High Energy Ignition Systems

by

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Abstract

The thesis describes research on high energy electrical igniters based on electrical discharge and laser induced plasma. The energy output of these specialized ignition systems is much higher than that of conventional "spark plug" igniters and is released in a chemically active form that enhances and promotes the critical steps of the chemical reactions of combustion. They have applications in various specialized fields of combustion which include aircraft turbine engine startup under adverse conditions, enchanced oil recovery burners and liquid propellant gun firing.

Plasma jet devices release the ignition energy in the form of a highly dissociated gas stream, usually described as low temperature plasma, into the combustion chamber and may operate in either a continuous or in a pulsed mode. The performance of an aerodynamically spun continuous plasma jet igniter was tested on an aircraft turbine combustor test rig under realistic "flight" conditions (low temperature and pressure) using air as the plasma medium. The plasma was injected to the combustor at sonic speed replacing the surface discharge igniter normally used in such applications. This series of experiments demonstrated the ability of the plasma jet device to ignite lean air/fuel mixtures under adverse conditions.

For applications requiring even higher energy releases, a pulsed plasma jet design using a liquid propellant as the plasma medium was investigated. The propellants used are liquid monopropellants based on aqueous solutions of nitric salts of hydroxylamonium and organic amines and have good electrical conductivity. This study was extended to investigate the possibility of optical initiation of the propellant fed plasma jet ignition process, using a Q-switched ruby laser operating at 693.4 *nm*. The interaction between the liquid propellant and the laser beam was studied in a series of experiments under constant pressure conditions in small "dilatometer", a device which allows the measurement of the generation of volume due to propellant decomposition under constant pressure. Following theoretical and experimental pointers suggesting enchancement of the reaction by oxides of nitrogen, the effects of precursory electrolysis and prolonged heating on the propellant behaviour during laser initiation were studied for various propellant combinations. It was found that precursory electrolysis and prolonged heating permanently increases the sensitivity of the propellant to laser initiation, although the extent of the change varies with the chemical structure of the propellant. It was also found that addition of light absorbing dyes in the propellant increase its sensitivity to laser initiation as well.

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CHAPTER 1

INTRODUCTION

An intensive research effort is currently taking place in many research institutions on novel high energy ignition systems. The term ''High Energy Ignition Systems'' is used to describe devices similar in shape and size to conventional spark plug igniters but capable of delivering larger amounts of energy, usually of the order of 2 to 150 J, to the combustible mixture and in such a form that it is used much more efficiently in achieving ignition. There is a wide range of applications for these novel igniters, typical ones being aircraft turbine engines, high intensity pulsed burners, liquid propellant guns, and burners of very lean mixtures.

In nearly all cases, initiation of a deflagration in a fuel/air system by an igniter takes place locally and then propagates to fill the combustion chamber. Temperatures near a spark ignition source are always high enough to create a small flame kernel, if the mixture is within the limits if flammability. The mechanism of flame propagation involves heat transfer and active chemical species diffusion from the flame region to the unburnt mixture. For flame kernels of small radius the rate of increase of area of the flame front is so high that the heat and chemical loses to the unburnt mixture may not be covered by the flame reactions and the flame kernel dies out, even if the mixture is combustible. High energy igniters produce initial flame kernels with sufficiently high temperature and/or free radical concentration so that their propagation beyond this critical stage is ensured. The use of such igniters is essential when combustion of very lean mixtures, combustion of very lean mixtures, combustion in higly turbulent flows and/or at low ambient pressure and temperature.

Most of these high energy igniters are based on the Plasma Jet principle. There are two main families of plasma jet igniters, ''continuous plasma jets'' and ''pulsed plasma jets'', the distinction being based on the mode of operation of the particular device. Their higher ignition performance is based on their ability to inject chemically reactive species deep into the combustion chamber, where conditions are more favourable for flame initiation. Additionally, they are capable of producing aerodynamic effects which contribute to the stability of the flame or pressure effects in the form of shock waves which can be used to initiate detonation in combustible mixtures.

The nature of continuous plasma jets makes them suitable both as igniters and as flame stabilizers of lean mixtures. They have high electrical efficiency but the whole ignition systems, including the feedstock and power supply units, tend to be relatively complicated. They have been tested mainly as flameholders for air engine applications, especially in experimental scramjets where they are used to stabilize supersonic combustion, by research teams at the University of Tokyo [Kimura et al, 1981] and NASA [Northam et al, 1984]. The design and evaluation of a continuous plasma jet igniter for conventional turbojet engines was the subject of a research programme at Imperial College [Warris and Weinberg, 1984; Cheriyan and Weinberg, 1986; Cheriyan et al, 1990]. The work discussed in chapters 2 and 3 of this thesis is the final part of this programme and involved the evaluation of the of the igniter under simulated high altitude conditions.

Pulsed plasma jets depend on simpler and lighter power supply units but suffer from lower efficiency. As they are relatively small, they can be used with internal combustion engines to replace the conventional spark plugs and allow them to ignite reliably and burn smoothly leaner mixtures and this is the subject of most applied research on these devices [Asik et al, 1977; Dale et al, 1978; Tozzi and Dabora, 1982; Vosen et al, 1988; Vince et al, 1984; Wyczalek et al, 1975]. Although these igniters have superior ignition performance than conventional spark plugs, they suffer from limited life of the electrodes. There is also some interest, mainly in the United Kingdom, to develop advanced aircraft jet engine igniters based on this principle. This line of investigation was based on fundamental work on plasma plugs done at Imperial College [Weinberg et al, 1978; Weinberg, 1986] and on flame initiation in lean mixtures under turbulent conditions at the University of Leeds [Boston et al, 1984]. A device called ''Focused Discharge Igniter'' was developed by Smiths Industries Ltd for Rolls-Royce plc and was subjected to an extensive test programme [Low et al, 1989].

Special high energy pulsed plasma jet igniters use a liquid propellant as feedstock and are capable of energy discharges of $50\,J$ or more. This makes them suitable for the most demanding applications.

The pulsed plasma jets studied in this thesis use aqueous monopropellants based on hydroxylamonium nitrate as feedstock and are capable of a very high energy release. Most early work on ignition of liquid propellants took place at U.S. Army Ballistic Research Laboratory [Klein, 1983] and at Imperial College [Klein et al, 1983; Carleton et al, 1985] and more recently at Sandia National Laboratories, Livermore, [Vosen, 1988] and elsewhere [Klingenberg et al, 1989; Kounalakis and Faeth,

1988; Russel and Brill, 1989], mostly under U.S. Army research contracts. The liquid propellants used as feedstock were developed initially for use with guns and most development work is still on military applications, although other potential applications have started to emerge [Chesters et al, 1981]. The work at Imperial College consists mainly of basic research on the initiation of reaction in these materials using mainly optical and calorimetric techniques. So far electrical initiation was studied in detail [Klein et al, 1983; Carleton et al, 1985; Carleton et al, 1987] and, more recently, the possibility of optical initiation was investigated. The work described in this thesis in the field of liquid propellant initiation is mainly a study of the parameters which affect the initiation of the propellant by laser beams. The results of this research can be used to evaluate the feasibility of laser triggered high energy plasma jet igniters. Factors which increase the sensitivity of the propellant to electrical or optical initiation, like precursory electrolysis, prolonged heating and dyeing are studied on a variety of hydroxylamonium based propellants. Some practical work was also undertaken in cooperation with Frazer-Nash Ltd and it involved the use of optical diagnostic methods (high speed schlieren and shadow photography) to study the operation of an electrically triggered liquid propellant plasma plug igniter and the results of these experiments were compared with previous work. Work relevant to particular topics is extensively reviewed in the relevant chapters, mainly chapter 2 for the continuous plasma jets and chapter 4 for liquid propellant fed plasma plugs and their applications.

CHAPTER 2

CONTINUOUS PLASMA JETS

2.1 Continuous Plasma Jets as High Energy Igniters and Flameholders

The term "Plasma" is used to describe a gaseous state that contains not only neutral molecules but also positive and/or negative species (ions, electrons) and free radicals. The plasma produced by the devices described here is usually described as "low temperature plasma" and its temperature is of the order of 5,000 to 20,000 K. At these temperatures a wide variety of chemical species survive long enough to produce interesting chemical effects, including ignition and promotion of flame propagation reactions.

A most common sources of low temperature plasma are flames [Weinberg, 1986], as their propagation mechanism involves rapid reactions that produce electrically charged intermediate products of rather short lifetime. This results to a zone of relatively high conductivity, perhaps 10000 times higher than the conductivity of hot combustion products.

The most important sources of plasma are, however, electrical discharges of various types in gases, usually described as sparks (low energy, high voltage) or arcs (low voltage, high current). It is also possible to produce plasma by electrodeless discharges using high frequency electromagnetic energy, up to the microwave frequencies, and focused laser beams.

The continuous plasma jet devices used in combustion applications usually operate with either DC current or short pulses of DC current. This current forms an arc between two electrodes, where a gas flow is established. The positive electrode is

called "anode" and the negative one "cathode", following the normal electrical conventions. The voltage across the electrode gap after initiation is of the order of some tens to a few hundred volts and the current varies from a few amps up to a few thousands amps. The power supply units normally work in a constant current mode. The gas flowing in the gap is usually called the "plasma feedstock". Many gases can be used as feedstock and hydrogen, air, argon, nitrogen and even methane have been tried. Some of these gases have special properties which make them better suited to specific applications than others [Harrison and Weinberg, 1971].

The first plasma jet designs applied to combustion were used mainly to increase the final flame temperature and control it independently of the fuel and air inputs by adding electrical energy to it [Chen et al, 1965]. Compared to more recent devices, they were inefficient, unstable, required bulky power supplies and cooling equipment and their operation was expensive as the cost of electrical energy is much higher than the energy released from ordinary gas or solid fuels.

Later it was demonstrated that by taking advantage of the chemical species present in the plasma flow, a large increase in the rate of reaction can be achieved. Harrison and Weinberg showed that the addition of a moderate amount of energy in the form of a nitrogen plasma which would increase the final flame temperature only by some 160 K, corresponding to less than a doubling of reaction rate on conventional kinetics, could increase the rate of reaction if nitrogen was present by as much as 700%. This observation initiated further research to determine the mechanism involved in this reaction rate increase.

Experiments with different feedstocks showed that if nitrogen is replaced with a chemically inert gas like argon, the increase in combustion rate is much smaller and compares to that achieved by bluff body aerodynamic flame stabilization [Warris and Weinberg, 1984]. Air gave similar results to nitrogen but attack of the hot cathode electrode by oxygen does not allow prolonged use of the device with air.

After aerodynamic effects were ruled out, further investigations using schlieren photography and conductivity measurements with an ionization probe [Behbahani et al, 1982] showed that the stream emerging from the nozzle of the plasma jet device is not homogeneous but consists mainly of relatively cold gas containing small pockets of very hot ionized material, which have a maximum diameter of 1.5 *mm*. In these pockets the free radicals, in this case free nitrogen atoms, survive long enough to reach the main combustion chamber.

The following explanation for the behaviour of nitrogen plasma jets was given: Nitrogen molecules are broken by the electrical arc into nitrogen atoms:

$$N_2 \rightarrow 2N \tag{2.1}$$

These free nitrogen atoms can survive in the hot pockets long enough to reach deep in the combustion chamber, because the third body nitrogen atom recombination reaction:

$$N+N+M \rightarrow N_2+M \tag{2.2}$$

is relatively slow and becomes slower with increasing temperature ($k2=3\times10^{14}\cdot\exp(500/KT)\ cm^6 mol^{-2} s^{-1}$). Free nitrogen atoms, when finally mixed with air, attack oxygen molecules and release free oxygen atoms, eliminating the energy barrier of oxygen dissociation:

$$N+O_2 \rightarrow NO+O \tag{2.3}$$

This reaction does not contribute to pollution by NO_x as NO is also reduced by free nitrogen atoms, releasing more free oxygen atoms [Behbahani et al, 1982]:

$$N+NO \rightarrow N_2+O \tag{2.4}$$

A new generation of plasma jets was designed based on these observations and they were tested initially as flameholders for lean fuel/air mixtures. They have also been tested with good results as flameholders for ''scramjet'' air engines [Kimura et

al, 1981; Northam et al, 1984] as replacement to the highly unstable and toxic chemicals used normally to keep the supersonic combustion going. The various technical problems presented by previous designs have been partially solved and the devices are available for tests in a wide range of combustion applications. An experimental arc heated stirred reactor was also based on the above findings [Kimura and Imajo, 1976].

Early continuous plasma jet devices suffered of arc instability, especially when nitrogen was used as feedstock. Usually an inert gas like argon was used as a carrier for the more active species but this reduced efficiency, as part of the electrical energy was used to heat the carrier gas instead of producing free nitrogen atoms. Also pressure fluctuations downstream would propagate in the arc region and cause additional instability problems. Regarding power supply units, resistors and inductors were used in series with constant voltage units so a relatively high percentage of the electrical energy was dissipated on the resistors in order to reduce arc instability.

The problem of arc instability in the plasma jet was solved with the addition of a nozzle downstream which produces a sonic flow into the combustion chamber and does not allow any pressure disturbances in the combustor to reach the gas flow in the discharge area which now has the form of a cavity.

The second serious problem to be solved was the melting of the point of the cathode. This was solved by redesigning the electrodes so that the cathode is in the shape of a square cut cylinder coaxially positioned in a conical cavity which acts as the anode. The arc now is struck between the sharp edge of the cathode and the nearest point on the anode. The arc is then forced to rotate about the axis of the electrode system by electromagnetic or aerodynamic forces. In the first case, a toroidal magnet is positioned around the electrodes and its field forces the arc to rotate around the cathode. In the second method, the gas is introduced tangentially into the cavity and the aerodynamic drag forces the arc to follow the gas rotation. As the arc

rotates the erosion of the cathode is distributed evenly around its edge and the gap length remains fairly constant.

It was also shown [Chan et al, 1980] that the optimum geometry of the cavity is that shown in figure 2.1, with an anode half angle of 45^o. This was based on the principle that the arc tends to avoid any change that increases its surface area (Steenbeck Minimum Principle). Having a half angle of 45^o ensures that small displacements would lead to maximum stretch and this would lead the arc to rotate around the cathode edge.

The two methods of arc rotation methods produce slightly different results, as the magnetic field does not affect the gas flow and so a higher degree of mixing is introduced between the bulk of cold gas and the highly ionized gas in the rotated arc region, while in aerodynamically spun jets the arc is dragged by the swirling gas stream. The two types of plasma jet are described as ''Aerodynamically Spun Plasma Jet'' and ''Magnetically Spun Plasma Jet''. The aerodynamically spun devices are more compact and were used in all experiments described in this thesis.

2.2 Description of the Plasma Jet Igniter

The plasma jet device used in this series of experiments (figures 2.2a and 2.2b) has been designed in the Dept. of Chemical Engineering, Imperial College [Cheriyan and Weinberg, 1986], specifically for combustion applications and has been constructed in the departmental workshops. The outer dimensions of the front part of the plasma jet are the same as the ''High Energy Igniter'' made by CHAMPION, which is a surface discharge plug for use in aircraft jet engines. As a result, it can easily replace the CHAMPION plug in test rigs or real jet engines.

The nozzle-shaped anode is made of copper and the square cut, cylindrical cathode is made of 2% thoriated tungsten and is positioned coaxially to to the anode.

The body of the plasma jet is made of ANSI ST-316 stainless steel. As it is physically impossible to feed the gas directly to the cavity and in order to avoid dissipation of the swirl due to the extended length of the plug between the gas inlet and the anode orifice, the swirl is introduced near the cavity by a quarl made of macor.

The quarl is a cylindrical rod 10 mm in diameter, with a 5 *mm* hole cut along its axis through which the cathode (either 3.2 *mm* or 4.0 *mm* diameter, a special quarl made for each cathode) is inserted. Along most of its length the diameter of the hole is larger than the diameter of the cathode. When the cathode has been inserted, an annular channel for the gas is formed. Over the last 10 mm the diameter of the hole is reduced, forming a nearly tight fit around the cathode. At the same end of the cylindrical quarl and on the outer surface there is a channel for an axial distance of 7 *mm*. This channel has a width of 2 *mm* and a depth of 1 *mm*, the projected angle between the axis of the rod and that of the helical channel being 60 degrees. The inlet of the channel is connected to the annulus through a radially cut hole.

The cathode is held in place by a stainless steel holder with a collet at the one end and a 17 *mm* long 3BA thread at the other. The holder passes through a cylindrical ceramic piston. The leaves of the collet tighten uniformly on the cathode when a nut is tightened at the opposite end of the holder.

The spacing between the cathode and the anode is adjusted by a screw cap made of phosphor bronze that holds the ceramic piston firmly against six compression springs. The opposite end of the springs rests against a metal washer that compresses a rubber O-ring. This way an air-tight seal is achieved between the piston and the body of the plasma jet. The screw cap is threaded with a 1 *mm* pitch. This means that a full rotation of the cap moves the cathode by 1 *mm*. Divisions of 0.1 *mm* are marked around the screw cap.

Three special converters have been made to allow the plasma jet to be inserted into various test rigs, one for the ''Spey-can'' rig at Smiths Industries plc, one for the

explosion bomb at Leeds University and one for the Lucas Aerospace Altitude Testing Facility. There are also two special tools, the ''quarl extractor'' and the ''anode support''. These tools are used to remove the quarl and to support the anode from inside the plasma jet when removing it using a screwdriver from the front.

2.3 Power Supply Unit

A specialized power supply unit (P.S.U.) has been designed and built for this particular applications. It derives from similar units used with pulsed plasma plugs or photographic flash lights. It gives the capability to experiment with various combinations of voltage and capacitance, which determine the duration and the total energy of the arc in order to select the most suitable for our application.

A detailed schematic of the power supply is shown in figure 2.3. It can be divided in three parts, namely the rectifier, the triggering circuit and the main storage and discharge circuit.

The rectifier part is very simple and allows us to charge the capacitors to any voltage between 0 and 350 V. The most interesting component in the power supply is the output inductor T3. This inductor consists of three coils, two main inductors T3a and T3b in series with the discharge and a smaller one T3c with only a few turns connected to a 8 μF capacitor via a TIC-126D thyristor and it serves two main purposes:

(i) It reduces (along with resistor R2) the rate of discharge of the capacitors, allowing for a longer discharge and protecting the plasma jet cathode

(ii) Generates a high break-down voltage that initiates a small spark between the electrodes. This spark opens an ionized path of low electrical resistance in the gas stream for the main discharge. The high voltage is generated from a steep 0.8 ms high current pulse flowing through the small coil T3c which consists of only a few turns compared to T3a and T3b.

The positive output terminal of the coil is connected to earth through the current limiting resistor R2. As the voltage across R2 is proportional to the current flowing through it, we can connect the vertical input of a storage oscilloscope at this point and see the current vs. time. Normally a dual trace Tektronix storage oscilloscope is used and the other vertical input is connected in parallel with the output socket so that the screen displays traces of both the voltage across the electrodes and the current flowing through them. A *Polaroid* camera is used to get a photograph for calculations. The total energy input to the plasma jet can the be calculated from the formula:

$$E_p = \int_0^T i(t) \cdot u(t) \cdot dt \qquad (2.5)$$

It should be emphasized that the amount of energy actually delivered to the gas and used to create active chemical species and increase its kinetic energy and heat content cannot be measured directly under these conditions. The efficiency of these devices was measured [Behbahani et al 1983] using the method of *NO* reduction. Measurement of the residual *NO* after a *NO* stream had reacted with the plasma jet showed that the efficiency of such a device in converting electrical energy to nitrogen atoms is surprisingly high, reaching 80%.

The power supply has been built into a 50×55×28 *cm* strong steel chassis in such a way that inspection, repairs, modifications and additions are made as simple as possible. There is no special provision for cooling as the use of the plasma jet is intermittent. The connection to the mains electrical supply passes through a special filter which eliminates electrical interference to other electrical apparatus, mainly digital computer equipment and timing devices. At a later stage an electronic timer circuit based on three NE-555 integrated circuits was added in order to control the gas flow through a solenoid valve and the ignition timing. As the timer was not used in the experiments presented in this thesis, it is not described here.

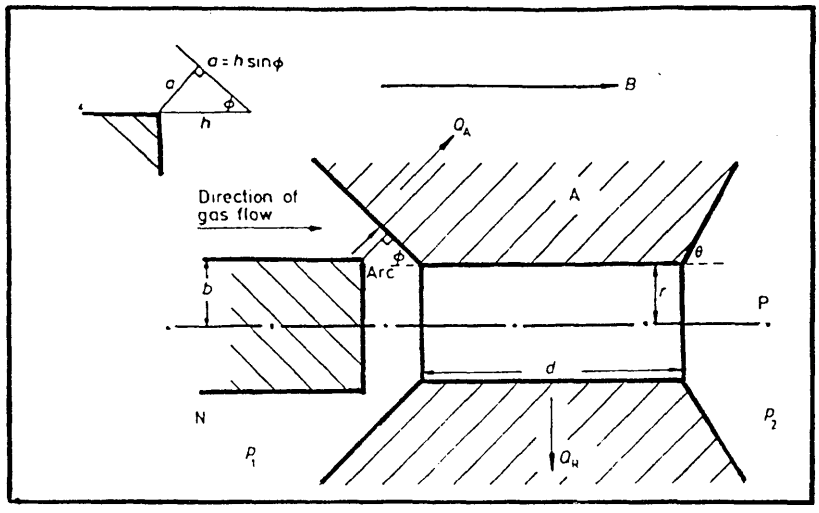


Figure 2.1 - Fine detail of cathode-anode arrangement.

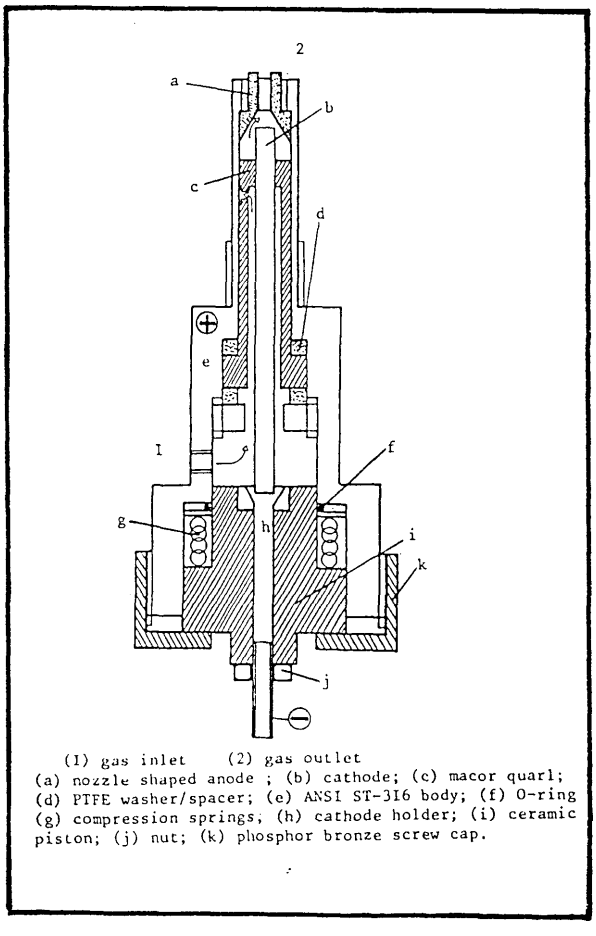
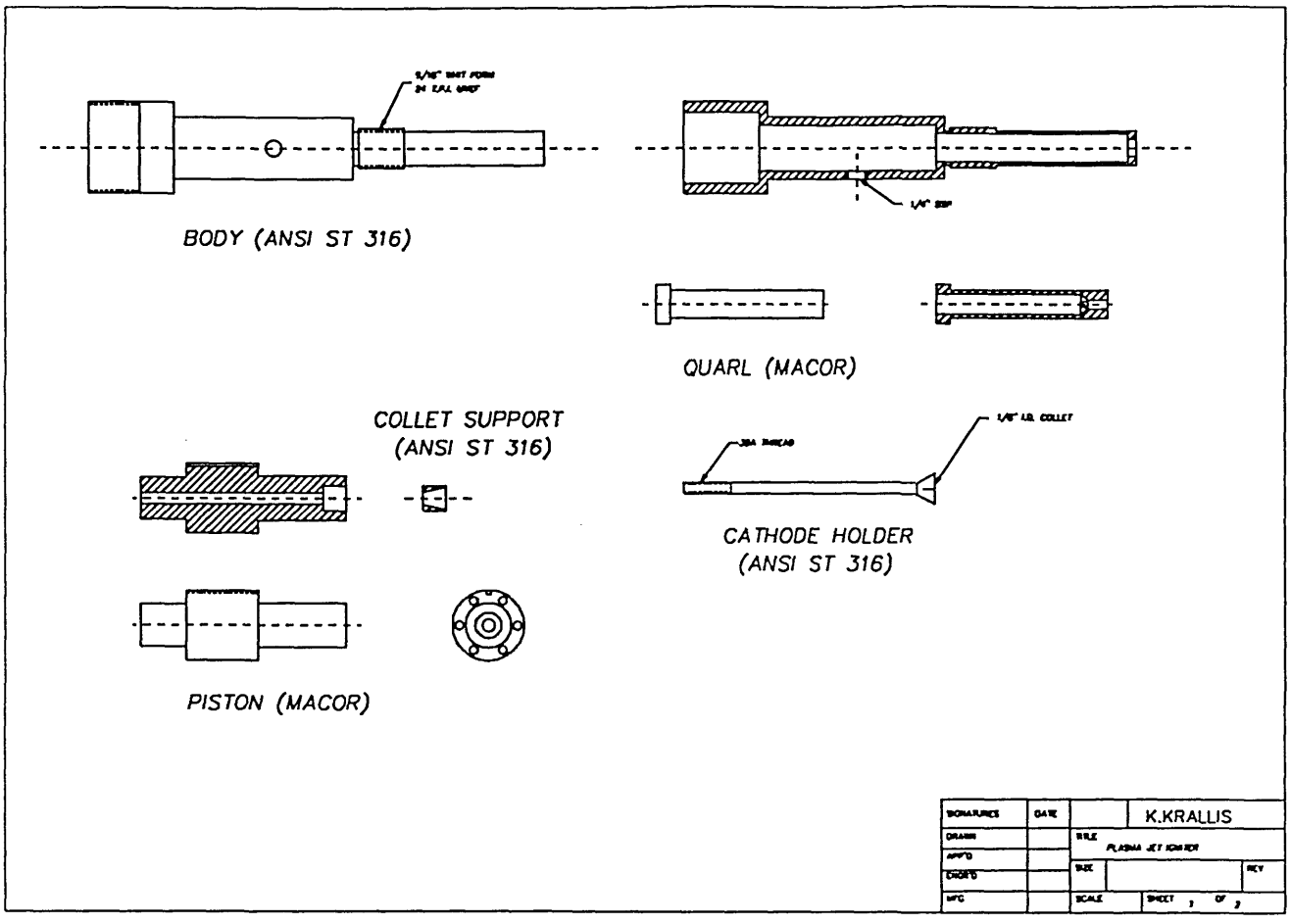


Figure 2.2a - Aerodynamically Spun Plasma Jet Igniter.



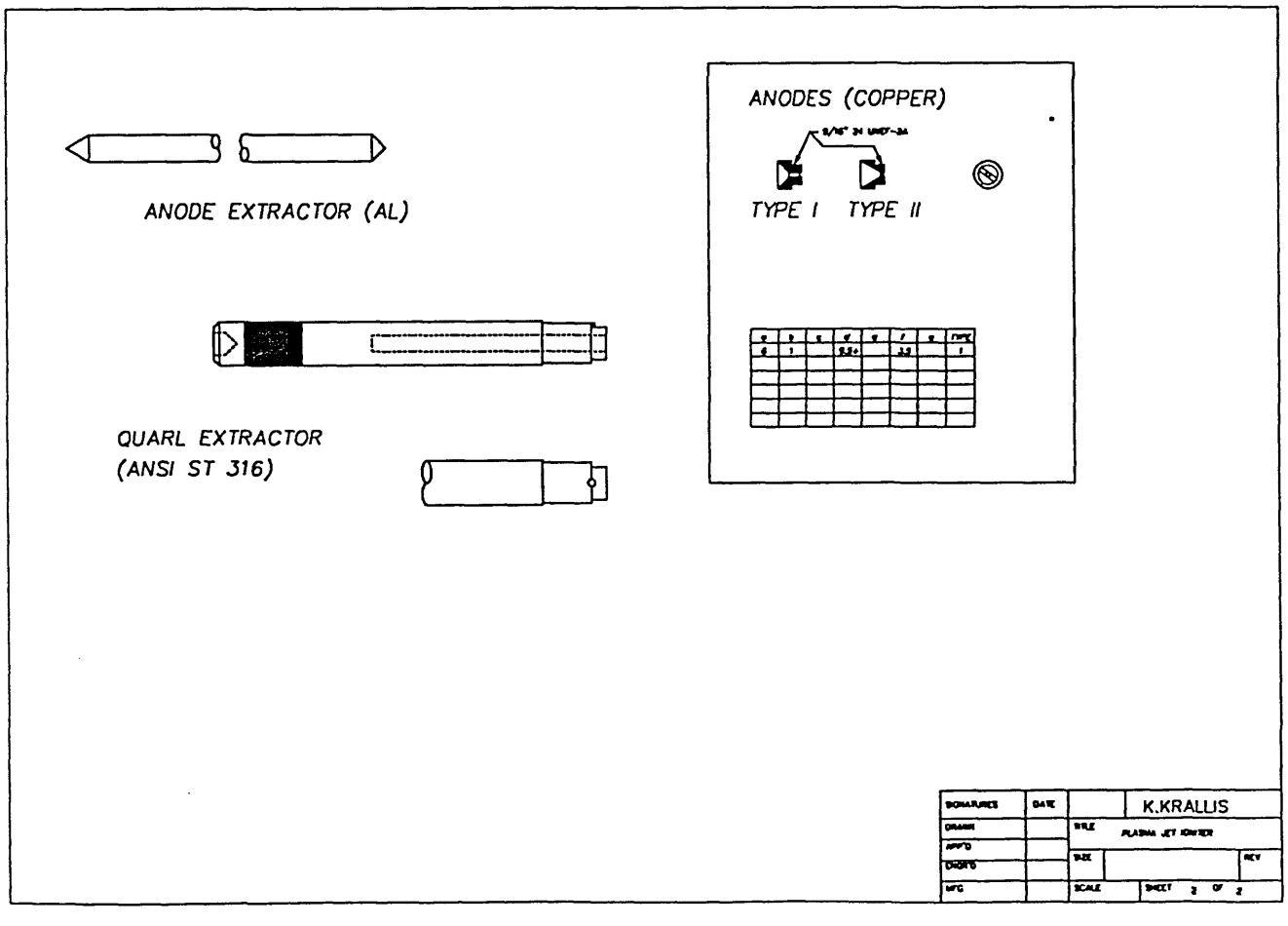


Figure 2.2b - Aerodynamically Spun Plasma Jet Igniter (cont.)

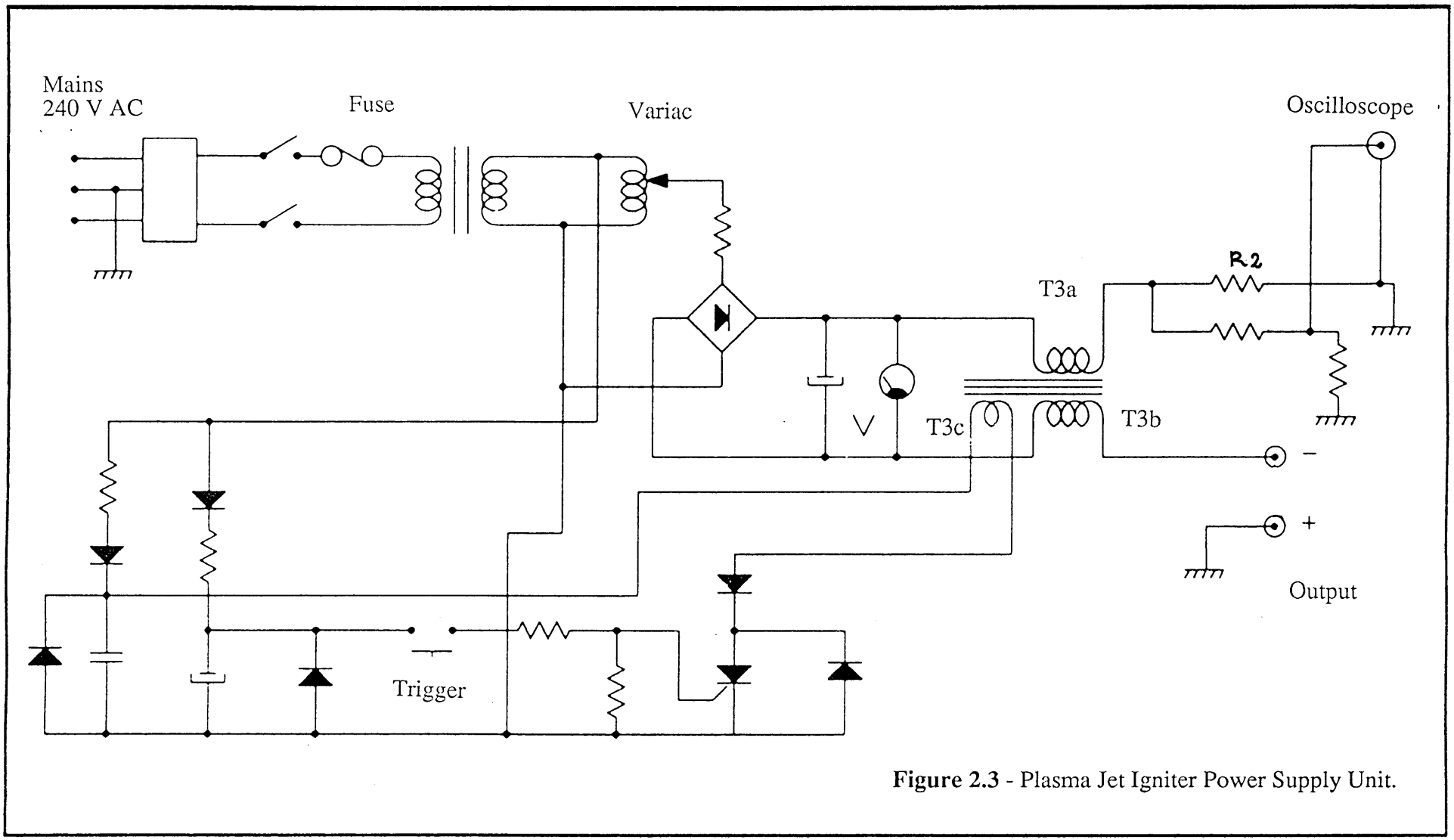


Figure 2.3 - Plasma Jet Igniter Power Supply Unit.

CHAPTER 3

EVALUATION OF A PLASMA JET AS AIRCRAFT ENGINE IGNITER

3.1 Introduction

Recently air engine manufacturers have been looking for more efficient igniters for air turbine engines [Low et al, 1989]. The main requirement is the ability to restart an engine in flight, under low temperature and pressure conditions and within set time limits, maybe 10 s maximum and preferably no longer than 3 s. When a flame-out situation occurs in an engine in flight, the pressure and temperature are too low to allow the engine to start again. Usually the aircraft has to descend to a much lower altitude where ignition becomes possible.

Starting a turbine engine is a difficult task, compared with reciprocating engines, mainly because of the high moment of inertia of the turbine and compressor assembly [Pellet, 1976]. The starting process involves the provision of an adequate and continuous volume of air at reasonably high pressure to the combustion chambers, effective atomization of the fuel and initiation of the combustion. As electrical motors capable of starting a large engine are quite heavy, pyrotechnic or pressurized air starting systems have been developed. If the flame is for some reason extinguished in flight, it is possible to restart the engine without the use of a motor, provided the aircraft flies low enough and fast enough to generate a reasonable pressure of air in the combustor. However the low temperature at high altitudes makes ignition of atomized fuel a difficult task.

The igniters used currently in aircraft engine combustors are of the coaxial surface discharge type. They work at relatively low voltages, about 2 kV, are capable of repeated action and deliver up to 12 J of energy in each spark. The spark takes place between a central electrode and the main body of the plug. A semiconductor pellet at the end of the plug allows a discharge to be struck at lower potentials. The operation is repeated automatically in 1 s intervals.

The front of the ignition plug is flush with the walls of the combustor in order to be protected from the high temperatures. This means that the initial flame kernel is near the cold wall of the chamber, far from the fuel rich area which exists near the fuel injector and flame propagation to fill the combustor chamber is difficult. More recent igniter designs, currently under test, are based on the pulsed plasma jet principle. In these igniters the discharge takes place in a small cavity at the end of the plug and the pressure developed in the cavity forces the plasma to be injected deep into the combustion chamber. The term ''focused plasma plug'' has been proposed to describe these devices.

The aerodynamically spun plasma jet described in the previous chapter has been tested for this application for two main reasons: its ability to project a sonic stream of gas deep enough in the combustion chamber while inducing a high level of turbulence and mixing effects and its ability to increase the reaction rate in the ignition zone by the injection of radicals using selected feedstock. Fortunately nitrogen and air are very effective feedstocks [Harrison and Weinberg, 1971] and pressurized air is often available aboard an aircraft.

A continuous plasma jet igniter suitable for use with the Rolls-Royce Spey engine was designed and built at Imperial College and later tested at the Smiths Industries facilities [Cheriyan and Weinberg, 1986; Cheriyan et al, 1990]. The results of the tests at atmospheric pressure and temperature were very encouraging, comparing well with the ignition systems used currently. In these initial tests the

duration of the arc in the plasma jet was longer than 1 *s* required the use of a large and heavy water cooled power supply connected to a 3-phase mains outlet, initially designed for flameholder applications. Figure 3.1 shows typical results of these experiments.

As the power supply used in these experiments was impractical for aircraft use, a small power supply based on capacitor discharge was designed, built and used in the phase of the work presented here. This power supply allows only short discharges, from a few milliseconds up to a few tenths of a second. Tests with this power supply were conducted in an ''explosion bomb'' [Boston et al, 1984], [Krallis, 1986] at the Dept. of Mechanical Engineering, University of Leeds. The effects of low pressure to the limits of flammability were investigated and showed that the continuous plasma jet igniter was very effective at pressures down to 0.2 *atma.* Additionally the behaviour of the plasma jet in the presence of high turbulence in the combustion chamber was investigated and the plasma jet was found to compare well with other ignition sources, including spark plugs and pulsed plasma plugs. Typical results of these experiments are shown in figure 3.2. It was decided then that the igniter should be tested under more realistic flight conditions.

3.2 Description of the Lucas Aerospace Altitude Testing Facility

The aerodynamically spun plasma jet igniter was evaluated as an aviation turbine igniter in a series of tests organized by Rolls-Royce plc at the Altitude Testing Facility, Burnley which is operated on behalf of the Ministry of Defence (Procurement Executive) by Lucas Aerospace Limited (now AIT Ltd), Fabrications Division. A test slot was made available by RAE Pyestock for the evaluation of ''State of the Art'' ignition technology. The test vehicle was supplied by Rolls-Royce plc in the form of a Spey triple sector rig Tay combustor.

Igniters were fitted in the port and starboard flame tubes with the plasma jet igniter in the port side. The standard igniter in the starboard position was not used. The plasma jet igniter was connected to the power supply described in chapter 2 and operated remotely from the control room. Approximately 4-5 discharges at 12 J could be achieved within 10 s when attempting an ignition test.

The test unit was installed in the Combustion Test Cell (CTC) as shown in the diagram of figure 3.3 [Lucas, 1988]. Air from the Cold Air Plant (CAP) was delivered to the rig through 15.2 *cm* diameter pipe via a controlling butterfly valve and air meter. Excess air was bypassed round the unit through a 23 *cm* diameter pipe and butterfly valve to exhaust. A dry compressed air supply system was connected to the plasma jet igniter. The air pressure was set by means of a manual valve and the air flow was controlled by means of a remotely operated solenoid valve.

An orifice plate metering device designed and installed to BS 1042 standards was used to measure the air mass flow entering the test unit along the 15.2 *cm* diameter pipe. The differential pressure across the metering device was measured using a water U-type manometer and the upstream static pressure at the meter was measured using an electrical manometer indicating in inches of mercury.

The air temperature at the meter was measured using the output from 2 resistance bulbs which was also used to indicate the air temperature to the unit. The temperature indication was displayed on digital meters in the test plan control room.

A copper-constantan thermocouple positioned at the rig inlet plane was used to measure the unit air inlet temperature. The temperature indication was by means of a digital meter situated on the test control panel. The inlet static pressure was measured from two off pressure tappings and displayed on an electrical manometer in inches of mercury. From this value, and the Rolls Royce plc Q-curves, the total inlet pressure was derived for a given inlet effective area of 0.012 m^2.

Indication of successful ignition was provided by six chromel-alumel thermocouples, two for each flame tube, positioned in the air stream near the exhaust plane. The thermocouples were connected to a pen recorder as was an event marker for the rig fuel solenoid valve. An additional thermocouple of the same type was positioned in the exhaust duct and connected to a digital meter to show exhaust temperature.

The fuel used throughout the test period was Avtur to specification DERD 2494 with a specific density of 0.800 @ 288 K (Appendix A). A diagram of the fuel supply system is shown in figure 3.4. The fuel was supplied from a header tank in the ATF fuel chamber and metered by float in tube type flowmeters before being pumped to through the ATF fuel cooler. The fuel passed from the cooler to a rig/spill solenoid valve system. The spill system incorporated a non-return valve and an adjustable restrictor to correspond with the flow number of the rig fuel sprayers together with a steam heated bath containing copper coils immersed in warm water to increase the fuel temperature to a nominal 290 K prior to return to the header tank. The delivery temperature of the fuel was measured using a copper-constantan thermocouple positioned in the supply line to the burner manifold. A thermocouple was also positioned in the fuel spill line to indicate fuel temperature stability before the flow to the rig was switched on. A pressure gauge just upstream the burner manifold indicated fuel delivery pressure.

3.3 Test Procedure

The procedure of the ignition tests was as follows:

(i) The required air inlet temperature, pressure and mass flow were set. Then the air supply to the plasma jet igniter was set to the required pressure for sonic flow through the nozzle.

(ii) The required fuel flow was preset through the spill system.

(iii) When the fuel temperature was stabilized at the required value, the fuel was switched from the spill system to the rig and a 5 *s* priming period started. Ignition was attempted for a maximum of 10 s which allowed for 4-5 discharges, each of 12 *J* energy.

(iv) The time to light was measured by stopwatch. A failure to light was recorded after 10 *s* of attempted ignition. A series of single search points was conducted to define roughly the limits of full ignition, partial ignition and no ignition. These were followed by detailed boundary definition. One failure to light on any of three ignition attempts classified the point as being in the non-ignition area. The time to light was taken as the longest of the three ignition attempts.

3.4 Results

Ignition points were conducted at the following conditions:

Air inlet pressure (*atm*):	0.41	0.54
Air inlet temperature (*K*):	265	286
Fuel temperature (*K*):	273	273
Igniter upstream pressure (*atm*):	1.5	2.0

The results obtained under these conditions are shown in figures 3.5 and 3.6. The igniter performed well at 286 *K* and the 10 *s* loop was well outside the stability envelope of the combustor. The 3 *s* loop follows the stability envelope and is slightly shifted towards the fuel rich area. Reliable ignition was possible even with a fuel-to-air ratio of approximately 0.01 by mass.

It seems that the plasma jet igniter was unable to ignite mixtures at the lower temperature of 265 K. The reason for this irregular behaviour could be attributed to the very low amount of fuel being in the vapour phase at this low temperature ranges. As the combustion enhancement mechanism of the plasma jet igniter when fed with nitrogen is based on the action of free radicals it involves reactions in the gaseous state and is not a particularly effective igniter of liquid sprays. The mean enthalpy of nitrogen is very low, approximately 15 $kJ \cdot mol^{-1}$ and is not very effective in evaporating enough fuel to produce combustible mixture.

3.5 Proposed use of Methane as Plasma Medium

The results of the experiments described in 3.4 prompted some investigation on the use of a fuel gas as feedstock to a plasma jet which would be more suitable for ignition of liquid sprays or dusts. When the continuous plasma jet was used as flame stabilizer, an application which demanded prolonged operation of the device, it was decided to avoid using hydrocarbon feedstock for two reasons: It would produce small amounts of cyanide gas thus introducing an unnecessary hazard in a research environment and elemental carbon would be released and deposited on the cathode electrode changing the gap dimensions and perhaps blocking the gas channel. As these potential problem sources would be much less important if the plasma plug operated in short bursts, it was decided to investigate the use of methane as a possible plasma medium. The inherent inability of the plasma jet igniter to ignite low temperature liquid sprays prompted us to consider this possibility.

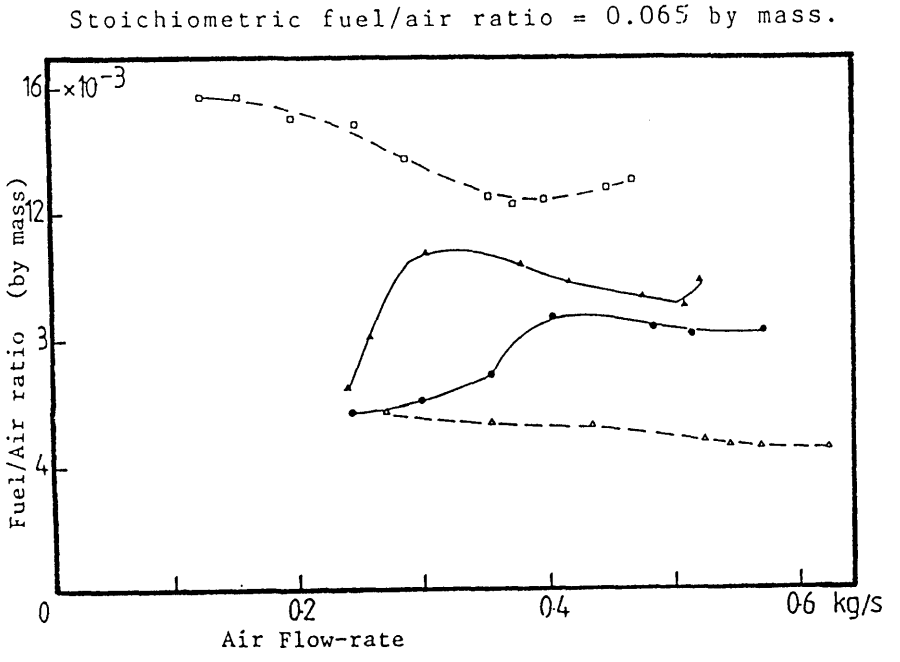
Only a few preliminary tests were actually done and a few cin´e sequences using the self-luminosity of the plasma were recorded (plate 3.1). The same electrical energy input of 12 J was used as in the previous experiments. It was found that a large flame plume is projected into the combustion chamber at the sonic velocity of

the jet and it lasts some 5 *ms*. After that the methane plasma jet remains active for another 5 ms. The flame plume reaches a length of approximately 25 *cm* and a maximum diameter of 3.5 *cm*.

It was also found that after repeated discharges through methane feedstock the amount of soot deposited on the cathode was actually very small and under these operating conditions (infrequent short bursts) a blocking of the gas channel or a short circuit between the electrodes is extremely unlikely. Plate 3.2 is a microphotograph of the cathode after repeated firings.

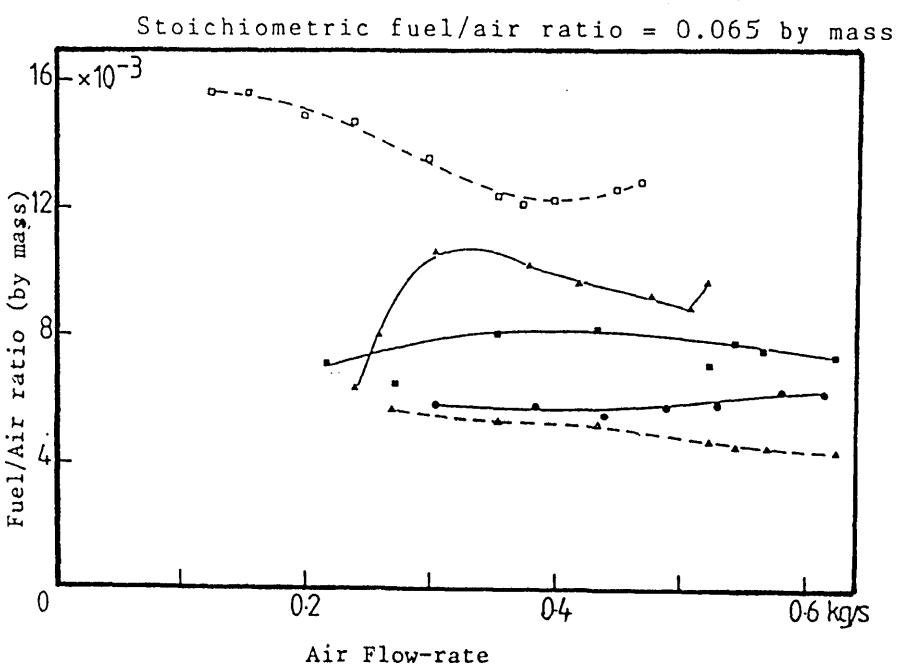
These results show that a very powerful igniter could be designed based on a fuel fed aerodynamically spun plasma jet. Such a device would overcome the problem of not having a rich fuel/air mixture to ignite, as the heat energy released by the combustion of the feedstock would vaporize enough fuel to sustain the combustion. Methane is not the only possible feedstock. The small masses of fuel required per firing could be contained in a tiny volume or ejected by a piston, though vaporized aviation fuel might be preferred for aircraft use [Cheriyan et al, 1990]. It seems likely that, with the possible exception of pyrotechnic devices, such an igniter would provide the most powerful combination of flame and chemically active plasma yet developed for use at low temperatures under fuel-deficient conditions.

Another possibility in this line of investigation would be to test a methane fed continuous plasma jet as a means to provide reliable ignition to coal and heavy oil burners. This would require perhaps a water cooled plasma jet igniter which would protrude deep enough in the combustor to reach the primary combustion zone of the burner.



Anode: cone angle 90 , Cathode: 2% thoriated tungsten; diameter I/8". Electrode spacing 300 m
Feed gas : nitrogen. Flow-rate : 300cc/s

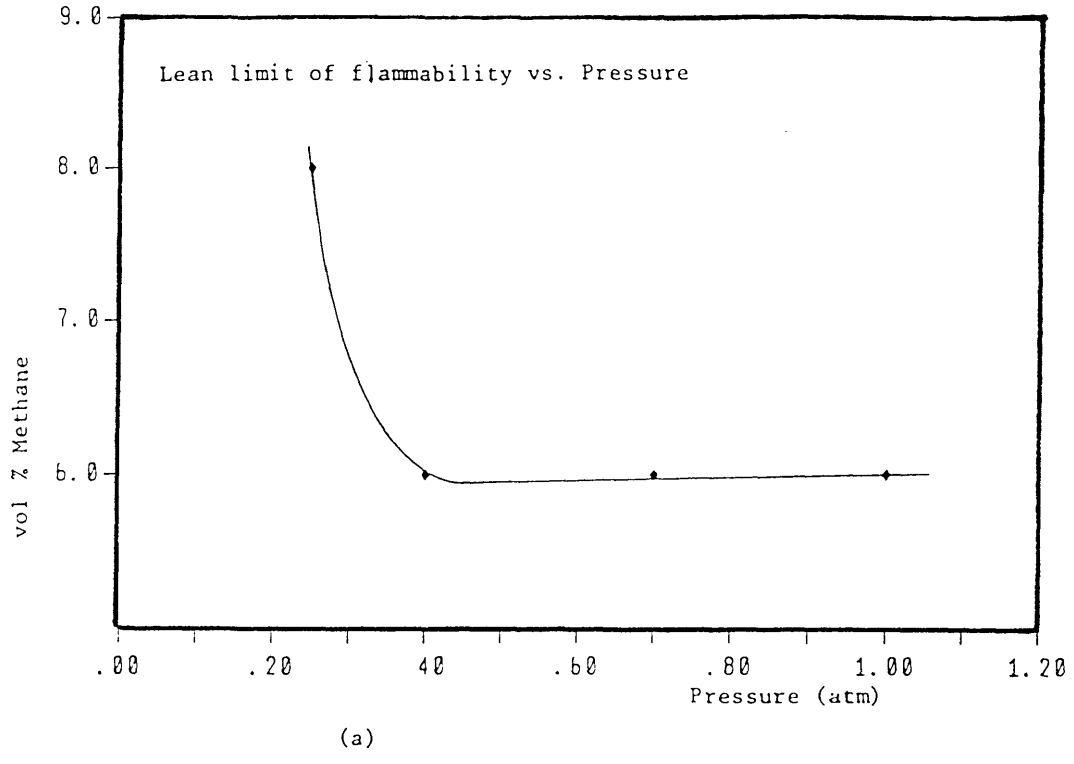
	Protrusion	Power input	Orifice dia.
(●)	39mm	I.75kW	2mm
(■)	35mm	I.69kW	2mm
(▲)	29mm	I.75kW	I.4mm
(□)	37mm	Standard igniter (i.e. surface discharge plug)	
(△)	Blow off characteristic of the "can"		



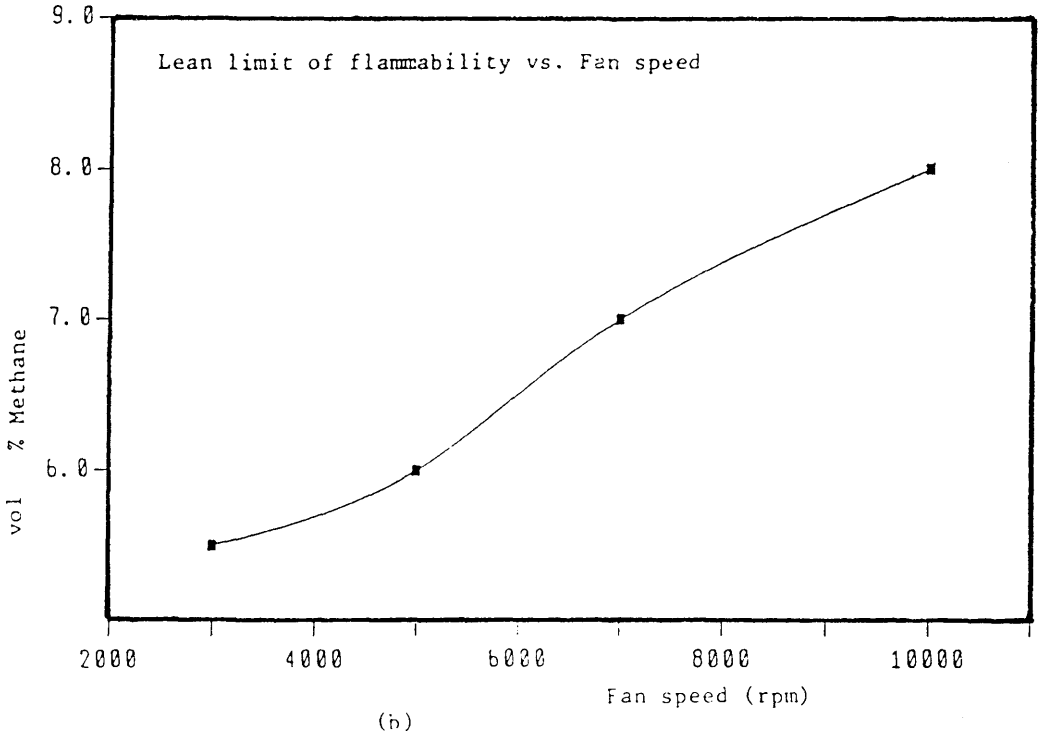
Anode: cone angle 90 , orifice diameter I.4mm
Cathode: 2% thoriated tungsten; diameter I/8"
Electrode spacing 300 m
Power input: I.75kW
Air flow-rate: 290cc/s. Nitrogen flow-rate: 300cc/s

	Protrusion	Gas
(▲)	29mm	Nitrogen
(●)	29mm	Air
(□)	37mm	Standard igniter (i.e. surface discharge plug)
(△)	Blow off characteristics of "can"	

Figure 3.1 - (a) Comparison between nitrogen and air plasma jets, (b) Effect of protrusion on the ignition loop.



(a)



(b)

Figure 3.2 - Lean methane/air ignitions. (a) Effects of pressure, (b) Effects of turbulence, (c) Comparison with other igniters.

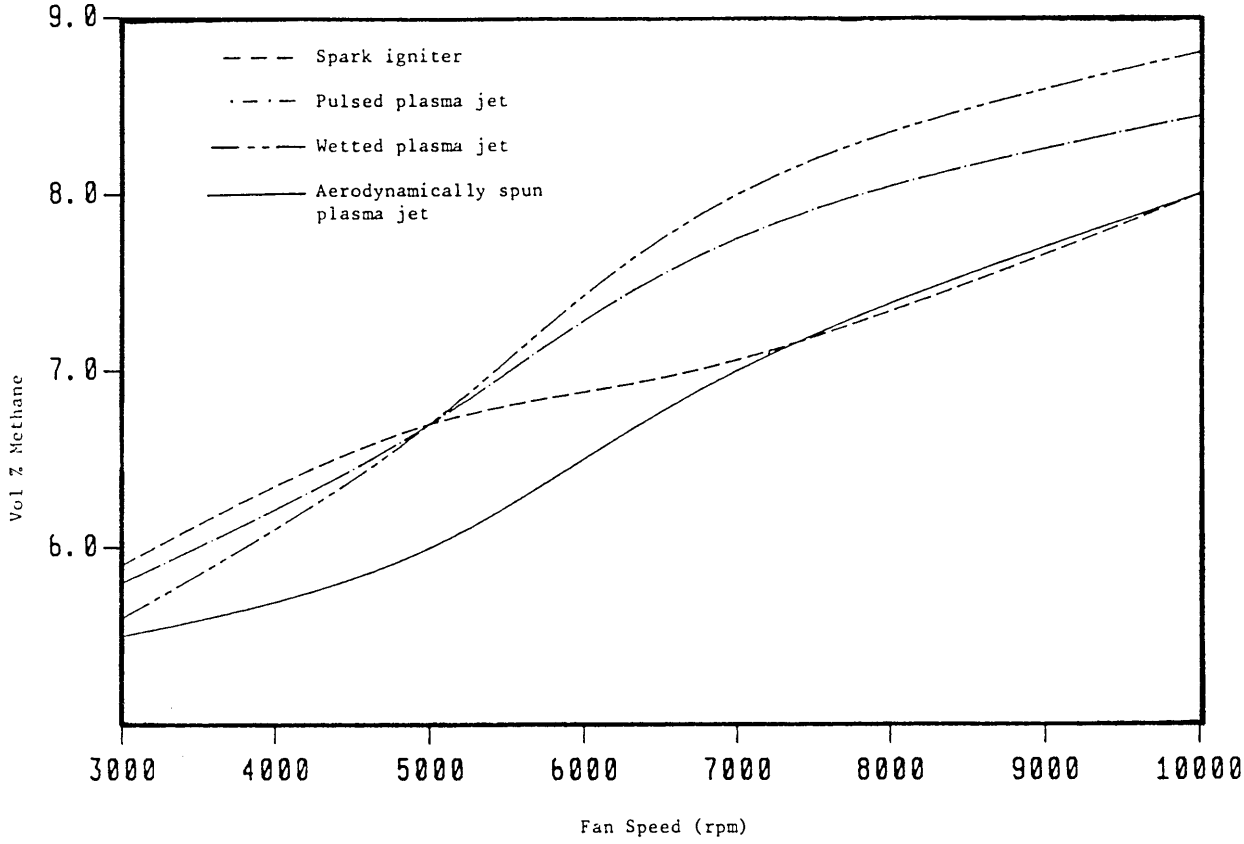

9.0
8.0
7.0
6.0
Vol % Methane
Spark igniter
Pulsed plasma jet
Wetted plasma jet
Aerodynamically spun plasma jet
3000
4000
5000
6000
7000
8000
9000
10000
Fan Speed (rpm)

Figure 3.2c.

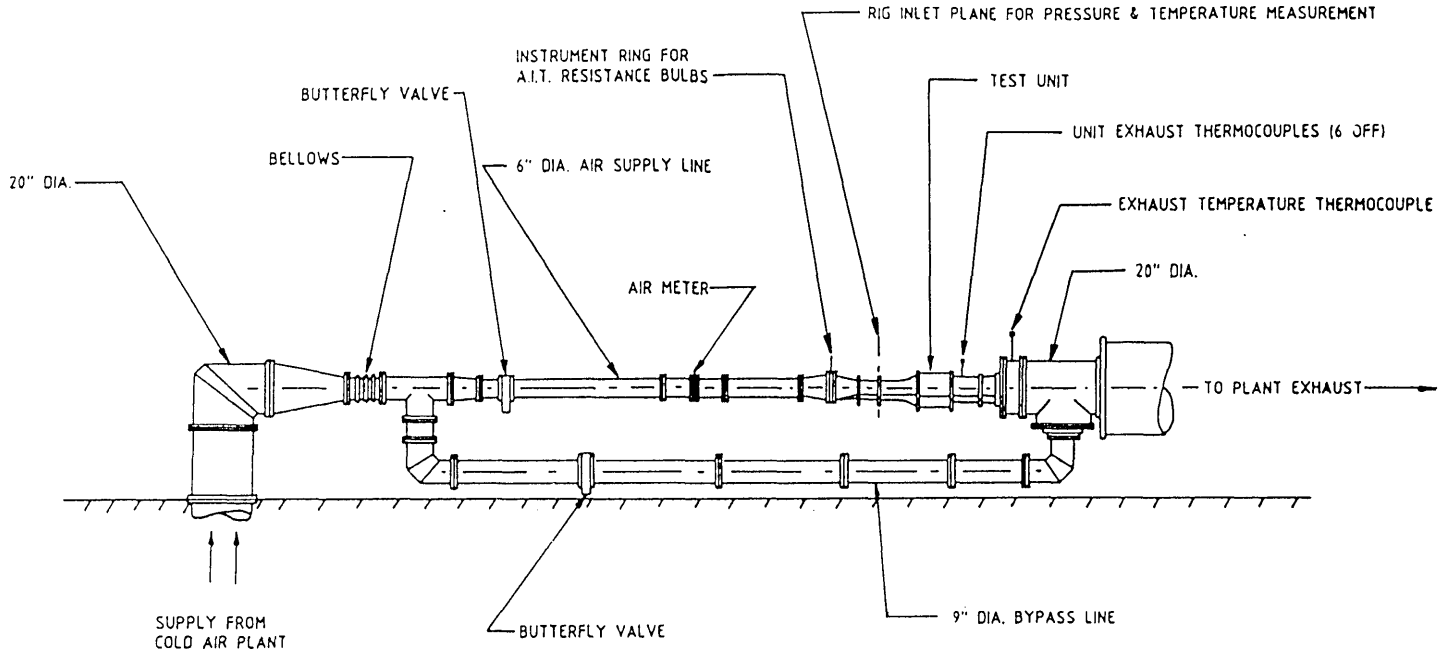


Figure 3.3 - Altitude Testing Facility, Burnley.

IGNITION TESTS ON A PLASMA JET IGNITER FITTED IN A TAY TRIPLE SECTOR RIG. DIAGRAM SHOWING RIG ARRANGEMENT IN COMBUSTION TEST CELL.		
REF. HC 2205	LUCAS AEROSPACE LTD. COMBUSTION TECHNOLOGY AND ENGINEERING CENTRE. ALTITUDE TEST FACILITY.	ATF 1095
DATE MAY 1988		FIG

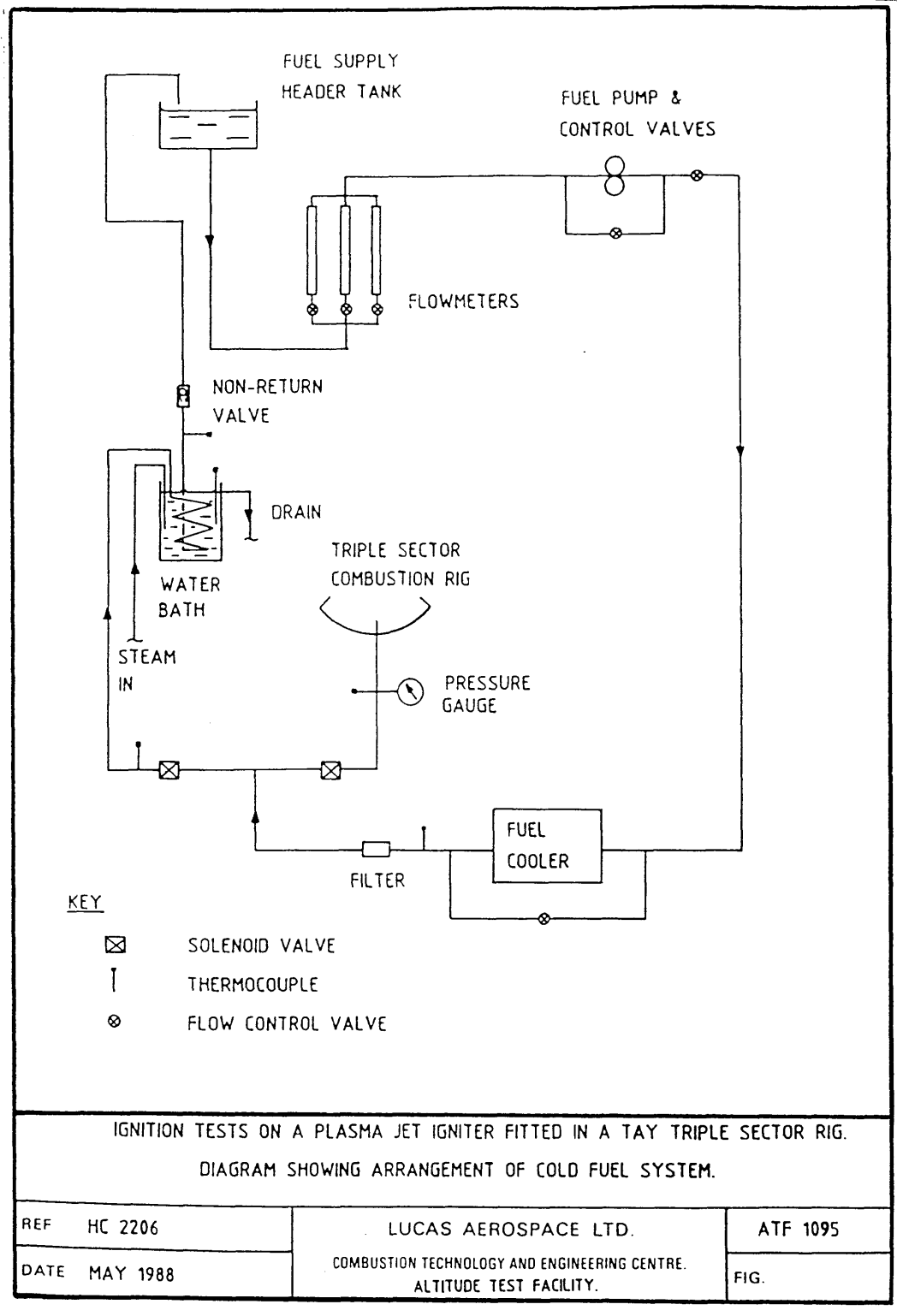


Figure 3.4 - Altitude Testing Facility - Fuel Supply System

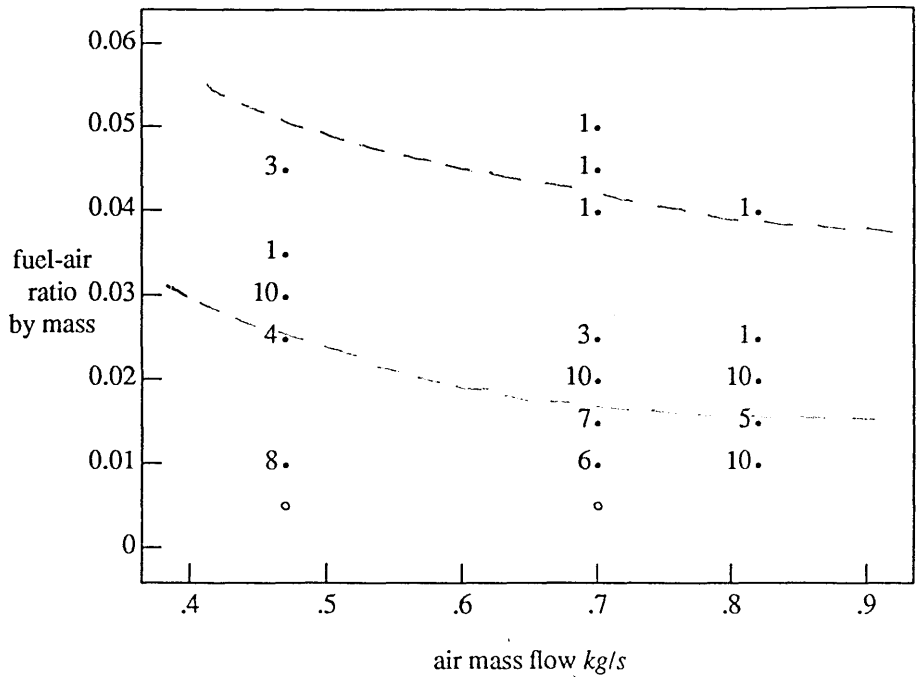


Figure 3.5 - Lucas ATF ignition results, 0.54 at, 286K. •: ignition at time shown, O: no ignition,

- - - : stability envelope of burner.

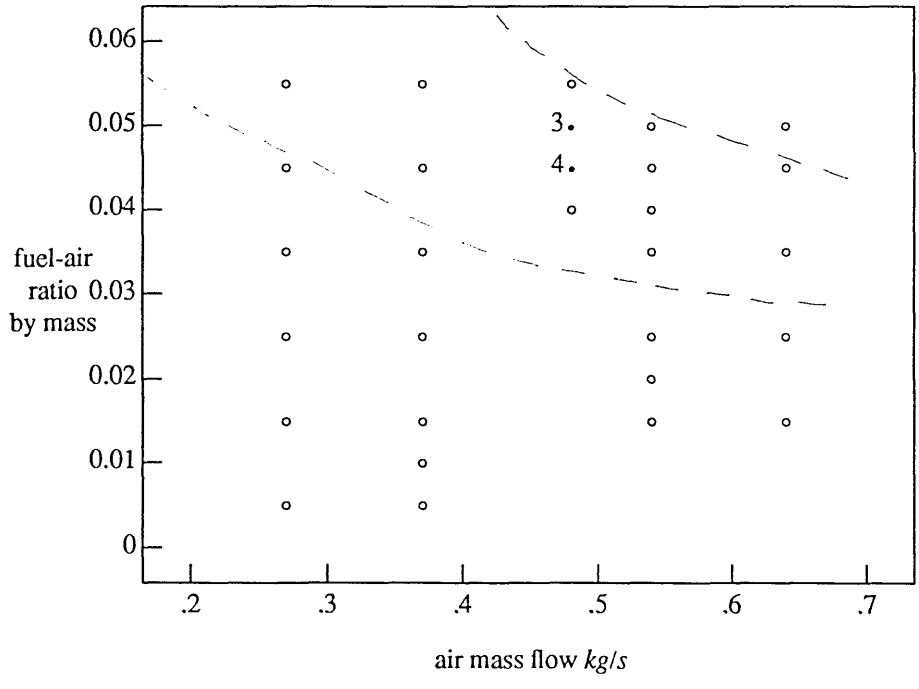


Figure 3.6 - Lucas ATF ignition results, 0.4 at, air temperature 265 K.

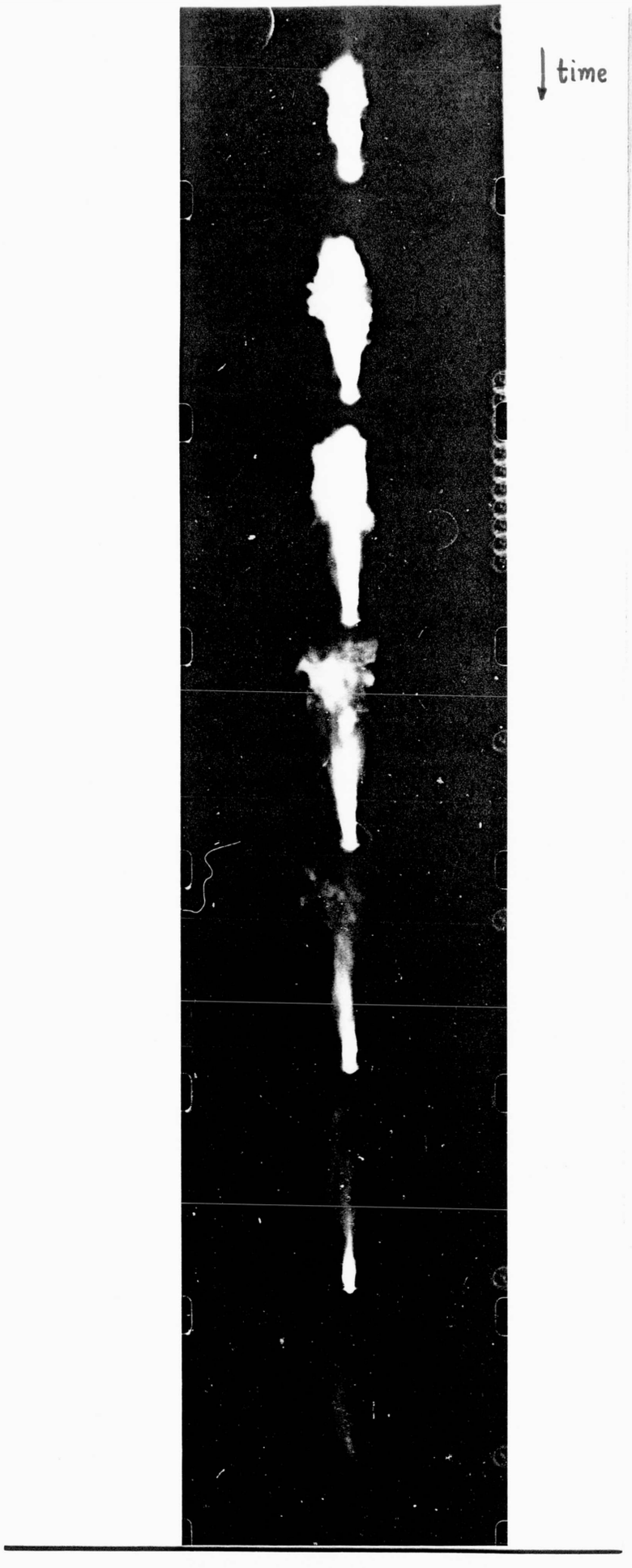


Plate 3.1 - Cine sequence of plume ignition at 800 f.p.s. Gas flow upwards from 1.2 *mm* diameter orifice.

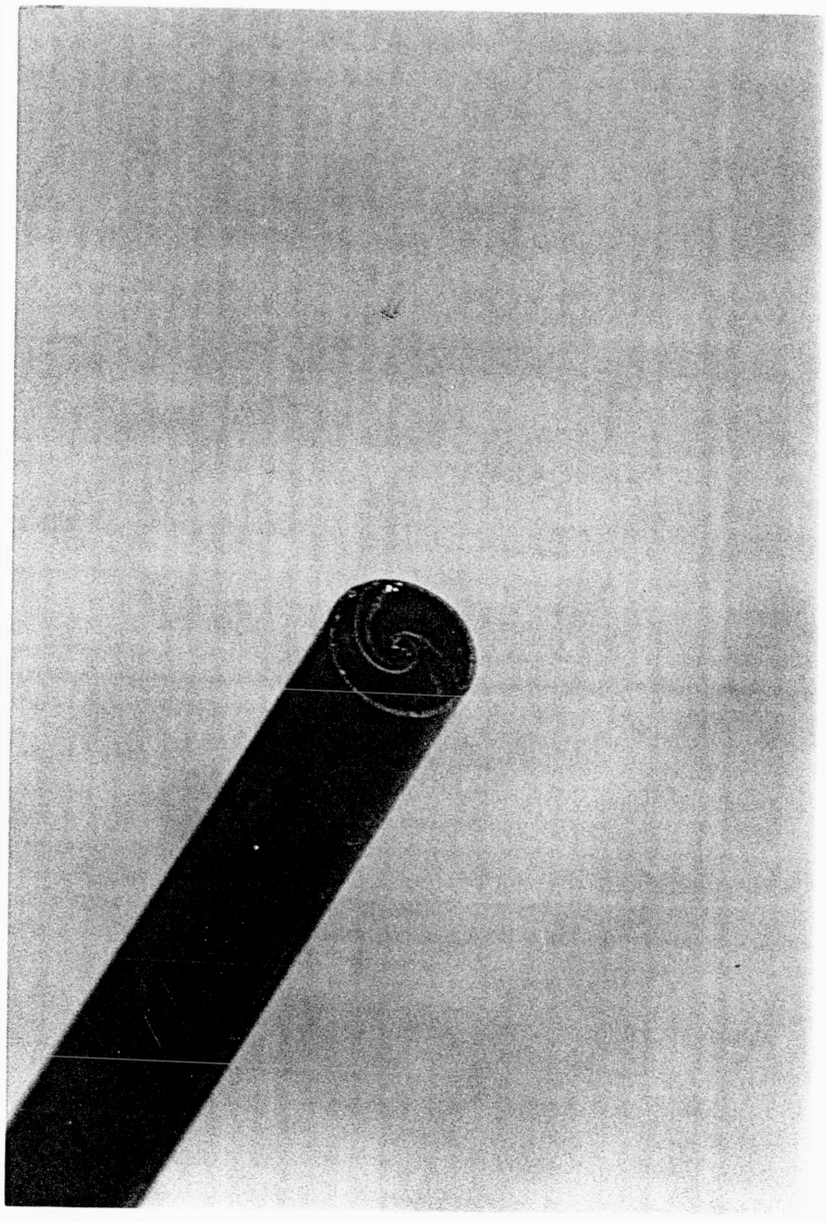


Plate 3.2 - Micrograph of cathode after 40 firings, with methane as plasma medium. Diameter: 4 *mm*.

CHAPTER 4

HAN BASED LIQUID PROPELLANTS AND THEIR APPLICATIONS

4.1 Pulsed Plasma Plugs - Applications - Liquid Propellant Guns

In addition to the continuous plasma jets described in chapter 2, there is another family of plasma generating devices, the pulsed plasma jets or plugs (PPJ), in which power is applied intermittently as a strong electrical pulse of high voltage and there is no continuous gas flow. The plasma ejection is produced by the heating effect of the discharge and, in special cases, by exothermal chemical reactions in the cavity.

The pulsed plasma plug devices evolved from the standard spark plugs used in internal combustion engines and the surface discharge plugs used for jet turbine ignition [Pallett, 1976] and they operate from power supplies of roughly the same physical size. Figure 4.1 shows typical pulsed plasma plug design [Weinberg, 1978; Weinberg, 1986]. Although they are similar in shape and size to spark plugs, the discharge does not take place directly in the combustion chamber but in a small cavity within the plug. The volume of the cavity is typically 30 μl, and its shape varies. The front of the cavity terminates in an orifice that injects the plasma at high velocities into the main combustor. In plugs used for research there is provision for a small diameter pipe which can be used to feed a fluid of our choice into the cavity, in order to produce specific plasma effects independently of the the nature of the gases contained in the main combustion chamber.

Power supplies used in conjunction with these plugs are based on capacitor storage and can typically supply pulses of up to 12 J to the electrodes. Capacitance is of about 50 μF and the capacitors are charged to voltages of a few hundred up to 2000 V.

The main parameters that can be varied in order to achieve specific results are the size and shape of the orifice aperture, the volume of the cavity, the feedstock and the amount and rate of electrical energy input. These parameters define the temperature, composition and depth of penetration of the plasma jet and the amount of turbulence induced in the combustor. The additional turbulence and mixing induced in the combustion chamber by the plasma jet igniter seem to be very effective means of accelerating flame propagation [Weinberg, 1978]. Acceleration of the flame front propagation by up to one order of magnitude has been reported with H_2 and CH_4 fed plasma plugs. In addition to increased mixing, free radicals like OH and H, produced by the fragmentation of the feedstock molecules, are injected in the combustor and they can accelerate the critical intermediate steps of flame propagation reactions [Vosen et al, 1984]. Often the cavity is filled with a specific gaseous feedstock which produces the desired free radicals. Sometimes liquid plasma media (for example light hydrocarbons and alcohols) are fed into the cavity and allowed to vaporize from a porous sleeve [Warris and Weinberg, 1984]. Metal hydrides have also been used and they produce hydrogen when heated by the discharge. Finally liquid propellant feedstock of high specific energy content can be used. Because of the large chemical energy release, such propellants are capable of producing very high energy plasma discharges, even of inducing detonations is a combustible mixture.

Pulsed plasma plugs were considered initially for use in internal combustion engines, especially for lean-burn engines working near the lean mis-fire limit, replacing standard spark plugs [Asik et al, 1977; Wyczalek et al, 1975; Tozzi and Dabora 1982; Dale et al, 1978]. Plasma jet igniters proved to be more insensitive to timing

than ordinary spark plugs and helped reduce the pollutant formation by burning leaner mixtures. Mis-fire normally was avoided with these novel igniters and reliable ignition was possible up to the normal lean limit of flammability. The effects on flame propagation and sooting for fuel rich mixtures has also been studied [Vince et al, 1984]. The main obstacles in use of pulsed plasma plugs in internal combustion engines are the high energy demand from the car electrical system and the high rate of erosion of the electrodes. Depending on firing rate and electrical energy input, the lifetime of a plug can be as low as a few tens of hours. These effects could be minimized by liquid-fed low energy plugs. Such obstacles are not limiting, however, in other applications, like aircraft turbine ignition [Boston et al, 1984; Low et al, 1989] and diesel engine starting under adverse temperature and/or pressure conditions, and for such applications pulsed plasma plugs may soon be seen in regular use.

Plasma plugs fed with conventional feedstocks release very little chemical energy compared to the electrical input and electrical efficiencies of up to 20% have been reported. If we want to release higher amounts of chemical energy, we can fill the cavity with an explosive condensed phase. A liquid monopropellant mixture is well suited for this application. Energy densities of liquid propellants are such that some $50\,J$ of chemical energy can be released from a $30\,\mu l$ cavity [Carleton et al, 1987]. With a larger cavity, the chemical energy can be one order of magnitude higher than the electrical energy release of the plasma plug. When such a large amount of energy is released, a significant rise in pressure in the form of a shock wave can originate from the plasma jet and propagate for some distance in the combustion chamber. Such plasma ejections accompanied by shock waves could be sufficiently powerful to initiate detonations in nearly stoichiometric gaseous mixtures. Such shock waves are desirable in some applications but present a serious hazards to others, like the liquid propellant gun described later.

There are some specialized applications which require such large amounts of ignition energy. One example is a special steam generator developed and tested by British Petroleum Company for enhanced oil recovery of viscous crude oils [Chesters et al, 1981]. This device consists of a high pressure (typically 70 *bar*) burner which is inserted in the production well and operates in quasi-detonation mode in order to decrease the rate of heat transfer to the walls of the burner so they don't melt. The burner can produce 0–10 *MW* of heat power when operated at an ignition frequency of 0–5 *Hz* and the intensity of combustion is approximately 1300 $MW \cdot m^{-3}$. The team who designed the burner were looking for a special igniter capable of producing the energy release required to initiate the detonation and which could be capable of repeated firing, so they considered the pulsed plasma plugs and found them well suited for their application. A plug which can directly produce a shock wave would be advantageous in this application. It seems however that this project was later shelved temporarily in favour of other oil recovery techniques, so no further development of detonation generating plugs was undertaken.

Another potential application for a high energy electrical igniter [Klingenberg et al, 1989] is the regenerative liquid propellant gun (RLPG). Liquid propellant guns (LPG) have been considered for a long time but only recently has the progress in propellant and gun technology made such weapons appear practical for military use. In the past the most important advantage of the liquid propellants were considered to be their high specific energy content. However, the results of recent studies show that the fluid nature of the propellant is more important in determining the value of LPGs.

The interior ballistic process of conventional guns is based on the rapid generation of gas by the combustion of a solid propellant charge. The gas generation rate depends on the (linear) burning rate and the total exposed surface of the propellant grains. These are determined by the chemical formulation of the propellant and the shape of the grains respectively. The shape of the grain determines production and

packaging techniques and generating the required pressure vs. time characteristics involves complex grain shapes and special packaging. All these requirements complicate packaging, storage and logistics of ammunition and the design of guns and combat vehicles.

In contrast to solid propellant guns, liquid propellant charges are formed inside the the gun by metering the propellant into the combustion chamber [Morrison et al, 1988]. The surface area required for combustion of the propellant charge on the time scale of the ballistic cycle is generated as the charge burns. This results in an increase in the complexity of the gun but has other important advantages: Propellant formulation and processing can be made simpler, cheaper and safer. Propellant packaging can be designed to simplify transport and storage efficiency.

There are three basic approaches to the design of a LPG: bulk loading (BLPG), externally powered injection and regenerative injection (RLPG). In the bulk-loaded gun, propellant initially fills the chamber behind the projectile. These guns use bipropellant or nonhypergolic monopropellant systems which require an external ignition source to initiate combustion. The surface area required for propellant combustion is generated by breakup of the gas-liquid interface separating the bulk of the liquid and the combustion products. For guns based on propellant injection, the propellant is pumped into the combustion chamber during the combustion cycle and the combustion process is, in some respects, similar to that taking place in a liquid propellant rocket engine. The rate of gas generation is controlled by the propellant injection process. If a bipropellant is used, the injection process provides breakup and mixing of the fuel and oxidizer. Vaporization of the droplets and diffusion of the vapour control the combustion process. Both hypergolic and nonhypergolic propellant combinations can be used in this application. If a monopropellant is used, breakup of the liquid jet in the combustion chamber creates the burning surface. The externally powered gun requires an external source of high pressure to inject the propellant. Pressurized air

has been considered as an external pressure source. The regenerative injection system uses the combustion chamber pressure, which is applied to the the propellant in a reservoir by a differential energy piston, to inject the propellant against the high pressure in the chamber.

Electric spark ignition, which is simple and reliable, is normally used in bulk loaded guns. Peak currents of up to 1400 A are produced by discharging a 50 μF capacitor charged to 2 kV. Total spark energies range from 25 J (unreliable) to 150 J (excessive). The duration of the pulse is 0.4 to 1 ms.

A simple RLPG is shown in figure 4.2. It consists of a standard gun tube attached to a chamber containing the regenerative piston. The head of the piston divides the chamber into the combustion chamber and the propellant reservoir. The length of the reservoir and its volume are defined by a breach element through which the the piston staff extends. A number of cylindrical channels are cut into the head of the plug. These channels are initially sealed to prevent leakage of propellant into the combustion chamber before ignition.

The pressure vs. time diagram of a RLPG firing [Morrison et al, 1988] is shown in figure 4.3. The igniter initiates the process by pressurizing the combustion chamber and forcing the piston backwards, pressurizing the propellant reservoir. As the area of the combustion chamber face of the piston is larger than the area in the storage chamber, it provides the differential pressure required for injection of the propellant.

The second phase is an ignition delay. During this period the piston continues to move backwards injecting propellant which accumulates in the combustion chamber. When the liquid ignites, the pressure grows until it reaches the operating pressure and the piston accelerates to its maximum velocity. Phase 4, is a quasi-equilibrium state in which the flow of the gas products down the barrel of the gun is balanced by freshly injected propellant. The final phase is the expansion of the combustion gases after combustion has ended.

It is obvious from the description of the RLPG operation cycle that a heavy duty igniter is required. Igniter designs for RLPGs used to be quite simple and robust. More recently experiments have been carried out with solid propellant charges burning in a small combustion chamber mounted outside the gun which injects high pressure hot gases into the main combustion chamber. Even secondary booster charges have been used in some cases to augment the primary ignition charge and prolong the gas generation. These systems tend to be complex and impractical for weapon systems, so different solutions have been investigated. One of them [Klingenberg et al, 1989] is using a small liquid propellant charge initiated electrically (figure 4.4). A liquid propellant system based on the plasma jet principle could be easily automated and use the same feedstock as the main gun charge, eliminating the logistic problems of separate solid propellant igniters. Such a system is being actively developed by General Electric, Inc. A 2-stage igniter based on the same principle has been designed and tested by U.S. Army, Ballistics Research Laboratory staff in which a 0.5 cm^3 liquid propellant charge is initiated and then vented into an antechamber containing a booster charge of 12 cm^3 of the same propellant.

4.2 Energetic Materials - Liquid Monopropellants

Liquid propellants are just one class of energetic materials. The term ''energetic materials'' covers nearly all materials, either pure substances or mixtures, that contain a large amount of chemical energy which can be released, under certain conditions and after some kind of initiation, in a short time in the form of a large volume of expanding hot gases. These materials are divided in two main families, ''(high) explosives'' and ''propellants''. Under the conditions of their normal use, (high) explosives detonate while propellants deflagrate. This does not mean that propellants are incapable of transition to detonation under different conditions, especially at higher pressures or if discontinuities exist in their mass. Some materials can be

classified both as propellants and as explosives [Fordham, 1980].

Propellants are stored in either solid or liquid form, as gases have too low an energy content per unit volume to be of any use [Kit and Everet, 1960]. Solid propellants are used mainly as gun and rocket propellants while liquid propellants have been used up to now only in rocket propulsion systems. There are also some other applications of propellants, such as engine starter cartridges and electrically actuated devices, which are normally classified as ''pyrotechnics''. Fuel and air mixtures used by air breathing engines of all kinds (turbojet, turboprop, ramjet, diesel etc) are not normally characterized as propellants although their chemical composition is very similar, as the oxidant is not carried in a condensed phase on the vehicle itself.

Solid propellants are necessarily monopropellants while liquid propellants can be either monopropellants or bipropellants. Hybrid systems of solid and liquid propellants have been developped as well. Monopropellants contain in the same liquid mixture (and sometimes in the same molecule) both the fuel and the oxidizing agent while bipropellants are systems of two liquids which are stored and fed to the combustion chamber separately. Some bipropellant systems, which are described as ''hypergolic'', ignite spontaneously when the two liquids come in contact. Typical hypergolic mixtures are those of fluorine and hydrazine. Nonhypergolic propellants systems, like hydrocarbon-LOX, always require some external source of ignition.

The requirements for a propellant substance or system, especially the ones used in critical aerospace applications, are quite strict. A propellant must be chemically stable and, if liquid, maintain its state (neither freeze or vaporize) under normal storage or operating conditions yet must decompose completely and immediately one it has been ignited. Also it must not be very corrosive. Some applications have special requirements regarding smoke release, electrical conductivity etc.

While there is a wide choice of solid propellants or liquid bipropellants, only a few liquid monopropellants have been found to fulfill the above requirements, the

most widely used being ethylene oxide ($(CH_2)_2O$), nitromethane (CH_3NO_2) and hydrogen peroxide (H_2O_2). A liquid monopropellant must be stored outside the combustion chamber and be pumped into it, so special precautions must be taken to avoid premature ignition.

4.3 HAN Based Aqueous Monopropellants

4.3.1 General

These propellants belong to a class of monopropellants characterized by water miscibility, ionic character and use of the nitrate ion (NO_3^-) as oxidizer. A variety of cations are combined with other substances to provide the desired properties of the propellant.

An aqueous monopropellant of historic interest which contains no carbon is a mixture of 30% hydrazine nitrate, 65% hydrazine and 5% water, which decomposes according to the scheme [Klein, 1988]:

$$4N_2H_5NO_3+N_2H_4 \rightarrow 7N_2+12H_2O \qquad (4.1)$$

Although this propellant is thermodynamically the best choice for a liquid propellant gun, it was abandoned because it is very toxic, thermally unstable, has a high freezing point and a poor rate of energy release. Some formulations using hydroxylamine ($NH_2{-}OH$) in place of hydrazine were also tried.

The hydroxylamonium nitrate mixtures were initially developed for applications involving presence of small quantities of water which would affect the performance of normal propellants in an unpredictable way. Their use as gun propellants was proposed by researchers at the Naval Ordnance Station, Indian Head, MD, USA. Many modifications and improvements have taken place and a series of mixtures to

suit specific applications have been produced.

The HAN based aqueous monopropellants are liquid systems [Klein, 1988] of at least three substances: hydroxylamonium nitrate (HAN) which contains a surplus of oxygen, a water soluble fuel with oxygen deficit, and water. They have good properties (low toxicity and low sensitivity) and a high electrical conductivity. They are described in more detail in the next paragraphs.

4.3.2 Hydroxylamine and Hydroxylamonium Nitrate

Hydroxylamonium nitrate (HAN) is the nitrate salt of hydroxylamine $NH_2–OH$ which can be considered a derivative of ammonia NH_3 with one of the hydrogen atoms substituted by a hydroxyl radical. Hydroxylamine is a weak base, about 2000 times less basic than ammonia. This is attributed to the electronegativity of the hydroxyl group compared with the hydrogen atom it substitutes. Because of the reduced basicity of hydroxylamine, HAN solutions in water have a lower pH than NH_4NO_3 solutions of similar concentration.

Regarding its behaviour against oxidizing and reducing agents, hydroxylamine can be viewed as a cross between hydrazine $NH_2–NH_2$ and hydrogen peroxide, $HO–OH$. Both hydrazine and its derivatives and hydrogen peroxide are widely used as components of rocket (bi)propellants, hydrazine as a very energetic fuel and hydrogen peroxide as a very active oxidizer. Hydroxylamine behaves as a hybrid of these two substances, having some of the oxidizing character of hydrogen peroxide and the reducing character of hydrazine. The nitrate ion is a stronger oxidizing agent than hydroxylamine so reaction between NH_3OH^+ and NO_3^- normally involves oxidation of the hydroxylamonium ion and reduction of the nitrate. As HAN contains more oxygen atoms than the number required for complete self-oxidation, it can be used as oxidizer combined with a suitable fuel to form an oxygen balanced

monopropellant system. The effects of concentration and pressure on the decomposition rate of aqueous HAN solutions were studied by Vosen of D.o.E. Sandia National Laboratories, Livermore, CA, USA, who demonstrated the importance of condensed phase reactions in HAN solutions [Vosen, 1989]

The presence of the hydroxyl group allows hydroxylamonium ions to form strong hydrogen bonds with water molecules and this explains the high solubility of HAN in water. Solutions with up to 95% HAN remain liquid at room temperature and have a relatively high boiling point which simplifies storage and field use. HAN-water mixtures show very little shock sensitivity.

4.3.3 Fuels

The fuels used in conjunction with HAN for aqueous monopropellants should have similar behaviour with water as has HAN. For this reason nitrate salts of aliphatic amines have been chosen and as there are many suitable aliphatic amines and substituted amines, a wide variety of propellant mixtures is possible. Aromatic amines and quaternary ammonium salts are ruled out because they are not reactive with HAN. Aliphatic amines are not easily oxidized by nitrate ions during normal storage and handling conditions, so propellants of this formulation are reasonably stable. Aliphatic amines with long carbon atom chains are thermally unstable and have reduced miscibility with water, so carbon chains of up to four atoms are normally used. An anhydrous liquid mixture of 67% HAN and 33% hydrazine nitrate has also been described and studied under fast thermolysis conditions recently [Russel and Brill, 1989]. Table 4.1 shows the physical properties of the C-4 amines and their nitrate salts. They correspond to a general chemical formula $C_4H_{12}N_2O_3$. Propellants based on solutions of these salts plus HAN in water so that a 11 M nitrate ion concentration is reached have a density of approximately 1.5 $g \cdot cm^{-3}$ and

thermodynamic calculations using the *BLAKE* computer program [Carleton et al, 1986] indicate an energy content of 1.5 $kJ \cdot g^{-1}$.

Table 4.1 - Properties of the C-4 Amines and Their Nitrate Salts

	Amines			Nitrate Salts	
Formula	Purity (%)	Density ($gm\ cm^{-3}$)	Boiling Point (^oC)	Melting Point (^oC)	Abreviation
$CH_3–CH_2–N–(CH_3)_2$	>99	0.670	36-37	83-85.5	EDMAN
$(CH_3)_3–C–NH_2$	>99.5	0.693	44-46	141-142	TBAN
$(CH_3–CH_2)_2–NH$	>99	0.704	55-56	88-91.5	DEAN
$(CH_3–CH_2)(CH_3)–CH–NH_2$	>99	0.724	63-65	51-53	SBAN
$(CH_3)_2–CH–CH_2–NH_2$	>98	0.773	67-69	66-67.5	IBAN
$CH_3–CH_2–CH_2–CH_2–NH_2$	>99	0.740	76-78	41-42	NBAN
$(CH_3)_2–CH–NH–CH_3$	?	0.703	50	-	MIPAN
$CH_3–CH_2–CH_2–NH–CH_3$	?	0.720	62-64	-	MPAN

The thermal stability of the propellant is easily compromised by the presence of impurities and the amine to be selected must be available to a high degree of purity. Substitution of hydrogen atoms in the aliphatic chain of the amine with hydroxyl groups increases miscibility with water because of the hydrogen bonds involved. The most successful propellants in use today, designated as LP-1845, LP-1846 and LP-101 use triethanolamonium nitrate for fuel. (LP-101 is the Royal Ordnance specification of the equivalent U.S.Army LP-1845. As the method of production and the source of raw materials may differ, propellant produced in Britain is always referred in this thesis as LP-101 to distinguish it from the U.S. equivalent.) Table 4.2 shows the composition of these propellant mixtures.

Recently some work has been carried out with support from U.S.Army on the thermodynamics of combustion of these propellants [Kunalakis and Faeth, 1988] and of their burning rates [Vosen, 1988]. Vosen's experiments showed, amongst other things, that the combustion of HAN-based propellants occurs in two stages, in which

Table 4.2 - Propellant Composition

Mixture	Density	Weight (%)			Concentration ($kmol/m^3$)		
	(kg/m^3)	HAN	TEAN*	Water	HAN	TEAN	Water
LP-1845	1455	63.2	20.0	16.8	9.62	1.38	13.16
LP-1846	1437	60.8	19.2	20.0	9.10	1.30	15.95
9.1 M HAN	1396	62.6		37.4	9.10		28.98

the liquid phase decomposition of HAN is followed by decomposition of TEAN. He also presented a simple chemical model of the combustion of these propellants, showing the reaction sequence of their components.

Theoretical work validated by experiments was conducted [Lee et al, 1988] on the combustion of propellant sprays under high pressure. The thermal decomposition characteristics of LP-1845 were also studied [Cronin and Brill, 1988] and a four-step chemical model that describes the major events occurring during the fast thermal decomposition and ignition of LP-1845 was presented.

Recently, a simple and easy to use deflagration model describing the combustion of the HAN based propellants was presented [Shaw et al, 1990]. This model used methods developed during previous work on the burning rates of perchlorates and nitramines and was based on the following major assumptions:

- Condensed-phase (liquid) chemistry is controlling the overall burning rate.
- The deflagration is a steady state, isobaric event and the flame front is flat.
- Multiphase flow effects are negligible.
- Chemical reactions take place in one step.
- All liquid species have the same specific heat.
- According to Shaw, HAN decomposition is described by an equation following the Arrhenius law:

$$\dot{W}_{HAN} = -\rho \cdot B \cdot \exp(\frac{-E}{RT}) \tag{4.2}$$

* TEAN: triethanolamonium nitrate

This model assumes that the expansion parameter, β is large compared with unity. The expansion parameter is given by:

$$\beta = \frac{E}{RT_s^2 C_{p,s}} \cdot \int_{T_0}^{T_s} C_p \, dT \tag{4.3}$$

According to this model, the burning rate is given by:

$$(\rho v)^2 = \frac{\rho R B \lambda T_S^2 \cdot \exp(\frac{-E}{RT_s})}{E \cdot Y_0 \, (\int_{T_0}^{T_s} C_p \, dT - \frac{q \cdot Y_0}{2})} \tag{4.4}$$

where the equation describing the chemistry is:

$$NH_4NO_3 + \phi H_2O \rightarrow \sum a_i P_i \tag{4.5}$$

and the heat of combustion is given by:

$$q = \frac{1}{W_{HAN}} (\bar{h}^0_{HAN} - \sum a_i \bar{h}^0_{P_i}) \tag{4.6}$$

The symbols in the equations above are the following: B: frequency factor, E: activation energy, M: molarity, P: product, R: universal gas constant, Y: HAN mass fraction, α: stoichiometric coefficient, β: expansion parameter, λ: thermal conductivity,

The analysis done by the authors of this article assumed the following stoichiometry:

$$N_2H_4O_4 \rightarrow aHNO_3 + bH_2O + cNO_2 + dNO + fN_2O + hN_2 \tag{4.7}$$

where $\frac{8}{5} \leq (b - \phi) \leq 2$. They used deflagration data given by Vosen of Sandia National Laboratory [Vosen, 1989]. Their analysis led to the conclusion that phase equilibrium is not approached in the HAN decomposition zone and predicted that the activation energy, E, should be in the range $9.6 \leq E \leq 10.7$ *kcal/mole*. This result is very close

to the value $E = 9.2\ kcal/mole$ estimated by other workers [Cronin and Brill, 1988].

4.4 Kinetics of HAN-based propellant initiation.

As electrical initiation of HAN-based propellants involve electrolysis as well as ohmic heating, some work has been done mainly at U.S. Army Ballistic Research Laboratory (BRL), MD, USA and their contractors on the chemical mechanisms of propellant initiation. The term "**initiation**", as apposed to "**ignition**", is used here to describe the first stages of the process which involve only HAN decomposition, before any combustion phenomena appear. Full ignition may or may not occur, because it depends heavily on pressure and confinement, while HAN decomposition is relatively independent of pressure. The first observation was that the initiation reactions involve only HAN and are independent of the exact fuel used and similar to initiation of HAN/water mixtures while combustion depends strongly on the fuel component used. It was also observed that the initiation process is essentially independent of pressure which strongly indicates that the reactions take place in the liquid phase. The overall reaction follows the stoichiometry:

$$7\,HAN \rightarrow 4N_2O + 4HNO_3 + 12H_2O \qquad (4.8)$$

Experiments and bibliographic research indicate that HAN can be chemically initiated by many substances, including NO, NO_2, especially nitric acid, nitrous acid and nitrite ions and nitronium salts. In a series of tests carried out we found that HAN solution exposed in a NO_2 atmosphere reacts vigorously as soon as some NO_2 is dissolved in it. It is suggested that the nitronium ion, NO_2^+, is the chemical species responsible for initiation of the reaction sequence. High concentrations of nitronium ions appear usually in anhydrous fuming nitric acid, which contains an excess of nitrtate ions. Because most of the water in the propellant is bound to other molecules with hydrogen bonds, a nearly anhydrous state with a high nitrate concentration exists

and small quantities of nitronium ions are present.

An irreversible reaction, attack of hydroxylamine by nitronium ions, produces nitroxyl, $H-N=O$ and nitrous acid, $HO-N=O$, both of which react with HAN. The reaction of hydroxylamine with nitrous acid is well documented in organic chemistry textbooks [Mellor 1967] and produces small amounts of hyponitrous acid, $HO-N=N-OH$, which then decomposes rapidly to N_2O. These reactions would essentially remove all nitrous oxide from the mixture, as there is a high initial concentration of HAN:

$$NH_3OH^+ + HO-N=O \rightarrow H_3O^+ + O=N-NH-OH \rightarrow HO-N=N-OH \quad (4.9)$$

$$HO-N=N-OH \rightarrow N_2O + H_2O \quad (4.10)$$

Nitroxyl $H-N=O$ produced from HAN decomposition can also react with hydroxylamonium ions and produce nitrogen gas and water. It can also be oxidized by the nitrate ions, the product being two molecules of nitrous acid:

$$NH_3OH^+ + H-N=O \rightarrow N_2 + H_2O + H_3O^+ \quad (4.11)$$

$$H-N=O + NO_3^- + H_3O^+ \rightarrow 2HO-N=O + H_2O \quad (4.12)$$

The products of the initiation reaction have been identified and they consist of 80% N_2O, 17% nitrogen and 3% NO and NO_2. NO and NO_2 are produced by the thermally unstable nitrous acid in later stages of the reaction. If reactions (4.10) and (4.11) dominated, they would result in equimolar yields of N_2O and N_2, in contrast to the yields observed in which the N_2O/N_2 product molar ratio is approximately 4. In a low pH environment, reaction (4.12) is more strongly favored than (4.11) and results in 2 moles of $HO-N=O$ to be produced for each mole of $H-N=O$ consumed [Klein, 1989; Carleton et al, 1990]. The overall stoichiometry established by the proposed reaction scheme is very close to the observed product yields.

Oxides of nitrogen (NO and NO_2) are products of the later stages of the reaction sequence. Nitrous acid is thermally unstable and decomposes to NO, NO_2 and H_2O and is the likely source of the gaseous products. The fact that TEAN is recovered essentially unreacted also supports the nonavailability of $HO-N=O$ for reaction late in the HAN decomposition. The reaction chain described is exothermic and the mixture is heated to a point where both water and HNO_3 appear as gases. Nitric acid in the gaseous state dissociates and produces the powerful oxidizing species OH and NO_2, both of which react with any reducing species.

It was also observed that full ignition can be achieved only under pressurization or confinement of the propellant sample, which indicates that at least one important step in the reaction chain takes place either in the gas phase completely or involves a two-phase gas-liquid reaction. As the reactions are sequential, adequate time must be available for the initiation reactions to proceed if full ignition is to take place. The presence of NO_2 gas facilitates ignition and reaction has been observed without thermal input or confinement if sufficient NO_2 is available.

Little of the fuel part of the propellant is consumed during the initiation reactions, but it is the oxidation of the fuel to CO_2, N_2 and water which releases most of the energy content of the propellant. The fuel molecules have a high oxygen deficit and the reactive oxidizing products of the HAN decomposition, mainly NO_2 and HNO_3, are required for complete oxidation.

The initiation process produces a spray of molten fuel (TEAN, SBAN, EDMAN etc) droplets in a cloud of NO_2, NO, N_2O, $HO-NO_2$ and water vapour. The molten fuel has a density of approximately $1.2\ g \cdot cm^{-3}$ and a droplet would require 30 times its volume of NO_2 at 1000^oC and $136\ atm$ for complete combustion. This explains the strond dependence on pressure of the combustion process. In the case of TEAN, which contains hydroxyl groups in its molecule, there is also the another reaction route which involves the formation of nitrate and, possibly, nitrite esters as

inermediate products. As these esters would remain in solution during the early stages of the reaction, this mechanism could be used to explain the slow reaction observed in TEAN droplets after they are ejected from pulsed plasma jet devices.

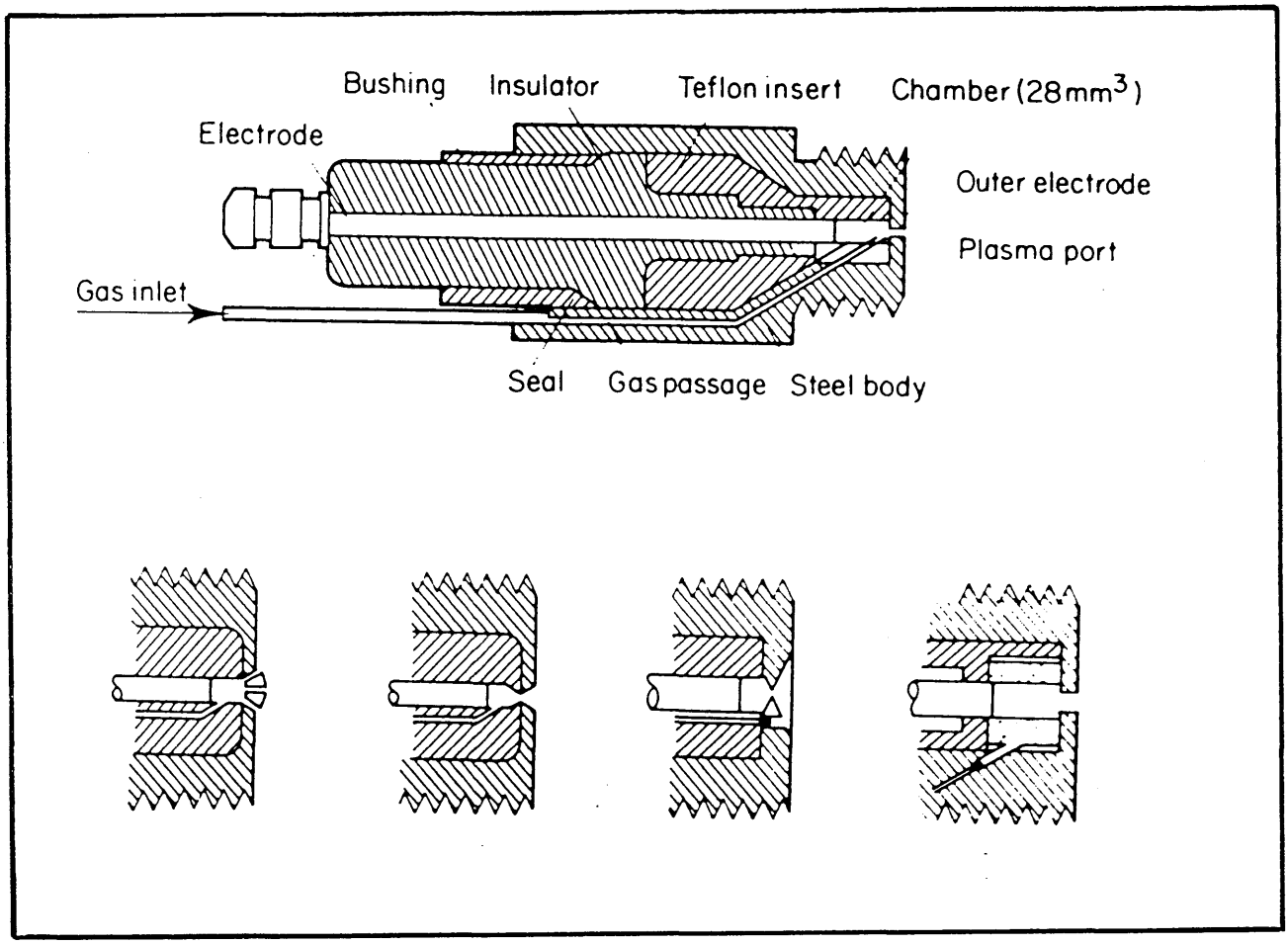


Figure 4.1 - Pulsed Plasma Plug igniter for automotive applications. Different nozzle geometries.

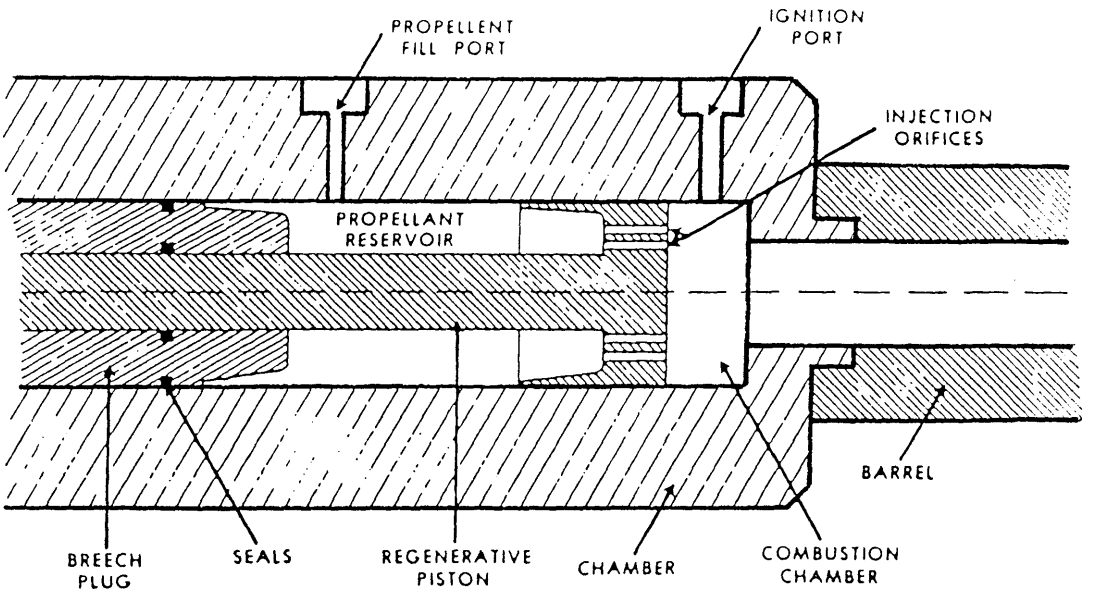


Figure 4.2 - Schematic of a simple in-line Regenerative Liquid Propellant Gun (RLPG) [Morrison et al, 1988].

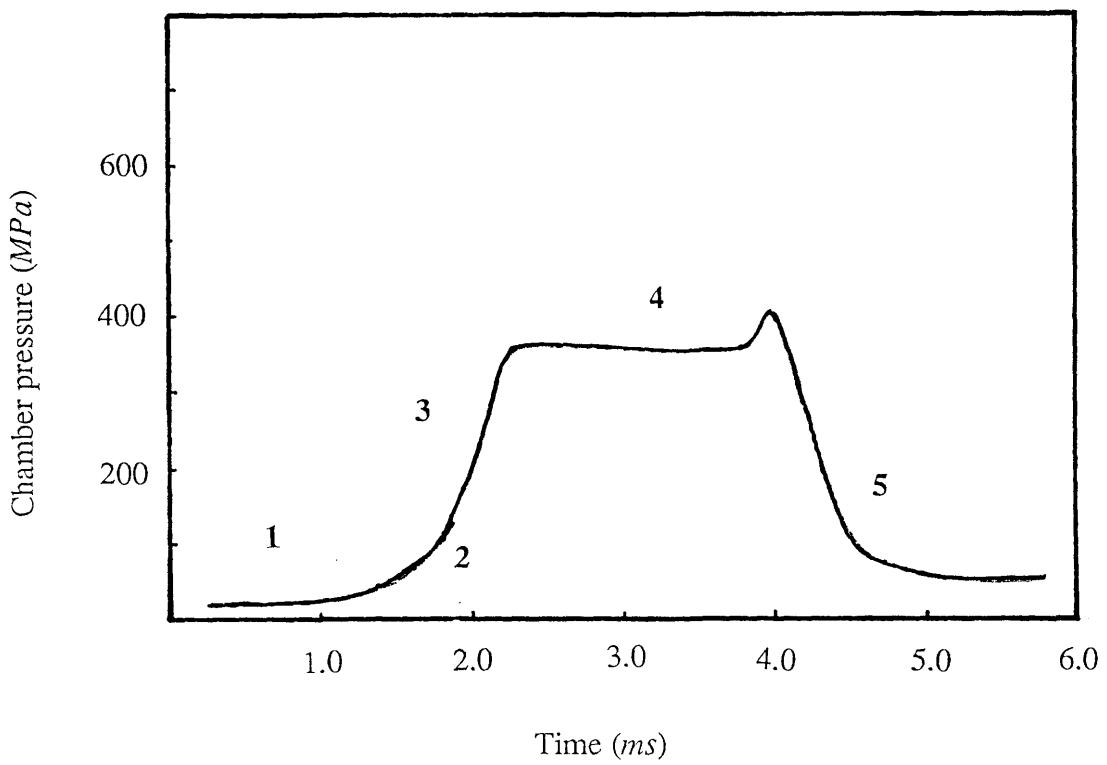


Figure 4.3 - Typical regenerative chamber pressure vs-time curve showing the five phases of the interior ballistic process.

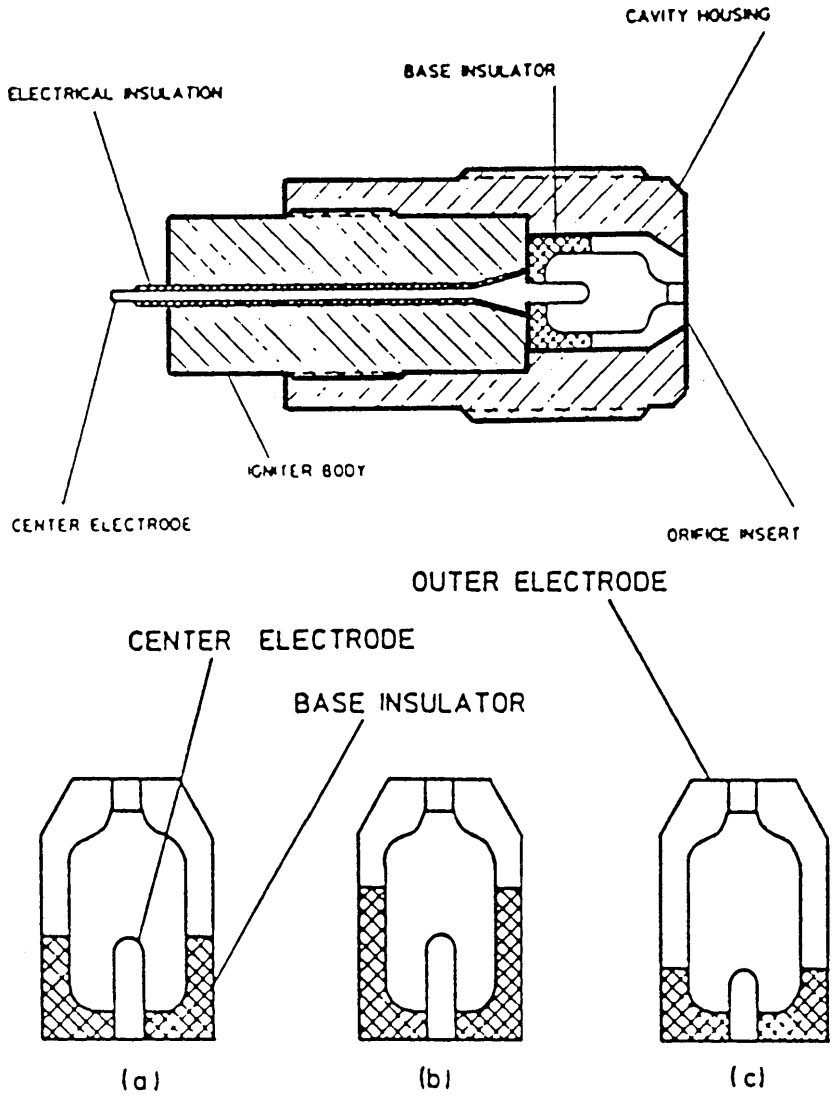


Figure 4.4 - Electrical liquid propellant single stage igniters.

[Klingenberg et al, 1989]

CHAPTER 5

ELECTRICAL INITIATION OF HAN-BASED PROPELLANTS

5.1 Ignition Phenomena in Energetic Liquids

The HAN based propellants described in the previous chapter are good conductors of electricity and, used in a plasma plug provide an interesting new possibility of study: Instead of generating the plasma by an electrical discharge in a plasma plug cavity, initiation of the reaction can be achieved by ohmic heating or by electrolysis of the sample or by arc formation. The electrical conductivity of these propellants could be an advantage in some applications as it makes the propellant safer in cases where static electricity could be accumulated on the electrodes. If a non-conducting propellant were used, a spark could occur and ignite it, while the conducting HAN based propellant would allow the electrical energy to discharge safely.

The first experiments on electrical initiation took place at Imperial College in 1982 by Klein, Carleton and Weinberg [Klein et al, 1983]. These involved the design and construction of a special electrical power supply which was used in many experiments later and of a series of pulsed plasma plugs (figure 5.1), specifically designed for use with HAN based propellants. The power supply (figure 5.2) included a 40 μF capacitor which could be charged to up to 1200 V and discharged through the propellant sample via a high voltage thyristor.

During these experiments it was observed that the current/voltage vs. time diagrams obtained during discharges of the plasma plug fell into either of two distinct

groups. Typical examples of each group are shown in figure 5.3. It can be seen from figure 5.3a that the maximum current is 127 *A* and that the pulse duration is approximately 560 μs. It should be noted that although the voltage across the plug is between 25 and 50 *V* during the pulse, it does not immediately fall to zero when the pulse ends. In figure 5.3b peak current is 48.5 *A* and pulse duration is again 560 μs but voltage is approximately 700 *V* and is maintained to a high value for about 1780 μs. Very different plug performance observations were associated with each of these current/voltage traces.

High speed shadow cin´e photography techniques showed that the trace of figure 5.3b corresponds to a vigorous event where a jet of liquid is ejected from the nozzle of the plasma plug and the event lasts approximately 1 *ms* while the tip of the jet traverses the entire 200 *mm* diameter test space. As the process continues, a plume of of fine spray begins to emerge from the vent and considerable turbulence is evident in the droplet column. Finally, after 5 *ms*, a plume of hot reacting gas begins to emerge from the plug vent. Shock waves reaching velocities of the order of *Mach* 3 were recorded during these sequences. The shock waves were analyzed using streak photography [Carleton et al, 1987], and the ''herring bone'' pattern recorded showed that the loud crack heard consists of a succession of shock waves generated during a 10 μs period.

The explanation proposed for these observations were the following: As the propellant charge is an electrolytic electrical conductor, as soon as the electrical pulse is applied to the plasma jet igniter, electrolysis accompanied by ohmic heating takes place and a thin non-conducting layer of gas is formed on the electrodes. An arc is then formed across the gas layer at a point of strong electric field. The discharge produces a column of extremely hot gas at an elevated pressure that reacts with the propellant sample in the cavity initiating a self-sustaining reaction. The partially decomposed propellant is ejected from the plug, and continues to react in the plume until

the event is complete. No flame appears, in agreement with other observations indicating that HAN-based propellant do not burn at atmospheric pressure, but reaction is still observed in the droplets of propellant. This slow reaction is attributed to the slower oxidation process involving nitrate esters of TEAN.

The trace of figure 5.3a can be obtained only from the plug design 5.2b. It is accepted that no arc is formed in this case. The sample is subjected to electrolysis and ohmic heating and the highest temperatures are achieved near the centre electrode where current density is higher and where decomposition begins. The various gaseous products, basically oxides of nitrogen, generate sufficient pressure to eject a column of cold unreacted propellant through the nozzle of the plug. No shock waves were recorded in any of these sequences.

This research project continued with support from U.S. Army B.R.L. [Carleton et al, 1985] and a series of flat transparent plugs suited for optical study were built from PTFE sheets and glass microscope slides, a typical design of which is shown in figure 5.2c. Optical records obtained when firing these plugs showed the following results:

- Ejection delay is increased when the volume of propellant in the plug is increased. This is caused by the longer duration of the current pulse and the higher pressure drop along the orifice which allows higher pressures to be built in the cavity.
- For full plugs, the ejection delay decreases with increased capacitor voltage, as expected.
- In all cases the vertical velocity of the plume front remains constant as time passes, although the volumetric flow changes
- Very small electrode separations (less than 1 *mm*) and high voltages (600 *V* or more) cause very vigorous reaction with current an order of magnitude higher, strong emission of light and a sharp cracking sound. Streak records of the shock

waves produced a "herring bone" pattern which revealed that they consist of a succession of shock waves, some of them generated after the end of the electrical pulse and attributed to propellant decomposition. Although they were separated by 100 μs intervals, they were heard as a single crack by a distant observer.

The most interesting result of these experiments is the graph of resistance vs. time shown in figure 5.4. This graph illustrates the two quite distinct events which occur when the electrodes are close enough and the voltage sufficiently high. They are described as ''event 1'' and ''event 2'' in most publications on the subject. The explanation proposed is that the passage of the electric current immediately causes the formation of a gas layer on the electrodes. This has also been confirmed microscopically. The first part of the graph is attributed to an inductive effect of the power supply circuit causing a delay in the current rise time. During the quasi-ohmic period which follows, there is no evidence of continuing growth of the gas layers and it is likely that some of the gas redissolves in the propellant. The vigorous event 2 which follows has all the characteristics of an arc discharge with very low resistance and is accompanied by light emission and a loud crack. The arc discharge is caused by the very strong electric field across the thin gas layer. Event 1 takes less time when voltage is increased or electrode separation is decreased but is always present, while there are cases where event 2 never happens, when electrode separation is too large (for example with the plug in figure 5.1b).

The research group at Ernst-Mach-Institut headed by G. Klingenberg and with U.S. Army financial support studied in great detail the design of practical electrical igniters [Klingenberg, 1989]. They studied the electrical field inside the cavity and based on this they modified the geometry of the cavity in order to achieve higher field strengths and current densities. They also studied the two-stage igniter developed by B.R.L. (chapter 4) for use with a regenerative liquid propellant gun (RLPG). They

concentrated on achieving arcless ignition as this would eliminate shock waves which might lead to detonation. The propellant they used was LP-1846 and their conclusions were the following:

i. It is feasible to ignite LP-1846 without arc breakdown.

ii. Electrostatic calculations support a cavity of parabolic shape.

iii. Both ohmic heating and electrolysis initiate the reaction.

iv. Electrochemistry takes place at both electrodes; it may start at the cathode.

v. The energy throughput depends on the length-to-diameter ratio of the igniter cavity and the surface of the centre electrode.

vi. For the optimized geometry of their igniter, negative voltage at the centre electrode yields smoother ignition than positive polarity.

We were able to confirm parts (i) and (iii) above with LP-101 as well. In many cases small samples of LP-101, when subjected to electrolysis and ohmic heating using a $6\,V$ source, started a self sustaining reaction at atmospheric pressure in a small open cavity without pressurization or confinement. The samples behaved as if they were exposed to a high concentration of NO_2.

5.2 Experiments on Electrical Initiation

A plug based on the work described earlier was designed and built by Frazer-Nash Limited of Epsom, Surrey. The cavity has a volume of approximately $30\,\mu l$ when the centre electrode is fully inserted. The orifice has a minimum internal diameter of 1.1 *mm*. The whole plug is of similar size and external appearance to a standard internal combustion spark plug. The cavity is made of stainless steel and the central electrode is a tungsten cylinder. Figure 5.5 shows details of the cavity.

Electrical energy to the plug is supplied by a capacitor discharge power supply unit. The capacitor is $40\,\mu F$ and is charged to a few hundred volts, typically 300–400 V. Only LP-101 propellant was used with this igniter.

Frazer-Nash has already used high speed video using the self-luminosity of the reacting propellant to investigate the plume emerging from the plug nozzle. A typical sequence obtained is shown in plate 5.1 and it shows clearly many, apparently burning, droplets emerging from the plug and continuing to radiate light in the air. The frame rates feasible with high speed video are very slow to distinguish between events 1 and 2 and what is seen is actually only event 2. For this reason a high speed (4000 frames per second) schlieren system was set up and used to photograph the emerging jet. Figure 5.6 shows the optical system set up. The main light source was a *Spectra Physics* 164 argon ion laser operating on 488 μm (blue) in CW mode. The beam was filtered via a spatial filter and a highly parallel beam of 0.20 m in diameter was produced by the first schlieren mirror which passed through the test space and was refocused on a knife edge by the second mirror. The schlieren image produced was recorded on 16 mm film (*Kodak* 7231 $Plus-X$) by a Hitachi high speed camera capable of speeds up to 20,000 frames per second. The camera motor was first started and the film was accelerated to the correct speed. When the final speed was reached, the camera controller closed a switch and triggered the electrical discharge. The negative was then processed in the departmental dark room facility.

Plate 5.3 shows a schlieren sequence where events 1 and 2 can be easily distinguished. They confirm the results obtained previously and described in the previous paragraph. Plate 5.2 shows the first pictures of a sequence in which a strong shock wave was produced. As explained earlier, shock waves are undesirable in most propulsion applications, but are desirable in others, like the BP enchanced oil recovery burner. Additional problems were caused by chemical attack of the electrode material. Some of the chemical species present in the initiation region (HNO_3,

NO_2 radicals) are strong oxidizers and attacked the centre electrode which was made of tungsten producing an insulating layer on its surface. When this happened, usually when the plug was left filled with propellant for considerable time periods, the plug failed to produce a vigorous plasma ejection. The presence of a high ohmic resistance layer was also confirmed with electrical measurements. The proper function of the device was restored after the cathode was rubbed with fine sandpaper which removed the layer of oxides.

These experiments provided us with some interesting optical records of liquid propellant plasma jets. They are also in agreement with previous observations and theories regarding initiation of HAN based propellants. The importance of the electrolysis stage and the need for confinement were confirmed. There was also support for the presence of strong oxidizing species in the initiation region and of the slow reaction path involving nitrate esters of TEAN.

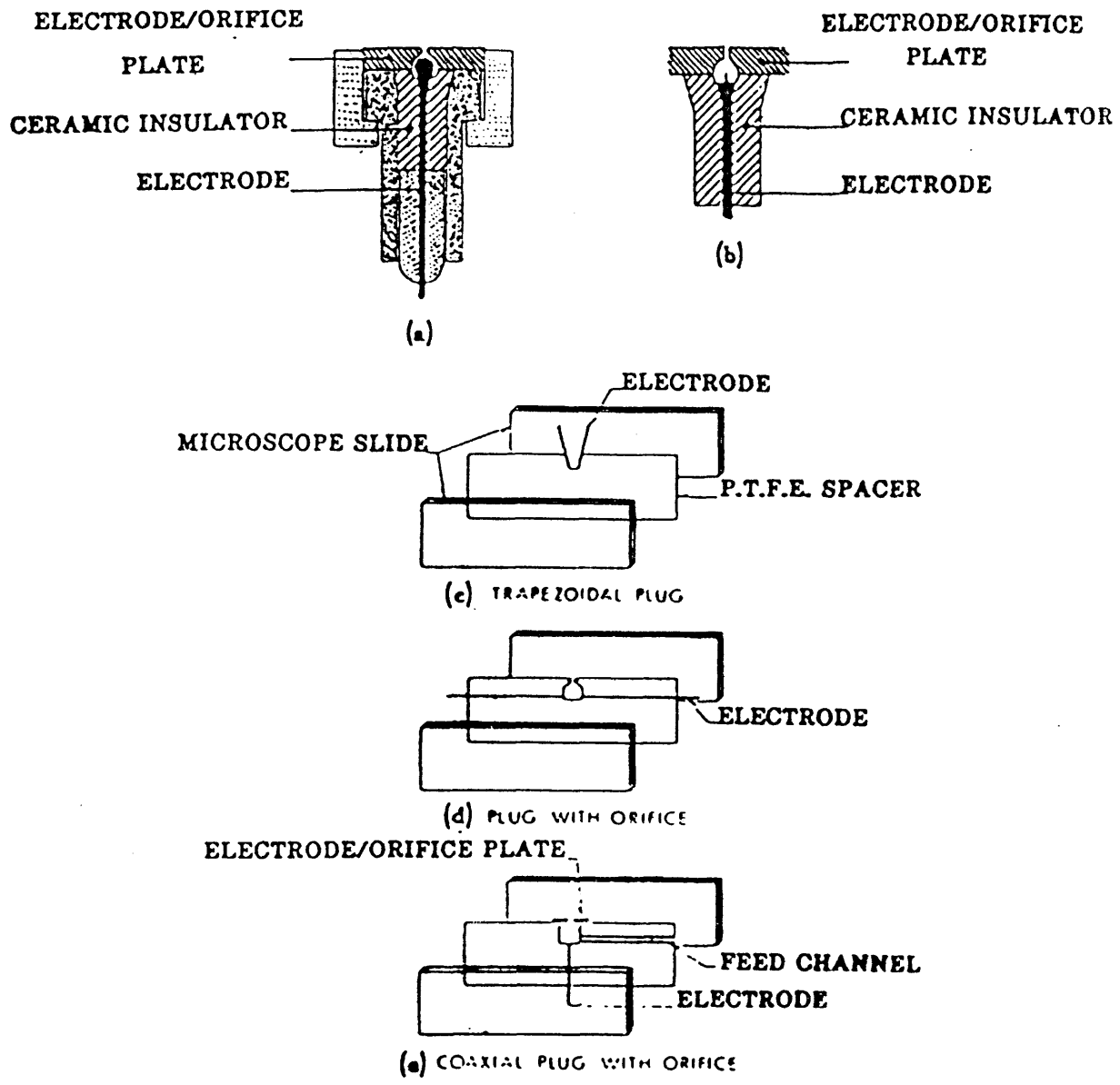


Figure 5.1 - Liquid propellant plasma plugs.

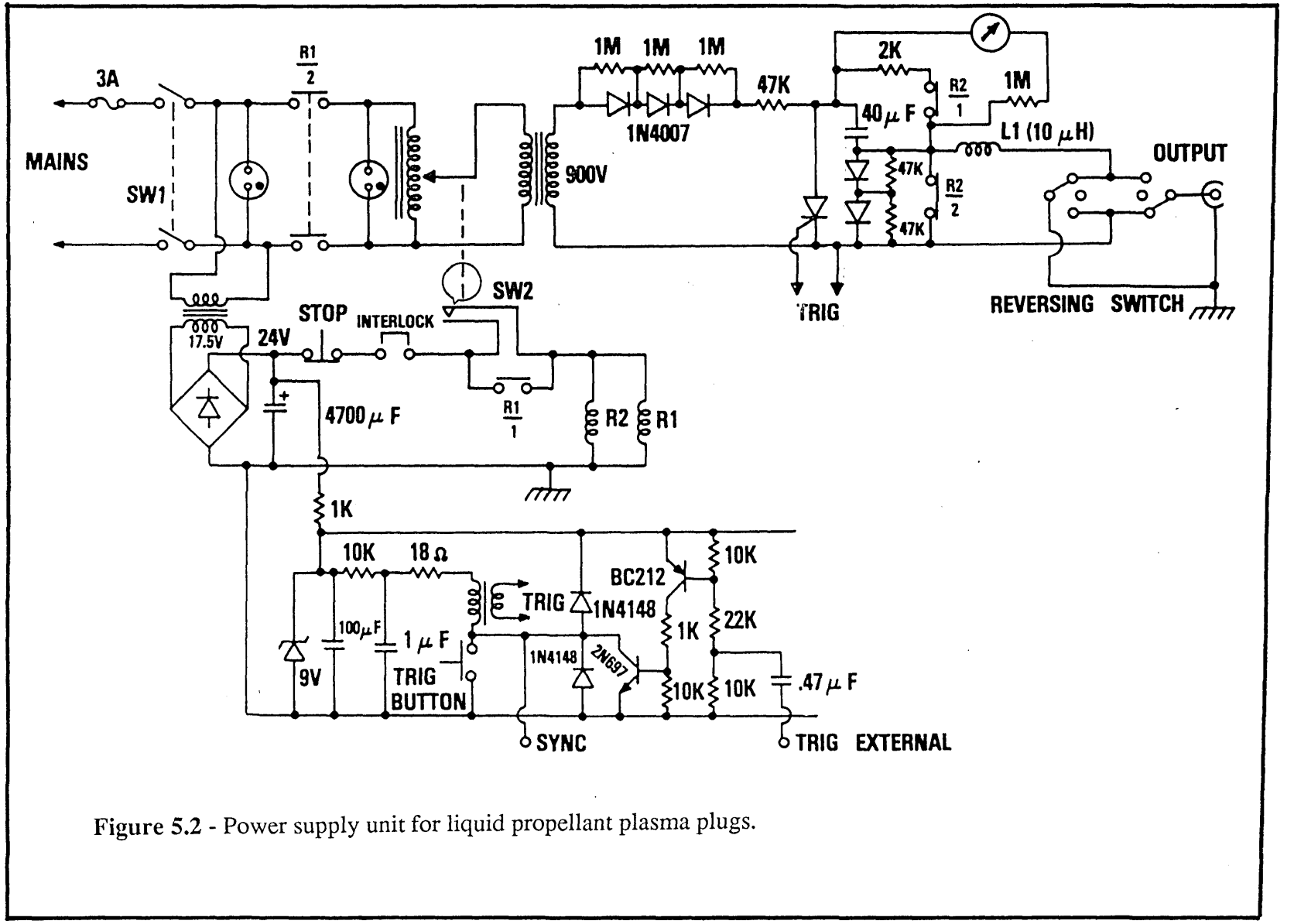


Figure 5.2 - Power supply unit for liquid propellant plasma plugs.

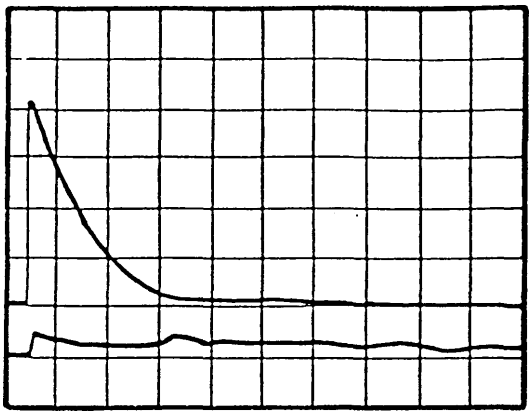


Figure 5.3a - Current-Voltage vs Time (Group 1) Upper trace = 30.3 *A/div*, Lower trace = 100 *V/div*, Horizontal = 200 μ*s/div*.

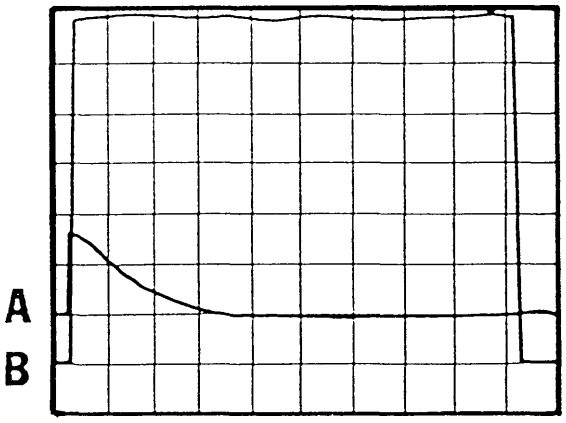


Figure 5.3b - Current - Voltage vs Time (Group 2) Upper trace (A) = 30.3 *A/div*, Lower trace (B) = 100 *V/div*, Horizontal = 200 μ*s/div*.

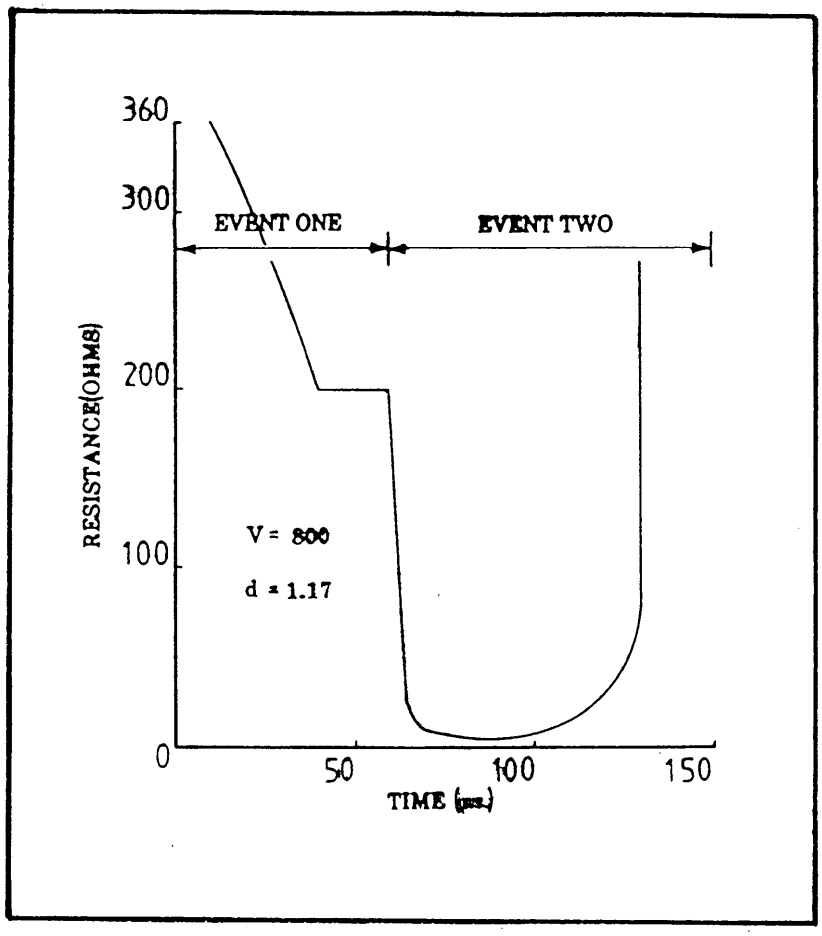


Figure 5.4 - Electrical resistance vs. time curve showing event 1 end event 2.

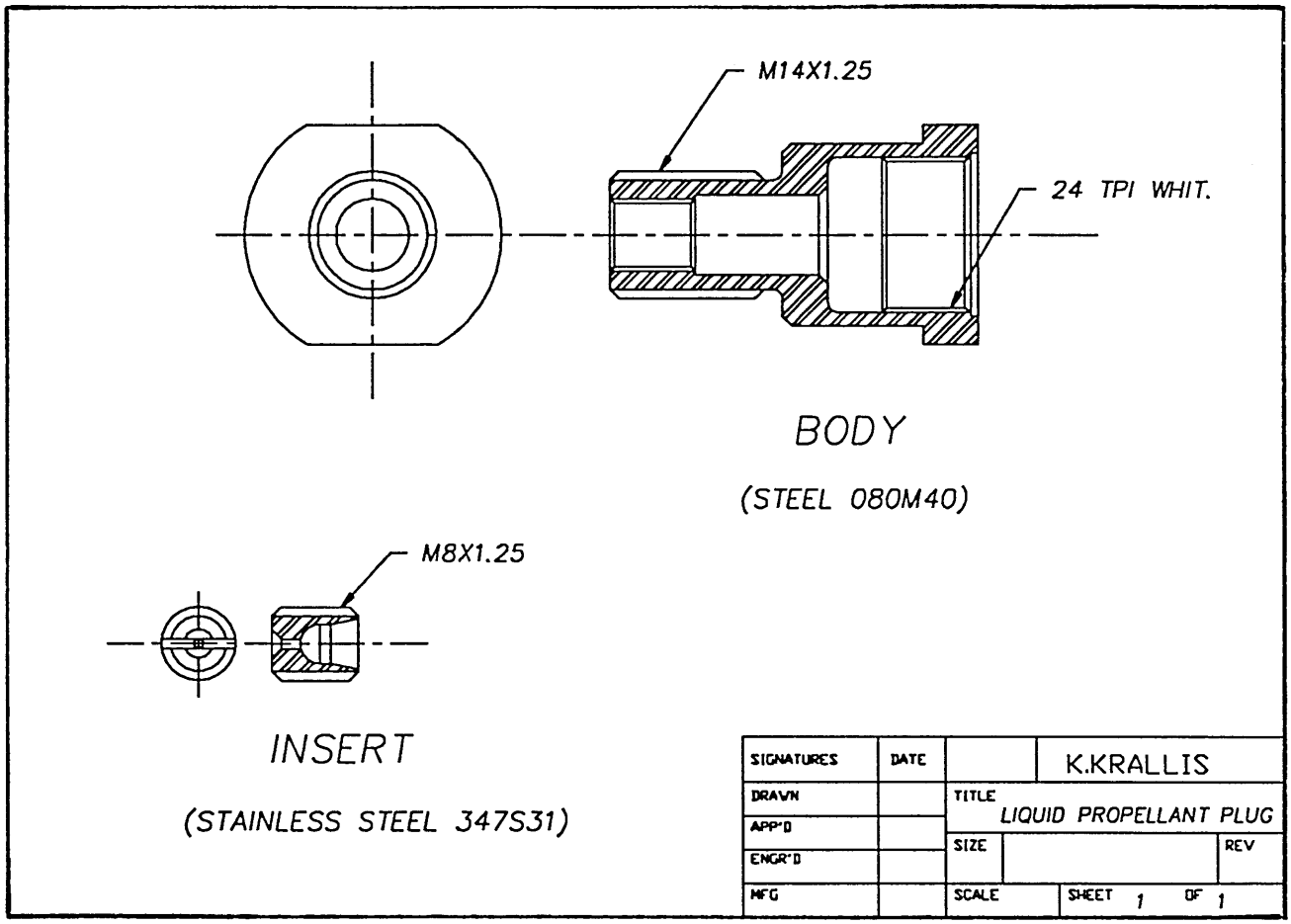


Figure 5.5 - The Frazer-Nash liquid propellant plug.

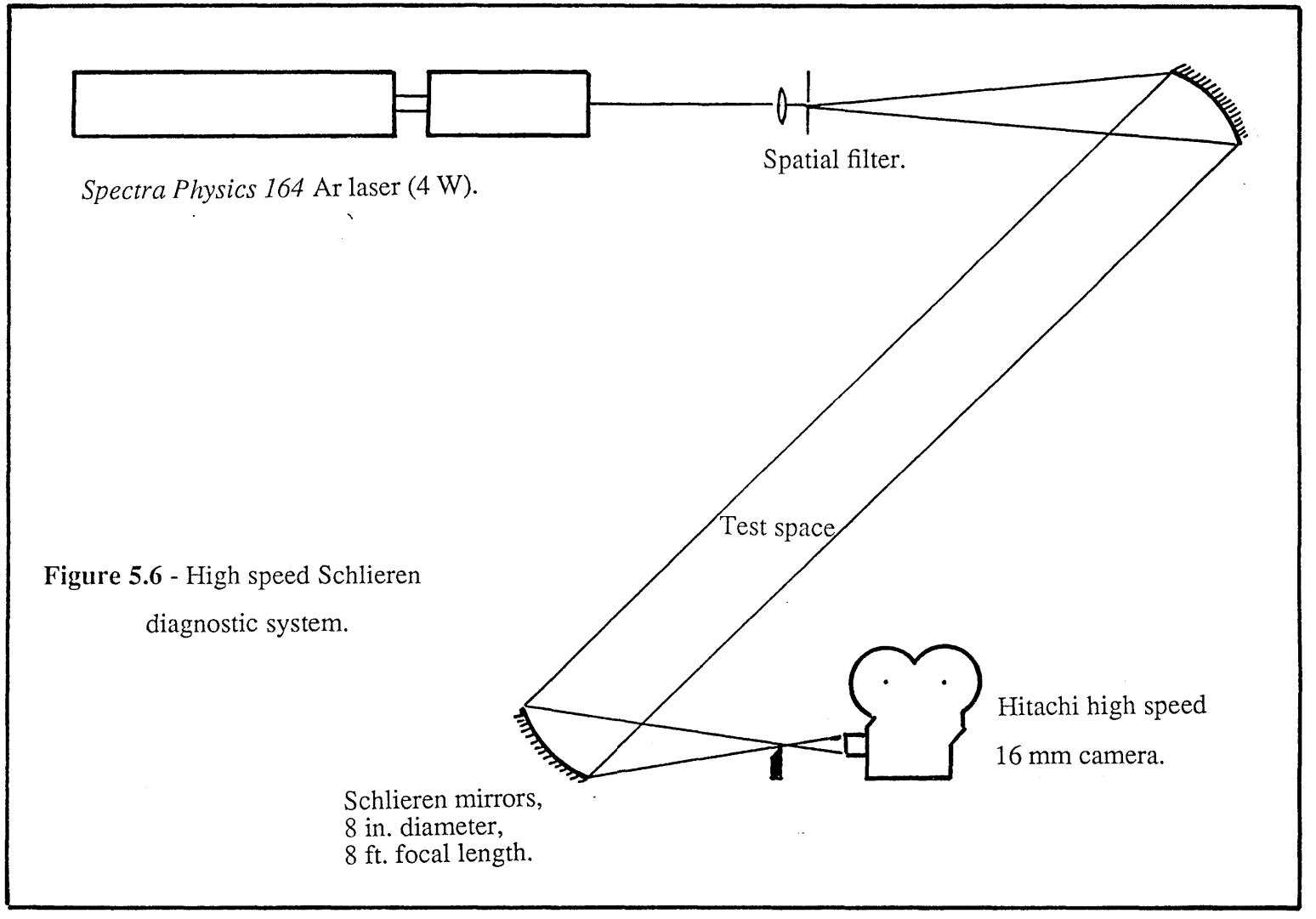


Figure 5.6 - High speed Schlieren diagnostic system.

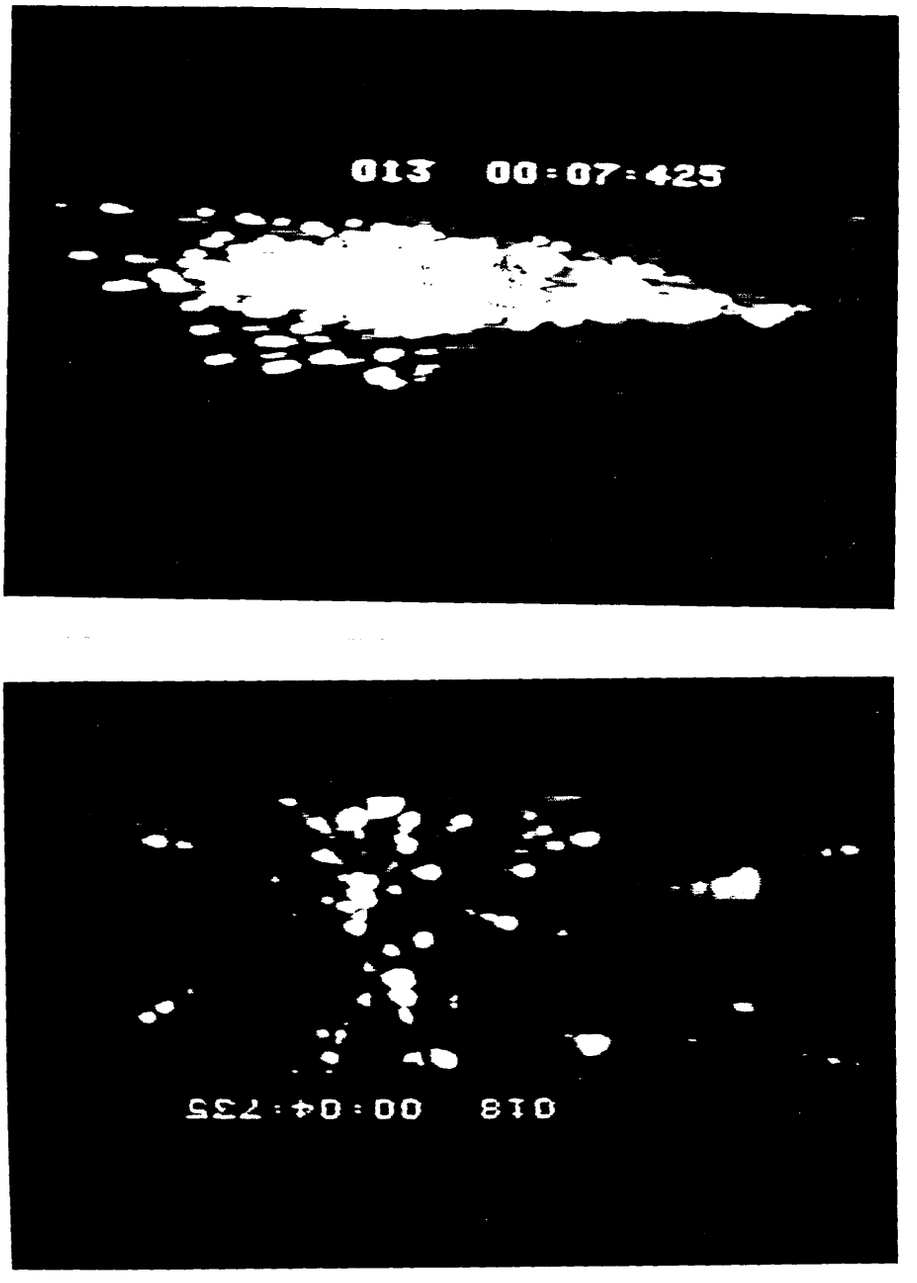


Plate 5.1 - High speed video pictures of reacting jet emerging from a liquid propellant plug (*Video by Frazer-Nash Ltd.*)

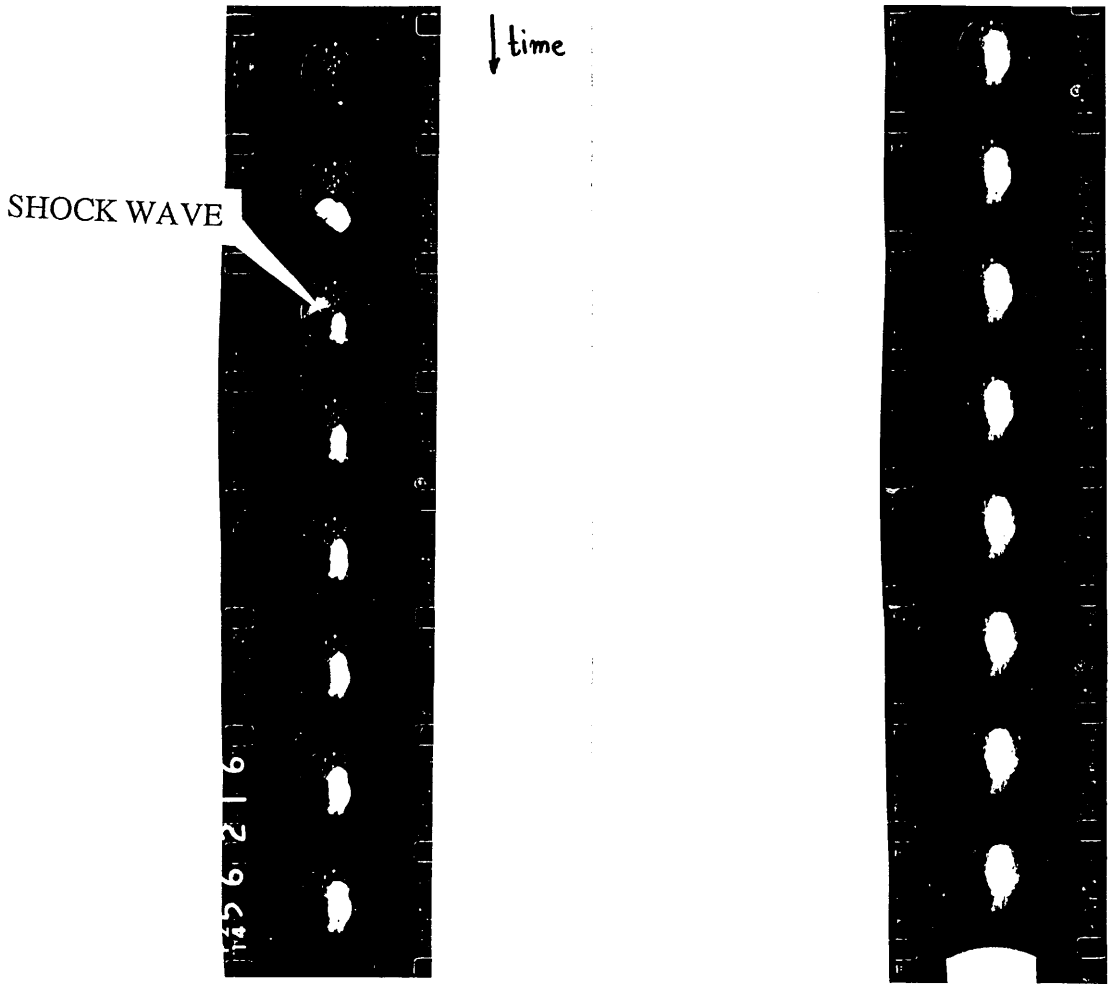


Plate 5.2

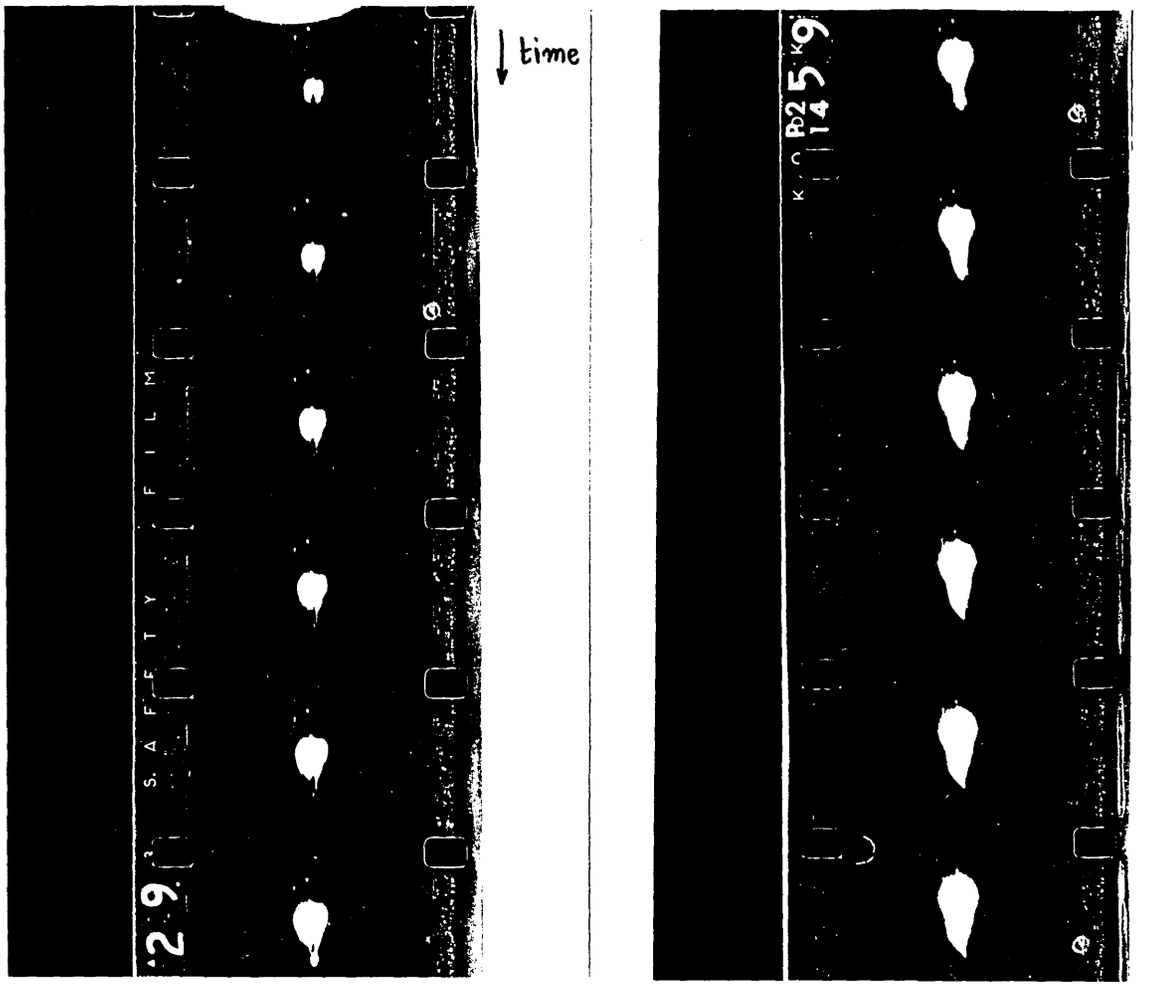


Plate 5.3

CHAPTER 6

LASER INITIATION OF HAN-BASED PROPELLANTS

6.1 Advantages of Laser Initiation

The ignition systems studied in chapters 4 and 5 depend on a pulse of electrical current passing through the mass of the propellant in order to start the chain of chemical reactions leading to full ignition. Electrical ignition systems are easier to design, build and operate but have some disadvantages which make other methods of initiation more attractive for special applications.

One problem is that use of electricity in places of high humidity or in presence of liquid is difficult and depends on special watertight cables and connectors. A minor insulation failure can lead to total loss of power and even damage to equipment, undesirable ignitions and fire hazard. Special equipment, which is often heavy, must be used in such applications and the installation procedure must be done carefully and the installed equipment tested thoroughly and frequently.

The second problem is the electromagnetic compatibility (EMC) of the electrical ignition system with other electrical and electronic equipment operated nearby. It is possible that switching of heavy electrical machinery (motors and generators) or high power radio transmissions can induce enough electrical energy to the ignition system to cause premature initiation. There are special rules regarding the proximity of electromagnetic energy sources to ignition systems used in mines etc. but in other applications there may be no way of avoiding electrical equipment operating nearby, a characteristic example being a naval vessel. In these cases the reliable behaviour of

the equipment depends on effective electromagnetic shielding which further increases the weight, size and cost.

The ignition system itself operates in pulsed mode and can interfere with the operation of sensitive radio navigation and RADAR receivers used aboard ships or aircraft. Extensive tests are always conducted following the integration of a new piece of electrical equipment in a sensitive environment which often lead to expensive equipment modification programmes.

The main source of electrical interference is the long cabling connecting the power supply and control unit to the igniter itself. The cables to the operator of the equipment carry very low currents and can be easily shielded against electromagnetic interference from other equipment. It is obvious that elimination of the main current leads would improve the reliability of the equipment, reduce its effects to other sensitive electrical apparatus and reduce the overall weight and cost. In some cases the power unit can be located very close to the igniter and this is the case with aircraft turbine ignition systems where it is often located on the shell of the engine itself. In other cases this is practically impossible and some other form of ignition energy source must be used. Most other energy sources are ruled out because they cannot be controlled reliably.

An alternative to electrical initiation which does not have the disadvantages described above but is easy to control is laser initiation. The advances in laser and optical fibre technology during the last few decades makes possible the transfer of large amounts of accurately controlled energy in the form of light pulses traveling along thin fibres of transparent material. Optical initiation of solid propellants has already been proposed for use with solid explosives used in pyrotechnic actuators [Barbour, 1981]. Figure 6.1 shows a typical fibre optic pyrotechnic actuator which uses a charge of solid propellant. Liquid propellants offer the possibility to design similar devices capable of repeated action.

This chapter describes a series of experiments involving the use of a laser source to initiate the same propellants studied in the previous chapter. The practical objective of the experiments described here is to explore an alternative configuration of plasma ignition plug in which electrical conductors are replaced by an optical light guide (optical fibre). On the fundamental side, we had the opportunity to study the effects of precursory electrolysis and heating of the propellant independently of each other and of the electrical discharge present in with electrical plugs.

6.2 Optical Study of Laser Initiation

6.2.1 General

The first experiments involved focusing laser light on a droplet of propellant suspended in a loop of thin platinum wire or between two such loops which, being electrically isolated, could be used as electrodes in studies involving electrolysis or electrical initiation of the reaction as well. Precise control of the position and separation of the electrodes was achieved by clamping them in a specially designed support structure, clamping heavier gauge copper wire which was used as lead to the fine gauge loops. The propellant used throughout this first series of experiments was exclusively HAN/SBAN.

Two initiating lasers were used during these experiments: a *Laser Associates* 211*A* pulsed ruby laser with a passive Q-switch device capable of up to 15 *J* of beam energy and an *Apollo* pulsed ruby laser with a Pockel cell Q-switch capable of 5 *J* of beam energy. Both lasers keep the temperature of the lamp and the ruby crystal constant with a closed circuit water cooling system.

The laser beam was focused on the droplet by a short focal length lens. Both ordinary glass lenses and plastic Fresnel lenses of short focal length (20–30 *mm*)

were considered but a preliminary study showed that plastic Fresnel lenses are not very efficient in transmitting the laser beam. In addition to the better efficiency we discovered that the surface of the lens facing the propellant droplet is covered by propellant and combustion products after each experiment and ordinary glass lenses can be cleaned much easier than plastic Fresnel lenses. It was decided then to use only glass lenses throughout the experiments described in this chapter. The final choice was a biconvex glass lens of 25 *mm* focal length and 20 *mm* in diameter for the initial experiments.

6.2.2 Optical Diagnostic System

A high time-resolution optical diagnostic system was used for these experiments. The system consisted of a light source, a high speed camera and an electronic timer circuit (figure 6.2a).

A Spectra Physics 164 argon ion CW laser operating at 488 *nm* was used as the primary light source. This laser is water cooled and powered from a 3-phase mains outlet and gives a light output of approximately 4 *W*. To this laser a cavity dumper is attached, forming an integral part of the resonant cavity. This device allows very fast switching of the laser beam, at frequencies of up to a few MHz corresponding to time periods of the order of 1 μs or less and can be controlled from either an internal pulse generator or an external signal source.

The output from the cavity dumper passed through a spatial filter (a pinhole at the focus of a lens) and was made parallel with a Schlieren concave mirror of 2.40 *m* focal length. The diameter of the parallel beam could be varied to up to 0.20 *m* in by

changing the focal length and position of a secondary lens located just beyond the spatial filter. A beam diameter of 3 in was chosen for this series of experiments.

The camera was a home made rotating prism camera (figure 6.2b) capable of speeds up to 200,000 frames per second. It was loaded with 1 m of 35 *mm* film which covered slightly less than the top half of the drum. A high speed electrical motor was used to rotate a hexagonal prismatic mirror which is located along the axis of the drum. The motor was operated from the 240 *V* AC mains through a *Variac* variable transformer, used to control the speed of rotation. The camera had a leaf shutter which was mechanically operated and when it opened a small electrical switch was closed. This switch starts the whole synchronization process described below. There was no lens attached permanently to the camera. A lens was positioned outside the drum and adjusted to focus the beam on the hexagonal rotating prism. This way the image was projected to the film while any stray light is out of focus and was dispersed on the image. The result was a shadow image of the event. In addition to the lens a blue filter (*Pentax* 80*C* ''flood'') was placed across the beam outside the camera to reduce the intensity of any red light scattered from the laser beam along the optical axis of the diagnostic system. As the light source was switched on and off, a series of images was formed on the film. The film used was *Ilford HP*−5 monochrome which is very sensitive to the blue light and has a sensitivity of 400 *ASA*.

The synchronization system consisted of a small switch located in the camera shutter, a variable delay pulse generator and a pulse train generator. The reason for the variable delay pulse generator was that it takes some 30 *ms* for the control circuit of the laser between closing the trigger switch and delivering the light pulse, so the beginning of the imaging process which was not subject to any delays, had to be delayed accordingly. The exact sequence of events is shown in the timing diagram, figure 6.2c. The shutter switch triggers both the laser control unit and the variable delay pulse generator. The output of the latter was fed into the trigger input of the

pulse train generator, which immediately started producing a preset number of pulses at a desired frequency. A frequency of 30.1 *kHz* was normally used and the sequences consisted of some 25-40 images, depending on the starting point on the film.

In order to reduce spurious triggering of the experiment, all cabling connecting the timing equipment was made with coaxial 50 Ohm cable type $RG-58/U$ with *BNC* connectors used throughout and all ground points were carefully tied together.

6.2.3 Experiments and Results

A series of experiments were carried out to study the interaction between the focused laser beam and the propellant droplets which were supported on single platinum wire loops. The variables studied included the position of the droplet with respect to the focal point, the focal length of the lens and the transparency of the propellant droplet to the red laser light which was varied by dyeing the propellant with methylene blue. The nitrate salt of methylene blue was used instead of the commonly used chloride in order to ensure that chloride ions do not interfere with the initiation reactions.

In the first series of experiments lenses of different focal lengths ranging from 20 to 200 *mm* were tested. Use of long focal lengths of 50, 100 and 200 *mm* always lead to shattering and dispersion of the droplets, with both Q-switched and non Q-switched laser beams. Dispersion of the liquid occurs in all directions but it appears not to be entirely symmetrical. A glass slide was positioned beyond the droplet and at the same distance as the distance between the lens and the droplet. It was observed that more liquid was consistently sprayed on the glass slide down-beam, the distribution being approximately 60:40. Although the results were reproducible, there was no evidence of droplet decomposition or initiation reactions taking place.

It has been observed [Weinberg and Wilson, 1971] that a Q-switched laser beam focused by short focal length lens (20 *mm* or less) will produce a breakdown in the air, which appears as a flash of light and a loud crack. The formation of the plasma is confined around the focal point of the beam where the electromagnetic field is strongest. No similar events were observed inside a liquid droplet, even if it is dyed with methylene blue. This was attributed to the much higher heat capacity per unit volume of the condensed phase.

Based on the above observations, a new series of experiments was carried out. In these the droplet was exposed to the plasma and the shock wave generated by by focusing the laser 1 *mm* in front of the propellant droplet. Using a lens of 25 *mm* focal length there was some indication of chemical reaction taking place. The droplet still broke up and liquid was splashed on the lens but a smoke puff and some carbon deposit on the loop were produced as well. These effects were not observed when the HAN/SBAN droplet was replaced by NaCl solution of similar conductivity.

After these encouraging observations, the optical system described earlier was set up and used to observe the interaction between the laser beam and the propellant droplet. Many events were recorded and three of them are shown in plate 6.1. The most important features recorded on the film are the plasma luminosity around the focal point of the Q-switched beam, the shock wave from the laser generated plasma, which has a very high Mach number initially, and its various reflections, the strongest one reflecting from the lens, and what appears to be the burning of the propellant spreading over the surface of the droplet from the initial plasma kernel. The observation is the most interesting feature and is absent when the propellant is replaced with sodium chloride solution. Careful study of the optical records shows that the shock wave generated by the breakdown shatters the droplet surface, while the inertia of the droplet is too high for the body to be moved at such a small timescale. Filaments of propellant emerge from the shattered propellant surface and they ignite when they

reach the plasma region.

As the propellant has to come in contact with the plasma in order to start reacting, the relative positions of the droplet and the beam focus become important factors and determine the effectiveness of the initiation process. This would be an important consideration if igniters were to be designed based on this principle.

The *Laser Associates* 211*A* Q-switched ruby laser used in these experiments has a tendency to produce double pulses quite often. They can be recognized both from the optical image and with a high-speed photodiode connected to a storage oscilloscope. Although this is an unwanted characteristic of the specific kind of Q-switch used with this laser, it gave us a few interesting sequences, a characteristic example being sequence 3 in plate 6.1. This shows clearly a second pulse interacting with the disintegrating and burning fragments of the droplet 220 μs after the main pulse and enhancing the rate of reaction.

6.3 The Dilatometer

The work described in the previous chapter was based on optical methods which give mostly qualitative information* on the various events taking place during propellant initiation.

In order to study the effects of various parameters on propellant decomposition a special "dilatometer" device was designed and constructed to measure the volume of gas released. The term was used to describe a similar device used previously in this project. It is basically a constant (atmospheric) pressure variable volume closed

* Optical records have been used previously to extract quantitative information as well, as is the measurement of energy release from shock wave velocities.

combustion chamber which allows measurement of increase in volume (dilatation) due to combustion taking place in it (figure 6.3).

The dilatometer consists of a hollow perspex cylinder of 30 *mm* diameter and 50 *mm* length. The front of the cavity is closed with a transparent window made of thin glass with refractive index $n_d = 1.52 \pm 10\%$ (BS 3836). A plano-convex lens with a diameter of 20 *mm* and focal length of 25 *mm* (*Ealing Electro –Optics* stock no 30-6829) is held against the front window by a brass screw-on cup. The modular construction of the dilatometer allows us to use a different lens of approximately the same diameter.

The opening on the back of the cavity is a cylindrical hole 20*mm* long and 10*mm* in diameter with a metric 10×1.5 thread. A brass piston with a matching and tightly fitting thread can be inserted in this hole. A small loop of platinum wire is glued on the front of the plug and can be positioned at or near the focus of the lens. A small quantity of propellant, typically 30 μl can be held on the wire loop. The empty space in the dilatometer when the plug is inserted to its final position is approximately 4 cm^3.

A different plug was designed for use with the electrolysis experiments described later in this chapter. This plug has the same outside diameter but a 5*mm* hole is cut along its axis. Two stiff electrically insulated wires were inserted into the hole and the void space left was sealed with epoxy glue. Two small platinum wire loops were soldered to the stiff wire ends. This system allows us to electrolyze the propellant immediately before firing the laser.

The cavity is connected to a small volume horizontal capillary glass tube via a short length of plastic pipe. A small droplet of mercury is inserted in the horizontal pipe and is free to move along its length. A ruler with 0.5*mm* markings is attached to the pipe and the movements of the mercury droplet can be measured on the scale. The capillary used in most experiments had an internal diameter of 1.15*mm* but a pipe of

2.30*mm* diameter was used in a few experiments producing larger volumes of gas products. A small plug made of glass wool is inserted in the pipe between the horizontal section and the combustion chamber. This damps any pressure surges or shock waves which might otherwise shatter the mercury droplet or force it out of the far end of the tube and allow the gaseous products to escape.

The dilatometer is secured on a three axis positioner which is placed on a short length of optical bench which is also supporting the *Laser Associates* 211*A* ruby laser so the dilatometer can be centered in the laser beam easily. A small size but strong light source placed between the ruby rod and the back mirror simplifies the alignment of the optical axis of the dilatometer so that it coincides with that of the laser beam.

6.4 Dilatometry

The use of the dilatometer is simple but care is required so that reproducible results are obtained. Occasionally erroneous readings are obtained which are caused by leaks in the pipe joints or along the rim of the glass window. A small leak usually causes a very high reading while a major leak (which rarely takes place if the experiment is conducted carefully) causes a low reading. The reasons will become clear after the experimental procedure is described.

The dilatometer and especially the window in the laser beam is cleaned and dried in a dry air stream. The lens is then put in place and the assembly is locked on the 3D positioner. A 30 μl droplet of propellant is then delivered on the wire loop of the plug using a microsyringe and the plug is carefully inserted to the body of the dilatometer. The thread of the plug is made airtight with PTFE tape. The plug is then screwed inwards until the droplet lies in the required position with respect to the focal point of the lens. A notch on the body of the dilatometer marks the plane where the lens focus lies. The light source described in the previous paragraph can be used to

confirm the proper focusing of the system.

The mercury droplet is then moved to the end of the tube nearest to the combustion chamber and the capillary is connected to it via a short length of flexible plastic pipe. Finally the dilatometer is closed and the laser can be fired.

The explosive gas and heat evolution following the propellant initiation by the laser pulse causes the mercury droplet to move towards the far end of the capillary. After that the gaseous product cools down and the water vapour condenses, causing the mercury to move back towards the combustion chamber but not, of course, to its initial position. The difference gives the volume of the permanent gaseous products of the reactions.

Initially the effect of varying the laser beam energy was studied. The energy of the laser beam was controlled by the voltage at which the power supply capacitors are charged and a calibration chart is included in Appendix C. Figure 6.4 shows the results of this experiment. The amount of gas products produced increases with beam energy. It is now accepted that no self-sustaining combustion can be reached under the atmospheric pressure conditions of the experiments and that some degree of confinement is essential in order to reach the stage of complete decomposition. Incomplete initiation gives us the opportunity to study the effects of various factors on the first stages of propellant initiation, especially the ones involving only HAN decomposition.

6.5 Effects of Precursory Electrolysis

As was explained earlier, electrolysis is a very important step in electrical initiation of the propellant. Two mechanisms are involved, a chemical (production of oxidizing species) and physical (formation of insulating layer leading to electrical discharge). It is possible now, by using laser initiation, to isolate the chemical effects

and study them separately.

The first series of experiments involved investigation of the effects of precursory electrolysis on propellant decomposition. HAN/SBAN propellant was used and a Q-switched laser beam was focused in the air, 1 *mm* in front of the droplet so that propellant initiation was caused by the plasma produced from a breakdown in air. Two measurements were taken for every firing, one immediately after electrolysis and just before firing and one a few minutes after firing, when the gas products had cooled down to ambient temperature. The results are shown in figure 6.5.

A quantity of LP-101 military grade propellant was acquired at this point and was tested under the same conditions. The results obtained with the new propellant were nearly identical to the ones obtained with HAN/SBAN.

The next step was to try focusing the laser beam inside the propellant droplet. Although the interaction between the laser induced plasma and the propellant is theoretically interesting, the design of a practical plasma plug based on this mode of initiation is difficult and such a device would be complicated and unreliable. A more practical approach would be the design of a plasma plug in which the laser beam is focused in the mass of the liquid propellant in the absence of any gas bubbles. Such a device would be based on figure 6.1, but with the optical window replaced with a short focal length lens of similar thickness. No indication of breakdown was observed when focusing in the droplet was attempted and propellant initiation was attributed to direct interaction between the constituents of the propellant and either the laser photons or the heating effects of the laser beam. As the liquid droplets have substantial heat capacity, the overall effect, in the absence of photochemical interactions, is the same with either a Q-switched picosecond pulse or a longer pulse of equal total energy. It was decided then not to use Q-switched laser beams in any experiments involving focusing on the droplet.

The first observation was that when focusing in the droplet, more reaction takes place than if the same amount of energy is used to produce a breakdown in the air next to the droplet. This was confirmed with both HAN/SBAN and LP-101 propellants.

There was already a theory that nitrogen oxides produced during electrolysis of the propellant increase its sensitivity and perhaps they can even start the initiation reactions. In these experiments, the laser was fired initially on the droplet immediately after electrolysis was completed. We decided to wait for 5 s after electrolysis and before firing the laser, so that the gas bubbles on the electrodes would dissolve in the propellant and have some time to react with it. The volume of gas produced under these conditions increased by 7.65% for LP-101 and 12.5% for HAN/SBAN compared to results obtained previously. This observation could possibly help to deduce the chemical mechanism of propellant initiation. It was decided then to electrolyse small quantities (1 cm^3) of propellant and leave it for periods of time ranging from 5 min to over 10 hours and then fire it in the dilatometer so that we could have some indications on the speed of the reaction between the propellant and the oxides. The results for LP-101 and HAN/SBAN propellant are shown in figures 6.6 and 6.7. Figure 6.8 shows the result of an additional experiment using HAN/SBAN and focusing in the air near the droplet. No further increase in the volume of gases products took place, so we concluded that the reactions which sensitize the propellant take place during the first few seconds after the current is applied and are irreversible with time.

The effect of the laser beam energy on propellant decomposition after electrolysis was studied next. Figure 6.9 shows the results with LP-101 and figure 6.10 with HAN/SBAN. The solid line represents the results with unmodified propellant and the dashed line represents results with electrolysed samples. The samples were treated the same way as those used in the experiment described in the previous paragraph. The increase of gas produced with increasing beam energy means that even with

sensitized propellant, full ignition is not achieved without confinement.

6.6 Effects of Heating and Dyeing

There were a few reports that LP-101 has shown unstable behaviour when heated in temperatures of $70^{o}C$ or more for prolonged periods of time and that samples of the propellant start reacting at random periods of time while held at this relatively high temperature. We decided to investigate heating as a method to sensitize the propellant without using precursory electrolysis. This decision was based on the assumption that heating would cause some decomposition of HAN and produce nitrogen oxides which would then dissolve in the propellant and increase its sensitivity. We don't know yet if this behaviour is specific to the british LP-101 propellant or is exhibited by the american LP-1845 as well.

Three propellant mixtures were used for this test, LP-101, HAN/SBAN and HAN/DEAN. The experiment involved heating many small (50 μl) of propellant in small glass containers held in a water bath of constant temperature $70^{o}C$. A larger vessel containing approximately 2 ml of propellant was also heated in each experiment and it was used for laser initiation experiments later. The temperature was held constant by an electrical heater switched on and off by a temperature controller. A stirrer and forced water circulation ensured that all samples were kept at the same temperature. The water was first heated to the final temperature and then the sample cylinders were immersed in it and kept in place for 7 hours.

Each propellant was heat treated in a separate series of experiments. When LP-101 was heated, one of the samples decomposed some 3 hours after it was immersed in the water bath. No sample of the other two propellants showed any sign of instability while heated in the water bath. No colour change resulted from the heating.

30 μl droplets taken from the larger samples of each run were then fired in the dilatometer. The results obtained with the LP-101 and HAN/SBAN propellants are shown in figures 6.11, 6.12 (dashed lines) compared to the standard propellant (solid lines). It appears that HAN/SBAN and HAN/DEAN are less affected by prolonged heating than LP-101. This sensitivity of LP-101 is not easily explained and it was not reported for LP-1845 which is its U.S. equivalent. It is possible that some factor introduced during its manufacture could be the cause, but this was not resolved as we were unable to obtain a sample of LP-1845.

As the propellant is a transparent liquid, we assumed that laser initiation is caused mainly by heating and that direct interaction between visible photons and propellant molecules is of little, if any, importance. To further investigate this aspect of laser initiation, we focused the laser beam on propellant samples dyed so that they would absorb in the visible and more specifically red part of the electromagnetic spectrum. One set of results was obtained with HAN/DEAN propellant dyed with a small quantity of black drawing ink. This ink consists of a dispersion of fine carbon particles in water so it simply absorbs light energy and converts it to heat without any chemical effects. The other sample was dyed with the nitric salt of methylene blue described earlier (Appendix B). Both samples gave near identical results and showed an increased sensitivity of the dyed samples compared to the undyed ones, while the mechanism appears to be again thermal initiation. The increase in the volume of gas products were approximately 30% for both dyes. As these results were obtained only with the red light (694.3 *nm*) of the ruby laser, they don't exclude the possibility that visible radiation of different colour or even ultraviolet radiation have a more pronounced effect on the propellant.

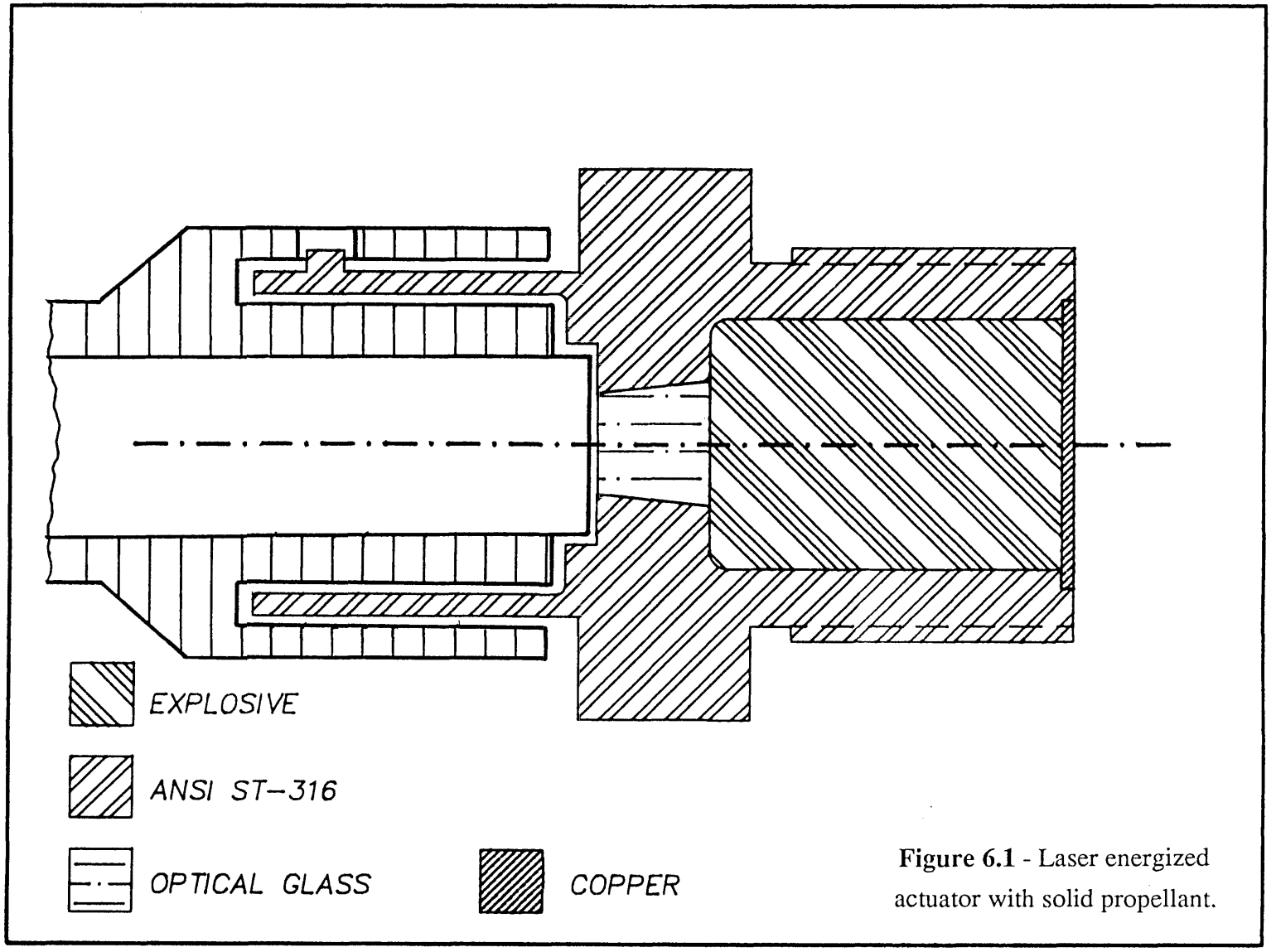
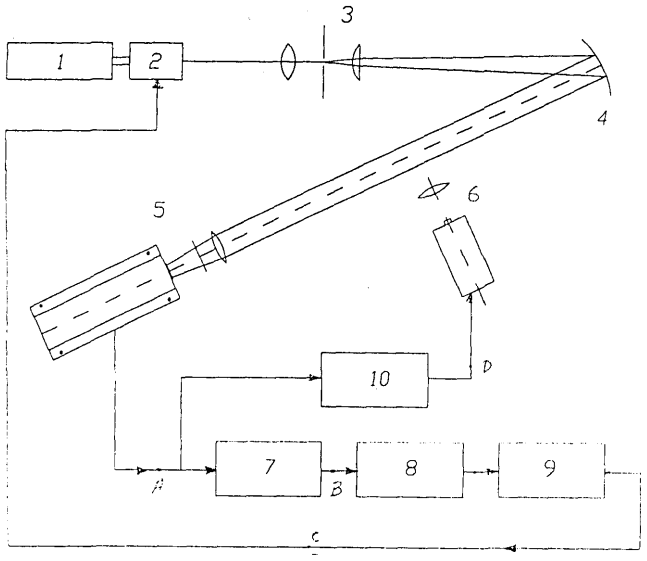


Figure 6.1 - Laser energized actuator with solid propellant.



1: Argon laser
2: Cavity Dumper
3: Spatial Filter
4: Concave Mirror
5: Camera
6: Ruby Laser
7: Delay circuit
8: Pulse generator
9: Cavity Dumper Controller
10: Ruby laser

Figure 6.2a

Optical diagnostic system for liquid propellant laser ignition studies.

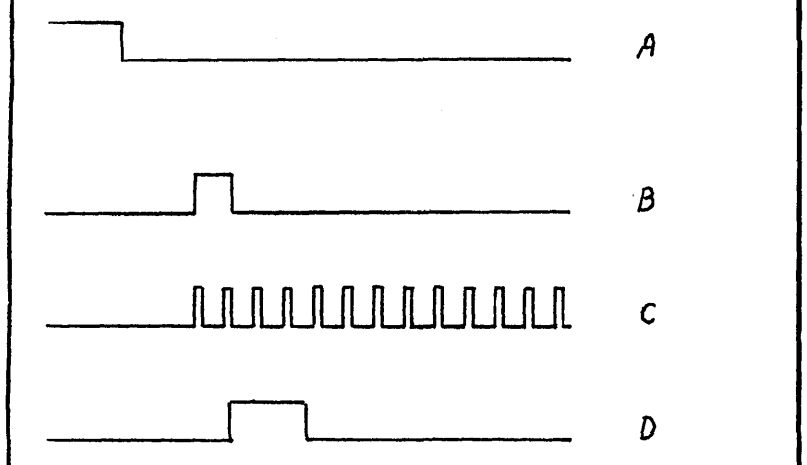


Figure 6.2c - Timing diagram for the diagnostic system.

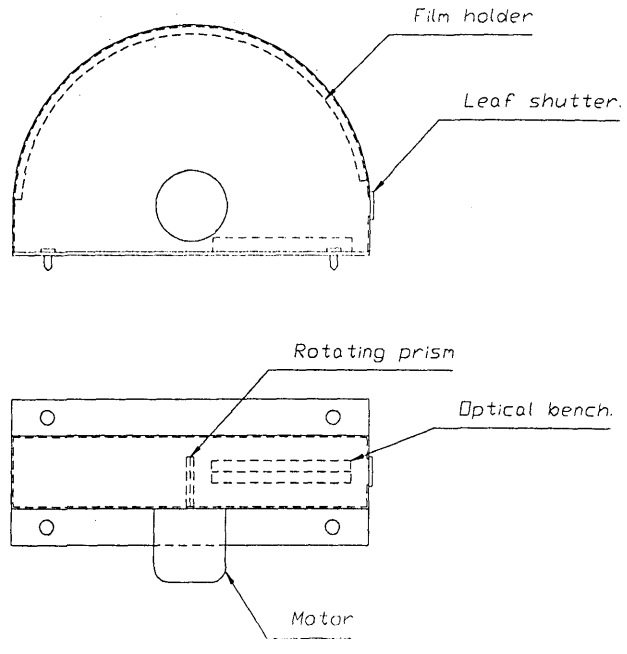


Figure 6.2b - Rotating prism high speed camera.

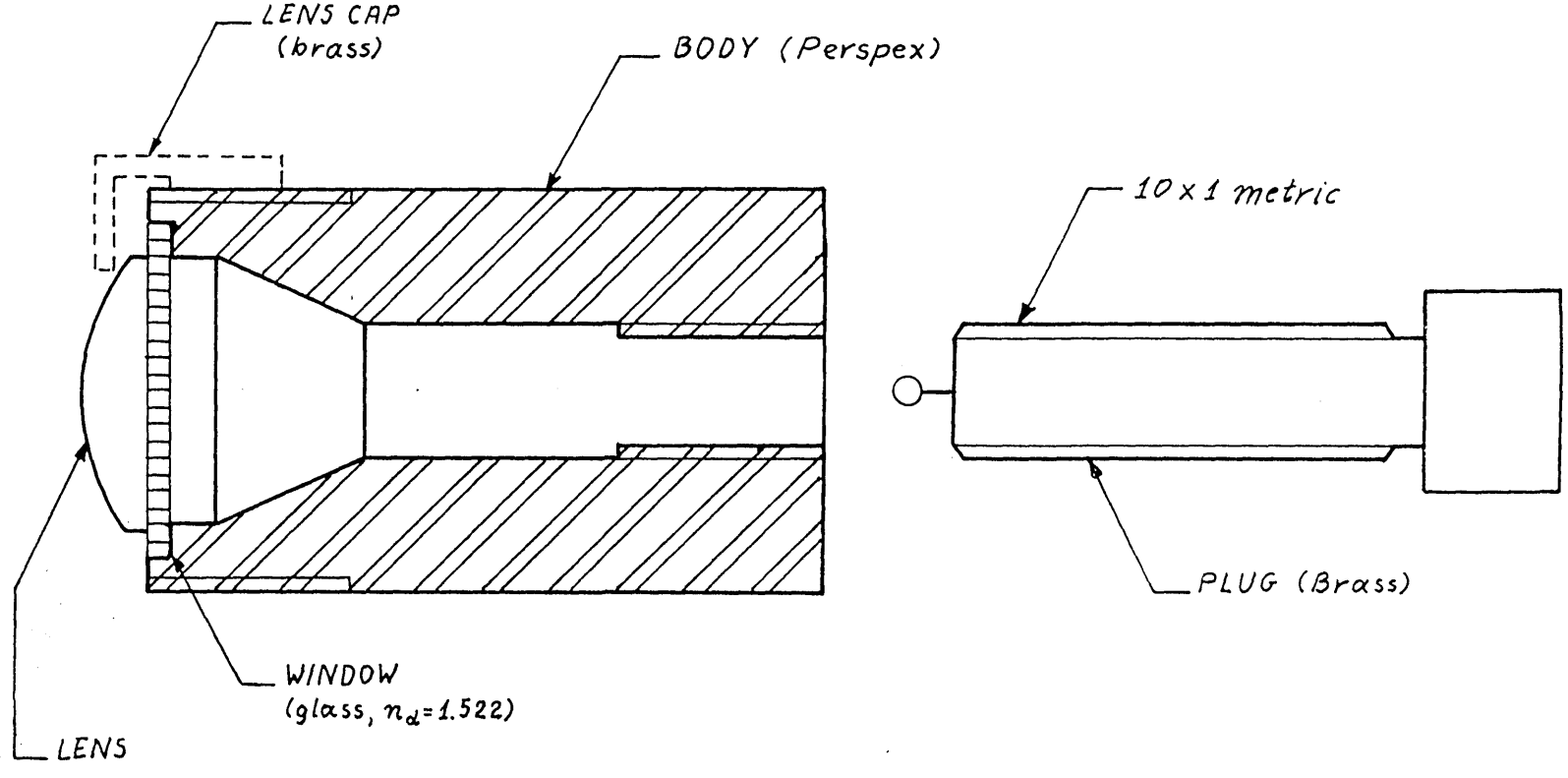


Figure 6.3 - The dilatometer.

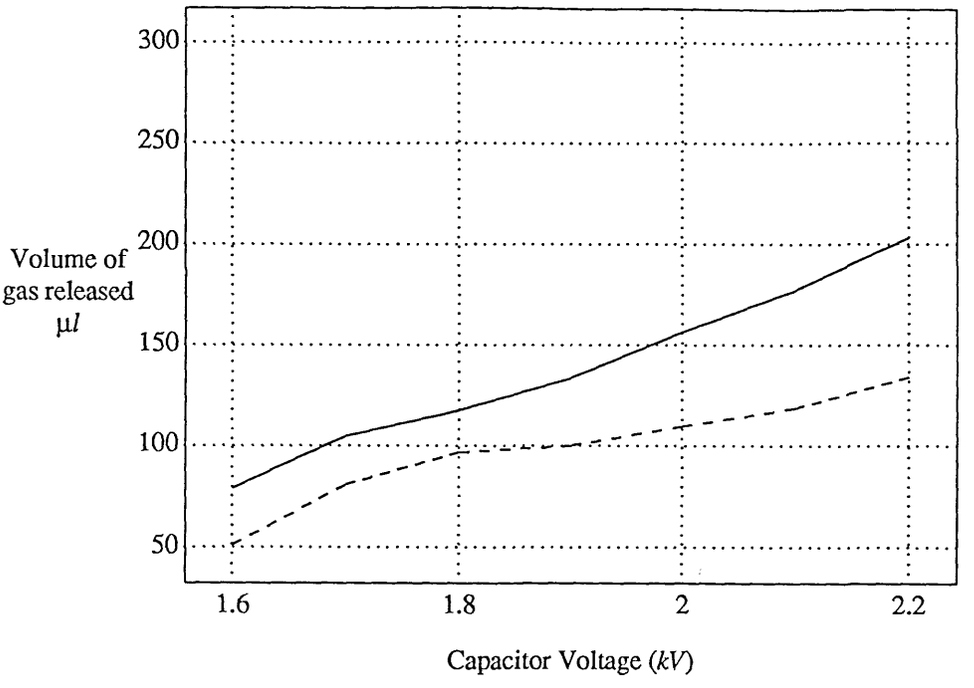


Figure 6.4 - Effect of laser beam energy on propellant decomposition. Solid line is for LP-101 and dashed line for HAN/SBAN.

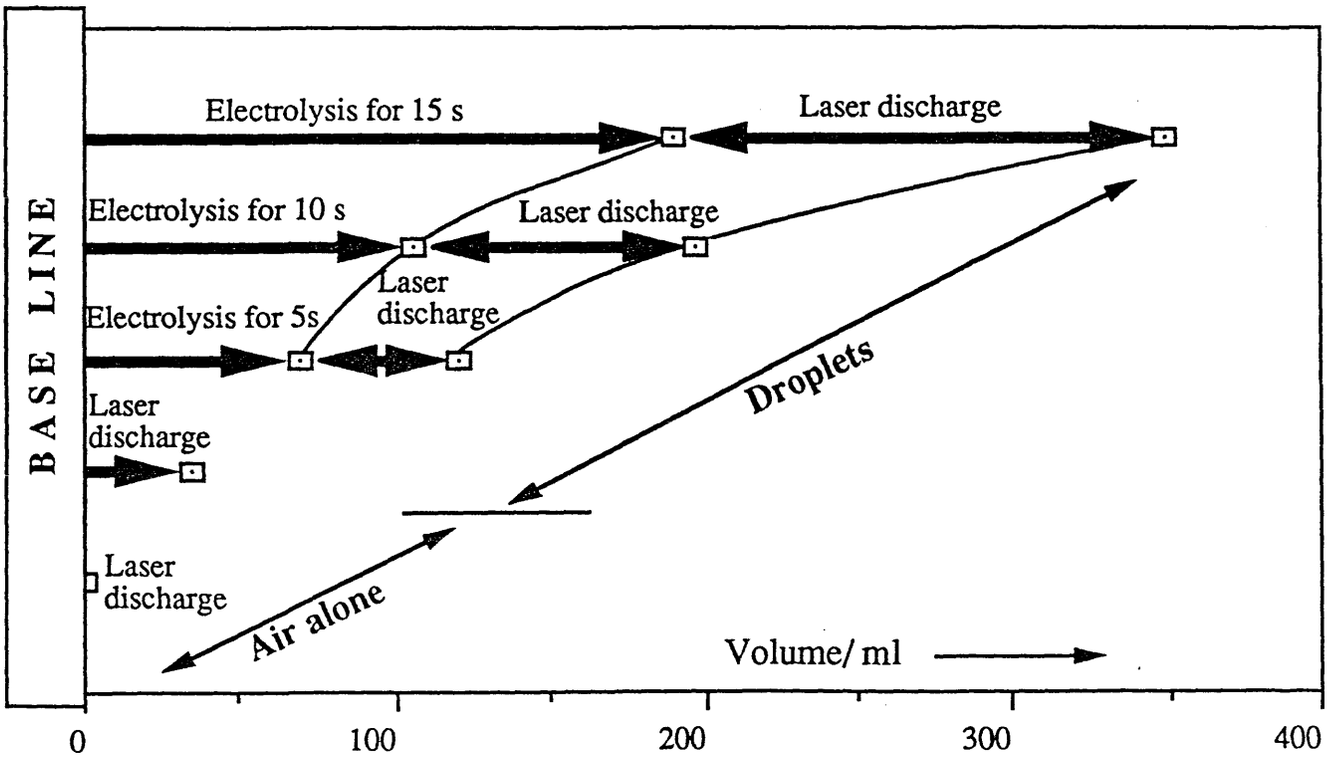


Figure 6.5 - Volume of gas initiation products with electrolyzed propelland samples.

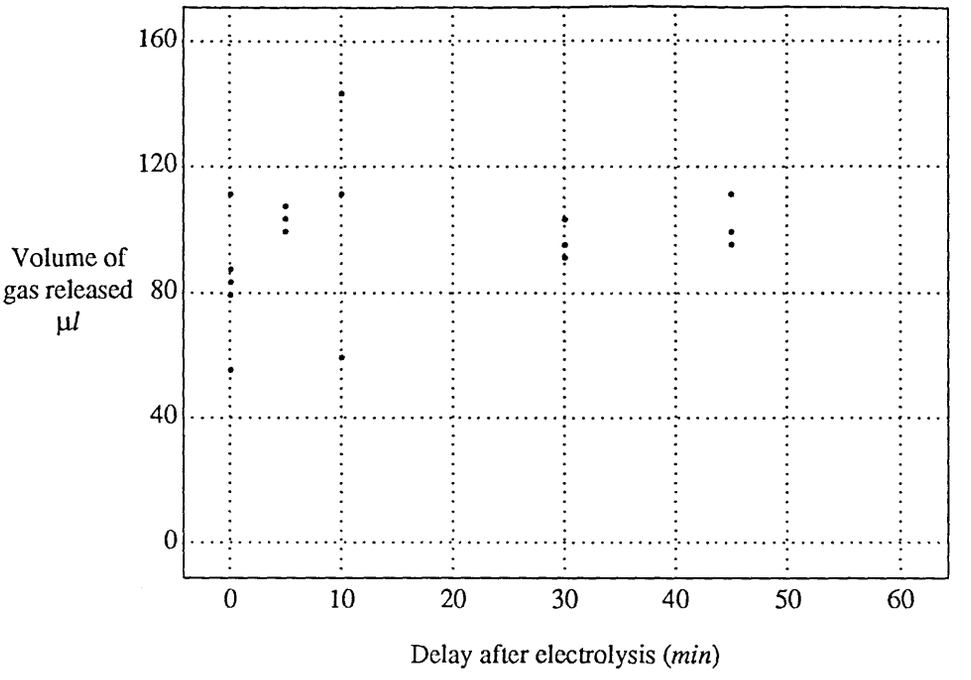


Figure 6.6 - Effect of delay after electrolysis on LP-101.

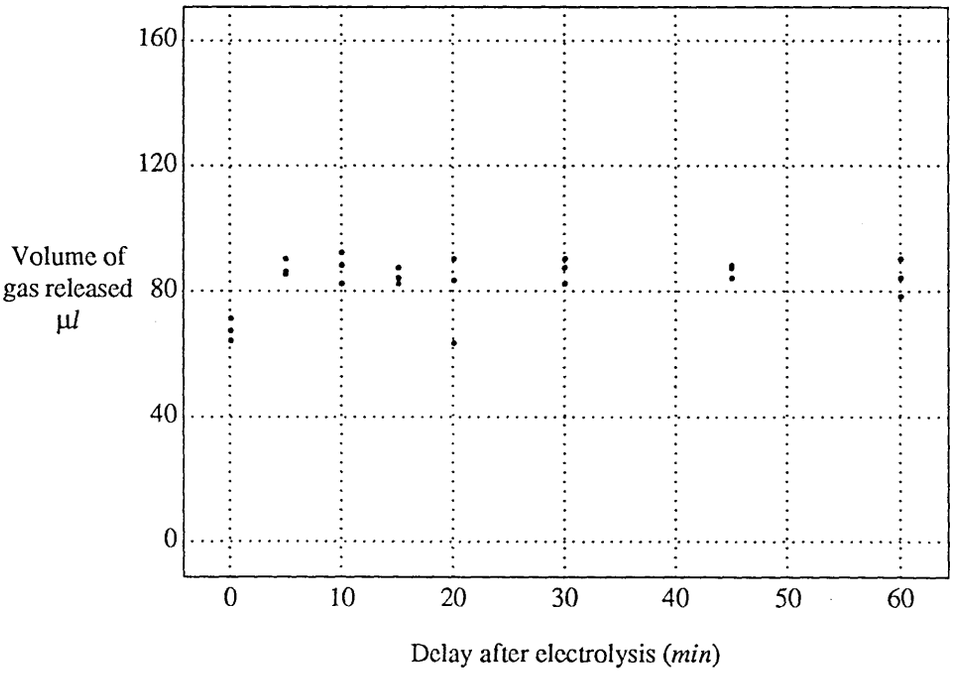


Figure 6.7 - Effect of delay after electrolysis on HAN/SBAN

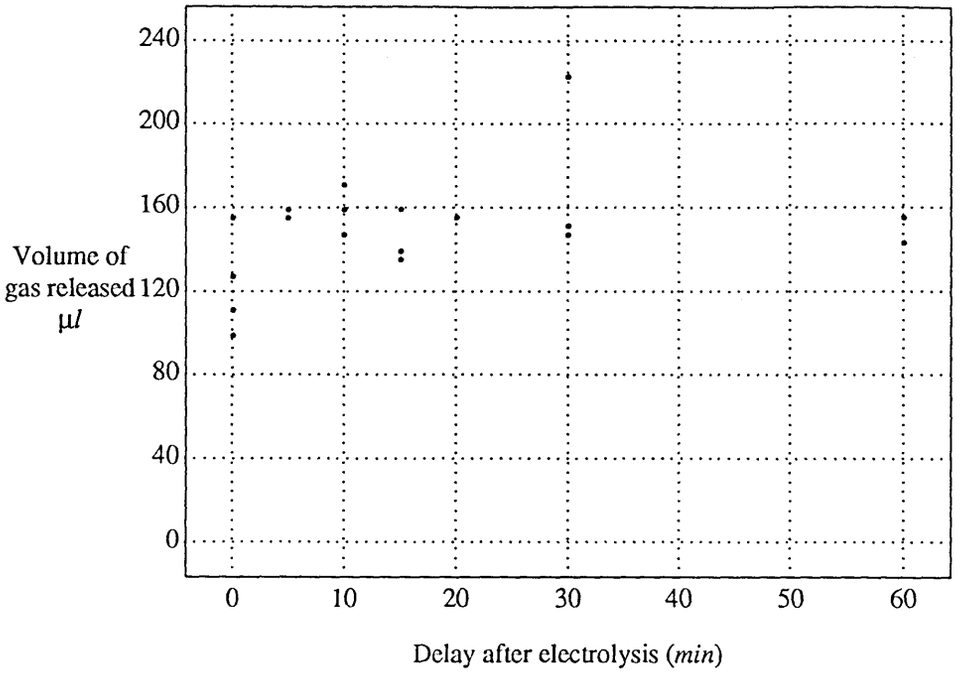


Figure 6.8 - Effect of delay after electrolysis on HAN/SBAN

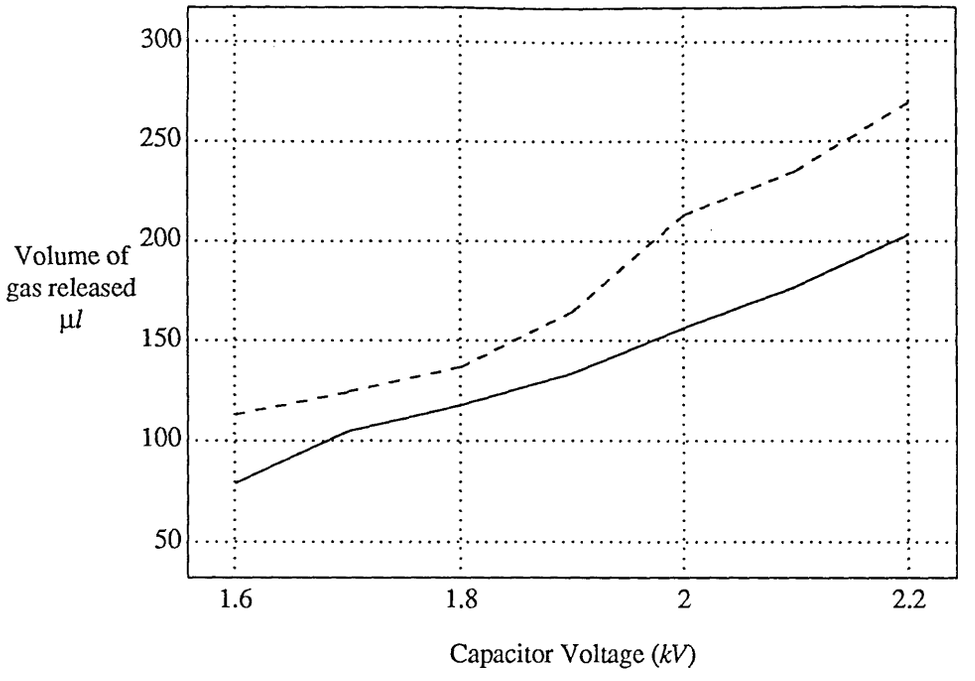


Figure 6.9 - Effect of electrolysis on LP-101.

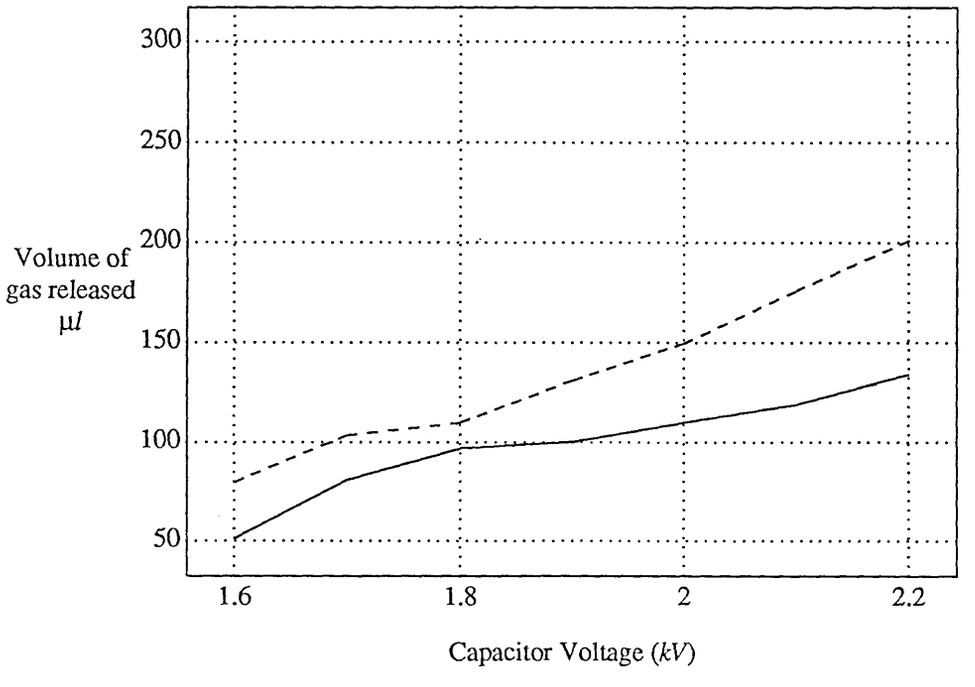


Figure 6.10 - Effect of electrolysis on HAN/SBAN

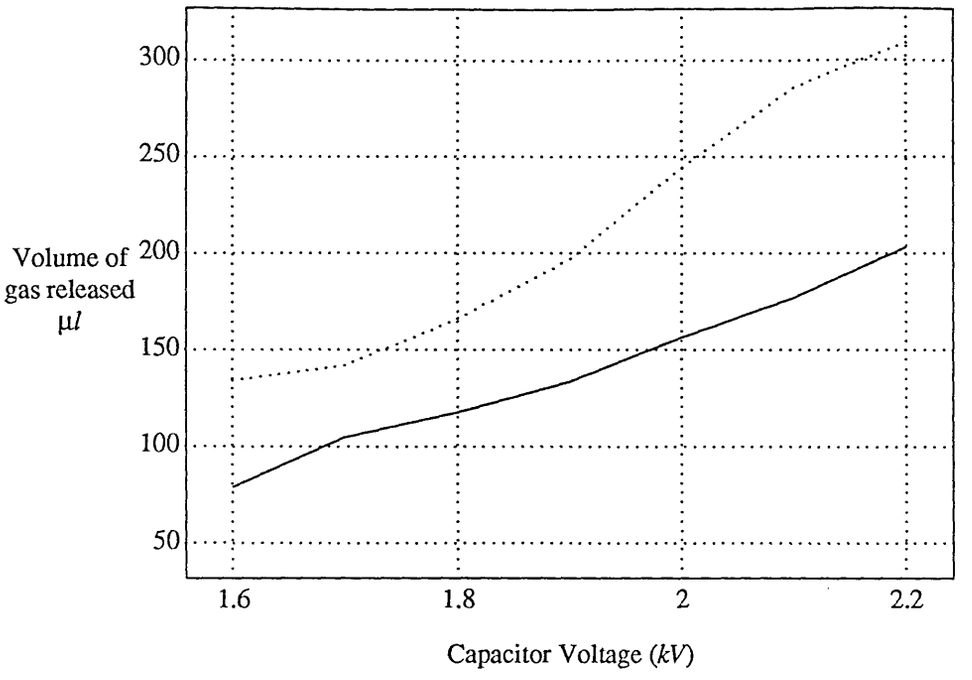


Figure 6.11 - Effect of heating on LP-101

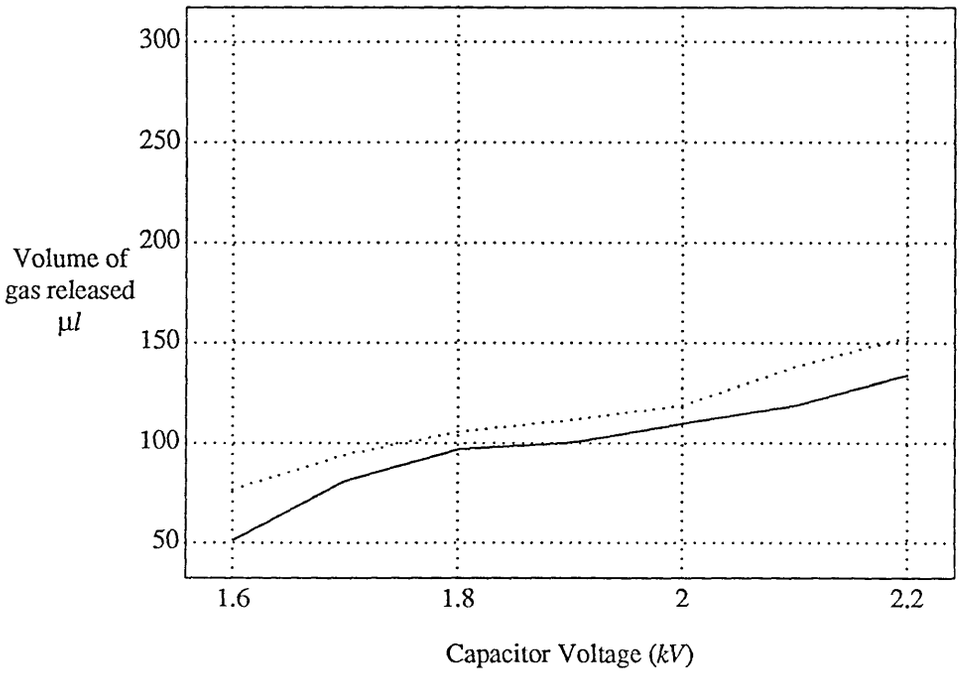


Figure 6-12 - Effect of heating on HAN/SBAN

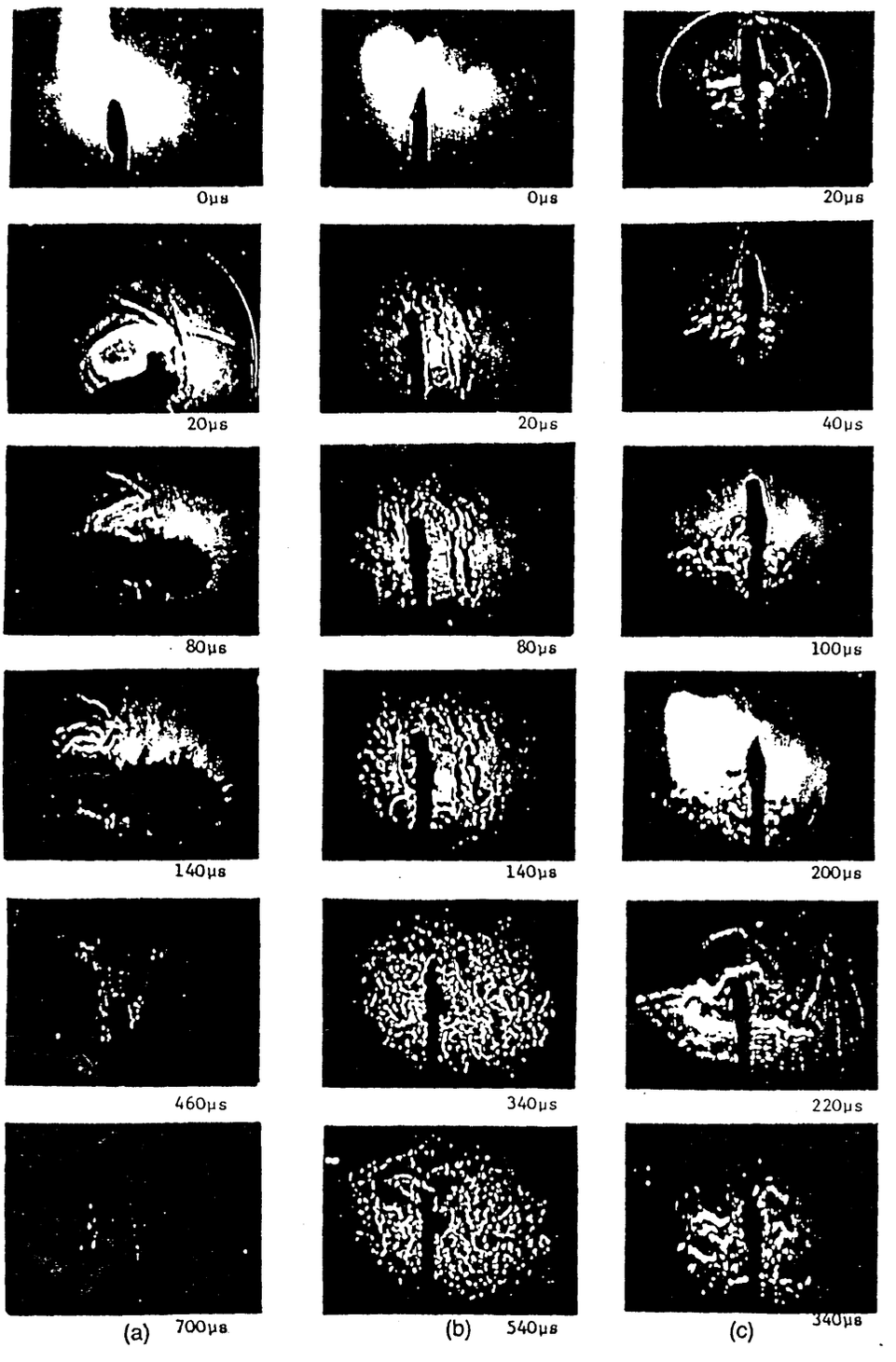


Plate 6.1 - Three shadow cine sequences illustrating the various interactions between stationary droplets and laser discharges: (a) liquid filaments extruded into plasma and secondary shock waves emerging from propellant droplet. (b) propellant replaced by NaCl solution, no reaction takes place, (c) the effects of laser double pulsing on a propellant droplet.

CHAPTER 7

DISCUSSION AND CONCLUSIONS

7.1 General

The work presented in this thesis has demonstrated the capabilities of various types of plasma jets when used as igniters under difficult conditions. The improved performance near the limits of flammability and the amount and form of the energy released make existing systems more reliable and allow the design of novel combustion systems ranging from pulsed supersonic burners to liquid propellant guns. The aerodynamically spun plasma jet igniter proved to be a very effective igniter and the feasibility of pulsed plasma plugs with liquid propellant feedstock energized by laser beams was demonstrated. We also have now a better understanding of the interaction between laser beams and hydroxylamonium based liquid propellants and the chemistry of initiation of such propellants.

7.2 Continuous Plasma Jets

The evaluation of the continuous plasma jet igniter demonstrated that a small size electrical power supply, which can be used aboard a jet aircraft, is feasible and can be constructed easily and at relatively low cost. As most aircraft electrical systems supply 28V DC, some design effort should be made towards a unit working at this voltage. Such a unit can be designed for minimum weight and size, which can be easily achieved, as the heavy Variac transformer can be eliminated from production units. The isolating transformer will need to be replaced by the transformer of a small solid state inverter and the capacitor voltage will be controlled electronically. Still an igniter of this type involves more complicated support hardware than other igniters currently considered for this specific application. This hardware is associated with the feedstock storage and control functions and consists mainly of a small tank, a solenoid control valve, a filling pipe and valve and a pressure meter. Such a system would be acceptable on an aircraft only if the improvement in ignition performance can outweight the problems posed by its size, complexity and weight and the logistics of feedstock supply.

The work described in this thesis demonstrated that nitrogen fed plasma jets of this type are very effective igniters of liquid sprays, except at relatively low initial temperatures. This limitation arises because the gas stream emerging from the igniter is relatively cold, partly as a result of the high electrical efficiency of these devices, and cannot vaporize enough liquid to produce a flammable gaseous air/fuel mixture. This problem could be possibly overcome by modifying the constitution of the gas feedstock. Fuel gas or vapour, like methane or aviation kerosene, could be mixed with nitrogen or used by themselves in order to produce fuel rich conditions locally in the ignition zone. Further experiments are required to show if such a system would be effective and practical as an aircraft turbine igniter. In a personal communication with staff from Rolls-Royce plc we were informed that the addition of a tank

containing flammable gas on an aircraft is undesirable so the option of using vaporized aviation fuel should be investigated.

Moreover, such a system could be quite useful as a high energy igniter for pulverized coal or heavy oil burners, provided a device which suits the geometry of these burners can be designed. If the igniter must protrude into the furnace, some method of cooling of its body, for example water cooling, will be necessary. For industrial furnace applications the complexity of the igniter and the storage of the feedstock would not normally be considered as serious disadvantages.

7.3 Liquid Propellant Plasma Plugs

Perhaps the most important practical result of this research is that laser initiation of the HAN based liquid monopropellants is possible and practical pulsed plasma jet igniters or gas generators which are free from electromagnetic interference are feasible. The next step should be to investigate the laser - propellant interaction under confinement, so that full ignition of the propellant is achieved. Finally a practical igniter must be designed and tested under realistic conditions. Such a device would be a hybrid of the igniters shown in figures 4.1 and 6.1 with the optical window possibly replaced by a suitable lens which will focus the beam into the mass of the propellant.

Regarding the fundamental aspects of HAN based propellant initiation, a reasonable chemical reaction scheme of the initiation process has been established as a basis for further research [Carleton et al, 1990]. This scheme, described in detail in pargagraph 4.4, explains the product yields and is further supported by the experimental results given in chapter 6. According to this model only hydroxylamonium and nitrate ions take part in the first critical parts of the initiation reaction. The most important initiating step seems to be the dissociation of nitric acid and production of strong oxidizing ions and radicals (NO_2, NO_2^+) which attack hydroxylamonium and lead to full reaction.

In a series of simple chemical experiments we conducted, we observed that the direct or indirect addition of nitrous acid or its salts, especially at low pH, immediately sets off a vigorous decomposition of the propellant, so we confirmed the important role of the reaction described by equation 4-9. The propellant reacted both to exposure to a NO_2 atmosphere which produces a mixture of nitric and nitrous acid and to addition of a solution of sodium nitrite in dilute nitric acid.

The initiation reactions were also set off by the addition of nitrate ions at low pH and this observation is in agreement with the nitronium ion hypothesis, as nitronium formation is favoured in near anhydrous low pH nitrate solutions. Generally we can say that our results are in agreement with the chemical mechanism described in chapter 4.

Other simple experiments demonstrated, independently of the Ernst-Mach Institute research team [Klingenberg et al, 1989], the feasibility of electrical initiation of LP-101 using low voltage electrolysis at relatively high current densities. A problem with this method is the variable delay before HAN decomposition sets off, which is avoided when an arc is formed in the cavity. This method of initiation is important

for some practical applications where shock wave which might develop into detonations must be avoided.

In previous work, when electrical initiation was used, the effects of electrolysis were partly masked by the arc discharge which followed. It is now possible, by using optical initiation, to isolate the effects of electrolysis and study them separately. These results are in agreement with the theory which predicts that nitrogen oxides are important intermediate products. They also show that propellants with relatively low sensitivity like HAN/SBAN can become as sensitive as LP-101 after short electrolysis. As this electrolysis can take place just before use, it is possible to store the propellant in a less sensitive form and electrolyse it immediately before or during loading in the igniter.

The experiments on thermal treatment of the propellant, which must be also confirmed with LP-1845, show an increased sensitivity and instability of LP-101 to prolonged heating at relatively high temperatures. In combination with the experiments on laser initiation using dyed propellant, they show that ohmic or laser heating is responsible for the generation of small quantities of active species from dissociation of nitrate ions. No photochemical reactions were observed with the 694.3 *nm* red light produced by the ruby laser, but the response of the propellant to laser beams of different wavelengths must be investigated. The first step would be to study the absorption spectrum of the propellant and correlate the various absorption bands with individual reactions. As all the propellants studied so far are clear transparent liquids, any absorption bands must be located outside the visible spectrum.

The experiments with the Frazer-Nash pulsed plasma plug design confirmed results of previous work at Imperial College and U.S. Army Ballistics Research Laboratory and demonstrated some practical problems which affect the operation of such systems, particularly the chemical attack of the electrodes by the aqueous propellant.

The development of the dilatometer was an important part of this work. This small instrument has good accuracy and reproducibility and was a valuable research instrument. It can be easily modified to suit other experiments which involve constant pressure combustion. Some practical problems faced during its operation in the form of minor gas leaks were solved easily. They can be eliminated completely by careful redesign of the seal between the window and the body of the dilatometer. Its main disadvantage is that it does not give a volume vs. time history of the event but only the volume after thermal equilibrium with the environment is reached.

Appendix A

Avtur Fuel Specification

Aviation kerosine, which is given the Joint Services Designation of **avtur**, is a colourless blend of relatively involatile hydrocarbon components with average properties roughly equivalent to $C_{12.5}H_{24.4}$ of molar mass 175 g/mol and of hydrogen content 14.06% by mass Avtur comprises by volume some 79% parafins and naphthenes, 20% aromatics and 1% olefins. Typically, avtur boils over the range 144-252^{o}C and has a density of about 0.8 kg/l.

Avtur is roughly equivalent to U.S.A. fuel Jet A-1 (NATO F-35, DERD Spec. No. 2494, ASTM D-1655) which has a low freezing point (-47°C) suited to international flights and contains FSII (Fuel System Icing Inhibitor, DERD Spec. No. 2451).

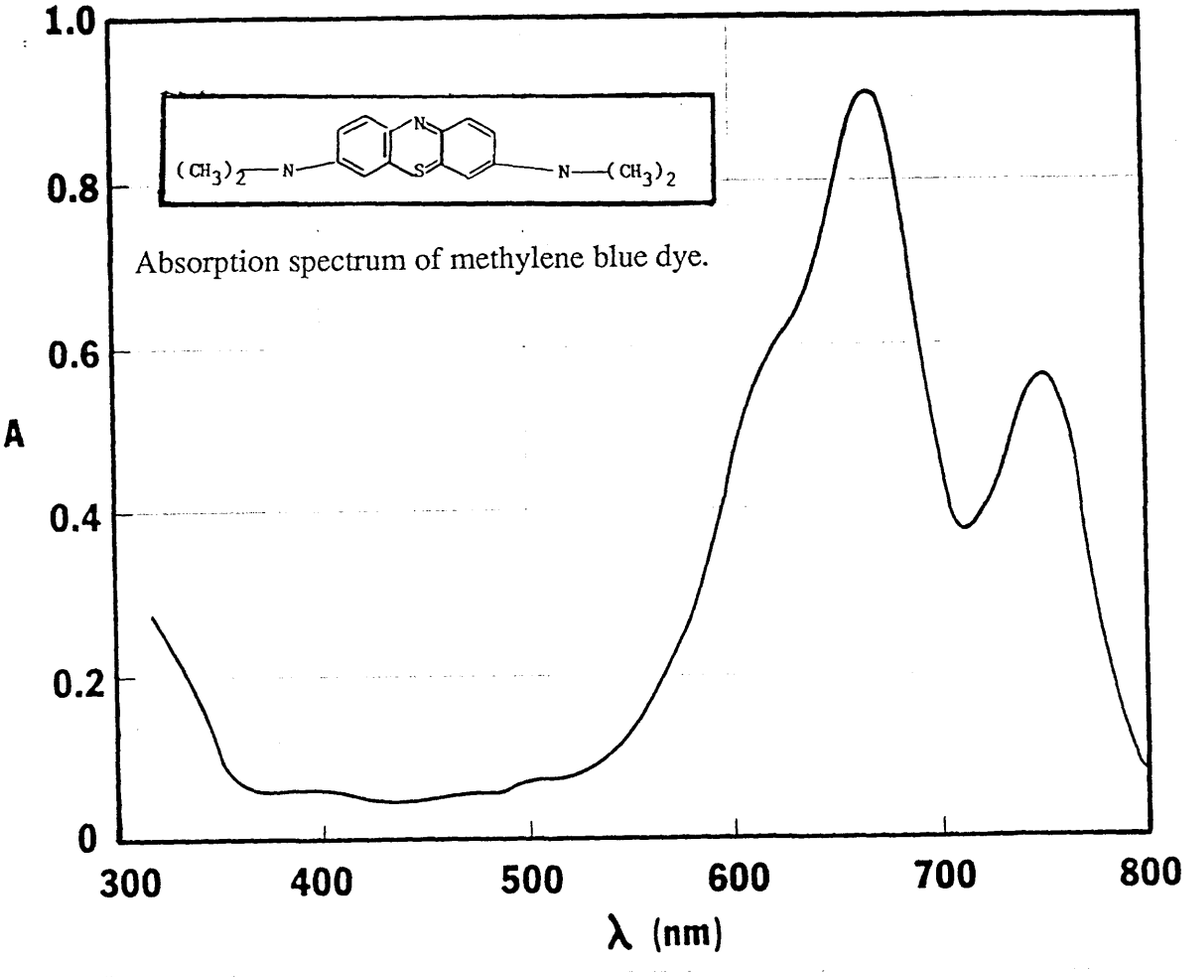
The specifications of Avtur fuel are the following:

Composition		
Acidity, total, $mg\ KOH/g$	max.	0.015
Aromatics, % vol.	max.	22.0
Olefins, % vol.	max.	5.0
Sulfur, total, % mass	max.	0.30
Sulfur, mercaptan, % mass	max.	0.003
Volatility		
Initial boiling point		Report
Fuel recovered		
10% vol. at ^{o}C	max.	205
20% vol. at ^{o}C	max.	Report
50% vol. at ^{o}C	max.	Report
90% vol. at ^{o}C	max.	Report
End point, ^{o}C	min.	300
Flash point, ^{o}C	min.	38
Density at 15^{o}C, kg/l	min.	0.775
	max.	0.830
Fluidity		
Freezing point, ^{o}C	max.	-47
Viscosity at $-20^{o}C, mm^{2}\cdot s^{-1}$	max.	8.0
Combustion		
Specific energy, net, MJ/kg	min.	42.8
or		
Aniline-gravity product	min.	4800
Smoke point, mm	min.	20
naphthalenes, %vol.	max.	3.0

Appendix B

Methylene Blue Dye

The ignition stimulus for laser initiation was supplied by a *Laser Associates* model 211*A* pulsed ruby laser producing a light pulse at 694.3 *nm*. In order to increase energy absorption is some experiments, a modified form of the "methylene blue" dye was used. Methylene blue is normally available as its chloride salt. It had previously been shown [Klein and Sasse, 1980] that the presence of small quantities of chloride ions (Cl^-) adversely affects the ignition and combustion characteristics of HAN based propellants. In order to avoid this potentially adverse condition, the nitrate salt of methylene blue was prepared. The preparation method was described by Dr. N. Klein [Klein et al, 1983]. Figure A-1 shows the absorption spectrum of the dye which has peaks at 664 *nm* and 750 *nm*.

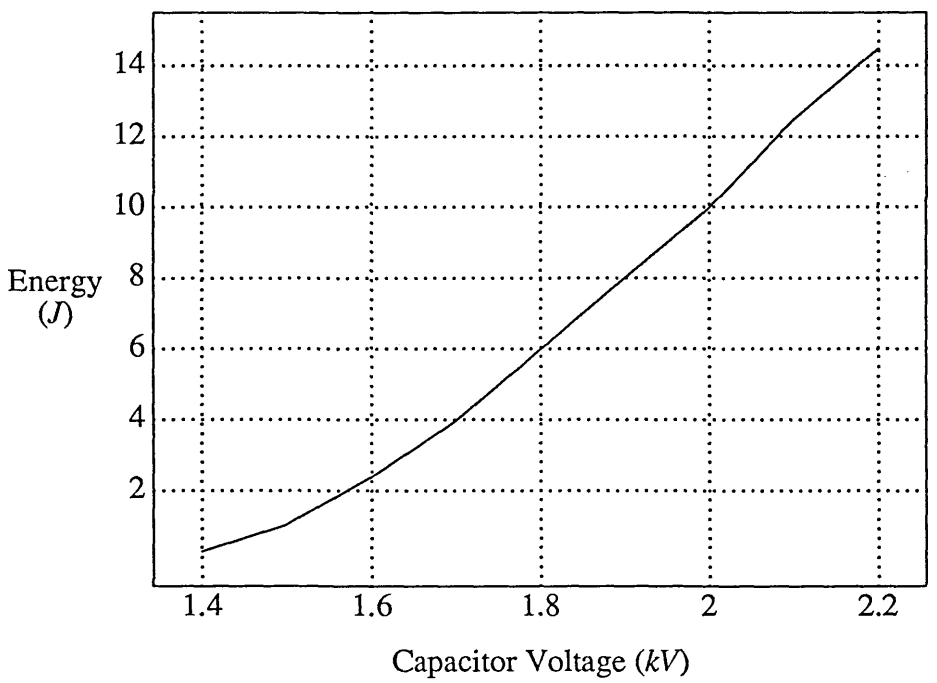


Absorption spectrum of methylene blue dye.

Appendix C

Laser Calibration (Energy vs. Voltage)

Calibration graph, showing beam energy vs. capacitor voltage for the *Laser Associates* 211A pulsed ruby laser operating at 694.3 *nm* (red) without Q-switch. A *5370 Monitor*, made by *Laser Instrumentation Ltd.* was used to measure beam energy.



Appendix D

Handling Instructions for LP-101 Liquid Monopropellant

The following instructions by B. H. Bonner, *dated 22-2-1989, are reproduced from an instruction sheet which accompanied the LP-101 sample supplied by Frazer-Nash Ltd.*

"LP-101" is the UK designation of an aqueous monopropellant with the composition:

63.2% hydroxylamonium nitrate
20.0% triethanolamonium nitrate
16.8% water

LP-101 is a clear, odourless liquid, density $1.46\ g \cdot cm^{-3}$, with a low vapour pressure. It freezes below $-50^{o}C$. Heating above $100^{o}C$ causes decomposition with the emission of oxides of nitrogen. The propellant will not burn if unconfined at atmospheric pressure.

HSE classification tests have shown that LP-101 is an explosive; UN Hazard Division **1.3 L1.**

If LP-101 is heated and held above $50^{o}C$ for extended periods, then there is a possibility of rapid explosive decomposition occurring in an unpredictable manner. Appropriate safety precasutions need to be taken in the design of aging and compatibility experiments particularly when LP-101 is held at elevated temperatures. Samples of LP-101 which have been exposed to elevated temperatures need to be handled and stored with caution.

The liquid is mildly acidic and will corrode aluminium and copper alloys and mild steel. Contamination with such materials can cause the propellant to become unstable and decompose. Contaminated propellant and spills must be diluted with copious quantities of water and washed into the site effluent system. The propellant must not be left confined and, after test, rig systems must be vented, drained and preferably flushed with water.

The liquid is moderately toxic and precautions must be taken to avoid ingestion and skin contact. Gloves and goggles must be worn and any splashes to the skin or clothing must be washed off with copious water. Splashes in the eyes must be treated by continuous irrigation with water for at least 10 minutes. The vapour is not toxic but

aerosol droplets produced by a fine spray could be harmful.

LP-101 must be stored away from amine and hydrazine fuels and away from nitric acid and nitrogen tetroxide oxidizers.

B. H. Bonner

22 February 1989

References

General

Barbour, 1981
barbour, R.T.: "Pyrotechnics in Industry", McGraw-Hill.

Bose, 1977
Bose, K.W.: "Aviation Electronics", Howard Sams.

Boston et al, 1984
Boston, P.M., Bradley, D., Lung, F.K.K., Vince, I.M. and Weinberg, F.J.: "Flame Initiation in Lean, Quiescent and Turbulent Mixtures with Various Igniters", *20th Symposium (International) on Combustion*, The Combustion Institute, Pittsburgh, p.1825.

Chesters et al, 1981
Chesters, D.A., Clarck, C.J. and Riddiford, F.A.: "Downwhole Steam Generation using a Pulsed Burner", *Proc. 1981 Euro. Symp. on Enchanced Oil Recovery*, p. 563, Elsevier Sequoia, 1981.

Fordham, 1980
Fordham, S.: "High Explosives and Propellants", Pergamon Press, 1980.

Hughes, 1987
Hughes, E.: "Electrical technology", 6th Edition, Longman.

Kit and Everet, 1960
Kit, B. and Everet, D.S.: "Rocket Propellant Handbook", McMillan, 1960.

Morrison et al, 1988
Morrison, W.F., Knapton, J.D. and Bulman, M.J.: "Liquid Propellant Guns", *Progress in Astronautics and Aeronautics*, **109**, Chap. 13, AIAA, Washington.

Pallet, 1976
Pallet, E.J.H.: "Aircraft Electrical Systems", Pitman Publishing, London.

Schwar and Weinberg, 1969
Schwar, M.J.R. and Weinberg, F.J.:"Laser Techniques in Combustion Research", *Combustion and Flame*, **13**, 335.

Continuous Plasma Jets

Behbahani et al, 1982
Behbahani, H.F, Fontjin, A., Muller-Dethlefs, K. and Weinberg, F.J.: " The Destruction of Nitric Oxide by Nitrogen Atoms from Plasma Jets", *Combust. Sci. and Tech.*, **27**, 123.

Behbahani et al, 1983
Behbahani, H.F., Warris, A.-M. and Weinberg, F.J.: "The Destruction of Nitric Oxide by Nitrogen Atoms from Plasma Jets: Designing for Thermal Stratification", *Combust. Sci. and Tech.*, **30**, 289.

Chan et al, 1980
Chan, A.K.F, Hilliard, J.C., Jones, A.R. and Weinberg, F.J.: "An electrically efficient, finely tunable, low-power plasma generator", *J. Phys. D: Appl. Phys.*, **13**, 2309.

Cheriyan and Weinberg, 1986
Cheriyan, G.K. and Weinberg, F.J.: "Plasma Jet Ignition Trials in a Spey Can Combustor", Final Report, London.

Cheriyan et al, 1990
Cheriyan, G.K., Krallis, K. and Weinberg, F.J.: "Adapting Continuous-Flow Plasma Jets for Intermittent Ignition in Gas Turbine Combustors", *Combust. Sci. and Tech.*, **70**, 171.

Harrison and Weinberg, 1971
Harrison, A.J. and Weinberg, F.J: "Flame stabilization by plasma jets", *Proc. Roy. Soc. Lond.*, A **321**, 95.

Hilliard and Weinberg, 1976
Hilliard, J.C. and Weinberg, F.J.: "Effect of Nitrogen-containing plasmas on stability, NO formation and sooting of flames", *Nature*, **259**, 556.

Kimura et al, 1981
Kimura, I., Aoki, H. and Kato, M.: "The Use of Plasma Jets for Flame Stabilization and Promotion of Combustion in Supersonic Air Flows", *Combustion and Flame*, **42**, 297.

Kimura and Imajo, 1976
Kimura, I. and Imajo, M.: "An Experimental Investigation of an Arc-heated Stirred Reactor", *16th Symposium (International) on Combustion*, The Combustion Institute, Pittsburgh, p. 809.

Krallis, 1987
Krallis, K: "Plasma Jet Ignition", *M.Sc. Thesis*, University of London (Imperial College).

Lucas, 1988
Lucas Aerospace Ltd: "Altitude Ignition Testing of a Plasma Jet Igniter Fitted in a Tay Triple Sectro Combustion Rig", *Report no ATF-1095*, Burnley.

Northam et al, 1984
Northam, G.B., McClinton, C.R., Wagner, T.C. and O'Brien, W.F.: *20th Joint Propulsion Conference*, Cincinnati, *AIAA Paper No. 84-1408.*

Warris, 1983
Warris, A.-M.: "Electric Plasmas for Flame Stabilization and Ignition in Fast Gas Streams", *Ph.D. Thesis*, University of London (Imperial College).

Warris and Weinberg, 1984
Warris, A.-M. and Weinberg, F.J.: "Ignition and Flame Stabilization by Plasma Jet in Fast Gas Streams", *20th Symposium (International) on Combustion*, The Combustion Institute, Pittsburgh, p.1825.

Weinberg, 1986
Weinberg, F.J. (Editor): "Advanced Combustion Methods", Chap. 5: "Electrical Discharge-Augmented Flames and Plasma Jets in Combustion", Academic Press.

Wilson, 1988
Wilson, C.W.: "Evaluation of the Imperial Colllege Plasma Jet Igniter in the Lucas ATF", *Rolls-Royce plc GN 29141*, Bristol.

Pulsed Plasma Jets

Asik et al, 1977
Asik, J.R., Piatowski, P., Foucher, M.J. and Rado, W.G.: "Design of a Plasma Jet Ignition System for Automotive Application", *SAE paper no. 770355.*

Dale et al, 1978
Dale, J.D., Smy, P.R. and Clements, R.M.: "The effects of a Coaxial Spark Igniter on the Performance of and the Emissions from an Internal Combustion Engine", *Combustion and Flamea*, **31**, 173.

Low et al, 1989
Low, H.C., Wilson. C.W., Adbel-Gayed, R.G. and Bradley, D.: *AIAA Publication No. 89-2944*, 25th Joint Propulsion Conference, Monterey.

Tozzi and Dabora, 1982
Tozzi, L. and Dabora, E.K.: "Plasma Jet ignition in a lean burn CFR engine", *19th Symposium (International) on Combustion, The Combustion Institute, Haifa, p.1467.*

Vosen et al, 1988
Vosen, S.R., Cattolica, R.J. and Weinberg, F.J.: "Chemical effects of plasma gases on flame kernel development", *Proc. Roy. Soc. Lond.*, A **418**, 313.

Vince et al, 1984
Vince, I.M., Vovelle, C. and Weinberg, F.J.: "The effect of Plasma Jet Ignition on Flame Propagation and Sooting at the Rich Limit of Flammability", *Combustion and Flame*, **56**, 105.

Weinberg et al, 1978
Weinberg, F.J., Oppenheim, A.K. and Teichman, K.: "Ignition by Plasma Jet", *Nature*, **272**, No. 5651, p.341.

Wyczalek et al, 1975
Wyczalek, F.A., Frank, D.L. and Neuman, H.G.: "Plasma Jet Ignition of Lean Mixtures", *SAE Paper no. 750349*

HAN-based Liquid Propellants

Carleton et al, 1985
Carleton, F.B., Cheriyan, G., Klein, N. and Weinberg, F.J.: "Optical Studies of Electrical Discharge-Liquid Propellant Interactions", *22nd JANNAF Combustion Meeting*, **1**, 201.

Carleton, F.B., Cheriyan, G.K., Klein, N. and Weinberg, F.J.:
"Plasma Propellant Jet Ignition", *22nd Symposium (International) on Combustion*, The Combustion Institute, p. 1885.

Carleton et al, 1987
Carleton, F.B., Klein, N. and Weinberg, F.J.: "Liquid Propellants in Pulsed Plasma Jet Igniters", *Combust. Sci. and Tech.*, **56**, 85.

Carleton et al, 1990
Carleton, F.B., Klein, N., Krallis, K. and Weinberg, F.J.: "Laser Ignition of Liquid Propellants", *26th Symposium (International) on Combustion*, The Combustion Institute, Orleans.

Cattolica and Klein, 1987
Cattolica, R.J. and Klein, N.: "Plasma Ignition of Liquid Propellant", *Combust. Sci. and Tech.*, **56**, 139.

Cronin et Brill, 1988
Cronin, J.T. and Brill, B.T.: *Combustion and Flame*, **74**, 81.

Klein et al, 1983
Klein, N., Weinberg, F.J. and Carleton, F.B.: "Ignition Phenomena in Energetic Liquids", U.S. Army Armament Research and Development Command, *Technical Report ARBRL-TR-02514.*

Klein, 1982
Klein, N.: "Isomer Effects on Liquid Propellant Performance", *19th JANNAF Combustion Meeting.*

Klein, 1983
Klein, N.: "Liquid Propelant Ignition Studies", *20th JANNAF Combustion Meeting*, p. 473.

Klein et al, 1982
Klein, N., Carleton, F.B. and Weinberg, F.J.: "Methods for Evaluation of Ignition Stimuli for Liquid Propellants", *19th JANNAF Combustion Meeting*.

Klein, 1988
Klein, N.: "Liquid Propellants for Use in Guns", *Progress in Astronautics and Aeronautics*, **109**, Chap. 13, AIAA, Washington.

Klingenberg et al, 1989
Klingenberg, G., Rockstroh, H, Knapton, J.D., DeSpirito, J. and Frieske, H.-J.: "Electrical Ignition of HAN-based Liquid Propellants", *11th International Symposium on Ballistics*, Brussels.

Kounalakis and Faeth, 1988
Kounalakis, M.E. and Faeth, G.M.: *Combustion and Flame*, **74**, 179.

Lee et al, 1988
Lee, T.W., Gore, J.P., Faeth, G.M. and Birk, A.: *Combust. Sci. and Tech.*, **57**, 95.

Mellor, 1967
Mellor: "Supplement to the Comprehensive Treatise on Inorganic and Theoretical Chemistry", **VIII**, Sup. II, Part II, p. 138, Longmans, 1967.

Pascal, 1956
Pascal, P.: "Nouveau Trait´e de Chimie Min´erale", Tome **X**, (Azote, Phosphore), Masson, Paris, p. 286.

Russel and Brill, 1989
Russel, T.P. and Brill, T.B.: *Combustion and Flame*, **76**, 393.

Shaw et al, 1990
Shaw, B.D., Williams, F.A. and Chung, S.H.: "Theory of Combustion of Liquid Propellants Based on Hydroxylamonium Nitrate", (Poster), *26th Symposium (International) on Combustion*, Orleans.

Solomons, 1980
Solomons, T.W.G.: "Organic Chemistry", p. 826, Willey, 1980.

Vosen, 1989
Vosen, S.R.: *Combust. Sci. and Tech.*, **68**, 85.

Zhu et al, 1987
Zhu, D.L. and Law, C.K.: *Combustion and Flame*, **70**, 333.