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

ON THE EFFECT OF PREHEATING ON THE IGNITION
OF CELLULOSIC MATERIALS

by

P. H. Thomas

Summary

There are some data of a limited character which suggest that heating
cellulosic materials makes them more easily ignitable or flammable and that
subsequent heating appears to reverse this trend. Such a reversal suggests
that either more than one reaction is involved in decomposition or that
there is some physical loss of active components. A theoretical model on
such lines is discussed and is shown to exhibit qualitative features of the
kind observed experimentally.

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1. Introduction

In Figure (1) is shown a curve obtained by Bardsley & Skeet [1]* for the ignition temperature of sawdust heated beforehand at 180°C and allowed to cool in air. The "ignition temperature" measured by heating the wood from cold after the period of heating first rises and then falls as the preheating period increases.

Webster has shown a similar effect of preheating on the flammability of cotton. Strips of cotton were kept in an atmosphere at 124°C, cooled and then subjected to the semicircular flammability test [2]. The time to spread 21 in. is shown in Figure (2) for different periods of heating. Only one specimen was tested for each duration of heating, but the data do show a fall in time of spread followed by a rise. The shorter the time of spread the greater the flammability and the lower the effective "ignition temperature". An inverse relation between flammability and "ignition temperature" has been calculated theoretically [3]. It is seen, despite the variation between the results, the results in Figure (2) have the same character as those in Figure (1).

A somewhat different experiment - the heating of wood at different levels of radiation for the same time - has given results which also have a similar feature to those above. Thus in Figure (3) are shown the times for spontaneous ignition of specimens subjected to a given intensity after previously being exposed to different intensities for the same time. It is seen again that there is evidence suggestive that some intermediate preheating condition has the greatest effect on the ease with which wood can be ignited spontaneously. The results for pilot ignition do not exhibit this feature to the same extent if at all.

The effect on "ignition temperature"^{T} (or, alternatively, on the ease of ignition) may not be large. In Figure (1) or (2) the effect on "ignition temperature" is of the order of 10 per cent. In Figure (3) it appears greater, but a difference in "ignition temperature" is magnified by the effects of conduction and surface heat loss and differences in ignition time are not indicative of differences in "ignition temperature" of the same magnitude.
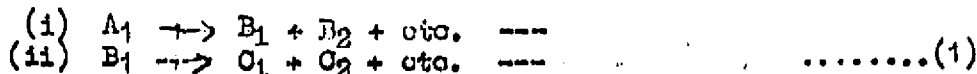
Even if the figure of 10 per cent is not of immediate practical importance, the result is of considerable interest. It shows that two factors are involved. The first may be assumed to be a primary decomposition, which produces some quantity which is necessary for self heating or which hastens it; the second is, presumably, some form of loss of decomposition product. This may be a physical loss by diffusion or a chemical loss by secondary decomposition. Klason [4] has shown that in the absence of air, wood decomposes in two main stages. It is assumed in what follows that the decomposition in air similarly follows two (or more) stages.

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*Some criticisms have been levelled at this work. For this reason only those results, i.e. for 180°C, which have been checked, have been quoted.

TThe term "ignition temperature" is used in a loose way. Strictly its definition involves the method of its measurement, but since for any one set of experiments the method is constant, the simple concept of "ignition temperature" is sufficient to demonstrate the change in the case of ignition brought about by preheating.

2. Discussion of general theoretical model

We consider first the decomposition of wood to follow two (or more) series of consecutive reactions, viz:

$$
\begin{array}{ll}
\text{(i)} & A_1 \longrightarrow B_1 + B_2 + \text{etc.} \quad ---- \\
\text{(ii)} & B_1 \longrightarrow C_1 + C_2 + \text{etc.} \quad ----
\end{array}
\qquad \ldots\ldots\ldots(1)
$$

The second of these can also be considered as a physical loss (see below)

For convenience, we denote the concentration of any of these components by the same symbol. Oxygen could also be included on the left-hand side of any one of these equations to represent oxidation following decomposition.

When a considerable part of the volatile decomposition products of wood have been driven off by heating, the carbonaceous residue may itself ignite but, confining ourselves to the ignition brought about by volatiles, we identify the components $B_1 B_2$, $C_1 C_2$ etc. as volatile precursors. If we identify the presence of one (or more) of the intermediate products as necessary for the ignition of wood, it follows that there is an optimum condition for such ignition, for example, the concentration of B_1, say, increases owing to the decomposition of A and decreases owing to its own decomposition or oxidation into $C_1 C_2$ etc. The concentration of B and all such intermediate products, thus passes through a maximum. In general, any weighted sum of B, C, etc. will also pass through such a maximum.

Considering the most general form of reaction with equilibria well over to the right-hand side of equation (1) we have a series of kinetic equations for each stage of the reactions. For example, B is here referring to any one of the series $B_1 B_2$ etc.

$$
\frac{dA}{dt} = -k_A f(A) \qquad \ldots\ldots\ldots(2)
$$

and

$$
\frac{dB}{dt} = -\frac{dA}{dt} - k_B g(B) \qquad \ldots\ldots\ldots(3)
$$

where k_A and k_B denote reaction constants (k_B could be related to a diffusion coefficient if loss of B were by diffusion) and $f(A)$ and $g(B)$ are functions which increase or remain stationary with increase in the argument A or B. $f(0)$ and $g(0)$ are both zero. Strictly speaking, the coefficient of $\frac{dA}{dt}$ in equation (3) is not unity but a fraction depending on the relative molecular weights of A and the particular component B under consideration. It should be pointed out that Stamm [5] has shown that heating wood reduces its mass in accordance with

$$
\frac{dm}{dt} \propto -m \qquad \ldots\ldots\ldots(4)
$$

If all the original wood is identified with one component A which all changes to one non-volatile component B then any loss of mass, say, through the formation of C products according to equations (2) and (3) could not follow equation (4). Loss of mass according to equation (4) can only be accommodated by introducing a second B component which escapes from the heated solid. Even then, the agreement of the two models is only approximate.
    A decreases with time and $f(A)$ is not a constant. B has the form shown in Figure (4). If $f(A)$ were constant B would have a sharp maximum when A became zero. Oxidation will follow similar equations if the oxygen is present in excess,
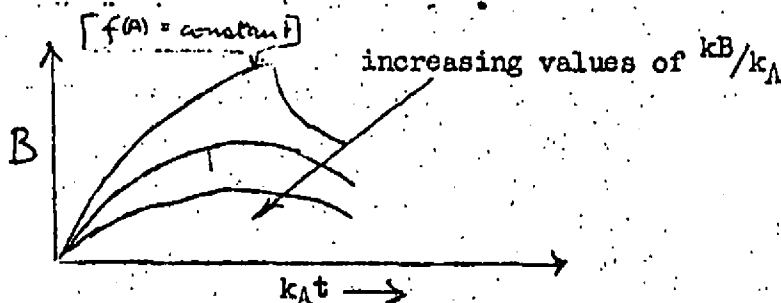

Figure 4. The variation of B with time

It is shown below that the curves for B versus $k_A t$ for different values of k_B/k_A do not intersect and that the maximum value of B increases as k_B/k_A decreases. One would expect that reducing the temperature and thereby reducing k_A and k_B would tend to increase the time at which the maximum occurs. While this is probably so for any practical situation, it does not follow logically from equations (2) and (3) unless restrictions are imposed on the nature of $f(A)$ and $g(B)$ and on the relative magnitude of k_A and k_B.

It must be mentioned here that the actual process of progressively heating the wood to ignition for the purpose of assessing its ease of ignition is not considered. Changes will occur during such an experiment and these will be of the kind in Figure 1 but at the higher temperatures they will be greatly accelerated. The mathematical treatment would be rather complicated because of the variation of temperature with time and the dependence of the k's on temperature but it would be reasonable to expect that the "ignition temperature" or the ease of ignition will depend directly on the condition of the material at the commencement of such an experiment, i.e. the condition after a time of preheating at a lower temperature.

For example, if the decomposition or oxidation in excess air of B is exothermic, a greater amount of B present initially will mean that exothermic heating at the commencement of heating to ignition will be greater and this will tend to hasten the onset of a condition where heat loss exceeds the heat generation and therefore of ignition itself.

We, therefore, do not consider the changes brought about by this second heating. We shall simply assume that the preheating time and preheating temperature determine an "initial" condition for the measurement of an "ignition temperature" or controlled by this "initial" condition.

From the above argument on the variation of B with preheating time, it would follow that the "ignition temperature" T_i will vary in a manner corresponding to the variation of B, i. e. it varies with preheating time 't_p' as in Figure (5), which has the same form as Fig. (1) and Fig. (2).
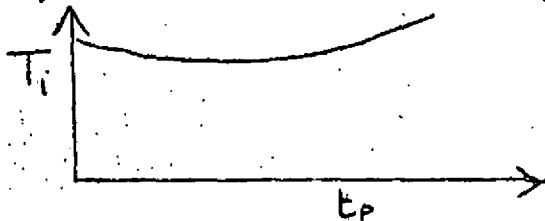

Figure 5. The effect of preheating time on ignition temperature T_i

2.1. The effect of the preheating temperature 'T_p' on the minimum value of T_i.

There are no reliable data with which to compare the theory for this section. It is included because it is possible to draw some useful conclusions from equations (2) and (3) in their general form, without imposing too severe a restriction on $f(A)$ and $g(B)$

It is possible to discuss how the minimum values of the "ignition temperature" T_i, for such curves as Fig.(5) vary with t_p the preheating temperature.

From equations (2) and (3) we can write generally

$$\frac{dB}{d\lambda} = F(\lambda) - \frac{k_B}{k_A} g(B) \qquad\qquad (5)$$

where $\lambda = k_A t$

and F is an undetermined but decreasing function of λ. Since $g(0)$ is zero, B versus λ curves for different values of k_B/k_A have the same slope at the origin, i.e. $F(0) = f(A)$, where the suffixes 'o' denotes the initial value.

Now, differentiating equation (5)

$$\frac{d^2 B}{d\lambda^2} = F'(\lambda) - \frac{k_B}{k_A} \cdot \frac{dB}{d\lambda} \cdot g' \quad \ldots\ldots\ldots\ldots(6)$$

the dash denoting differentiation.

F' is negative so that it follows from equation (6) that the higher is k_B/k_A the lower the $B - \lambda$ curve near the origin.

Consider two curves B_1 and B_2 corresponding to α_1 and α_2 (α equal to k_B/k_A) with

$$\alpha_2 > \alpha_1$$

At the origin they have equal slopes but B_2 tends to fall below B_1. Now if there is a subsequent intersection at X (see Figure (6)) $\left(\frac{dB_1}{d\lambda}\right)_X < \left(\frac{dB_2}{d\lambda}\right)_X$

Figure(6)
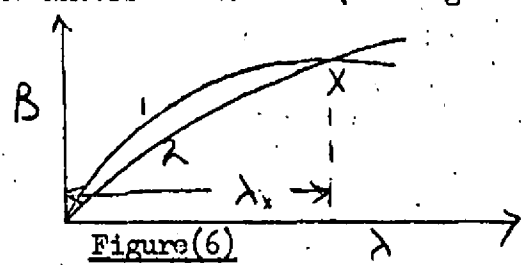
i.e. from equation (5)

$$F(\lambda_x) - \alpha_1 \, g(B_x) < F(\lambda_x) - \alpha_2 \, g(B_x)$$

Therefore

$$(\alpha_2 - \alpha_1) \, g(B_x) < 0$$

But $\alpha_2 > \alpha_1$ so there cannot be in fact an intersection.

It follows that the B_2 line is within the B_1 line throughout so that the maximum value of B decreases as α i.e. (k_B/k_A) increases. In particular, if α is zero (i.e. k_B is 0) B increases to the initial value of A i.e. A_0 while if k_B is ∞, B is zero throughout. Hence B varies with k_A/k_B as in Figure 7.
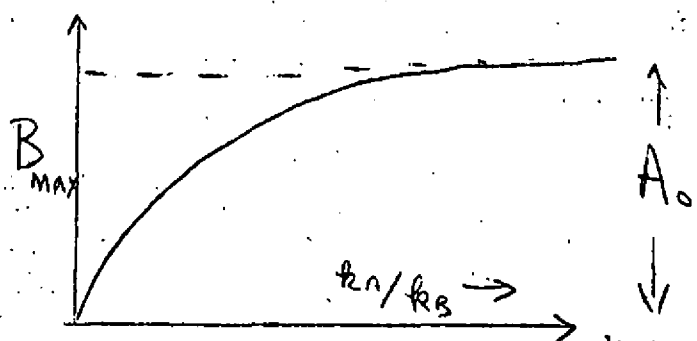

Fig. 7. Variation of B.max. with k_A/k_B

Now, assuming the Arrenhius relation

$$k = f \, e^{-E/RT} \quad \ldots\ldots\ldots(7)$$

where f is the frequency factor
E is the activation energy
R is the universal gas constant
T is the absolute temperature of preheating

it follows that

$$k_A/k_B \propto e^{-\frac{(E_B - E_A)}{RT}} \quad \ldots\ldots\ldots(8)$$

From the above discussion, it follows that, if $E_B > E_A$, the minimum "ignition temperature" for any preheating decreases, the lower the preheating temperature.

The fact that there is an upper limit to B max. implies that there is a maximum possible reduction in "ignition temperature" as a result of pre-heating.

On the other hand, if $E_B < E_A$ or the mechanism of the system were one of physical loss of material in which case k_B is constant, which is mathematically equivalent to putting E_B zero, the greater is the preheating temperature, the lower is the minimum "ignition temperature"

2.2. The variation of T_i with T_p for a given preheating time.

In the light of the above arguments, we can consider the variation of T_i with T_p for a given preheating time, t_p.

For a very low preheating temperature - say room temperature - we would not expect the amount of B produced in a certain time (hours rather than years) to be at all significant. Increasing the temperature T_p increases k_A and since at small values of T_p the curve of B against $k_A t_p$ tends to be independent of k_B (i.e. only the first reaction is proceeding) the amount of B produced will increase. If $E_B > E_A$ it follows that as T_p increases k_B/k_A also increases and B will pass through a maximum and then decrease. (See Figure 8.)
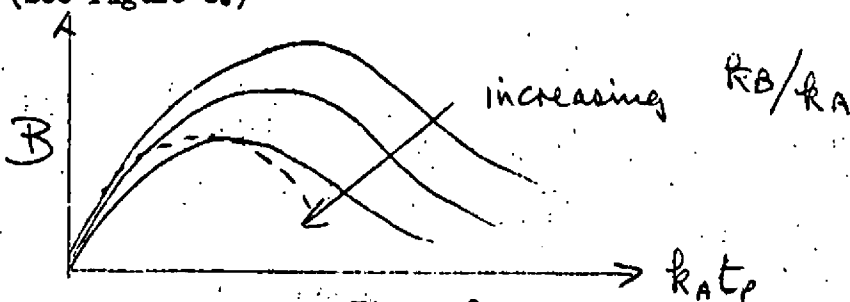

Figure 8

Dotted curve shows variation of B as the temperature of preheating T_p increases.
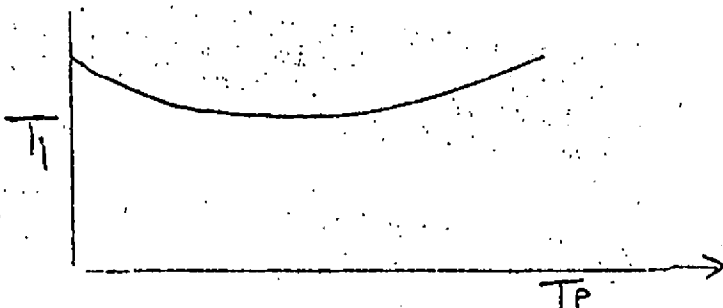

Fig. (9). The relation between preheating temperature & "ignition temperature"

The corresponding "ignition temperature" therefore decreases and then increases as shown in Figure (9) and may be compared with Figure (3).

3. Quantitative application

The above discussion has been conducted without imposing severe restrictions on the form of $f(A)$ & $g(B)$.

If $f(A)$ and $g(B)$ are proportional to A and B respectively, i. e. the reactions are first order then

$$A = A_0 e^{-k_A t}$$

Where A_0 is initial concentration of A
and

$$B = \frac{k_A A_0}{k_B - k_A} \left(e^{-k_B t} - e^{-k_A t} \right) \quad \dots\dots\dots\dots(9)$$

The variation in ignition behaviour with preheating temperature if known, could be used to evaluate E_B or E_A. For example, the time to reach the maximum of B is given by

$$t_m = \frac{1}{k_B - k_A} \log_e \frac{k_B}{k_A} \quad \dots\dots\dots(10)$$

$$i.e, \quad t_m \propto \frac{E_B - E_A}{RT} \frac{e^{E_A/RT}}{\left[1 - \frac{f_B}{f_A} e^{-\frac{(E_B - E_A)}{RT}} \right]} \quad \dots\dots\dots(11)$$

where f_B/f_A is independent of temperature.

For low values of T it follows from equation (11) that

$$\log_e T.t_m = \text{constant} + \frac{E_A}{RT} \qquad (E_B > E_A)$$

$$= \text{constant} + E_B/RT \qquad (E_B < E_A) \qquad \dots (12)$$

The temperature of heating corresponding to the minimum time to ignite in the preheating experiments at different radiation levels (Figure 3) which are nominal values, is not known accurately. The time of heating was approximately 150 hours and the temperature was in the range 150°C to 200°C. The result is, therefore, not sufficiently accurate.

For the heating at 180°C the time to reach the minimum ignition temperature is approximately 13 days (Figure 1) and for the heating of cotton at 125°C, 95 days (Figure 2). It is not possible to test whether in fact, there is a relationship such as that indicated by equation (12) but the value of E based on these two results alone, gives a minimum value equal to 13,000 cal/gm.mole. The values of E for wood, based on weight loss data [5] and ignition data [6] [7] are two to three times this value. It is not really possible to discuss this result, owing to the insufficiency of data, and the considerable assumption made in deriving it, but it is interesting that the result is of the right order.

Conclusions

The descriptive model of the reactions describe features of the preheating of cellulose which have been noted experimentally. These are:

(1) Progressive preheating wood at first increases its ease of ignition.

(2) This trend is reversed as preheating continues.

The theory suggests moreover that:

(3) The increase in the ease of ignition is dependent on the preheating temperature and is greatest for low temperature preheating if $E_A < E_B$ and least if $E_A > E_B$. There is, theoretically, a maximum possible reduction in ignition temperature as a result of preheating.

The experimental evidence from which these facts were obtained was of an exploratory nature. Even so, there seems to be sufficient grounds for further experimental work on such lines.

Acknowledgment.

I would like to thank Mr. P. C. Bowes for the helpful discussions I have had with him and the suggestions he has made and Messrs. Webster and Simms for the results of the experiments made by them.

References

(1) H. Bardsley and G. Skeet. The effect of preheating on the ignition of wood. F. C. Note No. 30/1950.

(2) British Standard 476 : Part II.

(3) P. H. Thomas and D. I. Lawson. The speed of Propagation of Flame on Fabrics. F. R. Note No. 278/1956.

(4) P. Klason. See E. Hagglund "Chemistry of Wood". Academic Press Inc. (1957) New York.

(5) A. J. Stamm. Ind. Eng. Chem. 1956. 48 (3) 413-417

(6) P. H. Thomas. Comments on the experiments on the self-heating of fibre insulating board. F.R. 306, 1957.

(7) P. C. Bowes. Estimates of the rate of heat evolution and activation energy for a stage in the ignition of some woods and fibreboards. ibid F.R. 266/1956.
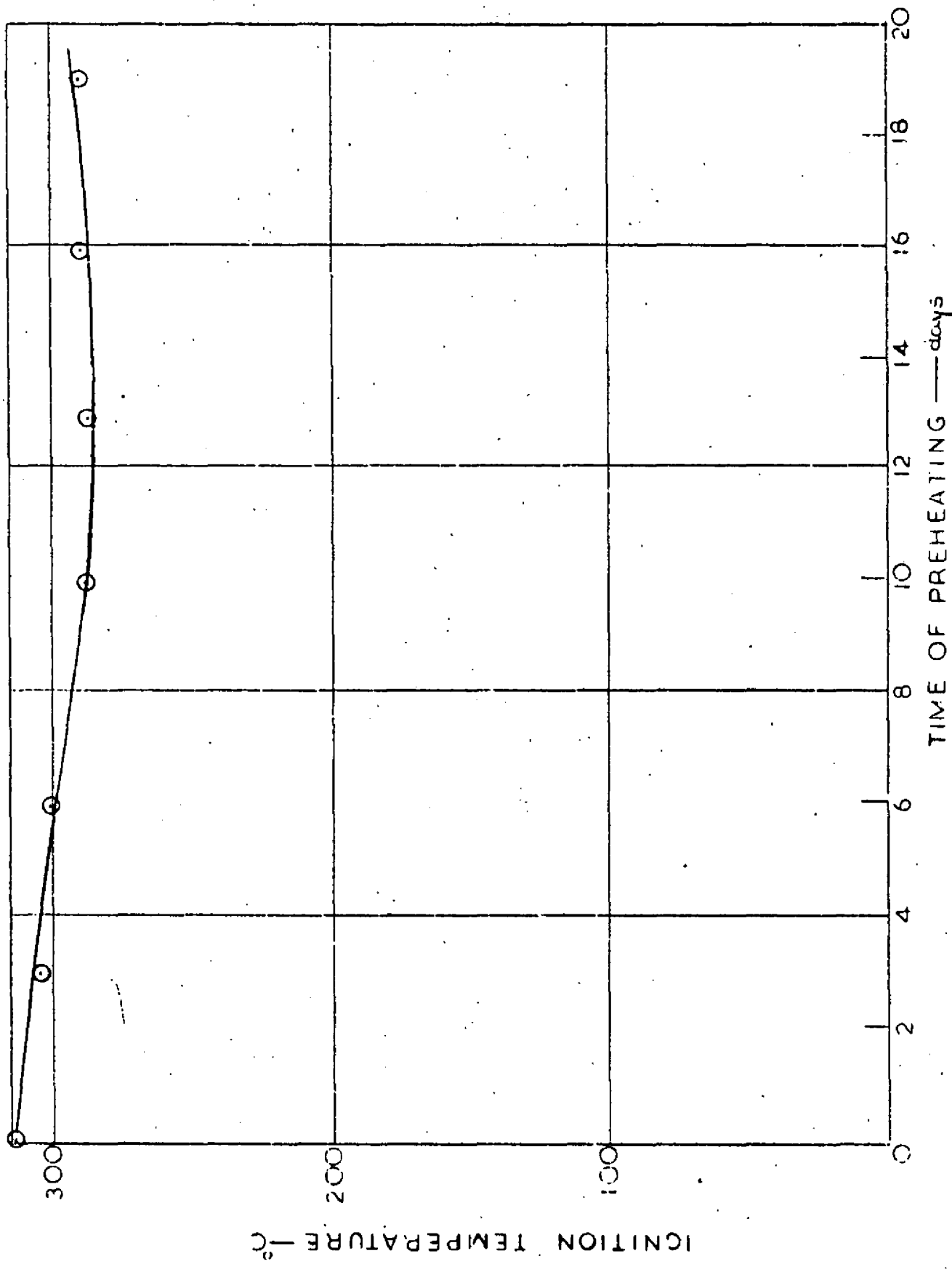
FIG.1 THE EFFECT OF PREHEATING ON "IGNITION TEMPERATURE"
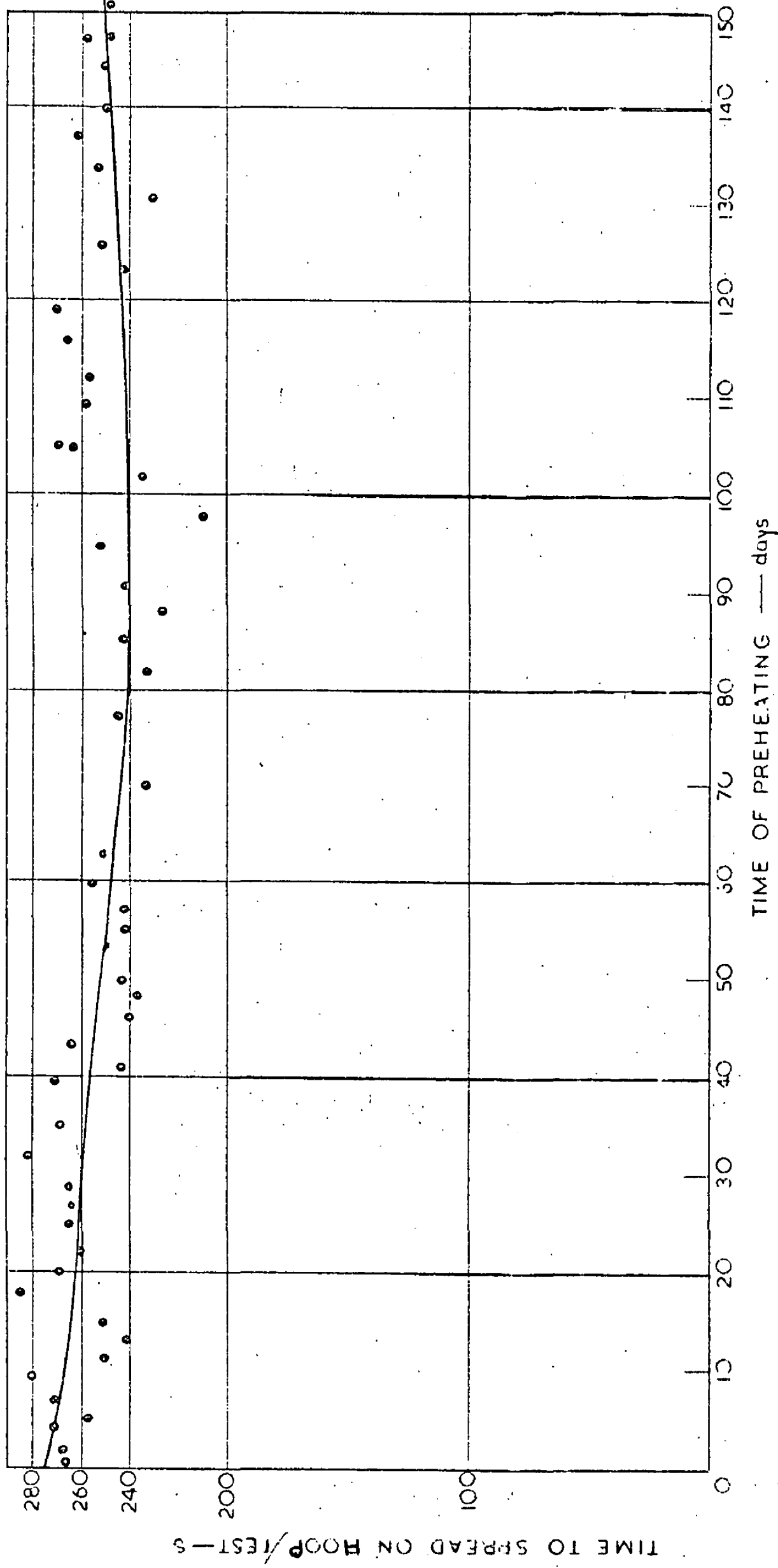(PREHEATING TEMPERATURE 180°C) FROM BARDSLEY & SKEET

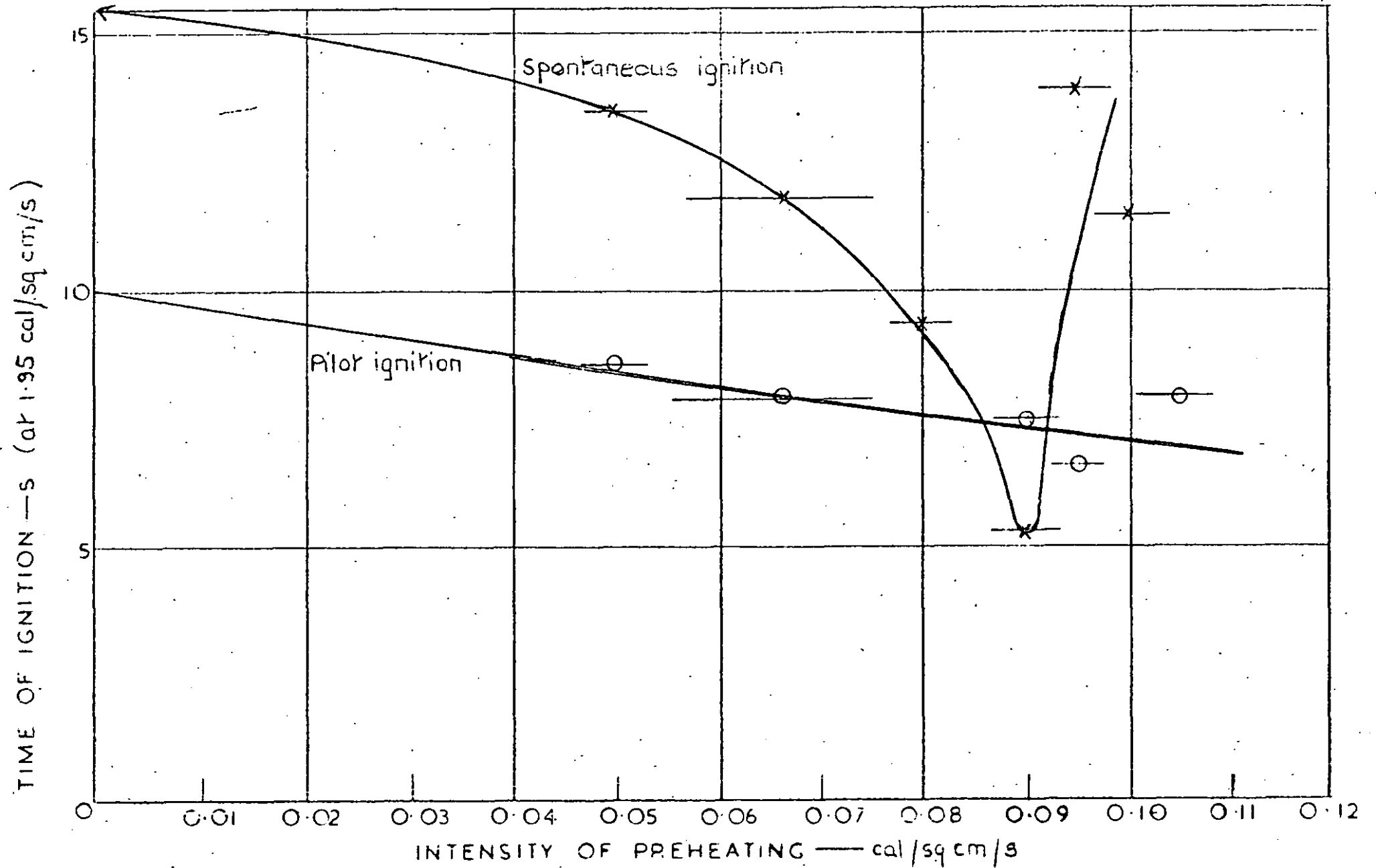FIG. 2. THE EFFECT OF PREHEATING ON THE FLAMMABILITY OF COTTON
(BY WEBSTER)

TIME OF PREHEATING — days

TIME TO SPREAD ON HOOP/TEST—s

FIG.3. IGNITION TIMES AS A FUNCTION OF PREHEATING FOR
150 HOURS. AT VARIOUS INTENSITIES OF RADIATION