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DEPARTMENT OF SCIENTIFIC AND INDUSTRIAL RESEARCH AND FIRE OFFICES' COMMITTEE
JOINT FIRE RESEARCH ORGANIZATION

METHODS FOR ASSESSING SPONTANEOUS HEATING AND IGNITION HAZARDS

I. - THE MACKEY TEST

by

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Summary

The Mackey test has been considered from the point of view of its suitability as a general method for assessing the spontaneous heating and ignition hazards of materials which are subject to atmospheric oxidation. An experimental study has shown that there is an optimum packing density for self-heating in specimens of oiled fibre in the Mackey tester.

The Mackey test can be used to show whether spontaneous heating can occur in a given material, and it may give an indication of the possibility of spontaneous ignition under practical conditions. But, if the test is to be used for classification of materials in order of their liability to spontaneous ignition, it may be necessary to determine the optimum test conditions for each material. Further experimental work is required to show if this extension of the test is practicable.

Introduction

With many materials which are capable of spontaneous heating and ignition the process is initiated by the reaction of the material with oxygen at ordinary atmospheric temperatures. The heat evolved in this oxidation causes an increase in the temperature of the material with a consequent acceleration of the reaction. In this way the temperature of the material may rise to the point of ignition; but, if the loss of heat to the surroundings is too high for this to occur, the temperature will rise to a maximum value lower than the ignition point and then fall as the oxidation approaches completion.

A laboratory method is needed which will be generally applicable for assessing the hazard associated with the storage of materials of this kind. In the course of studies on such materials different workers have used calorimetric methods, measurements of oxygen absorption, and small-scale reproduction of the heating accelerated by an elevated ambient temperature. The Mackey test [1,2] is of this last type and was devised specifically for assessing the spontaneous heating hazard of oils used in the textiles industry; although Mackey [2] found it of value for the examination of other materials. It has been widely used as a standard test for many years.

In the Mackey test a weighed quantity of the oil is spread on a weighed quantity of cotton sliver and enclosed in a chamber whose walls are maintained at a constant temperature of 100°C and through which air circulates by natural convection. The occurrence of self-heating is observed by means of a thermometer inserted in the specimen. If the temperature exceeds 200 °C in two hours or less the oil is regarded as unsafe [20].

The criterion by which oils are classified as safe or unsafe in the standard Mackey test [20] is based on practical experience with oils of known properties and it is applicable only for the normal use of oils in textile processing. It cannot be relied on as a guide to the behaviour of oxidisable oils in, for example, bales of oiled textile waste stored for long periods, or in oiled textile material exposed to unusually high ambient temperatures. The risk of unexpected self-heating or ignition in circumstances such as these is especially great when the presence of an antioxidant [3, 4, 22-24] or dilution with a mineral oil [5, 25] has increased the induction period in the oxidation of a hazardous oil sufficiently for the oil to pass the standard test, because the rate of oxidation and heating following such increased induction periods is usually almost as great as for the untreated oil.

By continuing a test to cover the whole oxidation and heating process the Mackey test can be used to assess the behaviour of oils under a wider variety of conditions than in textile processing. The test can also be used for observing the liability to spontaneous heating and ignition both of oxidisable oils supported on materials other than cotton, and of any oxidisable solid material. But, beyond the fact that materials which self-heat in the Mackey test may be expected to do so elsewhere, it is not clear at present how the results of tests are to be interpreted in terms of the relative hazard under practical conditions, especially as it is usually not certain that the tests have been carried out under the optimum test conditions for each material.

It is not expected that a single criterion for relative hazard would be possible, but, given optimum test conditions, materials could be classified initially in order of the maximum temperatures they attained. The materials giving maximum temperatures in any chosen range of values could then be compared in order of the times taken to reach the maximum; due attention being given to the occurrence of induction periods in the reactions responsible for heating.

Very little systematic work has been found, in the literature, on the effect of varying the conditions of the test, such as the size and packing density of the specimen and the amount of ventilation, although the importance of these factors is generally appreciated. Kehren [6] noted the effect of departure from the standard dimensions of the apparatus on the results of the standard test. Clogston and Nuckolls [7] and Thompson [8, 25] used a larger apparatus and specimen and obtained a degree of self-heating with olive oil and lard oil on cotton wool which showed that these oils might, in certain circumstances, be hazardous; although they are usually classed as safe by the standard test. The possibility of ignition occurring with olive oil was, however, demonstrated in Mackey's original tests [2] with specimens of the standard size but with prolonged heating. Thus, samples of olive oil on cotton self-heated to maximum temperatures of 235° to 241 °C in times between 3 hr 25 min and 5 hr 15 min.

The importance of the size of the specimen in tests for spontaneous ignition, carried out at constant ambient temperature, has been shown in a striking manner by Mitchell's tests [9] on wood fibreboard. The lowest ambient temperature at which a one-inch cube of the fibreboard heated spontaneously to ignition was 396 °F (202 °C), and ignition occurred in 18 min; but heating to ignition occurred with an ambient temperature as low as 228 °F (109 °C) when the specimen consisted of a solid octagonal prism of the fibreboard 22 inches between opposite faces, although the time required was 96 hr 40 min.

The reproducibility of results in the Mackey test is adequate only for a broad classification of oils. For example, Mackey [2] obtained maximum temperatures varying between 194° and 284 °C in eight tests on cottonseed oil, the maxima being attained in times varying from 1 hr 15 min to 1 hr 45 min; while some samples of olive oil and oleine did not exceed 104 °C in 1 hr 30 min.

Garner and Leach[10] claim that more reproducible results are obtained if the oil is incorporated into the cotton with the aid of hand cards, thus giving a more uniform distribution of the oil than is possible by the normal method of hand mixing; but the use of cards, with oleines especially, would appear to entail a risk of contamination by iron soaps sufficient to affect the rate of heating (see below). Chambard and Durande-Ayme[11] recommend that the thermometer should be contained in a copper tube to overcome the effects of uneven heating in the specimen.

A considerable amount of attention has been given to the effect of factors such as traces of metallic soaps and salts on the behaviour of textile oils in the test (see, for example, refs. 4, 6, 12-18); because of the marked acceleration of the heating produced by iron soaps in particular different workers have supported the specimen in, for example, a cylinder of platinum wire gauze[15], paper[17], a spiral of lead free glass[19], or in a bag made of cotton gauze[20].

In order to determine to what extent the principle of the Mackey test can be applied generally for assessing spontaneous heating and ignition hazards an investigation is being made of the effect of physical variables on the behaviour of materials in the Mackey tester. The system chosen for study is a drying oil dispersed on a vegetable fibre, since it is one in which heating is conveniently rapid and in which the concentration of oxidisable material can be adjusted readily. In the work described in this note the effect of the packing density of the specimen at constant volume has been studied.

The Mackey Tester

In Mackey's original test[1] the oiled cotton was packed into a cylinder of iron wire gauze and placed in an ordinary water-jacketed oven kept at the boil; the thermometer in the specimen projected through the roof of the oven. Mackey[2] later designed a special apparatus for the test which is shown diagrammatically in Fig. 1. A chimney system was fitted to provide for the circulation of air through the enclosure containing the specimen, whereas, in the original test, the air supply depended on the ventilators normally fitted to laboratory ovens. This form of the apparatus has been in general use until comparatively recently but, in this country, the standard test for textile oils which is prescribed by the Fire Offices' Committee[20] employs a more elaborate form known as Firth's 1934 Modification. This modified form is provided with a steam-jacketed chimney and interior baffles, and the specimen, packed in a bag made of cotton gauze and supported by a wire carrier, is inserted through an opening only 1.5 inches in diameter. This form was used in the work described below, except that the specimen was contained in a cylinder of stainless steel gauze.

Experimental

A search was made for a fine fibre on which the drying oil could be distributed easily without causing matting and which would give a uniform and stable packing within a wide range of densities. Of the fibres tested (cotton wool, jute, flax, and Sansevieria sp.) jute was found to have the desired properties. The variety used was Daisee jute (Corchorus olitorius). The fibre was cut by hand into lengths of about 1 cm, mixed, and stored in tins.

The drying oil used was a commercial sample of linseed oil which was found, by steam distillation, to contain about 10 per cent of white spirit. The characteristics of the oil were determined and were as follows:

	As used	For 100% oil
Iodine value	152	169
Saponification value	173	192
Free fatty acid (as oleic acid)	1.89	2.1

The self-heating tests were carried out on a mixture of equal weights of oil and fibre· the weights being appropriate to the desired packing density. The weighed quantity of oil was poured over the fibre in a porcelain dish and mixed by alternate hand kneading and teasing out; rubber gloves were worn for this purpose. In a series of tests to be described in a later report it was found that the loss of oil on the gloves and dish was 0.20 ± 0.02 g.

The oiled fibre was supported in the tester in a cylinder of stainless steel gauze 3.0 cm in diameter and 10.0 cm long. During the packing of the fibre, one end of the cylinder was closed with a rubber bung which had a glass rod projecting for 2 cm from the centre in order to form a hole in the centre of the specimen for the thermometer. The fibre was finally teased out and packed into the cylinder a little at a time with the aid of a glass rod and as uniformly as possible. The length of the packing was always 6.5 cm.

The specimen was not prepared until the temperature in the Mackey tester had reached 98° - 99°C. The time taken for the mixing and insertion of the specimen was about seven minutes.

From three to five tests were carried out at each packing density. In all cases the temperature in the centre of the specimen was recorded until the maximum was passed and cooling was in progress.

Results

The way in which the specimen temperature varied throughout a test is shown in Fig. 2 for two typical examples at different packing densities, and for which the difference in maximum temperature was large.

Charring of the interior of the specimens was pronounced in those in which temperatures of about 240°C and above were indicated. It was then mainly confined to the portion of the specimen below the thermometer, but was more extensive in specimens in which temperatures approaching 260°C were indicated. Darkening of the specimen was first noticeable in specimens which reached about 150°C. In general the distribution of discoloration and charring in the specimens after the tests showed that the maximum temperature indicated by the thermometer at the centre was less than the maximum temperature reached elsewhere in the specimen.

The mean observed maximum temperatures for each packing density, and the mean time taken to reach the maximum from the moment of insertion of the specimen in the tester, are given in Table 1, with standard deviations, and are plotted against the packing densities of the specimens in Fig. 3.

Table 1 - Results of Mackey tests

Packing density g/cm³	n	Maximum temperature °C	Time to maximum mins	Time to 85°C mins	Time from inflexion to maximum mins
0.131	3	133 ± 13	90 ± 9	16.2 ± 3.2	48 ± 5
0.174	5	177 ± 14	108 ± 8	22.3 ± 0.8	54 ± 6
0.218	5	241 ± 13	105 ± 7	26.6 ± 1.4	47 ± 7
0.262	3	264 ± 4	116 ± 8	33.4 ± 3.5	56 ± 7
0.303	3	262 ± 18	129 ± 7	34.0 ± 1.0	57 ± 3
0.349	3	248 ± 24	148 ± 11	35.7 ± 2.5	71 ± 13

n = number of tests

It is evident from Fig. 3 that there is an optimum packing density of about 0.28 g/cm^3 for the occurrence of the highest observed maximum temperature. It is reasonable to suppose that the highest actual maximum temperatures would also occur at this packing density.

The time taken to reach the maximum temperature (Fig.3) increases regularly as the packing density of the specimen is increased.

A characteristic of the rise in temperature of the specimen after insertion in the tester was an inflexion in the temperature/time curve between 97° and 99°C (Fig.2), which was close to the steady temperature of about 98°C reached in the interior of the tester when a specimen was absent. This indicated that the reaction responsible for self-heating did not occur at an effective rate until shortly before the inflexion. This delay is a normal feature of the heating of oiled fibres in the Mackey tester and is usually enhanced by the occurrence of an induction period in the oxidation process. The presence of moisture may result in a pause in the temperature rise near 100°C; Rosin [21] showed that it could be entirely responsible for such a pause in the self-heating of brown coal semi-coke. A separate test carried out with linseed oil on oven-dried jute confirmed that a delay in the heating occurred in the tests described in this note, which was not due to the presence of moisture. The inflexion occurred at mean times which increased from 43 to 77 minutes as the packing density was increased from 0.131 to 0.349 g/cm^3.

In view of the delay in self-heating it is possible to examine the effect of packing density on the heating time in two stages. For this purpose the mean time taken for the temperature to reach 85°C for each value of the packing density has been taken as characteristic of the heating of the specimen by the water jacket (at 100°C) alone before the reaction begins; and the mean time interval between the inflexion and the maximum temperature, for each value of the packing density, has been taken as characteristic of the self-heating stage in the specimen. These quantities are given with standard deviations in Table I, and are plotted against packing density in Fig. 4.

The linear increase of the time taken to reach 85°C, as the packing density increases to 0.26 g/cm^3 (Fig.4), must be related to the increase in thermal capacity of the specimen, and suggests that the rate of heat transfer through the specimen does not vary greatly in this range of densities. The sudden decrease in the rate of increase of the time at densities above 0.26 g/cm^3, however, can be explained only by an increase in the rate of heat transfer.

Below a density of 0.26 g/cm^3, the time interval between the inflexion and the maximum temperature is almost independent of the packing density, but it increases rapidly when the density exceeds 0.30 g/cm^3 (Fig.4).

Both of the sudden changes in the above time/density relationships occur at densities near the optimum for self-heating, i.e. 0.28 g/cm^3 (Fig.3). It is suggested that the increase in the heat transfer at these densities is due to a tendency for the voids in the specimen to become filled with oil instead of air. The decrease in maximum temperature at densities above 0.28 g/cm^3, and the increased interval between the inflexion and the maximum may then be due to increased heat losses or to reduced oxygen supply, or to both factors.

Discussion

It has been found that an optimum packing density exists for the spontaneous heating of specimens of jute impregnated with linseed oil in the Mackey test. It may be inferred that optima will exist similarly for other oiled fibres; but they will not necessarily occur at the same densities, and the optimum for a given oil and fibre may depend on the proportion of oil present.

The relatively abrupt change in the rate of heat transfer, which was indicated above certain densities, may be a factor which contributes to the existence of an optimum density for self-heating only in mixtures of solids and liquids such as oiled fibres. The postulated restriction of oxygen supply, however, is a factor which, alone, could result in an optimum density for self-heating in all oxidisable materials. But it would have to be determined by experiment whether the densities necessary for this restriction to be operative would be attained, by the normal methods of packing the specimen, with oxidisable materials in granular form. With a given granular material the range of possible packing densities (often only about $\pm$ 10% of the mean) is smaller than for fibrous materials and, therefore, the main factor controlling the degree of heating in a specimen of given volume may be the particle size rather than the packing density.

There is no doubt that the principle of the Mackey test, used either in the form of the present tester or some modification of it, is capable of showing whether spontaneous heating can occur in a given material. Further, if the size of the specimen used in the test is increased sufficiently, it may always be possible to reproduce ignition in a material which is capable of spontaneous ignition. But it is evident from the results so far obtained that, if the test is to be used for anything but the broadest classification of materials in order of their tendency to spontaneous ignition, it will be necessary to carry out a series of replicated tests to determine the optimum conditions for heating in each material. Since the different factors requiring adjustment are probably not independent, the number of tests to be carried out may be too numerous to make a classification by this method worthwhile. However, the experimental evidence at present available is inadequate for this to be decided.

It is probable that a classification of materials liable to spontaneous heating and ignition, under optimum conditions in a test of this kind, would indicate their relative hazard under practical conditions. This, it is felt, is sufficient to warrant carrying the investigation further. It must, however, be emphasized that the optimum conditions found for the different materials under test could not be expected to indicate more than qualitatively the nature of the optimum conditions for spontaneous ignition to occur in practice; the main obstacle to such a correlation is the change of scale.

Conclusions

From the results of an investigation of the effect of packing density on the heating of oiled fibre in the Mackey tester and a consideration of published work on the Mackey test, the following conclusions have been drawn:

1. An optimum packing density exists for self-heating in a specimen of oiled fibre of given dimensions.

2. The standard Mackey test employing temperature and time limits, is applicable only for comparison of the spontaneous heating and ignition hazards of textile oils subjected to normal use.

3. The test can be made more generally useful by following the whole course of the heating; continuing the test for several hours, if necessary, in order to allow for induction periods in the reactions responsible for heating.

4. The test may possibly be used to classify materials, which are subject to atmospheric oxidation, in order of their spontaneous heating and ignition hazard; provided they are compared under the optimum test conditions for each material. Further experimental work is required to determine whether this is, in fact, practicable.

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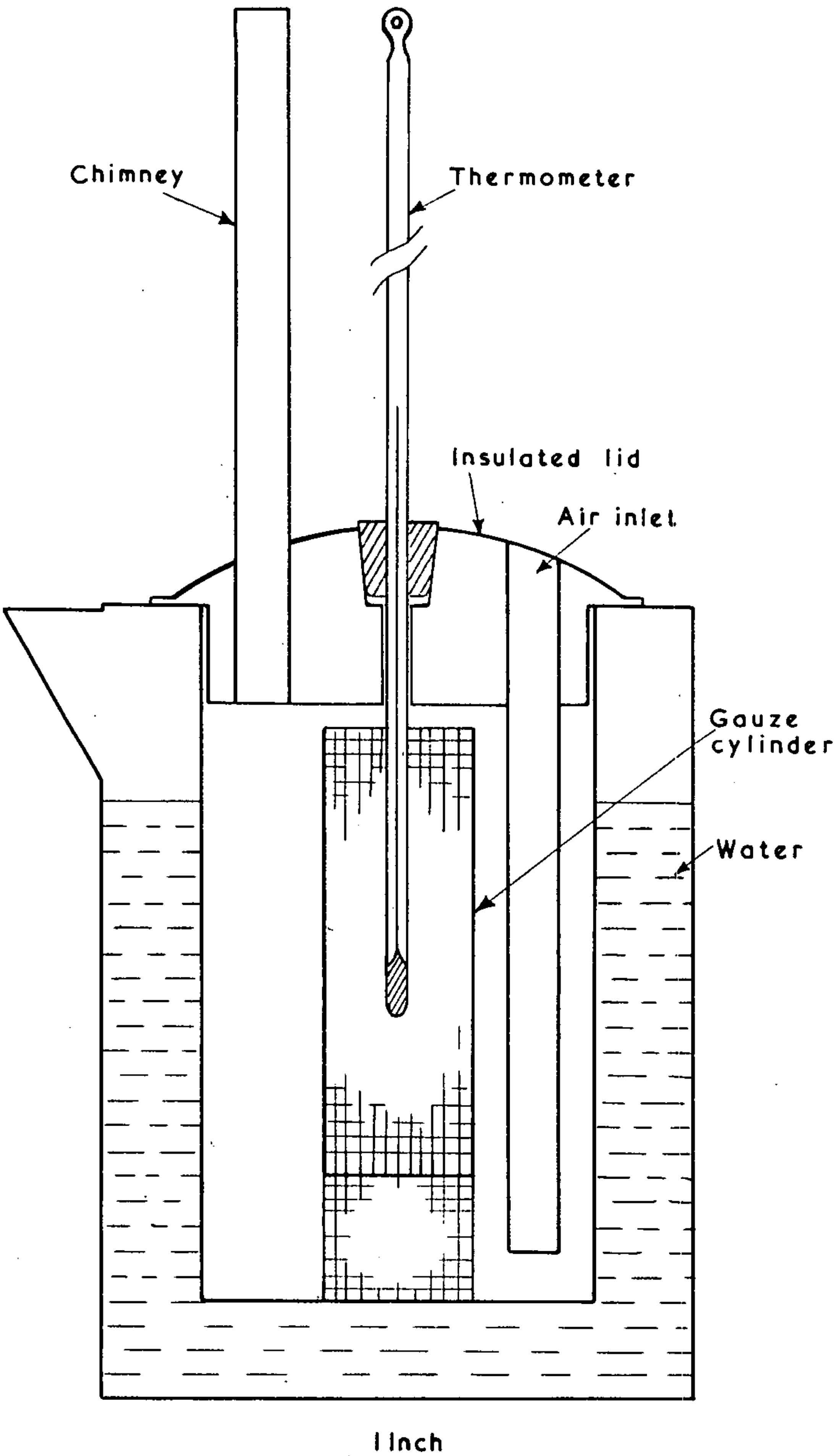
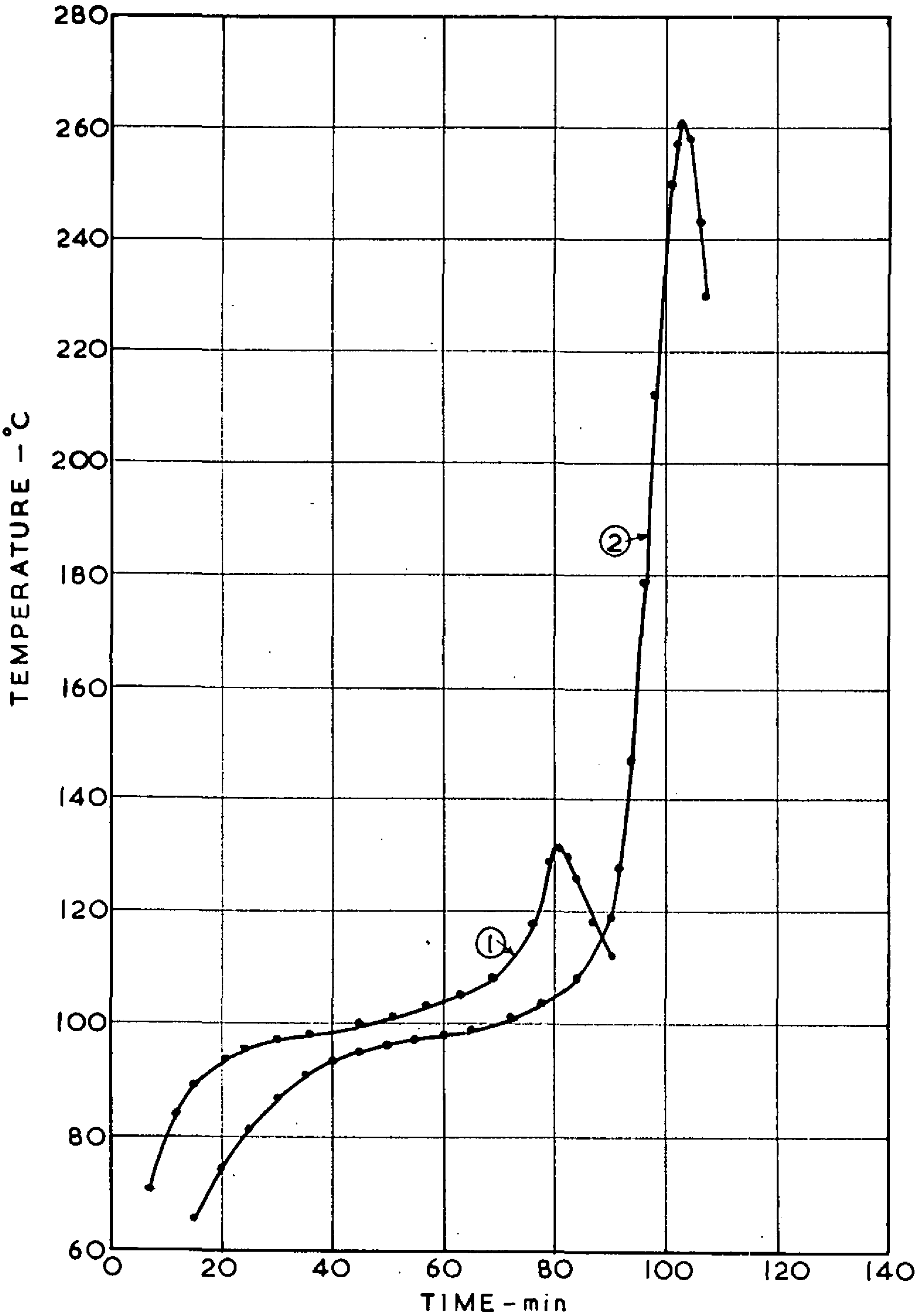


FIG. 1. MACKEY TESTER



① Packing density 0·131 g/cm^3
② Packing density 0·218 g/cm^3

FIG. 2. HEATING OF LINSEED OIL ON JUTE IN MACKEY TESTER

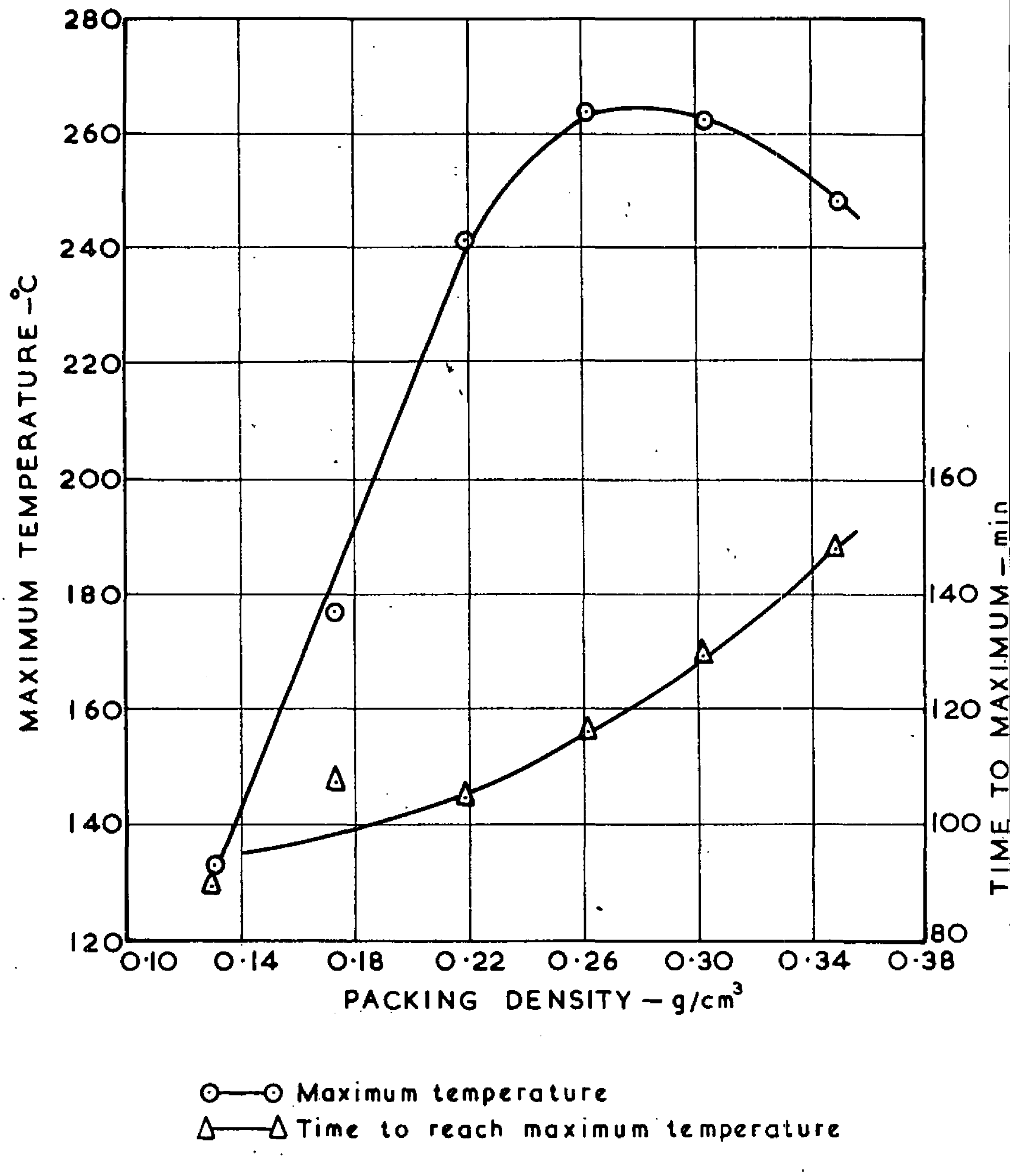


FIG. 3. EFFECT OF PACKING DENSITY OF SPECIMEN ON MAXIMUM TEMPERATURE IN MACKEY TEST.

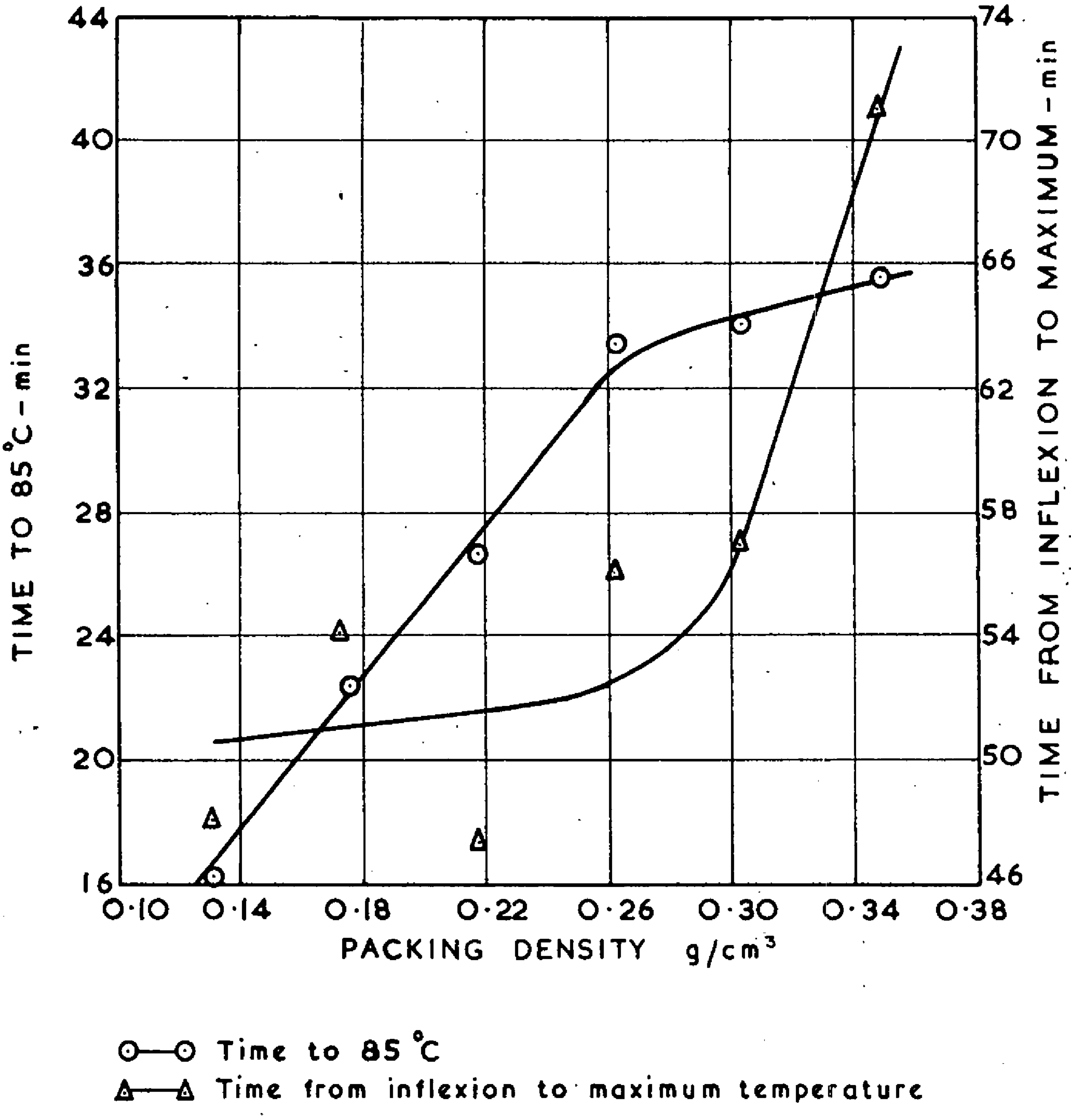


FIG. 4. EFFECT OF PACKING DENSITY OF SPECIMEN ON COURSE OF HEATING IN MACKEY TEST