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THE DETERMINATION OF THE MINIMUM EXPLOSIBLE CONCENTRATION
OF POLYVINYL CHLORIDE POWDER IN THE PRESENCE OF
METHANE AND AIR

by

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SUMMARY

The preparation of unplasticised polyvinyl chloride powder (PVC) by grinding can result in the release of vinyl chloride into the head space of grinders etc. Although PVC powder is non-explosible in the standard tests for the explosibility of dust clouds, the combination of PVC powder and vinyl chloride may be explosible.

Tests were undertaken to study the explosibility of PVC powder suspensions in an atmosphere of air and methane, below the lower explosible limits (LEL) of the methane.

Methane was used in place of vinyl chloride as a toxicologically safe substitute. It is concluded that methane exercises a strong influence on PVC powder suspensions causing the minimum explosible concentration to be reduced.

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1. INTRODUCTION

It is well known that coal dust and methane are able to exert an effect on one another, such that mixtures of gas and dust can jointly give rise to explosible concentration, even though each independent component is below its own explosible limit¹. However, information on such effects for other systems of flammable gas and dusts (hybrid systems) is extremely scarce.

Owing to concern in the PVC manufacturing industries (where in some circumstances, vinyl chloride can collect in concentrations below its LEI while in the presence of PVC powder), information was required on this system. The work described here employed methane in place of vinyl chloride as a toxicologically safe substitute.

The tests described here employed a small scale explosion tube similar in design to those used in dust explosibility work¹. An additional facility for the tests to be carried out at both room and elevated temperature was incorporated.

2. MATERIALS

The PVC powder used in the experiments, had been previously tested and classified as a 'Group (a)' dust. However, since the standard explosibility tests¹ used to determine the minimum explosible concentration of dusts use spark ignition with which PVC is non explosible, no figure for its minimum explosible concentration exists. The PVC powder had a bulk density of 467 kg/m³. The gases used were commercial grade methane and medical air.

3. APPARATUS

Figure 1 shows the apparatus in diagrammatic form and Plate 1 the general experimental arrangement. The apparatus was designed to permit the use of complex mixtures of gases, supplied via 5 gas lines of which only two (for air and methane) were used in the present tests.

The methane and air were supplied to the explosion tube via two flow meters (ranges 0-1.2 l/min and 0-22 l/min respectively). Adequate mixing of these took place in the gas supply line downstream of the flow meters. The gases for the dispersion of the powder of the same composition as the main supply of gas were supplied directly to a small pressure reservoir of capacity $4 \times 10^{-4} \text{ m}^3$, by means of taps connected to the methane and air lines. A bypass line to the metered flow-line, equipped with a solenoid valve, ensured that gas could be supplied to the explosion tube (of $2.085 \times 10^{-3} \text{ m}^3$ volume), from the pressure reservoir, without passing through the flow meters.

The gases were passed through an electrically operated pre-heating unit set at the appropriate temperature, and controlled by a solid-state temperature control device employing a chromel/alumel thermocouple as sensor. For all work carried out at temperatures above ambient, the explosion tube was replaced by a tube wound with a resistive heating wire coated with alumina cement.

The temperature inside the tube was controlled by a 36 SWG chromel-alumel thermocouple (suspended in the tube and away from its sides) operating a solid state temperature controller. The heated explosion tube is shown in Plate 2. The actual ignition was viewed by means of a mirror placed above the tube; this gave a clear view of the tube through a transparent plastic membrane covering the top of the tube.

The powder was ignited using an electrically heated coil, because PVC powder cannot be ignited by means of spark ignition¹ at the voltages which are normally employed. The coil was first allowed to reach approximately 1200°C before the powder was dispersed.

4. PROCEDURE

The required amount of PVC powder was placed in the 'dispersion cup' and the explosion tube was bolted into place. Gas of the required composition was then metered into the tube at a low flow rate ($10^{-2} \text{ m}^3/\text{min}$), in order to avoid disturbing the powder in the 'cup'. After 10 changes of atmosphere it was assumed that the correct gas composition had been achieved³. The gas supply was then stopped and

the pressure reservoir filled to a pressure of 420 kN/m^2 with gas of the same composition as measured by the method of partial pressures. This dispersion pressure was employed throughout.

The ignition coil was then brought to the desired temperature and the dispersion gases were released from the reservoir by operating a quick-acting solenoid valve. Ignition was deemed to have occurred when a flame was observed to propagate away from the ignition source within a few seconds of exposure. This is the criterion adopted in the UK, but other countries often have different criteria⁴.

Two ignitions are shown in Plates 3 and 4. Plate 3 shows a 'near-limit' explosion and Plate 4 a vigorous one. When the heated explosion tube was used, the explosion was observed through a mirror mounted above the tube as described above.

5. RESULTS

Results are summarised in Table 1.

These results indicate that PVC powder in the presence of methane enables combustion to occur below the lower limit concentration of either combustible. The table also shows that there is a marked change in behaviour within the concentration range of 0.5 per cent to 1.5 per cent, by volume, of methane in air. As might be expected from thermodynamic considerations, the results indicate that less PVC and methane is required to support combustion as the temperature rises, and that as the methane concentration is reduced, so more PVC is required to produce an explosible concentration.

The figures for the minimum explosible concentration of PVC powder alone, cannot be compared directly with literature values for other materials, because a heated coil was employed. In addition, the explosions produced may be regarded as fundamentally different from those observed with methane in air and PVC powder. The reason for this is that the former explosions were delayed by 40 seconds or more (and appear to be associated with the volatilised and pyrolysed products of the powder decomposed on the coil), while the latter occurred in under 1 second.

In the case of the determination of the explosibility of PVC suspensions in the presence of air and methane mixtures below the LEL, the maximum concentration of PVC powder employed in all but one test was 2.5 kg/m^3 .

TABLE 1

Minimum explosible concentration of PVC Powder in the presence of methane and air

Methane Concentration in per cent	5	4	3	1.5	0.5	0	Temperature
PVC Concentration in kg/m ³	$8 \pm 0.5 \times 10^{-3}$	$2.4 \pm 0.2 \times 10^{-2}$	$9.4 \pm 0.3 \times 10^{-2}$	$9.4 \pm 0.3 \times 10^{-2}$	'No go' (below 5 kg/m ³)	(8.7 ± 0.3) Non-explosible - see text	25°C
	$1 \pm 0.5 \times 10^{-3}$	$2 \pm 0.2 \times 10^{-2}$	$2 \pm 0.2 \times 10^{-2}$	$3.7 \pm 0.1 \times 10^{-2}$	'No go' (below 2.5 kg/m ³)	Not determined	55°C
	Not determined	$6 \pm 0.6 \times 10^{-3}$	$1 \pm 0.2 \times 10^{-2}$	$2.3 \pm 0.1 \times 10^{-2}$	'No go' (below 2.5 kg/m ³)	Not determined	85°C
	Not determined	$2.4 \pm 0.5 \times 10^{-3}$	$6.7 \pm 0.5 \times 10^{-3}$	$1.5 \pm 0.1 \times 10^{-2}$	$4.5 \pm 0.1 \times 10^{-1}$	(4.6 ± 0.3) see text	120°C

because the coil became heavily coated with PVC powder at concentrations of this magnitude, and dimmed noticeably until the bulk of the coating material had volatilised. Thus, explosions that did occur were delayed for about 30 seconds or more, and involved the volatilised products of PVC (rather than the powder) and methane in air.

6. DISCUSSION OF RESULTS

On examining the flammability of mixtures of organic gases and vapours in air there are found, often, certain common features. Thus such mixtures frequently obey Le Chatelier's Law and the calorific value times the lower limit (in per cent) is constant, and has a value of about 4600 kJ/mol which implies that most lower-limit mixtures provide approximately the same final flame temperature. There is, in comparison, a dearth of information on dust and flammable gas systems.

One of the few studies of significance is due to Singer et al⁶ who reported relationships

$$M = 351 - 0.24C - 0.0056C^2 \quad (1)$$

$$M = 37.0 - 0.49C \quad (2)$$

for downward and horizontal propagation respectively over a limited concentration range of coal-dust;

where M = concentration of methane (kg/m^3)

C = concentration of coal-dust (kg/m^3)

The latter relationship can be shown to be a form of Le Chatelier's Law; the intercept is the LEL of methane, and the slope has the absolute value of LEL of methane divided by the minimum explosible concentration of the coal-dust, under the conditions used in their tests.

Because the calorific value of PVC is small⁵ compared with methane⁶ (18,120 kJ/kg as compared with 52,500 kJ/kg) relatively large quantities of PVC are present.

The specific heat releases for the limiting mixtures in Table 1 have been calculated and are given in Table 2.

TABLE 2

Heat generated on thermodynamic consideration
for the PVC/methane/air system (kJ/m^3)

Methane concentration in per cent \ Temperature	5	4	3	1.5	0.5
25°C	1860	1810	2730	2220	170
55°C	1580	1610	1230	1140	160
85°C	Not determined	1250	1040	850	140
120°C	Not determined	1090	900	660	3040*

* This value has been adjusted to allow for the fact that the concentration of PVC, exceeded considerably the stoichiometric value for this experiment, and the calculation has been carried out as if 0.16 kg/m^3 of PVC (ie the stoichiometric value) had been consumed. This value given represents an upper limit for the heat generated per unit volume. The remaining values at 0.5 per cent methane represent the contribution from methane only.

Thus the three results for 0.5 per cent methane at 25°C, 55°C, and 85°C, for which no ignition occurs, represent the theoretical output of heat energy if there had been an explosion. The most important feature about them is that they are, in order of magnitude, less than the values for the minimum explosible concentration of PVC/methane and air. This suggests that there is some final flame-temperature for PVC powder/methane-air explosions such as is the case with many gas or vapour systems at these lower limits.

Le-Chatelier's law indicates that

$$\sum_{i=1} n_i / N_i = 1 \quad (3)$$

where N_i = lower limit for the i th combustible

n_i = percentage by volume of each combustible in any lower limit mixture

Table 3 gives the results for experiments at 25°C and 120°C, these being the only temperatures at which the lower-limit of PVC powder in air have been determined.

TABLE 3

	5%	4%	3%	1.5	0.5%
25°C $\sum n_i/N_i$	0.94	0.76	0.58	0.28	Not determined
120°C $\sum n_i/N_i$	Not determined	0.82	0.61	0.31	0.2

For these results the value of the lower-limit for PVC and methane have been expressed in kg/m^3 , and the value of the lower-limit for methane at 120°C has been calculated from an equation given by Coward and Jones⁷.

These results indicate that, at methane concentrations of less than 3 per cent, the PVC/methane/air system does not obey Le Chatelier's Law very well, and the disagreement increases as the concentration of PVC increases. It is important to note that 5 per cent methane/PVC mixture is in effect almost a one-component system in air and that by equation (3) it, and the results for no methane will automatically take a value of unity. It is in fact not surprising that the disagreement with Le Chatelier's Law increases with increasing PVC for it has been shown for gaseous systems that halo-carbons are able to cause significant deviation⁸, presumably, because the hydrogen halide affects the flame chemistry.

Finally, plots of the type proposed by Singer et al indeed produce a straight line curve as indicated by a plot of the methane concentration versus PVC concentration for ignition, Figure 2. The agreement to a curve of the type

$$M = a - bc \quad (4)$$

where M = Methane concentration (kg/m^3)
 C = PVC powder concentration (kg/m^3)
 a, b = constants

became much better above the concentration range of 1.5 per cent of methane as the temperature increased.

7. CONCLUSIONS

Although PVC is a relatively incombustible dust and is well known to produce HCl (a combustion inhibitor) both in combustion and pyrolysis⁹, the PVC/Methane/Air system has many features which can be explained on the basis of theory developed for gaseous systems.

However, the presence of the halogen makes PVC a very difficult material to examine in such studies, and would appear to lead to anomalous behaviour. There is therefore a need to work on simpler systems in which the interplay of physical and kinetic factors is not further complicated by the presence of halogenated material. Only then is sufficient information on hybrid systems likely to be gained in order to permit the elucidation of their behaviour.

This study has nevertheless clearly demonstrated a combined effect between PVC powder and methane in air. Also, the work indicates that we may expect such effects for any flammable gas and dust systems in which combustion is substantially homogeneous.

8. REFERENCES

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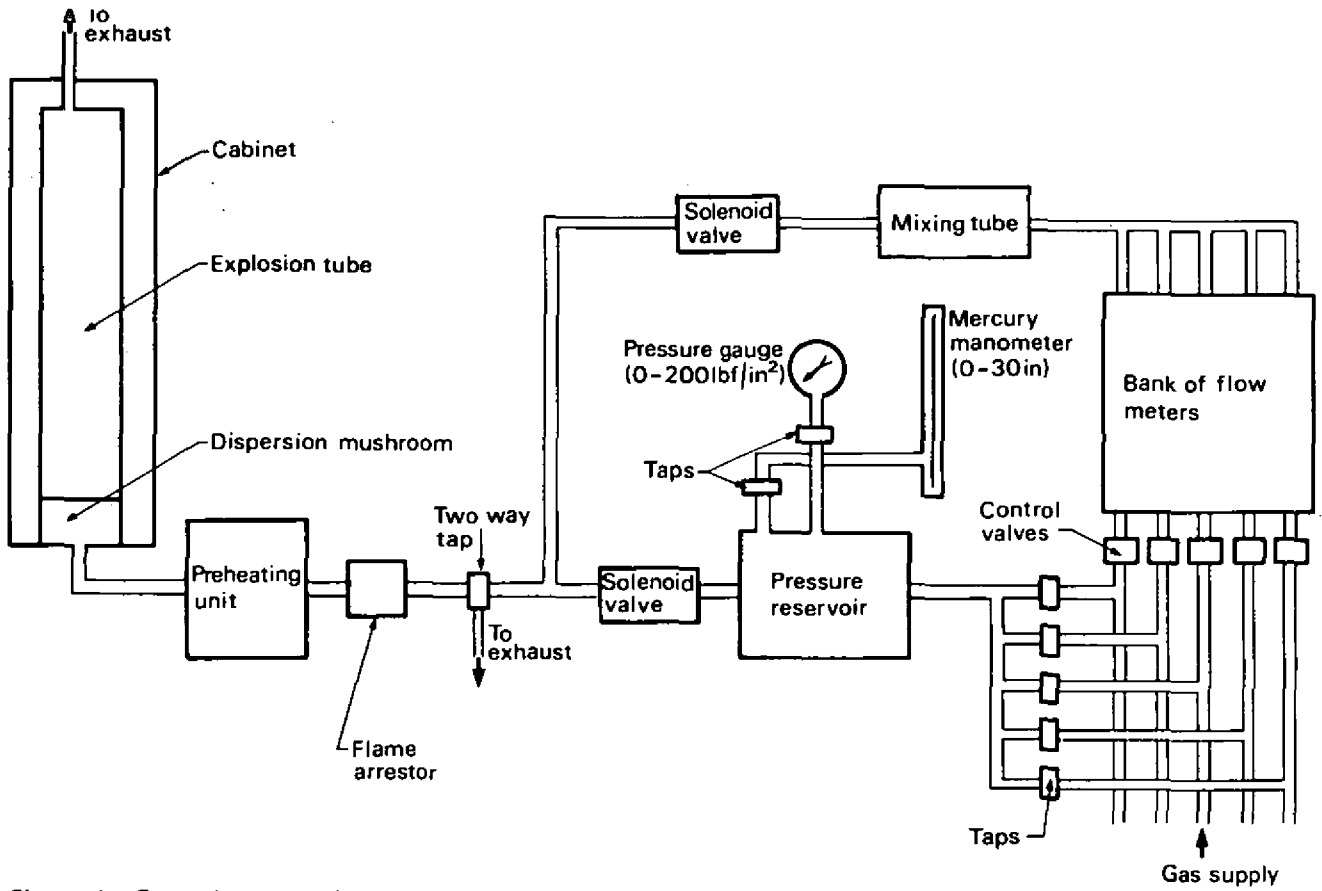


Figure 1 General layout of the modified explosion apparatus

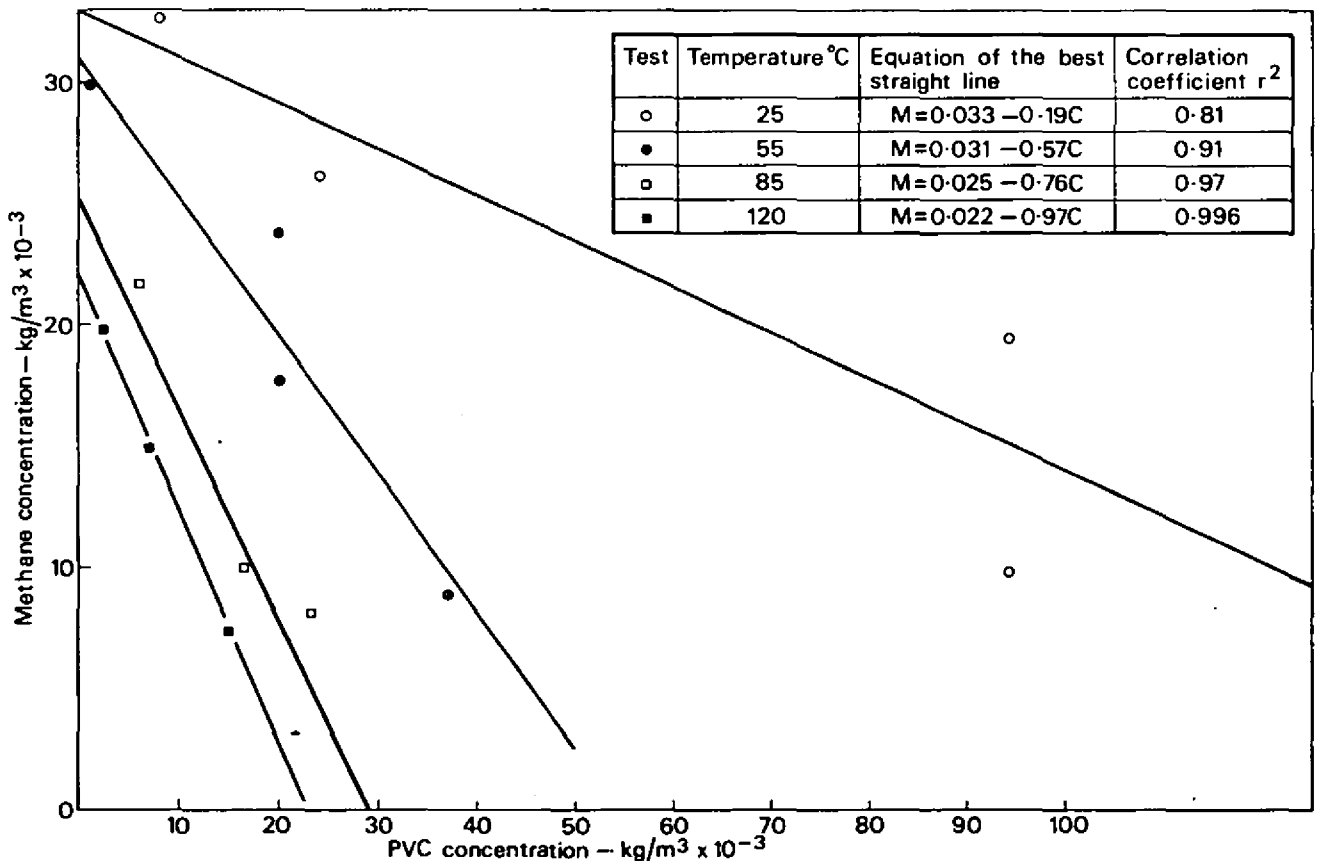


Figure 2 Methane concentration versus PVC powder concentration in kg/m^3 for ignition in a vertical tube

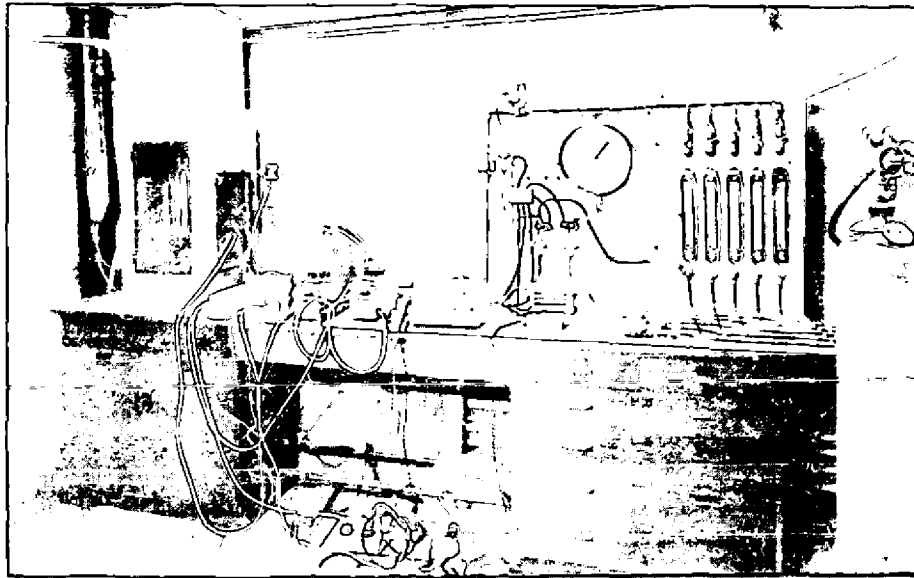


PLATE 1 THE LAYOUT OF THE APPARATUS

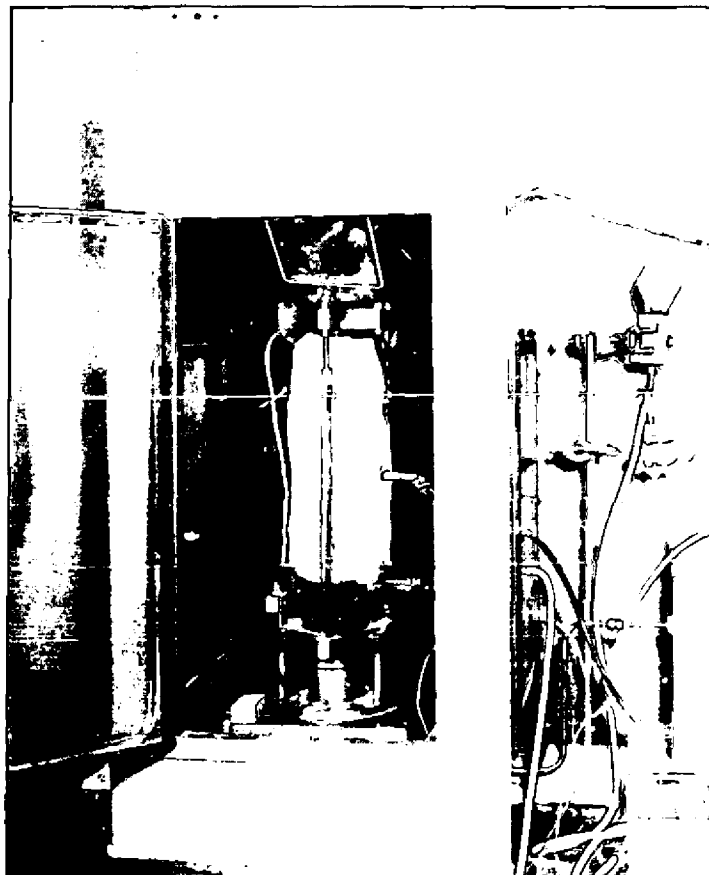


PLATE 2 THE HEATED EXPLOSION TUBE

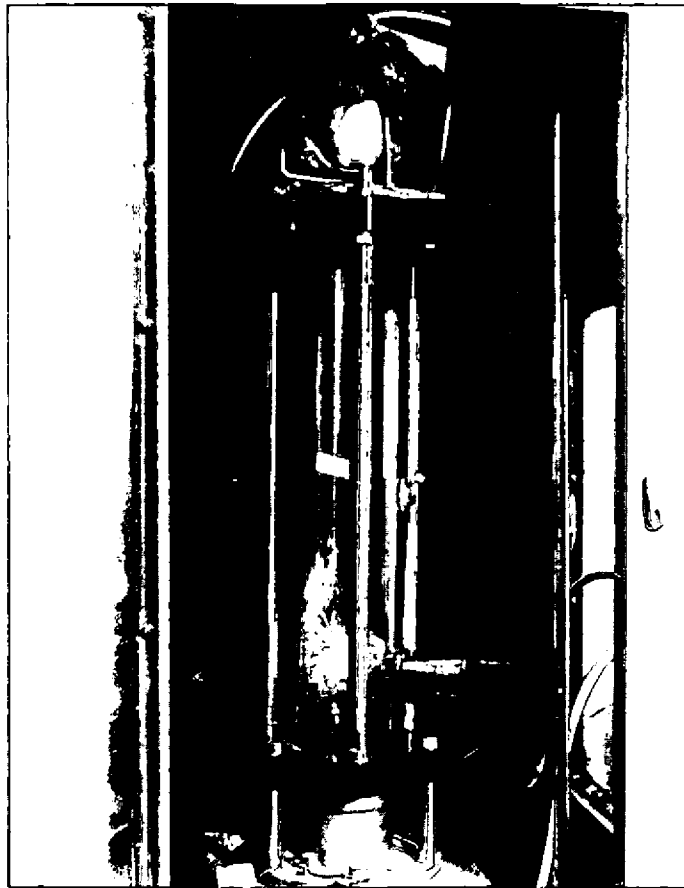


PLATE 3 'NEAR-LIMIT' EXPLOSION



PLATE 4 'VIGOROUS' EXPLOSION