THE DEVELOPMENT OF DETONATION OVER-PRESSURES IN PIPELINES

By A. D. CRAVEN* and T. R. GREIG*

SYNOPSIS

Experiments into the characteristics of gaseous explosions in pipes involving mixtures of ammonia and nitrous fumes have shown that the flame front may travel up to 30 feet or more before reaching a stable velocity consistent with classical detonation theory. During this period of development into a stable detonation the propagation of the unstable detonation is accompanied by the generation of pressures which are much greater than those associated with the stable detonation. It has been shown that this effect is increased with an increase in the diameter of pipe containing the explosive gas mixture.

The velocity of detonation of various mixtures of ammonia–nitrous oxide and ammonia–nitrous oxide–nitrogen are in good agreement with the values calculated according to classical detonation theory but the relationship between velocity and pressure observed during the unstable period of propagation cannot be accounted for in terms of a simple extension of classical detonation theory. By using a more complex model of the unstable detonation involving two discontinuities (one representing a weak shock wave and the other a classical detonation) one can account for the high increases in pressure which are generated by flame speeds that are only slightly higher than those associated with stable detonations.

Introduction

A few years ago we were called upon to investigate an explosion which had occurred in a pipeline on one of our chemical plants. The explosion had all the essential features of a gaseous detonation, damage being confined to blank ends and sudden changes in direction, particularly at T-junctions. Estimates, based upon an examination of the damage, indicated that local pressures of several thousand pounds per square inch had been involved although it was known that the normal working pressure in the pipeline was only about atmospheric. No one was injured in the explosion and the plant was soon brought on line again after certain modifications had been made to avoid the formation of potentially explosive mixtures in this system.

Although it was known that mixtures of ammonia and nitrous fumes could have been present in the pipe just prior to the explosion, the damage could not be accounted for in terms of a simple gaseous explosion. The maximum pressure which could be expected from, for example, the reflection of a detonation wave in a stoichiometric mixture of ammonia and pure nitrous oxide, initially at atmospheric pressure, would be only 1050 lbf/in^2 gauge whereas the estimates based on the damage to the pipe indicated pressures over five times as high as this.

There are some references in the literature[1–4] to the development of abnormally high pressures in gaseous explosions but the possibility of pressure piling cannot be ruled out in these references in which complex plant systems were involved. Under these circumstances the pressure in any particular vessel or line could be raised by a slow explosion in an adjacent vessel with the result that subsequent detonations could occur at an initial pressure higher than normal. Even in simple pipe systems which are closed at both ends a form of pressure piling can account for the high pressures which have been recorded experimentally.[5–7] In a closed pipe system, a slow deflagration can cause an increase in pressure throughout the pipe which may result in abnormally high local pressures being developed in the event of a local detonation.

Simple pressure piling of this sort could be ruled out in the case of the incident on our plant because the pipe system was essentially open-ended at one point. Henderson[8] has shown that abnormally high pressures can be produced in long pipeline systems as a transient feature of the establishment of normal detonation in turbulent gas streams. Turin and Huebler[9] made a more detailed study of this phenomenon in an open ended pipe with Toledo town gas–air mixtures in which the position of the flame front and the pressure front were recorded separately but simultaneously. It was shown by Turin and Huebler that a substantial shock wave precedes the flame front during the early stages of the development of a detonation wave and that abnormally high pressures are generated as the flame accelerates and eventually overtakes this primary shock wave. Various authors[10, 11] have stressed the importance of this primary shock wave in the development of detonation and Chu[12] has shown that it is a natural consequence of the accelerating combustion processes which take place before the onset of detonation.

From the work which has been done in recent years on the development of gaseous detonation it is evident that as the flame travels initially at subsonic velocities a shock wave is always formed ahead of the flame. As the flame accelerates and eventually overtakes the primary shock wave abnormally high pressures are produced.

As a result of the explosion a programme of experimental work was undertaken to investigate the detonation behaviour of mixtures of ammonia and nitrous gases in pipes. Although it is well known that pipe diameter has virtually no effect on the characteristics of a stable detonation wave, the processes of flame acceleration and hence the formation of the primary shock waves are affected by the type of confinement. We therefore confined our experiments to pipework similar to that which had been involved in the incident on the plant.

Experimental

Detonation pipe

The apparatus is shown diagrammatically in Fig. 1. The pipe which consisted of a number of flanged sections of 3 in. nominal bore ($3\frac{1}{4}$–$3\frac{1}{2}$ in. internal diam) could be arranged to

* I.C.I. Fibres Ltd., Harrogate, Yorkshire.

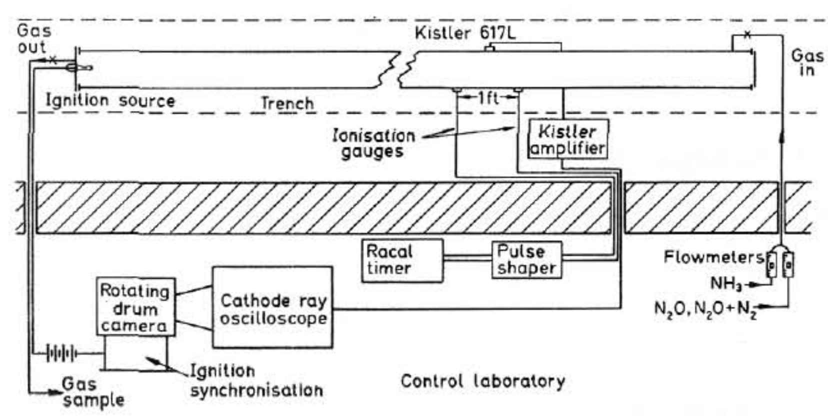

Fig. 1.—*Layout of the detonation tube*

provide a variety of lengths up to 120 ft. Similar pipe runs of 4 in. nominal bore ($4\frac{1}{4}$–$4\frac{1}{2}$ in. internal diam) were also available in lengths up to 60 ft. The pipe was seamless stainless steel with a wall thickness of 0·10 in. to 0·15 in. and was fitted with Table E flanges.

When the end remote from the ignition source was to be regarded as essentially open, a loosely fitting polythene bag was placed over the end to ensure the containment of the gas during charging. When this end was closed either a thick blank flange or a thin test-plate (shown in Fig. 2 and described below) could be fitted.

The pipe was situated in a trench and facilities for the preparation and analysis of gas mixtures and the measurement of velocity of propagation and pressure were situated in an adjacent laboratory.

The gas mixtures were prepared by calibrated flow and the pipe was filled with mixture by simple displacement. The efficiency of purging was checked by analysis before the inlet and outlet valves were closed prior to ignition.

Sparks or electrically operated match-head type igniters (non-percussive) were used to ignite the gas and the instant of ignition could be synchronized with the high speed camera attached to the oscilloscope. (See below). The ignition source was always situated one inch from a closed end.

Measurement of velocity

The velocity of flame propagation was determined by measuring the interval between the times of arrival of the flame front at two ionization gauges set one foot apart in the pipe wall. The interval, about 130 μs, for a stable detonation, was measured on a microsecond timer (Racal type S.A.535). It was necessary to introduce pulse-shaping circuits between the ionization gauges and the microsecond timers to compensate for the distortion of the signals between the ionization gauges in the trench and the timers which were located in the laboratory.

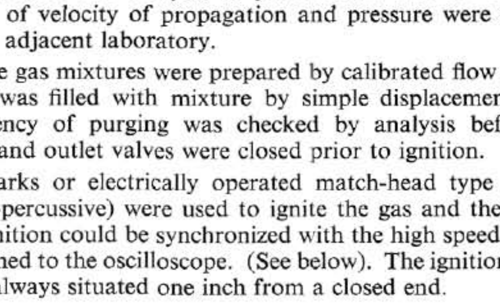

Fig. 2.—*Arrangement for holding test plates*

Measurement of pressure

INCIDENT PRESSURE

The incident pressures developed in the explosions were measured using a Kistler 617L piezo-electric type gauge screwed into the pipe wall with the sensing diaphragm parallel to the direction of propagation of the flame front. In this way the pressure was measured in the absence of any hydrodynamic effects due to reflection. The end of the pipe remote from the ignition source was either open (loose fitting polythene bag) or closed with a sufficient length of pipe, at least ten feet beyond the gauge, to prevent confusion between the initial detonation wave and the reflected wave.

The signals from the piezo-electric gauge were amplified (Kistler type Model 568) and displayed on the Minirack cathode ray oscilloscope and photographed with the rotating drum camera (Southern Instrument Co. Ltd.). The facilities for synchronizing the position of the drum with the instant of ignition and simultaneous " bright-up " of the C.R.O. beams were provided by the cam system which is a standard fitting on the Southern Instruments rotating drum camera. The natural frequency of Kistler 617C gauge is 150 kc/s giving a signal rise time of less than 10 μs. The camera paper speed was about 100 ft/s which made it difficult to resolve any event shorter than 50 μs.

REFLECTED PRESSURE

An alternative method was adopted for the measurement of reflected pressure for two reasons. In the first place signals from transducer gauges (Kistler 617L and Southern Instrument Co. Ltd. G319) were difficult to interpret because of excessive vibration and some permanent damage had been sustained on certain occasions by both types of gauges. Secondly, the purpose of the experiments was to demonstrate the ability of the explosions to inflict damage and not their ability to generate transient high pressures which may have had only a limited effect on plant pipe-work.

A method was adopted, therefore, which involved the permanent distortion of a realistic thickness of steel plate using the adaptor shown in Fig. 2. The test plate was fitted to the end section of the pipe and secured by eight bolts and a backing flange. (The provision of eight holes as opposed to the conventional four holes normally provided in a Table E flange was necessary to prevent the plate slipping during the sudden application of pressure). When tests were carried out in 4 in. nominal bore tube a special adaptor was fitted which reduced the area of application of pressure to that which occurred in the experiments in 3 in. nominal bore tube.

The results of a series of hydrostatic calibrations of this technique, using water from a hydraulic pump, are shown in Fig. 3 in which the permanent deflection of the centre of the plate is plotted against the applied pressure. It can be seen

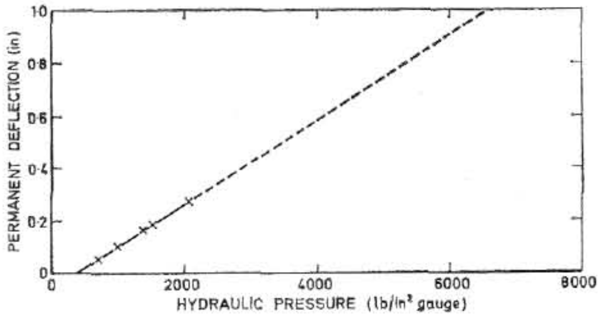

Fig. 3.—Hydraulic pressure calibration of test plates used for measurement of damaging power

that no permanent distortion of the plate takes place with pressures of less than 400 lbf/in^2 gauge the elastic limit, and that the calibration is then linear up to about 2500 lbf/in^2 gauge. Above 3000 lbf/in^2 gauge the calibration became difficult due to the development of slow leaks in the test rig and it was assumed for the sake of convenience that the linear relationship could be extended to 6000 lbf/in^2 gauge and beyond. There is some evidence (obtained from calibration by shock waves in water) to suggest that the slope of the calibration curve is less at higher pressures and the estimates of pressure based on a linear relationship will, therefore, tend to be low at high plate distortion. With this qualification the measurement of reflected pressure is quoted in terms of pressure (lbf/in^2) (damaging power) throughout this report in order to differentiate between absolute pressure measurements made with transducer gauges. It was subsequently shown that the reflected pressure expressed in these units was very close to the calculated value of the reflected pressure in the case of the stable detonation in ammoni and nitrous oxide.

Discussion of Results

Stable detonation in 120 ft of 3 in. nominal bore pipe

Early scouting experiments were conducted in the longest pipe available to us to establish the feasibility of gaseous detonation in mixtures of ammonia and nitrous fumes. Flame velocity measurements, made in those sections of the pipe farthest from the ignition source, confirmed that a wide range of mixtures of ammonia in nitrous oxide were capable of detonation. The observed velocities were close to those calculated by classical detonation theory (see below) and are given in Table I.

It was also shown that the reflected pressure of the stable detonation in a 50/50 ammonia/nitrous oxide mixture as measured by the damaging power technique, was 1100 lbf/in^2 (damaging power) compared with the calculated value of 1060 lbf/in^2 gauge. This is very much less than the estimates of pressure made after the examination of the damage to the pipe sections in the plant explosion.

TABLE I.—*Observed and Calculated Values of Detonation Velocities in Mixtures of Ammonia, Nitrous Oxide and Nitrogen.* (100 ft from ignition sources)

Mixture Composition	Detonation Velocity Observed (ft/s)	Detonation Velocity Calculated (ft/s)
50% NH_3/50% N_2O	7600 ± 60	7620 ± 10
40% NH_3/60% N_2O	7400 ± 60	7380 ± 10
30% NH_3/70% N_2O	6900 ± 50	6980 ± 10
30% NH_3/45% N_2O/25% N_2	6800 ± 50	6920 ± 10
20% NH_3/80% N_2O	6500 ± 40	6510 ± 10
12% NH_3/88% N_2O	6250 ± 40	6130 ± 10

Unstable detonation velocities in various lengths of 3 in. nominal bore pipe

When velocity measurements were made at various positions closer to the ignition source it was found that the flame accelerated to a maximum velocity and then decelerated to a stable velocity which then remained constant. It was also shown that although the velocity profile was complicated it was very reproducible. (Three velocity determinations were made over a period of two years, in the unstable region of a 50/50 ammonia/nitrous oxide explosion 18 ft from the ignition source. The time intervals for the passage of the wave on the three occasions were 118, 117, and 118 μs.) The results of four series of such experiments are shown in Fig. 4.

It can be seen from Fig. 4 that either a departure from stoichiometry or the introduction of inert gas results in the position of maximum velocity and the position where the velocity falls to the stable value being displaced farther down the pipe from the ignition source.

Unstable detonation pressures in various lengths of 3 in. nominal bore pipe

A full investigation into the pressures developed during the establishment of a stable detonation wave was made using 50/50 ammonia/nitrous oxide mixtures. The 50/50 mixture was selected for the purposes of the investigation because it took longer to reach the stable state than the stoichiometric mixture and it was much simpler to prepare and analyse than the ternary mixture containing nitrogen.

Pressure measurements made with the piezo-electric gauge at various points in an open-ended pipe are shown in Fig. 5, together with the corresponding velocity profile. It can be seen that the change in pressure in the pipe is similar to the change in velocity with the position of maximum velocity close to the position of maximum pressure. The point at which the pressure reaches the stable value is, however, farther down the pipe from the ignition source than the corresponding point of stable velocity.

The reflected pressure was determined by the test plate technique (damaging power) using various lengths of pipe and the results are shown in Fig. 6. The series of test plates obtained from these experiments is shown in Fig. 7.

It can be seen that the position of maximum damage is also at the same point as the position of maximum velocity in an open-ended pipe. The velocity profile shown in Fig. 6 is that obtained in open-ended pipe experiments also given in Fig. 5. Attempts were made to measure the ultimate velocity of a reflected detonation but this was not possible. Wherever the reflected pressure (damaging power) is compared with the velocity of propagation in this paper, it is the velocity associated with the explosion in an open ended pipe which is considered.

Velocity and pressure of unstable detonations in a 4 in. nominal bore pipe

It is known[13] that the distance which a flame must travel before the onset of detonation is greater in pipes of larger diameter. Experiments were therefore carried out in 4 in. pipe in which the damaging power was compared with the velocity of propagation in an open-ended pipe. The results of the damaging power experiments are shown in Fig. 7 together with those from the experiments on the 3 in. pipe and the profiles of damaging power and "open-ended-pipe" velocity measurements are shown in Fig. 8. It can be seen that the velocity and pressure maxima have both been dis-

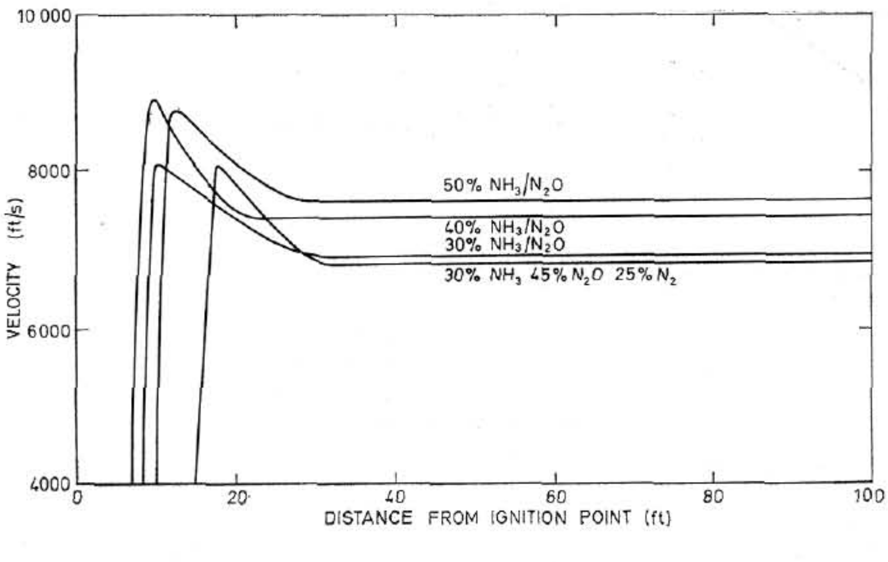

Fig. 4.—*Change of velocity with distance travelled by explosions in various mixtures of ammonia–nitrous oxide and nitrogen in 3 in, nominal bore pipe*

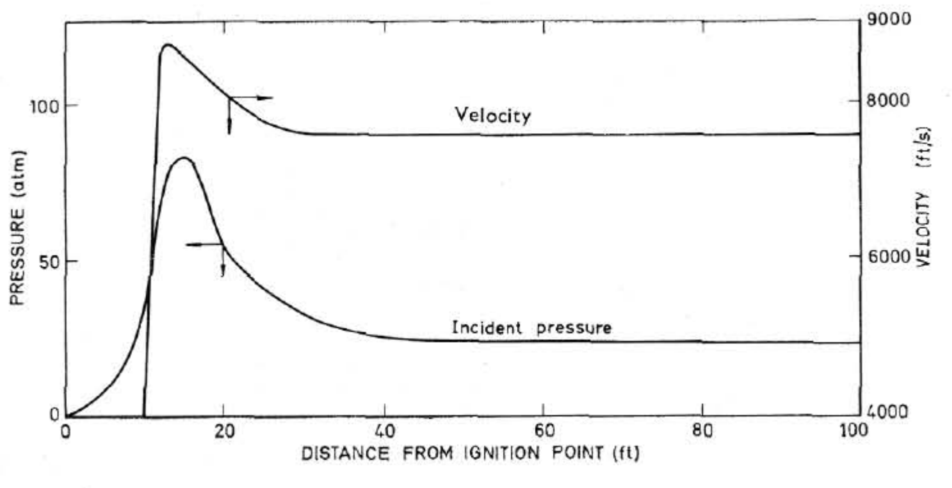

Fig. 5.—*Comparison of hydrostatic pressure (pressure gauge at right angles to direction of propagation) measured with pitzo-electro gauge at various distances in 50:50 ammonia–nitrous oxide mixtures*

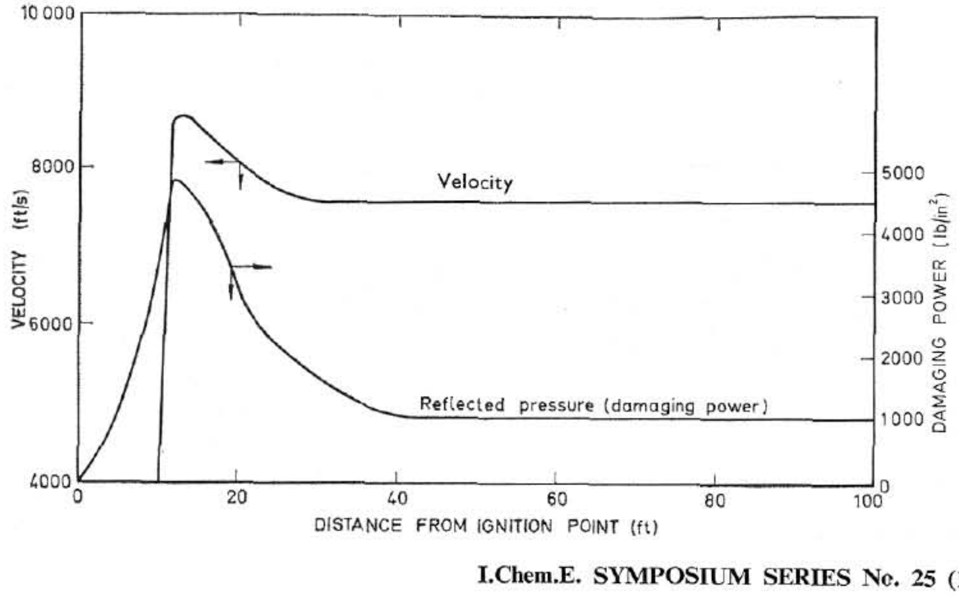

Fig. 6.—*Comparison of velocity and damaging power of explosions in 50:50 ammonia/nitrous oxide power mixtures in a 3 in. nominal bore pipe*

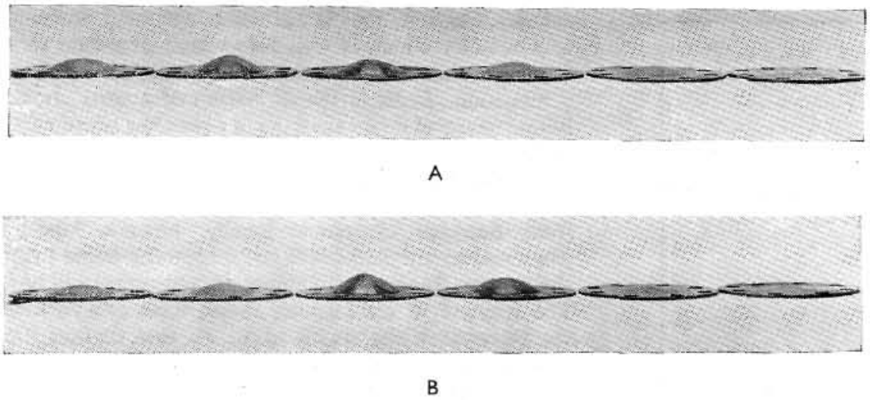

Fig. 7.—Permanent distortion of $\frac{1}{8}$ in thick test plates resulting from detonations of 50:50 ammonia–nitrous oxide mixtures in various lengths of 3 in. and 4 in. nominal bore pipe

placed farther along the pipe and both have slightly higher values. The pressure and velocity maxima for the experiments in the 3 in. and 4 in. pipe systems are given in Table II below together with the positions of these maxima relative to the ignition source.

TABLE II.—*Maximum Pressure and Velocity Values for* 50/50 *Ammonia–Nitrous Oxide Explosions in* 3 in *and* 4 in *Nominal Bore Pipes*

Pipe	Maximum Pressure (damaging power) (lbf/in^2)	Maximum Velocity (ft/s)	Position of maxima (ft from ignition)
3 in. N.B.	4770 ± 60	8770 ± 80	12
4 in. N.B.	5750 ± 60	9200 ± 90	15

Theory

Single discontinuity

The relationship between pressure, specific volume, and hence speed of propagation, for a single shock-type discontinuity can be derived from the Rankine-Hugoniot relationship:

$$\Delta E = \tfrac{1}{2}(P_1 + P_2)(V_1 - V_2) \quad . \quad . \quad (1)$$

where ΔE is the internal and chemical energy change across the discontinuity.[14] Calculated values of V_2, the specific volume of the gas in the wave front, are plotted against various values of P_2, the pressure in the wave front, in Fig. 9 as the curve BG. Point A corresponds to the initial state P_1, V_1 of a 50/50 ammonia–nitrous oxide mixture whereas points along BG are associated with the products of combustion. The final composition of the products and the associated change in the number of molecules occurring during the combustion process represented by equation (2):

$$NH_3 + N_2O \rightarrow aN_2 + bH_2O + cO_2 + dH_2 + eNO + fO + gOH + lH \quad (2)$$

were calculated using the appropriate thermodynamic data[5]. Curve BG is referred to as the Rankine–Hugoniot or R.H. curve.

The velocity of propagation of any shock wave is given by the square root of the tangent of the angle subtended at A between the X axis and by any particular point on BG. The unique solution of the stable detonation wave is that which travels at the minimum velocity and this corresponds to the point of tangency from the initial point A to touch the curve at C (Chapman[16]).

Overdriven detonations can be represented by points along BG between C and G and it can be seen that at all such points, the pressure and velocity of the wave will exceed those in the corresponding stable detonation. The relationships between pressure and velocity of propagation for this type of overdrive are plotted as curve I on Fig. 10.

Detonation wave velocities were calculated by introducing the condition of stability in the alternative form suggested by Jouget:[17]

$$\frac{dP_2}{dV_2} = \frac{P_2 - P_1}{V_1 - V_2} \quad . \quad . \quad . \quad (3)$$

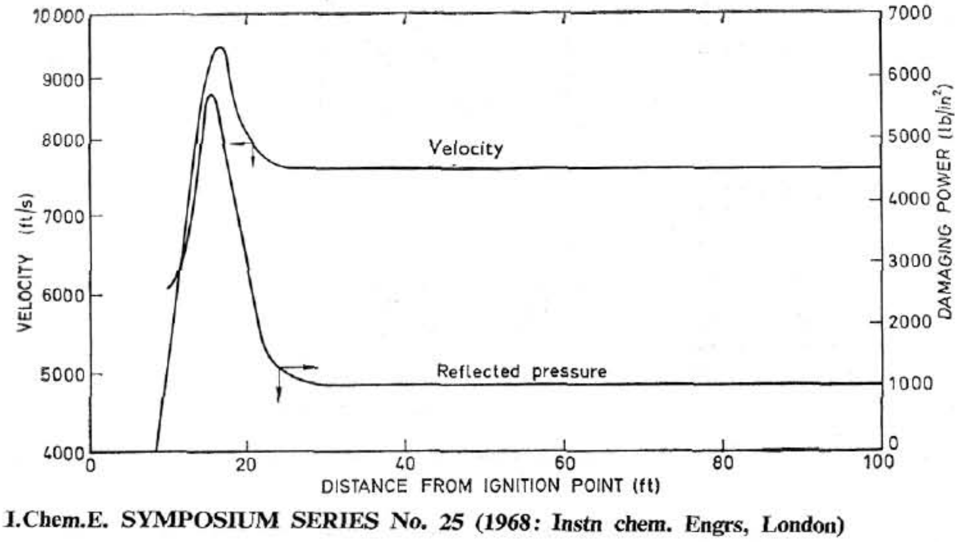

Fig. 8.—Comparison of velocity and damaging power of explosions in 50:50 ammonia–nitrous oxide mixtures in a 4 in. nominal bore pipe

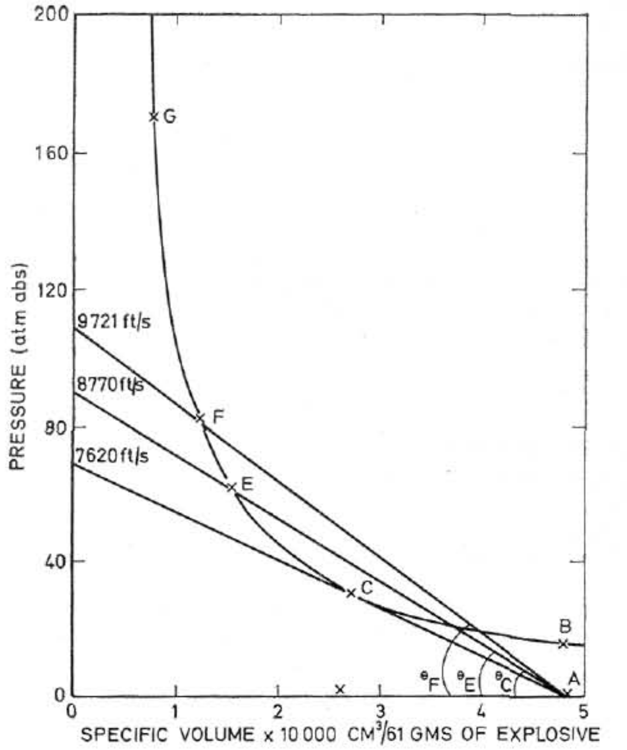

Fig. 9.—*Rankine–Hugoniot curve for reactive shock waves in 50:50 ammonia–nitrous oxide mixtures initially at 1 atm pressure and 18°C*

and not by the graphical method involving the point of tangency C in Fig. 9. Equations (1), (2), and (3) were solved simultaneously together with all the necessary equations governing the production of dissociated and undissociated species in the processes of combustion and the *P.V.* relationships of the burnt gases resulting from the net change in heats of formation and the total number of molecules. The method of Lewis and Friauf[18] involving a total of 18 simultaneous equations in the case of ammonia and nitrous oxide was adapted for the English Electric KDF9 computer.

Using this technique we computed the detonation velocities for a number of ammonia–nitrous oxide and ammonia–nitrous oxide-nitrogen mixtures using the basic thermodynamic data published by the National Bureau of Standards.[15] The computed values are given in Table I together with the observed values.

It was subsequently shown (see below) that although the stable wave parameters were predictable by C.J. Theory (Chapman[15]–Jouguet[16]), the high pressures observed during overdrive could not be accounted for on the basis of a single discontinuity.

Double discontinuity

When the development of the detonation wave is preceded by a weak shock wave the transient pressure and velocity of the unstable wave can be treated according to the simplified model shown in Fig. 11. This simplified model is based on the observations of Turin and Huebler[9] carrying out experiments in Toledo town gas–air mixture.

It can be seen that the wave form consists of two discontinuities, one involving a rise in pressure at some distance ahead of the flame and the other involving a much greater rise in pressure associated with the flame. This complex wave form is produced by a process which is admirably described in detail by Turin and Huebler[9] but which may be summarised as follows.

Upon ignition, the flame begins to travel down the pipe at a velocity which is well below that of sound in the unburnt gas ahead of the flame. The generation of pressure by combustion results in the formation of a weak shock which begins to travel down the pipe at about the speed of a sound. As the flame accelerates the pressure generated can reinforce the shock front so long as the flame is travelling subsonically relative to the gas behind the shock wave. When the flame front becomes supersonic locally, however, the pressure generated by the flame will not escape the flame front and a shock wave (the second pressure discontinuity) will be formed. The strength of the primary shock wave can be defined by the pressure in the shock front, P_s, and the gas "piston" behind the wave will have an associated velocity (particle velocity), U_p, according to the equation:

$$U_p = \sqrt{\left(\frac{P_s/P_1+\mu^2}{1+\mu^2}\right)} \qquad . \qquad . \qquad (4)$$

where $\mu^2 = (\gamma-1)/(\gamma+1)$ (γ is the specific heat ratio).

The gas behind the shock wave will also be at a temperature T_s which is above the ambient, T_1, according to the equation:

$$T_s = T_1 \cdot \frac{P_s}{P_1}\left(\mu^2\frac{P_s}{P_1}+1\right)\bigg/\left(\frac{P_s}{P_1}+\mu^2\right) \qquad . \qquad (5)$$

provided that:

$$T_s = \frac{P_s V_s T_1}{P_1 V_1} \qquad . \qquad . \qquad . \qquad (6)$$

i.e. it is assumed that there are no chemical changes in the primary shock.

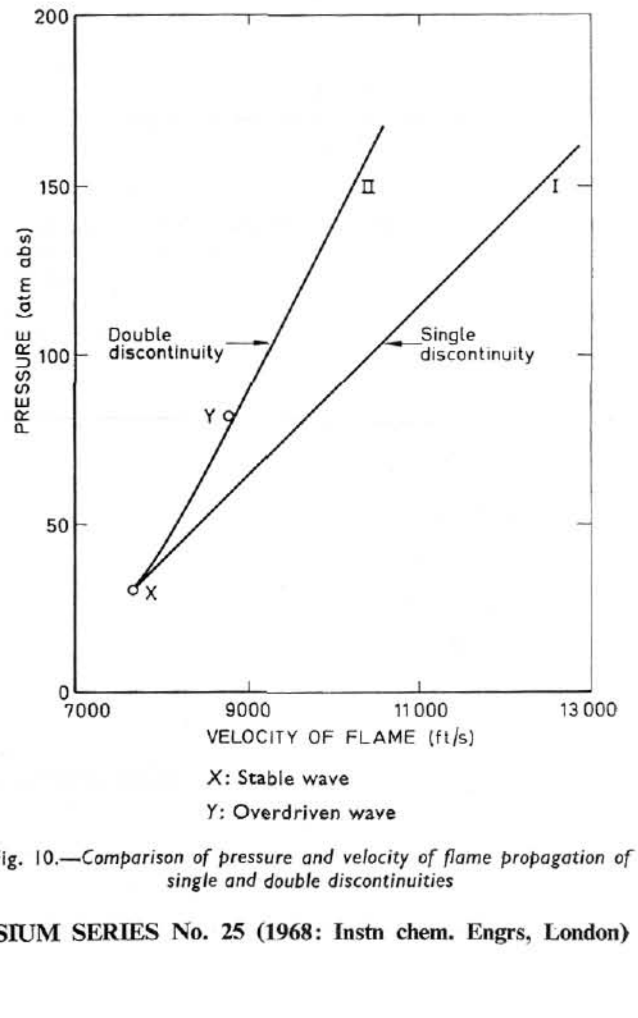

Fig. 10.—*Comparison of pressure and velocity of flame propagation of single and double discontinuities*

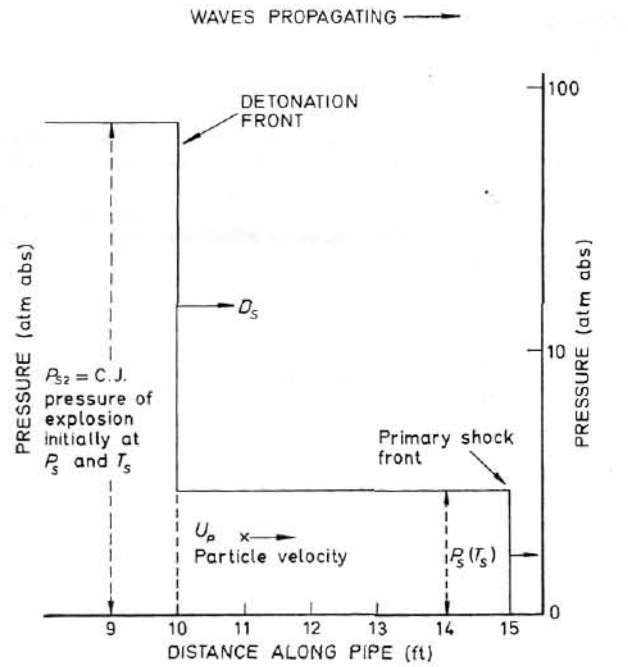

Fig. 11.—*Simplified model of overdriven detonation wave: double discontinuity. After Turin and Huebler*

We have assumed that the incident pressure of the gas behind the second discontinuity is that predictable by C.J. Theory where the initial temperature, T_s, and pressure, P_s, are those of the gas behind the primary shock wave. Thus for any given value of P_s, the primary shock pressure, the gas behind the second discontinuity will have a pressure P_{s2} and the detonation velocity relative to the gas behind the shock wave will be D_s'. The detonation velocity relative to a stationary observer (the ionization gauges) will be therefore:

$$D_s = D_s' + U_p \quad . \quad . \quad . \quad (7)$$

TABLE III.—*Characteristics of Overdriven Detonation in Open Ended Pipes based on the Double Discontinuity*

	Equation (5)	Equation (4)	Computed C.J. Theory	Computed C.J. Theory	Equation (7)
P_s (atm abs)	T_s (°K)	U_p (ft/s)	P_{s2} (atm abs)	D_s' (ft/s)	D_s (ft/s)
2	340	579	53·5	7675	8254
4	420	1241	88·1	7727	8968
6	500	1698	112·4	7759	9457
	Stable wave parameters (single discontinuity)				
1	298	0	30·0	7620	7620

Computed values of T_s, U_p, P_{s2}, D_s', and D_s are given in Table III for an initial set of values of P_s for a 50% NH3/50% N2O mixture. The computed values of P_{s2} and D_s are plotted on Fig. 10 as curve II.

The transient nature of the double discontinuity model is evident from the fact that D_s' is always much higher than U_p and the second discontinuity will, therefore, always overtake the first if the pipe is long enough.

Reflected detonation

The pressure multiplication which occurs on the reflection of normal shock waves depends upon the pressure in the incident shock but for the reflection of detonation waves Pfreim[20] derived the universal relationship:

$$\frac{P_3}{P_2} = 5\gamma + 1 + \sqrt{\left(\frac{17\gamma^2}{4\gamma} + 2\gamma + 1\right)} \quad . \quad (8)$$

where P_2 is the incident pressure and P_3 is the reflected pressure in the detonation wave. This is independent of the initial pressure. For all real gases at very high temperature, therefore, γ, the specific heat ratio will be approximately 1·3 and:

$$\frac{P_3}{P_2} = 2{\cdot}5 \quad . \quad . \quad . \quad (9)$$

Pfreim's equation is only applicable to a detonation wave at the C.J. point C (Fig. 9) and could not be used to predict the reflected pressure of a non-steady detonation wave whose pressure and density correspond to other points along the R.H. curve (BG; Fig. 9).

Reflection of the double discontinuity

Consider now the reflection of the double discontinuity model depicted in Fig. 11; the sequence of events is shown diagrammatically in Fig. 12.

The primary shock wave is first reflected from the closed end and the reflected wave returns to meet the oncoming second discontinuity (the detonation wave). A rise in pressure and temperature from P_s to P_R and T_s to T_R takes place in accordance with basic shock theory:[19]

$$P_R = P_s\left[(2\mu^2 - 1)\frac{P_s}{P_1} - \mu^2\right] \bigg/ \left[\mu^2\frac{P_s}{P_1} + 1\right] \quad . \quad (10)$$

and:

$$T_R = \frac{P_R}{P_S} \, . \, T_S\left(\mu^2\frac{P_R}{P_S} + 1\right) \bigg/ \left(\frac{P_R}{P_S} + \mu^2\right) \quad . \quad (11)$$

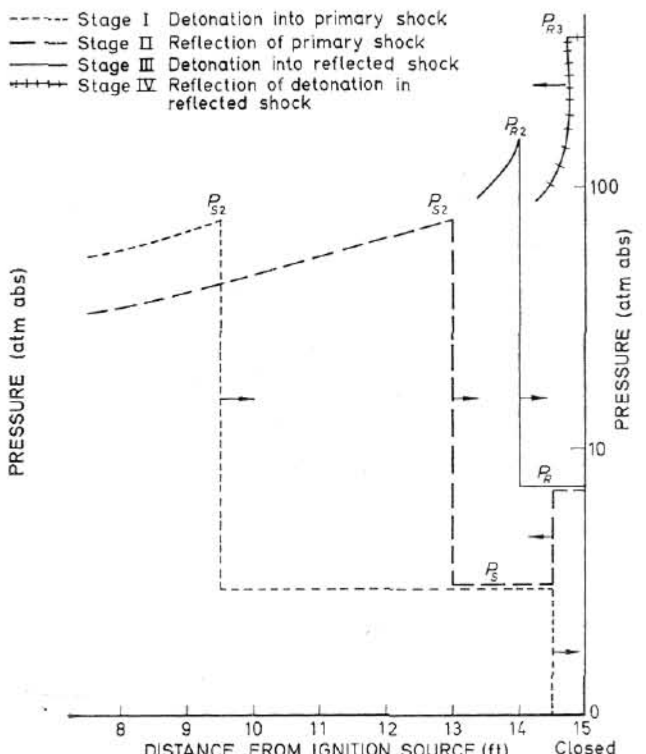

Fig. 12.—*Diagrammatic representation of the final stages of the approach and reflection of the overdriven detonation*

The gas behind the reflected shock wave is at rest and when the detonation wave meets the reflected shock the pressure in the detonation wave, P_{R2}, can be calculated from C.J. Theory by assuming that the initial temperature is T_R and the initial pressure is P_R.

As the gas ahead of the incident detonation is at rest, the pressure on reflection P_{R3} can be obtained by the Pfreim equation (equation (8).

The reflected shock parameters, P_R and T_R, for initial values of $P_s = 2$, 4, and 6 atm are shown in Table IV together with the C.J. pressure, P_{R2} (based on initial conditions P_R and T_R) and the reflected detonation pressure, P_{R3}.

Values of P_{R3} for 50/50 ammonia–nitrous oxide are plotted against the velocity (open-ended-pipe), for various primary shock pressures in Fig. 13. Also known in Fig. 13 are the damaging power and velocity maxima obtained in 3 in. and 4 in. nominal bore pipes with 50/50 ammonia/nitrous oxide mixtures.

TABLE IV.—*Characteristics of Reflected Overdriven Detonation in Closed Pipes based on the Double Discontinuity*

P_S (atm abs)	Equation (10) P_R (atm abs)	Equation (11) T_R (°K)	Computed C.J. Theory P_{R2} (atm abs)	Equation (8) P_{R3} (atm abs)
2	3·8	393	89·3	223·3
4	13·04	566	220·2	550·6
6	25·8	742	342·0	854·8
		Stable wave parameters		
1	(1)	(298)	30·00	75

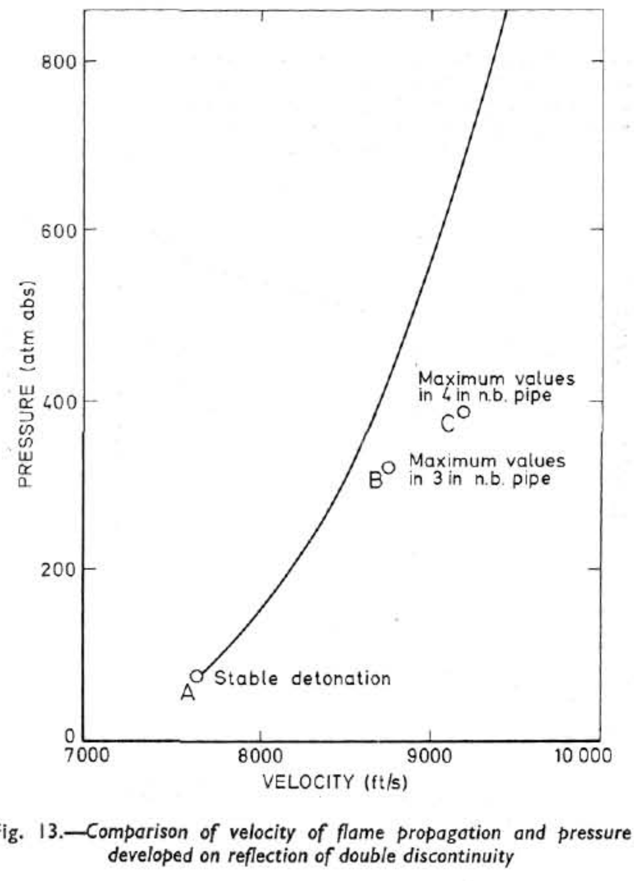

Fig. 13.—*Comparison of velocity of flame propagation and pressure developed on reflection of double discontinuity*

ZDN Spike

We considered the possible effect of the extension to the Chapman–Jouguet Theory proposed independently by Zeldovich,[21] Doring,[22] and von Neumann[23] in the early 1940's which predicts the existence of a sudden transient peak pressure (ZDN Spike) in the leading edge of the detonation wave. Although this pressure should in theory be higher than the C.J. pressure we consider that the time of application would be too short to affect our pressure gauges or our test plates.

Discussion

Before attempting to treat overdriven detonations theoretically, we compared the observed properties of the stable detonations in ammonia–nitrous oxide mixtures with those predicted by C.J. Theory. It can be seen from Table I that the agreement between the observed and calculated velocities of stable detonations is very good. We would therefore expect any theory regarding the structure of the overdriven detonation in these gases to stand up to similar mathematical analysis.

It can be seen that the relationship between the velocity and pressure in the overdriven detonation cannot be accounted for in terms of a transient excursion along the right-hand curve by a single discontinuity. The maximum observed velocity in a 3 in. pipe (50/50 ammonia–nitrous oxide) was 8770 ft/s which should correspond to a maximum incident wave pressure of about 60 atm (Point E, Fig. 9) whereas the observed pressure of 82 atm would require a wave velocity of 9720 ft/s (point F). The reflected pressures evident from Fig. 7 and shown in Figs 6 and 8 suggest an even greater departure from the single discontinuity theory.

The high incident and reflected pressures can, however, be explained by the double discontinuity theory. A comparison of the incident pressures and corresponding velocities predicted by the two alternative theories are shown in Fig. 10. Point X corresponds to the stable detonation and departures from stability (*i.e.* overdrive) are represented by points along the lines I (single discontinuity) and II (double discontinuity). For any particular velocity higher than the stable velocity, the double discontinuity theory predicts the higher wave pressure. In Fig. 10 the experimental point X taken from the region of stability in Fig. 5 (values between 40 and 100 ft from ignition) is in very good agreement with classical theory and the experimental point Y, taken from Fig. 5 at the point of maximum overdrive (12 ft from ignition), agrees with the double discontinuity theory.

The reflection of the double discontinuity model (Fig. 13) can, in theory, produce some very high pressures as shown in Fig. 14. This would account for the extreme damage which has been reported from time to time in plant explosions although the pressures appear to be, at first sight much, higher than those determined by our test plates (points B and C Fig. 13). We consider that this is due to the non-linear response of the test plates at very high permanent deflections. [It can be seen that the deflection sustained in stable detonation gives a point (A Fig. 13) which is in very good agreement with the predicition of theory.] The pressures experienced by the test pieces were probably very close to those predicted theoretically.

On the basis of the double discontinuity theory it is the primary shock wave which, although weak in itself, results in the high transient pressures and we refer to the whole process as shock piling in contrast with the more familiar process of pressure piling. We suspect that any factor promoting early acceleration of flame will reduce the effects of shock-piling since the primary shock wave has less time to develop. Conversely, when flames travel for relatively long

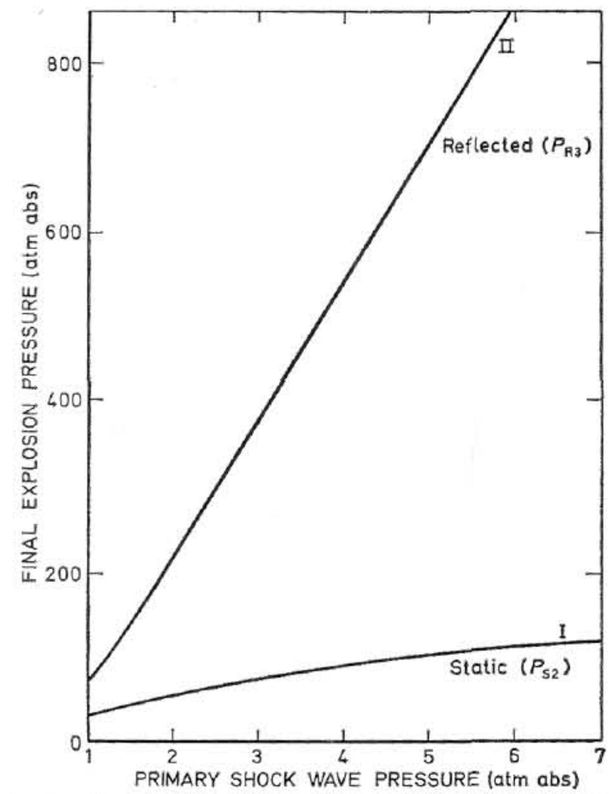

Fig. 14.—*Theoretical final pressures (static and reflected) of 50:50 ammonia–nitrous oxide explosion compared with primary shock pressure in the double discontinuity*

distances subsonically, the final effects of shock-piling may be extremely severe.

This effect is illustrated in our experiments in a 4 in. nominal bore pipe as compared with similar experiments in 3 in. nominal bore pipe. The increase in detonation induction distance results in an even higher ultimate pressure during shock piling. This presents problems of plant design particularly when scaling up from small plants to large ones. Experience based upon the manipulation of explosive gases in very narrow bore pipes may be of little value in assessing the hazard in large diameter pipes. In larger diameter pipes, the distance over which shock-piling is effective is much greater and, what is more important, higher maximum pressures may be generated.

Unfortunately there is no evidence from our experiments that the effect of shock-piling cannot continue to increase with increase in pipe diameter. There are, however, some theoretical reasons for believing that shock-piling cannot continue indefinitely. Thus, as the pressure in the shock front increases the temperature will rise according to equation (5). This temperature rise, for various initial shock pressures, is given in Table IV. For most gases T_S will be greater than 1000°K for primary shock waves between 10 and 20 atm and this will cause the gases to ignite spontaneously ahead of the flame front. This has been observed experimentally by Bone, Fraser, and Wheeler.[24] Under these circumstances the secondary flame front unites with the primary shock to form the new detonation wave which then proceeds down the pipe in accordance with C.J. Theory. This mechanism will set a limit to the extent to which the primary shock can continue to develop. However, it can be seen from Fig. 14 that reflection during shock piling can, in theory produce a final pressure of about 1000 atmospheres for a primary shock pressure of only seven atmospheres when the initial pressure is atmospheric.

Conclusions

(1). During the development of stable detonation waves in ammonia–nitrous oxide mixtures there is a period of overdrive when the flame front accelerates to a maximum velocity before it decelerates to a steady value predictable by classical (Chapman–Jouguet) theory.

(2). As the flame reaches peak velocity the incident and reflected pressures are several times higher than those associated with the stable wave.

(3). The pressure and velocity of propagation are not explicable in terms of a single discontinuity (excursion along the Rankine–Hugoniot curve) but are consistent with a double discontinuity in which the first is a neutral shock wave and the second is a classical detonation travelling into a section of gas whose temperature and pressure have been raised by the passage of the primary shock wave.

(4). By delaying the development of the detonation wave using a larger diameter pipe higher velocities and pressures are produced during the period of overdrive.

Acknowledgments

The authors wish to thank Miss J. M. Davidson and Dr. S. Paterson of Nobel Division of Imperial Chemical Industries Ltd for the helpful discussions and Miss S. Towers who adapted the method of calculating detonation parameters[18] for the English Electric KDF9 computer.

References

1 Jacobs, R. B., Bulkley, W. L., Rhodes, J. C., and Speer, T. L. *Chem. Engng Prog.*, 1957, **53**, 565.
2 Jacobs, R. B. *Proc. Am. Petrol. Inst.*, 1959, **39**, 15.
3 Pipkin, O. A. *Proc. Am. Petrol. Inst.*, 1959, **39**, 21.
4 Ginsburgh, L. and Bulkley, W. L. *Chem. Engng Prog.*, 1963, **59**, No. 2, p. 82.
5 Kogarko, S. M. *Zh. tekh. Fiz.*, 1958, **28**, 1875.
6 Rimarski, W. and Konschak, M. *Autogene Metallbearb.*, 1934, **27**, 209.
7 Alder, L. B. and Luker, J. A. *Combust. Flame*, 1959, **3**, 157.
8 Henderson, E. *Proc. Pacif. Cst Gas Ass.*, 1941, **32**, Sept., p. 98.
9 Turin, J. J. and Huebler, J. American Gas Association Research Project I.G.R. 59, Part I/1950, Part II/1951.
10 Oppenheim, A. K. in "*Fourth Symposium on Combustion*", 1952, p. 471. (Baltimore: Williams and Wilkins.)
11 Brinkley, S. R. Jr. and Lewis, B., in "*Seventh Symposium on Combustion*", 1958, p. 807. (London: Butterworths).
12 Chu, Boa-Teh in "*Fourth Symposium on Combustion*", 1952, p. 603. (Baltimore: Williams and Wilkins).
13 Bollinger, L. E., Fong, M. C., Laugrey, J. A., and Edse, R. *NASA tech. Note* D1983/1963.
14 Lewis, B. and von Elbe, G. "*Combustion, Flame, and Explosions of Gases*", 1961, 2nd Edition. (New York: Academic Press Inc.).
15 *Circ. U.S. natn. Bur. Stand.* 500/1952.
16 Chapman, D. L. *Phil. Mag.*, 1899, **47**, 90.
17 Jouget, E. *J. Math.*, 1905, p. 347: *Idem ibid.*, 1906, p. 6.
18 Lewis, B. and Friauf, J. B. *J. Am. chem. Soc.*, 1930, **52**, 3905.
19 Bradley, J. N. "*Shock Waves in Chemistry and Physics*", 1962. (London: Methuen & Co. Ltd.)
20 Pfreim, H. *Forsch Arb. Geb. IngWes.*, 1941, **12**, 148: *Idem ibid.*, 244.
21 Zeldovich, B. Ya. *Zh. éksp. teor. Fiz.*, 1940, **10**, 542.
22 Doring, W. *Annln Phys.*, 1943, **43**, 421.
23 von Neumann, J. "*Progress Report on Theory of Detonation Waves*".
24 Bone, W. A., Fraser, R. P., and Wheeler, W. H. *Phil. Trans. R. Soc.*, 1936, **A235**, 29.

The manuscript of this paper was received on 21 *April*, 1967.

DISCUSSION

THE CHAIRMAN (Mr. H. Stromberg) said that he noticed from the diagram of the apparatus that there was an ingenious method of detecting pressure which he presumed was an electronic method. There was a cathode ray oscilloscope which was photographed. He wondered if Craven and Greig would say something about this.

Mr. CRAVEN replied that the apparatus used for measuring the pressure in the detonation wave was quite standard. In the first place, Southern Instrument's capacitance gauges were used and later, the Kistler type piezo-electric gauge. There had been a little trouble at first because the trench was some distance from the laboratory and pulse shapers had to be used to tidy up the signals from the ionisation gauges but this trouble had not been experienced with the pressure gauges which were fitted with quite conventional amplifiers obtainable on the market. The cathode ray oscilloscope and rotating drum camera were standard equipment from Southern Instrument Co. Ltd.

Mr. T. THOMPSON said that it had now been ascertained how the shock waves were formed: had a way of stopping them been found?

Mr. CRAVEN replied that it was not possible to do anything to limit the formation of the primary shock wave since this arose as a natural consequence of the processes of fast combustion.

The work that they had described was valuable from the point of view of diagnostics; in regard to the accident which resulted in this work being carried out they had to know the precise nature of the explosion before preventative action could be taken. If the extent of the damage could not be attributed to gaseous explosion, a liquid or a solid explosive would have to be identified within the process. As a result of this work they were now satisfied that the steps they had taken to prevent the formation of explosive gas mixtures are adequate.

Dr. W. A. WOODS said that he was interested in the technique of using test plates to assess the damaging power associated with the reflection of waves. He suggested it might be possible to correlate the permanent distortion shown in Fig. 7 with the gas pressure subsequent to reflection. In this connection a useful starting point would be to use the work of W. Johnson of the University of Manchester Institute of Science and Technology.

In connection with the double discontinuity model proposed in Fig. 11 he asked if the authors knew of any experimental evidence such as measured pressure — time diagrams to support the existence of the two waves. He also asked if the authors' own ionisation gauges had detected the shock wave in front of the detonation wave.

Mr. CRAVEN said that he thought it true to say that the reason the experimental points did not lie on the curve (Fig. 13) was because of the lack of adequate calibration of the plates. An attempt had been made to calibrate them with shock waves in water but we suspected that the frequency of the shock waves in water was higher than the natural frequency of the plates. They really needed to be calibrated with shock waves in a gas of a known magnitude.

The primary shock wave had not been detected in the experiments reported. The trouble was that a pressure gauge sensitive enough to see a primary shock wave would be damaged by the second pressure wave which came along. The ionisation gauges were tuned to see the detonation waves but we could not get them to detect even the deflagration in the early stages and it was certainly not possible to see the primary shock wave with them. The authors would refer Dr. Woods to the paper by Turin and Huebler (Ref. 9 of the paper); their gauges saw the primary shock wave. There was also evidence of this primary shock wave in Refs 10 and 12 of the paper.

Mr. A. V. BAILEY asked if the authors had any ideas about the effects of bends in the piping on this system. Would there not be multiple reflections round the bends which would modify the behaviour of the system?

Mr. CRAVEN replied that a limited number of experiments had been done with bends. Experiments had been done with various pipe configurations, and if anything, the results indicated that any increase in the tortuous nature of the path tended to reduce the resulting detonation over-pressures. That was also true if orifice plates were placed in the pipe but the experiments they had made were very few in number.

These results were to be expected since the introduction of obstacles would tend to cause flame front acceleration as a result of which the primary shock wave had less time to become fully established before being overtaken by the flame. In all their experiments the greatest damage had been inflected in long straight pipes.

Mr. D. G. FURZEY asked whether, in that case, the authors would recommend the installation of pipe-lines in a tortuous path where there was a danger of detonation.

Mr. CRAVEN replied that as a result of the experiments they were now faced with something of a dilemma. If one was certain that the gas inside the plant would detonate, it might be advisable to reduce the effect of " shock-piling " by using bundles of small diameter pipes and even introducing bends. Unfortunately those conditions might well result in detonation in some gas mixtures which might otherwise only deflagrate. The moral they were always preaching was: try to avoid the handling of potentially explosive gas mixtures in large chemical plants.