LIBRARY REFERENCE ONLY

THE LIBRARY
BUILDING RESEARCH STATION
GARSTON WATFORD
HERTS.
FIRE RES. NO. 1078

Fire Research Note No 1078

THE CONSTRUCTION OF FLAMMABILITY DIAGRAMS FROM FLASH POINT MEASUREMENTS

by

P F Thorne and A A Briggs

November 1977

LIBRARY REFERENCE ONLY

FIRE RESEARCH STATION

56393

© BRE Trust (UK) Permission is granted for personal noncommercial research use. Citation of the work is allowed and encouraged.

Fire Research Station
BOREHAMWOOD
Hertfordshire WD6 2BL

Tel: 01 953 6177

Fire Research Note No.1078
November 1977

THE CONSTRUCTION OF FLAMMABILITY DIAGRAMS FROM FLASH POINT MEASUREMENTS

by

P F Thorne and A A Briggs

SUMMARY

Using a modified Abel closed cup flash point apparatus, both 'lower' and 'upper' flash points have been measured for the system n-hexane/carbon tetrachloride. From these experimental results a complete flammability diagram has been constructed.

The 'peak' flammability limit by this method was 9.7% carbon tetrachloride at a n-hexane concentration of 3.4%, compared with 11.5% and 3.2% respectively when determined by the standard limit apparatus.

© Crown copyright 1977

Department of the Environment Fire Research Station of the Building Research Establishment

LIST OF SYMBOLS USED

p_f, p_a	Partial vapour pressures of fuel and additive
p_f^o, p_a^o	Saturated vapour pressures of pure liquid fuel and pure liquid additive
x_f, x_a	Mole fractions of fuel and additive in the liquid mixtures
γ_f, γ_a	Activity coefficients of liquid fuel and additive
p_T	Total pressure (atmospheric)
y_f, y_a	Mole fractions of fuel and vapour in the vapour phase
L.E.L	Lower limit of flammability of the fuel vapour in air expressed as mole (volume) fraction
U.E.L	Upper limit of flammability of the fuel vapour in air expressed as a mole (volume) fraction

Fire Research Note No.1078
November 1977

THE CONSTRUCTION OF FLAMMABILITY DIAGRAMS FROM FLASH POINT MEASUREMENTS

by

P F Thorne and A A Briggs

INTRODUCTION

In previous publications[1,2] a theory was developed which enabled the lower limit limb of a flammability diagram to be partially constructed from the results of simple flash point measurements, using the Abel closed-cup apparatus in the standard manner. A knowledge of the vapour-liquid equilibrium of the particular mixture was also required. This theory extended the generally accepted concept that the 'closed-cup' flash point was synonymous with the lower explosive limit (LEL) of a single component fuel, to two component mixtures only one of which was flammable. For the system n-hexane/carbon tetrachloride it was found that liquid mixtures whose equilibrium vapour composition contained more than 7.5 per cent v/v of carbon tetrachloride were non-flammable. The value of 'peak' concentration for this system is 9.5 per cent v/v. It was suggested that the flash point measurements did not lead to an anomalous low 'peak' concentration but that the 'standard' flash point measurements could not lead to a complete definition of the lower limit limb.

Being synonymous with the LEL the flash point measured in the standard apparatus can be described as the 'lower (closed-cup) flash point'. It was Burgoyne and Williams-Leir[3] who first recognised that two distinct flash points existed, the other they described as the 'upper flash point'. It is with the 'upper flash point' that this note is concerned and the way in which it complements 'lower (closed-cup) flash points' in the construction of a flammability diagram.

FLAMMABILITY DIAGRAMS

A generalised flammability diagram is shown in Fig.1. The three well known properties of such diagrams are the lower explosive limit (LEL) of pure fuel vapour in air, the corresponding upper explosive limit (UEL) and the 'Peak' concentration (P) of inhibitor vapour. Superimposed upon this diagram are saturated vapour pressure (SVP) curves for different liquid mixtures of

flammable (fuel) and non-flammable (inhibitor) components. For these SVP curves, $x_{f_1} > x_{f_2} > x_{f_3} > x_{f_4}$. As each SVP curve is climbed from near the origin (O) the temperature of the liquid mixture increases. The point at which the SVP curves for x_{f_1} to x_{f_3} cross the flammability envelope corresponds to the 'lower' flash points, for those mixtures. As the mixture temperature is further increased and the SVP traverses the flammability envelope the liquid mixture continues to exhibit 'flash points' until it recrosses the flammability envelope at the 'upper' flash point. Thus points on the lower and upper limbs of the flammability envelope are established.

Special behaviour is exhibited by mixture x_{f_4} . Its SVP curve is tangential to the flammability envelope, the 'lower' and 'upper' flash points coincide, and only one flash point exists. Thus, it is seen that measurement of the 'lower' flash points will not enable the lower limb to be fully determined. If the SVP for mixture is considered where x_{f_3} is only slightly higher than x_{f_4} then it is seen that a 'lower' flash point is exhibited in the usual manner but on increasing the temperature, as described above, an 'upper' flash point is also found. This 'upper' flash point still corresponds to a point on the lower limb of the flammability diagram, ie it lies below the 'peak' concentration (P) and to its left. Thus, by measuring the upper flash point in addition to the lower flash point of liquid mixtures a complete flammability diagram can be constructed.

EXPERIMENTAL PROCEDURE

Previously[1,2] the Abel closed cup flash point apparatus had been used in its standard form[4] to make flash point measurements from which the lower limb of a flammability diagram had been partially constructed. Initially, therefore, in this work the standard Abel apparatus was used in order to see whether an 'upper' flash point could be measured with it, using n-heptane. As the temperature was increased above the normal (lower) flash point, inconsistent behaviour was observed above 20 per cent of the UEL; sometimes burning outside the cup took place, sometimes a normal flash (flame propagation across the cup) was seen. No flashes were recorded above 50 per cent of the UEL, and no change in behaviour occurred when the temperature was taken through the value corresponding to a saturated vapour pressure equivalent to the UEL. It was concluded that the Abel apparatus in its standard form was unsuitable for work above the 'lower' flash point.

The apparatus was modified in the following manner. The lid was replaced by a perspex plate resting on the rim of the cup. The standard mercury thermometer was mounted on, and passed through, the plate. A 10 mm diameter vent hole was provided in the plate and this vent was plugged except at the instant of firing the source of ignition, which was a spark. By moving the cover plate assembly, vigorous stirring of the vapour space could be effected. Several configurations of electrode design, spark position and energy were tried. The spark electrode mountings were led through the perspex cover plate and sealed into it.

The first electrode configuration tried consisted of two 1.2 mm diameter steel wires mounted on 4.5 mm diameter vertical pillars, forming a horizontal 6 mm gap. A nominal energy of 400 mJ was provided, discounting transformer losses. This spark energy was found to be adequate for a single component fuel; a flash point of $-4.5^{\circ}C$ was recorded for n-heptane compared with the literature value of $-4^{\circ}C$. However, this spark was found to be inadequate for igniting mixtures of n-heptane with carbon tetrachloride.

The energy available for causing a spark was increased substantially - nominally 11 J were provided although the actual energy of the spark was unknown. A further modification was the provision of 0.3 mm diameter platinum wire for the electrode assembly, the horizontal gap provided again being 6 mm. Most of these exploratory tests with n-heptane were carried out with the spark gap 2 mm above the liquid surface although some were made with the electrodes 10 mm above the surface. It was also found advantageous to modify the heating/cooling bath arrangements in order to eliminate an unacceptable temperature lag between the sample and the cooling medium when working below $0^{\circ}C$. The final version of the modified apparatus is shown in Fig.2. Cooling was achieved by placing all the components of the apparatus in a freezer, prior to each test. Table 1 summarises the results of both 'lower' and 'upper' flash point measurements made with these different arrangements. 'Lower' and 'upper' flash points of mixtures of n-hexane with carbon tetrachloride were measured using the modified Abel apparatus incorporating the platinum electrodes situated just above the liquid surface. Condensation of droplets, predominantly hydrochloric acid, on the underside of the 'perspex' lid were observed even when no visible flame had propagated. There was some doubt, near the limits, concerning the detection of weak flames due to the eye being dazzled by the vivid white spark. However, it is considered that errors due to non-detection were not unduly significant.

The n-hexane was > 99 per cent pure by GLC analysis, and the carbon tetrachloride was 'Analytical Reagent' grade.

The results for different mixtures with x_f ranging from 0.14 to 0.64 are shown in Table 2. Temperatures are recorded to the nearest 0.5°C. Using the known vapour/liquid equilibrium data for those mixtures, corresponding values of y_f and y_a were calculated viz

$$y_f = \gamma_f . x_f . P^\circ_f / P_T$$

Values of the activity coefficients (γ) were calculated using the Van Laar equations, assuming for the constants the values for the chemically similar n-Heptane[1]. The values of y_f and y_a are tabulated in Table 2 and plotted as a flammability diagram in Fig.3.

DISCUSSION

Figure 3 shows the complete flammability diagram for the system n-hexane/ carbon tetrachloride. It consists of pairs of points lying on the saturated vapour pressure curves for particular mixtures. The point nearest the origin is derived from the 'lower' flash point measurement and that furthest from the origin from the 'upper' flash point measurement. For illustration the saturated vapour pressure curves for two mixtures (x_f = 0.4 and 0.64) are shown. For comparison a flammability limit diagram for the same system measured by Coleman[5] using a standard limit apparatus[6] is also shown.

Whereas previously[1,2] 'lower' flash point measurements could only allow the lower limit limb to be partially constructed (up to 7.5 per cent carbon tetrachloride) the lower limit limb is completed by measurements of 'upper' flash points, as is the upper limit limb of the diagram.

It can be seen that the two diagrams are generally similar, but some notable differences are seen. Both the LEL (by extrapolation) and the UEL are lower but the 'peak' value is increased to 11.5 per cent at 3.4 per cent fuel compared with 9.7 per cent at 3.2 per cent fuel measured in the standard limit apparatus.

The differences between the standard Abel apparatus and the standard limit apparatus were summarised previously[1]. The results of this current work should be viewed in the light of the differences between the standard and the modified Abel apparatus. These are summarised in Table 3. It is not intended, however,

to enter the discussion area of the existence of 'absolute' limits nor that of the effect of apparatus geometry and detail on experimental results.

Although there are differences between the flammability envelopes produced by this method and those obtained by using the standard limit apparatus, for practical purposes, it is suggested that these differences are not greatly significant. For example, it is usual, when designing a fire extinguishing system, to add a 'safety margin' of at least ten per cent to the 'peak value' plus allowances for loss of extinguishing agent by leakage, poor distribution etc. Similarly when deciding the maximum allowable concentration of a flammable vapour in air to take only a fraction of the lower explosive limit, normally a quarter.

The present method has the advantage that it can be carried out more readily with economies in time and materials by less skilled personnel than required for the usual method for peak value involving a tube. For many practical purposes the adequacy of the present method would be sufficient.

CONCLUSIONS

It has been shown that it is possible to construct a complete flammability diagram from experimental measurements of 'lower' and 'upper' flash points of liquid mixtures and a knowledge of the equilibria of the mixtures.

A flammability diagram so constructed for mixtures of n-hexane with carbon tetrachloride is seen to be similar to that measured in the standard limit apparatus. There are some differences but these are not significant for many practical applications.

REFERENCES

1. THORNE, P F. Flash points of mixtures of flammable and non-flammable liquids. Fire Research Station, Fire Research Note 1022 (1975).
2. THORNE, P F. Flash points of mixtures of flammable and non-flammable liquids. Fire and Materials, 1976, 1, 134-139.
3. BURGOYNE, J H and WILLIAMS-LEIR, G. Inflammability of liquids. Fuel 28 (1949) 145-158.
4. Flash point by the Abel apparatus. IP 170/70. Institute of Petroleum (1970).

5. COLEMAN, E H. Technical Booklet No.11. Fire Protection Association. London, 1952.

6. COWARD, H F and JONES, G W. Limits of flammability of gases and vapours. Bulletin 503, United States Bureau of Materials, 1952.

TABLE 1

Values of 'lower' and 'upper' flash points (°C) of n-heptane measured in modified Abel apparatus

	Literature value	Experiment values			
		a	b	c	d
'Lower' flash point	-4	-6	-7	-7.8	-7.5
'Upper' flash point	27.3*	25.4	25.0	24.2	24.1

*Temperature corresponding to UEL of 6.7 per cent v/v[6]

a Steel/brass electrodes 2 mm from surface, gap = 6 mm

b Steel/brass electrodes 10 mm from surface, gap = 6 mm

c Platinum electrodes 2 mm from surface, gap = 6 mm

d As (c) but using modified water bath

TABLE 2

Results of 'lower' and 'upper' flash point measurements for mixtures of n-hexane with carbon tetrachloride

Mole fraction hexane	'lower' flash point (°C)	'upper' flash point (°C)	Lower y_f	Lower y_a	Upper y_f	Upper y_a
1.0	-	1.5	-	-	6.46	-
0.64	-24	5	0.914	0.41	5.0	2.31
0.40	-13.5	12	1.16	1.30	4.59	5.27
0.20	0.5	21	1.41	3.74	3.84	10.37
0.16	11	22.5	2.00	6.71	3.43	11.56
0.155	13	20.5	2.10	7.46	3.03	10.62
0.14	No flash					

TABLE 3

Comparison of standard and modified Abel apparatus

	Standard apparatus	Modified apparatus
Ignition point	At top of cup, ie 18 mm above liquid surface	Close to liquid surface, ie 2 mm above it
Source	Flame, 4 mm dia	Spark, 6 mm long
Direction of flame	Downwards	Upwards

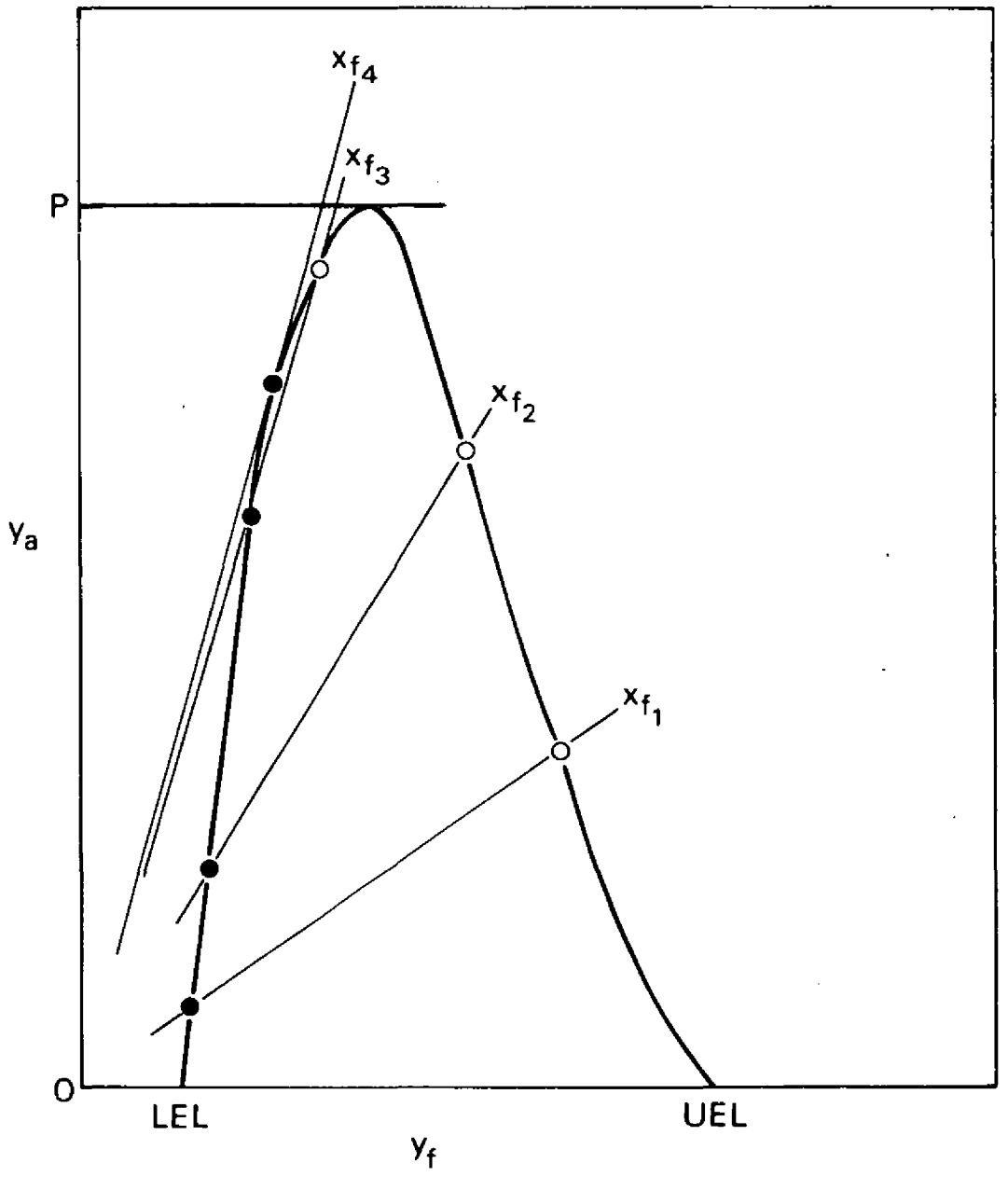

Figure 1 General flammability diagram

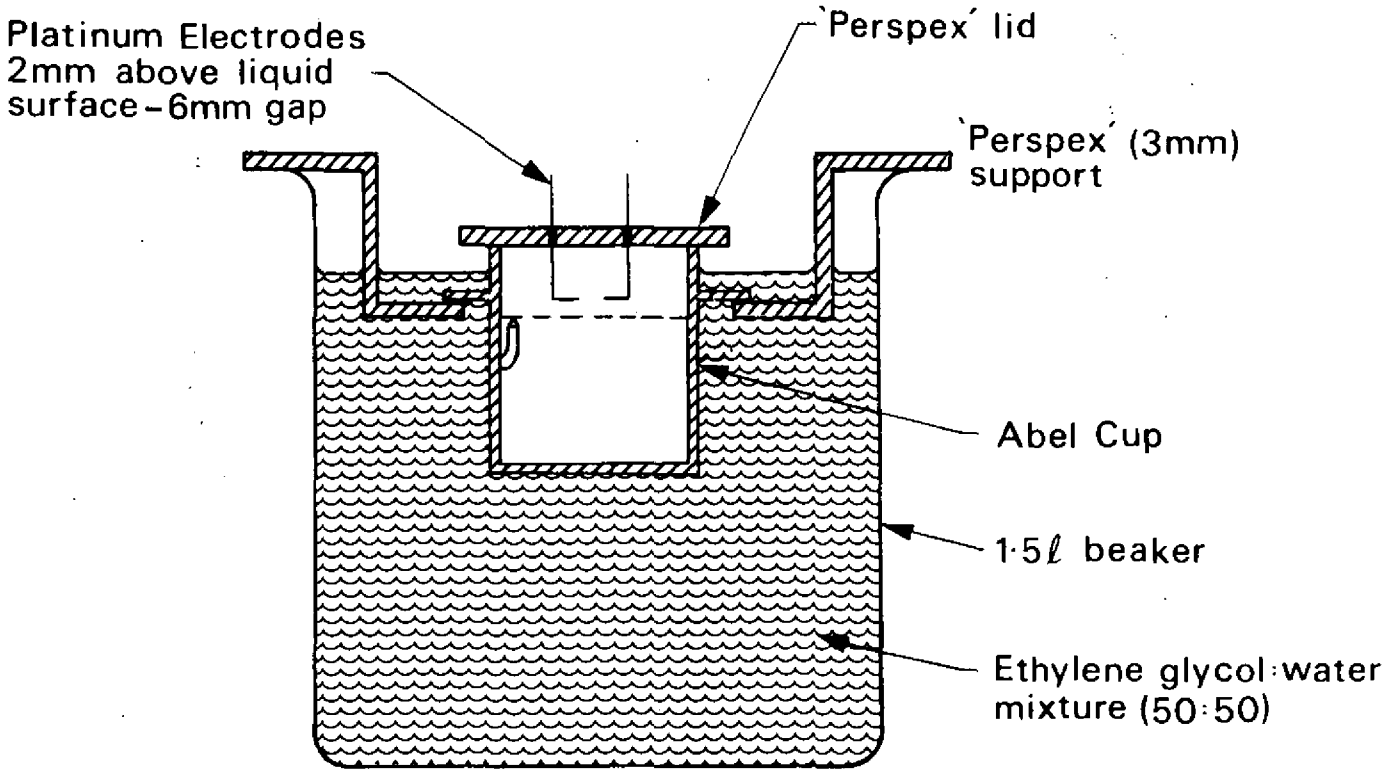

Figure 2 Schematic arrangement of final version of modified Abel Cup apparatus (thermometer and 10mm dia vent hole not shown)

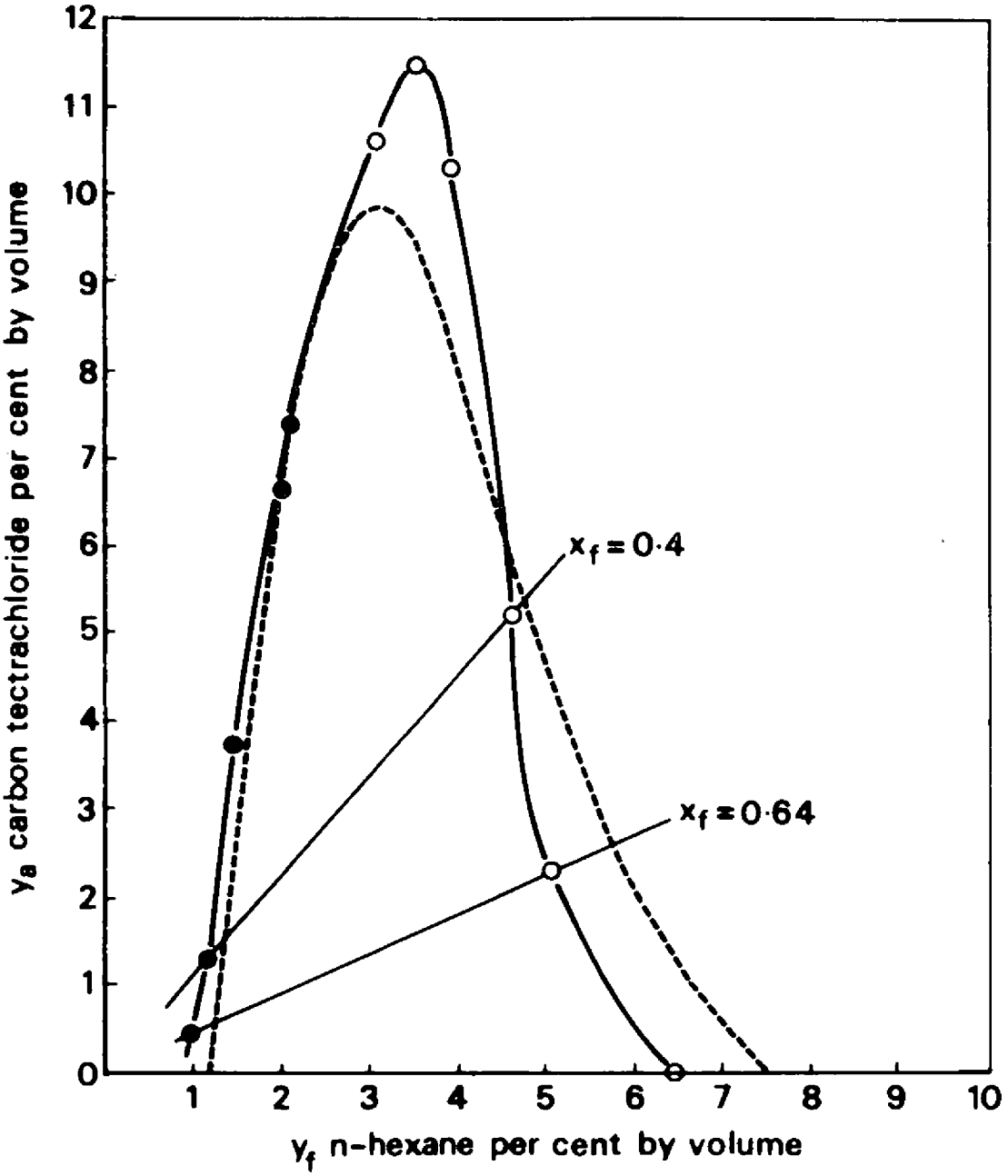

Figure 3 Flammability diagram constructed from 'lower' and 'upper' flash-point measurements

Printed in England for Her Majesty's Stationery Office by Studio Trade Plates Ltd., Watford, WD1 8SA.