A STUDY OF THE THERMAL BEHAVIOUR
OF FLAME-RESISTANT FIBRES AND FABRICS

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The thermal behaviour of a series of flame-resistant materials was studied, using the combined techniques of Differential Scanning Calorimetry and thermogravimetry. Materials were separated into three main groups according to the manner in which their flame resistance is achieved. The groups studied were
   (i) cellulosic materials which have been rendered flame-resistant by additives.
   (ii) chlorine-containing materials and
   (iii) high, temperature, resistant materials.
All studies were carried out in air at linear heating rates and the results within each group were compared.

Flame-resistant fibres are being used in ever increasing quantities to meet the demands made by the public and by legislation for safer fabrics. The end use of the fabric determines the degree of flame-resistance required.

The treated cellulosic and chlorine containing fabrics are used mainly for household purposes, such as curtains, carpets and upholstery fabrics and also clothing. The high temperature resistant materials are mainly used as protective clothing, e.g. for racing drivers, in the aerospace and aircraft industries and in other areas where the risk from high-intensity fuel fires is considerable.
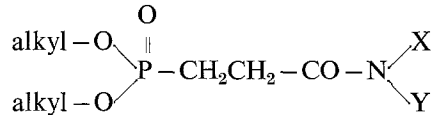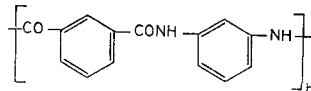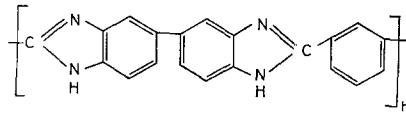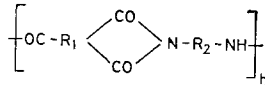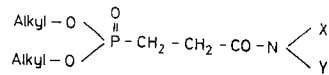
The thermal studies were carried out to assess the relative stabilities of each type of flame-resistant material.

At a later date it is hoped to establish a relationship between results obtained by these instrumental methods and those obtained from flammability tests. If such is possible it would simplify the task of predicting the performance of flame-resisting materials under practical conditions. The results of our findings will be published in due course.

The fibres considered in this article may be classified as follows:
(i) Cellulosic fibres:
This material burns readily, but fabrics made from it may be rendered more flame-resistant by treatment with a suitable flameproofing finish such as *Pyrovatex CP*. This finish belongs to the class of N-methylolated dialkyl phosphonopropionamides which have the general formula

$$\begin{array}{c} \text{Alkyl} - \text{O} \\ \\ \text{Alkyl} - \text{O} \end{array} \Big\rangle \overset{\overset{\text{O}}{\parallel}}{\text{P}} - \text{CH}_2 - \text{CH}_2 - \text{CO} - \text{N} \Big\langle \begin{array}{c} \text{X} \\ \\ \text{Y} \end{array}$$

$$\left[\text{OC} - \text{R}_1 \Big\langle \begin{array}{c} \text{CO} \\ \\ \text{CO} \end{array} \Big\rangle \text{N} - \text{R}_2 - \text{NH} \right]_h$$

$$alkyl - \text{O} \underset{alkyl - \text{O}}{\overset{}{\diagdown}} \overset{\overset{\text{O}}{\parallel}}{\text{P}} - \text{CH}_2\text{CH}_2 - \text{CO} - \text{N} \overset{\diagup \text{X}}{\diagdown \text{Y}}$$

where X = H or $-\text{CH}_2\text{OH}$; Y = $-\text{CH}_2\text{OH}$ and the alkyl groups are of the short chain type.

Fibres made from regenerated cellulose are made flame-resistant by incorporating an additive in the spinning mix. An example of this type of fibre is *Darelle*.

Chemical fire retardants may alter the thermal degradation process to give less flammable products and/or form surface barriers which interfere with oxidative reactions involved in combustion.

(ii) Fibres containing Chlorine:

(a) *Leavil* and *Clevyl* fibres are 100 per cent polyvinyl chloride.

(b) *Teklan* which is a mod-acrylic fibre, is a copolymer of polyacrylonitrile and polyvinylidene chloride in approximately equal proportions.

(c) *Acrilan Mod-Acrylic Fibre* is *Acrilan* with a flame-retardant added during the fibre production.

(d) *Polychlal* is a polyvinyl alcohol fibre which has polyvinyl-chloride emulsion added to the spinning solution. A 50/50 mixture of PVA/PVC may be obtained.

Materials containing chlorine derive their flame resistance from the liberation of hydrogen chloride gas during their thermal decomposition. The liberated gas extinguishes burning and prevents flame propagation.

(iii) High temperature resistant materials:

The fibres with the highest thermal stability are those constructed from stiff polymer chains. This stiffness is acquired by incorporating aromatic and/or hetero-cyclic rings along the length of the polymer chain. Examples of such polymers are:

(a) Polyamidimide *(Kermel)*. General formula:

PTO material is a strontium chelate of the above, and the degree of chelation determines the fire resistance.

(b) Polybenzimidazole *(PBI)*

(c) Aromatic polyamide *(Nomex)*

(d) Phenol-formaldehyde *(Kynol)*

This is a chain polymer in which the phenolic nuclei are connected by methylene bridges.

(e) Modified aromatic polyamides *(Durette)*

These materials are made by halogenation or oxyhalogenation of aromatic polyamides at high temperatures.

(f) Carbon *(Tayentex)*

These materials contain 80−95 per cent elemental carbon and are produced by heating certain polymers to temperatures well above their decomposition temperatures in an inert atmosphere.

Some of the precursor polymers used are viscose, polyacrylonitrile and poly-vinyl alcohol.

Experimental

A number of fibres from each of these three groups were selected and tested by the thermoanalytical techniques of Differential Scanning Calorimetry (DSC) and Thermogravimetry (TG). Duplicate tests were carried out on all samples and in all cases the duplicate curves were found to have excellent agreement.

DSC: A Perkin−Elmer DSC-1B instrument was used. The instrument was programmed for a temperature rise of 16°/min, and had a sensitivity of 8 milli-calories/sec. full scale deflection.

Test samples of between 5 and 6 milligrams were placed in sample pans with perforated lids which allowed any volatile degradation products from the sample to escape into the surrounding chamber and be swept away by the air flow (30 cc/min) which purges the system. All samples were allowed to come to equi-librium within the chamber before heating.

TG: Work was carried out using a Stanton Model HT-SM Thermobalance. The sample weights were 100−200 milligrams and samples were in an air atmos-phere under static conditions. The instrument was programmed for a heating rate of 6°/min.

Results and discussion

Referring to the curves of temperature versus percentage weight retained (Figs 1 −21) it can be seen that in general the samples show a major weight loss in one or two steps. The onset temperatures of these rapid weight losses are tabulated below:

Table 1

Sample	Temperature of first rapid weight loss, °C	Temperature of second rapid weight loss, °C
Cotton	330	—
Cotton (Pyrovatex Treated)	310	—
Darelle	240	—
Clevyl	270	440
Leavil	240	380
Polychlal	240	350
Acrilan	310	560
Acrilan Mod-acrylic	240	500
Teklan	220	460
50/50 Leavil/wool	240	470
50/50 Leavil/flax (Pyrovatex Treated)	260	430
Wool	220*	—
Flax (Pyrovated Treated)	280*	—
PBI	490	—
Durette	450	—
Durette (Heat Treated)	460	—
Kermel	440	—
Kermel (Heat Set)	440	—
Nomex	410	—
Kynol	370	—
Kynol/Nomex	390	—
Tayentex	360	—
Glass	—	—

* These values have been obtained from previous work.

(i) Cellulosic fibres (Figs 1 −3):

A comparison of the DSC traces of the cellulosic samples indicates that the course of the cellulosic degradation has been changed by the additives, since in the untreated cotton sample, two exothermic peaks occur between 100° and 200°, but in the *Pyrovatex* treated sample these exotherms have decreased in size and have been shifted to slightly higher temperatures. In *Darelle* only one exotherm is evident.

TG measurements confirm a change in mechanism. For cotton treated with *Pyrovatex* and *Darelle,* degradation begins at a lower temperature than for the untreated cotton (see Table 1). At about 500°, the untreated cotton loses no further weight and a carbonaceous residue is left, but for the treated samples this does not occur until above 700°. The non-flam additives would appear to change the decomposition in such a way that not only the rate of evolution but also the amount
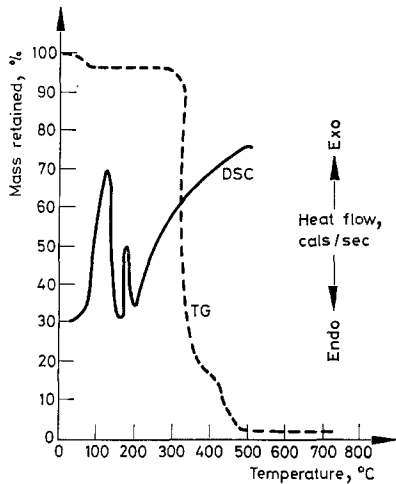

Fig. 1. DSC and TG traces of Cotton in air
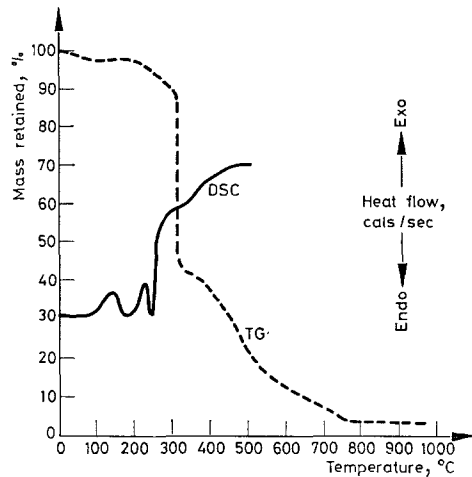
Fig. 2. DSC and TG traces of Cotton Pyrovatex treated in air
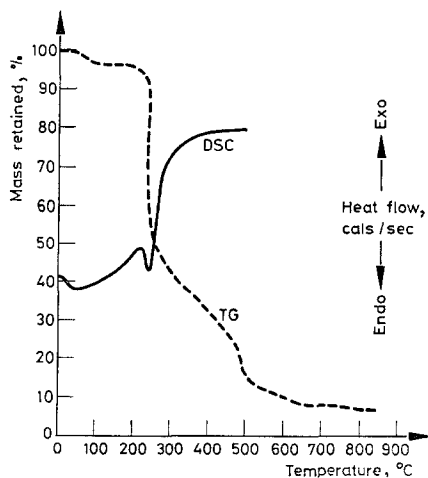
Fig. 3. DSC and TG traces of Darelle in air
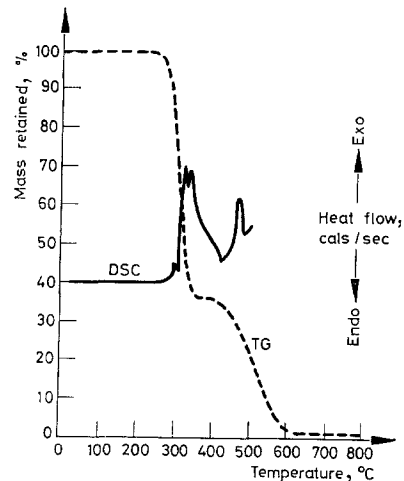
Fig. 4. DSC and TG traces of Clevyl in air

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of flammable volatiles is decreased, since the treated samples leave a greater weight of char.

(ii) Fibres containing chlorine:

The TG traces (Figs 4, 5, 6 ,8 and 9) show a two-step degradation process. The first rapid weight loss is associated with the liberation of hydrogen-chloride gas [1], and concurring with this in all of the corresponding DSC traces is a sharp exotherm. This exotherm is probably the net effect of bond rupture and formation.
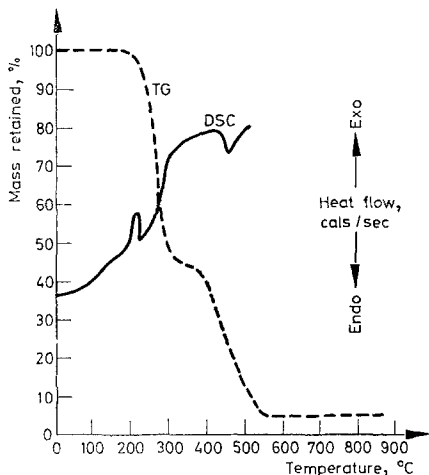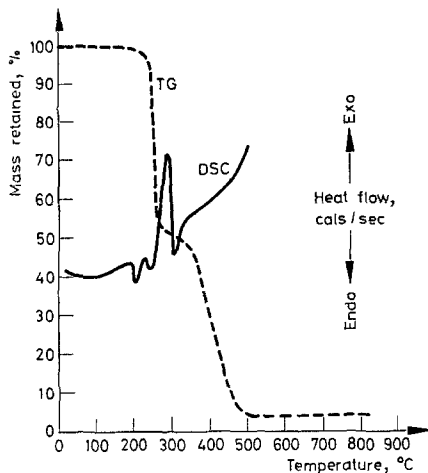

Fig. 5. DSC and TG traces of Leavil in air

Fig. 6. DSC and TG traces of Polychlal in air
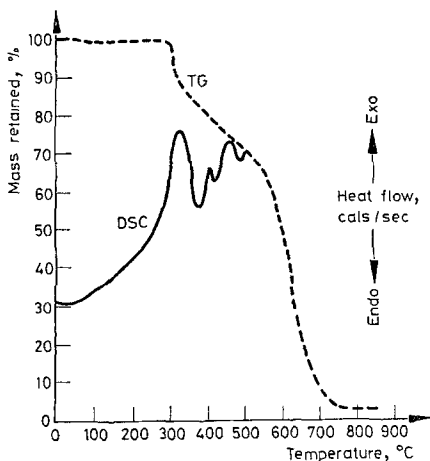
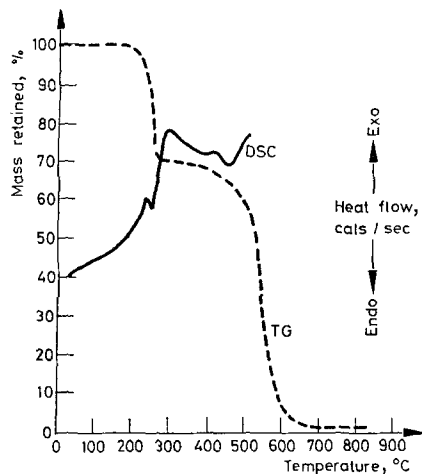Fig. 7. DSC and TG traces of Acrilan in air

Fig. 8. DSC and TG traces of Acrilan Mod-Acrylic in air

The associated weight losses vary from 64 per cent in the case of *Clevyl* to 30 per cent for *Acrilan Mod-Acrylic*.

Leavil which is a syndiotactic PVC (it has stereochemical regularity) shows 55 per cent weight loss in the first stage of its decomposition, whereas *Clevyl*, which is also a PVC but of different chemical configuration, loses 64 per cent. The decomposition behaviour is different for these two PVC fibres, for as well as a difference in initial weight loss, the second large weight loss occurs at 380° in
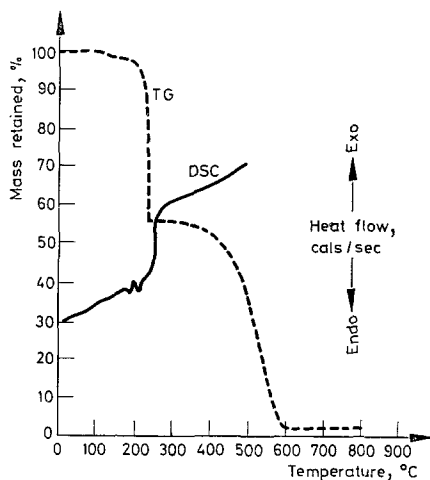

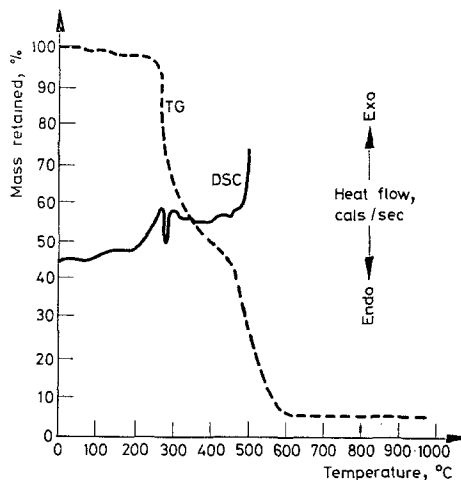Fig. 9. DSC and TG traces of Teklan in air

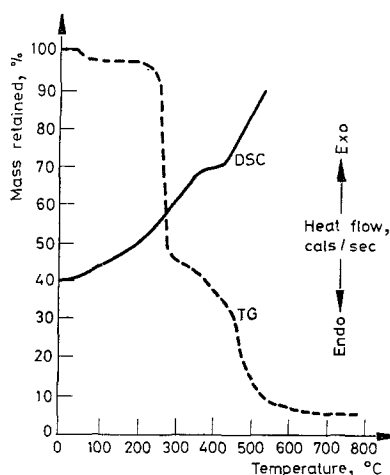Fig. 10. DSC and TG traces of 50/50 Leavil/ wool Blend in air

Fig. 11. DSC and TG traces of 50/50 Leavil flax blend in air. Pyrovatex treated

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Leavil and at 440° in *Clevyl*. *Leavil* leaves a greater char residue than *Clevyl*, indicating that there are less volatiles evolved in the decomposition. The DSC traces also show a different decomposition behaviour.

The TG (Fig. 7) of untreated *Acrilan* (a polyacrylonitrile fibre), shows a rapid decrease in weight at 310°, this is reflected in the DSC trace as a sharp exothermic peak, which is associated with cross-linking of the polyacrylonitrile chains by the elimination of hydrogen cyanide [2]. However, with *Acrilan Mod-acrylic fibre,*
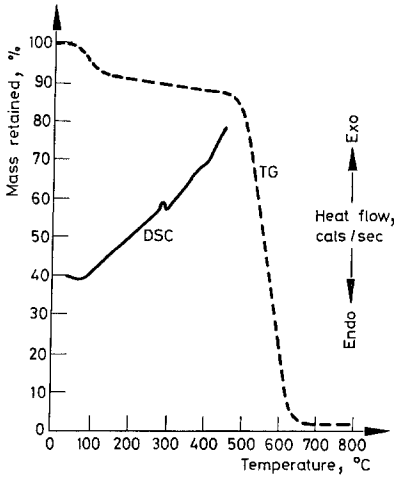
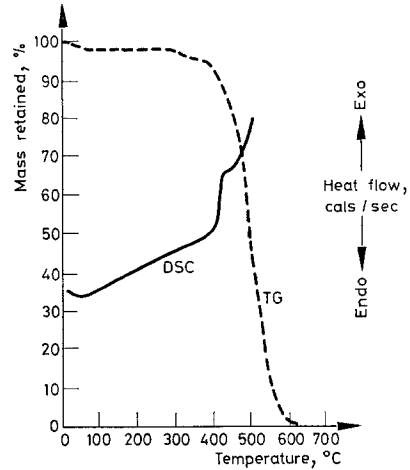Fig. 12. DSC and TG traces of PBI
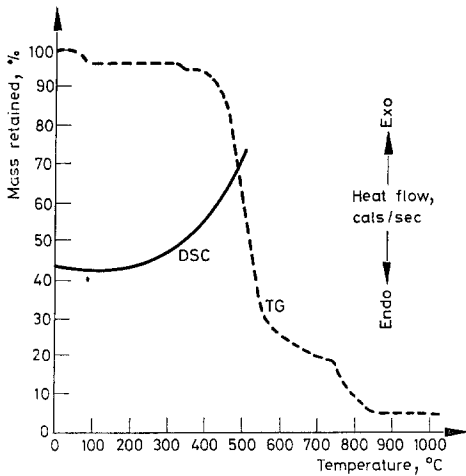in air

Fig. 13. DSC and TG traces of Durette
in air

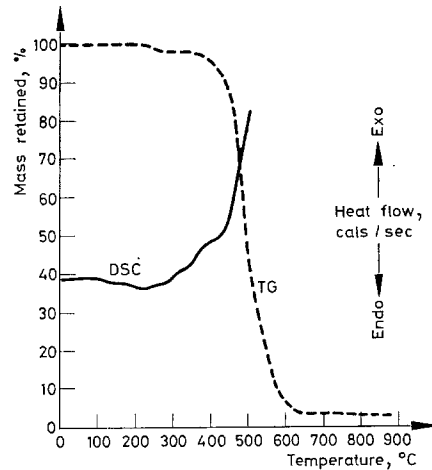Fig. 14. DSC and TG traces of Durette heat-
treated in air

Fig. 15. DSC and TG traces of Kermel
in air

which is *Acrilan* modified to confer more flame-resistant properties, the DSC and TG traces (Fig. 8) are of a different form. This change is also seen in *Teklan* which is a copolymer of polyacrylonitrile and polyvinylidene chloride. When the thermal traces of these materials (Figs 8 and 9) are compared with *Acrilan* (Fig. 7), it can be seen that there is a lowering of the temperatures at which the first and second rapid weight losses occur (see Table 1) and DSC traces show only one strong exotherm concurring with the first weight loss instead of a series of exo-
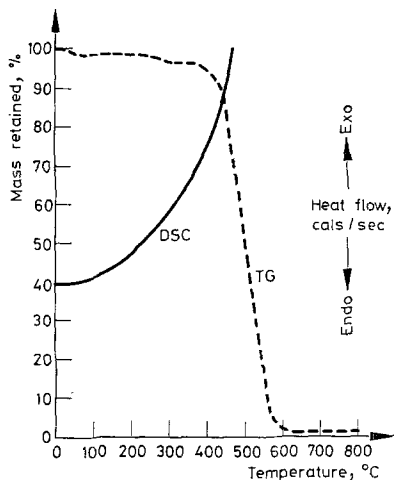

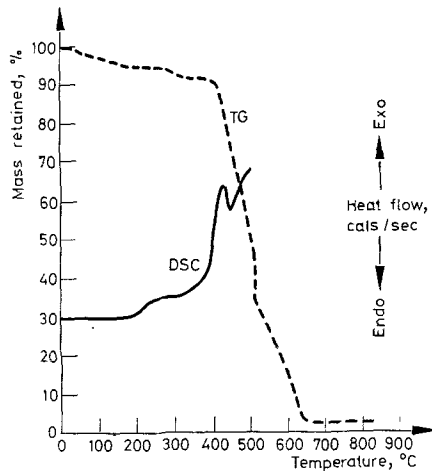Fig. 16. DSC and TG traces of Kermel heat-set in air
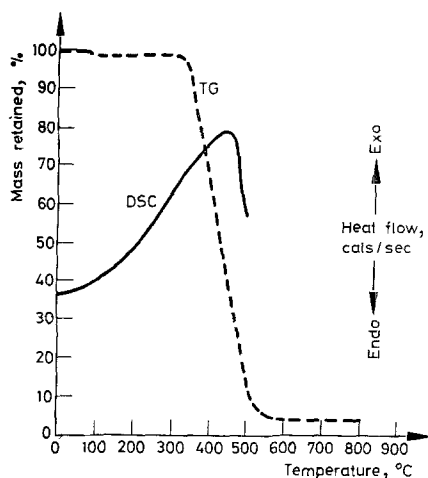

Fig. 17. DSC and TG traces of Nomex in air

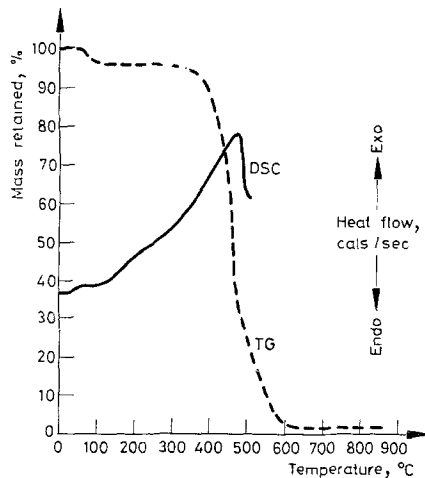Fig. 18. DSC and TG traces of Kynol in air

Fig. 19. DSC and TG traces of 50/50 Kynol/Nomex blend in air

thermic peaks. Overall the TG and DSC traces more closely resemble those of the PVC fibres rather than those of polyacrylonitrile.

Polychlal, a 50/50 mixture of polyvinyl alcohol and polyvinyl chloride, gives curves (Fig. 6) characteristic of the chlorine containing fibres. The initial degradation step begins at 240°, and the second step at 350°. Of the fibres examined within this class, *Polychlal* has the lowest secondary decomposition temperature.
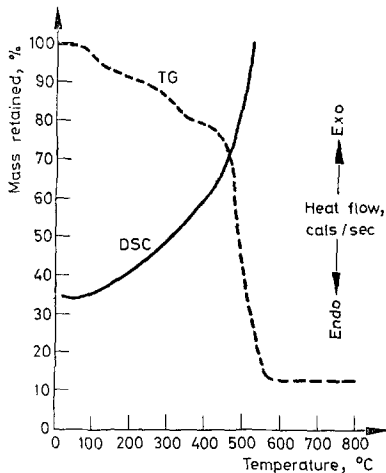

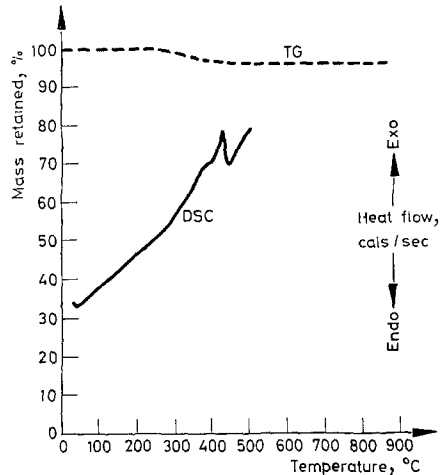Fig. 20. DSC and TG traces of
Tayentex in air

Fig. 21. DSC and TG traces of Glass
in air

When *Leavil* is blended with either wool or blended with flax and the fabric, then treated with *Pyrovatex* (Figs 10 and 11), wool would appear to have no effect on the temperature at which the initial degradation of the *Leavil* component takes place. With the treated flax blend material the initial degradation commences at a temperature between that of treated flax and *Leavil* when tested separately.

For *Leavil* the secondary decomposition step occurs at 380°, this is raised to 430° when combined with flax-and treated with flameproofing agent, and to 470° when combined with wool. It would appear that both the wool and the flax delay the second stage of the decomposition of the *Leavil* component. This could possibly be attributed to an endothermic reaction occuring in the natural fibre and opposing the further degradation of the *Leavil*. This opposing reaction is more noticeable with wool than with flax.

(iii) High temperature resistant materials (Figs 12 – 21):

These materials exhibit the highest thermal stability of any of the samples examined so far. No significant weight losses occur in most of the samples below 400°.

Two of the fabrics, *Durette* and *Kermel,* were given heat treatments. The treatment was given to the *Durette* by the manufacturer to confer greater flame-

resistance (details of the process are not available). The *Kermel* was heat-set at 250° for 5 minutes. This thermal pre-treatment affects the thermal stability of the *Durette* but the *Kermel* is unchanged. Heat treatment of the *Durette* delays the onset of decomposition by about 10°, and decreases the rate of decomposition. Comparing the TG traces for the two *Durette* samples (Figs 13 and 14), at 600° the *Durette* sample which had no prior heat treatment has completely decomposed, but at this temperature the heat treated *Durette* still retains about 25 per cent of its original weight and even at 1000°, total decomposition has not taken place.

Nomex and *Kynol* (Figs 17 and 18) start to degrade at 410° and 370°, respectively. When these two materials are blended in equal proportions, the thermal stability of the blend (Fig. 20) is found to be intermediate between that of the constituent components.

The blend starts to degrade at 390° and at any temperature thereafter the sample weight remaining is greater than that of *Kynol* alone but less than that of *Nomex*. This would indicate that the decomposition of the blend is a summation of the individual decompositions and that they are independent of each other. This has been confirmed by comparing the observed weight losses with a curve derived by combining the individual weight losses. The shape of the DSC traces also show this net effect.

The samples of *PBI, Durette, Kermel* and *Nomex* (Figs 12, 13, 15 and 17) have similar thermal curves but with slight differences in thermal stability. Under the stated test conditions the thermal stabilities in decreasing order would appear to be as follows: *PBI, Durette, Kermel, Nomex* (see Table 1).

These relative stabilities may perhaps be explained by comparing the general chemical structures. *PBI* has a very rigid polymer chain with 5 and 6 membered rings fused along its length, this leads to good thermal stability.

As *Durette* is an aromatic polyamide modified by a halogenation process, it would be expected to have thermal properties similar to *Nomex*. However it has been reported that the polymer undergoes a cross-linking reaction [3] as well as a substitution during halogenation and this would explain the greater thermal stability of *Durette*.

Glass shows a very high degree of thermal stability under these test conditions retaining over 95 per cent of its original weight at 1000°. The small loss in mass is possibly due to the loss of processing aids.

Conclusions

The two cellulosic materials which have been treated with flame-retardant agents, degrade at a lower temperature than the parent material and have higher carbonaceous residues.

Mod-acrylic, PVC and polychlal fibres thermally degrade in two distinct stages, the first stage being the mechanism by which flame-retardancy is achieved [1] and the second is the breakdown of the resultant structure.

The thermal stability of the high temperature resistant materials is related to

their chemical structure, the more rigid polymer structures conferring the greater stability.

In our opinion, more meaningful results were obtained from the TG measurements than from the DSC measurements. Interpretation of DSC traces becomes very complex during thermal decomposition. The decrease in sample weight causes an exothermic shift of the baseline, at the same time endothermic bond rupture is occurring, as a result, only the net effect is observed which can be misleading. The DSC, however, is useful in observing changes in reaction prior to the onset of decomposition.

<div align="center">*</div>

References

1. W. J. ROFF and J. R. SCOTT, Fibres, Films, Plastics and Rubbers, Butterworths 1971, Section 11.
2. Techniques and Methods of Polymer Evaluation, edited by P. E. SLADE and L. T. JENKINS. Volume 1, page 78. Edward Arnold (Publishers) Ltd. 1966.
3. United States patent No. 3607798.

RÉSUMÉ — On a étudié par analyse calorimétrique différentielle et par thermogravimétrie le comportement thermique de matériaux ignifuges. Trois groupes principaux de matériaux peuvent être considérés suivant leur caractère anticombustible:
  1. les matériaux cellulosiques rendus ignifuges sous l'effet d'additifs,
  2. les matériaux chlorés,
  3. les matériaux résistant aux températures élevées.
On a effectué toutes les études dans l'air, en utilisant des vitesses de chauffage linéaires et on a comparé les résultats obtenus dans chaque groupe de matériaux.

ZUSAMMENFASSUNG — Das thermische Verhalten einer Anzahl feuerbeständiger Stoffe wurde unter Anwendung der kombinierten Techniken der Differential-Abtast-Calorimetrie und der Thermogravimetrie studiert. Die Stoffe wurden je nach der Art ihrer Feuerbeständigkeit in drei Hauptgruppen eingeteilt. Die untersuchten Gruppen waren die folgenden:
  1. mittels Additivs feuerbeständig gemachte Cellulose-Stoffe,
  2. chlorhaltige Stoffe und
  3. hitzebeständige Stoffe.
Alle Untersuchungen wurden in Luft bei linearer Aufheizgeschwindigkeit durchgeführt und die Ergebnisse in jeder Gruppe verglichen.

Резюме — При использовании дифферендиального сканнирующего калориметра и термогравиметрии, изучено термическое победение рядапламя-угасящих вечеств. В соответствии со способом достиженя гасящего действия вещества разделены на три основные группы. Исследованы следующие группы:
  (i) Целлюлозные вецества в виде добавок
  (ii) Хлор- содержащие материалы и
  (iii) Вещества, выдерживающие высокую температуру.
Исследования проведены в атмосфере воздуха пру линейной скорости нагрева, результаты сравнены в каждой группе.