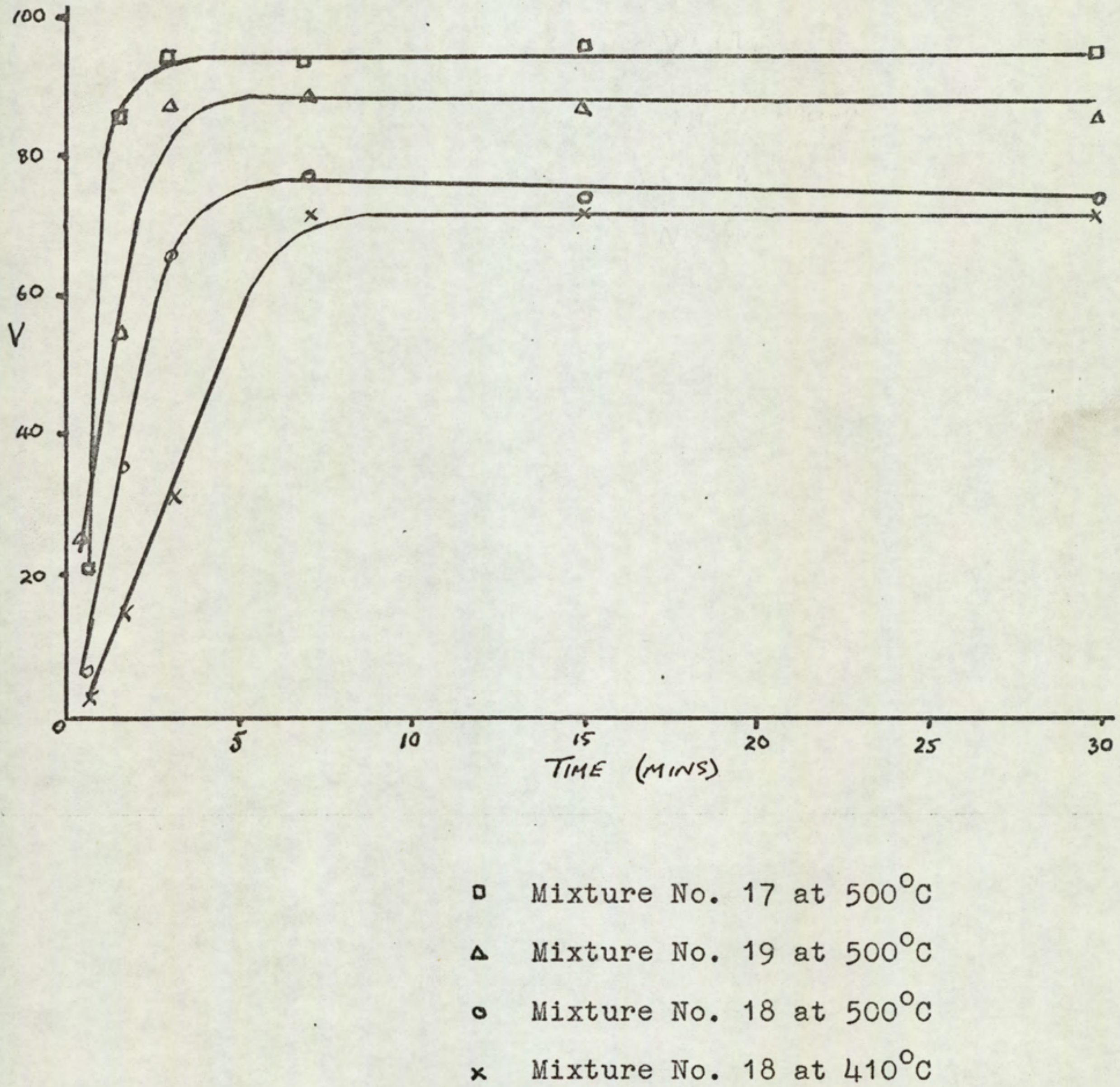
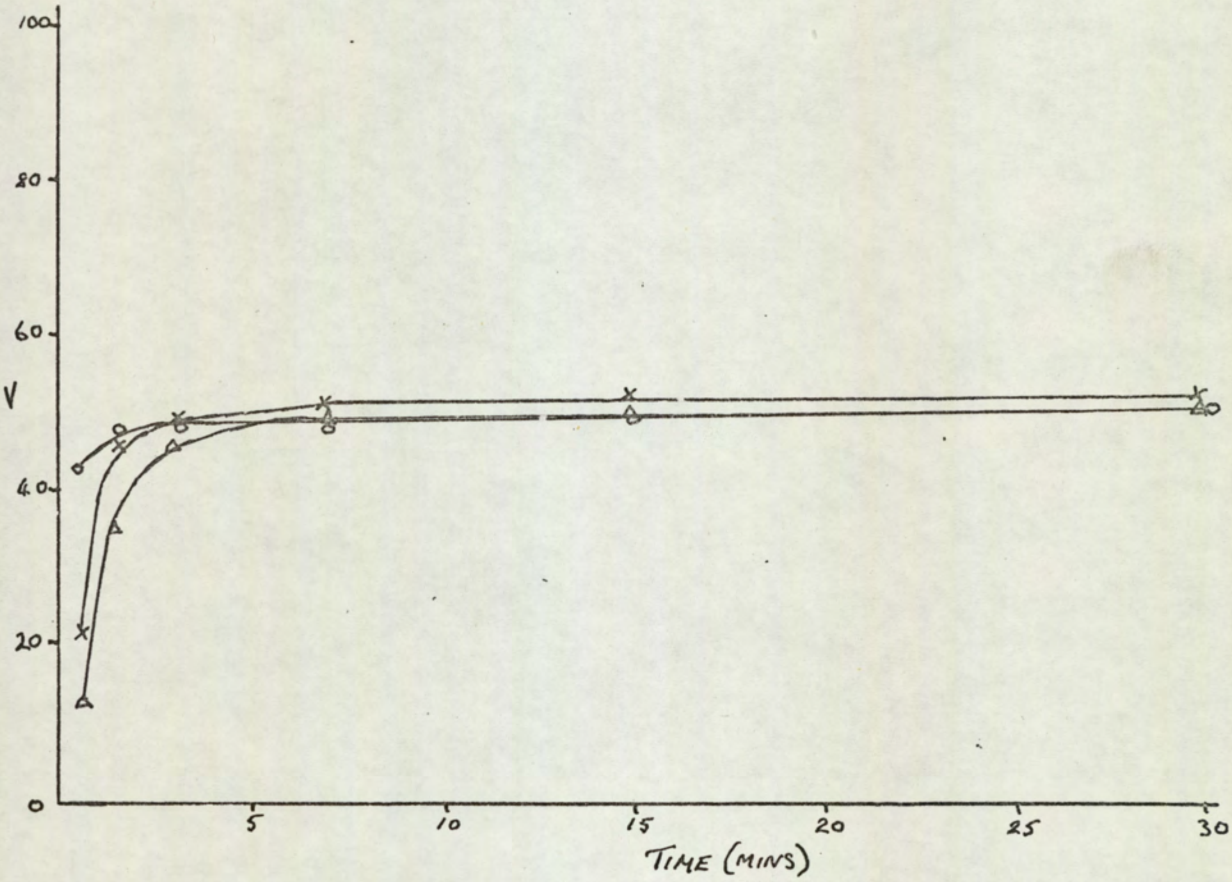


FIG. 23

THE EFFECT OF HEATING TOGETHER FLAMMEX 5BT AND ANTIMONY TRIOXIDE AT VARIOUS TEMPERATURES.



o Mixture No. 12 at 610°C

x Mixture No. 12 at 500°C

△ Mixture No. 12 at 460°C

FIG. 24

THE EFFECT OF HEATING TOGETHER FLAMMEX 4BS/ANTIMONY TRIOXIDE AND ALSO FLAMMEX 5AE/ANTIMONY TRIOXIDE AT 500°C

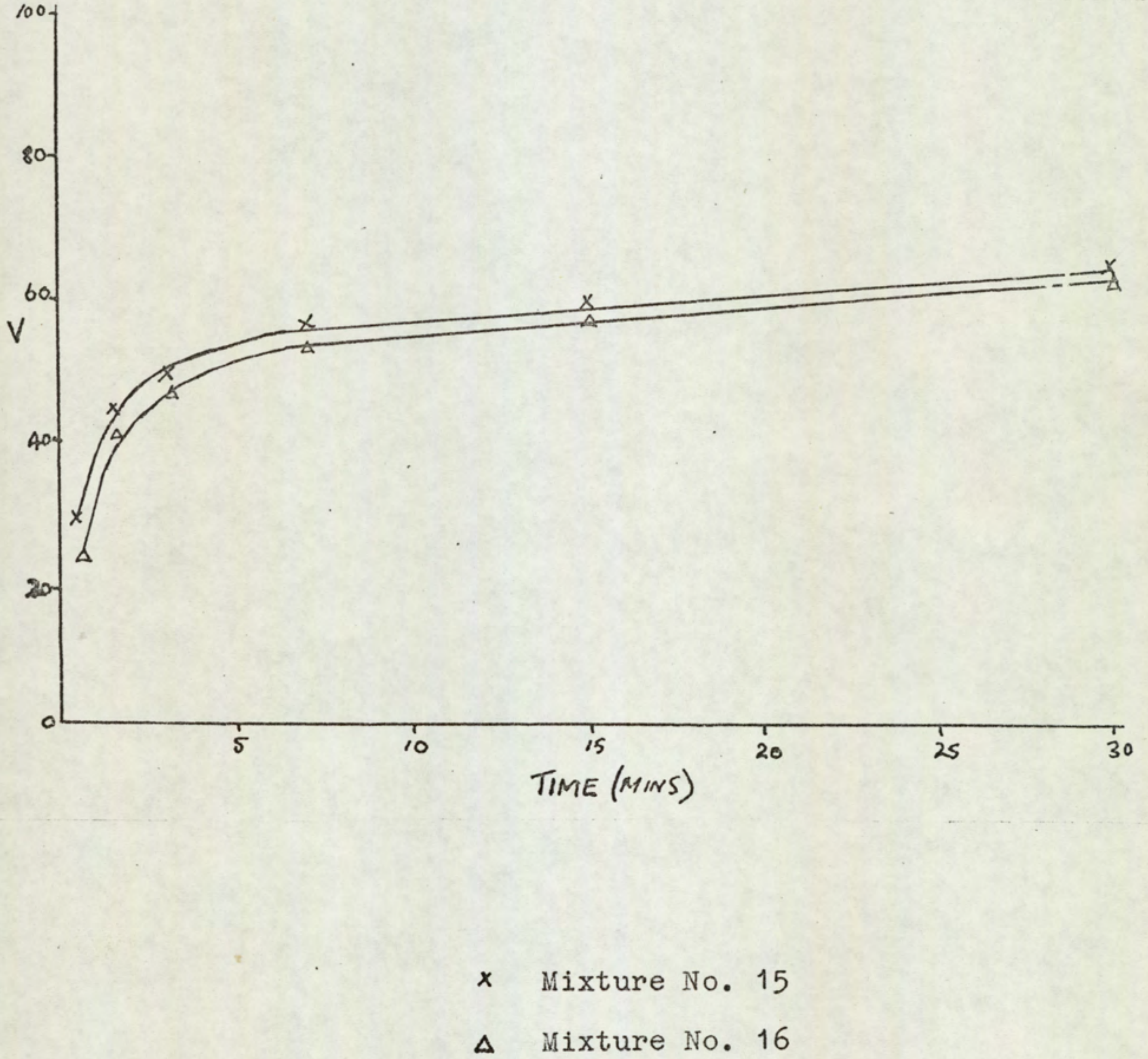


FIG. 25

THE EFFECT OF HEATING TOGETHER BROMOPARAFFIN/ANTIMONY TRIOXIDE AND ALSO BROMOPARAFFIN/ANTIMONY TRIOXIDE WITH DICUMYL PEROXIDE.

AT 500°C

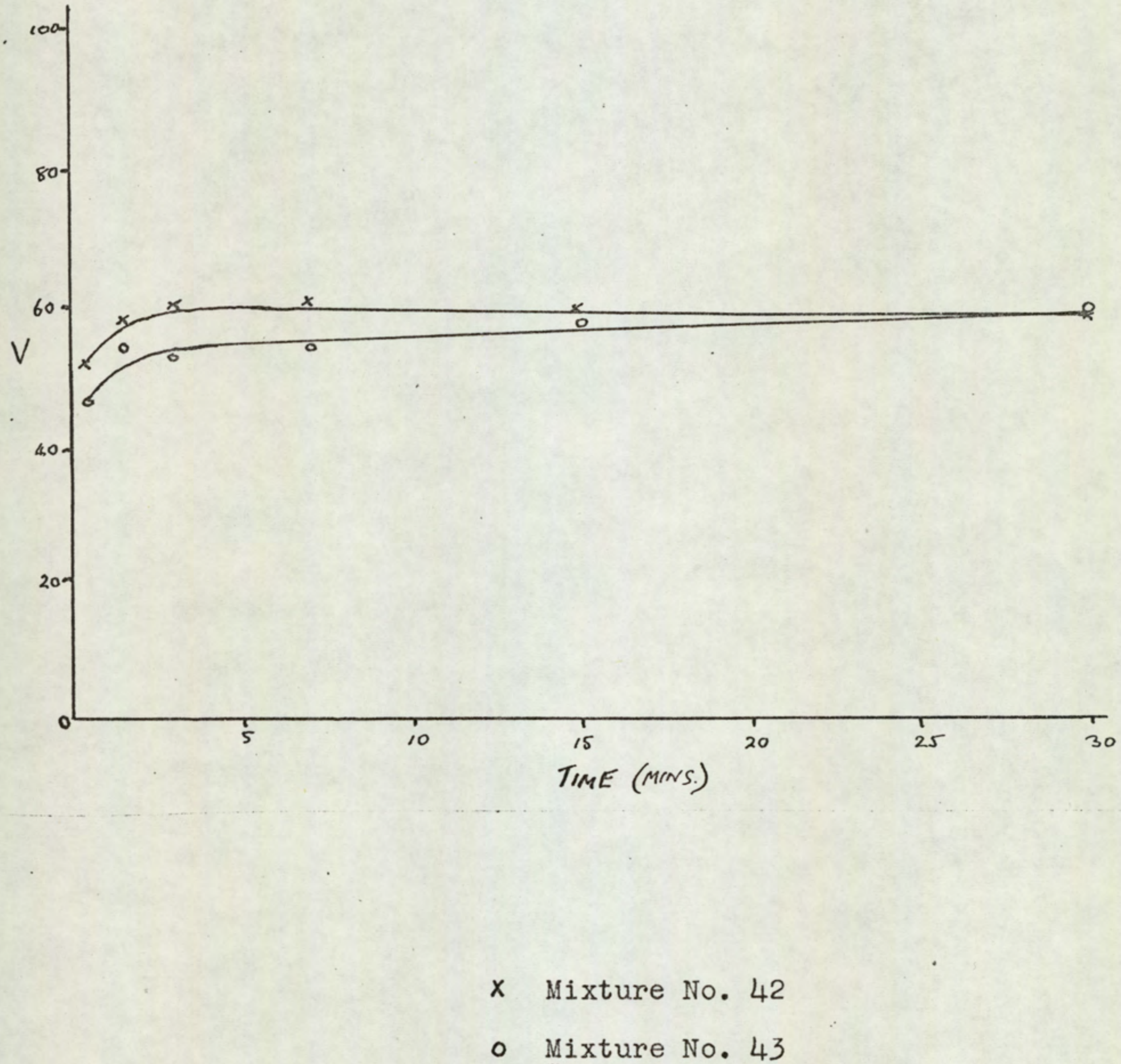
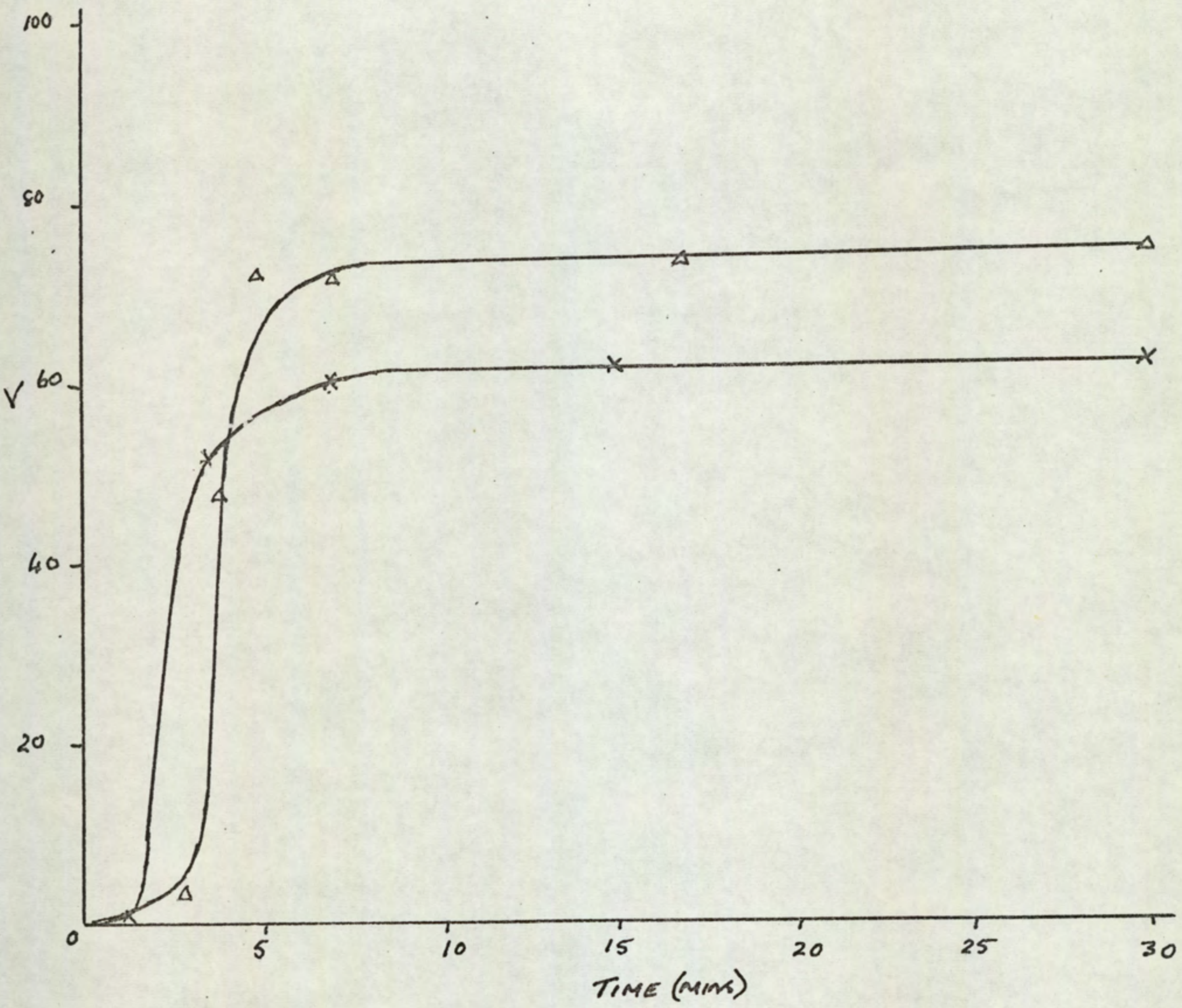


FIG. 25a

REACTIVITY OF PVC AND CERECLOR 70 WITH Sb_2O_3 AT 310°C



Δ Mixture No. 2

x Mixture No. 14

TABLE XIII

RANDOM WEIGHT LOSS EXPERIMENTS

Mixture No.	Time (mins.)	Temperature ^{o}C	V
13	15	500	96.3
14	15	500	85.0
22	30	460	39.7
22	15	460	35.3
22	30	500	41.8
22	15	500	40.0
23	30	460	44.7
23	15	460	41.5
24	30	460	30.2
24	15	460	27.1
25	30	500	47.5
25	15	500	40.8
26	30	500	34.9
26	15	500	35.2
27	30	500	45.4
27	15	500	38.8
28	30	500	53.4
28	15	500	48.6
29	30	500	69.5
29	15	500	54.6
30	30	500	30.6
30	15	500	29.4
31	30	500	51.2

Table XIII continued.../

Mixture No.	Time (mins)	Temperature °C	V
31	15	500	49.2
32	30	500	48.8
32	15	500	49.5
33	30	500	41.2
33	15	500	38.0
34	30	500	35.8
34	15	500	31.6
35	30	500	40.1
35	15	500	39.3
36	30	500	33.6
36	15	500	28.9
37	30	500	35.2
37	15	500	33.5
38	30	500	32.4
38	15	500	28.4
39	30	500	29.9
39	15	500	32.8
40	30	500	42.7
40	15	500	38.3
41	30	500	33.1
41	15	500	31.4

4.3. Thermal Stability of Cereclor

A simple distillation experiment was carried out on the Cereclor range of additives. These materials were individually heated in a glass still until only a char remained and the distillate was collected and weighed. It was apparent that heating under these conditions resulted in decomposition of at least part of the material, Infra Red Spectra were obtained on the original material and the distillate, in an attempt to assess the degree of decomposition. The chief differences were the appearance, in the spectrum of the distillate, of a weak to medium absorption band at 1620 - 1660 cm^{-1} and of a medium strength band at 960 - 980 cm^{-1} indicating the loss of some hydrogen chloride. Table XIV shows the weight percentage distillate obtained for each Cereclor and also the oxygen index of the corresponding resin mixture.

TABLE XIV

CERECLOR DISTILLATION AND RELATED DATA

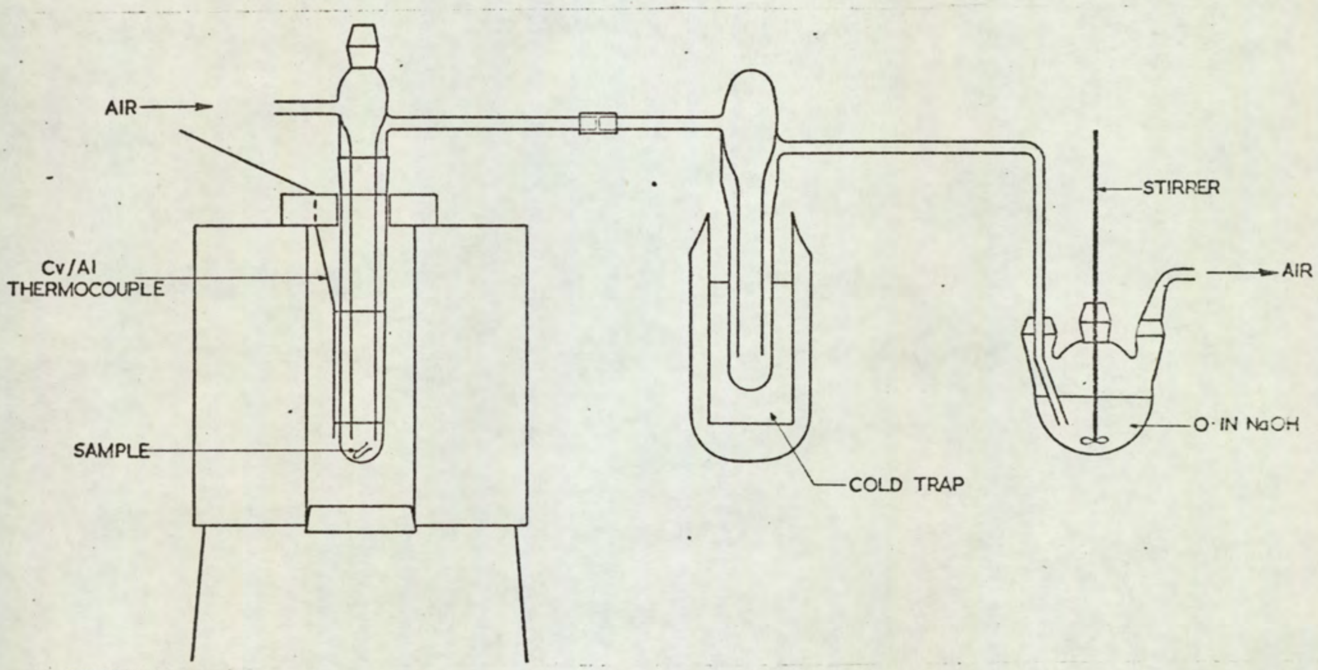
Additive	Distillate wt. %	Dist. Temp. range °C	Oxygen Index
Cereclor 70	-	-	0.350
" 70L	26.8	288 - 296	0.295
" 65L	51.0	274 - 280	0.287
" S52	54.1	256 - 262	0.260

4.4. Determination of Hydrogen chloride and Volatile SbIII

The apparatus used is shown in Fig. 26. The furnace was brought to the required temperature before introduction of the sample and this temperature was maintained throughout the experiments. The sample in a 'cut-off' ignition tube was dropped into the preheated apparatus, from the top. The materials which were volatile under test conditions were swept out of the heated part of the apparatus by a stream of air and passed through a liquid nitrogen trap and into a stirred solution of 0.1 N NaOH. Careful control of the air flow rate was necessary as too high a flow rate resulted in the volatile products of reaction between antimony trioxide and Cereclor 70 being carried into the alkali solution, resulting in hydrolysis and the production of hydrogen chloride. Too low a flow rate resulted in hydrogen chloride freezing out in the trap.

FIG. 26

EQUIPMENT USED IN DETERMINING REACTION PRODUCTS OF CHLORINE COMPOUNDS AND ANTIMONY TRIOXIDE



Hydrogen chloride was estimated by passing into 0.1 N NaOH solution and back titrating the excess with standard hydrochloric acid solution using methyl red indicator. Three determinations were made and the mean reported. The trapped material was carefully washed from the apparatus with the minumum concentrated hydrochloric acid solution and SbIII determinations were carried out by titrating with standard iodine solution using starch indicator according to the method described in Vogel[95]. Three determinations were made and the mean reported.

Reaction products were analysed from samples which had been heated in air at 500°C for 15 mins. in each case.

TABLE XV

REACTION PRODUCTS.

Mixture No.	Mean Hydrogen Chloride as wt. % of total Chlorine	Mean Hydrogen chloride as wt. % of total halogenated material	Volatile SbIII as % of Total Sb
1	87.5	61.3	
2	9.2	6.4	75.1
13	97.9	55.7	

The results of this work are generally in agreement with those obtained from the work described in the previous chapter. However, a few specific points appeared anomalous and it was concluded that a more severe test method would probably throw a light on this. The British Standard 476 fire propagation test was selected as a suitable method and these experiments are described in the next chapter.

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CHAPTER 5

B.S. 476 PART 6 FIRE PROPAGATION TEST

Results of work described in the previous two chapters have high-lighted the fact that the candle burning test and B.S.2782 Method 508A are useful in grading various flame retarded plastics materials under conditions of low thermal stress. However if a more complete picture is required it is probably necessary to examine materials under test conditions more closely resembling those found in a real fire. For this reason the B.S. 476 fire propagation test was chosen to examine selected resin formulations as a partial satisfaction of this need.

5.1. Development of the Test

Early experiments involving the study of the effect of room linings on the development of fire in rooms indicated that flash over time i.e. the time between the initial outbreak of fire and involvement of all of the combustible materials in the room depended upon the nature of the room lining but that once flash over had been reached the lining was relatively unimportant. The surface spread of flame test[88] had been used for the general assessment of lining materials but it was noted that the top class materials according to this test gave a wide range of flash over times. This was thought to be due to the open nature of the test. However, since it was not possible to change the criteria of the surface spread of flame tests in order to make the grading agree with results of model fires it was necessary to develop a new test designed to grade linings according to flash over times.

It was considered that a satisfactory test could be evolved by a suitable assessment of three factors:-

a. Ease of ignition of the lining by a small flame.

b. The ease of ignition of the lining by a larger source of heat.

c. The rate of liberation of heat after ignition of the lining together with a measure of the total amount of heat liberated.

The final test conditions and criteria which will be described in the next section were those which enabled a good correlation to be made between the performance of a range of materials on the test and their performance when used as linings in the model room experiments.

5.2. The Test

5.2.1. Apparatus

A very full description regarding the requirements of the apparatus is given in the British Standards specification[96] and as it would be tedious to detail these here it is proposed only to give a very brief general description.

Essentially the apparatus consists of a box, constructed from asbestos board, the box having internal dimensions of 190 mm. x 190 mm. x 90 mm. with one vertical face open. This open face was completed by a detachable wall which had facility for housing the material under test. The box was fitted with a vent and also a chimney hole, into the latter was fitted a steel chimney and muffle. At particular positions inside the box were fitted two 1 kW electrical heating elements and a bank of gas jets which when ignited liberated 7560 cal./min. The apparatus was so arranged that when the specimen was in position no air leakages other than the vent and chimney were present, the specimen constituting one vertical wall of the box. The muffle cowling had facility for attaching two thermocouples which measured the flue gas temperature.

5.2.2. Sample Preparation

Preliminary experiments using cast sheets were unsuccessful due to the sheets collapsing during the test, producing false results. For this reason it was decided to carry out these experiments using glass mat reinforced sheets. The resin to glass ratio was $2\frac{1}{2} : 1$ in every case. The glass mat used was supplied by Turner Bros. and was an E glass mat of $1\frac{1}{2}$ oz. per sq. ft.

When flame retardant additives were used these were incorporated into the resin using the method described in Chapter 3. The sheets were prepared using a hand lay up technique. These were cold cured between cellophane film backed with plate glass using $1\frac{1}{2}\%$ MEK peroxide (as 40% solution in DMP) as initiator and $1\frac{1}{2}\%$ of a 6% Cobalt Naphthenate solution as accelerator. Sheets of $\frac{1}{8}$ ins. thickness were readily reproduced using this method. When hard, the sheets were trimmed to the required dimensions (9 ins. x 9 ins.) by means of a circular saw, at the same time specimens suitable for candle burning tests were cut from the trimmings. At least three specimens were prepared of any one resin mixture. Before testing, the samples were allowed to equilibrate to normal laboratory conditions for at least 24 hours

TABLE XVI

RESIN MIXTURES TESTED

Resin Mixture No.	Formulation	
	Resin	Additives
1	100	-
2	100	15 Cereclor 70 + 15 Sb_2O_3
3	100	15 Dechlorane 4070 + 15 Sb_2O_3
4	100	15 Flammex 4BS + 15 Sb_2O_3
5	100	15 tris 2,3 dichloropropyl phosphate.

Note: details of the chemical nature and supplier of additives used may be found in Appendix I.

5.2.3. Test Procedure

Essentially the test consists of comparing the heat liberated through the chimney of the apparatus when a specimen is in position with that of an inert asbestos board of the same thickness.

The equipment was set up with the asbestos board in position and precautions were taken to see that the faces of the detachable wall were clean and air tight. The gas jets were ignited and the experiment timed from this point. After 2 minutes 45 seconds the electrical current was switched on to give an input of 1800 watts, this was reduced to 1500 watts after 5 minutes and remained constant at this for the remainder of the test. The temperature inside the muffle was recorded on a potentiometric recorder. The specification demands that a calibration curve falling within certain tolerances be obtained. The temperature rise above ambient was plotted against time over 20 minutes.

Similar temperature records were obtained for three specimens of the same resin formulation and the mean temperature rise above ambient calculated and plotted against time on the same graph as the calibration curve. Temperature readings of both the calibration curve and the test material were taken at ½ minute intervals up to 3 minutes and at 1 minute intervals from 4 minutes to 10 minutes and at 2 minutes intervals for 12 minutes to 20 minutes. From these readings the index of performance for the material was determined according to the specification.

$$I = \sum_{\frac{1}{2}}^{3} \frac{\theta_M - \theta_C}{10t} + \sum_{4}^{10} \frac{\theta_M - \theta_C}{10t} + \sum_{12}^{20} \frac{\theta_M - \theta_C}{10t}$$

where

I = index of performance

t = time in minutes from the origin at which the readings were taken.

θ_M = temperatures in degrees C of the mean curve for the material at time t.

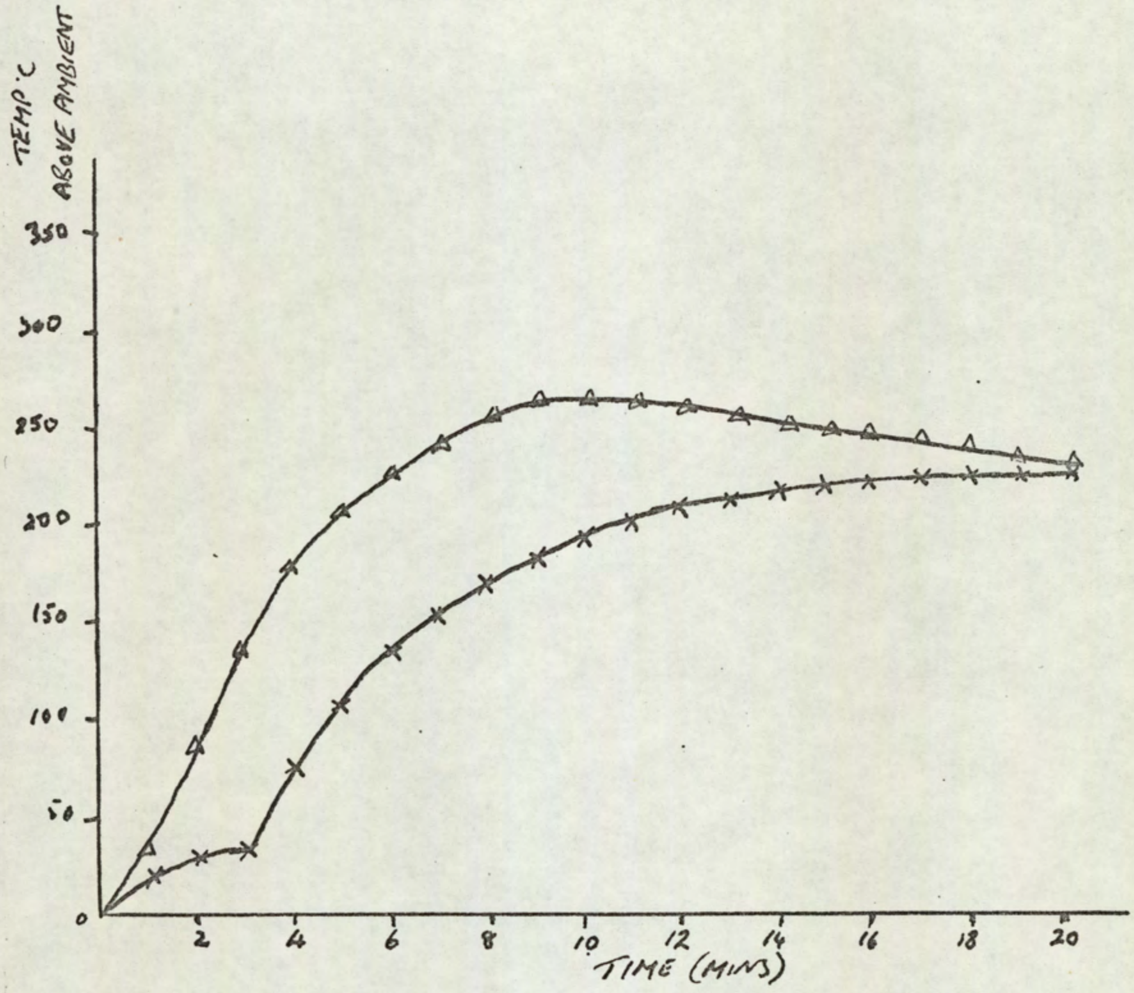
θ_C = temperature in degrees C of the calibration curve for the apparatus at time t.

5.3. Candle Burning Test

The apparatus and test procedure used was as described in Chapter 3.

FIG.27

STANDARD RESIN



× Calibration Curve

Δ Standard Resin

Performance Index

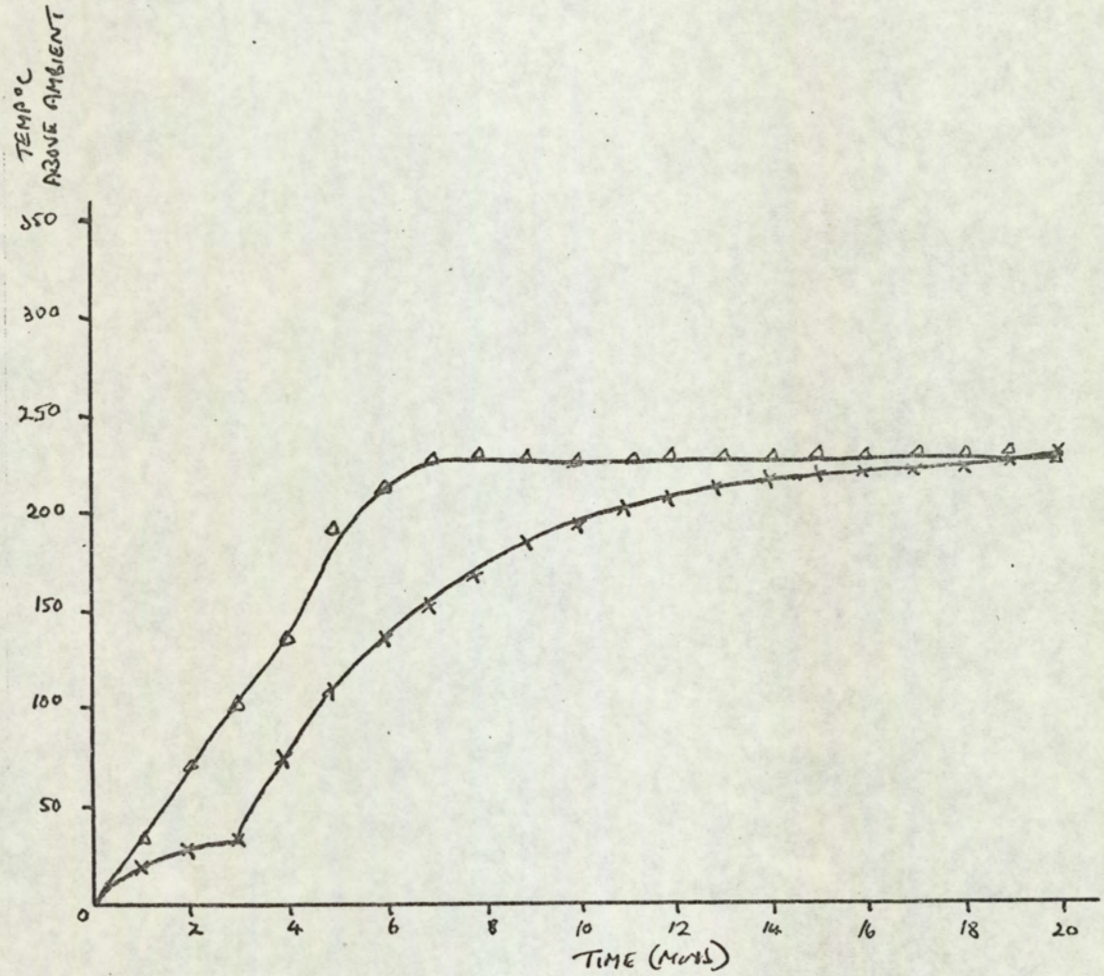
0 - 3 min.	14.8
4 - 10 min.	9.7
12 - 20 min	0.7
TOTAL	25.2

Candle Burning Test

	Cast Sheet	Reinforced
n	0.192	0.189

FIG. 28

CERECLOR 70/ANTIMONY TRIOXIDE



× Calibration Curve

Δ Resin Mixture (2)

Performance Index

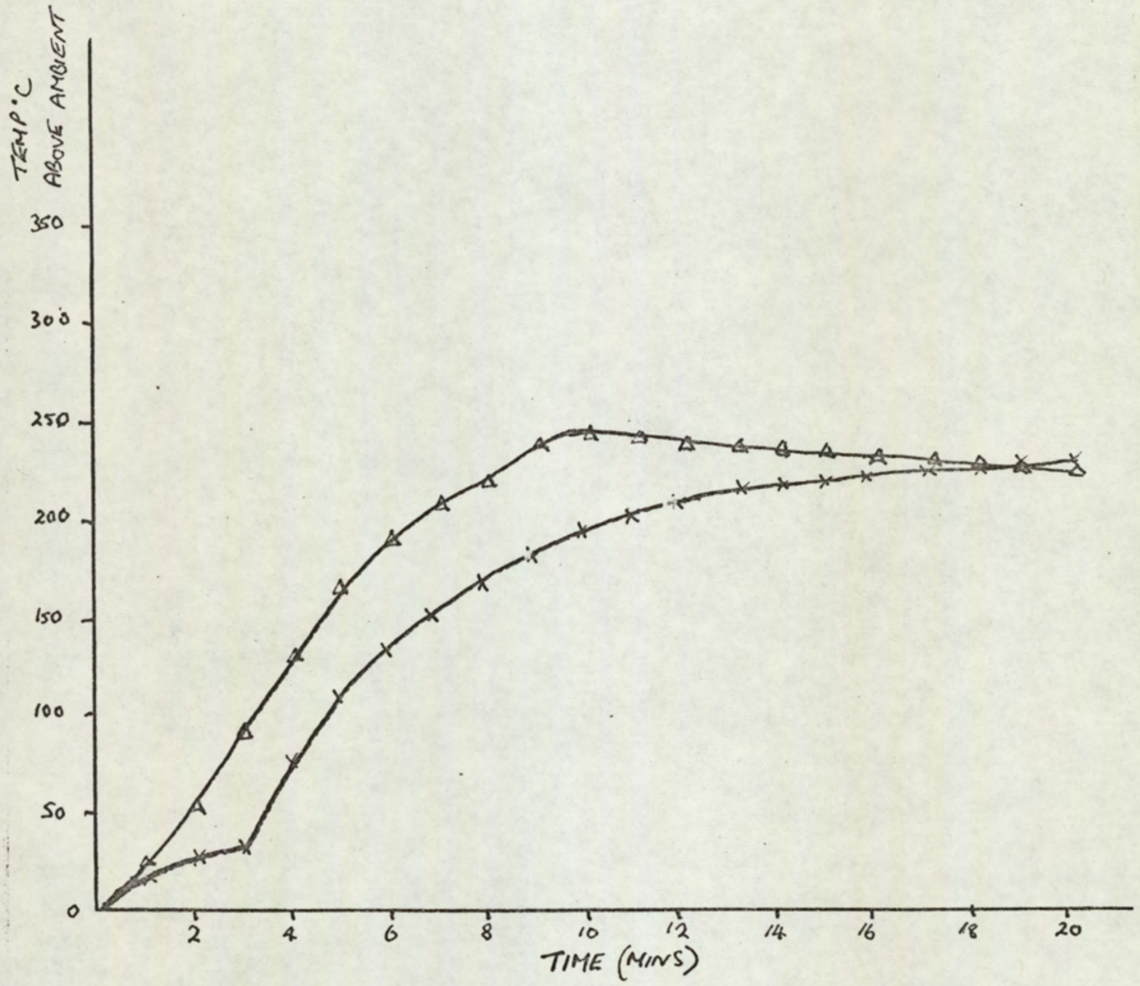
0 - 3 mins.	11.0
4 - 10 mins.	7.0
12 - 20 mins.	0.2
TOTAL	18.2

Candle Burning Test

	Cast Sheet	Reinforced
n	0.367	0.359

FIG. 29

DECHLORANE 4070/ANTIMONY TRIOXIDE



× Calibration Curve

△ Resin Mixture (3)

Performance Index

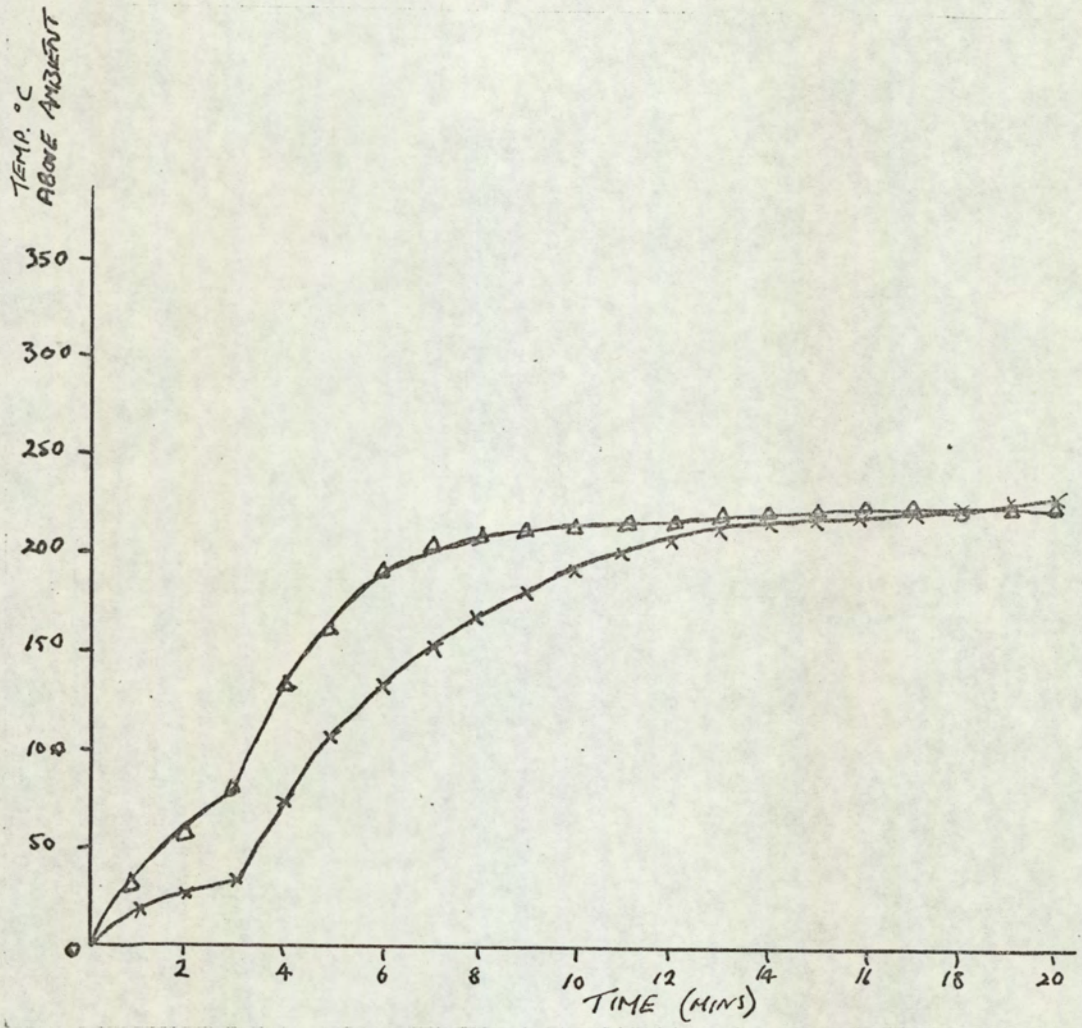
0 - 3 mins.	7.0
4 - 10 mins.	5.8
12 - 20 mins.	0.3
TOTAL	13.1

Candle Burning Test

	Cast Sheet	Reinforced
n	0.282	0.269

FIG. 30

FLAMMEX 4BS/ANTIMONY TRIOXIDE



× Calibration Curve

▲ Resin Mixture (4)

Performance Index

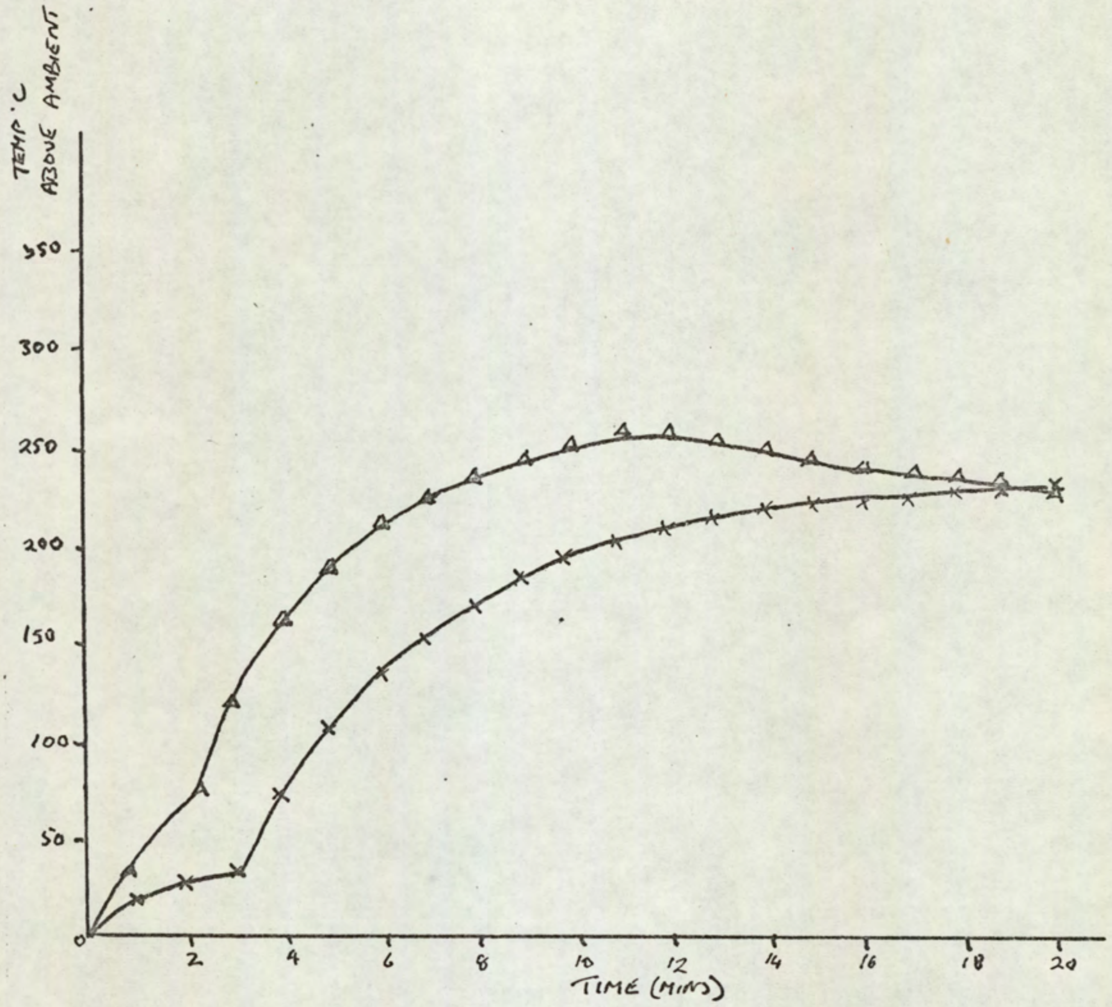
0 -	3 mins.	8.4
4 -	10 mins.	5.4
12 -	20 mins.	0.1
	TOTAL	13.9

Candle Burning Test

	Cast Sheet	Reinforced
n	0.346	0.353

FIG. 31

TRIS 2,3 DICHLOROPROPYL PHOSPHATE



X Calibration Curve

Δ Resin Mixture (5)

Performance Index

0 - 3 mins.	11.3
4 - 10 mins.	7.3
12 - 20 mins.	0.7
TOTAL	19.3

Candle Burning Test

	Cast Sheet	Reinforced
n	0.232	0.230

CHAPTER 6

THE EFFECT OF INHIBITORS ON MODEL FUEL DIFFUSION FLAMES

The combustion of solid materials involves a number of complex events occurring simultaneously and in order to study, more conveniently those which occur in the vapour phase it was decided to eliminate pyrolysis processes and study model flame systems. As the pyrolysis products of cross-linked polyesters have not been identified with any degree of certainty the choice of model fuels was fairly open and those materials selected were thought to be representative of some of the expected types of flammable pyrolysis products.

The burning of solid materials in real fires involve both diffusion and premixed flames. Diffusion flames rely on mixing of fuel and oxidant at the periphery of the flame envelope while in the case of premixed flames mixing of fuel and oxidant occurs prior to the flame zone. The present chapter describes work carried out to study the effect of inhibitors on diffusion flames.

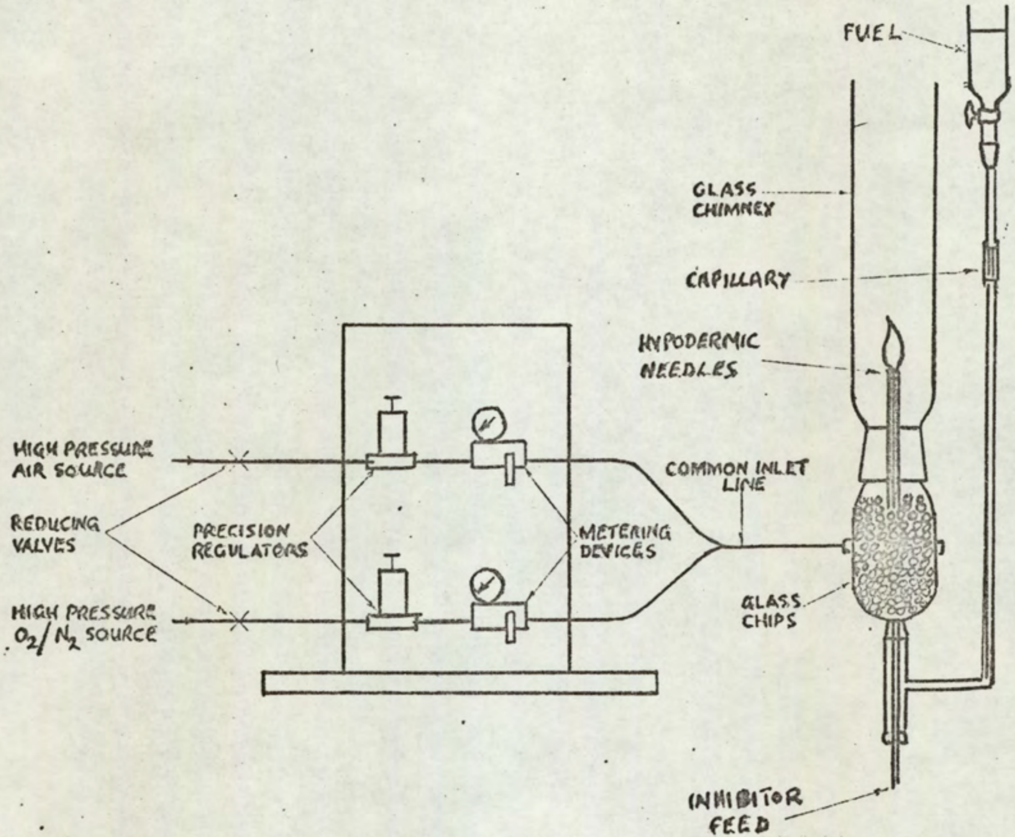
6.1. Experimental

6.1.1. Apparatus

Equipment modified from the candle burning test was used. The dimensions of the glass chimney were the same (8 cm. dia. x 60 cms. in length) and the atmosphere metering system was as described in Chapter 3. The main modification of the basic candle burning set up was the replacement of the polymer stick holder by a glass burner tube which was fitted with a sintered glass disc.

FIG. 32

THE DIFFUSION FLAME APPARATUS

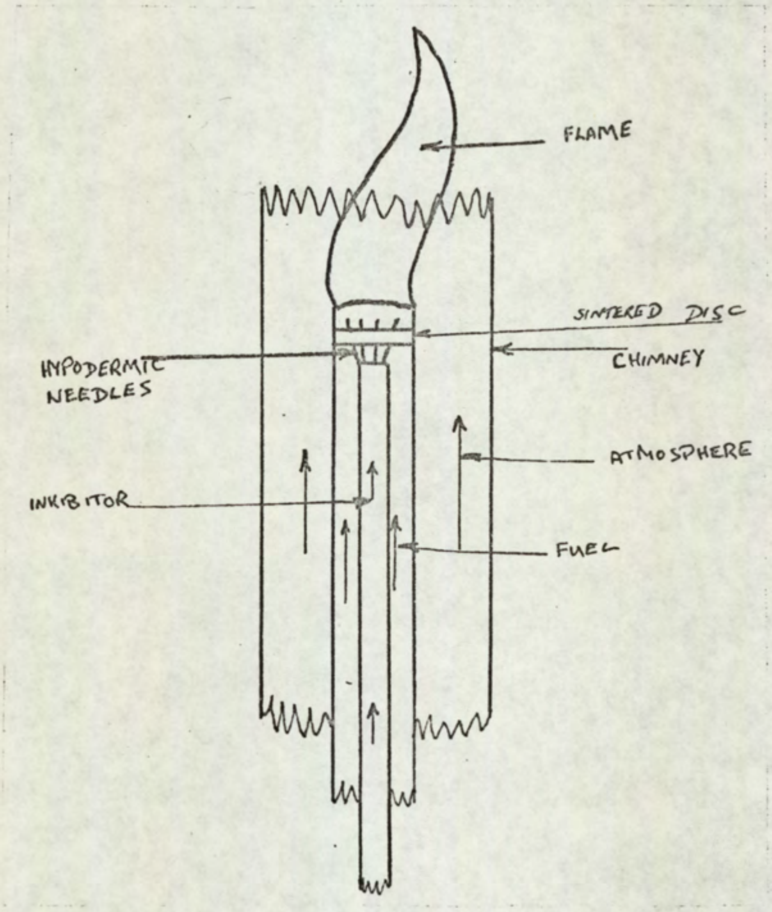


Five holes were drilled in the disc for insertion of hypodermic needles which were secured inside a glass tube by means of an epoxy adhesive. This tube was concentrically fitted inside the burner tube and was used for injection of gaseous inhibitors directly into the flame. A detail of the burner tube with hypodermic needles is illustrated in Fig. 33.

The burner tube was connected to a reservoir from which fuel was gravity fed through a flow restricting capillary. The rate of consumption of fuel was determined by allowing fuel to drain through the hypodermic needles and weighing the quantity collected over a time period. The rate of flow could be adjusted by insertion of a different capillary tube into the flow line. When not in use the inhibitor line was shut off at the inlet end.

FIG. 33

DETAIL OF BURNER TUBE



6.1.2. Preliminary Experiments with Uninhibited Flames

In order to best study the effect of inhibitors on model fuel flames it was considered necessary to obtain a 'standard' flame i.e. a flame which could readily be reproduced. Preliminary experiments with toluene and styrene monomer (polymerisation inhibitor free) indicated that suitable flames could be obtained by fuel delivery rates of 0.24 - 0.28 g./min. of styrene and 0.22 - 0.26 g./min. toluene. These ranges were suitable for air flow rates of the order of 10 litre./min. Under these conditions fairly stable flames of approx. 2½ ins. in height were obtained.

Values of oxygen index for toluene and styrene monomer, under these conditions, were obtained in a similar manner to that used in determining n values of polymer sticks. The fuel flow rate was determined as previously described and adjusted by use of a different size capillary if necessary. Air was allowed to flow through the chimney at 10 litres/min. and the fuel ignited by means of a coal gas flame. Nitrogen was allowed to flow into the common delivery line and its concentration was increased until the flame was extinguished. This occurred, in both cases, by the flame remaining quite large but lifting away from the burner tube. At oxygen concentrations just above the oxygen index it was possible to hold the flame ¾ ins. - 1 ins. above the burner tube. On increasing the nitrogen concentration the flame lifted further until feedback of heat was insufficient to vaporize more fuel. Values of oxygen index for 'Standard' toluene and styrene monomer flames are given in Table XVII.

TABLE XVII

OXYGEN INDEX OF STANDARD TOLUENE AND STYRENE FLAMES

	Toluene	Styrene Monomer
n	0.185	0.150

In practice it was found that little variation of fuel delivery rate outside of the ranges quoted above could be tolerated. Too high a delivery rate resulted in fuel running down the side of the burner tube causing the flame initially to become unstable followed by the flame consuming this fuel and hence greatly increasing in size. Alternatively too slow a rate resulted in fuel starvation and ultimately extinction of the flame.

Basically three techniques were used in adding inhibitors to the combustion system.

1. Incorporation of the inhibitor in the fuel supply.
2. Injection of the inhibitor into (a) the fuel (b) the oxidant side of the flame.
3. Introduction of solid material in pellet form into the flame zone.

6.1.3. Incorporation of the Inhibitor in the Fuel Supply

In the following experiments the inhibitor was dissolved in the fuel and fed through the fuel line in the normal way. This technique was found to be particularly suitable for those inhibitors which were of similar volatility to the fuel. When it was necessary to adjust the flow rate of the fuel/inhibitor mixture in order to maintain a flame of a fairly uniform size this was done but the flow rate was not determined in every case. The effect of fuel/inhibitor ratio on the oxygen index of a flame closely resembling the size of the standard flame was determined for various volatile liquid inhibitors. The results obtained for toluene and styrene monomer are illustrated in Figs. 34 and 35.

Other inhibitors were examined using this technique and in many instances it was necessary to increase the size of the restricting capillary as the added inhibitors considerably increased the viscosity of the solution. Fig. 36 illustrates the effect of various inhibitors on the oxygen index of styrene monomer at concentrations of 20 g. inhibitor dissolved in 100 g. styrene monomer.

FIG. 36

EFFECT OF INHIBITORS ON FLAMMABILITY OF STYRENE

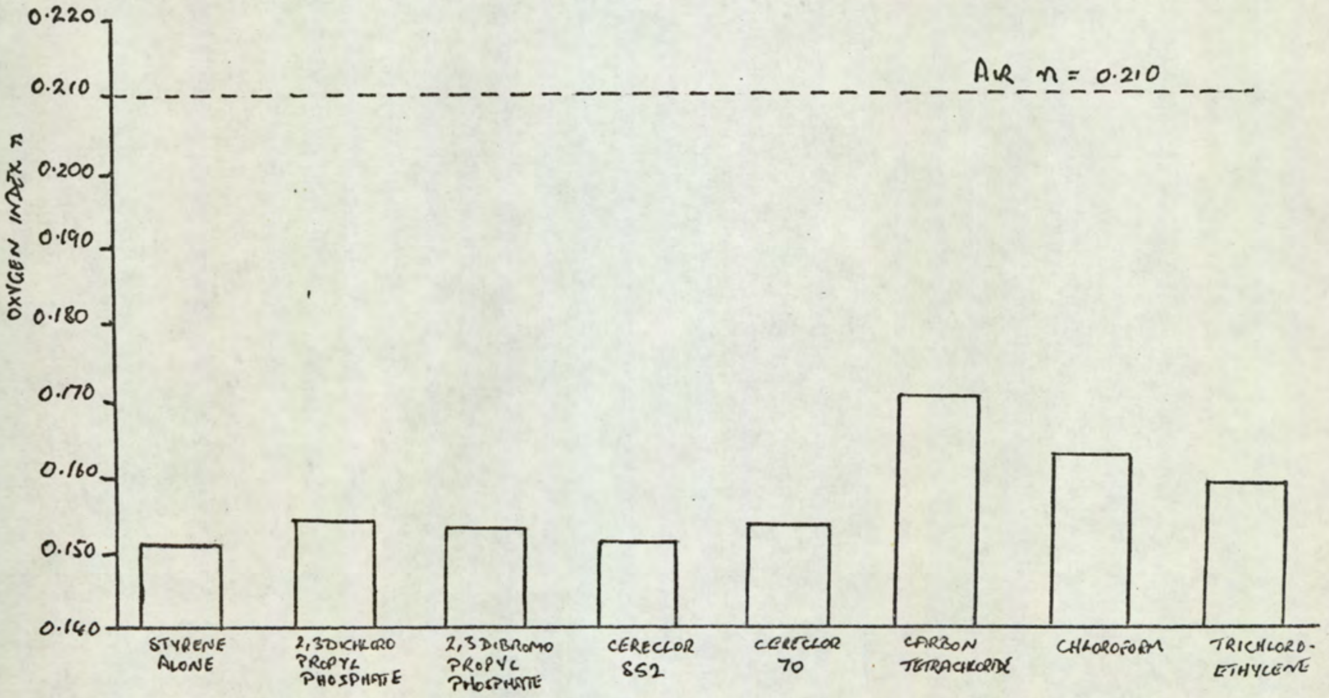


FIG. 34

THE EFFECT OF INHIBITORS ON THE OXYGEN INDEX OF STYRENE MONOMER

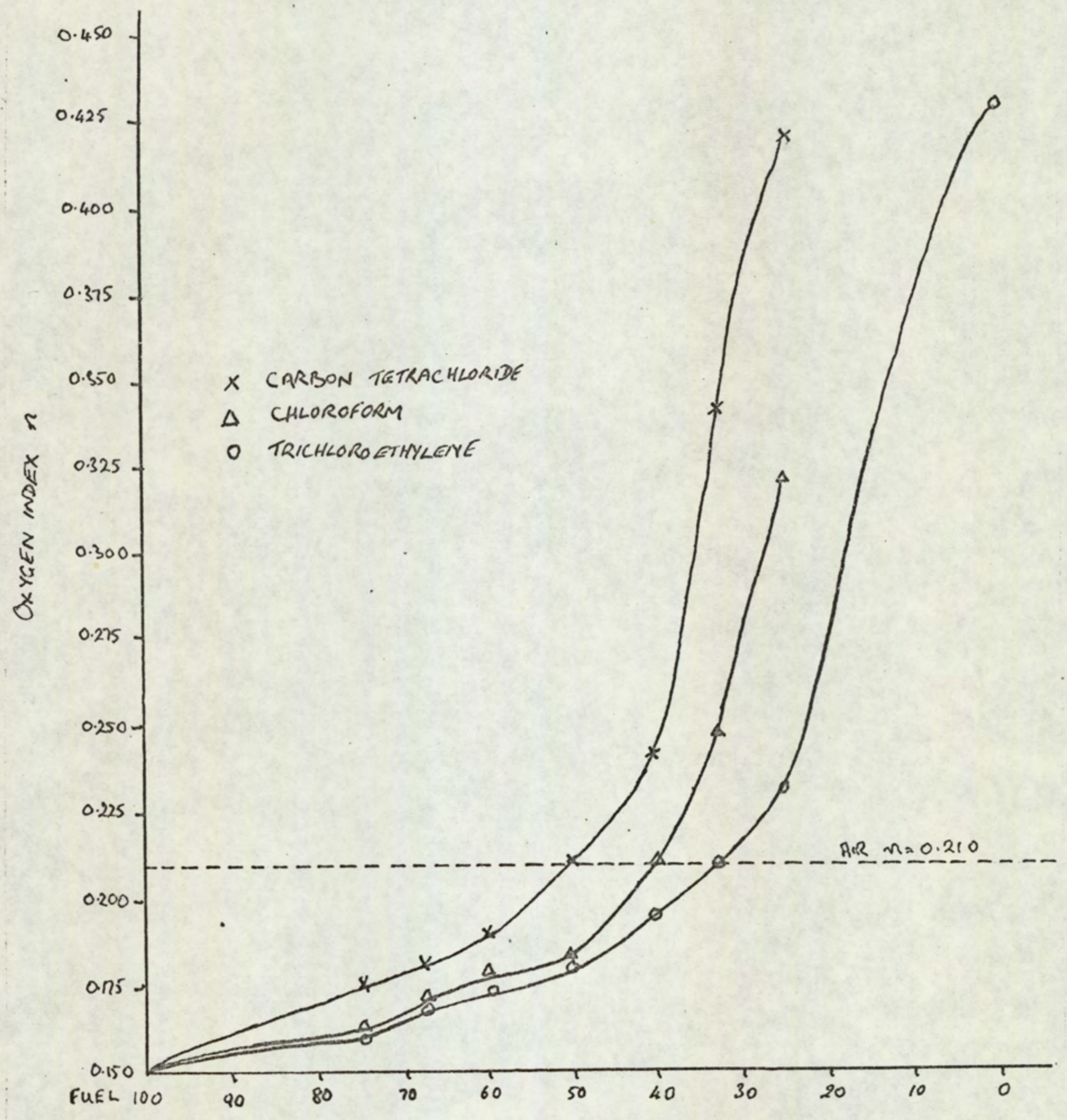
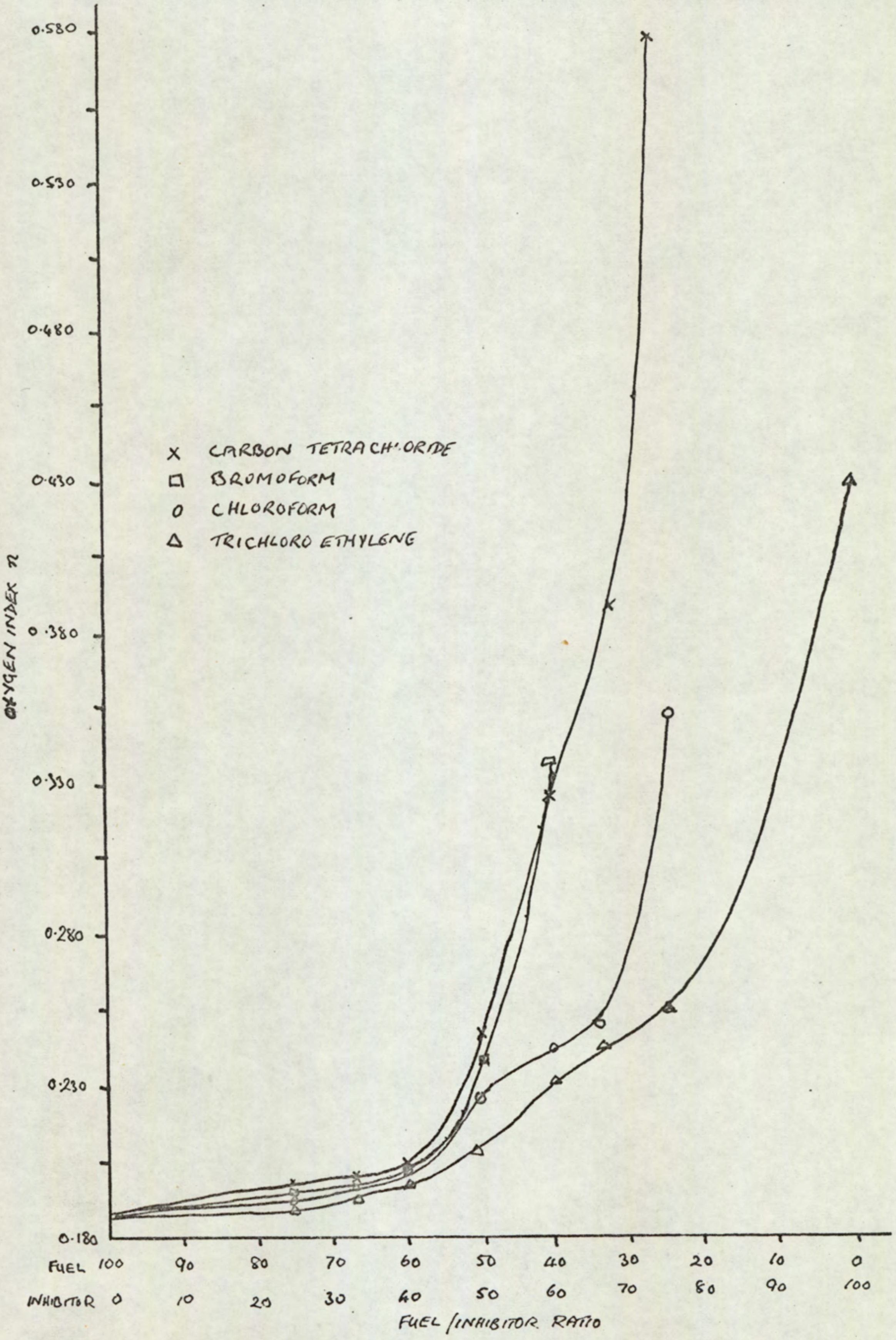


FIG. 35

THE EFFECT OF INHIBITORS ON THE OXYGEN INDEX OF TOLUENE

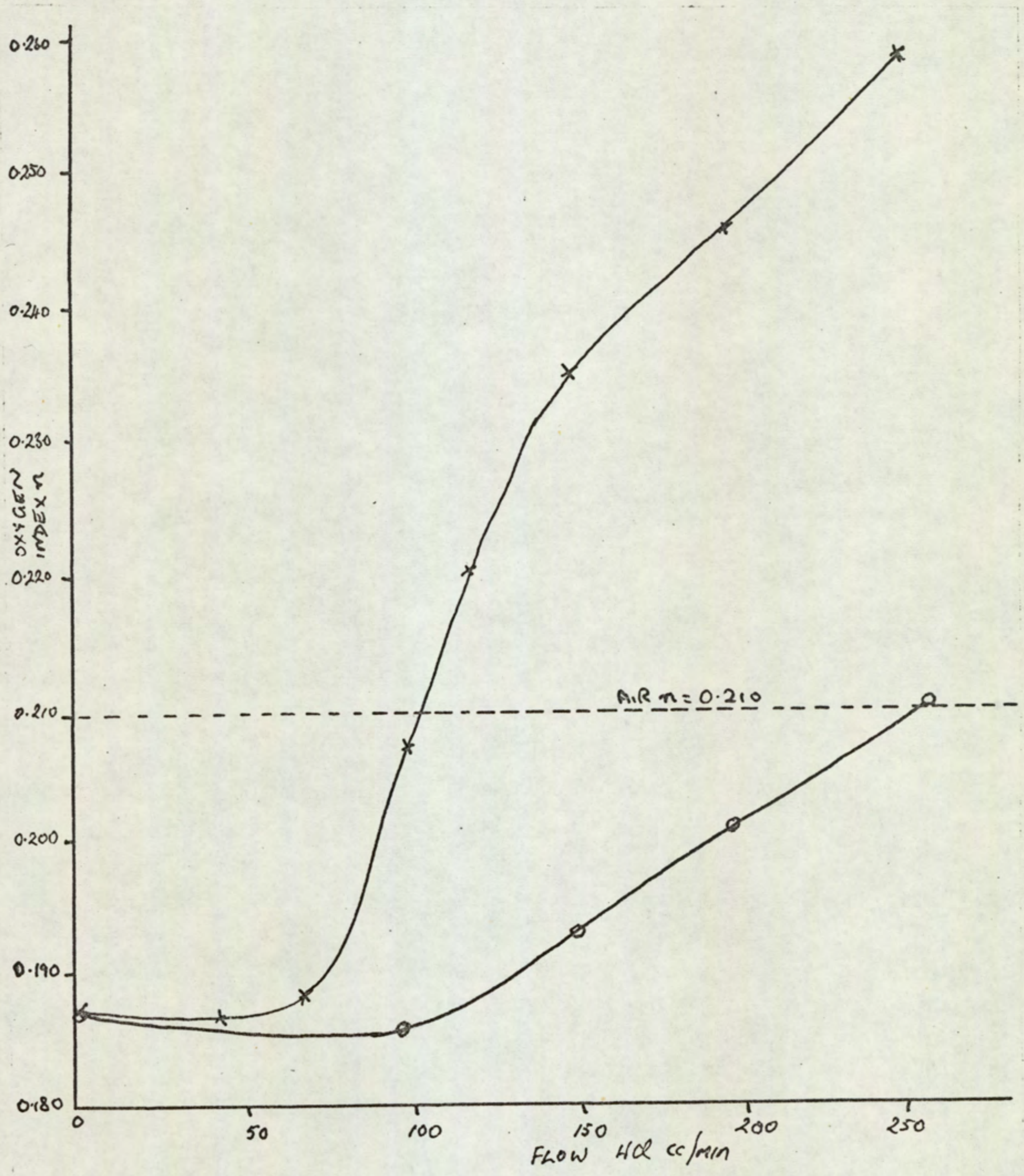


6.1.4. Injection of the Inhibitor into the Fuel and also the Atmosphere.

Calibrated rotameter type flow meters were used for metering anhydrous hydrogen chloride into the injection line. The technique involved obtaining a 'standard' toluene flame and metering hydrogen chloride at the required flow rate directly into it. For those n values of less than 0.210, nitrogen was added gradually to the atmosphere until the flame was extinguished. The highest concentration of nitrogen for which a flame was sustained was used in calculation of the oxygen index. For those n values above 0.210 it was necessary to commence burning in an oxygen rich atmosphere and approach the critical concentration by reduction of oxygen. This procedure was carried out at various flow rates of hydrogen chloride over the range 0 - 250 cc./min. A similar experiment was carried out by injection of hydrogen chloride into the atmosphere gases. Those mixtures which required very high concentrations of oxygen for burning produced copious quantities of soot and char which tended to obstruct the flame on prolonged burning. The results of these experiments may be found in Fig. 37.

FIG. 37

THE EFFECT OF HYDROGEN CHLORIDE WHEN ADDED TO THE FUEL AND OXIDANT SIDES OF A 'STANDARD' TOLUENE FLAME



o In the atmosphere

× In the fuel

Mean fuel consumption	0.24g toluene/min
Constant atmosphere flow	10.0 litre/min.
Anhydrous hydrogen chloride flow	0 - 250 cc/min.

Comparison of molar concentrations of anhydrous hydrogen chloride in the fuel and the atmosphere:

FLOW	CONCENTRATION (HCl)		OXYGEN INDEX	
HCl cc/min	Mole % in Toluene	Mole % in atmosphere	HCl in Toluene	HCl in atmosphere
250	76.6	2.03	0.260	0.210
200	71.8	1.56	0.246	0.201
150	65.4	1.21	0.235	0.193
100	56.2	0.80	0.210	0.185
50	39.5	0.39	0.186	0.185
0	0	0	0.185	0.185

Direct comparisons of the effect of hydrogen chloride in the fuel and atmosphere can therefore be only made between oxygen index values of 0.185 and 0.210.

Simmons and Wolfhard[11] determined the concentrations of methyl bromide required to quench diffusion flames over a range of total fuel and atmosphere flows and found that a peak concentration of inhibitor i.e. the concentration of inhibitor which would quench flames for all flow rates could be obtained. This has not been done in the present work only one set of conditions (as above) were used. However, ratios have been calculated for these conditions.

OXYGEN INDEX	CONCENTRATION (HCl)		$\frac{[HCl]}{[toluene]}$	$\frac{[HCl]}{[atmosphere]}$
	Mole % in toluene	Mole % in atmosphere		
0.210	56.2	2.03	1.282	0.0207
0.201	52.2	1.56	1.092	0.0158
0.193	48.7	1.21	0.949	0.0122

Simmons and Wolfhard[11] indicated that the concentration of inert gas required to quench fuel + oxygen diffusion flames gave a ratio [inert gas]/[oxygen] : [inert gas]/[fuel] very close to the stoichiometric ratio for the given fuel. They showed that this ratio was not true for diffusion flames inhibited by methyl bromide.

If air is considered to contain 21% by volume oxygen the above concentrations have been obtained for atmospheres containing 21% oxygen, 20.1% oxygen and 19.3% oxygen.

∴ Molar Stoichiometric Ratios:-

21% oxygen:- 1 toluene : 42.9 atmosphere
20.1% oxygen:-1 toluene : 44.8 atmosphere
19.3% oxygen:-1 toluene : 46.6 atmosphere

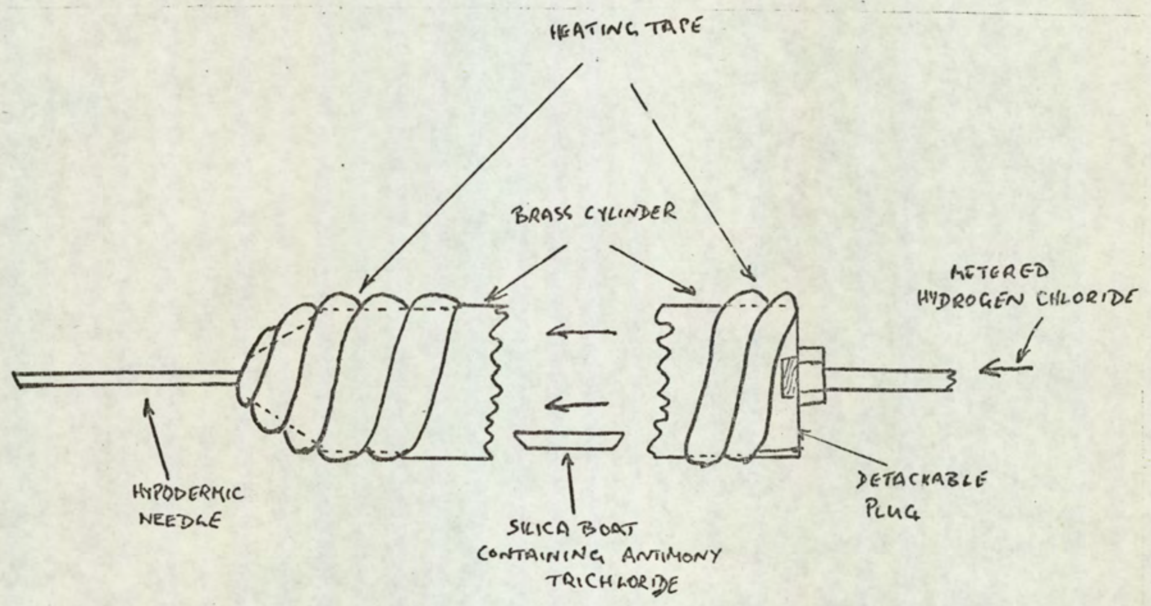
Calculated values of [HCl] / [toluene] : [HCl] / [atmosphere]

21% oxygen	1	:	62
20.1% oxygen	1	:	69
19.3% oxygen	1	:	78

Unsuccessful attempts were made at injecting antimony trichloride vapours into the flame. The apparatus shown in Fig. 38 was used. A hole of 0.060 ins. diameter was bored in the glass chimney at a point which corresponded with the top of the burner tube.

FIG. 38.

INJECTION EQUIPMENT



The hypodermic needle shown in the diagram was inserted until its tip just touched the base of the 'standard' flame. A weighed sample of antimony trichloride in a silica boat was inserted into the heated brass cylinder and the plug inserted. Hydrogen Chloride was metered into the cylinder. The objective was for antimony trichloride to be vaporized by the heat of the heating tape and for the stream of hydrogen chloride to pick the vapours up and transfer them through the hypodermic needle into the flame.

Qualitatively this was successful, antimony trichloride was shown to be an effective flame inhibitor, however quantitative information was much more difficult to obtain due to antimony trichloride gradually condensing out along the hypodermic needle and eventually blocking it.

6.1.5. Introduction of Solid Material in Pellet Form into the Flame Zone

As the attempt to inject antimony trichloride vapours into the flame zone was unsuccessful vaporization of solid antimony trichloride by feed-back of heat from the flame zone was attempted.

Pellets of antimony trichloride weighing between 0.5 - 1.0 g. were prepared in a pellet die. After weighing, these pellets were transferred to the top of the burner tube while a 'standard' toluene flame was burning. The pellet was supported on top of the hypodermic needles. The objective being that the feed-back of heat from the flame to vaporize the pellet, unfortunately the antimony trichloride readily melted and tended to block the sintered glass pad preventing fuel passing through thus the flame was extinguished by blockage of the fuel supply rather than interfering with flame reactions.

A modification of this technique involved suspending a wire gauze in the flame zone on to which a pellet was placed, however melting and dripping of the antimony trichloride again occurred and the drips again tended to block the sintered disc.

Attempts were made to prepare pellets of 50 : 50

mixtures of halogenated compounds and antimony trioxide these were difficult to make due to the dry nature of the powders, however a few were successfully prepared and suspended in the flame. It was found, however, that it was extremely difficult to reach a critical value of the oxygen concentration while the pellet was in the flame, as the evolution of reaction products occurred very rapidly. It was concluded that it was necessary to have much higher concentration of inhibitor, than could be practically used in pellet form, in order to obtain relevant information.

0-0-0-0-0-0

CHAPTER 7

INVESTIGATION OF THE QUENCHING ACTION OF METAL HALIDES AND OTHER MATERIALS ON PREMIXED FLAMES

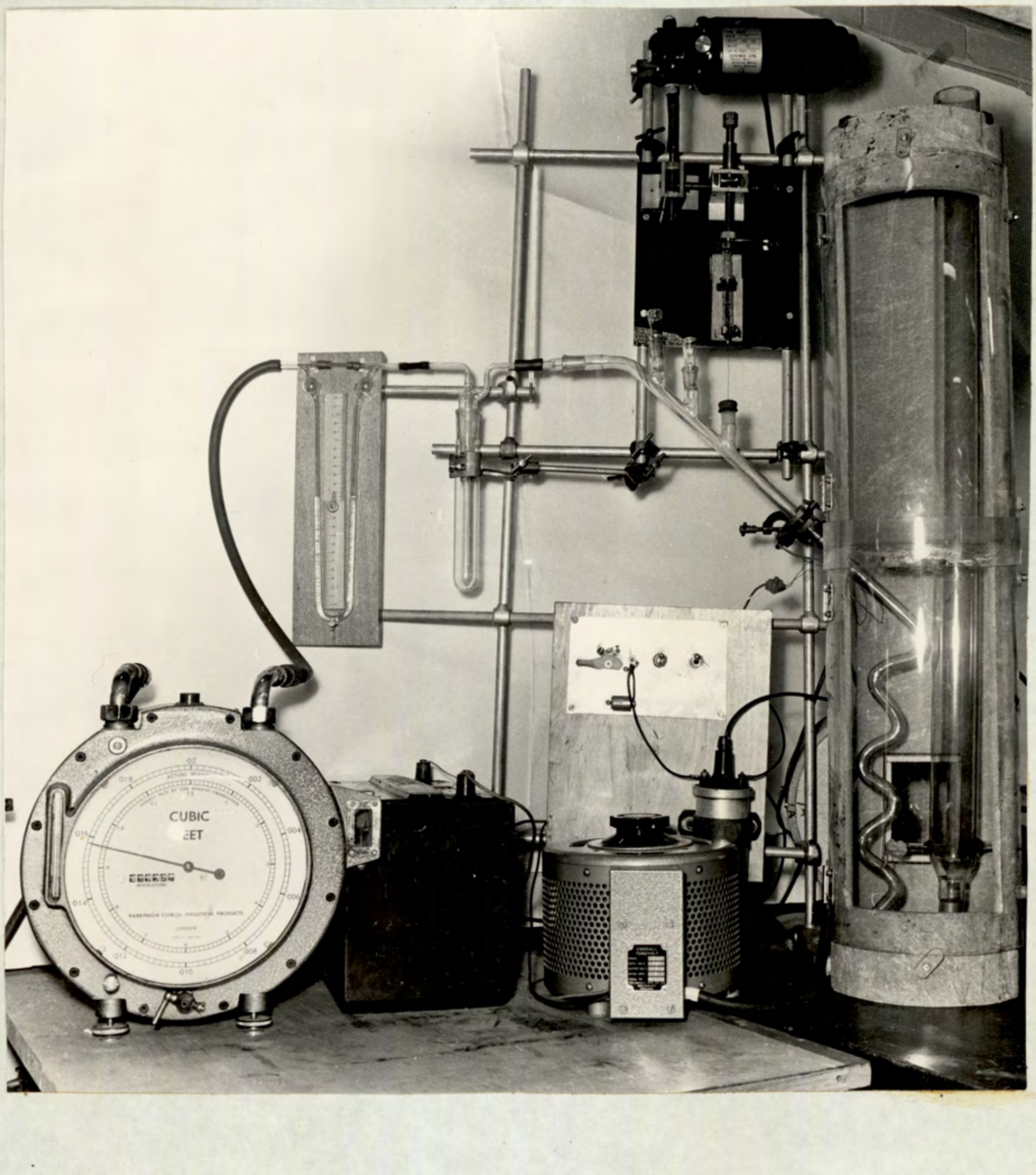
The work on diffusion flames indicated that before any useful information regarding inhibition by solid materials could be obtained a great deal of modification to the basic apparatus was required with no guarantee of success. For this reason it was decided to study the effect of inhibitors on the 'simpler' premixed flame system. For the same reasons as given in Chapter 6 model fuel systems were studied, these were all volatile liquids. It was first necessary to establish a technique which was capable of producing controlled flames in premixed liquid fuel/air mixtures. A search of the literature indicated that a development of an apparatus designed by Zabetakis et al[97] would probably be suitable.

7.1. Apparatus for Studying the Effect of Inhibitors on the Lower Flammability Limits of Model Fuels

Fig. 39 illustrates the equipment which was ultimately developed. Basically it consists of devices for metering air and fuel into a common flow line connected to a combustion tube which was fitted with an ignition source. The combustion and inlet tubes were encased in a cabinet which had provision for heating.

FIG. 39

APPARATUS FOR DETERMINING LOWER FLAMMABILITY LIMITS OF PREMIXED FLAMES



7.1.1. Air Metering Arrangement

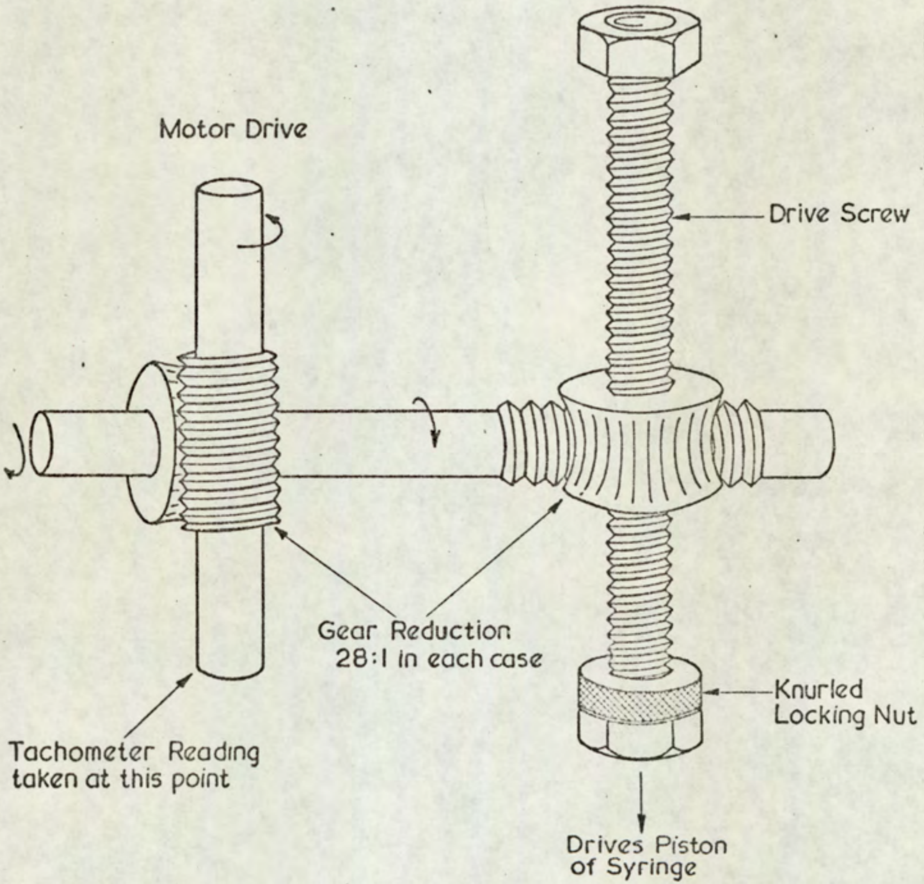
Total air flow over a given period was metered and recorded by means of a wet test meter. Steady flow was maintained by two precision regulators and a capillary tube flow meter (manometer type). The metered air was finally passed through a moisture trap before entering the apparatus.

7.1.2. Fuel Metering Device

In all cases a volatile liquid fuel was used. This was delivered from a glass hypodermic syringe at a constant rate, by means of a screw, driven through a suitably housed worm and gear train, which operated the piston of the syringe. Details of the gear train are shown in Fig. 40.

FIG. 40

DETAIL OF GEAR TRAIN



Two reductions were effected in the train both of 28 : 1. The gearing was driven by a laboratory 'stirrer motor' which had a speed range of 0 - 600 rpm but was found to operate most satisfactorily above 300 rpm. A fitting was provided for determination of motor speed by a hand tachometer. Infinite variation of rates of fuel delivery was made possible by variation of the dimensions of the syringe in use and also the speed of the motor.

7.1.3. Combustion Tube and Heating Cabinet

The combustion tube was constructed of pyrex glass tubing 36 ins. in length and diameter 2 ins. That part of the inlet tube inside the cabinet was bent in a zig-zag fashion in order to help vaporization and mixing of the fuel and air. Platinum electrodes for ignition were fitted at the inlet end of the combustion tube through capillary inlets.

The whole of the above was fitted inside a cabinet constructed from a 36 in. length of 7 in. diameter asbestos pipe. Two large openings were cut into the pipe one to accommodate the outlet part of a hot air blower, the other was fitted with shaped perspex doors to enable easy access to the combustion tube.

The hot air blower was also constructed from 7 in. diameter asbestos pipe. Three heating elements of total power rating 800 watts were sited off centre inside the pipe. Temperature was regulated by means of a Sunvic controller. The furnace was fitted with a small air blower which directed air over the hot elements. The ends of the furnace were enclosed leaving an outlet port of 4½ ins. x

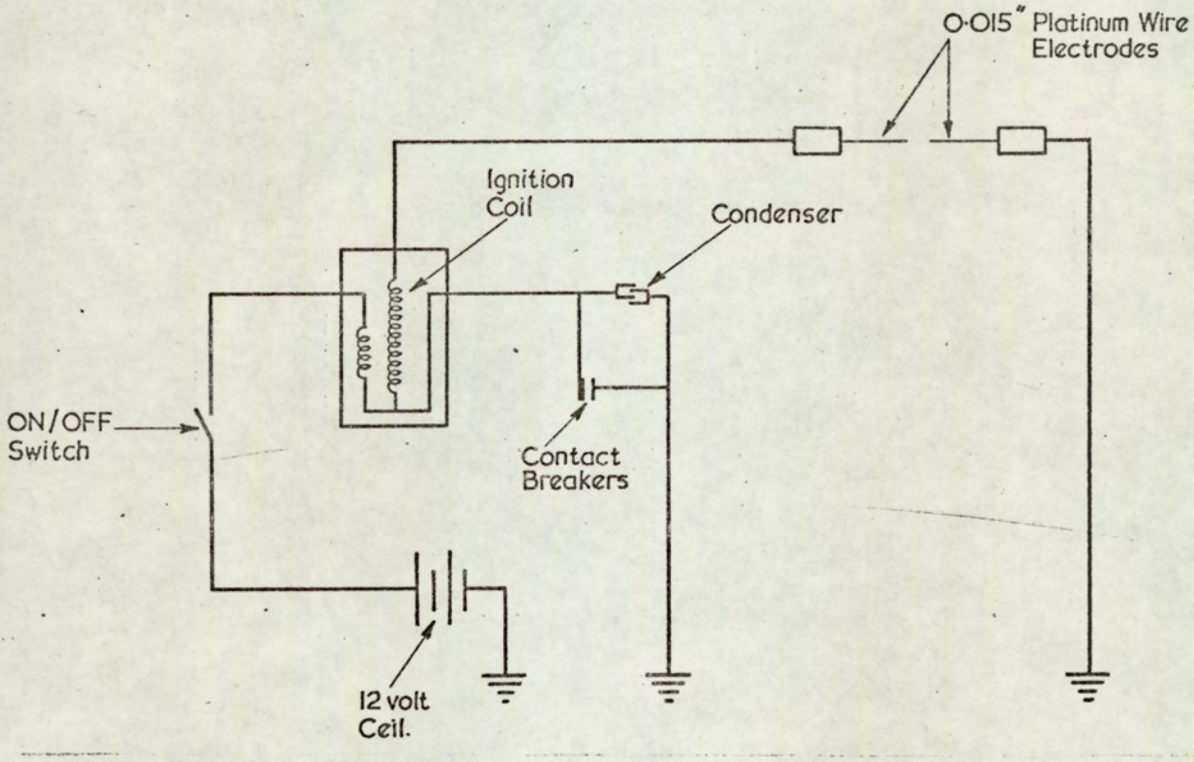
$3\frac{1}{4}$ ins. which was let directly into the vertical cabinet. A temperature of 100°C (at the electrodes) was readily achieved by this system.

7.1.4. Spark Ignition Source

Fig. 41 shows details of the ignition source. This was adopted from the ignition system of an internal combustion engine.

FIG. 41

IGNITION SOURCE



The electrodes were 0.015 ins. platinum wire with $\frac{1}{8}$ ins. spark gap. A spark was produced at the electrodes when contact breaker points were opened by means of a lever type mechanical switch.

7.2. Procedure for Determination of Lower Flammability Limits

The lower flammability limit of a fuel is defined as the lowest concentration of fuel in air through which a flame just propagates. The first series of experiments involved the determination of the effect of inhibitors on the lower flammability limits of model fuels. The general procedure adopted for the determination of lower flammability limits was as follows:-

The hot air blower was regulated so that a temperature of 100°C was obtained at the electrodes - this was measured with a thermocouple which entered the combustion tube through the capillary inlets. Air flow adjusted to give a constant delivery of between 2 - 3 lit./min. Preliminary experiments were carried out, adjusting the speed of the gear drive motor to give a constant slow delivery of fuel into the line. After allowing this mixture to flush through the apparatus for about 10 mins. a spark was passed between the electrodes and the propagation of the flame (if produced) was followed visually through the tube. Experience quickly indicated whether the flame was extremely fuel rich or only moderately so. By repeating this process, if a flame was produced, using a reduced motor speed, the approximate settings for the lower flammability limit were reached. Using these settings a precise determination was carried out by weighing the syringe filled with fuel, replacing to its fitting and switching on the drive motor, synchronous with this the wet test meter reading was taken and a stop clock started. After 10 mins. a spark was passed between the electrodes and any resulting flame propagation noted. The drive motor was then stopped and at the same time the reading of the wet test meter noted. The syringe was carefully removed from its fitting and reweighed. If a flame had propagated the length of the combustion tube the speed of the drive motor was reduced and the process repeated until a mixture was obtained for which a flame would not propagate the length of the tube. The lower flammability limit, expressed as percentage fuel in air by volume at NTP was calculated from the following:-

Per cent Fuel in air by volume at N.T.P. $= \dfrac{\left(\dfrac{\Delta W V}{M}\right)100}{\dfrac{\Delta W}{M} V + \dfrac{\Delta v P' T}{P T'}} = \left(\dfrac{V_1}{V_1 + V_a}\right)100$

where ΔW = weight of sample delivered during the time of the experiment.

V_1 = volume of liquid vapour (N.T.P.) corresponding to ΔW

Δv = volume of air at temperature T' fed into the system during the timed part of the experiment.

V_a = volume of air (N.T.P.) corresponding to Δv

V = 22.4 litres

T = 273°K

T' = temperature of air passing through the wet test meter.

P = 760 mm of Hg

P' = pressure of air passing through wet test meter.

Experiments were carried out using volatile liquid inhibitors. These were used as mixtures with the fuel under test and delivered in the normal way used for fuel metering. In some instances when large quantities of inhibitor were used it was necessary to increase the size of the syringe used, normally to 5 ml.

Usually it was found that when the equipment had not been used for several days it was necessary to thoroughly flush the system with fuel/air and ignite several times before reproducible results could be obtained. The model fuels used in these experiments were ethyl acetate, n-hexane and styrene monomer (polymerisation inhibitor free). The effects of bromoform, carbon tetrachloride and perchloro ethylene were studied on these fuels, the results are presented in Figs. 42, 43 and 44.

This type of inhibitor was fairly readily studied, as in the diffusion flame, but a study of the effect of metal halides on the flame was required so a basic modification to this equipment was necessary.

FIG. 42

THE EFFECT OF INHIBITOR ON THE LOWER FLAMMABILITY LIMIT OF STYRENE MONOMER

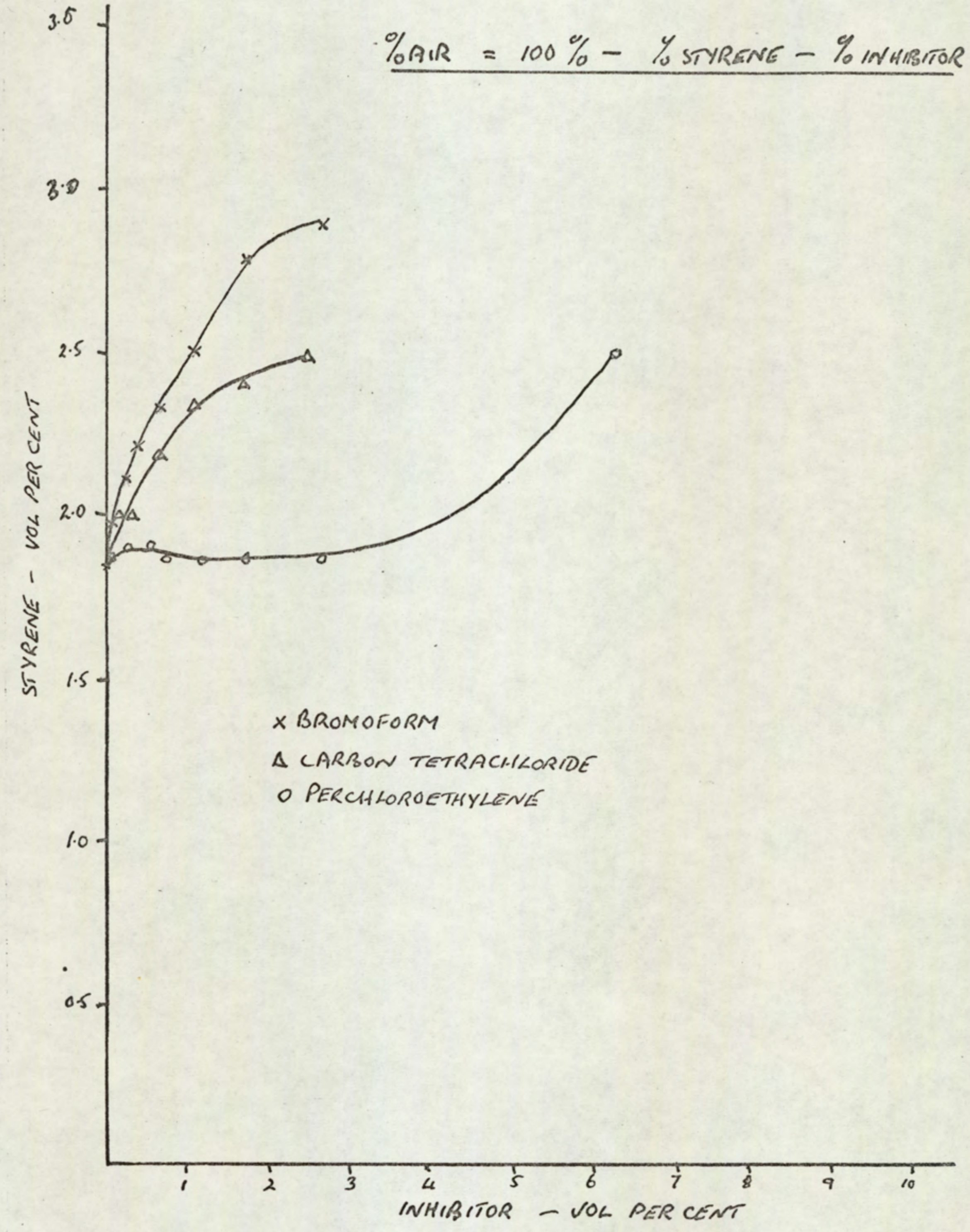


FIG. 43

THE EFFECT OF INHIBITOR ON THE LOWER FLAMMABILITY LIMIT OF ETHYL ACETATE

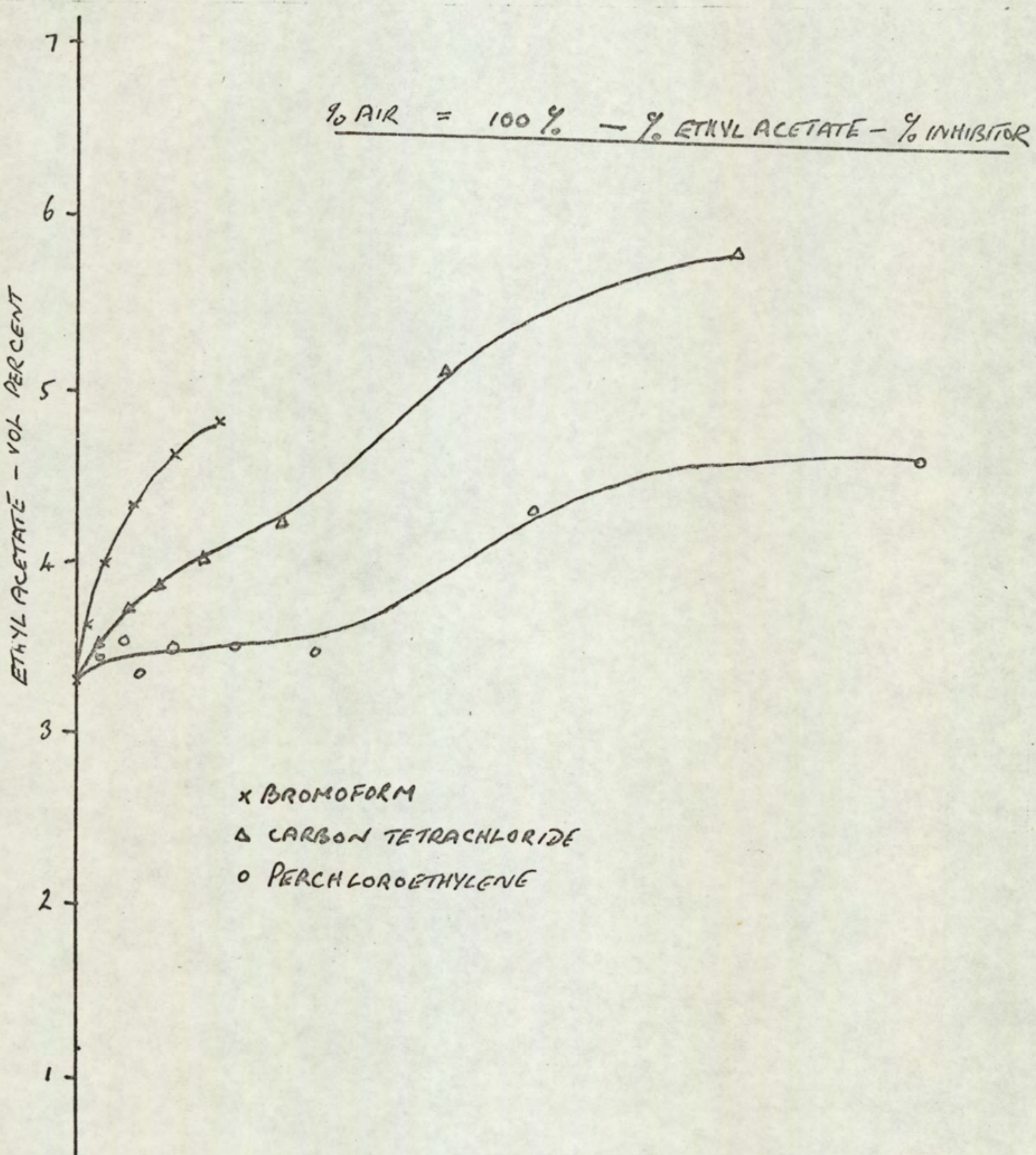
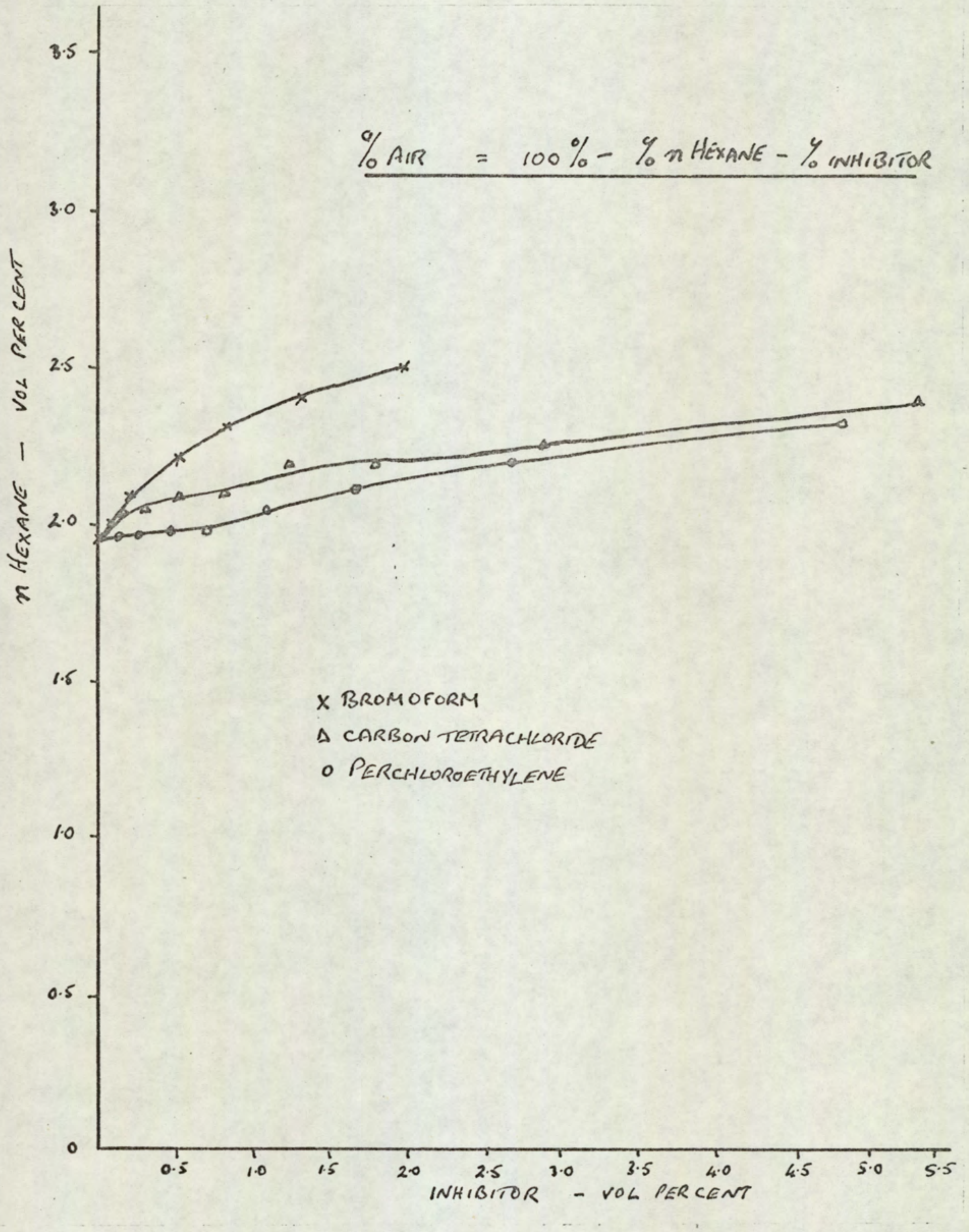


FIG. 44

THE EFFECT OF INHIBITOR ON THE LOWER FLAMMABILITY LIMIT OF n-HEXANE

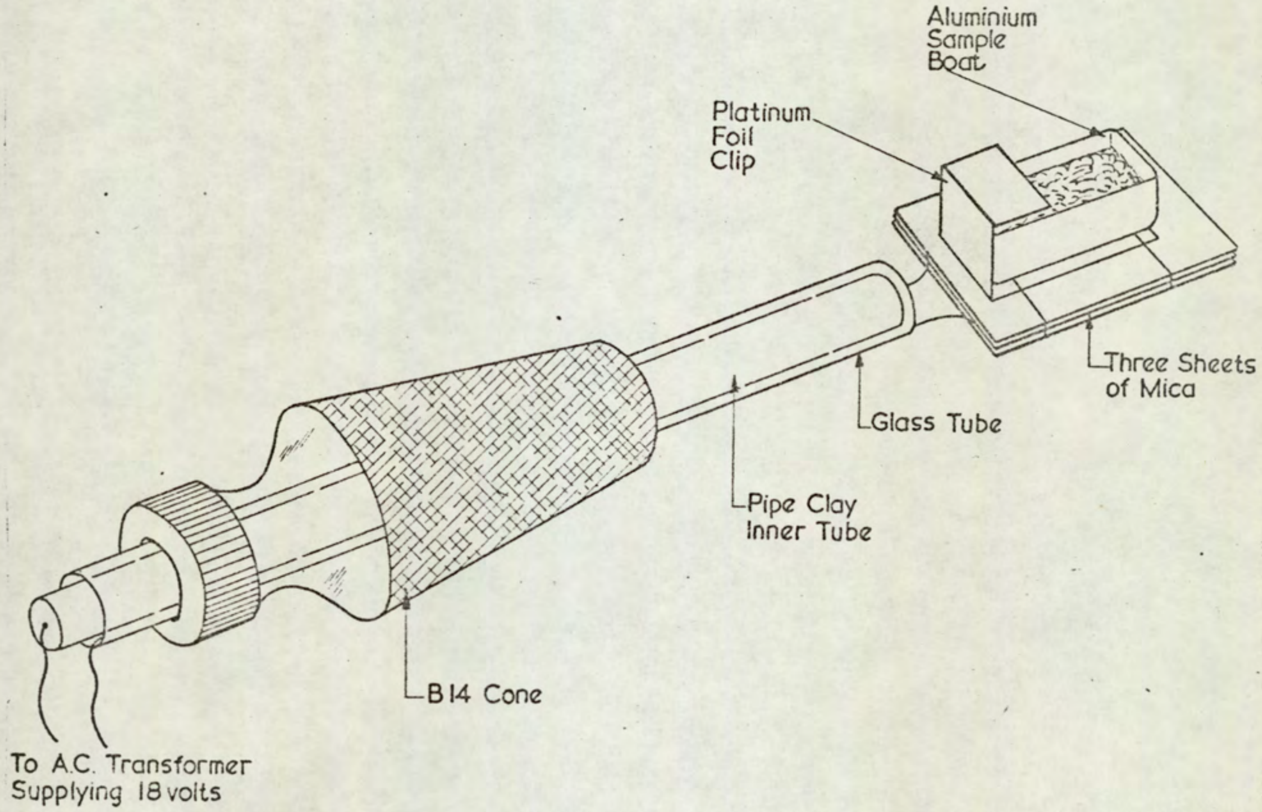


7.3. Apparatus used to study the effect of solid inhibitors in the flame

Essentially the equipment was the same as that described in the last section. The chief modification was the introduction of a ground glass B14 socket into the combustion tube, mid way along its length, used for housing a heating pad.

FIG. 45

DETAIL OF HEATING PAD

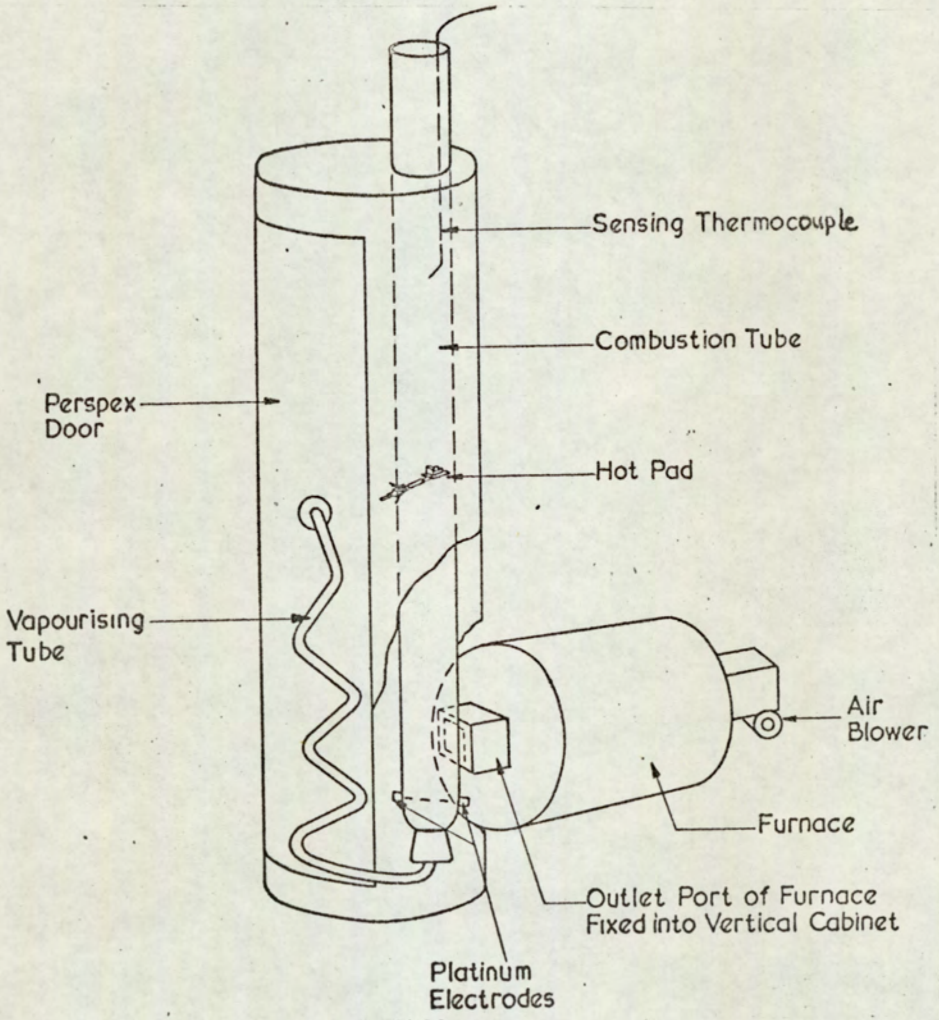


The heating pad primarily consisted of 5 turns of 0.005 ins. diameter nichrome resistance wire around 0.010 ins. thickness mica sheet. Mica sheet was bound to the top and bottom of this element for protection. The top of the pad was fitted with a clip of platinum foil for securing the sample boat. The boats were of aluminium and were supplied by Hewlett & Packard for use with a F. & M. Model 185 Analyser.

A 'sensing' thermocouple, was fitted with its tip at the centre of the combustion tube diameter, 12 ins. above the heating pad. This was 0.040 ins. stainless steel sheathed cromel alumel thermocouple, connected to a potentiometric recorder, having a full scale deflection of 10 Mv.

FIG. 46

ARRANGEMENT OF COMBUSTION TUBE AND FITTINGS IN THE HEATED CABINET



The objective of these experiments was to volatilise metal halides and similar materials into the path of the propagating flame and observe the quenching action of the inhibitor, using the thermocouple as a guide to the quenching efficiency of each compound.

7.3.1. Procedure

Experiments were again carried out at 100°C. The air flow was adjusted so as to give a constant delivery of 2.55 lit./min. At this rate one complete flushing of the apparatus with fuel/air mixture took approximately one minute. The motor driving the gear train was switched on and the apparatus allowed to be flushed with the mixture for about 10 mins. After this period a spark was passed between the electrodes and the flame progression through the combustion tube observed. The velocity and nature of the flame depended upon the concentration of fuel in air. The flame found to be most suitable for this work was a relatively slowly propagating blue flame which could be obtained just above the lower flammability limit of the fuel.

When conditions for producing this type of flame had been found the stop clock was started and a spark struck across the electrodes at three minute intervals. If a flame was propagated through the length of the tube at each of six repeats then the concentration of fuel in air was carefully determined as described in section 7.2.

At subsequent re-use of the equipment the same mixture was readily obtained by resetting the metering devices as for this experiment. It was not necessary to carry out this determination on every occasion.

When a flame passed completely through the mixture it was detected by the thermocouple and recorded as a sharp increase in temperature at the recorder. The object of the experiment was to determine the minimum concentration of inhibitor which, when volatilised from the sample boat, would quench the propagating flame before it reached the thermocouple.

A small quantity (1 - 10 mgs.) of inhibitor was weighed into the aluminium boat which was then transferred to the heating pad. The stop clock was reset and after 2 mins. 45 secs. (approximately) current was supplied to the heating element. When all of the material had volatilised (time depended upon the material under investigation) a spark was struck across the electrodes and the progress of the flame observed. If sufficient inhibitor was present to quench the flame before it reached the thermocouple then the procedure was repeated, reducing the amount of inhibitor used, by small quantities until a flame propagated completely through the tube.

The temperature attained by the heating pad was not accurately determined but it was estimated to be in the order of 700°C. At this temperature the 'life', of the element was approximately one hundred 'heatings'. Elements were relatively easy to construct and it was attempted to reproduce the dimensions as accurately as possible each time.

7.4. Samples

The fuel used for all of the experiments was laboratory reagent grade toluene.

TABLE XVIII

INHIBITORS USED

Inhibitor	Supplier
Antimony Trifluoride	Hopkins & Williams
Antimony Trichloride	
Antimony Tribromide	
Antimony Tri-iodide	
Arsenic Tri-iodide	
Arsenic Trioxide	
Aluminium Chloride	
Bismuth Trioxide	
Ammonium Chloride	
Ammonium Bromide	
Antimony Trioxide	Anchor Chemicals
Mercuric Chloride	Hopkins & Williams
Mercuric Bromide	
Mercuric Iodide	
Phosphorus Pentachloride	
Hexamine	
tris 2,3 Dichloropropyl Phosphate	Kingsley & Keith (Hooker Chemicals)
Polyvinyl Chloride	I.C.I. Ltd.
Cereclor 70	" "
Dechlorane 4070	Kingsley & Keith (Hooker Chemicals)

Table XVIII continued.../

Inhibitor	Supplier
Flammex 4BS	F. W. Berk & Co.,
" 5BT	
" 5AE	
Dicyandiamide	Hopkins & Williams

Some materials were used in the form of 50 : 50 by weight mixtures. The mixture components were hand mixed and intimately ground together with an agate pestle and mortar. Other materials were tested in the form of 50 : 50 mixtures with an inert material (alumina), in order to assist the accuracy of weighing very small quantities. The mixtures were prepared in a similar manner to those described before. In the case of these materials results are presented in terms of only the active species.

The results obtained from these experiments are presented in Tables XIX, XX and XXI. Q_{EX} is the minimum quantity in grammes of inhibitor which quenched the flame before reaching the thermocouple.

TABLE XIX

Q_{EX} VALUES OF MIXTURES

Inhibitors		Q_{EX}
1 pt. Cereclor 70	1 pt. Antimony Trioxide	0.0008 g.
1 pt. PVC	1 pt. " "	0.0013 g.
1 pt. Dechlorane 4070	1 pt. " "	0.0045 g.
1 pt. Flammex 4BS	1 pt. " "	0.0047 g.
1 pt. Flammex 5BT	1 pt. " "	0.0063 g.
1 pt. Flammex 5AE	1 pt. " "	0.0028 g.
1 pt. Cereclor 70	1 pt. Arsenic Trioxide	0.0022 g.
1 pt. Cereclor 70	1 pt. Bismuth Trioxide	0.0014 g.
1 pt. T23P	1 pt. Dicyandiamide	0.0026 g.

TABLE XX

Q_{EX} VALUES OF INORGANIC SINGLE SUBSTANCES

Inhibitors	Q_{EX}
Antimony Trichloride	0.00065 g.
Antimony Trifluoride	0.0014 g.
Antimony Tribromide	0.0005 g.
Antimony Tri-iodide	0.0005 g.
Arsenic Tri-iodide	0.0015 g.
Arsenic Trioxide	0.0022 g.
Aluminium Chloride	0.0022 g.
Ammonium Chloride	0.0028 g.
Ammonium Bromide	0.0032 g.
Mercuric Chloride	0.0030 g.
Mercuric Bromide	0.0027 g.
Mercuric Iodide	0.0028 g.
Phosphorus Pentachloride	0.0033 g.

TABLE XXI

Q_{EX} VALUES OF ORGANIC SINGLE SUBSTANCES

Inhibitors	Q_{EX}
Cereclor 70	0.0028 g.
Polyvinyl Chloride	0.0029 g.
Dechlorane 4070	0.0061 g.
Flammex 4BS	0.0025 g.
Flammex 5AE	0.0012 g.
Flammex 5BT	0.0030 g.
Hexamine	Increased burning velocity.

For clarity, histograms of the results presented in tabular form above, were drawn (Figs. 47, 48 and 49). It should be noted that the smaller the value of Q_{EX} the greater the efficiency of the inhibitor under these test conditions.

FIG. 47

Q_{EX} VALUES OF ORGANIC SINGLE SUBSTANCES

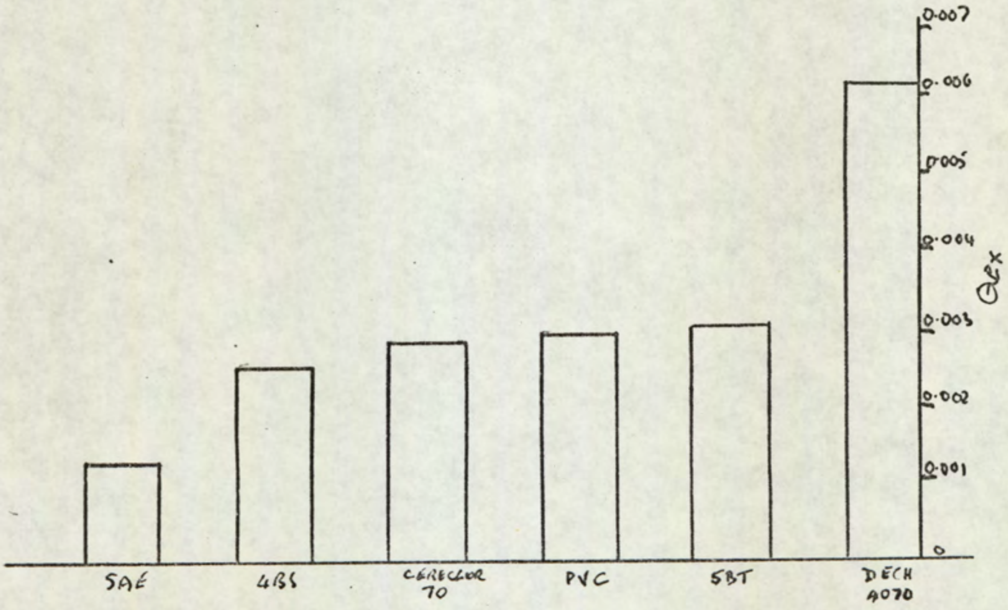


FIG. 48

Q_{EX} VALUES OF INORGANIC SINGLE SUBSTANCES

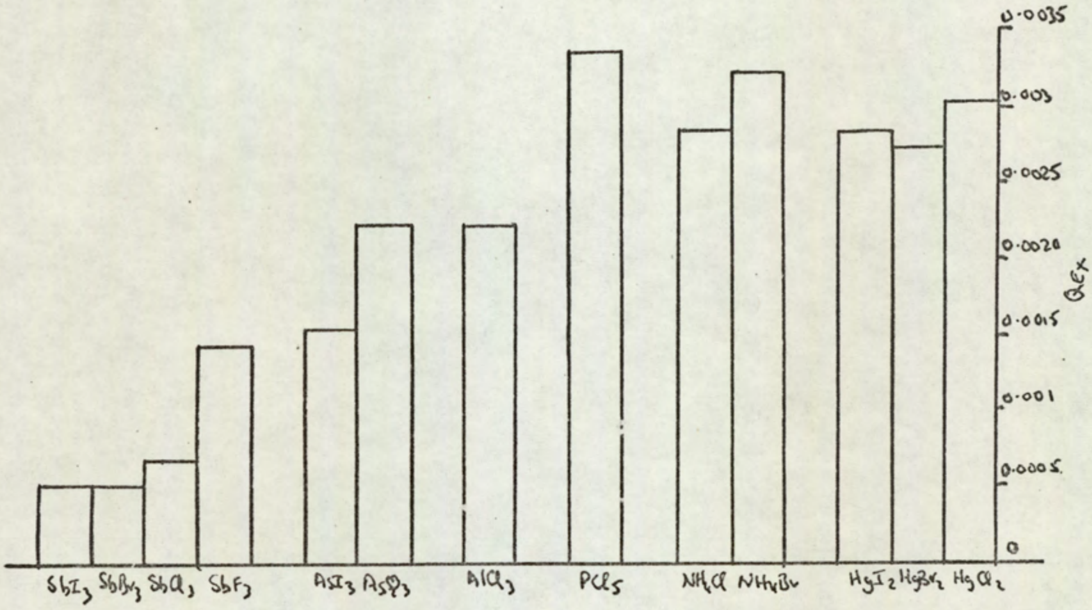
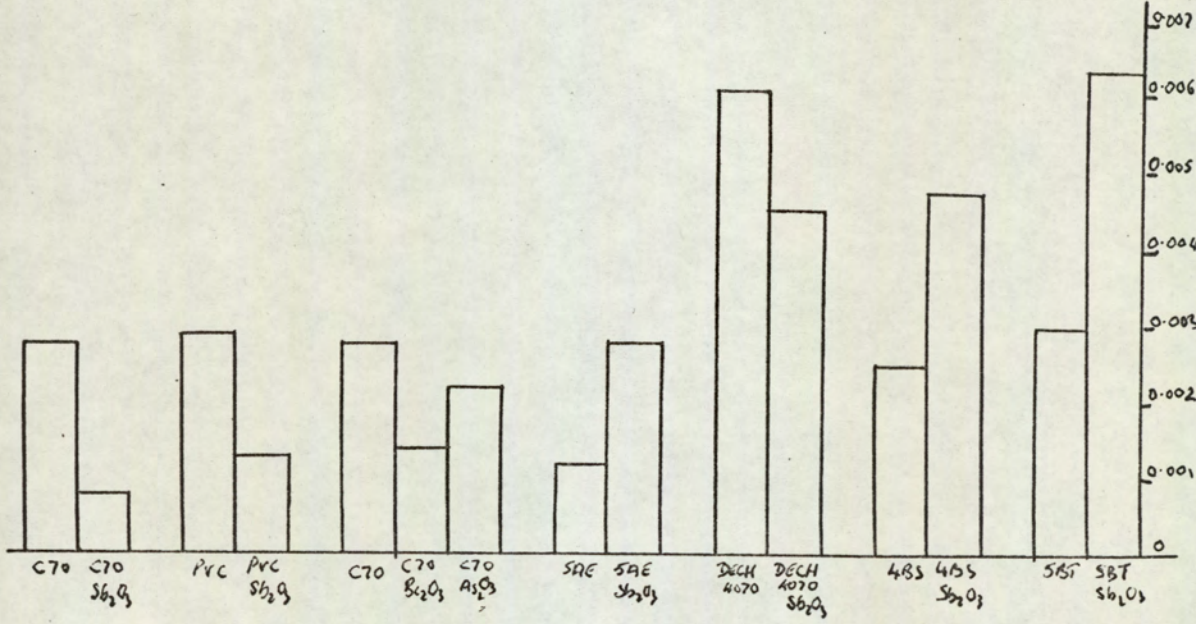


FIG. 49

Q_{EX} VALUES OF MIXTURES



CHAPTER 8

THE EFFECT OF METAL HALIDES AND OTHER COMPOUNDS ON THE FLAMMABILITY OF RESIN SYSTEMS

The study of the effect of inhibitors on model flames led to predictions regarding the requirements of efficient flame retardant systems. It was thought necessary, for the sake of completeness, to test some of these proposals in practical systems. A general purpose resin, from a different source to that used for previous work, was used. This was based on maleic and phthalic anhydride and propylene glycol cross linked with styrene, further details were not available but it was supposed that it was substantially the same as that used in the previous work.

The candle burning test was used for assessing the relative effectiveness of the systems.

8.1. Experimental

8.1.1. Sample Preparation

TABLE XXII

ADDITIVES USED

Trade Name	Chemical Nature	Supplier
-	Antimony Trichloride	Hopkins & Williams
-	Antimony Tribromide	
-	Mercuric Chloride	
-	Mercuric Iodide	
-	Ammonium Chloride	
-	Ammonium Bromide	
-	Dicyandiamide	
-	Arsenic Trioxide	
-	Bismuth Trioxide	

Table XXII continued.../

Trade Name	Chemical Nature	Supplier
-	Antimony Trioxide	Anchor Chemicals
Firemaster T23P	tris 2,3 (dibromopropyl) phosphate	Kingsley & Keith (Hooker Chemicals)
Cereclor 70	Solid chlorinated paraffin 70% Chlorine	I.C.I.
PVC P65-50	Polyvinyl Chloride	I.C.I.
Dechlorane 4070	Perchlorocyclodecane 70% Chlorine	Kingsley & Keith (Hooker Chemicals)
Bromoparaffin	Brominated paraffin	I.C.I. Dev. Prod.

TABLE XXIII

FORMULATIONS TESTED

Mixture No.	Resin	Additives
1	100	-
2	100	15 Antimony Trichloride
3	100	15 Antimony Tribromide
4	100	15 Mercuric Chloride
5	100	15 Mercuric Iodide
6	100	15 Arsenic Trioxide
7	100	15 Ammonium Bromide + 15 Antimony Trioxide
8	100	15 Ammonium Chloride + 15 " "
9	100	15 Cereclor 70 + 15 Arsenic Trioxide
10	100	15 Cereclor 70 + 15 Bismuth Trioxide
11	100	15 Dechlorane 4070 + 15 Bismuth Trioxide
12	100	15 PVC P65-50 + 15 Antimony Trioxide
13	100	15 T23P + 15 Dicyandiamide

Table XXIII continued.../

Mixture No.	Resin	Additives
14	100	3.75 PVC P65-50 + 7.5 Antimony Trioxide
15	100	7.5 PVC P65-50 + 7.5 " "
16	100	11.25 PVC P65-50 + 7.5 " "
17	100	3.75 Cereclor 70 + 7.5 " "
18	100	7.5 " 70 + 7.5 " "
19	100	11.25 " 70 + 7.5 " "
20	100	15 " 70 + 7.5 " "
21	100	18.75 " 70 + 7.5 " "
22	100	15 Bromoparaffin
23	100	15 Bromoparaffin + 15 Antimony Trioxide
24	100	10 Cereclor 70 + 5 Bromoparaffin + 7.5 Antimony Trioxide
25	100	7.5 Antimony Trioxide

Small batches only, were prepared of each mixture, therefore the procedure described in Chapter 3 could not be used. The additives were mixed, by hand in paper cups with wooden spatulas, until they appeared to have dispersed uniformly. Benzoyl peroxide was used as polymerisation initiator and the curing cycle was as described in Chapter 3. Antimony trichloride and also antimony tribromide tended to melt under these conditions and migrate to the surface of the cured sheet. This was removed by careful wiping before the specimen was tested. As a result of this it was not possible to be certain of the exact concentration of these compounds which was incorporated.

8.1.2. Test Procedure

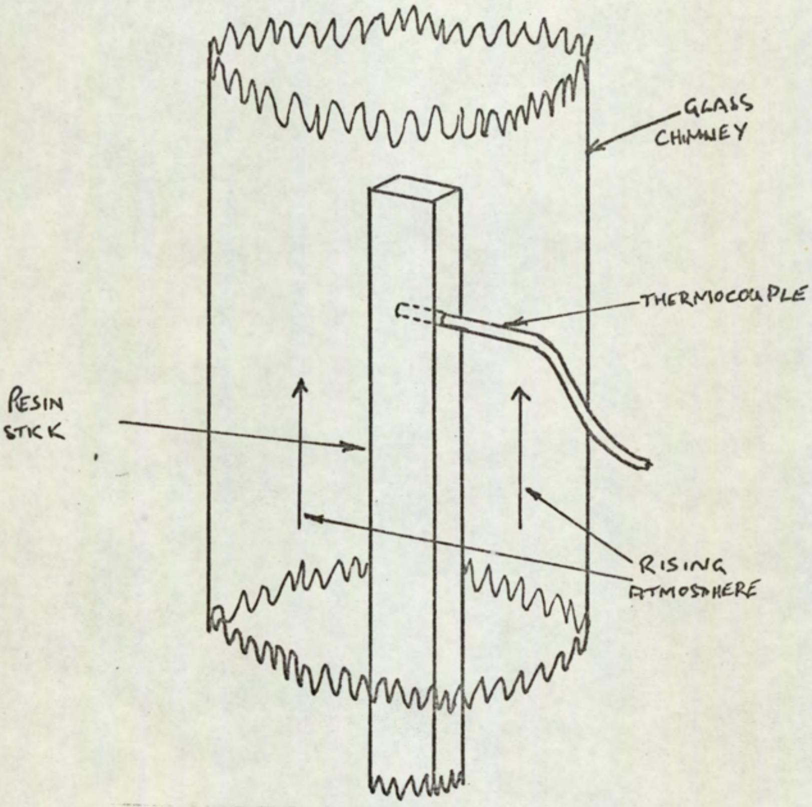
The candle burning test conditions were used in order to obtain temperature measurements inside the burning resin stick, at the critical oxygen concentration. Initially the oxygen index of each resin formulation was determined using the procedure as described in Chapter 3. These conditions were then used for the temperature measurements.

Holes were drilled into the thinnest edge of the resin stick. These were 0.045 ins. diameter and were drilled to a depth of half the width of the stick, 2 cm. from the top edge of the stick. A 0.040 ins. stainless steel sheathed cromel-alumel thermocouple was inserted in the hole through an orifice of similar diameter which had been made in the glass chimney. A detail of this arrangement is shown in Fig. 50.

The stick was ignited at the critical oxygen concentration and the temperature detected by the thermocouple was recorded. The maximum temperature attained as the combustion front spread past the thermocouple was observed. Two sticks of each mixture were burnt and the mean maximum temperature recorded. In a similar way flame temperatures for each sample was noted.

FIG. 50

DETAIL OF THERMOCOUPLE INSERTION



8.2. Results

TABLE XXIV

OXYGEN INDEX AND TEMPERATURE DATA FOR EACH RESIN MIXTURE

Mixture No.	n	Max. Temp. Resin °C	Flame Temp. °C
1	0.185	418	700
2	0.247	253	791
3	0.283	224	752
4	0.200	422	705
5	0.200	317	705
6	0.215	451	705

Table XXIV continued.../

Mixture No.	n	Max, Temp. Resin °C	Flame Temp. °C
7	0.254	326	766
8	0.289	288	714
9	0.292	398	800
10	0.265	351	771
11	0.252	468	705
12	0.269	248	733
13	0.263	278	700
14	0.220	441	705
15	0.254	446	705
16	0.260	446	705
17	0.220	341	705
18	0.270	408	705
19	0.292	379	705
20	0.287	315	655
21	0.283	467	664
22	0.220	353	674
23	0.276	315	705
24	0.299	363	788
25	0.204	357	687

The results above are illustrated in the following figures.

FIG. 51

THE EFFECT OF INORGANIC ADDITIVES ON THE OXYGEN INDEX OF THE RESIN

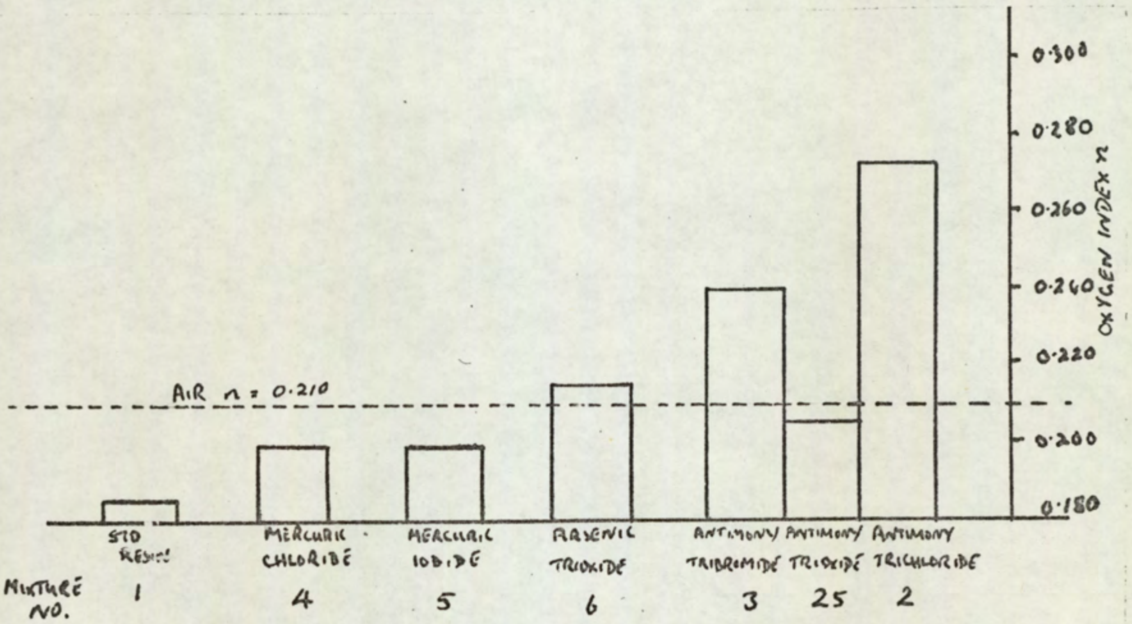


FIG. 52

THE EFFECT OF MIXTURES ON THE OXYGEN INDEX OF THE RESIN

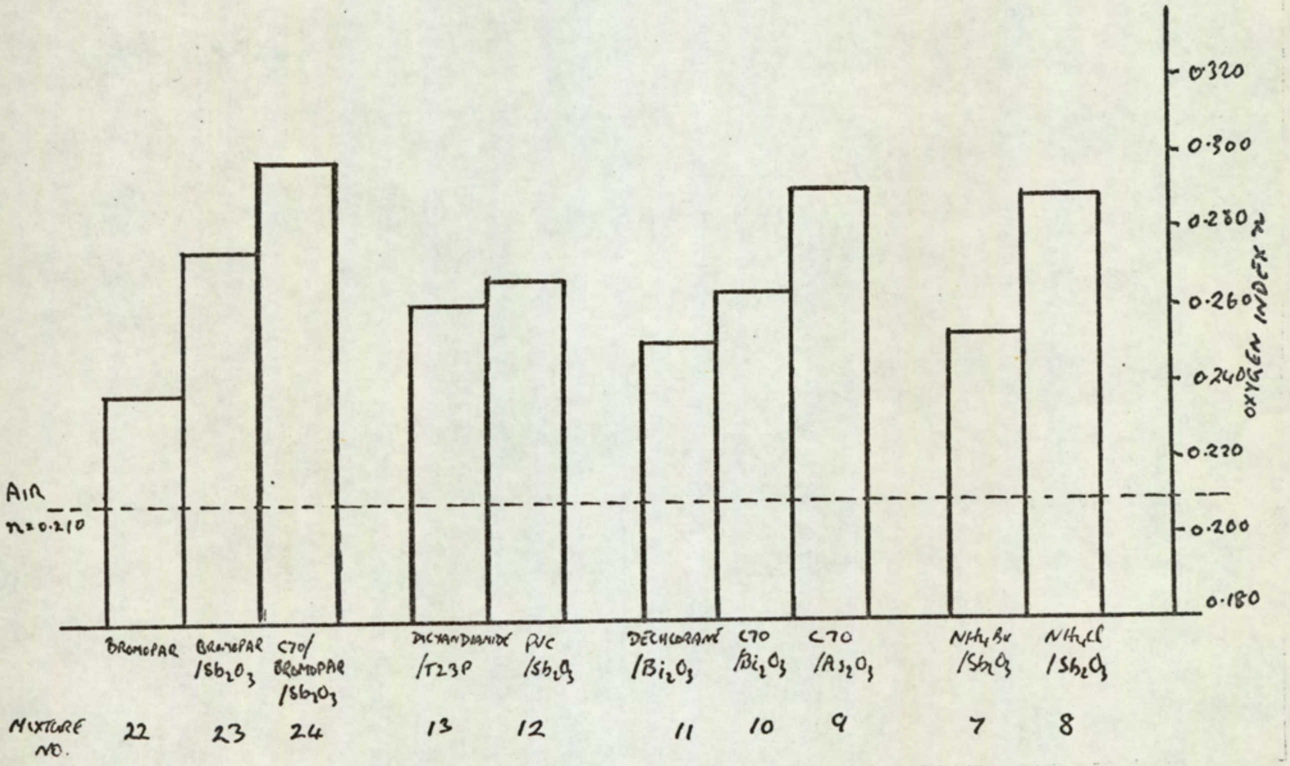
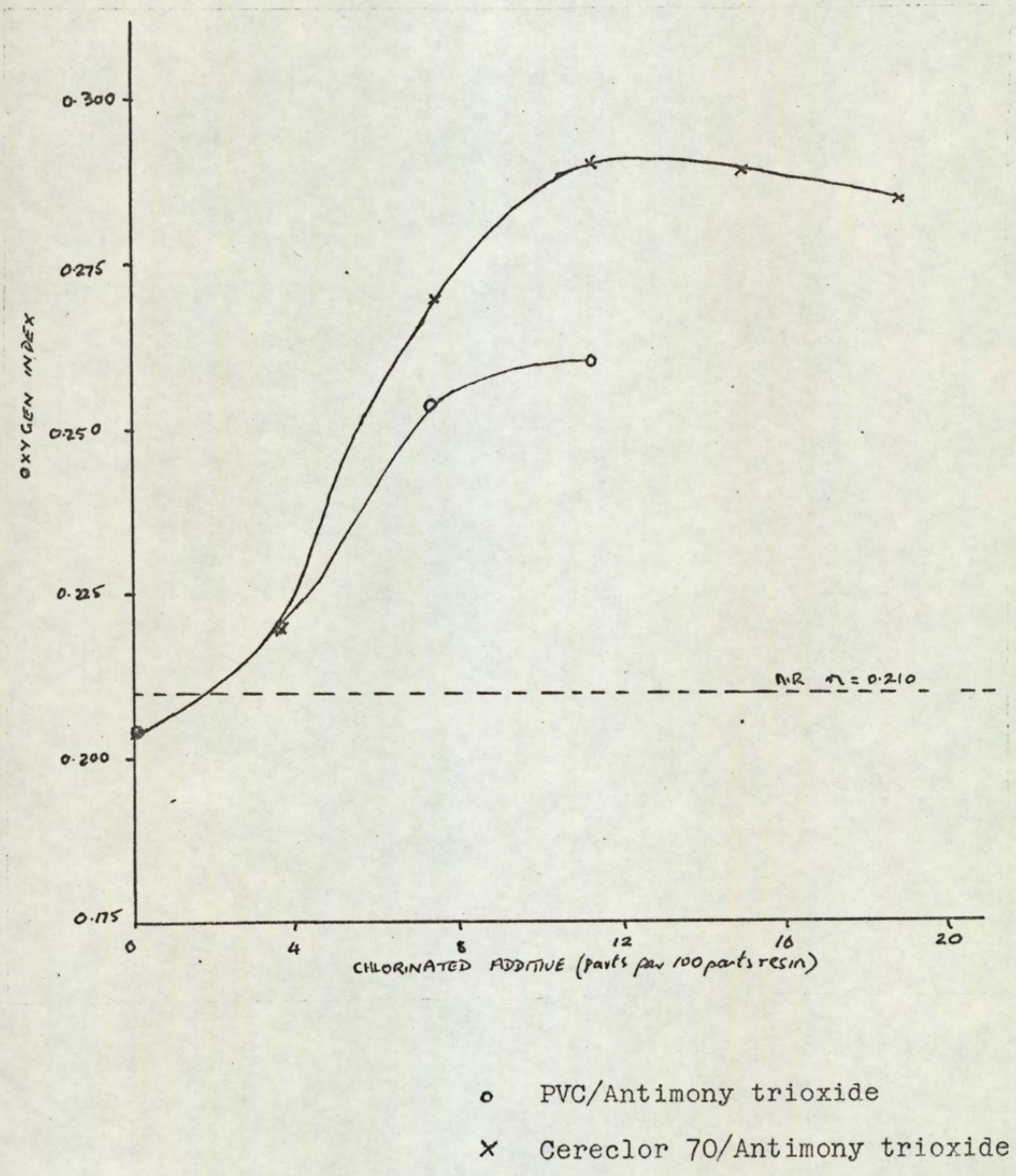


FIG. 53

THE EFFECT OF HALOGENATED COMPOUND/ANTIMONY TRIOXIDE RATIO ON THE OXYGEN INDEX OF THE RESIN



CHAPTER 9

DISCUSSION

The results presented in the experimental chapters are discussed and an attempt is made to interpret them. Each experiment is initially considered separately and the order in which the work was carried out is justified.

9.1. The Effect of a Series of Commercial Flame Retardant Additives on the Flammability of a general purpose Polyester Resin

9.1.1. Chlorinated Additives - Effect on Oxygen Index

The effect of chlorine in chlorinated paraffin, cyclic decane and chlorinated phosphate was examined. Addition of antimony trioxide greatly enhanced the effectiveness of the chlorinated paraffins and to a lesser extent the cyclic decane. Four chlorinated paraffins (Cereclors - see Appendex I) were studied, three of which were liquids and one solid. Probably the most significant result was the lower efficiency of the liquid Cereclor 70L compared with the solid Cereclor 70 both containing 70% by weight chlorine. The other two liquid Cereclors (65L and S52) were used at concentrations such as to give the same level of chlorine in each resin mixture, even so, oxygen indexes decreased with decreasing concentration of chlorine. Distillation experiments indicated that as the volatility of the Cereclor increased the flame retardant effectiveness decreased. It seemed likely therefore, that the flame retardant effectiveness depended upon the ability of the chlorinated compound to decompose whilst in the solid phase and that the parent molecular species was a relatively ineffective flame retardant.

From these facts it was possible to postulate two inhibition mechanisms.

1. Interference with solid phase degradation reactions by the decomposition of the halogenated material. It is known that heating chlorinated paraffins results in splitting out of hydrogen chloride, producing a randomly distributed polyene structure, along the carbon chain. At a suitable elevated temperature cyclisation (inter or intramolecular) may occur at these ethenic sites.

2. Reaction between the halogenated decomposition species (hydrogen chloride) and antimony trioxide producing a flame poisoning species (X).

Other workers[43, 44, 47] indicated that combinations of chlorinated additive with antimony trioxide were primarily active in the vapour phase, the above observations substantially agree with this.

In effect the action of three halogen species in the flame was observed (i) Hydrogen chloride (resin mixture No. 1) (ii) Chlorinated paraffin plus some (X) (resin mixture Nos. 4, 5 and 6). (iii) (X) alone (resin mixture Nos. 3 and 7). Oxygen indexes showed that resin mixtures likely to release (X) into the flame were less flammable than the others.

Doubling the concentration of antimony trioxide used for a given level of Cereclor 70 had little effect on the oxygen indexes (resin mixture Nos. 3 and 7). Probably indicating that an optimum ratio is around 1 : 2 antimony trioxide/Cereclor 70.

The two Dechloranes were less effective than the Cereclors probably because they decompose only at high temperatures and tend to sublime below this. Obviously this does not favour reaction with antimony trioxide.

Synergism between Cereclor 70 and a mixture of arsenic trioxide and bismuth trioxide was studied (resin mixture No. 23). A lower order of synergism was observed. The addition of tris 2,3 (dichloropropyl) phosphate had little effect on the oxygen index of the standard resin. Synergism was not observed when antimony trioxide was added to this system.

9.1.2. Brominated Additives - Effect on Oxygen Index

The effect of bromine, in different chemical environments, on the oxygen index of the standard resin was studied. Pentabromotoluene (Flammex 5BT - See Appendix I), tetra (pentabromo phenoxy) silane (Flammex 4BS), tribromophenyl allyl ether (Flammex 3AE), pentabromophenyl allyl ether (Flammex 5AE) and tris 2,3 (dibromopropyl) phosphate (T23P).

The first conclusion reached, on studying the results, was that under the conditions used the chlorine compounds tested were, broadly speaking, more effective than the bromine. This is not to say that in every case chlorine was a more effective flame inhibitor than bromine, differences in chemical environment must be considered.

It was established that the combinations of chlorinated additive and antimony trioxide were primarily active due to decomposition of the chlorine compound in the solid phase, producing a species which reacted with antimony trioxide resulting in a volatile antimony species (X). It was assumed that a similar sequence of events occurred in the case of the brominated compounds. Oxygen indexes of the resin mixtures containing 5BT, 3AE and 4BS with antimony trioxide (resin mixture Nos. 15, 16 and 17) could be explained with reference to the volatility of the bromine compound. 3AE and 5AE were substituted for part of the styrene monomer (to give concentrations equivalent to 15 pph resin). The mixture containing 5AE gelled on standing overnight and was discarded.

Appendix III shows that 4BS has a decomposition temperature of 380°C and is non volatile. 3AE decomposes at 200°C but sublimes above 150°C. 5BT has a decomposition temperature of 360°C but sublimes well below this. The oxygen indexes for resin mixtures 15, 16 and 17 were 0.346, 0.328 and 0.293 respectively. As 4BS and 5BT have about the same decomposition temperature the differences in oxygen index could only be attributed to the volatility differences. Had 3AE not been chemically bonded, in the form of cross links, an anomalous situation would have arisen.

9.1.3. Other Additives - Effect on Oxygen Index

The addition of TXP and TTP (resin Nos. 18 and 19) had little effect on the oxygen index of the standard resin. Antimony trioxide showed no synergistic activity with TTP (resin mixture No. 20).

Calcium and zinc metaborates were also investigated (resin mixture Nos. 21 and 22), these showed little effect. This was not particularly surprising as borates have previously been used in cellulosic materials which have different degradation mechanisms to polyesters. It was felt reasonable, therefore, to conclude that borates were specific in inhibiting solid phase degradation of cellulosic materials.

9.1.4. The effect of Additives on the Flame

The flame produced when the standard resin was burned tended to be small and stable. At the limiting oxygen concentration the size of the flame decreased until it was the same width as the stick. Below the limiting oxygen concentration the flame decreased still further in size until it was finally extinguished. This mode was common also for those mixtures which had low oxygen indexes. On the other hand, those materials with relatively high oxygen indexes, tended to burn with stable flames only in oxygen concentrations well above the limiting values. These were generally combinations of halogen compound with antimony trioxide, indicating that inhibition was mainly in the gas phase. This type of mixture burned with large flames and at the limiting concentration these were apt to flicker and sometimes lift completely away from the material. Extinction in these cases was invariably preceded by violent flickering.

9.1.5. The effect of Additives on After Glow Properties

In general, resin mixtures containing halogenated compounds, continued glowing after burning had ceased; this was particularly so in the cases of the mixtures with antimony trioxide. The phenomenon is attributed to the solid phase oxidation of carbon in the highly exothermic reaction:-

$$2C + O_2 \longrightarrow 2CO$$

Fig. 7 page 70 shows typical traces of temperatures recorded in ignition determinations on the standard resin, the resin containing halogenated organic compounds and antimony trioxide and the resin containing halogenated phosphorus compounds, with and without antimony trioxide. After glow was not seen in the standard resin or those materials containing phosphorus, but is a characteristic of those materials containing halogen compounds and antimony trioxide. Differential thermal analysis (d.t.a.) and thermogravimetric analysis (t.g.a.) would probably yield relevant information on this problem.

9.1.6. The Setchkin Ignition Test

In every case except those of the borates and T23P alone, addition of retardants to the standard resin raised the ignition temperature. No general trend was apparent in the numerical values of these temperatures but there were similarities in the mode of ignition of the various classes. Those materials containing halogenated compound/ antimony trioxide tended to ignite only after a series of explosions. These did not occur in the cases of the phosphorus containing additives, indicating that halogen compound/antimony trioxide mixtures were active in gas phase inhibition. It seemed that fuel gases and oxidant were present in concentrations favourable to burning and that ignition occurred but propagation of the flame was not possible, probably due to the joint effects of blanketing and flame poisoning. Further evidence in support of gas phase inhibition was that with those resins containing halogen and antimony trioxide, evolution of white fumes prior to ignition was apparent. Only after the rate of issue of these fumes had considerably decreased did ignition occur.

The traces (Fig. 7 page 70) show that although the shapes of the curves are different, for different additives, basically the same events occur. Initially a drop in temperature, due to sample introduction, followed by a warm up period when the sample attains the temperature of its surroundings. The sample temperature then increased above the initial temperature in the crucible, this is the self heating period and is due to exothermic decomposition reactions. On reaching a certain rate of reaction ignition occurred and burning continued in the vapour phase, sometimes followed by glow in the residue. After the flame was extinguished, or glow had ceased, a rapid reversion to the original temperature occurred.

It was apparent that those materials classed as self extinguishing according to BS.2782 Method 508A were more precisely defined in terms of their oxygen indexes. The candle burning test was useful in preliminary assessment of flame retardant mixtures.

The next stage of the work (Chapter 4) was concerned with elucidating the nature of (X) and also studying a number of analogous systems.

9.2. Quantitative Analysis of Reaction Products from Heating together Chlorinated Compounds with Antimony Trioxide

Total hydrogen chloride produced from the decomposition of Cereclor 70 and also PVC at 500°C over 15 mins. was determined. On attempting to determine excess hydrogen chloride from mixtures of Cereclor 70 and antimony trioxide it was found that volatile antimony chlorides were swept into the alkali solution and were hydrolysed, producing hydrogen chloride. Erroneous results were thus at first obtained. These volatile antimony chlorides were trapped out with liquid nitrogen, after careful regulation of the air flow. Reaction stoichiometries were thus easily calculated, from weight loss data and hydrogen chloride determinations. In order to confirm these quantities volatile antimony was also determined. SbIII was determined by iodine titration on the trapped out material and it was found that, within experimental error, all of the volatile antimony was trivalent.

9.2.1. Calculation of Reaction Stoichiometries

a. Cereclor 70/Antimony Trioxide

All data was obtained at 500°C over 15 mins.

From weight loss experiments:-

i. The degree of volatility V of Cereclor 70 was 88.0%.

ii. Cereclor 70/antimony trioxide V was 82.3%.

Assuming the Cereclor in the mixture had the same percentage volatility as when alone. The percentage antimony trioxide which reacted with hydrogen chloride:

= 2 x (82.3 - 44) = 76.6% of the total antimony trioxide.

Compare analytical determination of volatile SbIII:

= 75.1% of total Sb.

From hydrogen chloride determinations 87.5% of the total chlorine was evolved as hydrogen chloride. From hydrogen chloride determination on the mixture 9.2% of total chlorine was evolved as excess hydrogen chloride.

Chlorine, as hydrogen chloride which reacted with antimony trioxide = 87.5 - 9.2%

= 78.3% of total chlorine

Giving reaction stoichiometries of:-

$$\frac{76.6}{291.6} : \frac{78.3}{35.5} \times \frac{70}{100}$$

$$0.262 : 1.54$$

$$\underline{1 : 5.88}$$

Indicating:-

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

This was confirmed by the evidence for all of the volatile Sb being trivalent.

b. <u>PVC/antimony trioxide</u>

A similar conclusion to that for Cereclor 70/antimony trioxide was expected.

In this case weight loss experimental data and hydrogen chloride determination on the PVC only, was obtained. All data was obtained at 500°C over 15 mins.

From weight loss experiments:-

i. The degree of volatility V of PVC alone was 96.3%

ii. PVC/antimony trioxide V was 88.0%

Assuming that the PVC in the mixture had the same volatility as when heated alone then the percentage antimony trioxide which reacted with hydrogen chloride

= 2 x (88.0 - 48.2)%

= 73.6% of the total antimony trioxide

From hydrogen chloride determination on PVC alone it was seen that 98.0% of the total chlorine was evolved as hydrogen chloride. The stoichiometry of the reaction calculated below does not take into account excess hydrogen chloride which did not react with antimony trioxide.

Reaction stoichiometry

$$\frac{74}{291.6} : \frac{98}{35.5} \times \frac{56.8}{100}$$

$$0.254 : 1.57$$

$$\underline{1 : 6.17}$$

From this it seemed fair tc predict that the active species was again antimony trichloride.

It must be emphasised, however, that these determinations were made on the additives alone and these results represent ideal condition for reaction which would not be achieved on incorporation into the resin. However, it is probably fair to assume that the predicted reaction would be predominant.

It has therefore been shown that in the cases of antimony trioxide/Cereclor 70 and antimony trioxide/PVC the reaction product (X) was antimony trichloride. Further, production of this species is responsible for the so called synergistic effect between antimony trioxide and chlorine compounds.

9.3. Weight Loss Experiments

V was defined as that percentage of the original which was volatile at the temperature under consideration.

It was shown that effective flame retardant systems produced metal halides on heating, ideally these would be volatile near the decomposition temperature of the resin. Weight loss experiments were used as simple methods of assessing relative reactivity of various mixtures.

Fig. 9 illustrates that Cereclor 70 was relatively volatile at 310°C and that also at this temperature decomposition occurred, the resulting hydrogen chloride reacted with antimony trioxide producing antimony trichloride (antimony trioxide was shown to be 0.01% volatile at 500°C for 30 mins.) At this temperature (310° C) V for the mixture was higher than for the Cereclor alone, also, the curve for the mixture increased more steeply. This was probably important from a flame retarding point of view, as it seems likely to prevent initial ignition of the resin it is desirable that a reasonable quantity of volatile flame inhibitor be present early in the degradation mode of the resin.

Figs. 10 and 11 at 410°C and 500°C follow much the same pattern with the mixture reaching maximum volatility more quickly than the Cereclor alone.

Dechloranes were not considered to decompose appreciably below 400°C (see Appendix III). For this reason experiments were carried out at 410°C, 460°C and 500°C. At 410°C (Fig. 12) V for Dechlorane 4070 alone increased linearly between 5 and 30 mins. reaching a value of 92% at 30 mins. The shape of the curve of the mixture was completely different rising sharply and reaching a maximum of approximately 85% after 4 mins., indicating reaction.

NOTE: The times quoted should only be used for comparative purposes as they include a sample warm up period.

At 360°C for 60 mins. the mixture achieved a V value of 51%, confirming decomposition to be negligible, although Dechlorane 4070 was volatile at this temperature.

Fig. 13 and 14 at 460°C and 500°C follow much the same pattern, with Dechlorane 4070 reaching complete volatility.

It has been shown that both Dechlorane 4070 and Cereclor 70 react with antimony trioxide under the right conditions. The lower oxygen indexes of the Dechlorane mixture (resin mixture No. 8 page 58) was probably due to the higher decomposition temperature of the Dechlorane, i.e. Dechlorane 4070 is capable of volatilising below its decomposition temperature. It is therefore absolutely important to be clear of the difference between volatility and decomposition. The results suggest that if the Dechlorane 4070/antimony trioxide resin mixture was tested under more rigorous conditions then it may appear more effective. The candle burning test assesses the flammability of materials under conditions of low thermal stress but possibly does not describe their performance under conditions more closely resembling those found in a real fire.

Figs. 15, 16 and 17 compare values of V of the four Cereclors with antimony trioxide at 310°C, 410°C and 500°C. It is clear that at each of the three temperatures the Cereclor 70/antimony trioxide mixtures are most volatile, confirming the previous observations that Cereclor 70 decomposes predominantly in the solid phase. In every case the curves rise above a V value of 50%, indicating that reaction does occur.

The V values are in agreement with the oxygen index values obtained for these mixtures in the standard resin. The relevant mixture Nos. are 3, 4, 5 and 6 page 58. Giving oxygen indexes of 0.350, 0.295, 0.287 and 0.260 respectively.

Figs. 18, 19 and 20 compare the effect of incorporation of Cereclor 70/antimony trioxide mixtures on the volatility of the standard resin at various temperatures. At 310°C (Fig. 18) the rate of evolution of gaseous fuels from the standard resin was not great enough for ignition to occur. At this temperature appreciable reaction was observed between the Cereclor 70 and antimony trioxide which probably accounts for the increase in ignition temperature and the explosions which occurred prior to ignition.

The physical mixture of standard resin/antimony trioxide/Cereclor 70 tended to have a higher value of V than in the case where antimony trioxide/Cereclor 70 was incorporated into the resin, this was as expected. At 460°C (Fig. 19) however, the standard resin alone had a higher degree of volatilization and it is reasonable to assume that between 310°C and 460°C the rate of evolution of fuels increased to a point where ignition was possible. Figs. 19 and 20 show that the Cereclor 70/antimony trioxide mixture was more readily volatile than the standard resin, supporting what was previously said in accounting for the effectiveness of this mixture in initially preventing ignition and also for its high oxygen index rating.

Fig. 21 compares the reactivity of antimony, arsenic and bismuth trioxides with Cereclor 70. It is clear that reaction occurs in each case. The boiling points of the three trihalides are in the order bismuth trichloride > antimony trichloride > arsenic trichloride (see Appendix III) therefore the degrees of volatility are in the expected order. It is interesting to note the free energy changes for the corresponding reactions.

It is known that the algebraic sign of the free energy change for a given reaction indicates the ease of reaction.

i.e. ΔG = -ve the reaction occurs spontaneously

ΔG = 0 the system is at equilibrium

ΔG = +ve the reaction is not spontaneous.

The following reactions were considered at 500°C:-

$Sb_2O_{3(s)} + 6\,HCl_{(g)} \longrightarrow 2SbCl_{3(g)} + 3H_2O_{(g)}$ ΔG_{773} -22.7 Kcals

$Bi_2O_{3(s)} + 6HCl_{(g)} \longrightarrow 2BiCl_{3(g)} + 3H_2O_{(g)}$ ΔG_{773} -33.9 mole^{-}

$As_2O_{3(s)} + 6\,HCl_{(g)} \longrightarrow 2AsCl_{3(g)} + 3H_2O_{(g)}$ ΔG_{773} -25.6 "

$TiO_{2(s)} + 4\,HCl_{(g)} \longrightarrow TiCl_{4(g)} + 2H_2O_{(g)}$ ΔG_{773} +34.9 "

$SnO_{2(s)} + 4\,HCl_{(g)} \longrightarrow SnCl_{4(g)} + 2H_2O_{(g)}$ ΔG_{773} + 3.1 "

Values of ΔG_{773} were calculated from thermochemical data presented in Ref. 99.

It can therefore be predicted that under these conditions the trihalides of antimony, bismuth and arsenic are readily formed. The tetrahalides of titanium and tin will, however, not be expected to form under these conditions, this is in agreement with the weight loss experiments. The differences in total volatility (fig. 21) can therefore be attributed to the differences in boiling point of the respective trihalides.

Although the arsenic trioxide/Cereclor 70 had the highest total volatility this was not necessarily due to reaction, as arsenic trioxide itself has a very low sublimation temperature (below 300°C see Appendix III) under these conditions it would therefore be expected that a considerable amount of arsenic trioxide would be volatilised. It has been shown that in order to get antimony into the vapour phase it is necessary to form the halide, in the case of arsenic this is not necessary, therefore it may be predicted that mixtures of arsenic trioxide/Cereclor 70, or alternatively arsenic trioxide alone would be effective flame retardants.

Fig. 22 compares the effect of heating together ammonium halides with antimony trioxide. Ammonium bromide/antimony trioxide mixtures are considerably less volatile than ammonium chloride/antimony trioxide mixtures, at 500°C, probably due to a combination of reasons.

1. Ammonium chloride undergoes a considerably higher degree of dissociation than ammonium bromide.

2. Antimony trichloride is more volatile than antimony tribromide.

3. Although thermochemical data was not available it is likely that the tribromide is less ready to form than the trichloride.

The addition of 1 part dicumyl peroxide to 10 parts mixture had a surprising effect on the volatility curve suggesting possibly that the presence of the peroxide enhanced decomposition of ammonium bromide to hydrogen bromide.

The effectiveness of ammonium chloride in producing antimony trichloride with antimony trioxide suggests that it would probably make an effective flame retardant system.

Fig. 23 illustrates the effect of heating together Flammex 5BT (pentabromotoluene see Appendix I) with antimony trioxide, at various temperatures. Clearly no reaction occurred over the temperature range 460 - 610°C. On heating Flammex 5BT alone at 500°C for 15 mins. V was 98.4% its decomposition temperature is claimed to be 360°C but it tends to sublime well below this, suggesting that any decomposition occurs in the vapour phase.

Heating together Flammex 4BS/antimony trioxide and also Flammex 5AE/antimony trioxide at 500°C (Fig. 24) showed that a limited reaction does occur but each producing a V value of only approximately 60% indicating that antimony tribromide is not readily formed.

Fig. 25 compares the volatility of antimony trioxide/bromoparaffin and antimony trioxide/bromoparaffin with dicumyl peroxide. Dicumyl peroxide appears to have little effect on the total volatility of the mixture and it cannot be concluded that it enhances decomposition. Comparing the curve of the bromoparaffin with those of the three liquid Cereclors (Fig. 17) shows that they are very similar.

The main point to come from the work discussed so far is that combinations of Cereclor 70/antimony trioxide were the most effective flame retardant systems of those tested under candle burning test conditions but not under fire propagation test conditions due to:-

1. The decomposition of Cereclor 70 in the solid phase producing a high yield of hydrogen chloride (ammonium chloride and also PVC appeared to be effective chlorine donors).

2. The thermochemical ease of formation of antimony trichloride (bismuth and arsenic trichlorides have not been examined in sufficient detail in resin systems but it seemed possible that arsenic trioxide/Cereclor 70 or arsenic trioxide alone may produce effective flame retardant systems).

3. The decomposition temperature of the Cereclor and the boiling point of the antimony trichloride closely match the decomposition temperature range of the particular resin used.

It was shown that the volatility of halogen compound/metal oxide mixtures yield useful information regarding reactivity between the two types. In addition to those mixtures represented in figs. 9 - 25 other combinations were subjected to similar conditions, (Mixture Nos. 13 - 43 pages 77, 78 and 79). In general these did not show any reactivity or alternatively the reaction product was non volatile under test conditions, V values are presented in tabular form on pages 91 and 92. Consultation of thermochemical data and also physical properties of predicted reaction products indicate that the results obtained are feasible. In some instances (Mixture Nos. 19, 33, 34, 36, 37, 38, 39, 40 and 41) it was attempted to induce reaction by the addition of 'catalysts' these, however, were ineffective at the temperatures under consideration. It is possible that at a higher temperature these catalysts would induce reaction but the decomposition temperature of the halogen compound is considerably lower than the boiling points of the predicted halides therefore it is likely that the halogen decomposition product would be lost before reaction could occur.

9.4. BS.476 Fire Propagation Test

Selected resin formulations were tested under BS.476 fire propagation test conditions. As explained in Chapter 5 this test method was specifically designed to assess the relative fire hazard of room lining materials. It's use in the present research was essentially as a standard test method which provided conditions of considerably higher thermal stress than the candle burning test, the results obtained should therefore only be considered in this context.

The test procedure was not easy to carry out, difficulty mainly arising from achieving an air tight seal around the detachable wall. It was found that continual renewal of the asbestos paper gasket was necessary. Another source of difficulty was the siting of thermocouple tips inside the chimney cowling, slight differences in positioning resulted in significant differences in the temperature recorded. It was found, however, that once experience had been gained in using the equipment satisfactory results could be achieved.

The performance index is an aggregate of the calculated rates of temperature rise at specified intervals. The lower the index the safer the material. The results presented in Chapter 5 give values for 0 - 3, 4 - 10 and 12 - 20 minute intervals. The first section indicates the ease of ignition of the material by a small flame. The second the ease of ignition by a larger source of heat while the overall performance index indicates the total heat liberated by a particular sample. Table XXVI lists the resin mixture in order of effectiveness.

TABLE XXVI

COMPARISON OF CANDLE BURNING TEST AND BS.476 RESULTS

	Candle Burning Test	BS.476
Increasing Flame Retardancy ↓	Standard Resin	Standard Resin
	tris 2,3 dichloropropyl phosphate	tris 2,3 dichloropropyl phosphate
	Dechlorane 4070/antimony trioxide	Cereclor 70/antimony trioxide
	Flammex 4BS/antimony trioxide	Flammex 4BS/antimony trioxide
	Cereclor 70/antimony trioxide	Dechlorane 4070/antimony trioxide

The BS.476 fire propagation test obviously rates Cereclor 70/antimony trioxide and Dechlorane 4070/antimony trioxide in reverse positions of effectiveness compared with the candle burning test. This result is in agreement with the results obtained in the weight loss experiments.

In some instances (figs. 29, 30 and 31) the curve for the material under test just crossed the calibration curve this was due to sooting up of the thermocouples during the test. On consultation with users of similar equipment it appeared that it was necessary to remove the thermocouples and brush any soot away periodically during the test. This was not carried out due to the difficulty in replacing the thermocouple tips in exactly the same positions.

Detailed discussion of these results seemed unnecessary, the anomalous situation which arose from the weight loss experiments has been explained. It may therefore be concluded that while the candle-burning test is useful as a semi-quantitative small scale test, in order to obtain a more detailed picture of the effectiveness of a particular system it is necessary to test performance under conditions of higher thermal stress.

As explained in previous chapters, a dual approach to the problem of flammability of plastics was adopted, this particular thesis being devoted to the study of inhibitors in the gas phase. The preliminary work using resin systems was carried out, initially to provide a bank of background information and also to attempt to identify those classes of additives which were effective by gas phase inhibition. In order to more easily study flame inhibition the pyrolysis stage of the combustion of plastics was dispensed with and model fuel diffusion and premixed flames studied.

9.5. The Effect of Inhibitors on Diffusion Flames

The oxygen index was used as a measure of inhibition effectiveness. The method proved satisfactory for assessing the relative effectiveness of gaseous and liquid inhibitors but practical difficulties arose on attempting to meter solid inhibitors quantitatively into the flame zone.

Reproducible flames of model fuels were used to study the effect of liquid and solid inhibitors dissolved in the fuel. In many instances this seemed to increase the viscosity of the fuel considerably. Fig. 36 indicates that at a level of 20g inhibitor per 100g fuel all of those tested produced only negligible increases in oxygen index. It is clear that the volatilization of the additive relied on adequate feedback of heat from the flame zone and in the case of the less volatile materials feedback often was not great enough and a deposit of additive tended to form in the bowl of the burner, obstructing the passage of fuel, hence the flame extinguished through fuel starvation. The more volatile additives, however, did not suffer from this failing and were evaporated into the flame zone. While this method is unsuitable for incorporation of viscous liquids and solids it is satisfactory for the more volatile liquids.

Figs. 34 and 35 illustrate the effect of inhibitors on the oxygen index of styrene monomer and toluene flames respectively. In each case a relatively shallow increase in oxygen index was observed for mixtures below 50 : 50 by weight.

In the case of styrene flames it was not possible to burn mixtures containing greater than 75% by weight carbon tetrachloride or chloroform. However, trichloroethylene alone burned with an oxygen index of 0.430 and it seemed likely that it was behaving as a fuel and also inhibitor under these conditions. Carbon tetrachloride and chloroform probably decompose under flame conditions and inhibit flame reactions by the mechanism proposed by Rosser et al in reactions such as:-

$$HOO^{\bullet} + X^{\bullet} \longrightarrow HX + O_2 \;\ldots\ldots\ldots\ldots\; 1$$

$$OH^{\bullet} + HX \longrightarrow X^{\bullet} + H_2O \;\ldots\ldots\ldots\ldots\; 2$$

Reaction (1) representing hydrogen abstraction from the fuel and (2) the destruction of the highly active $OH^{\bullet}$ radical. X atoms are regenerated, thus the inhibition cycle is self perpetuating.

Even for additives such as bromoform a high concentration is essential before significant inhibition occurs. While this may be practicable in the case of flame extinguishment (halogenated organic compounds, particularly fluorine containing materials, are frequently used as fire extinguishers), when considering flame proofing the smallest possible concentration of retardant is desirable. Hence the use of synergists such antimony trioxide with halogenated compounds.

Figure 37 illustrates the effect of introducing anhydrous hydrogen chloride to both the fuel and atmosphere sides of a toluene diffusion flame. The results have been calculated on a molar concentration basis and it is seen that hydrogen chloride introduced to the atmosphere side of the flame is a considerably more effective inhibitor than when introduced with the fuel. This is in agreement with the results of Creitz and Simmons and Wolfhard.

As the minimum oxygen concentration in the atmosphere was taken as the criteria of effectiveness only those concentrations of hydrogen chloride which quenched under similar oxygen concentrations may be compared i.e. oxygen index values

0.185 - 0.210.

The ratios $[\mathrm{HCl}]/[\mathrm{toluene}] : [\mathrm{HCl}]/[\mathrm{atmosphere}]$ were not the stoichiometric ratios for toluene indicating that hydrogen chloride was not acting purely as an inert diluent.

Attempts to inject vaporized antimony trichloride in a stream of hydrogen chloride was quantitatively unsuccessful but it was shown that qualitatively antimony trichloride was an effective flame inhibitor. It was found necessary to aim the hypodermic needle at the base of the flame, this lead to large holes appearing in the flame until stability was completely upset and the flame lifted and was extinguished. Injection at higher points in the flame caused holes to appear but it was extremely difficult to get complete extinguishment. It seemed, therefore, that the stability of the leading edge of the flame was important and quite small concentrations of antimony trichloride upset this stability.

The pellet method of introducing metal halides into the flame was also unsuccessful. It was clear that considerable practical difficulties would have to be overcome before inhibitors could be successfully screened using the diffussion flame equipment. For this reason the modified Zabetakis equipment was built in order to use a premixed flame system as it was expected that this would be more readily adaptable to the aims of this work.

9.6. The Effect of Inhibitors on Premixed Flames.

As previously explained the main objective in setting up this equipment was that it should serve as a means of assessing the relative effectiveness of inhibitors. The types of inhibitor which were of primary importance were those which could be directly incorporated into, or could be developed, in plastics materials under conditions of combustion.

The experiments illustrated in figs. 42, 43 and 44 were therefore only carried out in order to test the equipment and observe any 'in use' peculiarities.

It was expected that flames near the lower flammability limit would be the most suitable for assessing the effectiveness of inhibitors as these would not be complicated by the presence of excess fuel, therefore figs. 42, 43 and 44 present data obtained only near the lower flammability limit. The normal procedure for presenting data on the effect of inhibitors on premixed flames is to consider fuel concentration in oxidant up to the upper flammability limit. Thus a curve may be obtained describing the limits of flammable mixtures for fuel/oxidant/inhibitor.

Zabetakis (U.S. Bureau of Mines Bull. 627) quotes lower flammability limits of ethyl acetate, styrene and n-hexane in air as 2.2%, 1.1% and 1.2% at 25°C. This compares with 3.3%, 1.8% and 1.95% obtained here at 100°C. The reason for the difference in values is the relatively low power of the ignition source used. This discrepancy was probably not important as fundamental information was not required.

The experiments using solid inhibitors were considered separately in groups. A broad distinction was made between those which were thought to volatilize unchanged and those which decomposed and/or reacted to give volatile reaction products.

9.6.1. Compounds thought to Volatilize Unchanged

The four trihalides of antimony were studied, these showed a tendency toward increasing quenching efficiency with increasing atomic weight of the halogen.

Under flame conditions it may be expected that all of these compounds would be more or less readily oxidised to the trioxide. Ease of oxidation is expected to be in the order iodide > bromide > chloride > fluoride. The other product of oxidation is the free halogen, which according to Rosser et al could be expected to readily abstract hydrogen from the fuel. The inhibition mechanism described in section 9.5. may be represented by the general equations:-

$$H\alpha \quad + \quad X^{\bullet} \longrightarrow HX \quad + \quad \alpha$$

$$\beta \quad + \quad HX \longrightarrow X^{\bullet} \quad + \quad H\beta$$

where $H\alpha$ is the fuel, X a halogen atom, HX the hydrogen halide and β such species as $OH^{\bullet}$, $H^{\bullet}$, $O^{\bullet}$, $CH_3^{\bullet}$ etc. The substitution of these active species, which are responsible for important exothermic chain branching and propagation reactions obviously results in reduced intensity in the flame zone.

Assuming the above proposal to be correct the important point is the role of the antimony trioxide in the flame zone.

Salooja[25], while investigating the anti-knock properties of lead-tetraethyl in hydrocarbon fuels showed that combustion inhibition due to this compound was entirely attributable to the lead monoxides formed. He showed that for the hydrocarbons hexane, 2 methyl pentane and 2,2 dimethyl butane the presence of either allotropic form of lead monoxide eliminated the formation of hydrogen peroxide and organic peroxide intermediates which in the absence of lead monoxide were formed in substantial quantities. He showed also that the presence of both forms of lead monoxide substantially reduced the formation of aldehyde and ketone intermediates but hydrocarbon intermediates were increased.

Cheaney et al[98] showed that the alkyls of bismuth, lead and thallium are all effective anti-knock agents whilst those of mercury are not. This was explained by the lower decomposition temperature of mercuric oxide producing volatile mercury metal. Alkyls of each of the other metals were capable of producing solid oxide particles in the form of fogs.

It would seem that an analogous situation occurred in the flame quenching properties of the halides of antimony. The higher efficiency of the iodide may be explained by its being more readily oxidised and that iodine is produced on oxidation, which in its own right is a more effective flame inhibitor than fluorine or chlorine. On the other hand, the lower efficiency of the other inorganic inhibitors may also be explained by the above argument. Of the materials studied, only the antimony halides were capable of producing solid or liquid particles in the flame. Arsenic trioxide, with a sublimation temperature of around 300°C obviously was not present as solid particles in the flame zone. Arsenic triiodide would be readily oxidised to the trioxide under these conditions and the increased effectiveness may only be attributed to the release of free iodine.

Aluminium chloride is unlikely to be oxidised to any large extent under flame conditions, hence it would be mainly present as the volatile halide, which is less effective than solid particles in the flame. Alternatively, the mercuric halides have readily decomposable oxides which yield volatile mercury. The ammonium halides obviously are not capable of yielding solid particles under these conditions, similarly with phosphorus pentachloride.

Therefore, in order for a material to be an effective flame inhibitor it must readily undergo oxidation or some other reaction forming low energy solid or liquid particles in the flame zone. A flame retardant to be used in a plastics material must also be volatile at or near the decomposition temperature of the plastics material.

9.6.2. Mixtures and Materials which Decomposed on Heating

9.6.2.1. Chlorinated Compounds

The effect of antimony trioxide in 50 : 50 mixtures with both Cereclor 70 and PVC was to reduce the total weight of mixture required to quench the flame, indicating that antimony trichloride was readily formed under these test conditions. A similar effect was observed with Dechlorane 4070 but to a lesser degree.

Dechlorane 4070 alone, however, was considerably less effective than either PVC or Cereclor 70 alone. Dechlorane 4070 would obviously be decomposed under flame conditions but it seemed likely that under these conditions Dechlorane 4070 was volatilised largely unchanged. Thus the propagating flame front meets a cloud of Dechlorane 4070. In the case of the Cereclor 70 and PVC the propagating flame front first meets hydrogen chloride. This therefore seems to be further evidence in support of the proposal that stability of the leading edge of the flame is critical and that hydrogen chloride is far more effective in reducing this stability (probably by Rosser et al's mechanism), than the whole molecular species.

Cereclor 70 with arsenic trioxide proved to be a less effective mixture than either bismuth trioxide/Cereclor 70 or antimony trioxide/Cereclor 70. This supports the hypothesis of the solid particle in the flame being the active inhibitor. Bismuth trichloride would undergo oxidation to the solid oxychloride or trioxide whilst arsenic trichloride would be oxidised to the volatile trioxide and furnish no solid particles.

9.6.2.2. Brominated Compounds

Addition of antimony trioxide had no synergistic activity on any of the compounds studied under these conditions. On the contrary, at least twice as much 50 : 50 mixture was required to produce the same effect as the bromine containing compound alone. This appeared to indicate that reaction did not occur between these materials, however, this is not in agreement with previous work where it was shown that a certain degree of reaction does occur between Flammex 4BS and antimony trioxide and also Flammex 5AE/ antimony trioxide at elevated temperatures. The probable explanation for this is that the hot plate did not provide sufficient heat to decompose the brominated compound in the vicinity of the oxide, enabling reaction to occur.

Although it seems that antimony tribromide was not formed under these conditions it is suggested that formation of the tribromide is to be preferred due to its greater ease of oxidation.

When producing volatile metal halides 'in situ' it has been shown that a number of factors decide the ultimate flame retardant effectiveness when incorporated into plastics materials:-

a. Decomposition temperature of the halogen compound relative to that of the plastics material.

b. Decomposition products of the halogen compound.

c. Lowest temperature of formation of the metal halide.

d. Ease of oxidation of the metal halide.

e. The formation of solid particles on oxidation.

Failure to match each of these conditions may result in a lower efficiency of the system as a whole. It has been demonstrated that antimony trioxide, while not being unique in its reaction with organic halides produced halides which fulfil most of the above requirements.

9.7. Further Experiments Involving Resin Systems

The proposals suggested by the results discussed above were tested in practical systems. The oxygen index was used in assessing the relative effectiveness of the systems. In general the results support the proposals made from the model flame experiments. Appendix III gives tables of some physical properties of the additives used.

The two antimony halides (resin mixture Nos. 2 and 3 page 141) both migrated to the surface of the cast samples, it was therefore not possible to be sure of the concentration incorporated, nominally 15 pph resin. Even so the oxygen indexes obtained were considerably higher than for the other inorganic additives (Fig. 51.) Arsenic trioxide, mercuric chloride and mercuric iodide (resin mixture Nos. 4, 5 and 6 page 141) were considerably less effective than the antimony compounds, which supports the hypothesis of solid particles in the flame.

Fig. 52 illustrates the effect of various mixtures on the flame. Comparing mixtures of ammonium chloride/antimony trioxide and ammonium bromide/antimony trioxide (resin mixture Nos. 7 and 8 page 141) support the observation made from the weight loss experiments. Comparison of the oxygen indexes produced by arsenic trioxide/Cereclor 70 and bismuth trioxide/Cereclor 70 (resin mixture Nos. 9 and 10 page 141) showed that the arsenic trioxide produced the more effective system. This is not in agreement with the model flame experiments, but weight loss experiments showed that mixtures of Cereclor 70/arsenic trioxide gave considerably higher total volatilization than bismuth trioxide/Cereclor 70. In this instance the much greater concentration of volatile inhibitor outweighed the effect of smaller concentrations of bismuth trichloride. It was thought that combinations of Dechlorane 4070/bismuth trioxide would yield a higher concentration of bismuth trichloride, however it seems that under candle burning test conditions (i.e. low thermal stress) Dechlorane 4070 probably tended to sublime out before decomposition, coupled with this the fact that thermochemical data has shown that bismuth trichloride is less readily formed than antimony or arsenic trichlorides.

Combination of PVC and antimony trioxide (resin mixture Nos. 12, 14, 15 and 16) gave surprisingly low results probably due to the low decomposition temperature of PVC forming hydrogen chloride under less favourable reaction conditions.

Resin mixture Nos. 22, 23 and 24 showed that synergism does occur between bromoparaffin and antimony trioxide. Weight loss experiments showed that at 500°C a total volatility of only approximately 60% was achieved, indicating that the relatively small amount of antimony tribromide formed is an effective flame inhibitor. The addition of Cereclor 70 to the Bromoparaffin/antimony trioxide mixture enhanced the effectiveness.

Fig. 53 shows the effect of the halogen compound/ antimony trioxide ratio on the oxygen index of the standard resin. The curves indicate that for a constant level of 7.5 pph resin of antimony trioxide an optimum level of Cereclor 70 is reached at around 12 pph resin of Cereclor 70, which to a certain extent agrees with the earlier work carried out on resin systems (Chapter 3).

The results obtained for this work cannot be directly compared with the earlier experiments as a different resin and also a different incorporation technique was used. Oxygen indexes of the two standard resins were 0.192 for the resin used in the earlier work and 0.185 for that used in these experiments. The latter resin was thus inherently more flammable. Comparison of two equivalent formulations (ie resin mixture No. 3 page 58 and resin mixture No. 20 page 142)give oxygen indexes of 0.350 and 0.287 respectively. It seems unlikely that this difference was entirely due to the difference in resins (as they were basically similar) but it is probable that the mixing technique is quite important, a much more efficient dispersion being possible in the ball mill.

The temperature measurements were carried out in order to investigate whether the proposed reactions were feasible. However, the temperatures obtained were not very meaningful, particularly those taken in the resin. In each case the thermocouple was under a slight tension when inserted in the resin, as the flame front progressed down the stick the area around the thermocouple degraded until the thermocouple broke out of the hole. Thus, the temperature measurement was more a measure of the physical strength of the compound than an accurate temperature. However, it was interesting to note that the stronger materials recorded temperatures up to 468°C inside the resin indicating that true temperatures were in excess of this. Flame temperature were more consistent, producing values of around 700°C in most cases, however sooting up of the thermocouple frequently occurred and true temperatures were probably in excess of those recorded.

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CHAPTER 10

CONCLUSIONS

While one of the original aims of this work was modified, i.e. the study of the mechanisms of flame inhibition, equipment was developed which should prove useful in assessing the relative effectiveness of retardants which operate by flame inhibition.

It would seem that the various techniques available for measuring the flammability of plastics materials are to a certain extent complementary but a degree of caution should be adopted in interpreting results from one individual method. Although numerical correlation between Setchkin ignition temperatures and oxygen index values was not possible it was possible to conclude that the most effective systems i.e. the halogenated compound/antimony trioxide mixtures were mainly active by gas phase inhibition. It was also concluded that effective flame retardance depended upon the volatility of the halogenated additive, it seemed necessary that the halogen compound should decompose in the solid phase providing more favourable conditions for reaction with antimony trioxide.

The chief reaction product on heating together antimony trioxide/Cereclor 70 and antimony trioxide/PVC was antimony trichloride. Although these represented near ideal conditions the same reaction was expected to be predominant when incorporated into the resin. Assuming, as in this case, the product of reaction was volatile under test conditions, the degree of reactivity could readily be followed by measuring the total volatility of mixtures over time periods. Consultation of free energy data showed that antimony trichloride, bismuth trichloride and arsenic trichloride would all be expected to be readily formed under the experimental conditions. Many other metal oxide/halogenated compound mixtures were studied but the Group V halides were most readily formed and had boiling points near the degradation range of the resin. Dechlorane 4070/antimony trioxide volatility curves indicated that the mixtures should have received a better rating according to the flammability tests. Results suggested that the candle burning test assessed performance under conditions of low thermal stress and performance indexes of B.S.476 fire propagation test confirmed this.

The apparatus devised for assessing the effect of inhibitors on model fuel diffusion flames was adequate for studying volatile liquid or gaseous inhibitors but practical difficulties arose on attempting to study solid inhibitors. Qualitatively, it was shown that the stability of the leading edge of the flame was important.

The technique developed for studying the effect of volatilised solid inhibitors on premixed model fuel/air flames was largely successful. The results of this work, considered in conjunction with other published work suggested that the effectiveness of the antimony trihalides was possibly due to their ability to form solid oxide particles in the flame zone.

It may be predicted that high energy species such as $OH^{\cdot}$, $O^{\cdot}$ and $H^{\cdot}$ radicals are absorbed at the surface of these particles which would result in an overall decrease in energy of the flame system. Again the leading edge of the flame was shown to be important. Volatilization of whole halogenated organic molecules into the flame was relatively less effective than decomposition and liberation of hydrogen chloride prior to the flame zone. The hydrogen chloride was then probably effective by the mechanism proposed by Rosser et al.

General conclusions made from these model experiments were confirmed by the later work using practical resin systems.

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APPENDIX I

SUPPLEMENTARY INFORMATION ON THE COMMERCIAL ADDITIVES USED

Trade Name	Nature of Additive	Supplier
Cereclor 70	Solid chlorinated paraffin containing 70% chlorine	Imperial Chemicals Industries
Cereclor 65L	Liquid chlorinated paraffin containing 70% chlorine	"
Cereclor S52	Liquid chlorinated paraffin containing 52% chlorine	"
Bromoparaffin	Liquid brominated paraffin	"
Timonox	Antimony Trioxide Sb_2O_3	Anchor Chem. Ltd.
Dechlorane 4070	Perchloropenta-cyclodecane 78% chlorine	Kingsley & Keith Chemicals Ltd.
Dechlorane Plus 515	Perchloropenta-cyclodecane 65% chlorine	"
Firemaster T23P	tris 2,3 dibromo-propyl phosphate	"

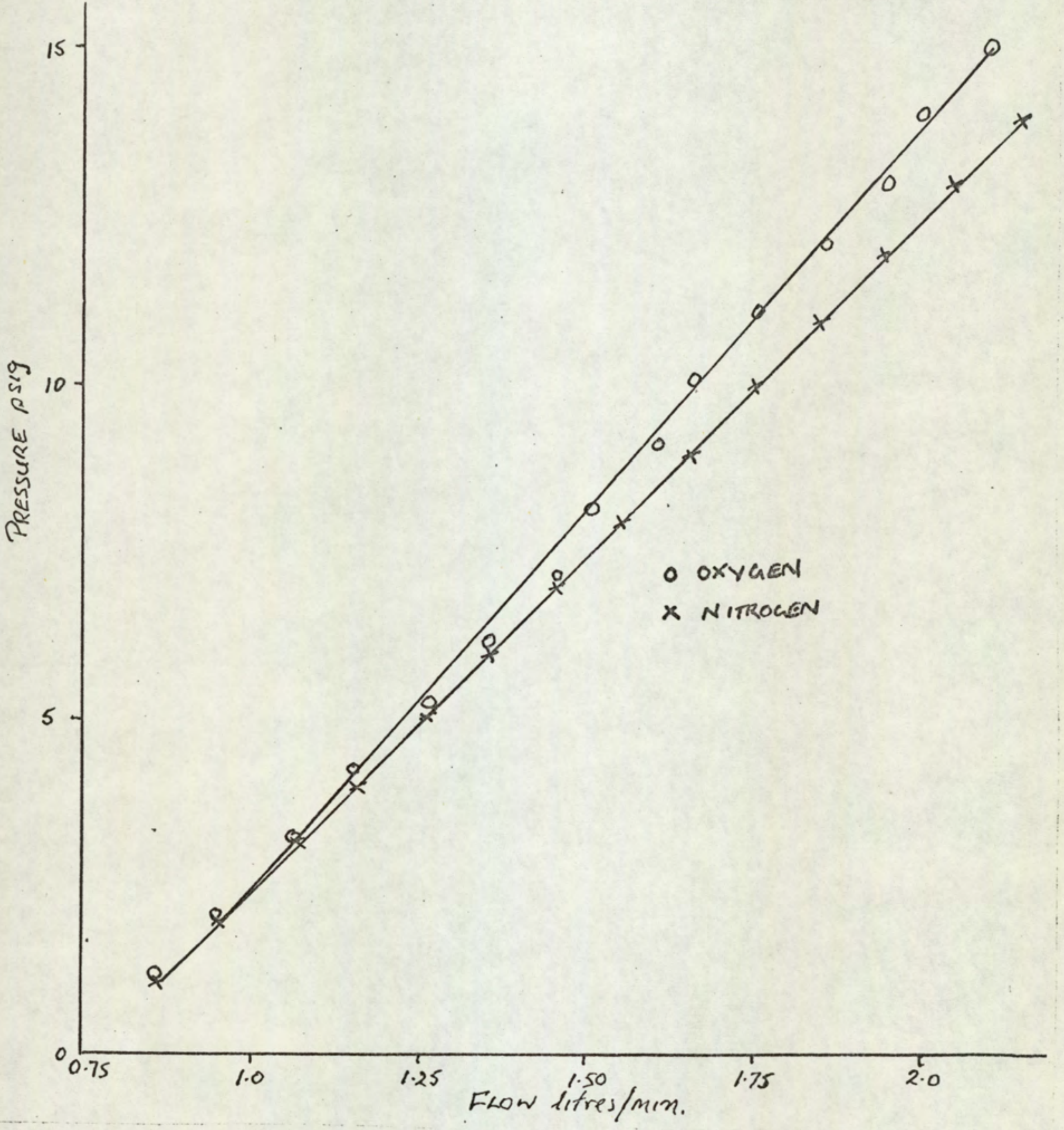
Appendix I continued

Trade Name	Nature of Additive	Supplier
-	tris 2,3 dichloropropyl phosphate	Albright & Wilson Ltd.
TTP	Tritolyl phosphate	"
TXP	Tri Xylyl phosphate	"
Flammex 4BS	Tetra (pentabromophenoxy) silane	F. W. Berk Ltd.
Flammex 5BT	Pentabromotoluene	"
Flammex 5AE	Pentabromophenylallyl ether	"
Flammex 3AE	Tribromophenylallyl ether	"
Zinc Borate 9506	$Zn\ (BO_2)_2 2H_2O$	Joseph Storey Ltd.
Calcium Borate 9578	$Ca(BO_2)_2 2.5H_2O$	"

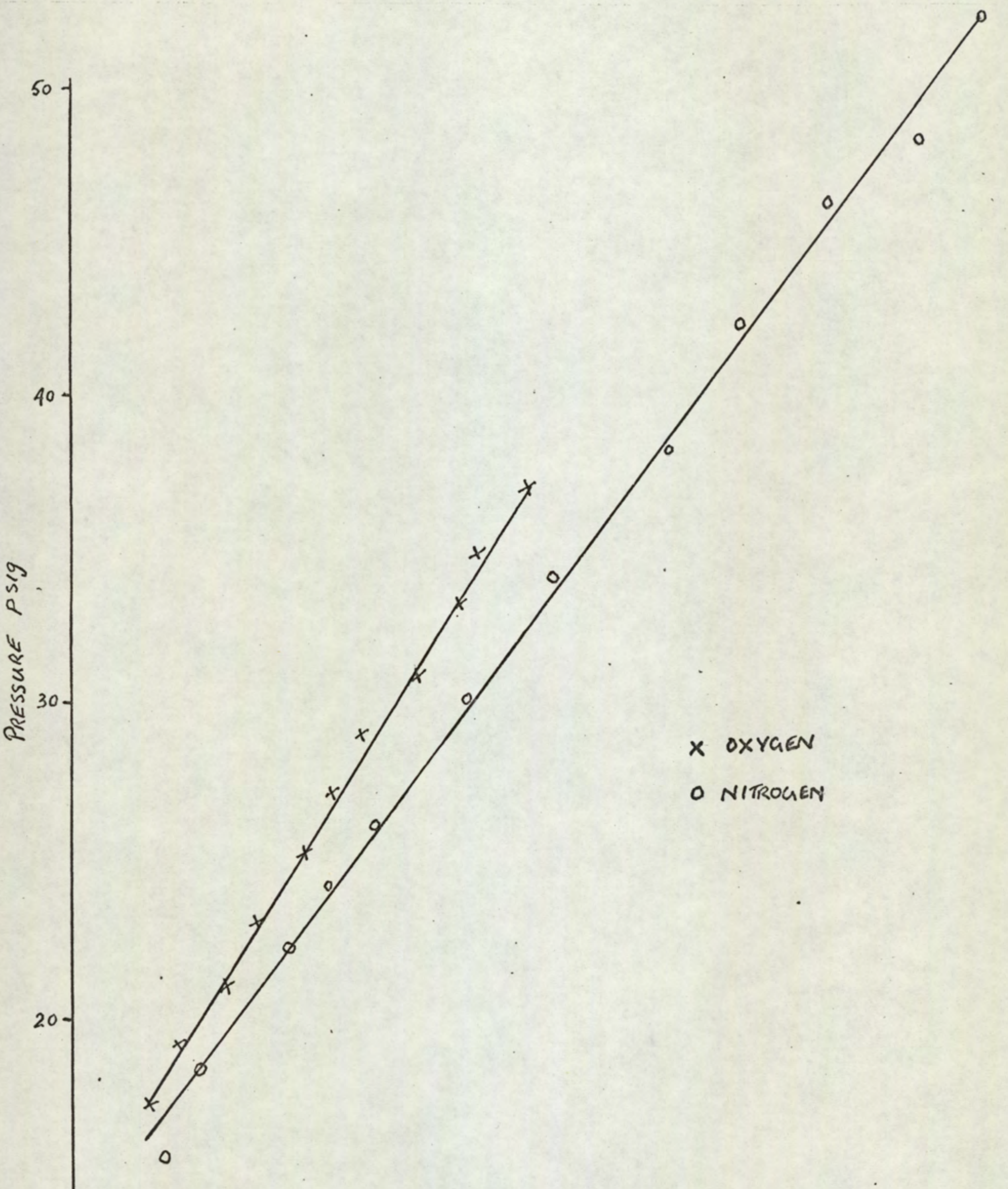
APPENDIX II

CALIBRATION AND OTHER DATA FOR USE WITH ATMOSPHERE METERING SYSTEMS

Oxygen and nitrogen, 0.0135 ins. diameter orifice No. 2 Meter

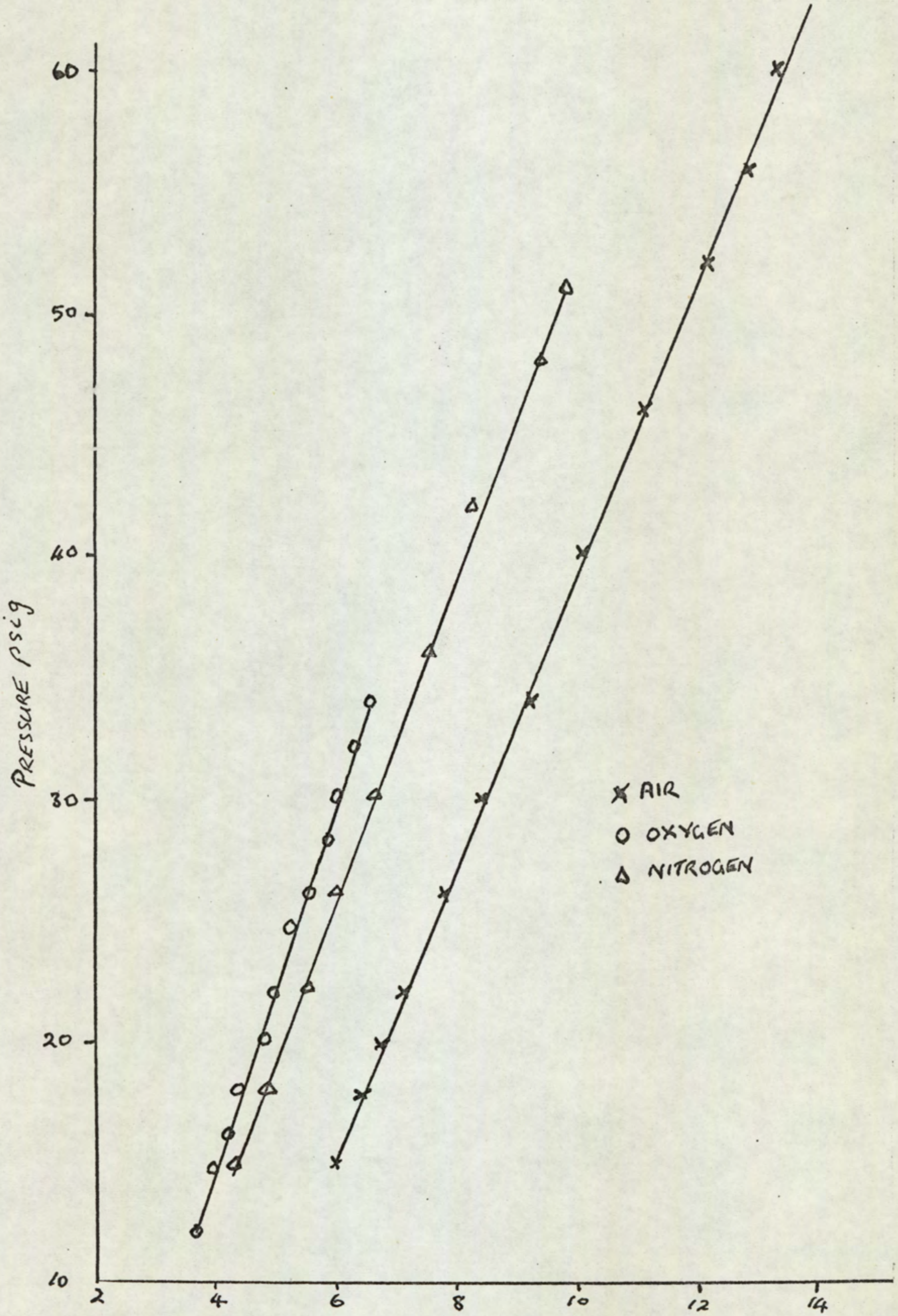


Oxygen and nitrogen, 0.0135 ins. diameter orifice No. 2 meter

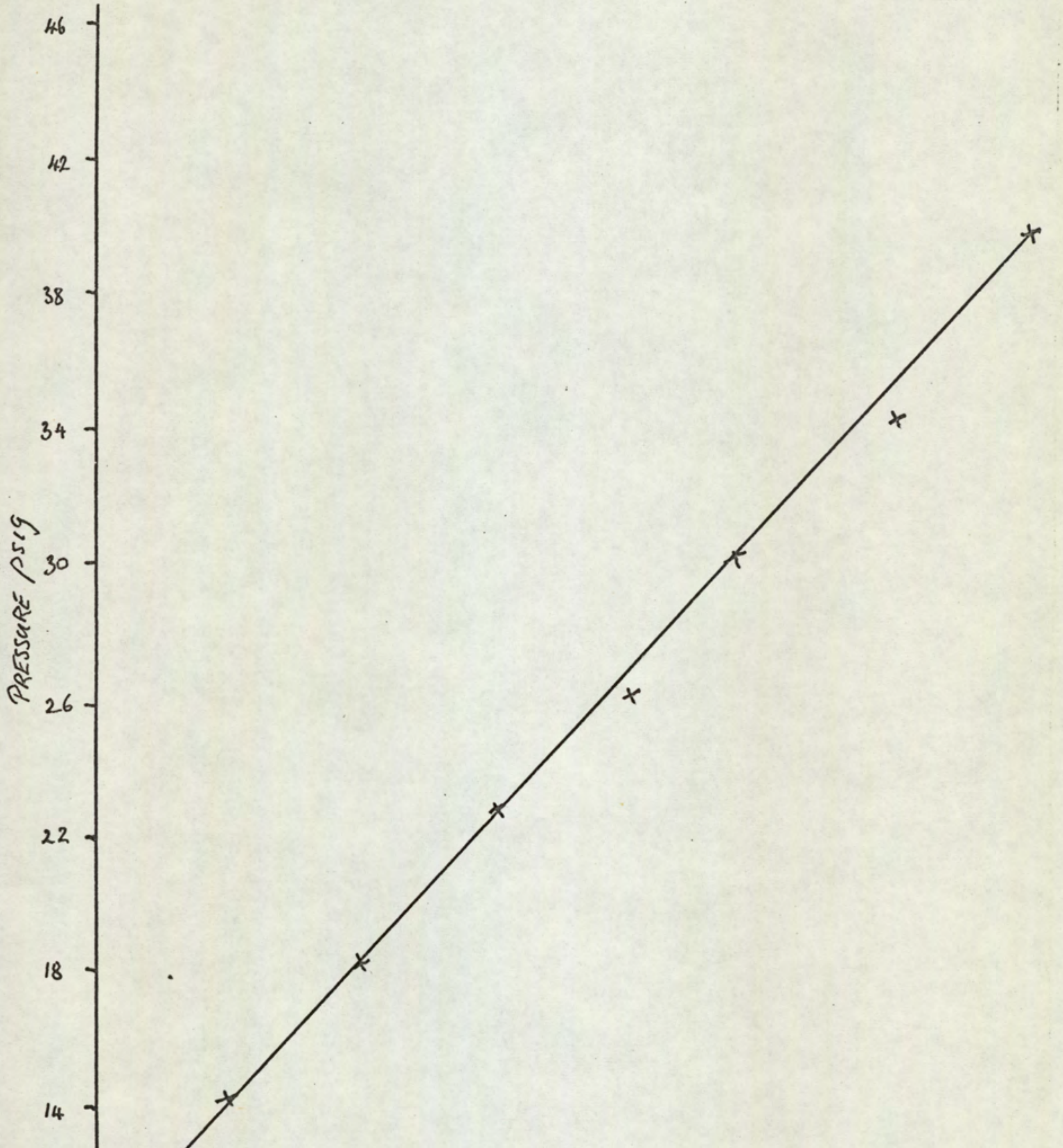


Air, oxygen and nitrogen 0.021 ins. diameter orifices

Nos. 1 and 2 meters



Air, 0.035 ins. diameter orifice No. 1 meter



ELLIOT 803 COMPUTER PROGRAMMES FOR OXYGEN INDEX VALUES

a. Air flow rates between 10 - 40 lit./min. with 0 - 4.0 lit./min. oxygen

```
AIR CALIBRATION CHART 5'
BEGIN INTEGER I' REAL A' LINEPRINTER'
      PRINT ££S50?AIR CALIBRATION CHART£L3??'
      FOR A:=0 STEP 0.2 UNTIL 4.0 DO PRINT SAMELINE,DIGITS(5),A'
      FOR I:=10 STEP 1 UNTIL 40 DO
      BEGIN PRINT ££LS2??,DIGITS(2),A'
      FOR A:=0 STEP 0.2 UNTIL 4.0 DO
      PRINT SAMELINE,ALIGNED(1,3),(2.1+A+(I-10)*0.21)/(I+A)'
       END
END OF PROGRAM'
END OF LINEPRINTER PACKAGE'
```

b. Air flow rates between 10 - 40 lit./min. with 0 - 4.0 lit./min. nitrogen.

```
AIR CALIBRATION CHART 6'
BEGIN INTEGER I' REAL A' LINEPRINTER'
      PRINT ££S50?AIR CALIBRATION CHART£L3??'
      FOR A:=0 STEP 0.2 UNTIL 4.0 DO PRINT SAMELINE,DIGITS(5),A'
      FOR I:=10 STEP 1 UNTIL 40 DO
      BEGIN PRINT ££LS2??,DIGITS(2),A'
      FOR A:=0 STEP 0.2 UNTIL 4,0 DO
      PRINT SAMELINE,ALIGNED(1,3),(2.1+(I-10)*0.21)/(I+A)'
       END
END OF PROGRAM'
END OF LINEPRINTER PACKAGE'
```

OXYGEN INDEX VALUES AIR/NITROGEN

NITROGEN lit/MIN.

AIR lit/MIN.	0.0	0.2	0.4	0.6	0.8	1.0	1.2	1.4	1.6	1.8	2.0	2.2	2.4	2.6	2.8	3.0	3.2	3.4	3.6	3.8
10	0.210	0.206	0.202	0.198	0.194	0.191	0.187	0.184	0.181	0.178	0.175	0.172	0.169	0.167	0.164	0.162	0.159	0.157	0.154	0.152
11	0.210	0.205	0.203	0.199	0.196	0.192	0.189	0.186	0.183	0.180	0.178	0.175	0.172	0.170	0.167	0.165	0.163	0.160	0.158	0.156
12	0.210	0.207	0.203	0.200	0.197	0.194	0.191	0.188	0.185	0.183	0.180	0.177	0.175	0.173	0.170	0.168	0.166	0.164	0.162	0.159
13	0.210	0.207	0.204	0.201	0.198	0.195	0.192	0.190	0.187	0.184	0.182	0.180	0.177	0.175	0.173	0.171	0.169	0.166	0.164	0.163
14	0.210	0.207	0.204	0.201	0.199	0.196	0.193	0.191	0.188	0.186	0.184	0.181	0.179	0.177	0.175	0.173	0.171	0.169	0.167	0.165
15	0.210	0.207	0.205	0.202	0.199	0.197	0.194	0.192	0.190	0.187	0.185	0.183	0.181	0.179	0.177	0.175	0.173	0.171	0.169	0.168
16	0.210	0.207	0.205	0.202	0.200	0.198	0.195	0.193	0.191	0.189	0.187	0.185	0.183	0.181	0.179	0.177	0.175	0.173	0.171	0.170
17	0.210	0.205	0.205	0.203	0.201	0.198	0.196	0.194	0.192	0.190	0.188	0.186	0.184	0.182	0.180	0.179	0.177	0.175	0.173	0.172
18	0.210	0.208	0.205	0.203	0.201	0.199	0.197	0.195	0.193	0.191	0.189	0.187	0.185	0.183	0.182	0.180	0.178	0.177	0.175	0.173
19	0.210	0.208	0.206	0.204	0.202	0.200	0.198	0.196	0.194	0.192	0.190	0.188	0.186	0.185	0.183	0.181	0.180	0.178	0.177	0.175
20	0.210	0.208	0.206	0.204	0.202	0.200	0.198	0.196	0.194	0.193	0.191	0.189	0.187	0.186	0.184	0.183	0.181	0.179	0.178	0.176
21	0.210	0.208	0.206	0.204	0.202	0.200	0.199	0.197	0.195	0.193	0.192	0.190	0.188	0.187	0.185	0.184	0.182	0.181	0.179	0.178
22	0.210	0.208	0.206	0.204	0.203	0.201	0.199	0.197	0.196	0.194	0.192	0.191	0.189	0.188	0.186	0.185	0.183	0.182	0.180	0.179
23	0.210	0.208	0.206	0.205	0.203	0.201	0.200	0.198	0.196	0.195	0.193	0.192	0.190	0.189	0.187	0.186	0.184	0.183	0.182	0.180
24	0.210	0.208	0.207	0.205	0.203	0.202	0.200	0.198	0.197	0.195	0.194	0.192	0.191	0.189	0.188	0.187	0.185	0.184	0.183	0.181
25	0.210	0.208	0.207	0.205	0.203	0.202	0.200	0.199	0.197	0.196	0.194	0.193	0.192	0.190	0.189	0.188	0.186	0.185	0.184	0.182

OXYGEN INDEX VALUES AIR/OXYGEN (1)

OXYGEN lit/min.

AIR lit/min	0.0	0.2	0.4	0.6	0.8	1.0	1.2	1.4	1.6	1.8	2.0	2.2	2.4	2.6	2.8	3.0	3.2	3.4	3.6	3.8
10	0.210	0.225	0.240	0.255	0.269	0.282	0.295	0.307	0.319	0.331	0.342	0.352	0.363	0.375	0.383	0.392	0.402	0.410	0.419	0.425
11	0.210	0.224	0.238	0.251	0.264	0.276	0.288	0.299	0.310	0.321	0.332	0.342	[illegible]	0.361	0.370	0.379	0.388	0.397	0.405	0.413
12	0.210	0.223	0.235	0.248	0.259	0.271	0.282	0.293	0.303	0.313	0.323	0.332	0.342	0.351	0.359	0.368	0.376	0.384	0.392	0.400
13	0.210	0.222	0.234	0.245	0.256	0.266	0.277	0.287	0.297	0.306	0.315	0.324	0.333	0.342	0.350	0.358	0.366	0.374	0.381	0.389
14	0.210	0.221	0.232	0.242	0.253	0.263	0.272	0.282	0.291	0.300	0.309	0.317	0.326	0.334	0.342	0.349	0.357	0.364	0.372	0.379
15	0.210	0.220	0.231	0.240	0.250	0.259	0.269	0.277	0.286	0.295	0.303	0.311	0.319	0.327	0.334	0.342	0.349	0.356	0.363	0.370
16	0.210	0.220	0.229	0.239	0.248	0.256	0.265	0.274	0.282	0.290	0.298	0.305	0.313	0.320	0.328	0.335	0.342	0.348	0.355	0.362
17	0.210	0.219	0.228	0.237	0.246	0.254	0.262	0.270	0.278	0.286	0.293	0.301	0.308	0.315	0.322	0.328	0.335	0.342	0.348	0.354
18	0.210	0.219	0.227	0.235	0.244	0.252	0.259	0.267	0.274	0.282	0.289	0.296	0.303	0.310	0.316	0.323	0.329	0.336	0.342	0.348
19	0.210	0.218	0.226	0.234	0.242	0.250	0.257	0.264	0.271	0.278	0.285	0.292	0.299	0.305	0.311	0.318	0.324	0.330	0.336	0.342
20	0.210	0.218	0.225	0.233	0.240	0.248	0.255	0.262	0.269	0.275	0.282	0.288	0.295	0.301	0.307	0.313	0.319	0.325	0.331	0.336
21	0.210	0.217	0.225	0.232	0.239	0.246	0.253	0.259	0.266	0.272	0.279	0.285	0.291	0.297	0.303	0.309	0.314	0.320	0.326	0.331
22	0.210	0.217	0.224	0.231	0.238	0.244	0.251	0.257	0.264	0.270	0.276	0.282	0.288	0.293	0.299	0.305	0.310	0.316	0.321	0.326
23	0.210	0.217	0.224	0.230	0.237	0.243	0.249	0.255	0.262	0.267	0.273	0.279	0.285	0.290	0.296	0.301	0.306	0.312	0.317	0.322
24	0.210	0.217	0.223	0.229	0.235	0.242	0.248	0.254	0.259	0.265	0.271	0.276	0.282	0.287	0.293	0.298	0.303	0.308	0.313	0.318
25	0.210	0.216	0.222	0.229	0.234	0.240	0.246	0.252	0.258	0.263	0.269	0.274	0.279	0.284	0.290	0.295	0.300	0.305	0.309	0.314

OXYGEN INDEX VALUES AIR/OXYGEN (2)

OXYGEN lit/min

AIR lit/hour	4.0	4.2	4.4	4.6	4.8	5.0	5.2	5.4	5.6	5.8	6.0	6.2	6.4	6.6	6.8	7.0	7.2	7.4	7.6	7.8	8.0
10	0.436	0.444	0.452	0.459	0.466	0.473	0.480	0.487	0.494	0.500	0.506	0.512	0.518	0.524	0.530	0.535	0.541	0.546	0.551	0.556	0.561
11	0.421	0.428	0.436	0.443	0.450	0.457	0.464	0.470	0.477	0.483	0.489	0.495	0.501	0.506	0.512	0.517	0.523	0.528	0.533	0.538	0.543
12	0.407	0.415	0.422	0.429	0.436	0.442	0.449	0.455	0.461	0.467	0.473	0.479	0.485	0.490	0.496	0.501	0.506	0.511	0.516	0.521	0.526
13	0.398	0.403	0.410	0.416	0.423	0.429	0.436	0.442	0.448	0.454	0.459	0.465	0.471	0.476	0.481	0.486	0.492	0.491	0.501	0.506	0.511
14	0.386	0.392	0.399	0.405	0.412	0.418	0.424	0.430	0.436	0.441	0.447	0.452	0.458	0.463	0.468	0.473	0.478	0.482	0.488	0.493	0.497
15	0.378	0.383	0.389	0.395	0.402	0.407	0.413	0.419	0.425	0.430	0.436	0.441	0.446	0.451	0.456	0.461	0.466	0.470	0.476	0.480	0.485
16	0.368	0.374	0.380	0.386	0.392	0.398	0.404	0.409	0.415	0.420	0.425	0.431	0.436	0.441	0.446	0.450	0.455	0.460	0.464	0.469	0.473
17	0.360	0.367	0.372	0.378	0.384	0.390	0.393	0.400	0.406	0.411	0.416	0.421	0.426	0.431	0.436	0.440	0.445	0.450	0.454	0.458	0.462
18	0.354	0.359	0.365	0.371	0.376	0.382	0.387	0.392	0.397	0.403	0.407	0.412	0.417	0.422	0.427	0.431	0.436	0.440	0.445	0.449	0.453
19	0.347	0.353	0.359	0.364	0.369	0.375	0.380	0.385	0.390	0.395	0.400	0.404	0.409	0.414	0.418	0.423	0.427	0.431	0.436	0.440	0.444
20	0.342	0.347	0.352	0.358	0.363	0.368	0.373	0.378	0.383	0 386	0.392	0.397	0.402	0.406	0.410	0.415	0.419	0.423	0.428	0.432	0.436
21	0.336	0.342	0.347	0.352	0.357	0.362	0.367	0.372	0.376	0.381	0.386	0.390	0.395	0.399	0.403	0.407	0.412	0.416	0.420	0.424	0.428
22	0.332	0.337	0.342	0.347	0.351	0.356	0.361	0.366	0.370	0.375	0.379	0.384	0.388	0.392	0.397	0.401	0.405	0.409	0.413	0.417	0.421
23	0.327	0.332	0.337	0.342	0.346	0.351	0.356	0.360	0.365	0.369	0.373	0.378	0.382	0.386	0.390	0.394	0.398	0.402	0.406	0.410	0.414
24	0.323	0.328	0.332	0.337	0.342	0.346	0.351	0.355	0.359	0.364	0.368	0.372	0.376	0.380	0.384	0.388	0.392	0.396	0.400	0.404	0.407
25	0.319	0.324	0.328	0.333	0.337	0.342	0.346	0.350	0.355	0.359	0.363	0.367	0.371	0.375	0.379	0.383	0.387	0.390	0.394	0.398	0.401

APPENDIX III

MELTING AND BOILING TEMPERATURES OF MATERIALS USED OR PREDICTED REACTION PRODUCTS

1. Commercial Additives

Material	M. Pt. °C.	B. Pt. °C
Cereclor 70		-
Cereclor 70L		288 - 296
Cereclor 65L		274 - 280
Cereclor S52		256 - 262
Bromoparaffin		
Dechlorane 4070	485	sub. 360, d.410
Dechlorane Plus 515	350	
Firemaster T23P		
tris, 2,3 dichloropropyl phosphate		175 (0.1 mm Hg)
TTP		420
TXP		
Flammex 4BS	355 - 360	Non volatile d.380
Flammex 5BT	280 - 284	Sub. 200, d.360
Flammex 5AE	160 - 165	Vol. 150, d.200
Flammex 3AE	75 - 77	Vol. 150, d.200
Timonox	656	sub. 1550
Calcium Borate		
Zinc Borate		
PVC P65-50		

2. General Purpose Reagents

Material	M. Pt. °C.	B. Pt. °C.
Bismuth Trioxide	820	1890
Arsenic Trioxide	sub. 300	
Magnesium Oxide	2800	3600
Aluminium Oxide	2045	2980
Stannic Oxide	1127	sub. 18 - 1900
Zinc Oxide	1975	
Lead Monoxide		
Red Lead	d. 500	
Stannous oxide	d. 1080	
Ferric Oxide	1565	
Titanium Dioxide	1830 - 1850	2500 - 3000
Manganese Dioxide	- [O] 535	
Ceric Oxide		
Antimony Trifluoride	292	sub. 319
Antimony Trichloride	73.4	283
Antimony Tribromide	96.6	280
Antimony Triiodide	170	401
Arsenic Triiodide	146	403
Aluminium Chloride	190 (2.5 atm)	182.7
Ammonium Chloride	Sub. 340	520
Ammonium Bromide	sub. 452	232 (vac)
Mercuric Chloride	276	302
Mercuric Bromide	236	322
Mercuric Iodide	259	354
Phosphorus Pentachloride	d. 166.8	sub. 162

Material	M. Pt. °C	B. Pt. °C
Hexamine	sub. 285 - 295	
Dicyandiamide		
Arsenic Tribromide	32.8	221
Magnesium Chloride	708	1412
Stannic Chloride	- 33	114.1
Stannous Chloride	246	652
Zinc Chloride	283	732
Lead Chloride	501	950
Ferric Chloride	306	d. 315
Titanyl Chloride	- 25	136.4
Manganese Chloride	650	1190

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FLAMMABILITY OF PLASTICS

I. RELATION BETWEEN PYROLYSIS AND BURNING

By G. S. LEARMONTH, A. NESBITT and D. G. THWAITE

The fundamental basis of the burning of polymers is reviewed and the planning of the present investigations is justified. Preliminary results are given on the effect of chlorinated additives on the pyrolytic decomposition of polyesters.

Introduction

There is an increasing interest in the use of plastics for structural and decorative applications in the building and transport industries. Consequently, a good deal of work has been done to investigate the flammability of polymer-based materials. This topic has been previously reviewed[1,2] and information is available from various government organisations. However, as already pointed out, most of the work recorded has been confined to an empirical nature and there is scope for considering the matter more fundamentally.

In general a solid or liquid plastics material will not burn, and the phenomenon which is recognised as burning is dependent on the presence over the surface, of vapour or other low molecular weight fragments derived from one or other of the ingredients of the plastics compound. Solid-phase burning is discussed later. Burning will in fact follow the sequence: (i) all or part of the material is heated from an external source, enough to produce a vapour or a concentration of volatile fragments from polymer degradation; (ii) when sufficient concentration of fuel is in the vapour phase it can ignite and a flame results – this is a high-energy zone in which rapid free radical reactions occur, and is of the type known as 'diffusion' flame, controlled by the rate of diffusion of fuel gases into the flame zone; the net results of reaction in the flame are the oxidation of organic matter to oxides of carbon, and a certain amount of 'cracking' may occur, resulting in the formation of carbonaceous smoke or soot; (iii) the flame heats the plastics material and more vapour is formed which perpetuates the cycle; and (iv) some polymers degrade to leave a residue of graphitic carbon in a more or less orientated state; if the temperature is high enough, the residue can burn in the solid phase, but the kinetics are different and the reaction rate is at least an order of magnitude less than gas reactions.

Mechanism of pyrolysis

In any plastics material, the course and results of pyrolysis are dependent on the polymer used. In the general case, pyrolysis occurs in three stages.[3-5] At moderate temperatures, below about 300° functional groups react or are eliminated from the main polymer skeleton. In some cases these are groups residual from condensation reactions, or such groups as catalyst residues. Otherwise, elimination is of a single species of low molecular weight such as HCl from polyvinyl chloride or H_2O from cellulose, and this may be accompanied by regular changes in the nature of the main polymer chain or network.[6] Between 250° and 550° thermal movement of the polymer chain or network segments is sufficiently energetic to give bond scission in the main structure. This may be located at random with the production of polymers of much lower molecular weight and some small amount of volatile fragments, or may be at chain ends giving 'unzipping' and the formation of monomer or very small polymer units, which are volatile and leave the original material only slightly lowered in molecular weight. In cases such as PVC and cellulose, the reactions which have occurred in the first stage may be prerequisite to the fission stage.[7] Some polymers always, and most polymers under some conditions, give some recombination of the fragments produced in this stage of pyrolysis, and it is usual for this to result in an aromatic or condensed ring structure irrespective of the nature of the original chain or network.[8] In such cases a third stage occurs; in this the structure is increasingly condensed, and all elements other than carbon are gradually eliminated, leaving a carbon 'char' the exact composition of which depends mainly on the temperature reached.

Relation between pyrolysis and burning

At any time during the burning of a polymer there is a vapour phase in which the actual flame reactions are occurring and a solid phase, usually in the form of a surface, which may be partly carbonised, in which fuel for the gas reactions is being produced.[9] It seems that there are two ways in which flammability may be controlled namely, modification of the course of the reactions in the solid phase to produce less volatile matter, or alternatively to prevent burning in the gas phase. The latter may be simply a matter of diluting the mixture of fuel and air or oxygen with an inert gas, or cooling it by some endothermic reaction, or introduction of some alien species to inhibit the free radical reactions involved in the flame formation.

In addition to the normal methods of control mentioned, it is also possible in some cases that an inert surface gaseous layer forms and has some specific effect on burning. This effect is often cited, but is difficult to verify in practice.

The experiments described in this paper are intended to find out the effect of various common 'flame-proofing' agents on the solid-phase reactions and the flame as defined above. The polymers used are unsaturated polyesters dissolved in styrene, and cross-polymerised by free radicals from organic peroxides. In addition, both polystyrene and polypropylene are under investigation.

Polymer degradation reactions

Degradation of polystyrene has been described by several workers. The process is not simple, in that the main reaction is preceded by a random fission. However, the effect is that there is a steady formation of monomer with smaller amounts of dimer and trimer, with the degradation proceeding from an activated chain end in each case.[10]

Polypropylene gives very little monomer, and is apparently degraded almost entirely by a random scission process.[10]

Unsaturated polyesters give a complex pattern, and little clear information is available, though some work on model compounds and on saturated polyesters such as polyethylene terephthalate are relevant.[11] The polyester network is composed of polyester chains of molecular weight about 1500 crossed by styrene–fumaric acid copolymers of molecular weight, about 15,000. Usually the polyester chain is derived from fumaric and phthalic acid and a simple glycol such as 1,2-propylene glycol, but sometimes other raw materials are used. The typical reaction of an ester in degradation is formation of an olefin and a carboxylic acid fragment, but there are many side reactions such as decarboxylation of the main chain fragments. In crosslinked polyesters this may be complicated by degradation of the styrene (or other monomer) crosspolymer, about which there seems to have been nothing published.

The course of pyrolysis and thus of flammability can be greatly affected by additional materials in the plastics compound.[12] As these are many and varied, the situation tends to be complicated. Usually inorganic additives, such as silica, asbestos or glass, mainly affect the thermodynamics of the system by increase or decrease in the thermal demand, but sometimes they may affect the pyrolysis. In some other cases the mechanism is fairly clear. For example, the addition of potential acids such as phosphates to cellulose results in the removal of water and this considerably alters the course of pyrolysis.[9] Thus instead of production of many small fragments, most of the carbon present appears as char. Also in the case of PVC, where the first step in degradation is loss of HCl, not only is the original dehydrochlorination very sensitive to traces of some metals, but all technological materials contain stabilisers. These either prevent dehydrochlorination or affect subsequent degradation of the polyene structure left when all the HCl is gone. In most other cases the mechanisms are not too clear. For example, when chlorine is added to polyesters it will reduce flammability, whether it is in an additive or part of the polymer structure, but it is not yet clear whether this is by modification of the pyrolysis or inhibition of the flame reactions.

Pyrolysis in the solid state

The reactions involved in degradation of the solid polymer have been described above in general terms. Where there are no complicating circumstances, the reactions in every case involve bond splitting, and are therefore endothermic. In the presence of air, however, oxidative reactions may either precede or follow the main scission, and sometimes the balance of heat changes may be exothermic. In a complete evaluation of these reactions, it is therefore necessary to follow both changes in weight due to loss of fragments, and the accompanying thermal changes. Such reactions in the condensed phase can be studied either by studying the composition and thermal changes taking place in the solid state, by differential thermal analysis (d.t.a.), thermogravimetric analysis (t.g.a.)[13] or related techniques, or alternatively by analysing the products of pyrolysis under different conditions.

T.g.a. involves heating a few mg of the sample material in a recording balance, usually by raising the temperature by about 10 or 20°/min. Although there are techniques for extracting kinetic information from t.g.a. curves, it is truly a diagnostic technique, enabling the overall pattern of weight loss with temperature to be seen from a single experiment. The earlier techniques[3–5,14,15] derived kinetic results from a single analysis. These methods yield rates averaged over a wide range of events, and Anderson,[16] Friedman[15,17] and Reich[18] have developed better expressions, using a series of t.g.a. curves at different heating rates. For accurate estimation of reaction rates it is necessary to work isothermally. By following the weight loss against time at a series of temperatures in separate experiments, it is usually possible to relate specific reaction rate with activation energy and a pre-exponential factor in the Arrhenius equation. The only disadvantages of this procedure are the time involved in making the separate experiments, and the time required to heat the sample to operating temperature. An error is introduced by this latter factor, because the sample is presumed to decompose during the heating period, and an extrapolation is necessary to find the initial reaction rate.

In d.t.a. the sample is heated so that the temperature rises steadily in a similar manner to t.g.a. but in this case its temperature is continuously compared with that of an inert reference material. Only the net result of the reactions occurring at any given time is measured; nevertheless this technique gives useful information about the successive stages of thermal degradation.[14]

The alternative process of analysing the volatile products of pyrolysis at constant temperature has been described[10] and is usually achieved either by pyrolysis direct into a gas–liquid chromatography column, or in a vacuum rig from which several fractions are recovered and analysed by conventional means.

Reactions in the flame

Usually control of the flame in burning plastics compounds is achieved by the introduction of chlorine or bromine and sometimes antimony oxide. Knowledge of the way in which these operate is scanty and often speculative, and it may be of interest to review the possibilities.[19] There is a synergistic effect when halogen and Sb_2O_3 are present together but this is also not well understood.

There is a possible 'blanketing' effect in which inert gas or some other pyrolytic species is present in high concentration immediately on the gas side of the interface. This could effectively lower the temperature of the solid side of the interface and slow down pyrolysis, though there seems little evidence for the effect. However, it must be that the species expelled from the surface will move into the flame zone by diffusion, upon which will be superimposed some movement related to the gas velocity (the gas stream may be turbulent, which would steepen the concentration gradient considerably; see Fig. 1 and Table I).

The injection of volatile fragments from the surface into the gas side will cause some cooling, especially if the fragments can react endothermically thereafter.

It is known that flame can be extinguished by injection, into the reaction zone, of finely divided particles which

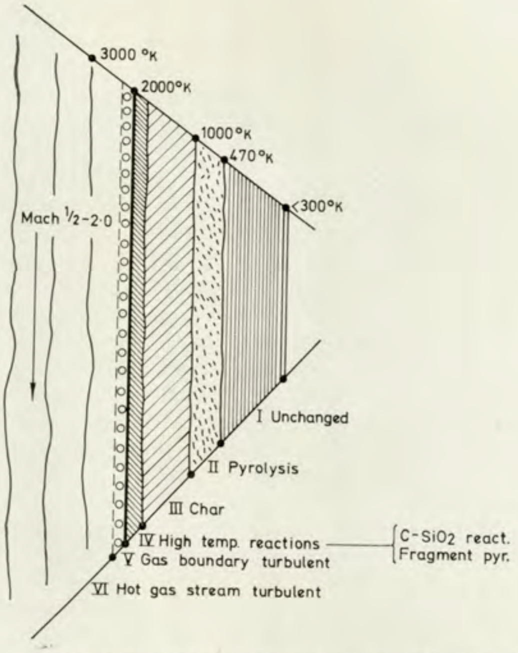

Fig. 1. *Effect of burning plastic compound in a flame*
Compound used contained 38% phenol resin and 62% glass

TABLE I

Composition of plastic compound subjected to burning
Compound used contained 38% phenol resin and 62% glass

Zone (see Fig. 1)	C	H	O	N	Mineral
I	28·25	2·15	7·66	0·34	61·6
II	27·77	1·93	6·87	0·13	63·3
	27·04	1·59	5·75	0·17	65·5
III	23·32	0·37	1·40	0·12	74·8
	26·96	0·16	0·93	0·10	71·9
IV	33·30	0·09	—	0·20	66·6

absorb the reactive species in the reactions. It is possible that antimony oxide acts in this way.[20]

It is probable that effective inhibition of flame is due to the removal of active free radicals by transfer reactions. Various assumptions have been made about the form in which chlorine, bromine and antimony appear in the gas phase. Rosser & Wise[21,22] have studied the inhibition of hydrocarbon flames and concluded that HBr is the active species. Volans[19] further studied the effect of bromine on burning of polystyrene and also believes that HBr is the active fragment. However he was working under non-oxidative conditions. In connexion with diffusion flames Creitz[23] found that organically combined halogen was active.

Experimental techniques

The 'candle-burning test', described by Fenimore & Martin[24] seems of special interest. A stick of plastics material is burned in an enclosed tube where the atmosphere can be controlled. The concentration of oxygen at which burning is just sustained is used as an index of flammability. Martin used various atmospheres and developed a theoretical model of the system in which stability of the leading edge of the flame is critical. He found that halogen was only really effective if added to the plastics material, and the effect of adding it to the atmosphere was trivial. When the atmosphere was N_2O instead of oxygen, bromine was much less effective.

The only standard test which seems relative to the dual approach to flammability is the Setchkin test.[25–27] This consists of heating a small sample of plastics compound in a special furnace with preheated air, and provision of dynamic temperature control. The temperature at which the emission of active species is rapid enough to burn is measured under one of a number of specified circumstances.

Finally, it is probably relevant to study the burning of a model flame, i.e. one based on the species known to be emitted from the solid surface, and equipment similar to that for the candle-burning test, or that from which it is adapted, is required.[19,24,28]

Experimental

Apparatus

Simultaneous t.g.a. and d.t.a. measurements were made using the Linseis thermobalance Mk I. (Linseis Prufgeratebau A-G., Selb, Bavaria.

The standard Setchkin equipment[26,27] was used for ignition tests as described in A.S.T.M. standard D1929-62T.

Equipment for the 'candle-burning test' (after Fenimore & Martin) was made in this laboratory and is described in detail in Part II.[29]

Materials

Solid-phase reactions

I Standard resin + 10% Sb_2O_3 + 10% Dechlorane +
II ,, ,, ,, ,, ,, Cereclor 70
III ,, ,, ,, ,, ,, pentabromotoluene
IV ,, ,, ,, ,, ,, tetra (pentabromophenoxy) silane

Gas-phase reactions

V Standard resin
VI ,, ,, + 15g/100g Cereclor 70
VII ,, ,, ,, Timonox (antimony oxide)
VIII ,, ,, ,, Cereclor 70 + 15g/100g Timonox
IX ,, ,, ,, ,, + 7·5g/100g Timonox
X ,, ,, ,, Cereclor 70L + 7·5g/100g Timonox
XI ,, ,, + 16·2g/100g Cereclor 65L + 7·5g/100g Timonox
XII ,, ,, + 20g/100g Cereclor S52 + 7·5g/100g Timonox

Results and Discussion

The d.t.a. and t.g.a. thermograms obtained during pyrolysis of a standard polyester resin system, and the same resin with various additives, are shown in Figs 2 and 3 and Table II.

From Fig. 2 it can be seen that the thermogram has five separate zones, and the temperatures which appear to separate them are recorded in Table II. Firstly there is the normal loss of up to 20% by wt. up to about 300°, followed by the rapid loss in weight characteristic of the thermal reforming stage. At about 400° there is an apparent halt point up to about 450°, corresponding to a loss of under 5%. Between 450° and 550° a further loss of 15% appears. Finally the curve levels out.

Fig. 4 (a) shows the thermograms normalised with reference to the second stage of pyrolysis and this shows not only the various stages designated, but also the effect of various chlorinated additives. Fig. 4 (b) contains curves which show the thermal changes. Because conditions were oxidative, all changes are exothermic and the large exotherm should be associated with the second loss in weight between 450–550° (Fig. 3). In it, the presence of halogen gives a slight increase in exotherm, and a slight lowering in peak temperatures. The smaller first exotherm on the other hand is distinctly decreased. In the initial part of the weight curves, there is not a great deal of difference between the various materials except that the brominated materials are losing weight faster.

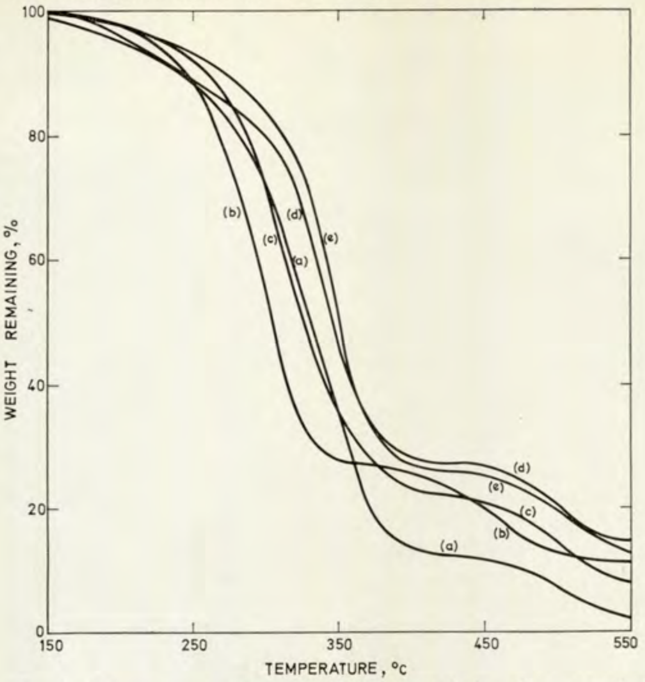

Fig. 2. *Thermograms obtained during pyrolysis of a standard polyester resin and with various additives*
(a) No additive; (b) with Dechlorane +; (c) with Cereclor 70; (d) with pentabromotoluene; (e) with tetra (pentabromophenoxy) silane

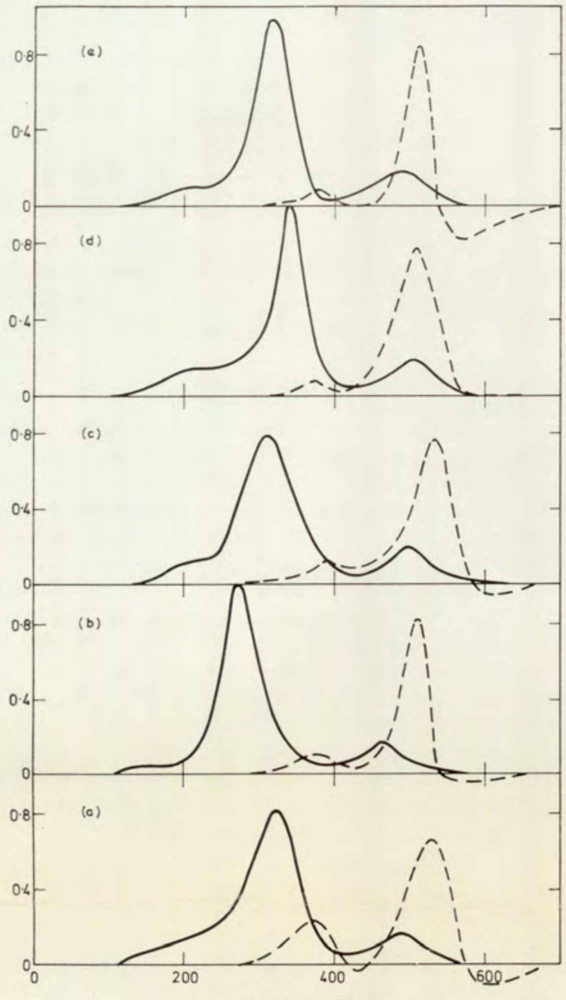

Fig. 3. *Differential thermogravimetric analyses* (———) *and differential thermal analyses* (— — —) *for standard polyester resin and with various additives*
(a)–(e) as for Fig. 2

TABLE II

Thermogravimetric analyses
(Apparent points of inflexion—Fig. 2)

Sample	A	B	C	D	Temp. for 50% residue	Residue, %
I	260	370	425	525	310	10
II	265	370	450	550	325	5
III	275	375	470	525	345	15
IV	300	370	475	550	350	10
Resin alone	265	370	450	540	330	2

The general shapes of these curves agree with those of Anderson & Freeman[30] and of Moore *et al.*[31] It is suggested by Anderson & Freeman that the first stage of weight loss is due to hydroperoxidation of the styrene in the crosslinking chain, followed by rearrangement and cleavage to give benzaldehyde as one of the products of degradation. The second stage is thought to be due to bond rupture, with the formation of phthalic anhydride and decarboxylation to give CO_2 and propylene; the final weight loss is thought to be due to solid-phase oxidation of the residual carbon. Anderson & Freeman support these suggestions with calculations of energies of activation, reaction orders and frequency factors.

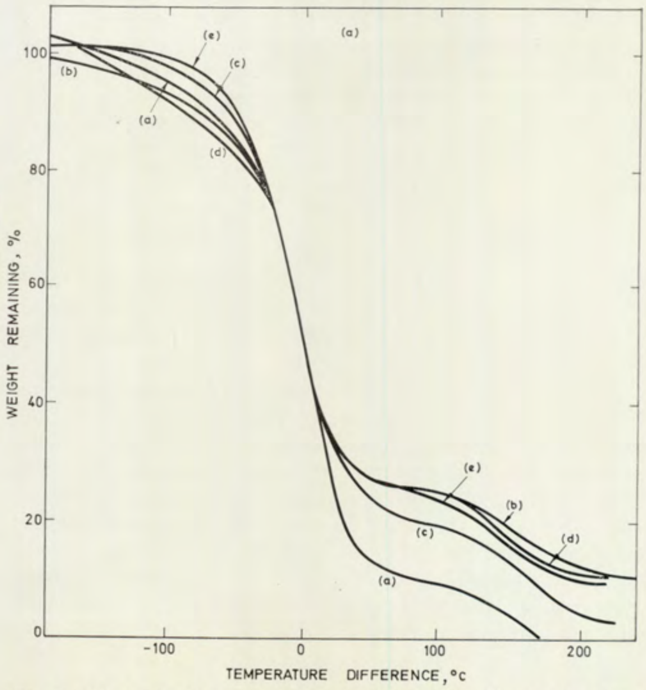

Fig. 4. (a) *Resin thermograms normalised with reference to second stage of pyrolysis*
(a)–(e) as for Fig. 2

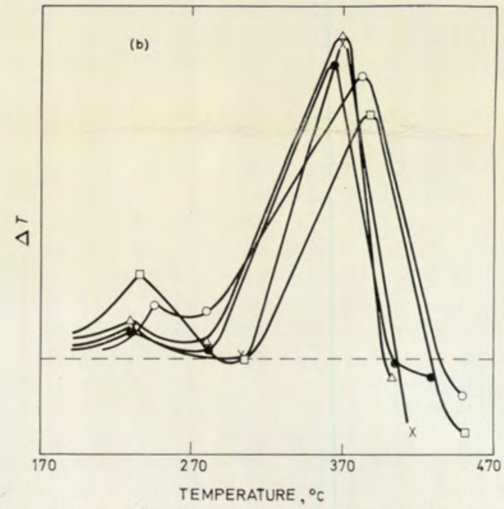

Fig. 4 (b) *Thermal change of plastic with increasing temperature*
□ No additive; ● with Dechlorane +; ○ with Cereclor 70; △ with pentabromotoluene; × with tetra (pentabromophenoxy) silane

Thermal volatization analysis thermograms obtained in this laboratory, which will be reported later, generally take the form of the differential thermograms without the final peak which has been assigned to oxidation of the carbon residue. This accords with the suggested mechanisms, if it is assumed that sufficient peroxide residues are present initially in the cured network for the hydroxyperoxidation of the styrene.

It is not possible at this stage to explain the effects of the various halogenated additives on this general pattern of degradation, without extensive analysis of the products of pyrolysis, which are being continued. It is to be noted, however (Fig. 2) that in every case, the use of an additive decreases the total loss in weight and that this difference has occurred by the end of the second stage of pyrolysis. The weight loss due to the final solid-phase reaction is approximately equal, whether or not an additive is present. The fact that the exotherm associated with the second stage of weight loss is

TABLE III

Oxygen index vs linear gas flow

Gas flow rate, cm/sec	Oxygen index
4·1	0·191
4·4	0·192
5·6	0·192
7·9	0·192
9·6	0·192
11·3	0·192
12·0	0·193
14·8	0·196

larger than for those with additives (Figs 3 and 4) also suggests that it is in this stage of the overall reaction that the flame retardants act.

Table III shows the results of preliminary tests using the 'candle-burning test' to find the range over which varying rates of flow in the chimney would give constant oxygen index figures. Above 12·5 cm/sec flow was too rapid and the flame tended to blow out.

It can be seen how the addition of various materials has affected the burning of the standard resin (Table IV). Materials with an oxygen index above 0·260 would correspond to the qualitative description of self-extinguishing. The synergistic effect of using both halogen and antimony oxide can be seen (compounds VII, VIII and IX for example). Furthermore, the differences between the various additives are shown.

The differences between the several chlorinated materials (Cereclors) with antimony oxide are greater than might be expected, especially between compounds IX and X. These differences arise from the difference in physical state of the Cereclors, as the mixtures cited all have similar chlorine contents. Cereclor S52, 65L and 70L are all liquids, while No. 70 is a solid. It is thought that heating tends to decompose the solid Cereclor to a higher degree than the liquids, which partly distil undecomposed. There is therefore more HCl available from the solid material, for reaction with the Sb_2O_3.

No definite relation is apparent between the ignition temperature and oxygen indices, but the addition of a flameproofing material produces an increase in ignition temperature above that of the standard resin in every case.

TABLE IV

Effects of Cereclor and antimony oxide

Compound number	Oxygen index	Ignition temperature, °C
V	0·192	459
VI	0·235	483
VII	0·233	466
VIII	0·367	506
IX	0·350	480
X	0·295	479
XI	0·287	483
XII	0·260	472

The resin mixture VII which contains the only additive not likely to be volatile below the ignition temperature of the standard resin gives only a slight increase in ignition temperature. This is taken to confirm that the flame-retarding effect of the additives is largely due to inhibition of reactions in the vapour phase. This proposal agrees with observations that in all mixtures containing both halogen and antimony, ignition was preceded by a series of explosions, probably indicating that the ratio of fuel to oxygen was suitable for combustion and ignition did in fact occur, but the flame was snuffed out by the initial presence of volatile inhibitors in sufficient concentration to prevent flame propagation.

Conclusions

From this preliminary report, it is clear that there are several techniques capable of estimating the effect of added materials on the flammability of a polyester resin, and in general giving a series of index figures which will enable quantitative results to be obtained.

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FLAMMABILITY OF PLASTICS

II.* EFFECT OF ADDITIVES ON THE FLAME

By G. S. LEARMONTH and D. G. THWAITE

Setchkin ignition tests and candle-burning tests have been shown to provide a numerical index of the effect of flame retardant agent on polyesters. Experimental details for a number of commercial halogenated retardants, which were tested, are given and some conclusions are made about the nature of their action.

Introduction

Burning of plastics materials involves two series of events: (i) the breakdown of the solid material under thermal stress resulting in gaseous and volatile liquid fragments; and (ii) at a suitable concentration and temperature, spontaneous reaction between these fuels and the oxidant, resulting in a flame.

In an earlier paper[1] the fundamental basis of the burning of polymers was reviewed and it was concluded that there was scope for a more basic approach to the problem of flammability. It was shown that a logical approach lay in a 'two-pronged' attack, i.e. investigating solid-phase thermal degradation pathways and means of altering them with a view to reducing the concentration of evolved flammable components, and interfering with flame reactions.

The present paper reports the suitability of equipment and procedures for investigating the effect of reactions occurring in the vapour phase. The candle-burning test equipment was developed by Fenimore & Martin[2] for use with plastics. The test consists essentially of burning a stick of polymer in a candle-like manner in an atmosphere which has a variable oxygen concentration. The limiting oxygen concentration which allows a test piece to completely burn is determined and is expressed in terms of the ratio:

$$n = \frac{[O_2]}{[O_2] + [N_2]}$$

where $[O_2]$ and $[N_2]$ are the volume concentrations of oxygen and nitrogen in the atmosphere; for air n is taken to be 0·210.

Work described here was carried out with an unsaturated polyester resin based on maleic and phthalic anhydrides and propylene glycol, cross-polymerised with styrene monomer $[-CH_2-CH(C_6H_5)]$. Chemicals likely to be active in reducing the flammability of this resin were added; these are listed in Table I. The object of the work was to obtain a correlation between the results of the proposed test methods with the well-known technological effects of certain materials. It is proposed to follow this work by studying the effect of these and other compounds on the burning of model flames. Thus by eliminating the solid phase and therefore the pyrolysis reactions a study of the action of these retardants on the flame will be made slightly less complex.

Experimental

Sample preparation

The solid linear resin was dissolved in styrene monomer by rotation in a Pascall ball-mill for 48 h.

Retardants in all but two cases were added to the resin solution and rotated on the Pascall ball-mill until good dispersion was achieved, normally after about 30 min. The initiator was added to this mixture and rotated for 10 min.

2% by wt. of benzoyl peroxide was used as a polymerisation initiator.

Samples of cured resin for testing were prepared using a cure cycle of 1 h at 70° followed by a post-cure of 24 h at 70°. These are listed in Table II.

Three types of test specimen were cast.

TABLE I

Additives used to reduce flammability of resins

Additive Trade Name	Chemical nature of additive	Supplier
Cereclor 70	Solid chlorinated paraffin containing 70% chlorine	I.C.I. Ltd.
,, 70L	Liquid chlorinated paraffin containing 70% chlorine	,,
,, 65L	Liquid chlorinated paraffin containing 65% chlorine	,,
,, S52	Liquid chlorinated paraffin containing 52% chlorine	,,
Timonox	Antimony trioxide (Sb_2O_3)	Anchor Chemical Co. Ltd.
Dechlorane 4070	Perchloropentacyclodecane (78% chlorine)	Kingsley & Keith Chemicals Ltd. (Hooker Chemicals)
,, Plus 515	Perchloropentacyclodecane (65% chlorine)	,, ,, ,,
Firemaster T23P	tris(2,3-dibromopropyl) phosphate	,, ,, ,,
—	tris(2,3-dichloropropyl) phosphate	Albright & Wilson Ltd.
TTP	Tritolyl phosphate	Geigy (U.K.) Ltd. Industrial Chemicals Div.
TXP	Trixylyl phosphate	
Flammex 4BS	Tetra(pentabromophenoxy) silane	F. W. Berk Ltd.
,, 5BT	Pentabromotoluene	,,
,, 5AE	Pentabromophenyl allyl ether	,,
,, 3AE	Tribromophenyl allyl ether	,,
Zinc borate 9506	$Zn(BO_2)_2.2H_2O$	Joseph Storey & Sons Ltd.
Calcium borate 9578	$Ca(BO_2)_2.2\frac{1}{2}H_2O$	,, ,, ,, ,,

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*Part I: Preceding paper.

TABLE II

Composition of resin mixtures used

Additives	Sb_2O_3, nil	Sb_2O_3, 7·5g/100g	Sb_2O_3, 15g/100g	Bi_2O_3, 7·5g/100g + As_2O_3, 7·5g/100g
Cereclor 70	1	3	7	23
,, 70L		4		
,, 65L		5		
,, S52		6		
Dechlorane 4070			8	
,, Plus 515		10	9	
Flammex 4BS			15	
,, 5BT			16	
,, 3AE			17	
Firemaster T23P	14		13	
tris(2,3-dichloropropyl) phosphate	12		11	
TTP	18		20	
TXP	19			
Zinc borate 9506	21			
Calcium borate 9578	22			
None			2	

Ignition samples

These were blocks of dimensions $\frac{3}{4}$ in × $\frac{3}{4}$ in × $\frac{1}{2}$ in cast into a pre-heated mould capable of producing six specimens. The mould was coated with a mould release agent, and the top face of the specimens was covered with a strip of cellophane film. On completion of the curing cycle the specimens were trimmed to a regular weight on a linishing machine. A satisfactory weight range was found to be 4·9–5·5 g.

Candle-burning sticks

These were cast in the form of sheets in frame moulds 8 cm^2 × 3 mm thick between cellophane film backed with plate glass. When heated the film became taut, which gave the resin casting a smooth finish. An initial attempt to cut test specimens from the fully cured sheet was abandoned owing to loss of material through shattering. A method of cutting the material with a sharp knife when gelled but not hard proved the most satisfactory. The time taken for a sample of the material to reach this state depended upon the additive present.

Strips for B.S. 2782 *Method* 508*A*

A similar technique to that just described was used. The test specimens required the dimensions 6 in × 0·5 in × 0·060 in and were cut from sheets 6 in^2 × 0·060 in.

Vickers Pyramid Hardness Numbers (V.P.N.) were used as a simple test to indicate the extent of cure which was aimed at being complete. Specimens prepared for ignition determinations were tested using a load of 2½ kg applied for 5 sec. Five impressions were taken, and the mean was reported. Table III shows hardness numbers of one batch of the standard resin cured for various times.

TABLE III

Vickers Pyramid Hardness Numbers (V.P.N.) of standard resin cured for various times at 70°C

Cure time, min	V.P.N.
10	—
15	26·9
20	27·3
25	27·3
35	27·3
45	25·8
60	28·3
120	27·3

Table IV gives V.P.N. values for six batches of the standard resin prepared at different times but under the same conditions.

It is apparent that a sufficiently high degree of cure may be achieved by heating for 1 h at 70° followed by a post-cure of 24 h at 70°.

The addition of flame retardant additives affected the curing properties of the resin as indicated in Table V which shows the optimum cutting time for B.S. 2782 Method 508A. These times were the period between the material entering the oven in a pre-heated mould and the time when they were most easily cut, i.e. between gelled and hard states.

TABLE IV

Vickers Pyramid Hardness Numbers (V.P.N.) of different batches of standard resin cured at 70°C

Resin batch	V.P.N.	
	Post-cure 22 h	Post-cure 38 h
1	29·9	29·8
2	29·9	29·6
3	29·3	30·1
4	30·2	29·0
5	29·2	29·5
6	29·8	30·4

TABLE V

Optimum cutting time for B.S. 2782 Method 508A for various resins

Resin mixture No.	Cutting time, min	Resin mixture No.	Cutting time, min.
Standard resin	25–30	12	40–45
1	35–40	13	55–60
2	45–50	14	40–45
3	45–50	15	40–45
4	50–55	16	35–40
5	50–55	17	45–50
6	50–55	18	50–55
7	40–45	19	60–65
8	40–45	20	45–50
9	40–45	21	35–40
10	40–45	22	35–40
11	40–45	23	40–45

Additives and in particular organic liquids increase the time before gelation.

These followed the expected pattern, i.e. the addition of organic materials to the resin decreased the hardness in accordance with the viscosity of the added material. It was noted that the resin containing Flammex 3AE had a V.P.N. of less than 10, presumably because of the low crosslinking efficiency of 3AE compared with styrene. Addition of inorganic compounds had no effect on the ultimate hardness of the material although they did tend to delay the gel time. As expected those materials which most effected the gel time of the resin were the organic compounds, particularly the liquids.

Apparatus and test procedures

Candle-burning test

Fig. 1 shows the apparatus, which consists of a vertical glass chimney 8 cm dia. × 60 cm high, into which mixtures of air with oxygen or air with nitrogen may be passed. The gas-flow metering devices (Fig. 2) are essentially orifices set in the inlet gas stream with a Bourdon gauge on the high-pressure side of the orifice. In practice the orifices are bored in a brass disc. By rotating the disc the required size of orifice may be placed in the way of the gas stream. The pressure reading on the gauge will depend upon the size of the restricting orifice and the source pressure. When gas is allowed to flow into the barrel a Teflon seal seats itself against the disc and prevents leakage. The flow of gas into the barrel may be adjusted accurately by means of precision regulators.

On leaving the metering devices the gases are mixed in a common outlet line and fed into the base of the glass chimney where further mixing is effected by passing them through a layer of glass chips. Gas-flow calibration curves were obtained over a wide range of gauge pressures for each orifice.

The resin strip was ignited from the top by means of a coal gas flame supported at the end of a glass tube 12 in long. It was found advisable to commence burning in an atmosphere rich in oxygen and reduce this when a steady flame had been attained. An average of 35 sticks of each material were burnt in order to obtain values of oxygen index. An Elliott 803 computer was programmed to prepare a table of *n* values for

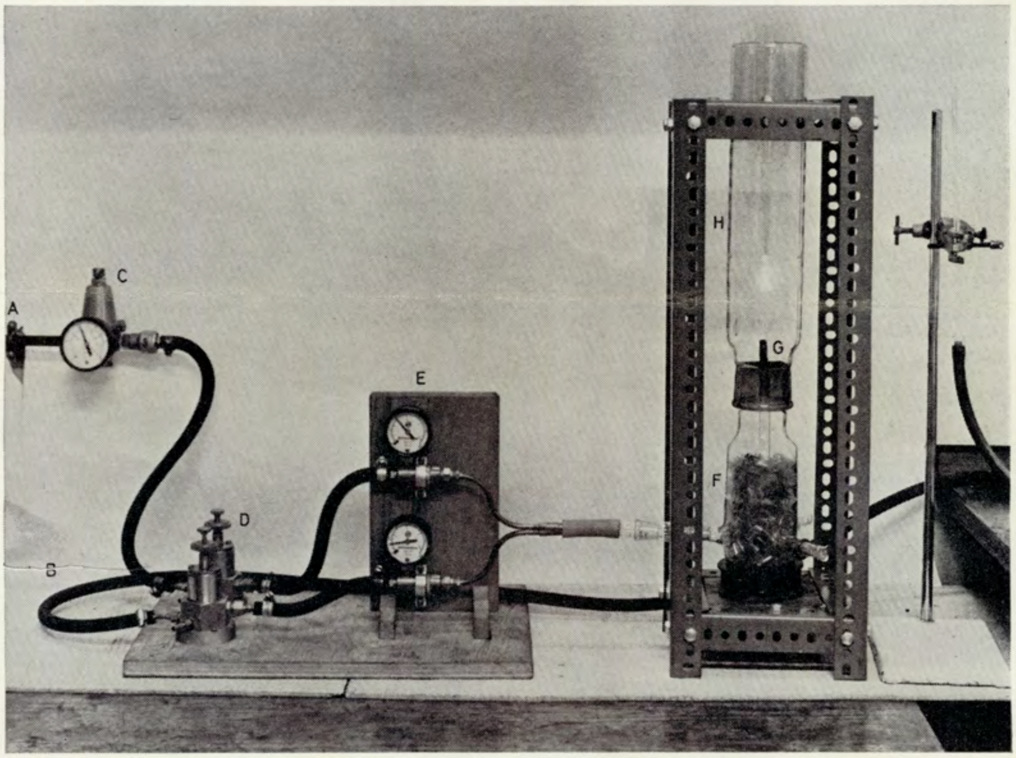

Fig. 1. *Candle-burning apparatus*

A, High pressure air source; B, high pressure O_2/N_2 source; C, reducing valves; D, precision regulators; E, metering devices; F, glass chips; G, polymer stick; H, glass chimney

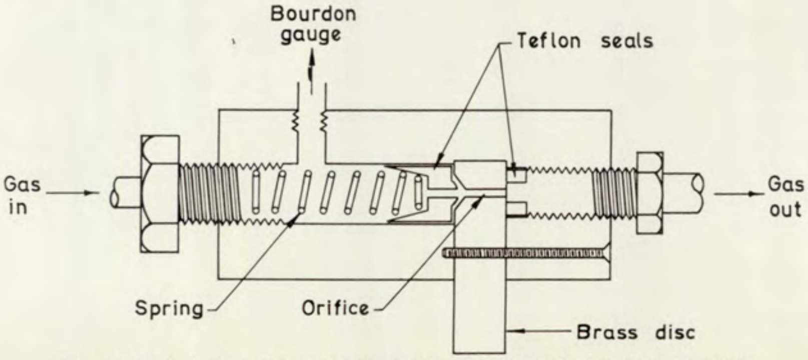

Fig. 2. *Detail of gas-flow metering equipment of candle-burning apparatus*

mixtures of air–oxygen and air–nitrogen; by means of this table, equivalent oxygen indices for varying rates of gas flow through the chimney were readily available. In practice wherever possible the value of the oxygen index was tested for at least two different total gas-flow rates. Fenimore & Martin[2] maintained critical flow at all times but the present authors found this was not possible when the gas mixture approached a value of $n = 0{\cdot}210$, i.e. when the diluent gas was at a very low concentration. In fact it was found impossible to accurately determine values between 0·205 and 0·210 and also values between 0·228 and 0·210, owing to the very low concentration of diluent gas required to obtain these values. It was found, however, that few materials fell into these categories.

Setchkin ignition test

Previous to the development of this test by Setchkin[3] methods of determining ignition temperatures of plastics have probably not, in fact, determined the lowest temperature at which ignition would occur. Techniques used include: bringing a heated porcelain rod into contact with the material and estimating the temperature of the rod at which spontaneous ignition occurs;[4] placing a specimen in a pre-heated furnace at a temperature known to be above the ignition temperature, recording temperatures at various points inside the sample at ignition and estimating from these the surface temperature at ignition;[5] and surrounding the sample under test with an electrical coil and determining the time lag between the production of volatile materials and ignition by high-tension sparking plugs.[6] Results obtained using these techniques were not reproducible and their mean values differed numerically among themselves.

The apparatus devised by Setchkin is shown in Fig. 3. Essentially it consists of a vertical tube furnace, in the centre of which a sample is sited in a crucible. Inside the furnace, a coronite tube of dia. ½ in less than the bore of the furnace stands on a tripod. Metered air is passed down between the furnace and the tube, and then circulated up through the inner tube around the sample which is in its path.

The test determines the minimum air temperature at which ignition occurs. Temperatures are recorded at the sample surface, immediately below the sample holder and at the furnace coils. Adjustment in temperature is made with reference to the latter thermocouple.

A slight modification of the procedure was adopted for the determination of spontaneous ignition temperatures of plastics. It required an approximate ignition temperature to be determined by raising the furnace temperature at a rate of 500°/h for linear air flow rates of 5, 10 and 15 ft/min consecutively, and observing which flow rate produced minimum ignition temperatures. It also required isothermal determinations to be made, near this ignition temperature at the air flow rate producing minimum ignition temperatures. These runs were carried out by decreasing the temperature at each run until ignition failed to occur. The temperature above this was taken to be the ignition temperature of the material.

In practice it was found that a temperature rise of 500°/h was not sufficient, especially with resins containing flame retardants, as most of the combustible volatiles had been released before the ignition temperature had been reached. A temperature rise of 2,400°/h produced ignition in every case.

Initial experiments on the standard resin to determine the air flow rate which produced the lowest ignition temperature, showed that a flow of 5 ft/min through the apparatus was appropriate, and this was adopted for all later experiments.

Rate of burning (*Test B.S.* 2782 *Method* 508*A*)

The equipment used in this test is shown schematically in Fig. 4. The tests were conducted according to the specification, which requires two pencil lines to be drawn on the

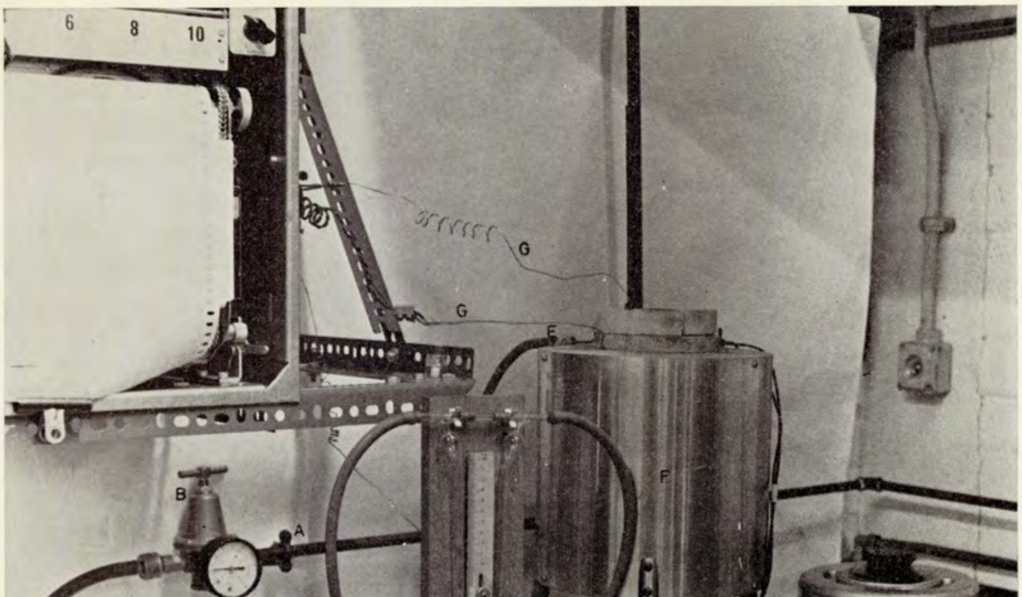

Fig. 3. *Ignition temperature determination equipment*

A, High pressure air source; B, reducing valve; C, precision regulator; D, flow meter; E, air flow through base of furnace; F, furnace containing sample holder; G, thermocouples

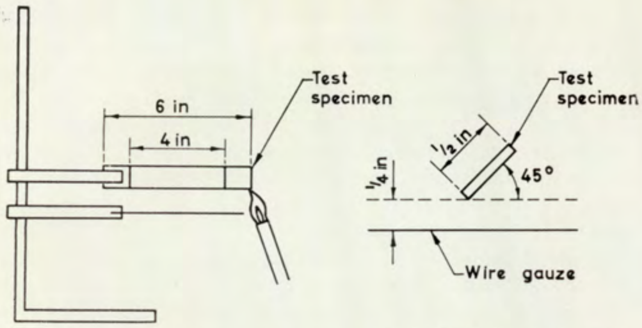

Fig. 4. *Rate of burning test equipment* (*B.S.* 2782 *Method* 508*A*)

specimen 1 in and 5 in from the same end and the strip to be held at an angle of 45° above a wire gauze. A coal gas flame, non-luminous and ½ in. in height is held to the free end for 10 sec and the time for the flame to spread between the two lines is observed. If the flame fails to spread to the first line the material is designated self-extinguishing according to this specification. The rate of burning is then easily calculated in in/min. Five specimens of each resin mixture were tested and the mean value was reported.

Thermal stability of Cereclor

A simple distillation experiment was carried out on the Cereclor range of additives. These materials were individually heated in a glass still until only a char remained, and the distillate was collected and weighed. It was apparent that heating under these conditions resulted in decomposition of part of the material. Infra-red spectra were obtained on the original material and the distillate in an attempt to assess the degree of decomposition. The chief differences were the appearance, in the spectrum of the distillate, of a weak to medium absorption band at 1620–1660 cm^{-1} and of a medium strength band at 960–980 cm^{-1} indicating the loss of some HCl.

Table VI shows the wt.-% distillate obtained for each Cereclor compound and the oxygen index of the corresponding resin mixture.

Results

Table VII lists values of oxygen index, spontaneous ignition temperature, rate of burning (according to B.S. 2782 Method 508A) and Vickers Pyramid Hardness Number for each of the materials listed earlier.

Discussion

Effect of additives on after-glow properties

In general it was observed that materials which contain halogenated additives tended to glow after ignition had ceased. This was especially so in the cases of mixtures of Sb_2O_3 and halogenated organic materials in the standard resin. After-glow was readily seen in the residues of burnt sticks of these materials in the candle burning test. The ignition test also clearly showed the occurrence of after-glow in these materials.

After-glow is the name given to the phenomenon of quite intense glowing in the charred residue of a burnt plastic material after the flame has gone. This phenomenon is attributed to the solid phase oxidation of carbon in the highly exothermic reaction:

$$2C + O_2 \longrightarrow 2CO$$

Fig. 5 shows typical traces of temperatures recorded in ignition determinations on the standard resin, the resin containing halogenated organic compounds and antimony trioxide, and the resin containing halogenated phosphorus compounds with and without antimony trioxide.

TABLE VI

Oxygen index and wt.-% distillate of some Cereclor additives

Additive	Distillate, wt.-%	Dist. temp. range, °C	Oxygen index
Cereclor 70	—		0·350
,, 70L	26·8	288–296	0·295
,, 65L	51·0	274–280	0·287
,, S52	54·1	256–262	0·260

TABLE VII

Rate of burning and other data for resins tested

Resin No.	Oxygen index	Ignition temp, °C	V.P.N.	Rate of burning, in/min
Standard Resin	0·192	459	29·7	0·83
1	0·235	483	26·2	0·72
2	0·233	466	29·6	0·58
3	0·350	480	29·8	s.e.*
4	0·295	479	27·6	s.e.*
5	0·287	483	21·5	s.e.*
6	0·260	472	15·9	s.e.*
7	0·367	506	30·9	s.e.*
8	0·282	495	30·7	s.e.*
9	0·286	515	38·4	s.e.*
10	0·252	492	33·8	s.e.*
11	0·238	506	22·1	s.e.*
12	0·232	459	18·0	s.e.*
13	0·295	456	32·0	s.e.*
14	0·255	420	28·9	s.e.*
15	0·346	481	27·5	s.e.*
16	0·293	461	26·3	s.e.*
17	0·328	463	< 10	s.e.*
18	0·210–0·228	482	14·2	0·74
19	0·210–0·228	476	14·6	0·81
20	0·210–0·228	486	22·3	0·67
21	0·205–0·210	386	31·1	0·90
22	0·205–0·210	397	29·9	0·76
23	0·295	489	35·3	s.e.*

*s.e. = self-extinguishing

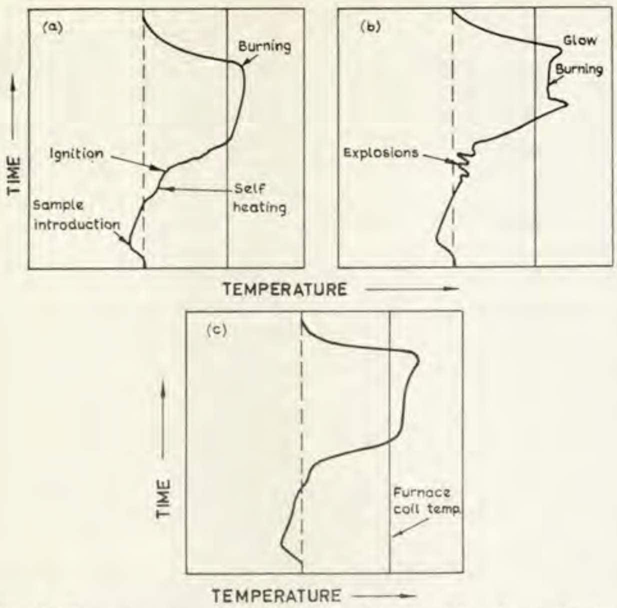

Fig. 5. *Time–temperature traces recorded in ignition determinations* (a) Standard resin, (b) resin containing halogenated organic compounds $+Sb_2O_3$, (c) resin containing halogenated phosphorus compounds with and without Sb_2O_3

It is clear that after-glow is not occurring in the standard resin or those materials containing phosphorus but is a characteristic of those materials containing halogen compounds and antimony trioxide.

It is expected that differential thermal analysis (d.t.a.) and thermogravimeteric analysis (t.g.a.) will be useful in the study of after-glow.

Effect of additives on the flame

The flame produced when the standard resin was burnt tended to be small and stable. At the limiting oxygen concentration the size of the flame decreased until it was the same width as the stick. Below the limiting oxygen concentration the flame decreased still further in size until it was finally extinguished. On the other hand those materials with relatively high *n* values tended to burn with a stable flame only in oxygen concentrations well above the limiting value. These flames were extremely large, and when the limiting oxygen concentration was approached the flames remained large and were apt to flicker and sometimes lift completely away from the solid material. Extinction in these cases was invariably preceded by violent flickering.

A general trend was apparent in the way in which extinction occurred. Those materials with low *n* values, i.e. those which burn more readily in air, burned with a reasonably stable flame even near their limiting oxygen concentration and below this the flame decreased in size until it went out. As the *n* value increased, the size of the flame at the limiting oxygen concentration also increased but stability decreased.

The experiments reported fall broadly into three separate groups which are concerned with (a) investigation of chlorine as a flame retardant, (b) investigation of bromine as a retardant and (c) investigation of the effect of various other flame-retarding species.

Candle-burning test

Chlorine as a flame retardant

The effect of chlorine in chlorinated paraffins, cyclic decane, and chlorinated phosphates on the flammability of the standard resin was investigated. If the results obtained are compared against each other in groups it is clear that for 15g/100g chlorinated paraffin (or equivalent, for lower chlorine contents) and 7·5g/100g antimony trioxide (resin mixture Nos 3, 4, 5 and 6), the effectiveness of the solid Cereclor 70 is greater than that of the three liquids. It is also apparent that the effectiveness of the liquid Cereclors increases with chlorine content of the compound although the total chlorine concentrations are equivalent. Comparison of oxygen indices of resin mixtures 3 and 7 show that increasing the concentration of Sb_2O_3 from 7·5–15g/100g has little effect.

Probably the most significant result is the decreased oxygen index for resins containing the liquid chlorinated paraffins compared with those containing solid chlorinated paraffin both with 70% chlorine concentration. The distillation experiments showed that those materials which are more volatile were the least effective as flame retardants. It is therefore suggested that the fire retardant effectiveness of the chlorinated paraffin depends upon the ability to decompose whilst in the resin rather than distil out as a whole species.

The increase in fire retardant effect produced by the increased residence time of the solid Cereclor in the resin enables two mechanisms to be postulated. (1) Interference with solid-phase degradation reactions by the decomposition of the halogenated material–it is known that on heating, HCl splits out of these paraffins resulting in a randomly distributed polyene structure along the carbon chain; at a suitable elevated temperature cyclisation (inter- or intra-molecular) may occur at these ethenic sites. (2) Reaction between the halogenated decomposition species (HCl) and Sb_2O_3 producing flame-poisoning species (X) – this could be a combination of antimony trichloride and oxychlorides of antimony.

Assuming the proposal that the liquid Cereclors largely distil out unchanged to be correct, then in effect the action of three halogen species in the flame has been investigated. These are (i) HCl (resin mixture No. 1), (ii) chlorinated paraffin plus some X (resin mixture Nos 4, 5 and 6) and (iii) X alone (resin mixture Nos 3 and 7).

The oxygen indices showed that the resin mixtures which are likely to release X into the flame are less flammable than the others.

It has been shown that in order to observe synergism it is necessary for the chlorinated compound to decompose whilst in the resin. The two Dechloranes tested showed inferior effects to both the solid and the liquid Cereclors. This is probably due to part of the Dechlorane being sublimed out of the resin below its decomposition temperature. Comparing oxygen indices of the two resin mixtures Nos 9 and 10 it may be seen that a greater increase in oxygen index is obtained by doubling the Sb_2O_3 concentration for the Dechlorane than for the Cereclor (resin mixtures Nos 3 and 7). This may be because the Dechlorane decomposes to a much smaller extent and thus an increase in Sb_2O_3 in the solid phase will increase the chance of reaction occurring between the halogenated decomposition species (probably Cl_2 in this case) and Sb_2O_3.

Experiments with resin mixture No. 23 investigated the synergistic action between Cereclor 70 at 15 and 7·5g/100g Bi_2O_3 + 7·5g/100g As_2O_3 and showed that synergism occurred although of a lower order than for antimony.

The addition of 15g/100g tris(2,3-dichloropropyl) phosphate to the standard resin has virtually no effect and when 15g/100g Sb_2O_3 is added to this no synergistic effect is observed.

Bromine as a flame retardant

The effect of bromine in the form of pentabromotoluene, tetra(pentabromophenoxy) silane, tribromophenyl allyl ether, pentabromophenyl allyl ether, and tris(2,3-dibromopropyl) phosphate has been investigated.

At first sight it may appear that the chlorinated materials gave a superior performance to the brominated compounds but on closer inspection it will be seen that only in the case of tris(2,3-dichloro)- and tris(2,3-dibromopropyl)-phosphates can a direct comparison be made, and here the bromo compound was superior.

Flammex 5BT and 4BS were added to the standard resin at levels of 15g/100g with 15g/100g Sb_2O_3 (resin mixtures Nos 15 and 16). Flammex 3AE and 5AE were substituted for a part of the styrene monomer and assumed the role of crosslinking agents. Sufficient was substituted to give an equivalent bromine concentration in the final resin to that used for 5BT and 4BS (i.e. 15g/100g). The resin containing 5AE gelled on standing over night and was discarded. 15g/100g Sb_2O_3 was added to the resin containing 3AE (resin mixture No. 17).

If the oxygen indices of these resin mixtures are considered in terms of the volatilities of the brominated compounds then the same arguments put forward for the chlorine compounds are valid: 4BS has a decomposition temperature of 380° and is non-volatile; 3AE has a decomposition temperature of 200° and tends to sublime at temperatures greater than 150°; 5BT has a decomposition temperature of 360° and tends to sublime well below its decomposition temperature. The oxygen indices of the resin mixtures from these compounds were 0·346, 0·328 and 0·293 respectively. As 4BS and 5BT have about the same decomposition temperatures, the differences in oxygen indices can only be attributed to the volatility differences of the compounds. Had 3AE not been chemically bonded into the resin in the form of crosslinks then an anomalous situation would have arisen. However, the bonding prevents sublimation, and therefore when heated, the material loses HBr and/or Br_2 which is able to react with Sb_2O_3.

Fire retardants other than chlorine and bromine

Resin mixtures Nos 18, 19 and 20 respectively show the effect of 15g/100g TTP, 15g/100g TXP and 15g/100g TTP + 15g/100g Sb_2O_3 on the standard resin. Only a slight increase in oxygen index over the value for the standard resin was obtained, and the addition of Sb_2O_3 had no synergistic effect.

The insensitivity of the pressure gauges noted earlier made it possible to assign only a range of oxygen index values to these materials, and all fell between 0·210 and 0·228.

Calcium metaborate, $Ca(BO_2)_2.2\frac{1}{2}H_2O$, and zinc metaborate, $Zn(BO_2)_2.2H_2O$, at concentrations of 15g/100g were also investigated. Each produced only a slight increase in oxygen index over the standard resin, both falling in the range 0·205 to 0·210. These observations are not surprising as borates are primarily used in fire-retardant preparations in textiles and cellulosics, for which degradation pathways are different from those of polyesters. It may therefore be concluded that borates are probably specific, in that their fire-retarding action occurs in the solid phase of cellulosic materials and possibly in materials which thermally degrade in a similar manner.

Ignition temperature determinations

In every case except those of the borates and of T23 P alone, addition of retardants to the standard resin raised the ignition temperature.

No general trend is apparent in the numerical values of these temperatures but there are similarities in the mode of ignition of the various classes. Those materials containing halogenated compounds, and antimony trioxide tended to ignite only after a series of explosions had occurred. This phenonemon was not characteristic of the phosphorus-containing additives. This observation suggests that gas-phase inhibition is occurring with these materials. It seems that fuel gases and oxidant are present in concentrations favourable to burning and that ignition occurs, but propagation of the flame is not possible, probably owing to the joint effects of blanketing and flame poisoning.

With those resins containing halogen and antimony trioxide, evolution of white fumes prior to ignition was apparent, and only after the rate of issue of these fumes had considerably decreased did ignition occur.

The presence of phosphorus in the additive effectively removes the after-glow, which appears to be induced by the halogen species.

It is predicted from the low ignition temperatures obtained for borates that interference with degradation reactions causes the evolution of fuels to occur at a lower temperature.

The traces show that although the shapes of the curves are different for different additives, basically the same events are occurring. Initially a drop in temperature is observed due to the introduction of the sample. This is followed by a warming up period when the sample attains the temperature of its surroundings. The sample then increases above the initial temperature in the crucible; this is the self-heating period and is due to exothermic decomposition reactions. On reaching a certain rate of reaction, ignition occurs and burning continues, in the vapour phase; sometimes this may be followed by glowing in the solid residue. After the flame is extinguished or glow has ceased, a rapid reversion to the original temperature takes place.

Those materials classed as self-extinguishing according to B.S. 2782 Method 508A are more precisely defined in terms of their oxygen indices.

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FLAMMABILITY OF PLASTICS III

Studies of the Reactions between Sb_2O_3 and Organic Halogenated Flame Retardants with Reference to their Performance in a Cross Linked Polyester Resin

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INTRODUCTION

An earlier paper (1) reports on the performance of a number of commercial flame retardants incorporated into an unsaturated cross-linked polyester resin under test conditions suitable for investigating reactions in the vapour phase. A general conclusion drawn from this work was that combinations of halogenated organic compounds and Sb_2O_3 produced species which inhibited flame propagation. More specifically it was found that equal concentrations of Cereclor 70 and Sb_2O_3 proved the most successful retardant, of those tested, by the oxygen index rating. It was pointed out that the effectiveness of this system was probably due to decomposition of the Cereclor 70 in the solid phase evolving hydrogen chloride which reacted with Sb_2O_3 producing one or a number of species active in limiting flame propagation. This paper reports on work undertaken in an attempt to elucidate the nature of the species evolved on heating together organic halogenated materials and Sb_2O_3.

EXPERIMENTAL

1. Materials Tested

TABLE I

Additive Trade Name	Chemical Nature of Additive	Supplier
Cereclor 70	Solid chlorinated paraffin containing 70% chlorine	Imperial Chemical Industries
Cereclor 70L	Liquid chlorinated paraffin containing 70% chlorine	" "
Cereclor 65L	Liquid chlorinated paraffin containing 65% chlorine	" "
Cereclor S52	Liquid chlorinated paraffin containing 52% chlorine	" "
Timonox	Antimony Trioxide Sb_2O_3	Anchor Chem. Co. Ltd
Dechlorane 4070	Perchloropentacyclodecane 78% Chlorine	Kingsley & Keith Ltd (Hooker Chemicals)
Flammex 4BS	Tetra (pentabromophenoxy silane)	F. W. Berk Ltd.
Flammex 5BT	Pentabromotoluene	"
Corvic P65-50	Polyvinyl Chloride	Imperial Chemical Industries

2. Sample Preparation

The powdered samples were accurately weighed and intimately ground with an agate pestle and mortar. The resin samples were ground with a bronze pestle and mortar with dry ice to produce a powder which passed through a 36 mesh and collected on a 100 mesh sieve. A sample weight of between 0.2 and 0.4 gm. was tested in all experiments. All Sb_2O_3/halogenated organic compound mixtures were 50 : 50 by weight.

The techniques employed were very simple and the experiments took two distinct forms:-

2.i. Weight Loss Experiments

Specimens were heated under isothermal conditions and the percentage of the material which was volatile was followed with time.

The experiments were conducted in a stream of air passing at approximately 6 lit./min., through the Setchkin furnace. Samples in 'cut-off' ignition tubes were dropped into the silica crucible which was suspended in the preheated furnace. The temperature inside the crucible was measured with a Cr/Al thermocouple. On completion of the required heating time the crucible and ignition tube were removed and a lid placed over the crucible to exclude air from the cooling sample, prior to weighing.

2.ii. Determination of Hydrogen Chloride and Volatile SbIII

The apparatus used is shown in Fig. (1).

The apparatus was brought to the required temperature before introduction of the sample and this temperature was maintained throughout the experiment. The sample in a 'cut-off' ignition tube was dropped into the preheated apparatus, from the top. The materials which were volatile under test conditions were swept out of the heated part of the apparatus by a stream of air and passed through a liquid nitrogen trap and into a stirred solution of 0.1 N NaOH. Careful control of the air flow rate was necessary as too high a flow rate resulted in the volatile products of reaction between Sb_2O_3 and Cereclor 70 being carried into the alkali solution, resulting in hydrolysis and the production of hydrogen chloride. Too low a flow rate resulted in hydrogen chloride freezing out in the trap.

Hydrogen chloride was estimated by passing into 0.1 N NaOH solution and back titrating the excess with standard hydrochloric acid solution using methyl red indicator. Three determinations were made and the mean reported.

The trapped material was carefully washed from the apparatus with the minimum concentrated hydrochloric acid solution and SbIII determinations were carried out by titrating with standard iodine solution using starch indicator. Three determinations were made and the mean reported.

3. Samples

TABLE II

a. Weight Loss Experiments

Experiment I	(i)	Cereclor 70
	(ii)	1 pt. Cereclor 70 + 1 pt. Sb_2O_3
Experiment II	(i)	Dechlorane 4070
	(ii)	1 pt. Dechlorane 4070 + 1 pt. Sb_2O_3

TABLE II continued

Experiment III	(i)	1 pt. Cereclor 70 + 1 pt. Sb_2O_3
	(ii)	1 pt. Cereclor 70L + 1 pt. Sb_2O_3
	(iii)	1 pt. Cereclor 65L + 1 pt. Sb_2O_3
	(iv)	1 pt. Cereclor S52 + 1 pt. Sb_2O_3
Experiment IV	(i)	Polyester Resin
	(ii)	Physical mixture of polyester resin + 15 pph Sb_2O_3 + 15 pph Cereclor 70.
	(iii)	Polyester resin with 15 pph Sb_2O_3 + 15 pph Cereclor 70 incorporated prior to curing.
	(iv)	1 pt. Cereclor 70 + 1 pt. Sb_2O_3
Experiment V	(i)	1 pt. Cereclor 70 + 1 pt. Sb_2O_3
	(ii)	Flammex 5BT
	(iii)	1 pt. Flammex 5BT + 1 pt. Sb_2O_3
	(iv)	Corvic PVC P65-50.
	(v)	1 pt. Corvic PVC P65-50 + 1 pt. Sb_2O_3

b. Determinations of Hydrogen Chloride and Volatile SbIII

Hydrogen Chloride det.	(i) Cereclor 70
	(ii) Corvic PVC P65-50
	(iii) 1 pt. Cereclor 70 + 1 pt. Sb_2O_3
Volatile SbIII det.	(i) 1 pt. Cereclor 70 + 1 pt. Sb_2O_3

RESULTS

Throughout the following let V be defined as that percentage of the original mixture which was volatile at the temperature under consideration.

a. Weight Loss Experiments

These fall into five separate sections:-

(I) Experiments comparing the degrees of volatilization of the Cereclor 70/Sb_2O_3 mixture and Cereclor 70 alone at 310°C, 410°C and 500°C

Curves of V vs. time are plotted in Figs. (2), (3) and (4).

(II) Experiments comparing the degrees of volatilization of the Dechlorane 4070/Sb_2O_3 mixture and Dechlorane 4070 alone at 410°C, 460°C and 500°C

Curves of V vs. time are plotted in Figs. (5), (6) and (7).

(III) Experiments comparing the degrees of volatilization of mixtures of Cereclor 70, 70L, 65L and S52 with Sb_2O_3 at 310°C, 410°C and 500°C

Curves of V vs. time are plotted in Figs. (8), (9) and (10).

(IV) Experiments showing the effect of 15 pph Sb_2O_3 + 15 pph Cereclor 70 on the degree of volatilization of the standard resin at 310°C, 460°C and 500°C

Curves of V vs. time are plotted in Figs. (11), (12) and (13).

(V) Random experiments observing the reactivity between Sb_2O_3 and various halogenated organic materials at various temperatures.

A list of V values are shown in Table III.

TABLE III

Temp. °C	Time mins.	Sb_2O_3 Alone	Flammex 5BT/ Sb_2O_3	Flammex 5BT	Flammex 4BS/ Sb_2O_3	PVC/Sb_2O_3	PVC Alone
500	120		50.5				
500	30	0.01					
500	15		48.2	98.4	63.6	85.0	96.3
450	15		48.2		28.3		
410	15				10		
380	30				10		
380	15				6.9		
360	30		48.9				
360	15		48.4				

b. Quantitative Determination of Hydrogen Chloride and Volatile SbIII

All decompositions were carried out in air at 500°C for 15 mins. The results are listed in Table IV.

TABLE IV

	Mean Hydrogen chloride as wt % of total Chlorine	Mean Hydrogen chloride as wt. % of total halogenated material	Volatile SbIII as % of total Sb
Cereclor 70	87.5	61.3	
1 pt. Cereclor 70 + 1 pt. Sb_2O_3	9.2	6.4	75.1
Corvic PVC P65-50	97.9	55.7	

DISCUSSION

It is convenient to discuss independently results obtained from the separate experiments listed in the previous section.

a. Weight Loss Experiments

Experiment I

It is clear from Fig. (2) that Cereclor 70 is relatively volatile at 310°C and that also at this temperature decomposition must occur with evolution of hydrogen chloride which reacts with Sb_2O_3 producing volatile antimony species (Sb_2O_3 has been shown to be 0.01% volatile in air at 500°C for 30 mins.).

At this temperature V for the mixture is higher than for the Cereclor alone. While the Cereclor alone is gradually volatile over 15 mins. to a maximum of approx. 68% it is interesting to note that the curve of the mixture rises much more steeply and reaches a maximum of approx. 74% after only 5 mins.

N.B. These times to reach maximum volatilization should be used only for comparative purposes as they include a sample warm up period.

The effect of mixing Sb_2O_3 and Cereclor 70 at 310°C is therefore to increase the total V and also, probably more important from a flame retarding point of view, volatilization occurs more readily than for the Cereclor alone. It is suggested that it is important for prevention of initial ignition that volatile flame inhibiting species be present early in the decomposition of the resin.

Figure (3) shows that at 410°C V for the Cereclor alone is greater than that of the mixture, reaching approx. 86% and 79% respectively. It is important to note that the curve of the mixture again rises more steeply than the Cereclor alone and that total V for the mixture is achieved after approx. 1½ mins. whilst the curve of the Cereclor alone begins to flatten out after six minutes.

Figure (4) follows much the same pattern as figure (3) but with an increase in total V of both the Cereclor alone and the mixture, at this temperature. Maximum values of V are also reached more quickly.

Experiment II

Dechloranes are not considered to decompose appreciably below 400°C. For this reason experiments were carried out at 410°C, 460°C and 500°C.

Figure (5) shows that at 410°C the V for Dechlorane 4070 alone increases linearly between 5 and 30 mins. reaching a value of 92% at 30 mins. The shape of the curve of the mixture is completely different rising sharply and reaching a maximum of approx. 85% after 4 mins.

At 360°C for 60 mins. the mixture achieved a V value Of 51% confirming decomposition to be negligible, although the Dechlorane alone is volatile at this temperature.

At 410°C, however, it is clear that the Dechlorane does decompose, evolving species which react with Sb_2O_3 producing volatile antimony compounds.

Figure (6) gives the V vs. time curves at 460°C. At this temperature the Dechlorane alone is 100% volatile after 15 mins. The value of V for the mixture reaches a maximum of 84% after 2½ mins. At 410°C and 460°C it has been shown that reactivity does occur between Sb_2O_3 and Dechlorane decomposition products resulting in volatile species.

At 500°C (figure 7) the Dechlorane alone has been completely volatilized after 7 mins. The V vs. time curves of both the Dechlorane alone and the mixture follow the same line - the mixture attaining a total V of 85%.

Comparing the Dechlorane 4070/Sb_2O_3 and Cereclor 70/Sb_2O_3 curves it is apparent that both Dechlorane and Cereclor react with Sb_2O_3 to a comparable extent. The reason for the lower oxygen index of the resins containing Dechlorane is probably due to the higher decomposition temperatures of the Dechlorane. From this it may be concluded that under conditions of higher thermal stress as encountered in a fire these materials and also the brominated additives, which have higher decomposition temperatures will be comparable if not superior to the Cereclor 70/ Sb_2O_3 mixture.

It should be pointed out that the candle-burning test by its very nature, assesses the flammability of the material only under conditions of low thermal stress. It is likely, therefore, that whilst this test is excellent for assessing the performance of a material with regards to its being a fire initiator the oxygen index rating probably does not describe its performance under conditions of greater thermal stress as may be encountered in actual fire conditions.

For this reason it will be interesting to compare the performance of these additives under BS.476 part 6 - fire propagation test conditions.

Experiment III

At 310°C the highest value of V is attained by the Cereclor 70/Sb_2O_3 mixture reaching approx. 73% after 5 mins. Cereclor S52 and 70L follow much the same pattern but reach only 55% and 59% respectively. The curve of Cereclor 65L rises much less steeply and flatten out at approx. 60% after 5 mins. At this temperature it is clear that decomposition of all four cereclors does occur (all mixtures achieve total values of V greater than 50%). The higher value of V for the solid Cereclor 70 mixture than with the liquid Cereclor 70L mixture may be due to a lower degree of decomposition in the liquid producing less hydrogen chloride, or alternatively the liquid probably decomposes to a certain extent whilst in the vapour phase resulting in the hydrogen chloride not being in position favourable for reaction with Sb_2O_3.

Figure (9) shows the curves obtained at 410°C, at this temperature the solid Cereclor mixture reaches a markedly higher total V. A trend in time for maximum V to be reached emerges i.e. the primarary slope of the curve is increased with increasing

Cl_2 content of the Cereclor.

Figure (10) provides further evidence for the higher reactivity between the solid Cereclor and Sb_2O_3, whilst a direct comparison of V vs. time curves of the Cereclor 70L mixture and Cereclor 70 mixture may be made it must be remembered that both Cereclor 65L and S52 have lower Cl_2 contents and will therefore not be expected to react to the same extent.

The V values for the Cereclor/Sb_2O_3 mixtures are in agreement with the oxygen index values obtained for these materials in the standard resin. The relevant values of oxygen index were 0.350, 0.295, 0.287 and 0.260 for Cereclor 70, 70L, 65 and S52 respectively at concentration of 15 pph, or equivalent for lower Chlorine content paraffins, with 7.5 pph Sb_2O_3.

Experiment IV

Four materials were studied at three temperatures i.e. 310°C, 460°C and 500°C.

At 310°C (fig. 11) the rate of evolution of gaseous fuels from the standard resin is not great enough for ignition to occur. At this temperature appreciable reaction was observed between the Cereclor 70 and Sb_2O_3 probably accounting for the increase in ignition temperature and explosions occurring prior to ignition.

The physical mixture of standard resin/Sb_2O_3/Cereclor 70 tended to have a higher value of V than in the case where Sb_2O_3/Cereclor 70 was incorporated into the resin, this was as expected.

At 460°C (fig. 12), however, the standard resin alone has a higher degree of volatilization and it is reasonable to assume that between 310°C and 460°C the rate of evolution of fuels increases to a point where ignition is possible. If the concentration of flame inhibiting species are not high enough at this temperature than ignition will occur.

It is clear from figs. (12) and (13) that the Cereclor 70/ Sb_2O_3 mixture is more readily volatile than the standard resin this therefore supports what was previously said in accounting for the effectiveness of this mixture as rated by its oxygen index.

Experiment V

Experiments were carried out on various halogenated organic compounds alone and in mixtures with antimony trioxide under various conditions. These were not carried out over specified time periods as in the previous experiments but under random conditions to see if any pattern could be obtained between reactivity and oxygen index.

Flammex 4BS

Tetra pentabromophenoxy silane has a decomposition temperature of 380°C and is non volatile. V for a 4BS/Sb_2O_3.mixture at 500°C for 15 mins. is only 28.3%. It would therefore seem that decomposition of 4BS occurs at a temperature too high for the full effect to be found in the standard resin. However, the oxygen index of 0.346 is relatively high taking this into consideration and although the antimony bromine compound is not being evolved at the ideal time relative to the decomposition of the resin a comparatively 'good' material is produced. From this it is possible to deduce that bromine has a greater efficiency than chlorine and if a brominated compound initially decomposing around 320°C were used then a marked decrease in flammability may be expected.

Flammex 5BT

On heating the pentabromotoluene with Sb_2O_3 at 500°C over 2 hours, the total V was only 50.5% other experiments on the mixture and lower temperatures and over shorter periods resulted in percentage volatilities of approx. 50%. While heating 5BT alone for 15 mins. at 500°C was 98.4%. It may be assumed from this that negligible reaction occurs on heating pentabromotoluene and Sb_2O_3 together.

The oxygen index of the standard resin containing 15 pph Sb_2O_3 and 15 pph 5BT was 0.293, from the above it appears that synergism does not occur between 5BT and Sb_2O_3, therefore it may be expected that the removal of Sb_2O_3 from the resin mixture would not result in a marked reduction in oxygen index in fact a value of 0.256 was obtained. This is perhaps a little lower than may have been expected but it does indicate that synergism does not occur to any great extent between Sb_2O_3 and pentabromotoluene.

It would seem that the increase in oxygen index on addition of 15 pph Sb_2O_3 to the resin mixture results from the Sb_2O_3 interfering to a certain extent with propagation of flame across the polymer surface - rather than being due to the presence of volatile antimony as flame poisoning species.

PVC

A sample of Corvic P65-50 was heated alone and with Sb_2O_3 at $500^{\circ}C$ for 15 mins. in order to investigate any similarities between this and heating Cereclor 70 and Sb_2O_3 together under the same conditions. The stoichiometries of these reactions are later calculated.

b. Hydrogen Chloride and Volatile SbIII Determinations

Total hydrogen chloride produced from the decomposition of Cereclor 70 and PVC at $500^{\circ}C$ over 15 mins. was estimated by the method described earlier. On attempting to determine excess hydrogen chloride from reaction of a mixture of Cereclor 70 and Sb_2O_3 it was found that volatile antimony chlorides were swept into the alkali solution where they were hydrolysed, producing hydrogen chloride. Erroneous results were thus at first obtained. These volatile antimony chlorides were trapped out with liquid nitrogen after carefully regulating the air flow.

Reaction stoichiometries were thus easily calculated from the weight loss data and hydrogen chloride determinations. In order to confirm these quantities volatile Sb was also determined. SbIII was determined by iodine titration on the trapped out material and it was found that within experimental error all of the volatile Sb was present as SbIII.

Calculation of Reaction Stoichiometries

i) Cereclor 70/Sb_2O_3

All data was obtained at 500°C over 15 mins. From weight loss experiments.

1. The degree of volatility of Cereclor 70 alone is 88.0%.
2. Cereclor 70/Sb_2O_3 50 : 50 mixture V is 82.3%.

Assuming that the Cereclor in the mixture has the same percentage of volatility as when heated alone. Then the percentage of Sb_2O_3 which reacts with hydrogen chloride:

= 2 x (82.3 - 44) = 76.6% of the total Sb_2O_3

Compare analytical determination of volatile SbIII

= 75.1% of total Sb is volatile.

From hydrogen chloride determination we have 87.5% of the total Cl_2 is evolved as hydrogen chloride. From hydrogen chloride determinations on the mixture we have 9.2% of total chlorine is evolved as excess hydrogen chloride.

∴ Chlorine as HCl reacting with Sb_2O_3

= 87.5 - 9.2

= 78.3% of total chlorine.

∴ We have reaction stoichiometry of

$$\frac{76.6}{291.6} : \frac{78.3}{35.5} \times \frac{70}{100}$$

$$0.262 : 1.54$$

$$1 : 5.88$$

Indicating a reaction stoichiometry of

$$Sb_2O_3 + 6\,HCl \longrightarrow 2SbCl_3 + 3H_2O$$

This is confirmed by the evidence for all of the volatile Sb being SbIII.

ii) $\underline{PVC/Sb_2O_3}$

A similar conclusion to that for Cereclor 70/Sb_2O_3 may be expected.

In this case weight loss experiment data and hydrogen chloride determination on the PVC only were obtained. All data was obtained at 500°C over 15 mins.

From weight loss experiments:-

1. The degree of volatility of PVC alone is 96.3%
2. PVC/Sb_2O_3 50 : 50 mixture V is 88.0%.

Assuming that the Cereclor in the mixture has the same percentage volatility as when heated alone then the percentage volatile Sb_2O_3 i.e. the percentage Sb_2O_3 which reacts with hydrogen chloride

$$= 2 \times (85.0 - 48.2) = 73.6\% \text{ of the total } Sb_2O_3.$$

From hydrogen chloride determinations on PVC alone it is seen that 98.0% of the total Cl_2 is evolved as hydrogen chloride. The stoichiometry of the reaction calculated below does not take into account excess hydrogen chloride which did not react with Sb_2O_3.

∴ We have reaction stoichiometry of:

$$\frac{74}{291.0} : \frac{98}{35.5} \times \frac{56.8}{100}$$

$$0.254 : 1.57$$

$$\underline{1 : 6.17}$$

From this it seems fair to predict that the active species is again $SbCl_3$.

It must be emphasised that these determinations have been made on the additives alone and these results represent maximum efficiency of reaction which is not expected to be achieved on incorporation in the resin. However, it is probably fair to assume that the predicted reaction is predominant.

CONCLUSIONS

It has been demonstrated that synergism between Sb_2O_3 and the halogenated additives arises out of reaction between these materials at elevated temperatures producing flame poisoning species.

In the case of Cereclor 70/Sb_2O_3 mixtures and also for PVC/Sb_2O_3 mixture this flame poisoning species has been shown to be predominantly $SbCl_3$.

0-0-0-0-0-0

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2. Learmonth G.S., Nesbitt A. and Thwaite D.G. Brit. Polym. Journal 1969.
3. Vogel A.I. A textbook of Quantitative Inorganic Analysis p.365
4. B.S.S.476 pt. 6. 1968. Fire Propagation Test for Materials.

KEY TO DIAGRAMS

Figs. 2, 3 and 4

a. Cereclor 70/Sb_2O_3

h. Cereclor 70 Alone

Figs. 5, 6 and 7

i. Dechlorane 4070/Sb_2O_3

j. Dechlorane 4070 Alone

Figs. 8, 9 and 10

a. Cereclor 70/Sb_2O_3

b. Cereclor 70L/Sb_2O_3

c. Cereclor 65L/Sb_2O_3

d. Cereclor S52/Sb_2O_3

Figs. 11, 12 and 13

a. Cereclor 70/Sb_2O_3

e. Cereclor 70/Sb_2O_3 each equivalent to 15 pph in a physical mixture with the standard resin.

f. 15 pph Cereclor 70 + 15 pph Sb_2O_3 incorporated into the standard resin.

g. Standard Resin Alone.

FIG 1.

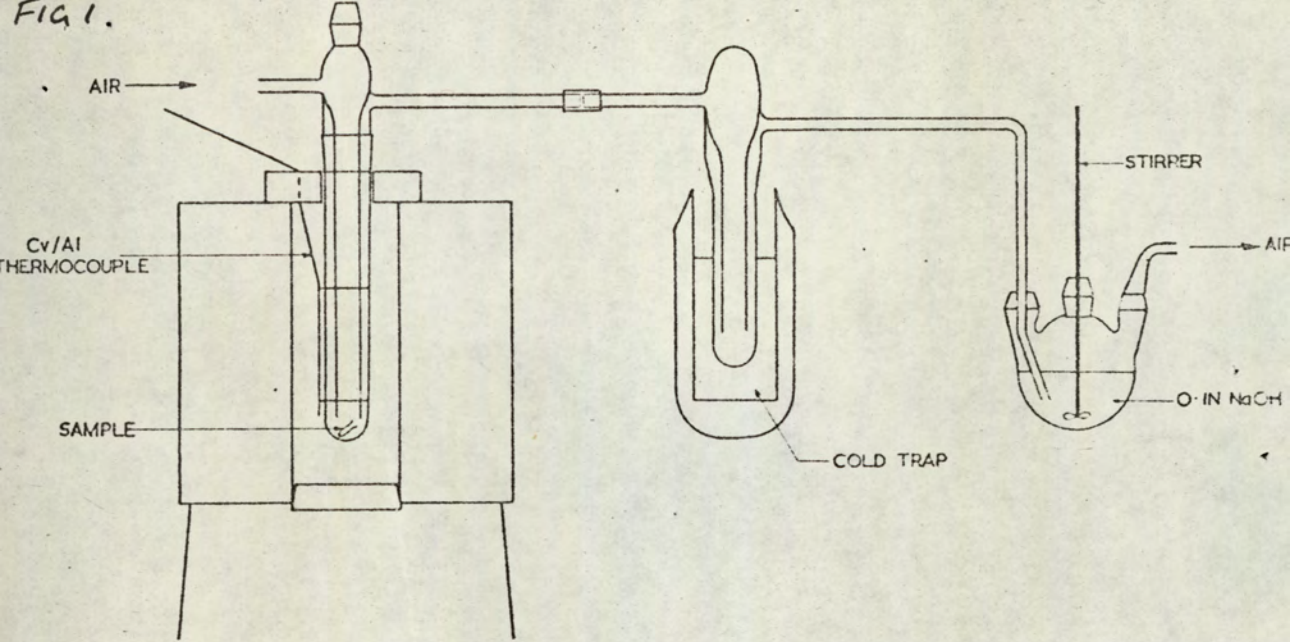

AIR
Cv/Al THERMOCOUPLE
SAMPLE
COLD TRAP
STIRRER
AIR
0·1N NaOH

FIG 2

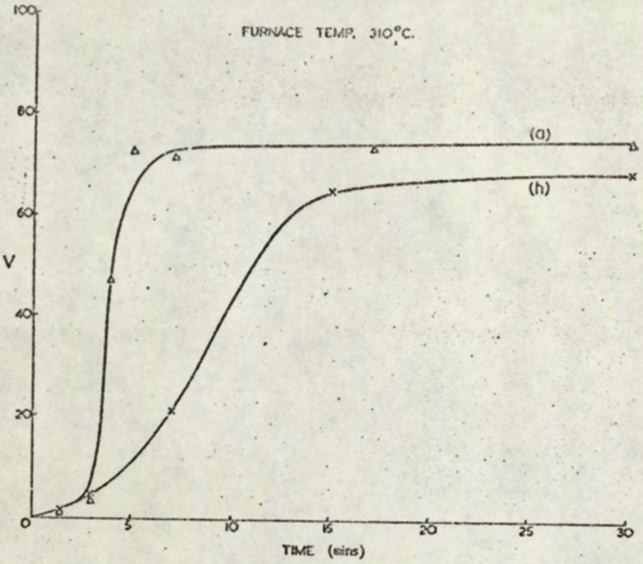


FIG 3

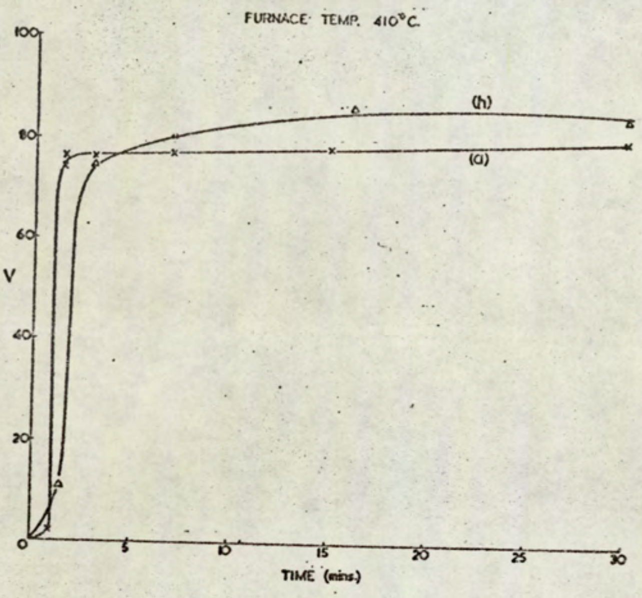


FIG 4

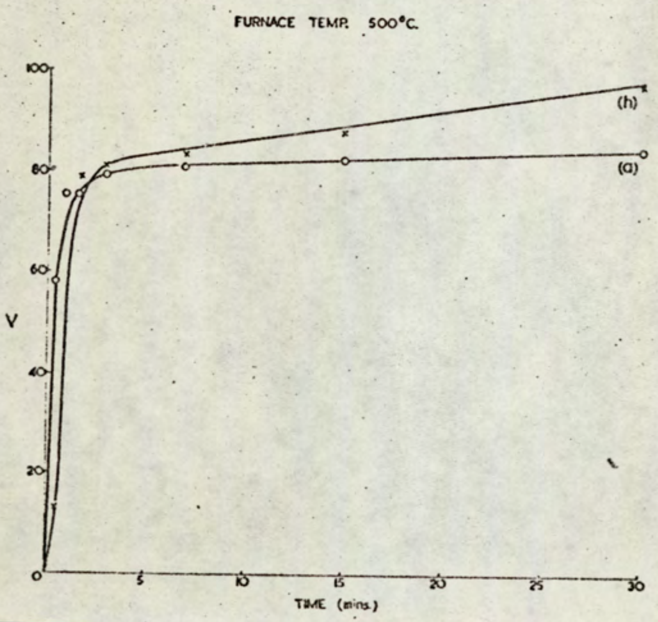


FIG 5

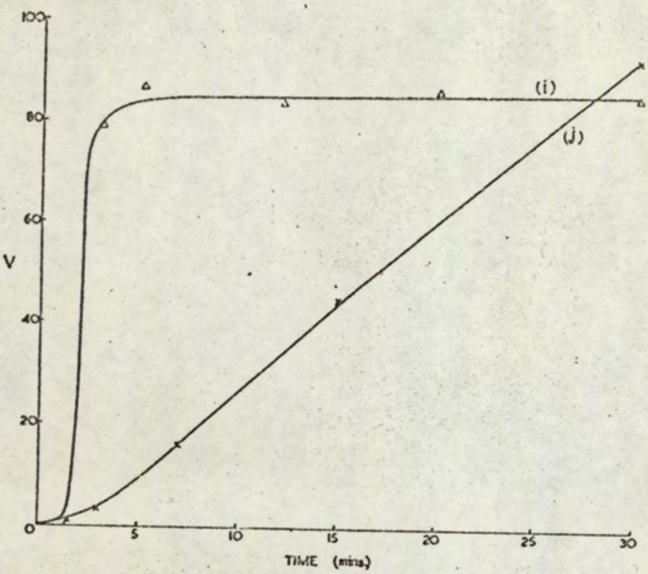

FURNACE TEMP. 420°C.

FIG 6

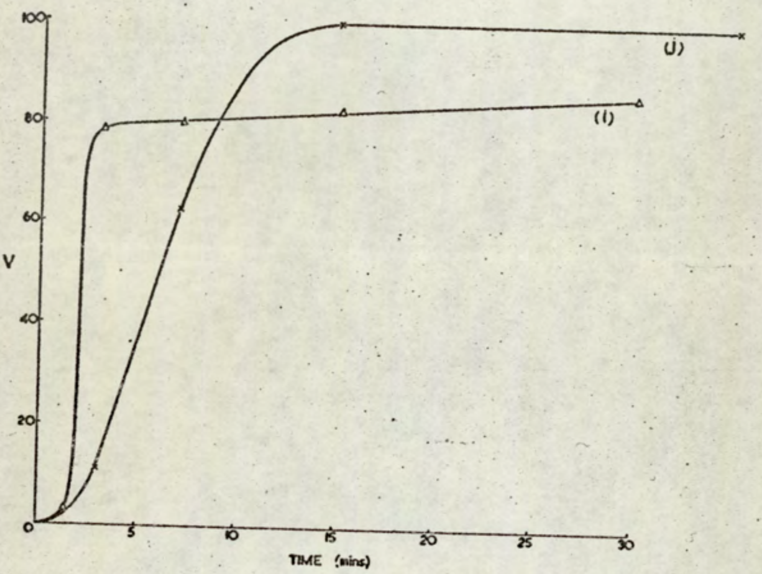

FURNACE TEMP. 460°C.

FIG 7

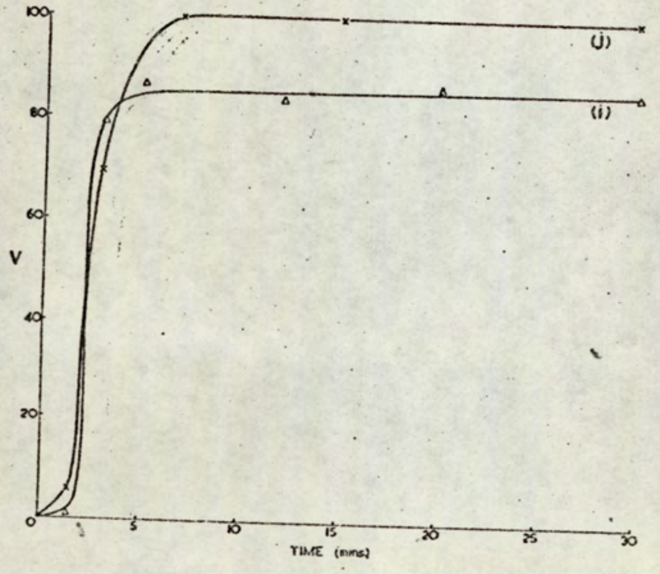

FURNACE TEMP. 500°C.

FIG 8

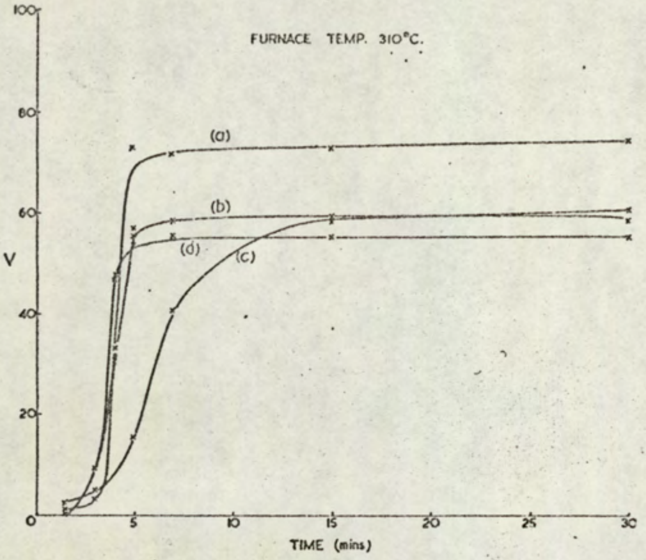


FIG 9

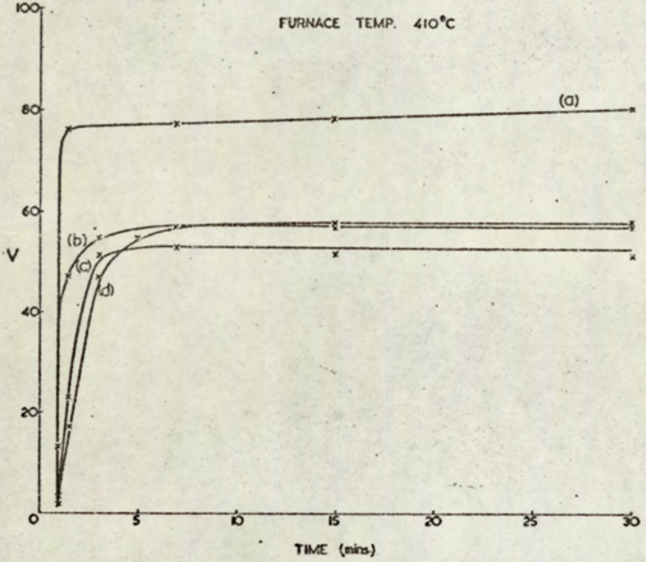


FIG 10

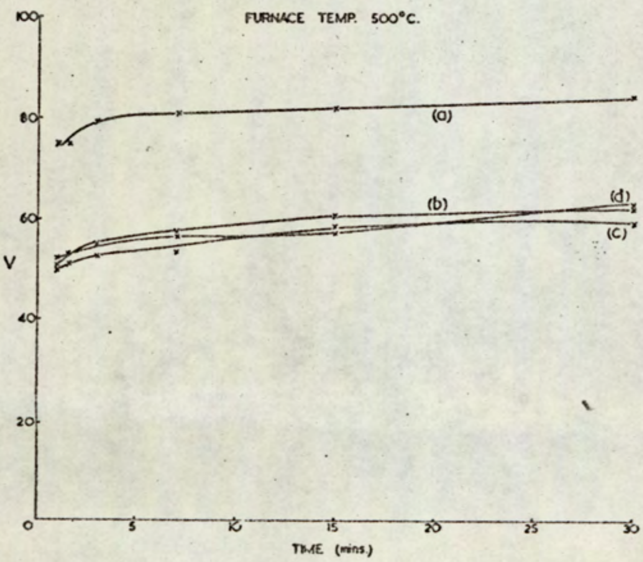


FIG 11

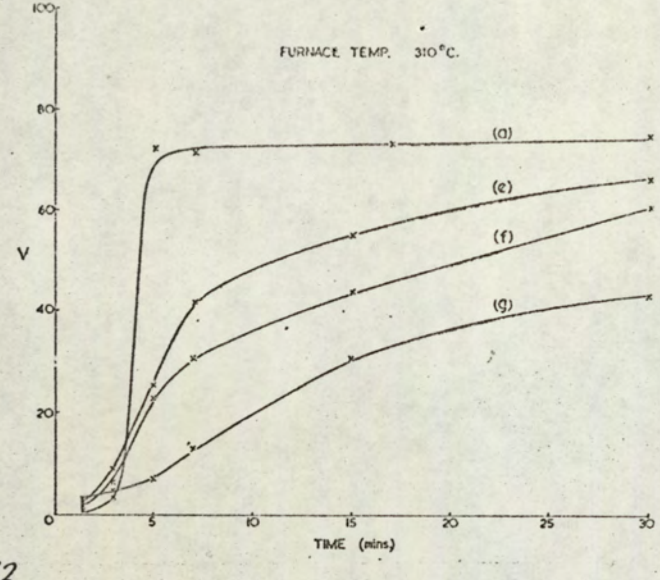


FIG 12

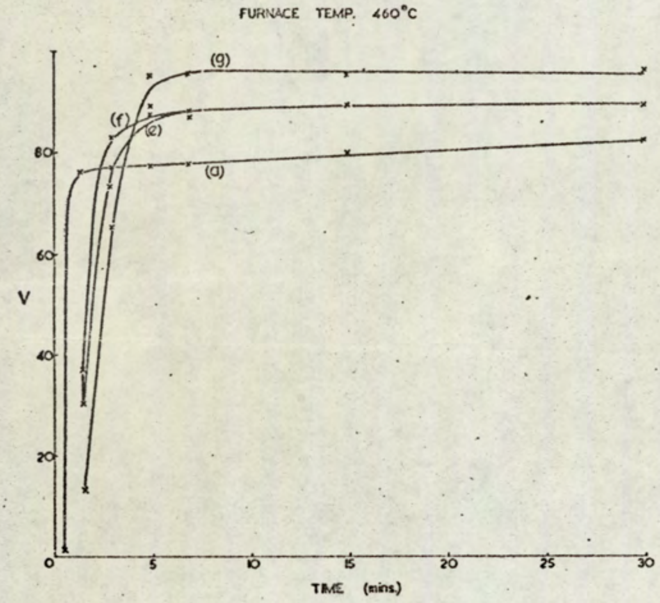
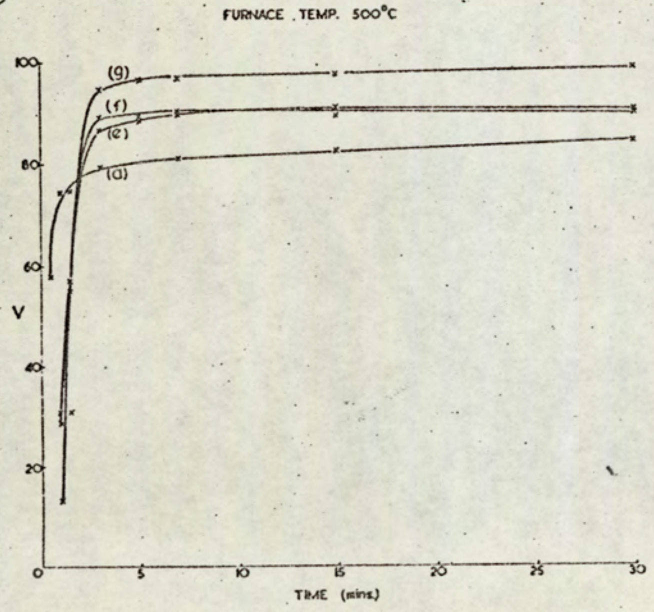


FIG 13



FLAMMABILITY OF PLASTICS IV

An Apparatus for Investigating the Quenching Action of Metal Halides and other Materials on Premixed Flames

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SUMMARY

A technique is described for assessment of the relative quenching effects upon 'premixed' flames, of volatile materials such as metal halides. The effect of a number of compounds has been investigated and semiquantitative results are reported. Some suggestions as to the nature of the quenching mechanism are discussed.

INTRODUCTION

Earlier work carried out in this laboratory demonstrated the efficiency of mixtures of antimony trioxide and various halogen donors in controlling the burning of cross linked polyester resins.(1) In subsequent work, concerned with heating together various halogenated materials with antimony trioxide, it was shown that where mixtures of equal weight of polyvinyl chloride and antimony trioxide or of 'Cereclor' 70 and antimony trioxide were used, the chief product of reaction was the relatively volatile antimony trichloride. (2) It was concluded that the reduced flammability of polyester resins containing these materials, and the so called 'synergistic' effect of antimony trioxide could be attributed to the formation of antimony trichloride.

Burning of a plastics material involves its thermal breakdown within the temperature range 250 - 550°C, providing volatile fuels. In presence of air or oxygen the fuel vapours are oxidised, exothermically in the gas phase, to yield a mixture of oxides of carbon and some other products. It was thought that the antimony trichloride was effective in inhibiting the complex of gas phase reactions involved in the phenomenum of flame. Therefore it seemed necessary to study in some detail the effects of antimony trichloride and related materials on the propagation of flame.

The present investigation is concerned with the study of polyester resins which decompose in the solid state. As this process is very difficult to control and its elimination would simplify the study of flame quenching, it was proposed to study the reactions of the solid and gas phases separately. Accordingly, this investigation is concerned with the burning of toluene as a model fuel of a type similar to that expected from the pyrolysis of a styrene cross linked unsaturated polyester. When precise information is available regarding the nature of the products of pyrolysis, the investigation will be extended to include them.

In order to obtain a highly reproducible system, fuel and air were premixed and the propagation of the flames resulting from their combustion was followed visually in a metre long glass tube. A means was provided for introducing vaporised metal halides or other material halfway up the tube, and the relative efficiency of various materials in quenching the flame was studied.

EXPERIMENTAL

1. Apparatus

The apparatus fig. (1) is a development of that developed by Zabetakis et al (3) for determining the lower flammability limits of hydrocarbon gases and liquids at elevated temperatures.

It consists essentially of devices for metering air and fuel into a common flow line connected to a combustion tube. The combustion and inlet tubes are encased in a cabinet which may be heated. A spark ignition source, a hot pad for volatilising materials into the flame path and also a 'sensing' thermocouple are fitted.

1.1. Air Metering Arrangement

Total air flow over a given period was metered and recorded by means of a wet test meter. Steady flow was maintained by two precision regulators, and a capillary tube flow meter (manometer type). The metered air was finally passed through a moisture trap before entering the apparatus.

1.2. Fuel Metering Device

In all cases a volatile liquid fuel (toluene) was used. This was delivered from a 2 ml glass hypodermic syringe at a constant rate by means of a screw, driven through a suitably housed worm and gear train, which operated the piston of the syringe. Details of the gear train are shown in Fig. (2). Two reductions were effected in the train, both of 28 : 1. The gearing was driven by a laboratory 'stirrer motor' which had a speed range of 0 - 600 r.p.m. but was found to operate most satisfactorily above 300 r.p.m. Infinite variation of rates of fuel delivery was made possible by varying the dimension of the syringe in use and also the speed of the motor.

1.3. Combustion Tube and Heating Cabinet

The combustion tube was constructed of pyrex glass tubing 36 ins. in length and diameter 2 ins. That part of the inlet tube inside the cabinet was bent in a zig-zag fashion in order to help vaporization and mixing of the fuel and air.

Platinum electrodes for ignition were fitted at the inlet end of the combustion tube through capillary inlets. Mid-way along the length of the combustion tube a ground glass socket was positioned for insertion of the hot pad.

The whole of the above was fitted inside a cabinet constructed from a 36 ins. length of 7 ins. diameter asbestos pipe. Two large openings were cut into the tube, one to accommodate the outlet port of a hot air blower, fitted with shaped perspex doors, to enable easy access to the combustion tube.

The hot air blower was constructed from 7 ins. diameter asbestos pipe. Three heating elements of total power rating

800 watts were sited off centre inside the tube. Temperature was regulated by means of a Sunvic controller. The furnace was fitted with a small air blower which directed air over the hot elements. The ends of the furnace were enclosed leaving an outlet tube of $4\frac{1}{2}$ ins. x $3\frac{1}{4}$ ins. which was let directly into the vertical cabinet. A temperature of 100°C (at the electrodes) was readily achieved by this system.

1.4. Spark Ignition Source, Hot Pad and Sensing Thermocouple

Fig. (4) shows details of the ignition source. This was adopted from the ignition system of an internal combustion engine. The electrodes were 0.015 ins. platinum wire with $\frac{1}{8}$ ins. spark gap. A spark was produced at the electrodes when the contact breaker points were opened by a lever type mechanical switch.

A heating pad was constructed as shown in fig. (5). This primarily consists of five turns of 0.005 ins. diameter nichrome resistance wire around 0.010 ins. thickness mica sheet. Mica sheet was bound to the top and bottom of this element for protection. The top of the pad was fitted with a clip of platinum foil for securing the sample boat. The boats were of aluminium and were supplied by Hewlett and Packard for use with a F. & M. Model 185 analyser.

The 'sensing' thermocouple, situated with its tip 12 ins. above the hot pad was a 0.040 ins. stainless steel sheathed Cromel-Alumel thermocouple. This was connected to a potentiometric recorder having a full scale deflection of 10 Mv.

2. Procedure

The hot air blower was regulated so that a temperature of 100°C was obtained at the electrodes. Air flow was adjusted so as to give a constant delivery of 2.55 lit./min. At this rate one complete flushing of the apparatus with fuel air mixture takes approximately one minute. The motor driving the gear train was switched on and the apparatus allowed to be flushed with the mixture for about 10 mins. After this period a spark was passed between the elctrodes and the flame progression through the combustion tube observed. The velocity and nature of the flame depends upon the concentration of fuel in air. The flame which was found to be most suitable for this work was a relatively slowly propagating blue flame which could be obtained just above the lower flammability limit of the fuel.

When conditions for producing this type of flame had been found the stop clock was started and a spark struck across the electrodes at three minute intervals. If a flame was propagated through the length of the tube at each of six repeats then the concentration of fuel in air was carefully determined as follows:-

2.1. Determination of Fuel in Air

The syringe plus fuel was accurately weighed and set into position. A stop clock was started synchronous with starting the drive motor and noting the reading on the wet test meter. At the end of 15 mins. the motor was stopped, the wet test meter reading noted and the syringe plus fuel reweighed.

The volume concentration of fuel in air (at normal temperature and pressure) was calculated from the expression:-

$$\text{\% Fuel in air by volume at N.T.P.} = \frac{\left(\frac{\Delta w\, V}{M}\right)100}{\frac{\Delta w}{M}V + \frac{\Delta v\, P' T}{P T'}} = \left(\frac{V_1}{V_1 + V_a}\right)100$$

where Δw = weight of sample delivered during time of the experiment

V_1 = volume of liquid vapour (N.T.P.) Corresponding to Δw

Δv = volume of air at temperature T^1 fed into the system in the time interval of the experiment.

V_a = volume of air (N.T.P.) corresponding to ΔV

V = 22.4 litres.

T = 273°K.

T^1 = Temperature of air passing through the wet test meter.

P = 760 mm of mercury.

P^1 = pressure of air passing through the wet test meter.

At subsequent re-uses of the equipment the same mixture was readily obtained by resetting the metering devices as for this experiment. It was not necessary to carry out the determination on every occasion.

When a flame passed completely through the mixture it was detected by the thermocouple and recorded as a sharp increase in temperature at the recorder. The object of the experiment was to determine the minimum concentration of inhibitor which when volatilised from the sample boat would quench the propagating flame before it reached the thermocouple.

A small quantity (mgs) of inhibitor was weighed into the aluminium boat which was then transferred to the heating pad. The stop clock was reset and after 2 mins. 45 secs. (approx.) current was supplied to the heating element. When all of the material had volatilised (time depends upon the material under investigation) a spark was struck across the electrodes and the progress of the flame observed. If sufficient inhibitor was present to quench the flame before it reached the thermocouple then the procedure was repeated, reducing the amount of inhibitor used by small quantities until a flame propagates completely through the tube.

The temperature attained by the heating pad has not been accurately determined but it was estimated to be in the order of 700°C. At this temperature the 'life' of the element is approximately one hundred 'heatings'. Elements were relatively easy to construct and it was attempted to reproduce the dimensions as accurately as possible each time.

3. Samples

The fuel used for all of the experiments was laboratory reagent grade toluene.

TABLE I

Materials Used

Material		Supplier
Antimony trifluoride	General Purpose Laboratory Reagent Grade	Hopkins & Williams
Antimony trichloride		
Antimony triiodide		
Arsenic triiodide		
Aluminium Chloride		
Arsenic trioxide		
Bismuth trioxide		
Antimony trioxide		Anchor Chemicals
Cereclor 70		Imperial Chemical Inds.
Polyvinyl Chloride		" " "
Dechlorane 4070		Hooker Chemicals
Flammex 4BS		F. W. Berk & Co., Ltd.
Flammex 5BT		
Flammex 5AE		

Some materials were used in the form of 50 : 50 by weight mixtures. The mixture components were hand mixed and intimately ground together with an agate pestle and mortar. Other materials were tested in the form of 50 : 50 mixtures with an inert material (alumina) in order to assist the accuracy of weighing very small quantities. The mixtures were prepared in a similar manner to those described before. In the case of these materials results are presented in terms of only the active species.

Results

In the following tables Q_{EX} is the minimum quantity in grammes of inhibitor which will quench the flame before reaching the thermocouple.

TABLE II

Q_{EX} Values of Mixtures

Materials		Q_{EX}
1 pt. Cereclor 70	1 pt. Antimony Trioxide	0.0008 g.
1 pt. PVC	1 pt. " "	0.0013 g.
1 pt. Dechlorane 4070	1 pt. " "	0.0045 g.
1 pt. Flammex 4BS	1 pt. " "	0.0047 g.
1 pt. Flammex 5BT	1 pt. " "	0.0063 g.
1 pt. Flammex 5AE	1 pt. " "	0.0028 g.
1 pt. Cereclor 70	1 pt. Arsenic Trioxide	0.0022 g.
1 pt. Cereclor 70	1 pt. Bismuth Trioxide	0.0014 g.

TABLE IIIa

Q_{EX} Values of Inorganic Single Substances

Materials	Q_{EX}
Antimony Trichloride	0.00065
Antimony Trifluoride	0.0014
Antimony Triiodide	0.0005
Arsenic Triiodide	0.0015
Arsenic Trioxide	0.0022
Aluminium Chloride	0.0022

TABLE IIIb

Q_{EX} Values of Organic Single Substances

Materials	Q_{EX}
Cereclor 70	0.0028 g.
Polyvinyl Chloride	0.0029 g.
Dechlorane 4070	0.0061 g.
Flammex 4BS	0.0025 g.
Flammex 5AE	0.0012 g.
Flammex 5BT	0.0030 g.

DISCUSSION

For interpretation of the results the materials are classified into groups. A broad distinction was made between those which were thought to volatilise unchanged and those which decomposed and/or reacted to give volatile reaction products. Further sub-divisions were made within the two classes.

This work was carried out specifically to study the effect of materials of flame reactions. For this reason care should be taken not to apply the results obtained out of context.

Compounds thought to volatilise unchanged

Three trihalides of antimony were studied i.e. the fluoride, chloride and iodide these showed increasing quenching efficiency with increasing atomic weight of the halogen.

Under flame conditions it may be expected that all of these compounds would be at least partially oxidised giving the trioxide. Ease of oxidation would be expected to be in the order iodide > chloride > fluoride. The other product of oxidation is the free halogen which according to Rosser et al (4) could be expected to readily abstract hydrogen from the fuel. They propose a general inhibition mechanism where the active species is the hydrogen halide. The mechanism may be represented by the general expressions:-

$$H\alpha + X^{\cdot} \longrightarrow HX + \alpha$$
$$\beta + HX \longrightarrow X^{\cdot} + H\beta$$

where $H\alpha$ is the fuel, X a halogen atom, HX the hydrogen halide and β such species as $OH^{\cdot}$, $H^{\cdot}$, $O^{\cdot}$, $CH_3^{\cdot}$ etc. The substitution of these active species which are responsible for important exothermic chain branching and propagation reactions will obviously reduce the intensity of the flame reactions.

The important point, however, is the action of the antimony trioxide formed in the flame zone.

Salooja (5) while investigating the anti-knock properties of lead tetra ethyl in hydrocarbon fuels showed that combustion inhibition due to this compound was entirely attributable to the lead monoxides formed. He showed that for the hydrocarbons hexane, 2 methyl pentane and 2,2 dimethyl butane the presence of either allotropic form of lead monoxide eliminated the formation of hydrogen peroxide and organic peroxide intermediates which in the absence of lead monoxide were formed in substantial quantities. He showed also that the presence of both forms of lead monoxide substantially reduced the formation of aldehyde and ketone intermediates but hydrocarbon intermediates were increased.

Cheaney et al (6) showed that the alkyls of bismuth, lead and thallium are all effective anti-knock agents whilst those of mercury are not. This is explained by the lower decomposition temperature of mercuric oxide producing volatile mercury metal. Alkyls of each of the other metals are capable of producing solid oxide particles in the form of a fog.

It would seem that an analogous situation occurs in the flame quenching properties of the halides of antimony. The higher efficiency of the iodide may be explained by its being more readily oxidised and that iodine is produced on oxidation which in its own right is a more efficient flame inhibitor than fluorine or chlorine.

On the other hand the lower efficiency of arsenic trioxide is also readily explained by this idea, with a volatilization temperature of only 350°C no solid particles, are present in the flame zone and hence the highly reactive intermediate species are less readily eliminated. Arsenic triiodide will be readily oxidised to the trioxide under these conditions and the increased effectiveness may only be attributed to release of the free iodine

Aluminium chloride was shown to be less effective than the antimony halides, this may also be explained on the same grounds. The relative stability of aluminium chloride to oxidation means that solid particles of aluminium oxide are not readily formed in the flame and the volatile chloride is less efficient in destroying intermediates.

From this it may be assumed that in order for a material to be an efficient flame inhibitor it must readily undergo oxidation or some other reaction forming low energy solid or liquid particles in the flame zone. A flame retardant to be used in a plastic material must also be volatile at or near the decomposition temperature of the plastics materials.

Mixtures and Materials which Decompose on Heating

Chlorinated Compounds

The effect of antimony trioxide in 50 : 50 mixtures with both Cereclor 70 and PVC was to reduce the total weight of mixture required to quench the flame, indicating that antimony trichloride is readily formed under these test conditions. A similar effect was observed with Dechlorane 4070 but to a lesser degree.

Dechlorane 4070 alone, however, was considerably less effective than either PVC or Cereclor 70 alone. The inhibition mechanism proposed by Rosser et al (4) would seem to be applicable here, i.e. the ready formation of hydrogen chloride from PVC and Cereclor 70 while Dechlorane 4070 appears to volatilise mostly unchanged under these conditions. This supports the idea that the hydrogen halide and not the whole halogenated molecule is the active flame inhibitor.

Cereclor 70 with arsenic trioxide proved to be a far less effective mixture than either bismuth trioxide/Cereclor 70 or or antimony trioxide/Cereclor 70. This supports the hypothesis of the solid particle in the flame being the active inhibitor. Bismuth trichloride would undergo oxidation to the solid oxychloride or trioxide whilst arsenic trichloride would be oxidised to the volatile trioxide thus furnishing no solid particles in the flame.

Brominated Compounds

Addition of antimony trioxide had no synergistic activity on any of the compounds studied under these conditions. On the contrary, at least twice as much 50 : 50 mixture was required to produce the same effect as the bromine containing compound alone. This appears to indicate that reaction does not occur between these materials, however, this is not in agreement with previous work carried out in this laboratory where it has been shown that reaction does occur between Flammex 4BS and antimony trioxide at elevated temperatures (2). A possible explanation is that the hot plate did not provide enough heat for the formation of antimony tribromide.

Although it seems that antimony tribromide was not formed under these conditions it is suggested that formation of the tribromide is to be preferred due to its greater ease of oxidation

When producing volatile metal halides 'in situ' therefore, it is clear that a number of factors will decide the ultimate flame retarding efficiency in the plastics material.

a. Decomposition temperature of the halogen compound relative to that of the plastics material.

b. Decomposition products of the halogen compound.

c. Lowest temperature of formation of the metal halide.

d. Ease of oxidation of the metal halide.

e. The formation of solid particles on oxidation.

Failure to match each of these conditions will result in a lower efficiency of the system as a whole.

It has been shown that antimony trioxide while not being unique in its reaction with organic halides produces halides which fulfill most of the above requirements.

CONCLUSIONS

The test apparatus and procedure is adequate for assessing the relative flame quenching efficiencies of systems involving solid materials which are volatile at moderate temperatures.

It has been demonstrated that the synergism observed between organic halogenated compounds and antimony trioxide is due to the formation of volatile antimony trihalides which under flame conditions are more or less readily oxidised, yielding solid particles of antimony trioxide in the flame. These particles are active in destroying energetic chain propagating and branching intermediates.

0-0-0-0-0-0

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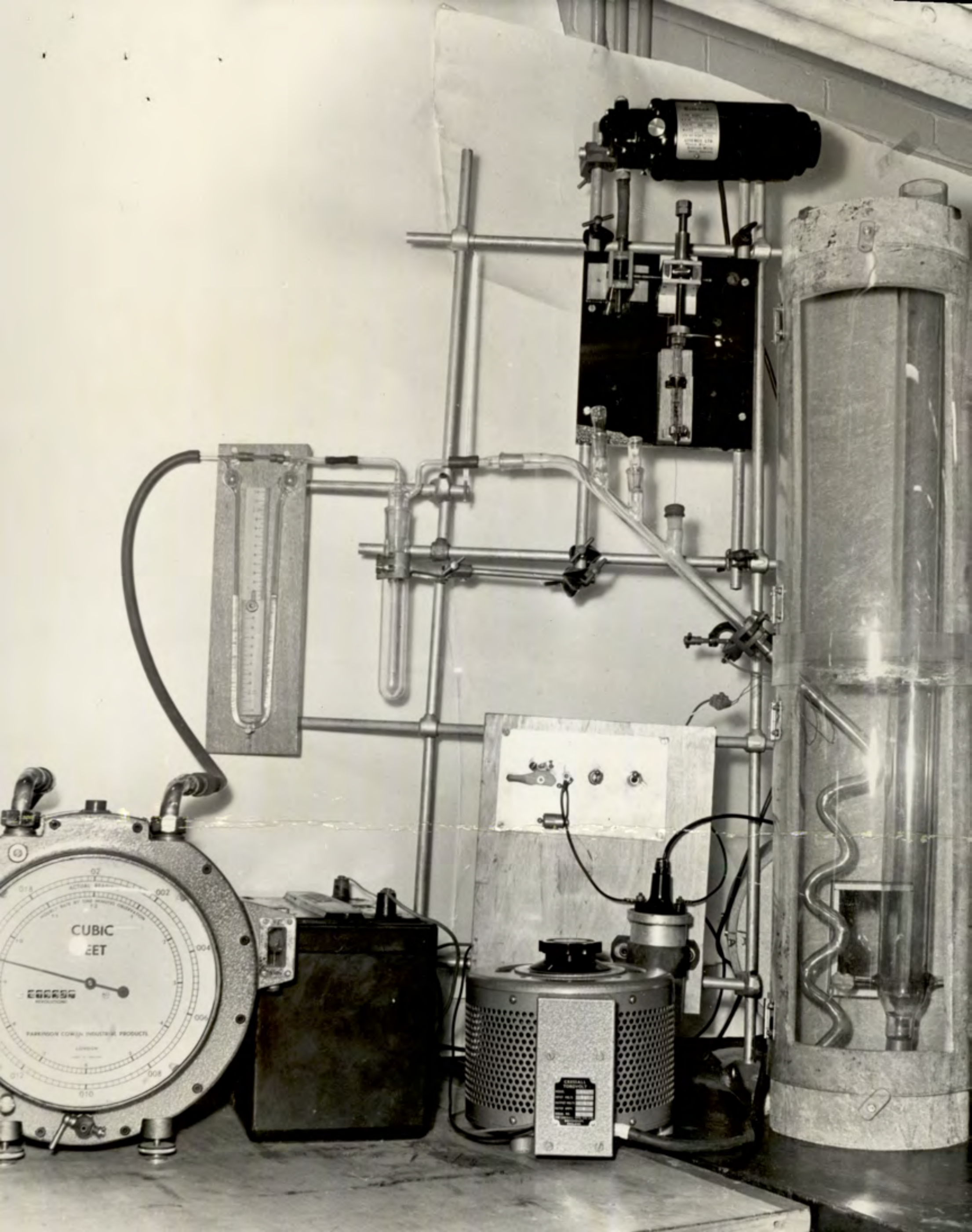
CUBIC
EET
02
018
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ACTUAL
REVOLUTIONS
PARKINSON COWAN INDUSTRIAL PRODUCTS
LONDON

FIG. 2

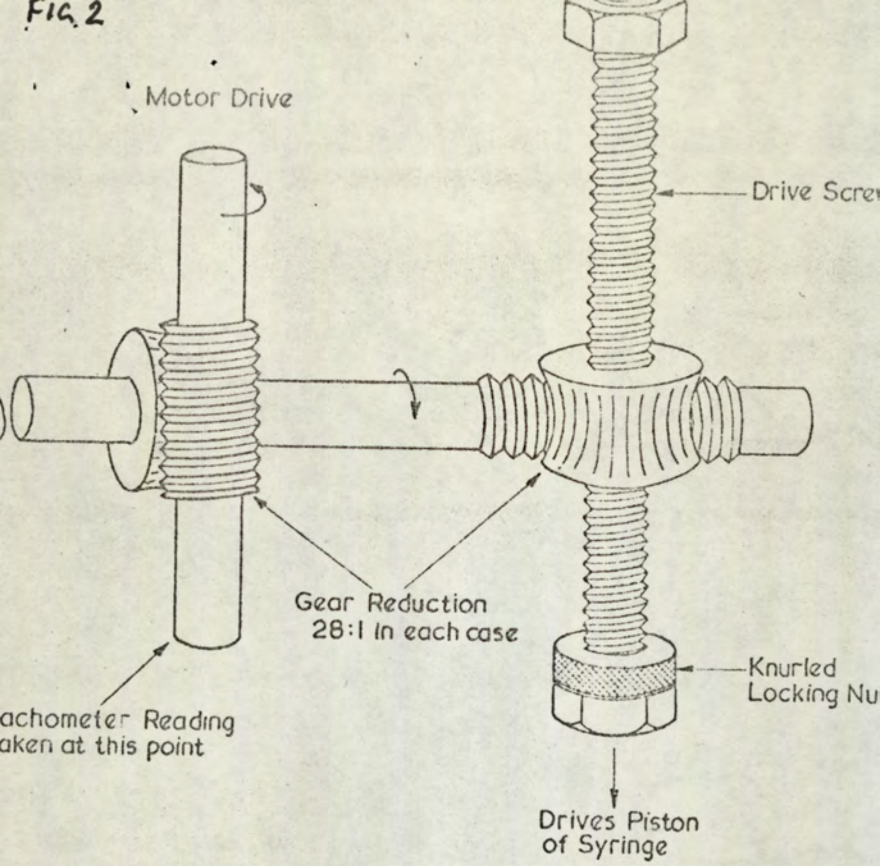

Motor Drive
Drive Scre
Gear Reduction
28:1 in each case
Knurled
Locking Nu
achometer Reading
aken at this point
Drives Piston
of Syringe

FIG 4

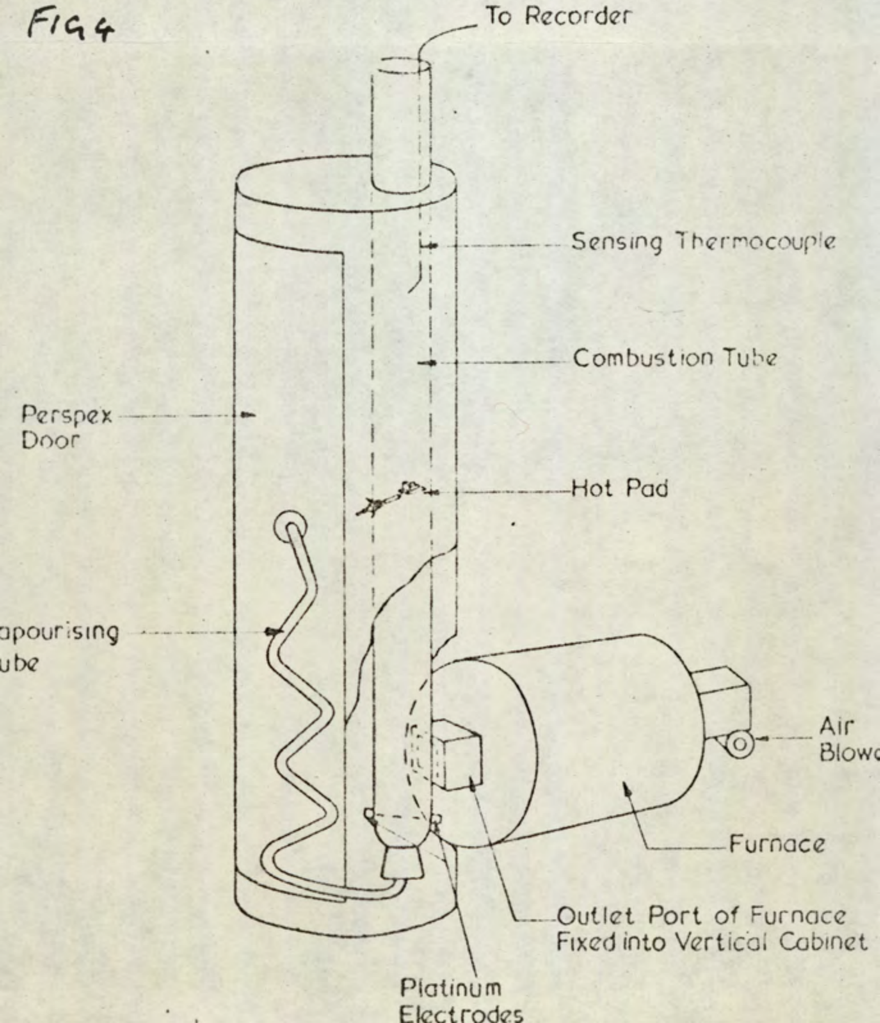

To Recorder
Sensing Thermocouple
Combustion Tube
Perspex
Door
Hot Pad
apourising
ube
Air
Blow
Furnace
Outlet Port of Furnace
Fixed into Vertical Cabinet
Platinum
Electrodes

FIG 5

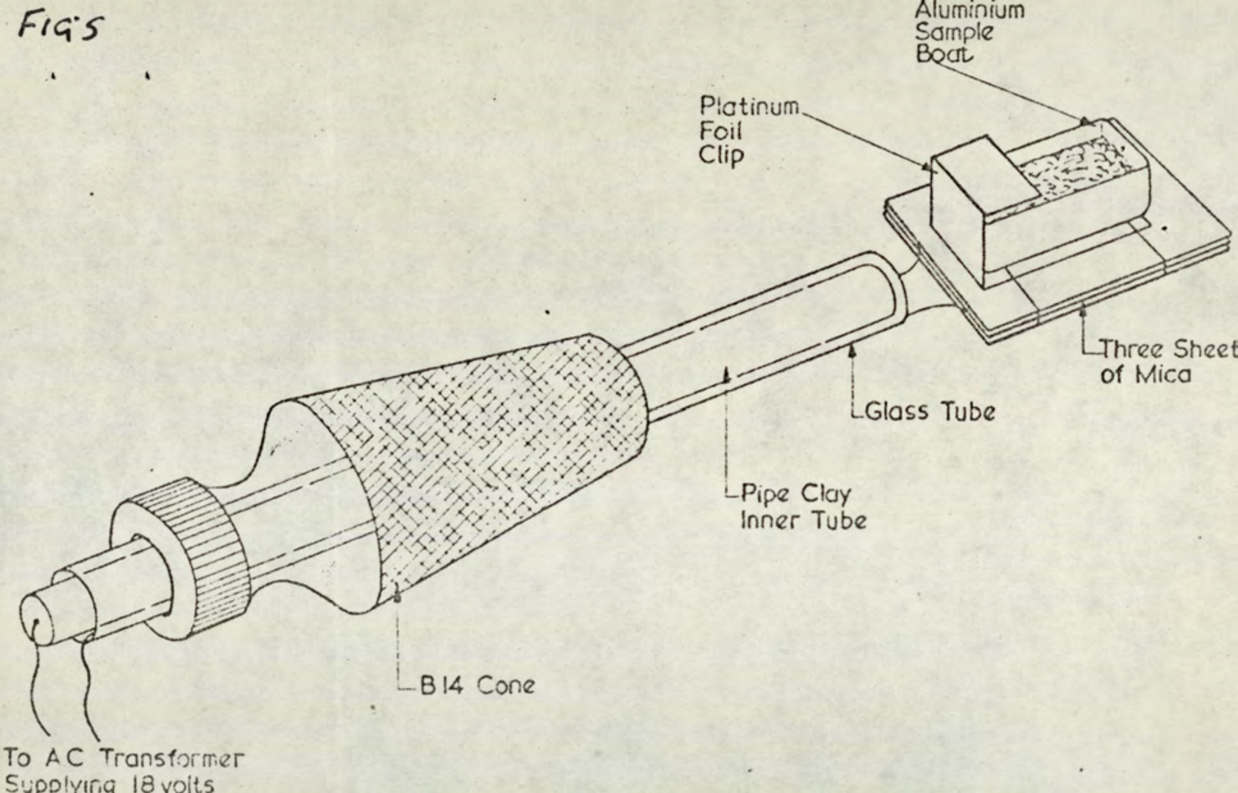
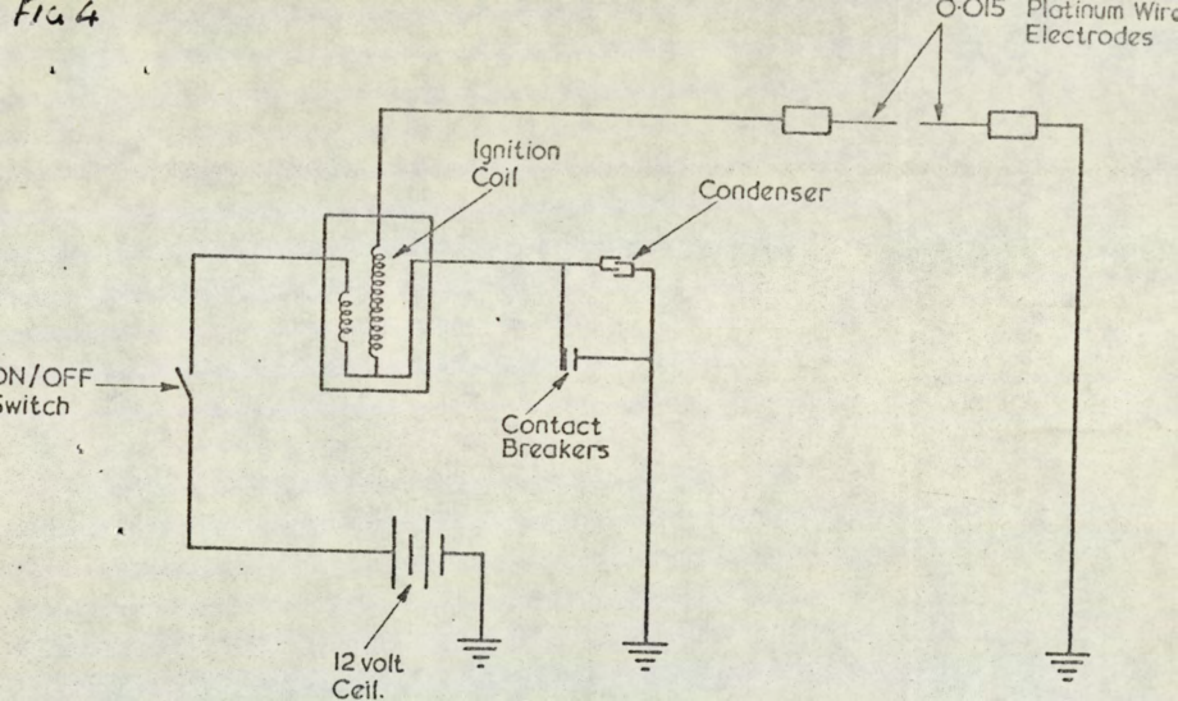

Aluminium Sample Boat
Platinum Foil Clip
Three Sheet of Mica
Glass Tube
Pipe Clay Inner Tube
B14 Cone
To AC Transformer Supplying 18 volts

FIG 4


0·015 Platinum Wir
Electrodes
Ignition
Coil
Condenser
ON/OFF
Switch
Contact
Breakers
12 volt
Ceil.