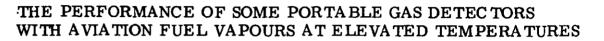


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PART 1 - TESTS WITH N-HEXANE, 'AVTAG' and 'CIVGAS' VAPOURS

by

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FIRE RESEARCH STATION

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THE PERFORMANCE OF SOME PORTABLE GAS DETECTORS WITH AVIATION FUEL VAPOURS AT ELEVATED TEMPERATURES PART 1 - TESTS WITH N-HEXANE, 'AVTAG' AND 'CIVGAS' VAPOURS

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SUMMARY

A method of testing portable flammable gas detectors at elevated temperatures is described and results are given for tests on five proprietary instruments with n-hexane, 'Avtag', and 'Civgas' vapours at 65° C, and n-hexane vapour at 25° C.

In general, the actectors gave a low response to 'Avtag' and 'Civgas' vapours and there is evidence that the readings are changed significantly with increase of ambient temperature. Possible reasons for the low response are given.

KEY WORDS: Explosimeter, detector, flammable vapour, aircraft fuels.

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• INTRODUCTION

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(a) General Introduction

The estimation of flammable gas concentration by the heat generated when the gas is oxidised on a heated filament, was first attempted by Liveing¹ (1880) and since that date the various phenomena associated with catalytic oxidation have been studied^{2,3,4} resulting in the production of various types of detector.

The catalytic-filament type flammable gas detectors, commonly known as "explosimeters", are now widely used for giving an indication of the explosive nature of a mixture of flammable gas or vapour and air. Reviews^{5,6} of the general properties of these instruments are available, but these are concerned in the main with the detection of the vapours of simple, pure compounds at moderate ambient temperature and humidity.

These gas detectors do, however, find application in testing for the vapours of mixtures of compounds such as are found in the petroleum fuels. In particular, use of these instruments in newly emptied and purged aviation fuel storage tanks, in tropical areas where the ambient temperature may be as high as 65° C with a relative humidity of 10 per cent at that temperature, has led to doubt as to the accuracy and reliability of the readings obtained. Since decisions, such as when it is safe to enter such a tank, use tools or carry out hot cutting or welding, are often confirmed by detector readings, it was considered desirable to subject some proprietary instruments to laboratory tests at 65° C with typical aviation fuel vapours, and to study also the effects of humidity changes.

(b) Principle of operation of the detectors

With all the detectors tested for this report, the flammable vapour or gas/air mixture, is allowed to pass over a heated catalytic filament, where oxidation takes place. The heat evolved raises the temperature and hence the resistance of the filament. The filament forms one arm of a Wheatstone bridge circuit, and the out of balance current, due to the resistance change, is registered on a galvanometer. Figure 1 shows a generalised circuit diagram to illustrate the measuring principle. The compensating filament serves to allow for temperature fluctuations and battery drift whilst the instrument is in use.

It was found by Le Chatelier⁷ that the heats of combustion of equal volumes of the lower explosion limit (L.E.L.) concentration of many flammable gases and vapours, are similar, and this makes it possible to calibrate these detectors in "per cent L.E.L." although they cannot be assumed to have universal application. Calibration curves or data can be supplied by some manufacturers, but these are normally for the vapours of single pure compounds at an unspecified temperature and humidity.

(c) Design of the detectors tested

The detectors differed in the mode of transferring the flammable vapour or gas/air mixture from the sample to the catalytic filament. Some instruments were fitted with a hand operated aspirator bulb and sampling line, allowing the gases to be sucked into the instrument; others relied upon diffusion of the test gases through a sintered bronze plug or steel grille before reaching the filament. Some details of each detector are given in Table 1.

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Detector	Sampling mode	Calibration gas*	Scale ranges (L.E.L.)	Power source	Other: features
A B	Aspiration "	Methane Leaded petrol	0-100%) 0-10%) 0-100%)	Replaceable leakproof cells	
C C	Diffusion Diffusion or	Methane n-pentane	0-100% 0-100%	Rechargeable battery . "")Preset)audible)and visual
E	Aspiration Aspiration	Avtag	0–100% 0– 10%	Replaceable leakproof, cells)alarm

Table 1. Some details of the tested detectors

*As stated by manufacturer.

With detectors A and B the compensating filament was not exposed to the, gas stream, but with C and D this filament was exposed but so coated as to be non-catalytic. With the latter arrangement, the cooling effect of the vapour is compensated for.

2. EXPERIMENTAL

(a) Test Apparatus

Figures 2 and 3 show the test apparatus. The fuel to be used was placed in one of the two reservoirs (the other reservoir will be used for water in future experiments for examination of humidity effects) from where it was metered into a heated vaporiser by a calibrated pump.

Air from a compressor was passed into the large vessel R which served to eliminate any pulsations. The air left vessel R via a pressure regulating valve, whose low pressure outlet was set at a pressure of somewhat less than that inside R, thus ensuring a steady flow. The air was then passed through a flowmeter and into the vaporiser where it became mixed with the fuel vapour. This vapour/air mixture passed through a stainless steel tube fitted with a pressure gauge, (this gauge enabled a correction for "back pressure" to be applied to the flowmeter reading) to a coil of stainless steel tubing inside a thermostatted oven. This coiled tube enabled the vapour/air mixture to assume the temperature of the oven. The end of this tube was fitted with a "tee" piece,

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one arm connecting with a standard flammable or explosion limits tube via a tap and flame trap, the other connecting with the detector sampling line via a tap and through the detector (A or B) or into a perspex box containing the detector (C or D) or housing the probe (E). The effluent gases were pumped (via a flowmeter) outside the laboratory.

(b) <u>Tests carried out</u>

Table 2 below gives some details of the fuels used for these tests. Table 2. Some details of the fuels used for the tests

Fuel	Description	Lower explosion limit 65°C (mass per cent)	Source
n-hex a ne*	S traight chain C ₆ hydrocarbon (analytical standard grade)	3•56 /	Chemical Suppliers
'Civgas'	Petrol B.S. 4040 Pt 1."4 Star"	3.41	Local garage
'Avtag'	Wide cut aviation turbine fuel (Min. of Aviation Supply Ref.No. D. Eng RD 2486, N.A.T.O. Ref. No. F-45)	3.49	R.A.F.

* not used as a fuel (

 \neq at 25°C

All detectors were initially tested with n-hexane at 25° C and 65° C to determine temperature effect and this compound was also used when a check on the reliability of the test method was carried out using gas-chromatography. For this check, samples of n-hexane vapour/air mixtures at several nominal concentrations were withdrawn from the detector sampling line with a gas syringe and transferred to a gas-chromatograph, previously calibrated with n-hexane vapour/air mixtures. The concentrations of n-hexane vapour obtained were compared with the concentrations expected from the test apparatus settings.

The detectors were all tested with 'Avtag' and 'Civgas' vapours at 65°C. No attempt was made in this series of experiments to artificially increase the relative humidity - the ambient relative humidity was monitored during the tests with a whirling hygrometer. The effects of increased humidity will be studied and reported later.

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(c) Test procedure

Before testing began, the vaporiser was switched on, and set at a temperature of 300°C for tests with 'Avtag' and 'Civgas' or 100°C for tests with n-hexane, thus ensuring complete vaporisation of the fuel. The thermostatted oven enclosure was switched on and set at the desired temperature. All detectors for test were placed inside the oven, and testing only begun when a thermocouple showed that the instruments were at the oven temperature. The compressor was started and the whole system purged with air to remove traces of fuel from previous experiments. The air flow rate was then adjusted to give a convenient steady value and the fuel pump started. With the tap to the detector under test closed, and the tap to the explosion limits tube open, various concentrations of fuel vapour in air, obtained by adjusting the fuel pumping rate, were passed into the tube and ignition attempted by an electric spark near the base of the tube in each case.

When a vapour concentration was found, which when exceeded, gave rise to a self-propagating flame of more than 0.61m (2 ft) above the spark electrodes, this was taken as the lower explosion limit concentration. The tap to the detector was then opened, and this lower explosion limit mixture (100 per cent L.E.L.) drawn through the detector by a small suction pump at a rate equivalent to that obtained with a hand operated aspirator bulb, 0.8 - 1.5 1/min, (in the case of instruments A and B) or into the perspex box containing the detector or probe at about 10 1/min (in the case of instruments C, D and E). The maximum steady reading of the detector was noted, together with the time taken to reach it. The concentration of vapour was then lowered (by maintaining a steady air flow rate and reducing the fuel pump delivery rate) to give mixtures of nominally 80 per cent, 50 per cent, 20 per cent and, in the case of n-hexane, 10 per cent of the lower explosion limit concentration. These mixtures were similarly passed through the detectors and the readings noted in each case. Between fuels, the **var**ious filters and flame traps fitted to some of the detectors were cleaned, and when using 'Civgas' vapour, detector A was fitted with the manufacturer's lead inhibitor filter.

3. RESULTS

Table 3 gives the results of the gas-chromatography analysis carried out on the n-hexane vapour/air mixtures issuing from the sampling line.

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Table 3. Comparison of theoretical n-hexane vapour concentration with concentration obtained by gas-chromatography

Nominal concentration of n-hexane vapour in air per cent by mass	Concentration of n-hexane vapour in air by gas- chromatography per cent by mass	Per cent lower explosion limit (nominal)	
3.56*	3.61	100.0	
3.56	3.65	100.0	
3.56	3.54	100.0	
1.81	1.84	50.8	
1.81	1.74	50.8	
1.81	- 1.87	50.8	
0.77	0.74	21.6	
0.77	0.98	21.6	
0.77	0.66	21.6	
0.39	0.49	11.0	
0.39	0.38	11.0	
0.39	0.28	11.0	

*Accepted literature value 3.5 per cent - see Refs 8 and 9

Figures 4 - 8 show the response of each detector to n-hexane vapour in air at 25° C and 65° C and 'Avtag' and Civgas' fuel vapours in air at 65° C. The broad line on each graph represents the ideal conditions where scale reading and per cent lower explosion limit are coincident. When working with vapour concentrations of less than 25 per cent of the lower explosion limit concentration, instruments A and B did not give a steady reading and the mean of the values at the limits of pointer swing was used as a point on the graph. These pointer swing limits are also recorded on the graphs. Readings taken above 50 per cent of the lower explosion limit were generally quite steady and all readings were reached within fifteen seconds of passing the vapour/air mixture through instruments A or B, and within 25 seconds of starting to fill the perspex box containing instruments C or D or the probe of instrument E. The relative humidity varied between a minimum of 47 per cent R.H. and a maximum of 66 per cent R.H. at 20°C (1.08 per cent and 1.52 per cent by volume respectively at 760 mm Hg pressure) during the series of experiments.

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None of the detectors showed any visual sign of deterioration as a result of operating at elevated temperatures, and battery performance was normal. With detector D the reading pulsed rhythmically in step with the alarm signal. The alarm was, however, easily muted, and steady readings were then obtained. No evidence of condensation in the sampling line was noticed with these fuels.

4. DISCUSSION

The gas-chromatography results summarised in Table 1 show that above about 50 per cent of the lower explosion limit concentration, the apparatus is capable of giving accurately known concentrations of n-hexane vapour in air. Below about 25 per cent of the lower explosion limit concentration, the method is not so reliable, and this may account for the fluctuating readings obtained with detectors A and B when tested with these mixtures. This variation in vapour concentration is probably due to limitations of the fuel pump when pumping small volumes, and also the design of the nozzle at the end of the fuel delivery tube inside the vaporiser. Experiments are in hand to overcome this problem, and it is hoped to be able to study detector performance in the O-10 per cent L.E.L. range and report this later.

These detectors may be used in two ways. Either they may be used to give an alarm when the concentration of a flammable gas or vapour exceeds a certain value, or they can be used to give quantitative readings of the flammable vapour or gas concentration over the range 0-100 per cent L.E.L. although this latter use may extend beyond the manufacturer's intentions. The seriousness of the deviations from the ideal line of Figs 4 - 8 depend on which of these two criteria is adopted, since obviously, more reliability can be expected when only one reading of per cent lower explosion limit is needed rather than readings throughout the per cent L.E.L. range.

Although these experiments were concerned with the effect of increased ambient temperature on detector performance, other factors which could modify the readings were almost certainly operative due to the nature of the fuels tested. Probably the two most important of these factors are, firstly, that the fuels contain a great number and variety of hydrocarbons and their derivatives, each with a different heat of combustion, thermal conductivity, normal boiling point and vapour phase diffusion coefficient (into air). This latter parameter is important since the different fuel vapour components will be arriving at different rates at the filament surface and the composition of the vapour actually being catalysed (and hence giving rise to the detector reading), would be different from that present in the sampling line. Thus, Le Chatelier's results (see 1 (b)) would not apply here and a depression of the detector reading from

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Besides the fuels mentioned in this report other aviation fuels were tested during the same period. These other fuels, however, gave a condensate in the test apparatus. Thus, although the 100 per cent lower explosion limit concentration could be determined, and the detector checked with this mixture, lower concentrations could not be accurately produced, due to the unknown contribution to the flammable vapour from the condensate. Tests using these latter fuels with a modified procedure are in hand and will be reported later.

- 5. CONCLUSIONS
- (1) The detectors as tested did not give accurate indications of the concentration of 'Avtag' or 'Civgas' vapours in air and care is thus needed in interpreting the readings if the instruments as calibrated are to be used for quantitative measurements.
- (2) A significant change in response with all detectors was observed with increase of temperature from 25°C to 65°C when testing for n-hexane vapour in air.

6. ACKNOWLEDGMENT

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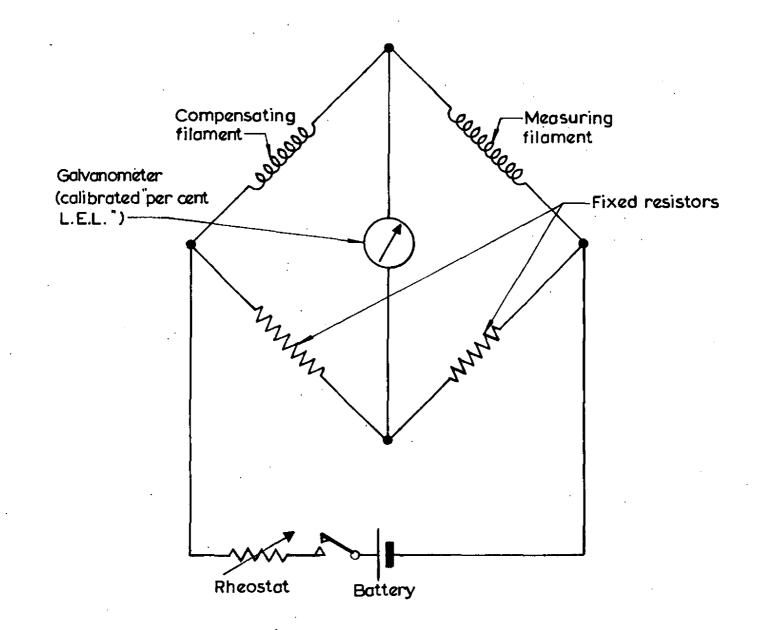
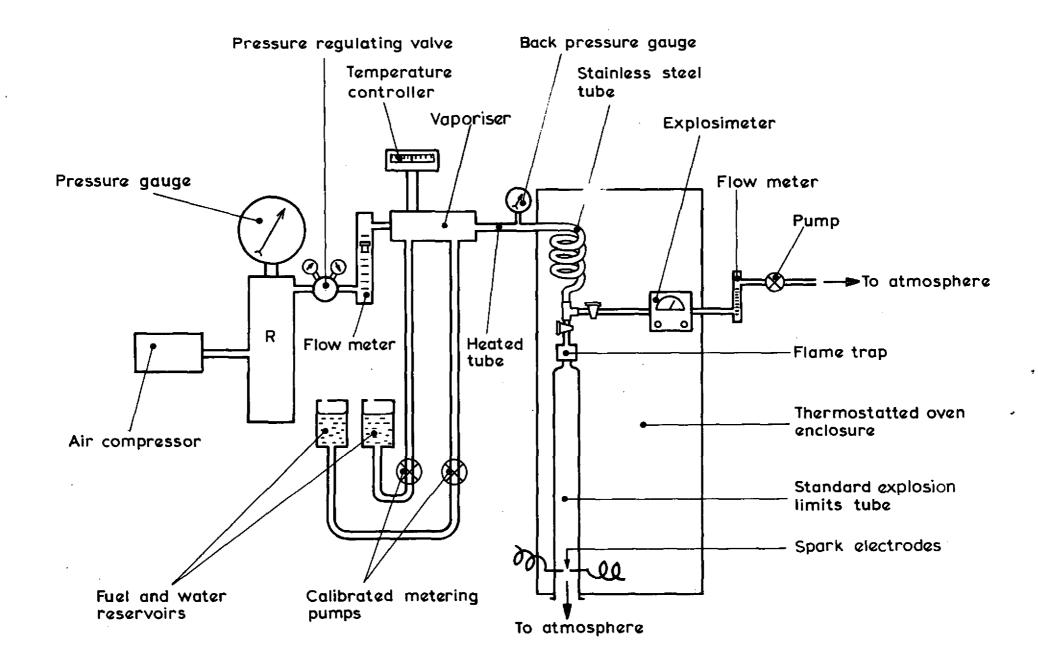


FIG.1 SIMPLIFIED CIRCUIT DIAGRAM OF A TYPICAL PORTABLE FLAMMABLE GAS DETECTOR

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FIG.2 EXPLOSIMETER TEST APPARATUS

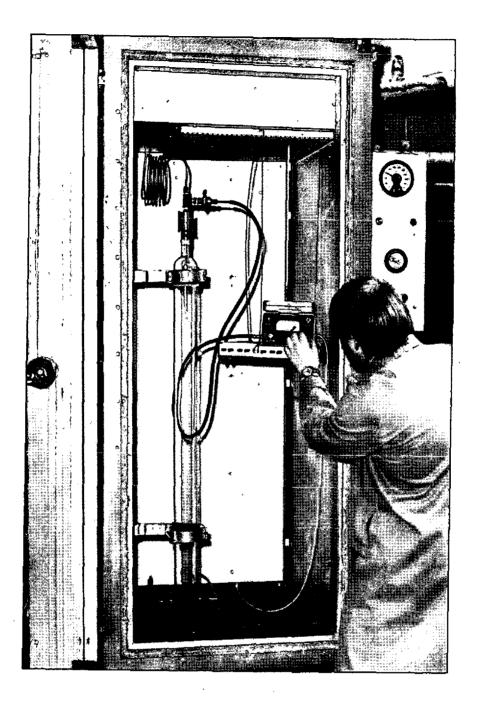


FIG. 3. EXPLOSIMETER TEST APPARATUS IN USE

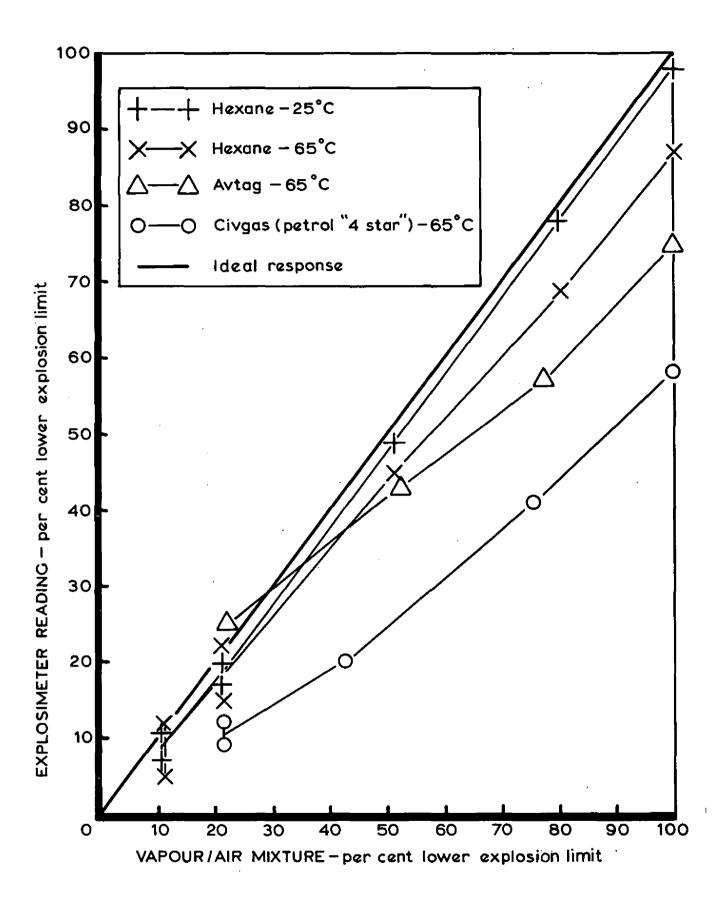


FIG.4 RESPONSE CURVES FOR DETECTOR A"

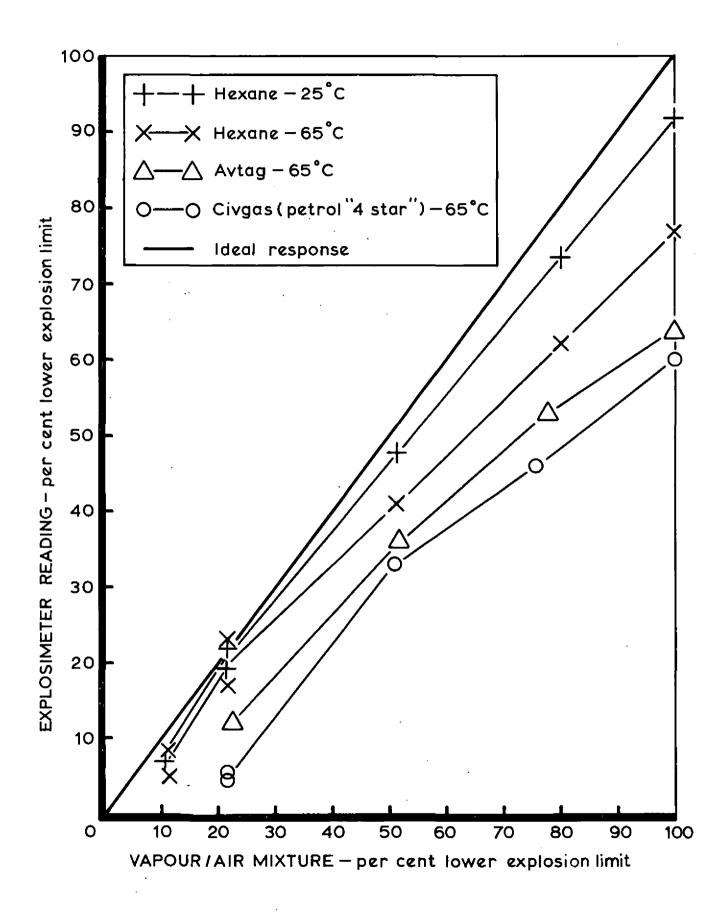


FIG.5 RESPONSE CURVES FOR DETECTOR"B"

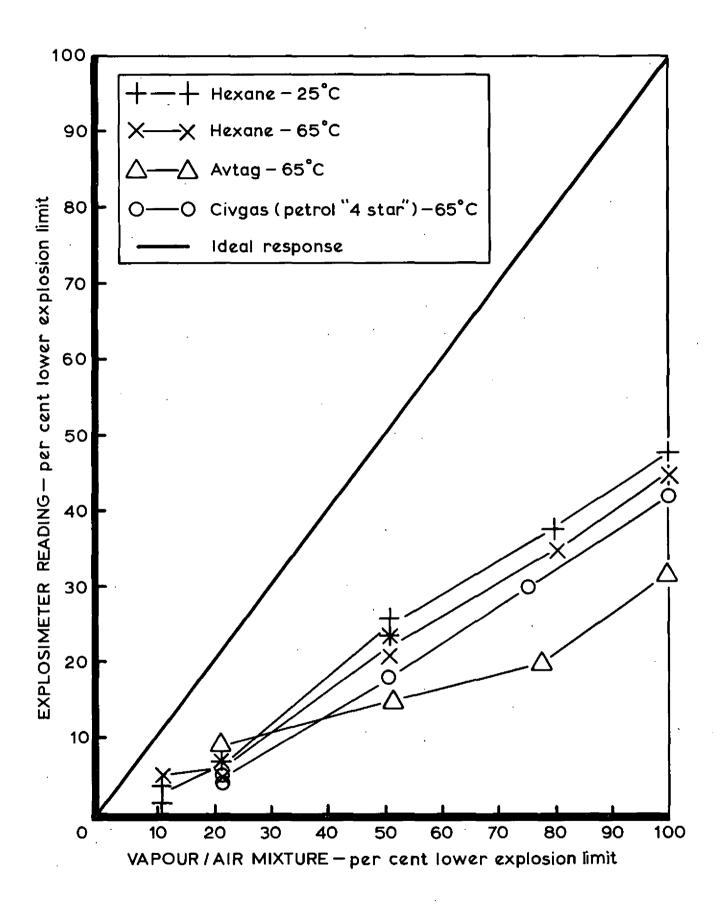


FIG.6 RESPONSE CURVES FOR DETECTOR "C"

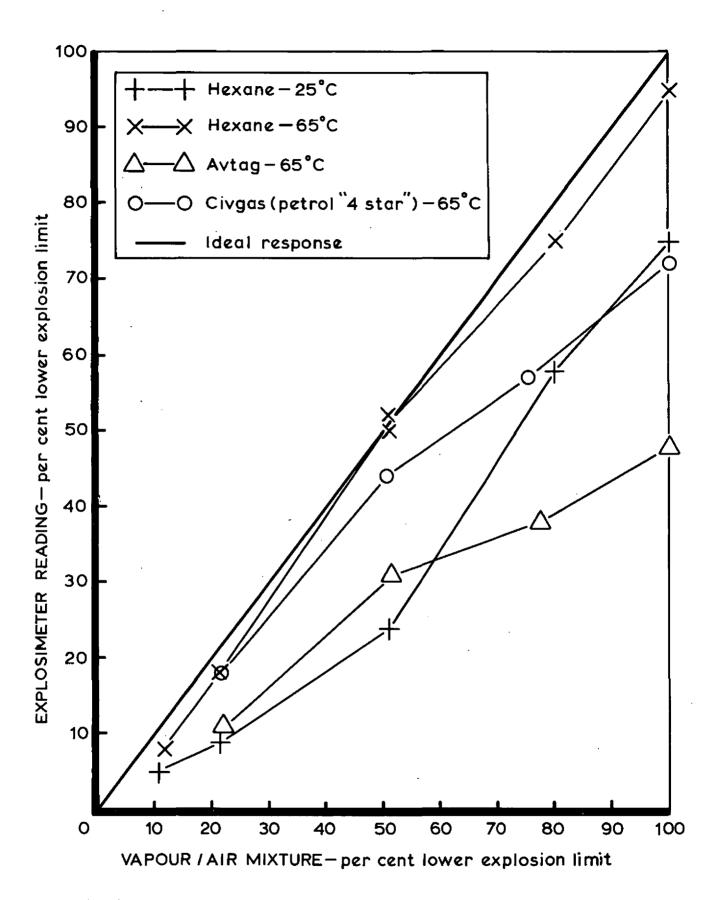


FIG.7 RESPONSE CURVES FOR DETECTOR D

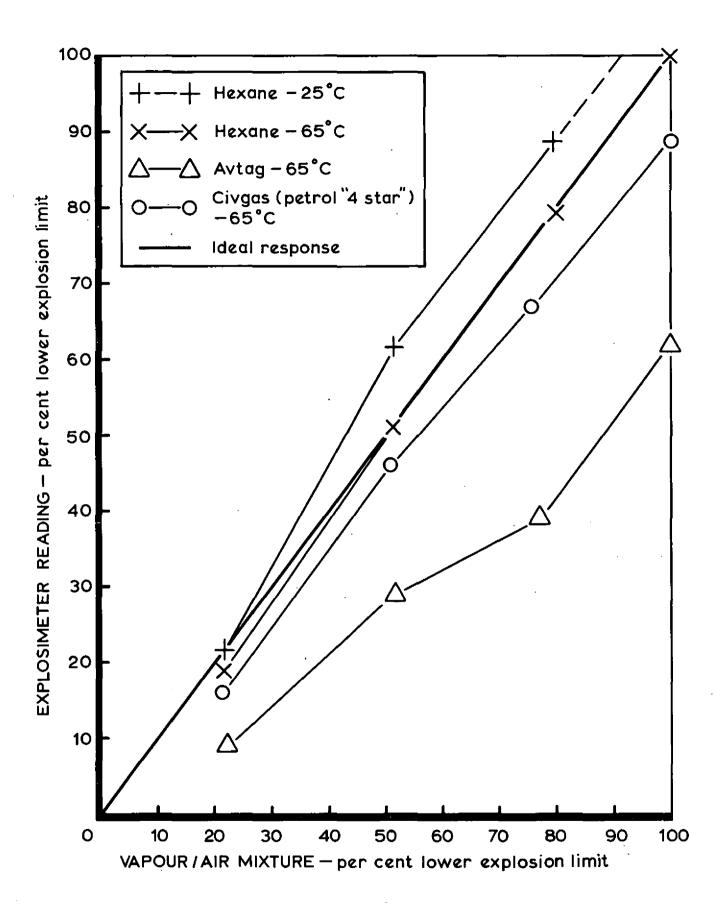


FIG.8 RESPONSE CURVES FOR DETECTOR "E"

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