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COMPARISON OF THERMAL CHARACTERISTICS OF MATERIALS EXAMINED BY THERMOGRAVIMETRY AND FLAMMABILITY TESTS

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This paper deals with the examination of various types of flame resistant fabric in fire conditions, standard flammability tests and thermogravimetry. It shows how it may be possible to determine the protection afforded by a garment using very small samples and instrumental laboratory techniques. This could be important in the development of new materials where a quick assessment could be made of the protective qualities of the material.

Different flame resistant fabrics afford different degrees of protection to a wearer under conditions of fire and this is perhaps one of the critical factors which needs to be known as far as protective clothing is concerned. However, existing test methods do not differentiate between them in this respect. The standard flammability test, where a strip of fabric is held vertically and ignited at, or near the bottom, gives results which indicate that there is little difference between the flame resistant fabrics – they do not propagate flame after removal of the igniting source, and have relatively short char lengths. While radiant panel tests do show differences between the fabrics these cannot be related to the practical behaviour of garments made from the materials. Radiant panel tests can be criticized on the grounds that

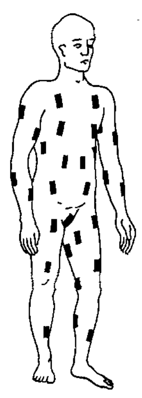

Fig. 1. Nude manikin with temperature indicators mounted in position

the spectral characteristics of flames and the panel are not the same, but it is debatable whether the difference in intensities of the wavelengths has a significant effect on the decomposition of the fabric.

In a crash involving a helicopter or a racing car there is a high probability of a fuel leakage. If this is ignited the occupant must escape through the blazing fuel. The type of clothing worn is not usually designed to protect the body against such an intense fire because it would be extremely uncomfortable to wear as an everyday work garment. This is especially true in the case of pilots.

Because of the nature of the fires under consideration we decided to use the pit test as our standard method of test for the fabrics under investigation and to see if we could devise a laboratory method which would correlate with it. The pit test has been used in the United States to evaluate many flame resistant fabrics. In the pit test the "skin" temperature of a manikin clothed with the appropriate material is measured. Figure 1 shows a nude manikin with the temperature indicators mounted in position. Skin damage is known to occur when the skin reaches a temperature of 45° [1]. The degree of damage is assessed by the temperature the skin reaches and the time the temperature is above 45°.

In the test, the manikin is clothed in an untreated cotton shirt and shorts and a coverall of the material under investigation. The dressed manikin is pulled through a pit of blazing JP-4 jet fuel, having a flame temperature range of 1000° to 1200° and the "skin" temperature is measured at the various points. From the measurements the time for 20 per cent damage of the skin is calculated.

Experimental

In the work discussed here eight different fabrics of approximately the same mass per unit area (150 g/m^2), thickness and cover were examined. The fabrics selected as being representative of materials which are considered flame resistant were the following:

'PBI' (polybenzimidazole)
'Nomex' (aromatic polyamide)
'Kermel' (polyamidimide)
'Kynol' (phenolic)
'Durette' (chlorinated and cross-linked aromatic polyamide)
'Leavil' (polyvinyl chloride)
'Proban'-treated cotton
'Kynol'/'Nomex' (50/50 blend)

Five similar fabrics tested by the fire pit method gave the results shown in Table 1 [2].

The other fabrics were subjected to laboratory testing, firstly using method 5905 of Federal Test Method Standard No. 191. This method uses a flame having a

Table 1

Sample	Estimated protective time for 20% skin surface damage, seconds
PBI	4.0
Kynol	2.5
Nomex	2.0
Durette	2.0
Proban-treated cotton	1.4

flux of about 2 $cal/cm^2/sec$. Observations are made as to the time of after flame and extent of damage sustained by the test specimen.

For a material to get good ratings in the fire pit test another important property besides material stability and resistance to thermal transmission is that sustained flaming is not induced by exposure to JP-4 fuel fire of the pit test. Such a fire has an energy flux of 2 to 4 $cal/cm^2/sec$. By flaming the fabric can provide a significant amount of energy at the manikin surface and thus increase measurements related to burn severity.

From experience gained in the United States using these laboratory methods and critical oxygen index values it is estimated that if the Kermel, Leavil, and Kynol/Nomex blend fabrics were subjected to the pit test, the blend fabric and the Kermel would give results comparable to Nomex and Durette and the Leavil would give a lower protective time than the treated cotton. This would give a ranking from the fire pit test as shown in Table 2.

Table 2

Sample	Estimated protective time for 20% skin surface damage, seconds
PBI	4.0
Kynol	2.5
Nomex, Durette, Kermel, Kynol/Nomex	2.0
Proban-treated cotton	1.4
Leavil less than	< 1.4

Thermogravimetric methods

The samples of fabric were examined using a Stanton Redcroft TG 750 thermobalance. 2.5 mg samples were punched from the fabrics and subjected to heating rates of 5°/min and 100°/min, in an air stream flowing at 10 cm^3/min. The temperature of the onset of degradation was determined (procedural decomposition temperature). In all cases the degradation took place in one step except for the treated cotton and Leavil which were two step processes. The procedural decomposition temperatures are given in Table 3.

Table 3

Sample	Procedural decomposition temperature, °C	
	heating 5° C/min	heating 100° C/min
PBI	520	609
Kermel	405	476
Nomex	400	457
Durette	400	439
Kynol/Nomex	326	443
Kynol	321	410
Proban-treated cotton	248	300
Leavil	180	231

The tests made at the lower heating rate put the samples in approximately the same order but, of course, gave lower procedural decomposition temperatures.

The order based on procedural decomposition temperature is approximately the same as that for the pit test except for the Kynol sample which has a lower de-

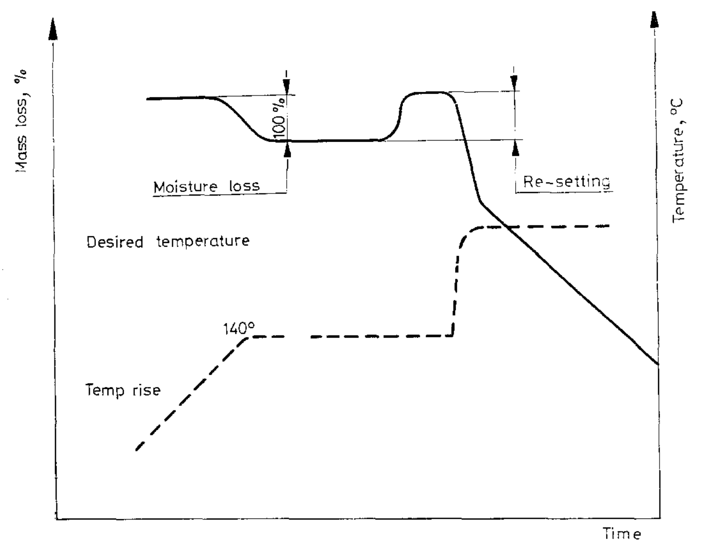

Fig. 2. Typical curve illustrating the loss in mass as temperature is rises

composition temperature than the group of fabrics ranked immediately below it in the pit test. At the lower heating rate the procedural decomposition temperature of the Kynol/Nomex blend fabric is closer to that of Kynol than that of Nomex, whereas at the higher heating rate it is closer to that of Nomex.

These results were obtained by heating the fabrics at a relatively slow rate, which we consider not to be the case when a sample is in an actual fire situation. Therefore we decided to subject the samples to isothermal holds at various elevated

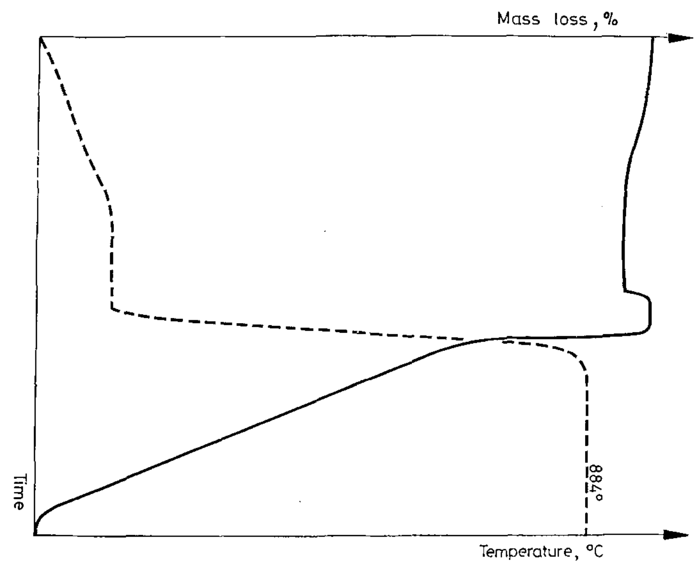

Fig. 3. Actual curve for Kynol illustrating mass loss at isothermal temperature of 884°

temperatures up to 1000°, the limit of the instrument, and examine their behaviour. 2.5 mg samples were placed in the furnace and heated to 140° at a rate of 100°/min. The samples were held at this temperature until a constant mass was reached, i.e. until all the moisture was removed. The chart recorder was re-set so that this mass now corresponded to the total mass, i.e. 100 per cent. The samples were then heated at a rate of approximately 3000°/min to the desired temperature. A typical curve is shown in Fig. 2, and an actual curve of Kynol at 884° in Fig. 3.

Examination of the curve shows that, initially, there is very rapid mass loss followed by a slowing down of the rate. This pattern is exhibited by all but one of the fabrics, namely PBI.

From the curves, the mass retained at the point where the decomposition rate changes can be determined and plotted against the corresponding isothermal temperature (Fig. 4). The order of stability of the fabrics at an isothermal temperature of 950° is compared in Table 4.

The manner in which a fabric behaves in the pit test must depend on the thermal characteristics of the fabric. The thermogravimetric studies carried out at high heating rates puts the fabrics in the same order as the fire pit test, and their positions relative to each other are almost identical. It would appear therefore that the high heat flux of the source is the overriding influence on the behaviour of the fabric. It should therefore be possible to estimate the protective time for the various fabrics using the mass retained figures in Table 4 and the protective time for one

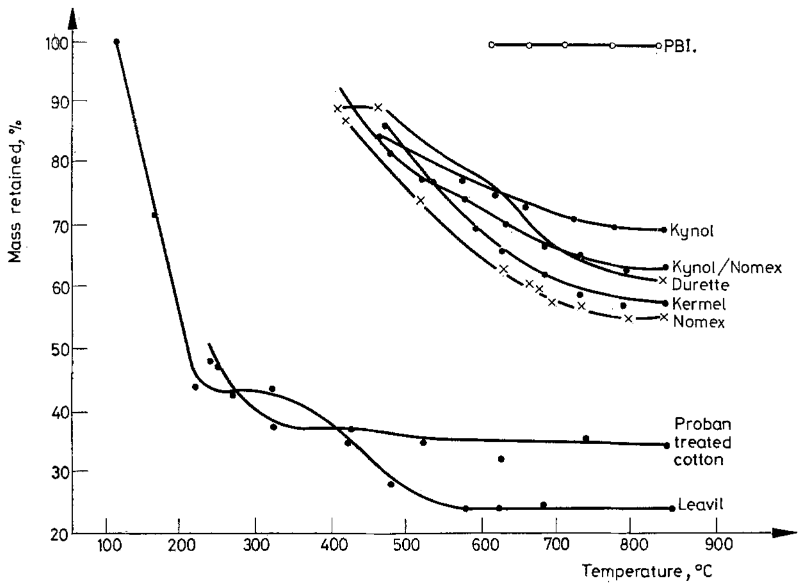

Fig. 4. Mass retained at point of inflection under isothermal conditions

Table 4

Sample	Mass retained at 950° at point where decomposition rate changes, %
PBI	100
Kynol	70
Durette	63 } mean 59
Kynol/Nomex	61 } mean 59
Kermel	57 } mean 59
Nomex	55 } mean 59
Proban-treated cotton	35
Leavil	24

particular fabric. This is done in Table 5 for two cases for values taken from Table 1:

(1) using the protective time of 4 seconds for PBI and
(2) using the protective time of 2.5 seconds for Kynol.

The result of this scaling operation is shown in Table 5.

Table 5

Sample	Protective time (seconds)	
	based on PBI	based on Kynol
PBI	4.0	3.6
Kynol	2.8	2.5
Nomex, Durette, Kermel, Kynol/Nomex	2.3	2.1
Proban-treated cotton	1.4	1.3
Leavil	1.0	0.9

A comparison of the times in Table 5 with those in Table 1 shows that the protective times derived from the mass retained figure, using Kynol as the known standard, are almost identical with those obtained in the pit test – with the exception of PBI which gives a lower time.

Use of protective times based on PBI (Table 5) gives values which are not quite so comparable with those in Table 1 as the Kynol-based one. However, they still show a very fair degree of correlation.

This high degree of correlation would lead one to posit that, providing fabrics exhibit the same pattern of behaviour under isothermal conditions during thermogravimetry, it is possible to predict how they will behave in the fire-pit test and hence in practice.

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RÉSUMÉ — On examine différents types d'étoffes ignifuges du point de vue de l'inflammabilité et par thermogravimétrie. On montre la possibilité de déterminer à l'aide des techniques instrumentales de laboratoire, l'action protectrice d'un vêtement en utilisant de très petits échantillons. Cela pourrait être important lors du développement de matériaux nouveaux où l'on pourrait soumettre à analyse rapide les qualités protectrices des étoffes.

ZUSAMMENFASSUNG — Es wird die Prüfung verschiedener feuerfester Gewebe unter Feuerbedingungen bei standardisierten Entzündbarkeitsprüfungen und durch Thermogravimetrie beschrieben. Es wird gezeigt, wie der durch ein Kleidungsstück gewährleistete Schutz mit sehr kleinen Proben und durch Laboratoriumstechnik bestimmt werden kann. Dies könnte bei der Entwicklung neuer Materialien von Wichtigkeit sein, wo eine Schnellbestimmung der Schutzeigenschaften des Materials durchgeführt werden muß.

Резюме — Данная статья касается исследования различных типов огнестойких волокон в условиях пожара, стандартных тестов воспламеняемости и термогравиметрии. Показывается возможность определения защиты, даваемой одеждой, используя очень малые образцы и инструментальную лабораторную технику. Это представляется важным для разработки новых материалов, для которых может быть проведена быстрая оценка их защитных качеств.