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EXPLOSIVES RESEARCH AND
DEVELOPMENT ESTABLISHMENT

Rules Governing the Routine Operation
of the South Site Proof Stand

WALTHAM ABBEY,
ESSEX

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RULES GOVERNING THE ROUTINE OPERATION OF THE
SOUTH SITE PROOF STAND

Building No's. P.725 and P.753

Object

These rules are intended to formulate a method of safe working of the South Site Proof Stand, and are intended to be observed with those laid down in the Safety Rules Handbook.

I Procedure in the Hot and Cold Store
Building No.P.727

1. All handling of rounds involving the use of hot or cold chests will be carried out only when at least two persons are present.

2. Except in case of emergency, no person is to enter a hot or cold chest without at least one other person standing nearby and observing.

II Inspection of Rounds Prior to Assembly
and Firing

1. Each round will be inspected by the Laboratory Worker-in-Charge of Firing prior to assembly and firing.

2. Any round defects, e.g. cracks, badly torn propellant, off-centre conduit, distortion, faulty inhibition, propellant in threads, defective metal parts, will be reported to the Officer-in-Charge.

3. No defective rounds may be fired without the express approval of the Officer-in-Charge.

III Storage of Rounds in the Assembly Bays

1. Under no circumstances must rounds be left in the bays over-night.

2. On no occasion must more than the equivalent of one day's firing be allowed to accumulate in the assembly bays.

IV Transport and Handling of Rounds

All rounds larger than 2" Air-to-Air must be transported between buildings on an approved truck.

V Handling of Igniters

When assembled in live rounds the bare ends of the Igniter Leads should be twisted together to ensure that both leads are at the same potential.

VI Approaching and Entering an Empty Firing Pit

1. All rounds larger than 2" air-to-air will be brought into the Proof Stand by the rear entrance.

2. Before a round is brought into the Firing Pit it is the responsibility of the person with the Safety Plug (para. XII 8 below) to see that:

(a) Everyone (except the Firing Pit Team, the Officer-in-Charge and approved Visitors) vacates the Proof Stand Building.

(b) All material and equipment not required in the Firing Pit is removed.

3. When this has been done he will then ensure that the gate at the rear entrance to the Proof Stand is closed and secured.

4. The round may then be brought into the Firing Pit.

5. The gate at the rear entrance to the Proof Stand will remain closed and secured until the round is removed from the Firing Pit.

VII Setting up a Round and Vacating the Proof Stand Building

1. The round will be set up in accordance with instructions given by the Officer-in-Charge.

2. The safety of visitors will be the responsibility of the Officer-in-Charge, who must be informed of their presence, if he is not present at the time.

3. The round having been set up,

(a) the person having the Safety Plug will then ensure that the Firing Pit is vacated by all other members.

(b) The members of the Firing Pit Team, who will be in the Switch Room, must ensure that no-one enters the Firing Pit by the front entrance.

(c) The person with the Safety Plug will then connect the Igniter Leads to the Firing Leads.

(d) He will then vacate the Pit, bolt the iron door and proceed to the Switch Room.

4. On the arrival of the person with the Safety Plug at the Switch Room:

(a) the Ignition Switch will be placed in the FIRE position.

(b) the 'Round On' Switch will be placed in the ON position.

(c) the Fan Motors will be started.

5. The person with the Safety Plug will then ensure that the Proof Stand Building is vacated and will himself be the last to leave.

VIII Preparation for Firing and Firing in Building P.721

1. As far as possible, all preparation for firing must be made before the sounding of the warning signal.

2. The ignition circuit will be tested with the Igniter Tester before each firing and any abnormal reading reported immediately to the Officer-in-Charge. Normal readings are defined as:

66 to 80 for a single igniter and
56 to 70 for two igniters wired in parallel.

5. To avoid the possibility of injury if flame started coming from the rocket nozzle, until the round is cold no person will place himself or any part of his person in a position from which any part of the inside of the venturi can be seen.

6. No-one may attempt to re-enter the Firing Pit by the rear entrance when a live round, a spent round or a misfire is in the Firing Pit. (A live round is defined in Section XI below. A spent round is one which has fired normally and a misfire is defined in Section XII.

X Re-entering the Proof Stand and Firing Pit after a firing which evolves toxic product

All solid propellants evolve toxic products on firing and sufficient time must be allowed for these to disperse. Since this time is largely dependent on the prevailing weather conditions it is not possible to stipulate a fixed waiting period without involving, on occasions, an unnecessary wastage of time.

1. When propellants which give unusually toxic products are to be fired, the Officer-in-Charge will inform the Firing Pit Team and will also stipulate a minimum waiting period between the end of firing and re-entry to the Proof Stand.

XI Re-entering the Proof Stand and Firing Pit When a Live Round (not classified as a misfire) is present

(A live round is defined as one having its Igniter Leads connected to the Firing Leads, no attempt having been made to fire the Igniter).

1. Specific instruction must be obtained from the Officer-in-Charge before an entry can be made.

2. The procedure will be that given in paragraph IX but with the following modifications:

(a) There must be at least two persons who enter the Proof Stand.

(b) The person with the Safety Plug will be the only one to enter the Firing Pit, other member(s) remaining in the Switch Room.

(c) Another member of the Firing Pit Team is permitted to enter the Firing Pit only during an emergency involving the safety of the person with the Safety Plug.

3. After the necessary work or inspection is completed the Proof Stand will be vacated in accordance with paragraph VII.

XII Misfires

For the purpose of these rules a misfire will be defined as any firing or attempted firing in which the charge is not ignited or is incompletely burnt. Misfires may be classified into four types:

- Type 1: Igniter fails to function.
- Type 2: Igniter fires but fails to ignite charge.
- Type 3: Charge ignites but is extinguished before being completely consumed.
- Type 4: Motor explodes.

XIII Detection of Misfires

- Type 1: If there is no detectable pressure pulse or change in pressure it may be assumed that a Type 1 misfire has occurred.
- Type 2: This is distinguished by an initial sharp pressure peak falling to zero in a time negligible in comparison with the expected burning time.
- Type 3: This is distinguished by a falling off to zero pressure before the elapse of the expected

burning time. This falling off may be sudden (e.g. when a choke is blown out) or gradual (e.g. due to a wrongly designed motor).

- Type 4: This is usually distinguished by an increase in pressure to a level well above the expected value followed by a sudden decrease to zero pressure. It may not always be possible to distinguish between this and Type 3 (e.g. it is possible for the pressure to be normal but the motor explodes due to a flaw in material).

In some cases the milliammeter connected to the Kintel D.C. Amplifier will show an abnormal steady deflection indicating that the pressure or thrust measuring device attached to the motor, or the cable, has been damaged.

XIV Action to be taken after a Misfire

1. After a misfire the following procedure will be observed and in this order:

(a) The misfire warning switch will be applied.

(b) The Officer-in-Charge will be informed.

(c) The barriers sealing the path will be raised at the discretion of the Officer-in-Charge.

(d) The pressure record will be developed for his inspection.

2. The Officer-in-Charge will then decide on further action to be taken.

3. The Officer-in-Charge will take possession of the Safety Plug and will be the first to enter the Firing Pit, the procedure up to this instant being in accordance with paragraph XI.

4. The Firing Pit Team will then act according to instruction received at the time from the Officer-in-Charge.

XV Approval for Firing

1. No firing may take place without the written approval of the Officer-in-Charge. For this purpose a Firing Sheet will be prepared and given to the Laboratory Worker-in-Charge of Firing showing details of the

rounds approved for firing. A diary will also be kept by the Officer-in-Charge in which the complete firing programme will be given. This diary will be freely available to the Laboratory Worker-in-Charge of Firing and will contain the Officer-in-Charge's signature of approval for firing.

2. The Laboratory Worker-in-Charge will enter the rounds in a firing record book in the order that they are fired.

XVI Conditions for Firing

1. Firing can only be carried out when the Officer-in-Charge is present in building P.721 or the Hot and Cold Store, building P.727.

2. It is the duty of the Officer-in-Charge to announce his arrival as soon as possible. The Firing Pit Team will then assume that the Officer-in-Charge remains in the vicinity unless otherwise instructed.

3. It is the duty of the Officer-in-Charge to announce his departure and the name of the new Officer-in-Charge or, if no other Officer-in-Charge is available, to order firing to cease.

4. If firing ceases for any cause and the Firing Pit Team leaves the vicinity of building P.721 (e.g. for lunch break, medical inspection etc.) it is the duty of the Laboratory Worker-in-Charge on their return to ensure that the Officer-in-Charge is still present before resuming firing.
5. Preparation of a round for firing in accordance with paragraphs I, II and paragraph VII section 1, may be carried out before the arrival of the Officer-in-Charge.
6. The Officer-in-Charge will be either Mr. R. Pape or Mr. E. Speller.
7. The Laboratory Worker-in-Charge will normally be Mr. E. Clements. He will be in over-all control of firing operations, and of preparation of rounds for firing.
8. Subject to the instructions of the Officer-in-Charge, the Laboratory Worker-in-Charge will normally nominate a member of the Firing Pit Team to take possession of the Safety Plug, and to be in charge for the time being of firing operations up to and including operation VIII 5 above, when the Safety Plug is handed over to the Firing Operator.

XVII Firing in Small Proof Stand, Building
No. P.753

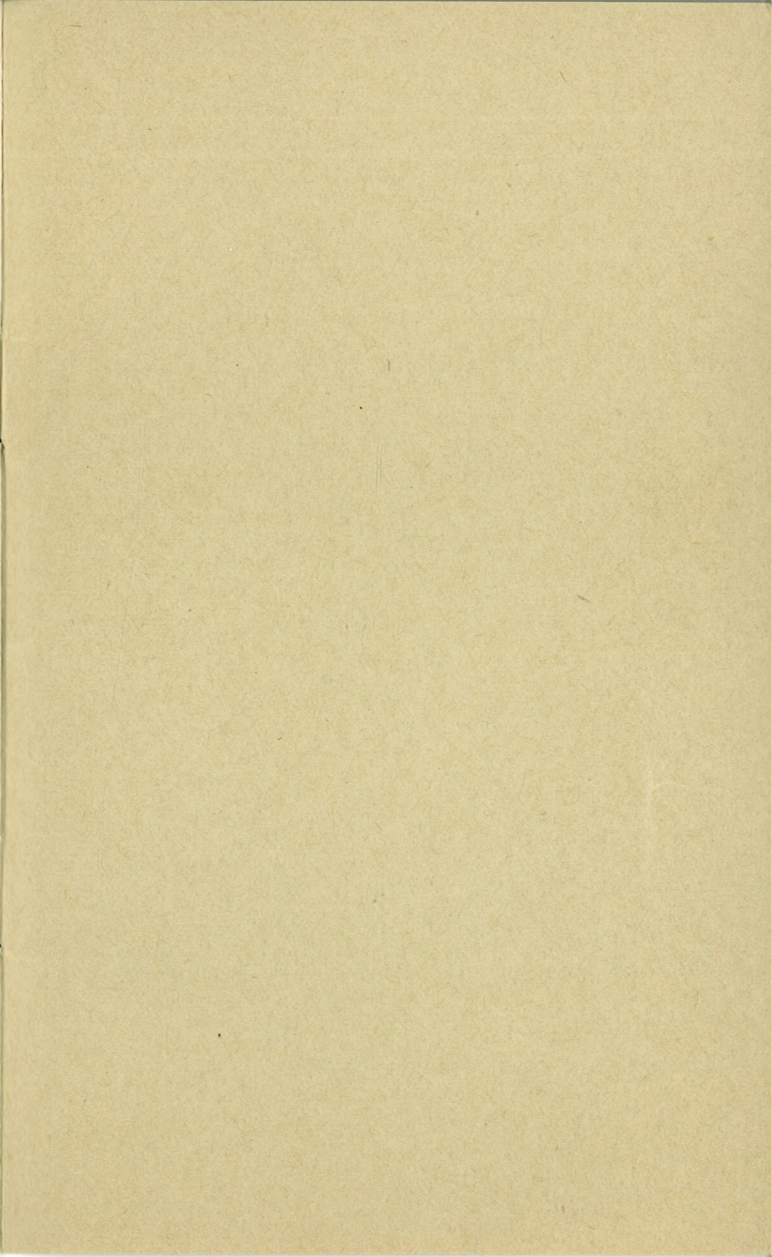
1. No round other than a K round will be fired in this building without specific instructions to the contrary from the Officer-in-Charge.
2. Where applicable, the firing procedure will be as laid down in the preceding paragraphs.

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THE HISTORY OF THE UNITED STATES

The history of the United States is a story of growth and expansion. From a small collection of colonies on the eastern seaboard, it grew into a vast nation spanning two continents. The early years were marked by struggle and the fight for independence, leading to the formation of a new government. The westward expansion brought new challenges and opportunities, shaping the nation's identity and destiny. The Civil War was a pivotal moment, resolving the issue of slavery and preserving the Union. The Reconstruction era followed, a period of rebuilding and reform. The late 19th and early 20th centuries saw industrialization and the rise of a powerful nation, culminating in World War II. The post-war period has been characterized by global leadership, technological advancement, and the pursuit of peace and prosperity.



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THE CHEMISTRY OF SOLID PROPELLANT COMBUSTION: NITRATE ESTER OR DOUBLE BASE SYSTEMS*

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Abstract—During the last decade there has been a great increase in the scale of application of solid propellants in rocketry and a corresponding increase in our empirical knowledge of the internal ballistics of solid propellants. Superficially, it would appear that our understanding of the detailed mechanism of their combustion has failed to keep pace.

In this lecture an attempt will be made to review the current state of knowledge in this field and to place it in perspective in relation to the general field of combustion chemistry. We shall discuss the broad trends in research on flame propagation during the last ten years and examine their relevance to problems of solid propellant burning. At the beginning of this period there was a tendency to regard the combustion of all solids and liquids as a gas-phase flame coupled to the surface of the condensed phase by heat and mass transfer processes. The successes and failures of this simple picture will be examined with reference to nitric ester propellants.

1. INTRODUCTION

The chemistry of propellant combustion has occupied the attention of scientists for many years. The burning of a solid propellant provides a striking example of the conversion of chemical energy into heat and energy of motion. Moreover, we have learned to control the rate of conversion of chemical energy. In physically homogeneous, or monopropellant, systems, this control is basically a problem in chemical kinetics, an application of the principle that substances undergo chemical change at a rate which is determined by the forces of interaction between atoms and the frequency and energy of collision processes between molecules. The science of the chemistry of propellant combustion is part of the more general field of flame chemistry. This has largely been concerned with the reaction of relatively simple fuel molecules with molecular oxygen. Even so, we still have a long way to go in understanding the detailed nature of the elementary chemical reactions which occur in such flames and which determine the speed of flame propagation. In solid propellant combustion we are usually concerned with the reactions of oxygen atoms chemically combined with other atoms in relatively complex molecules. The detailed chemistry of the combustion process is very different from hydrocarbon-oxygen systems although the physico-chemical principles involved are the same.

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It is interesting to consider the broad trends in the development of combustion research. We can distinguish three phases. In the first we find the experimental study of the relation between the speed of flame propagation and the chemical composition of the combustible, together with the influence of environmental factors such as pressure and initial temperature. This leads to a recognition of the importance of the rate of chemical reaction and its dependence on the chemical nature of the reacting substances together with the temperature and pressure in the flame.

We then see the development of the theory of flame propagation, the progressive understanding of the quantitative relation between the speed of movement of the wave of chemical reaction and the rate of the processes which control that reaction. Once the difficulties in the formulation of this type of problem were overcome, and the advent of modern computing techniques made it possible to solve the resulting set of simultaneous differential equations for reaction schemes of an arbitrary degree of complexity, it became apparent that the major problem was to identify the elementary chemical reaction steps and to obtain quantitative data on their chemical kinetic properties. Thus we find evidence in the literature of an intensive experimental study of the structure of the reaction zone in flames and of the kinetics of elementary reactions of the type we should expect to occur in flames.

This suggests a suitable order of presentation of the subject of this lecture. We shall restrict the scope to that of the mechanism of combustion of double base solid propellants, since it is with these that the chemistry has a predominant effect on the internal ballistic properties. Furthermore, although our knowledge of the chemical mechanism is far from complete, the chemistry is essentially that of the combustion of nitrate esters and the reactions of nitrogen oxides, both of which have been studied more intensively than the inorganic perchlorates which are the major constituents of composite solid propellants.

2. THE INTERNAL BALLISTIC PROPERTIES OF SOLID PROPELLANTS

The characteristic property of a useful propellant explosive is that under a given set of environmental conditions it has a unique burning rate. The burning surface regresses in the direction normal to itself at a steady rate, determined by the composition of the propellant and the external conditions, giving a flow of gaseous combustion products away and normal to the surface. It is not a difficult experiment to measure this rate in laboratory equipment and to determine its variation with composition and with the initial temperature of the propellant sample and with the external gas pressure [1]. Under rocket chamber conditions other factors, such as gas flow parallel to the surface, can influence the burning rate but we shall here only consider these first three factors. The earlier solid rocket propellants were derived from gun propellants of the cordite type: nitrocellulose plasticized with nitroglycerine and organic coolants and chemical stabilizers. At gun pressures the mass burning rate varies with very nearly the

first power of the pressure and at a fixed pressure depends mainly upon the thermochemical energy or calorimetric value of the composition. It was fortunate from the point of view of the application to rocket propulsion that the burning rate varies more slowly with pressure at pressures of 5000 psi and below. Figure 1 shows the linear burning rate plotted against the pressure on a log-log scale for Cordite S.C. This composition has been used for many years as a ballistic standard, its rate-pressure behavior has been measured by a variety of experimental techniques and is known accurately.

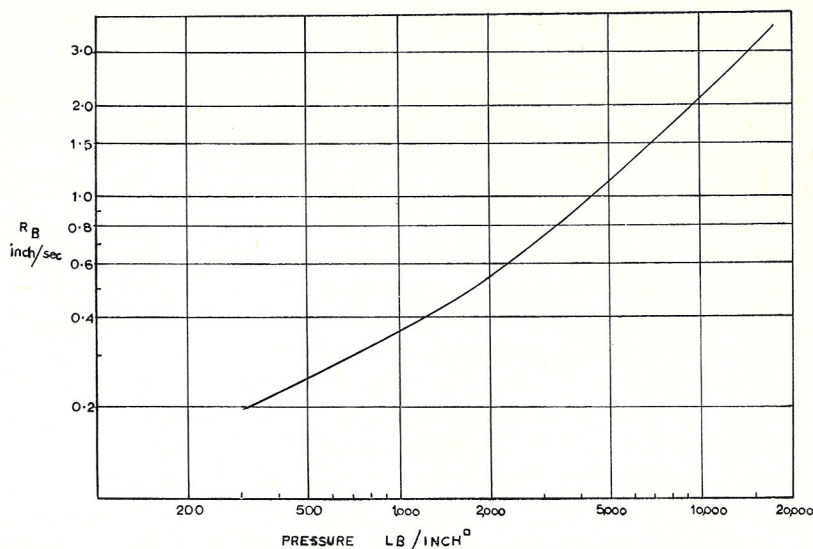
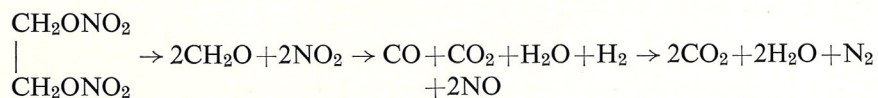


FIG. 1. Burning rate as a function of combustion pressure for Cordite S.C.

The burning rate can be represented in terms of the now standard exponential formula $r = cp^n$ with n taking different values over different ranges of pressure. For S.C. Cordite, n varies from 0.5 below 2000 psi to a value of 1 above 10,000 psi. Most double base propellants of this simple type show a qualitatively similar behavior although as the burning rate is increased by raising the calorimetric level, the pressure exponent tends to increase to the value of unity at lower pressures [5]. We now know that this ballistic property, essential for rocket propellants, is in fact not typical of organic explosives as a class. The great majority have pressure exponents of burning rate close to unity at all pressures. We also find that comparing the burning rates of a wide range of explosive compounds at a fixed pressure they are not only a function of the calorimetric level but are also dependent upon the chemical structure of the explosive molecule (Fig. 2).

The calorimetric level of explosives is known not to be a good indication of the flame temperature in low pressure combustion where the extent of chemical reaction to final products near the burning surface is incomplete. However, if we compare the burning rates of some simple nitrate esters with their experimentally

measured flame temperature, the latter is still not the only factor in determining rate. The structure of the parent molecule or the detailed mechanism of reaction of its decomposition products must play an important part in determining the rate of burning. The conventional representation of the combustion of nitrate ester propellants is in terms of three formally simple and consecutive reactions: decomposition to aldehydes and nitrogen dioxide followed by oxidation first by nitrogen dioxide and then by nitric oxide [2], for example,



As we shall demonstrate, this simple sequence of chemical reaction steps, although adequate in this particular example of ethylene glycol dinitrate, cannot be representative of nitrate ester combustion in general.

Nitrocellulose appears to have special ballistic properties in that it not only burns at some rate three times that of the liquid ester component of a double base propellant (at equal calorimetric level) but also in that it lowers the pressure exponent of a mixture of the two components over a considerable range of concentration. It also confers the property of susceptibility to catalysis of rate of burning at low pressures by metallic compounds.

Two recent papers [6, 7] have given examples of the effect of the addition of various lead compounds to double base propellants. The addition of a few per cent of lead oxide or salts of aliphatic acids to compositions of low calorimetric value, and therefore relatively low burning rate, can increase the rate at low pressures by factors of three or more. The increase in burning rate diminishes with increasing combustion pressure so that the overall result is to give regions of very low pressure exponent (Fig. 3). At higher pressure, and with compositions of high energy and burning rate, the catalysis by these lead compounds is small but a similar effect can be induced by more thermally stable lead compounds such as salts of aromatic acids (Fig. 4).

Finely divided carbon black has a synergistic effect with lead compounds in that it enables the catalysis to persist at higher pressures [7]. Some other finely divided, thermally stable, pigments are reported to show a similar effect [7] (Fig. 5).

The effect of additions of lead compounds to the burning rate of the liquid component of the propellant is relatively small. It cannot be said to be completely specific to nitrocellulose since it is promoted by non-explosive polymers such as cellulose acetate and, to a lesser extent polymethyl methacrylate and acrylate. The monomers of these materials do not promote the catalytic effect of lead. It appears that a condensed phase surface above some minimum temperature is necessary. In a subsequent section we shall discuss other evidence on the cause of this effect of lead compounds.

Although we may now have access to a considerable volume of empirical ballistic data on solid propellant compositions, data which are essential for the development and application of solid propellants, this has not, of itself, led to

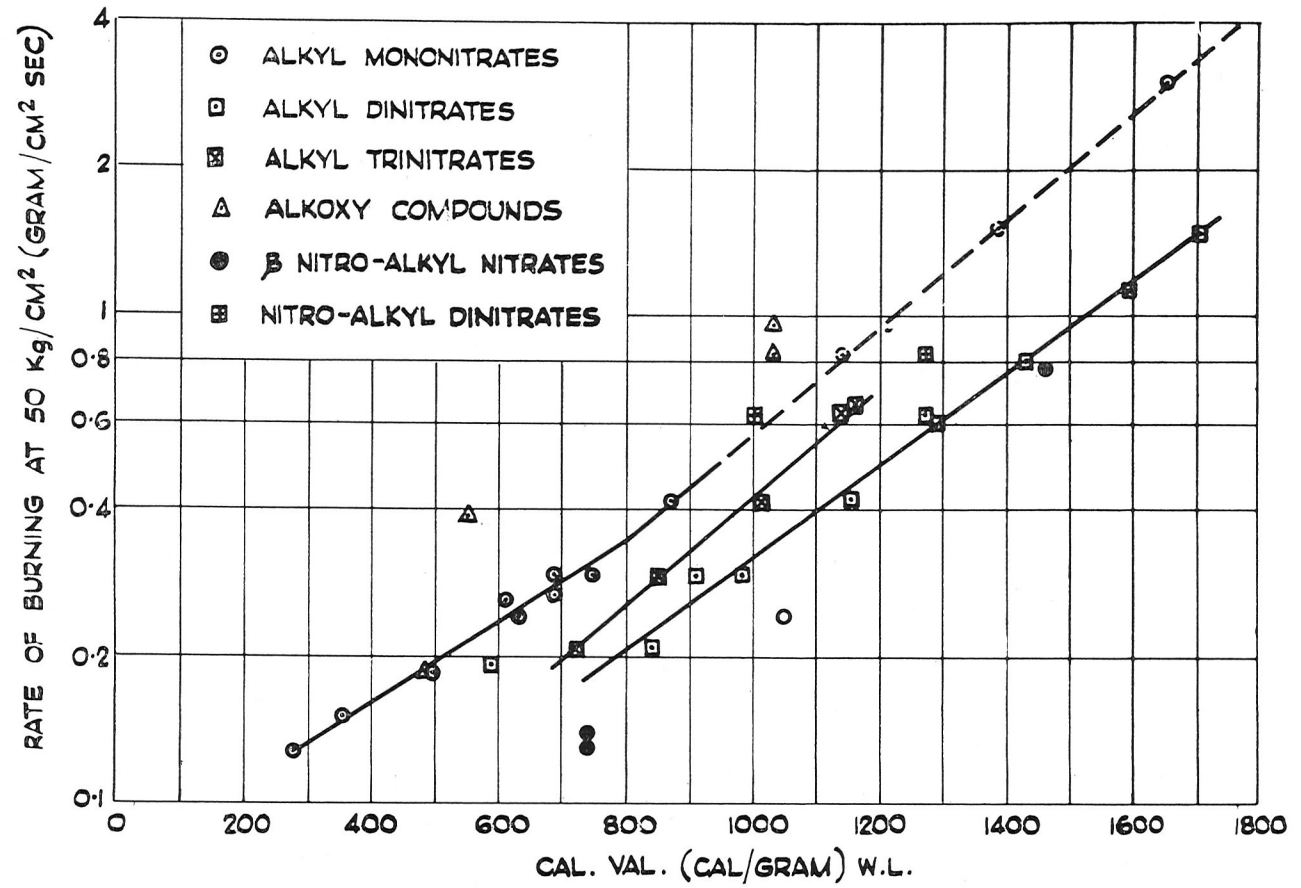


FIG. 2. Burning rate at 50 kg/cm² for nitrate esters as a function of calorimetric value.

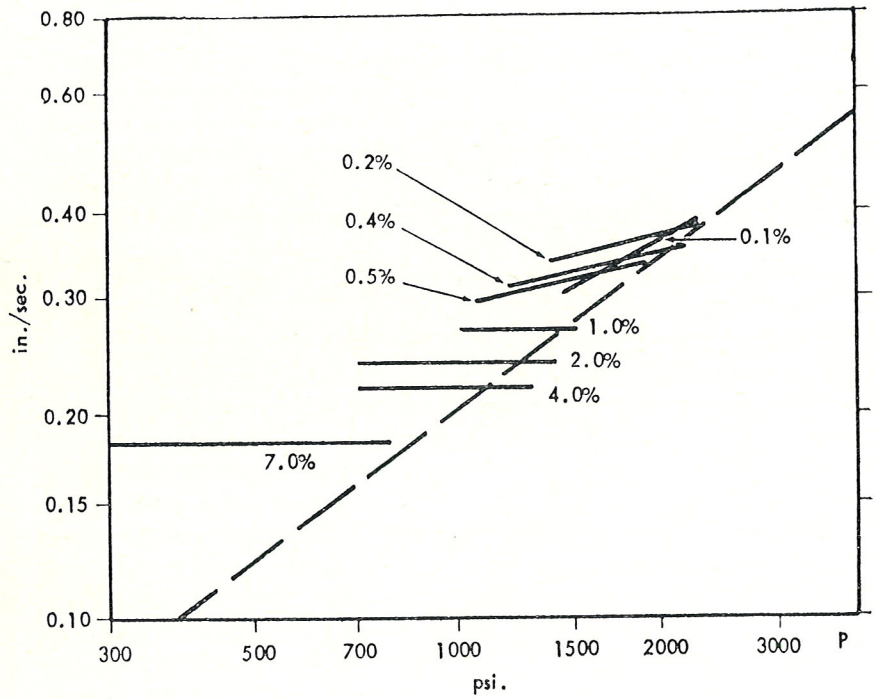


FIG. 3. Burning rate as a function of pressure for double base propellants containing x wt. % of lead stearate. Dashed curve is the unmodified propellant cal. val. = 800 cal/g. (After Preckel [6].)

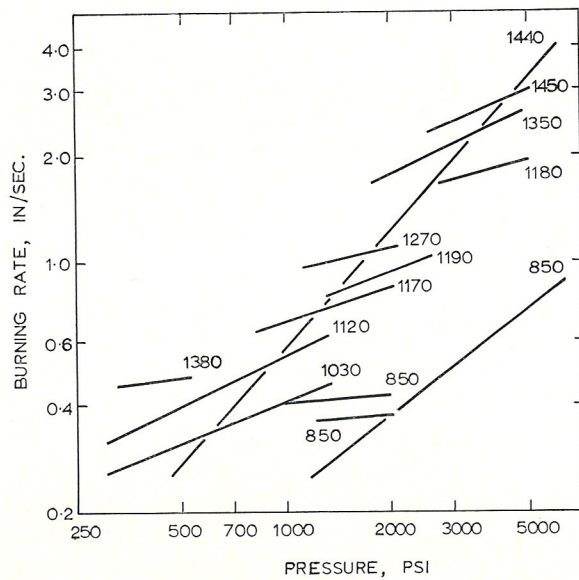


FIG. 4. Plateau ballistics with aromatic lead compounds. Numbers signify cal. val. (cal/g.) (After Preckel [7].)

any improved understanding of the mechanism of the combustion process. It will provide a proof, in the original sense of the word, of any views of the mechanism which we can obtain in other ways. A prerequisite of such tests is an understanding of the theory of the propagation of a flame supported by the pyrolysis or vaporization of a condensed phase and which, even in the simplest conception, involves a sequence of chemical reactions in the gas phase.

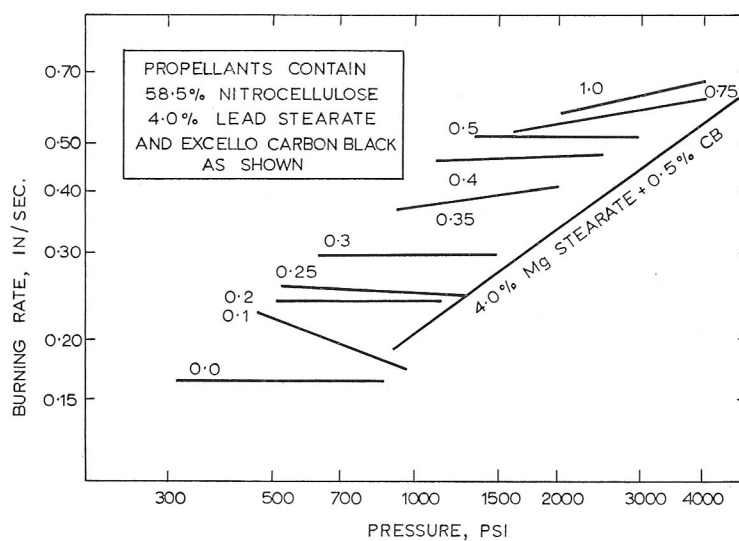


FIG. 5. Effect of carbon black on plateau ballistics. (After Preckel [7].)

3. THE THEORY OF THE BURNING OF HOMOGENEOUS PROPELLANTS

The theory of steady laminar flame propagation in a gas undergoing a single exothermic chemical reaction is now well understood [8-10]. The problem is essentially that of determining the value of the mass flux which enables the temperature and concentration distributions to satisfy the boundary conditions imposed in the unreacted and the completely reacted regions of the flame.

The spatial variation of temperature and reactant concentrations are determined by the solution of the differential equations of mass and energy conservation together with the diffusion equations for the reacting species. For plane, one-dimensional flow these can be written as:

$$\text{Mass conservation: } M \frac{dG_i}{dx} = -w_i \quad (1)$$

where M is the total mass flux, MG_i the fractional mass flux for component I , x the space coordinate, and w_i the net rate of loss of component I due to chemical change. It is assumed that w_i can be specified in terms of chemical reaction rates which are functions of the local concentrations and temperature.

$$\text{Diffusion: } MG_i = MY_i - \rho D_i \frac{dY_i}{dx} \quad (2)$$

where ρ is the mass density and Y_i is the mass fractional concentration of component I of mass diffusivity D_i .

$$\text{Energy conservation: } \frac{d}{dx} \left[M \sum G_i h_i - \lambda \frac{dT}{dx} \right] = 0 \quad (3)$$

where h_i , the component enthalpies per unit mass, are defined by

$$h_i = \Delta h_{f_i} + \int^T c_p dT \quad (4)$$

Δh_{f_i} is the standard heat of formation of species I . The summation in eqn. (3) is taken over all components of the system and λ is defined as the bulk thermal conductivity.

If there is no heat loss from the combustion products and the system tends to a state of chemical equilibrium, the derivatives vanish at the hot boundary downstream of the flame. The total enthalpy then tends to a constant value and equation (3) can be integrated to give the upstream temperature gradient in terms of the local component mass fluxes and enthalpies.

$$\lambda \frac{dT}{dx} = M \sum G_i h_i - M (\sum G_i h_i)_{\text{hot boundary}} \quad (3a)$$

Since the space variable appears only as a differential, it is possible to eliminate it from the equations and to use the temperature as the independent variable. If the Lewis numbers are unity, $\rho D_i = \lambda / c_p$, and if the enthalpy tends to a constant value at the hot boundary, it is well known that equations (2) and (3) can be combined and integrated to give the result that the local enthalpy remains constant from the hot through to the cold boundary. This result can also be expressed in terms of an implicit relation between the concentrations of the initial and intermediate reactants and the local temperature:

$$\sum Y_i (\Delta h_{f_i} - \Delta h_{f_m}) = \int_{T'}^{T_m} c_p dT \quad (5)$$

where Δh_{f_m} is the standard heat of formation of the final product species, T_m is the temperature reached at the hot boundary where $Y_m = 1$, and c_p has been assumed independent of composition. The important feature of these relations between the temperature and reactant concentrations and between the temperature gradient, temperature and the component mass fluxes is the fact that they have been obtained by specifying only the hot boundary conditions; they are independent of the conditions to be imposed at the upstream boundary.

If we take the case of a single reaction step, $A \rightarrow B$, unit Lewis number, and constant heat capacity, the problem reduces to the integration of a single first

order equation for the variable G_a and the temperature T .

Thus combining

$$M \frac{dG_a}{dT} = - \frac{w_a}{dT/dx} \quad (1)$$

and

$$\lambda \frac{dT}{dx} = M(\Delta h_{f_a} - \Delta h_{f_b})G_a - M\bar{c}_p(T_b - T) \quad (3b)$$

we obtain

$$\frac{dG_a}{dT} = \frac{\lambda w_a}{M^2[\bar{c}_p(T_b - T) - (\Delta h_{f_a} - \Delta h_{f_b})G_a]} \quad (6)$$

where w_a can be expressed as a known function of temperature since a dependence on the reactant concentration Y_a can be eliminated by using the relation (5) which becomes:

$$(\Delta h_{f_a} - \Delta h_{f_b}) Y_a = \bar{c}_p(T_b - T) \quad (5a)$$

The integral curves for equation (6) which pass through the point $T = T_b$, $G_a = 0$ have been obtained by Hirschfelder, Curtiss and Campbell [8], and are illustrated in Fig. 6. The curves intersect the line $G_a = 1$ at a temperature, T_1 ,

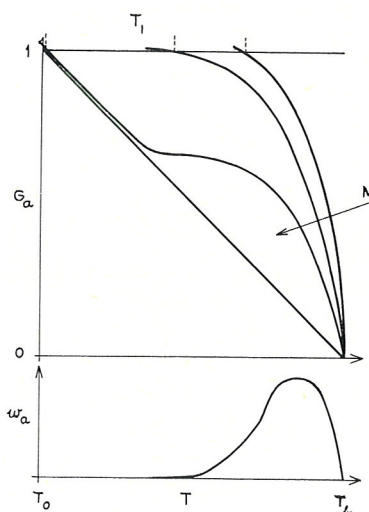


FIG. 6. G_a - T curves for varying mass flux values, M . (After Hirschfelder, Curtiss and Campbell [8].)

which decreases as the value of the total mass flux, M , increases. This temperature can be regarded as the cold boundary condition which is necessary to determine a unique flame speed. If the chemical reaction term remains finite and positive with decreasing temperature, the integral curve cannot cross the line defined by setting the denominator of the R.H.S. of (6) equal to zero and intersects the $G_a = 1$ line no matter how large is the value of the total mass flux. The

rate of heat loss at the upstream boundary can be determined by setting $G_a = 1$ and $T = T_1$ in the energy flux equation (3b):

$$\frac{\lambda}{M} \left(\frac{dT}{dx} \right)_1 = (\Delta h f_a - \Delta h f_b) - \bar{c}_p (T_b - T_1) \quad (7)$$

The concept of a flameholder abstracting heat at the cold boundary of the flame was introduced by Hirschfelder [8] to resolve the problem which results from an attempt to allow dT/dx to vanish at the cold boundary while allowing the reaction rate to remain finite. He points out that the temperature dependence of the reaction rate function is normally such that the flame speed is insensitive to the values assigned to the cold boundary conditions so that the empirical association of a unique steady flame speed with a given inflammable gas at a given initial temperature is not contraverted.

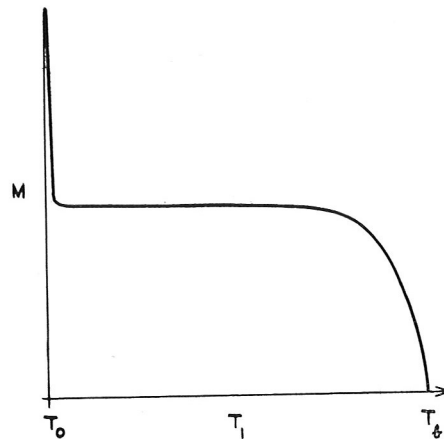


FIG. 7. M as function of cold boundary temperature, T_1 . (After Hirschfelder, Curtiss and Campbell [8].)

The degree of dependence of the mass flux through a steady flame on the upstream boundary condition is a crucial point in the understanding of combustion supported by a condensed phase and involving a sequence of reactions. The relation of the mass flux to the cold boundary conditions at a constant final flame temperature is shown schematically in Fig. 7. The left hand region illustrates the fact that provided the reaction rate is everywhere finite and there is no heat loss downstream of the cold boundary, the reaction will still go to completion at very large values of the mass flux. In the middle portion of the curve the mass flux is very insensitive to variations in the upstream boundary condition. As T_1 approaches T_b the mass flux falls to zero as an increasing proportion of the area under the reaction rate curve is cut off by the upstream boundary.

Let us apply this result to the simple $A \rightarrow B$ reaction supported by evaporation from a condensed phase. The concentration-temperature relation for species A

in the gas phase is determined by the final flame temperature and the enthalpy difference between the two gas phase species. If the required mass evaporation rate is much less than the kinetic vacuum evaporation rate, an equilibrium condition will hold at the interface which provides a second relation between the fractional concentration and the temperature:

$$(Y_a)_s P = P_a^* \exp\left(\frac{-L}{RT_s}\right) \quad (8)$$

where P_a^* is a constant reference vapor pressure, P is the total pressure and L the heat of evaporation at T_s .

From (5a) and (8) the surface temperature, T_s , is determined by the equation:

$$(\Delta h_{fa} - \Delta h_{fb}) P_a^* \exp\left(\frac{-L}{RT_s}\right) = P \bar{c}_p (T_b - T_s) \quad (9)$$

It is independent of the mass flux but increases with increasing pressure. The fractional concentration of the gaseous reactant at the surface, $(Y_a)_s$, is always less than unity and decreases with increasing pressure.

We may also conclude that, so long as T_s is in a temperature region where the rate of the gas phase reaction is small compared to its maximum value, the mass burning rate is almost independent of T_s or, at a fixed flame temperature, the heat of evaporation, L . The mass flux for the gaseous flame supported by a condensed phase, its pressure exponent and its dependence on flame temperature will be the same as that of the flame propagating through the gaseous reactant at the same flame temperature.

If the mass flux is comparable with the kinetic evaporation rate or if the gasification process is a surface pyrolysis, the surface temperature is determined by the mass flux rate through an equation of the form:

$$M = k \exp\left(\frac{-E}{RT_s}\right) \quad (10)$$

In this case, the surface temperature at constant pressure will vary with the mass flux and, if the mass flux for the gas phase reaction increases with pressure, the surface temperature will also increase with pressure. $(Y_a)_s$ is again less than unity and is a function of M . At high pressures where T_s approaches the final flame temperature, the mass flux tends to a constant value determined by the rate of the surface reaction at $T_s = T_b$.

Spalding [11] has used this variation of the surface temperature with pressure to develop a theory of inflammability limits for the burning of solid or liquid monopropellants based upon radiative heat loss from the surface of the condensed phase to the surroundings. If the heat absorbed by the surface is small compared with that radiated, then the final flame temperature will be less than the adiabatic value T'_b by the amount

$$T'_b - T_b = \sigma \epsilon \frac{T_s^4}{M \bar{c}_p} \quad (11)$$

where σ is Stefan's constant and ϵ is the emissivity. This equation expresses the fact that the change in the heat flux in the burnt gases must equal the rate of loss of heat by radiation.

Spalding defines a dimensionless heat loss intensity:

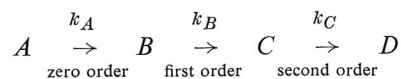
$$Q = \frac{\sigma\epsilon(T'_b)^3}{\bar{c}_p M} \quad (12)$$

He shows that if this exceeds a critical value, no steady value of the mass flux is obtained. Thus if M decreases with decreasing pressure, there will be a lower pressure limit for steady burning. An upper pressure limit may exist for a gaseous flame supported by an equilibrium evaporation process if the exothermic reaction does not occur in the condensed phase. Although upper pressure limits for some monopropellant systems have been observed experimentally [12, 13], this explanation seems an unlikely one because chemical reaction rates do not in fact vanish in a condensed phase.

The dependence of the steady state mass flux upon the boundary conditions for a single step reaction can be used to examine the behavior of a combustion process involving a number of consecutive reaction steps. If each reaction rate is assumed to depend upon a different power of reactant concentration, the mass flux satisfying given boundary conditions for each step in the sequence will vary in a different way with pressure. The steady mass flux for each step can easily be shown to vary as $P^{n/2}$ where n is the order of the chemical reaction. With suitable assumptions as to the reactive magnitudes of each reaction rate at a given pressure and temperature, we can consider the overall reaction to consist of a series of reaction zones located at different distances from the propellant surface and occurring at different temperature levels in the flame. The total mass flux is the same for each zone so that the boundary conditions at their junctions must satisfy this condition.

When the junction boundary conditions have been determined, the steady state mass flux is also determined. Several authors have used this method to determine the variation of burning rate with pressure for a hypothetical combustion model involving a sequence of reactions of increasing reaction order. Early treatments [2, 3, 4] assume that diffusion in the gas phase could be neglected. A more recent paper by Vilyunov [14] attempts to solve the diffusion equation but makes the arbitrary assumption that the mass fractional concentration of gaseous reactant at the surface of the condensed phase is equal to unity irrespective of the value of the surface temperature. We have seen that this is not generally true because the concentration-temperature relation is determined by the downstream boundary conditions in the gas phase.

Let us consider a solid A undergoing an exothermic, zero order, reaction to give a gas phase product B which then is converted to a stable product D in two stages of first and second order respectively:



The mass rates of each successive reaction are proportional to P^0 , P^1 , and P^2 respectively, and at a given temperature there will be a pressure below which each successive rate will be negligibly small compared with that of the preceding rate. We assume that each reaction commences only when the preceding one has gone effectively to completion. Then in the first reaction zone $G_a + G_b = 1$, $G_c = G_d = 0$; in the second $G_b + G_c = 1$, $G_a = G_d = 0$; in the third $G_c + G_d = 1$, $G_a = G_b = 0$.

If the overall process is adiabatic and leads to a final temperature T_a , the energy flux equation can be integrated to obtain:

$$M \sum_a^d G_i (\Delta h_{f_i} - \Delta h_{f_a}) - \frac{\lambda dT}{dx} = M \bar{c}_p (T_a - T) \quad (13)$$

Using the mass flux fraction relations for the first reaction zone, we find that in this zone:

$$M G_a (\Delta h_{f_a} - \Delta h_{f_b}) + M (\Delta h_{f_b} - \Delta h_{f_a}) - \frac{\lambda dT}{dx} = M \bar{c}_p (T_a - T) \quad (14)$$

There is a minimum surface temperature T'_s defined by setting the temperature gradient in the gas phase adjacent to the surface equal to zero in (14) and putting $G_a = 0$, to give

$$(\Delta h_{f_b} - \Delta h_{f_a}) = \bar{c}_p (T_a - T'_s) \quad (15)$$

If we use this relation to eliminate T_a , equation 14 becomes:

$$M G_a (\Delta h_{f_a} - \Delta h_{f_b}) - \frac{\lambda dT}{dx} = M \bar{c}_p (T'_s - T) \quad (16)$$

The differential equation for G_a as a function of T is then:

$$\frac{dG_a}{dT} = \frac{\lambda w_a}{M^2 [\bar{c}_p (T'_s - T) - G_a (\Delta h_{f_a} - \Delta h_{f_b})]} \quad (17)$$

This equation is to be integrated from the cold boundary where $G_a = 1$ to the propellant surface where $T = T_s$, $G_a = 0$. Using the thermochemical relation defining the initial temperature T_0 :

$$\bar{c}_p (T'_s - T_0) = \Delta h_{f_a} - \Delta h_{f_b} \quad (18)$$

we may write (17) as:

$$(T'_s - T) dG_a - (T'_s - T_0) G_a dG_a = \frac{\lambda w_a}{M^2 \bar{c}_p} dT \quad (17a)$$

The LHS of equation (17a) can also be expressed as:

$$(T'_s - T_s) dG_a + (T_s - T) dG_a - (T'_s - T_0) G_a dG_a \quad (17b)$$

If E_a/RT_s is large and we restrict the solutions to those which cross the $G_a = 1$ line nearly horizontally, G_a becomes close to unity for small values of $T_s - T$

so that the second term is small compared with the last term. A first approximation to the solution passing through $G_a = 0$, $T = T_s$ is given by

$$\frac{G_a^2(T'_s - T_0)}{2} - (T'_s - T_s)G_a = \frac{1}{M^2 \bar{c}_p} \int_T^{T_s} \lambda w_a dT \quad (19)$$

and an approximate value of the mass flux is found by putting $G_a = 1$ in this equation. We assume that $w_a = \rho_a k_a \exp(-E_a/RT)$ and that the term on the right-hand side can be written as

$$\frac{\lambda_a \rho_a k_a}{M^2 \bar{c}_p} \int_T^{T_s} \exp\left(\frac{-E_a}{RT}\right) dT$$

This integral is insensitive to the value of the lower limit, T , and we can obtain a first approximation for the mass flux as:

$$M^2 = \frac{2\lambda_a \rho_a k_a}{\bar{c}_p(2T_s - T'_s - T_0)} \frac{RT_s^2}{E_a} \exp\left(\frac{-E_a}{RT_s}\right) \quad (20)$$

This is identical with that given by Vilyunov. Better approximations can be obtained by writing the integral on the R.H.S. of (19) in terms of a series involving powers of RT_s/E_a and by correcting for the term $(T_s - T)dG_a$ in (17b). These do not differ by more than 10 per cent from the first approximation for values of $E/RT_s > 20$.

The differential equation for G_b in the second stage of the flame is obtained by a similar procedure as

$$\frac{dG_b}{dT} = \frac{\lambda w_b}{M^2 [\bar{c}_p(T'_c - T) - G_b(\Delta h f_b - \Delta h f_c)]} \quad (21)$$

where T'_c is the adiabatic flame temperature for the reactions $A \rightarrow B \rightarrow C$.

Strictly, for a first order gas phase reaction, G_b and Y_b cannot become zero at any temperature below the maximum final flame temperature, T_d . If the reaction rate is strongly temperature dependent, the G_b versus temperature curves decrease from a value close to unity to a value close to zero over a small temperature range. In these conditions it is possible to define a temperature T_c greater than T'_c but less than T_d at which G_b and Y_b effectively vanish and G_c becomes equal to unity.

The variation of M^2 with the boundary conditions can be found as for the first zone, by integrating equation (21) from $G_b = 0$, $T = T_c$ to give the approximate equation:

$$\frac{G_b(T'_c - T'_s)}{2} - (T'_c - T_c)G_b = \frac{1}{M^2 \bar{c}_p} \int_T^{T_c} \lambda w_b dT \quad (22)$$

where we have again neglected the term $(T_c - T)dG_b$ on the assumption that

G_b becomes near to unity at a value of T close to T_c . Inserting the boundary condition $G_b = 1$ at $T = T_s$ we obtain:

$$\frac{M^2 \bar{c}_p (2T_c - T'_c - T'_s)}{2} = \int_{T_s}^{T_c} \lambda w_b dT \quad (23)$$

The dependence of M^2 on T_s arises from the R.H.S. of this equation. The integral can vary with T_s through the lower limit of integration and through λw_b if this is a function of both T and T_s . Differentiating M^2 with respect to T_s we obtain

$$\frac{\bar{c}_p (2T_c - T'_c - T'_s)}{2} \frac{d(M^2)}{dT_s} = -\lambda w_b(T_s) + \int_{T_s}^{T_c} \frac{\partial(\lambda w_b)}{\partial T_s} dT \quad (24)$$

The first term on the R.H.S. of this equation depends on the reaction rate at the solid surface boundary, if $w_b(T_s) \ll w_b(T_c)$, it gives rise to a negligible decrease in M with increasing T_s . Since $\lambda w_b = \lambda \rho Y_b k_b \exp -(E_b/RT)$, it can have a partial derivative with respect to T_s only if the gas composition is a function of T_s . If we neglect any small dependence of $\lambda \rho$ on composition, this depends upon whether Y_b is a function of T_s .

We have seen that, for a single gas phase reaction step, the reactant concentration depends only on the downstream boundary conditions. This is still true for a multiple gas phase reaction steps. The relation between the reactant concentration and the temperature in the second reaction zone where $Y_a = 0$ is, for Lewis numbers of unity:

$$Y_b(\Delta h_{fb} - \Delta h_{fa}) + Y_c(\Delta h_{fc} - \Delta h_{fa}) = \bar{c}_p(T_a - T) \quad (25)$$

If we assume that T_b tends to zero at T_c and that, because of the temperature coefficient of w_b and w_c , the B and C reaction zones occupy small temperature intervals at T_c and T_a respectively, we can put $G_b = 1$ throughout most of the region between T_s and T_c and $G_c = 1 - G_b$ throughout this region. The diffusion equations for dY_b/dx and dY_c/dx can be combined to give:

$$\frac{dY_c}{dY_b} = \frac{Y_c - G_c}{Y_b - G_b} \quad (26)$$

where $G_b = 1$ and $G_c = 0$, this can be integrated to give

$$Y_c = C(Y_b - 1) \quad (27)$$

The constant of integration C can be determined from the condition that $Y_b = 0$ at T_c . Then from (25)

$$Y_c(T_c) = \frac{\bar{c}_p(T_a - T_c)}{(\Delta h_{fc} - \Delta h_{fa})} \quad (28)$$

and, for $T < T_c$,

$$Y_c = \frac{\bar{c}_p(T_a - T_c)}{\Delta h_{fc} - \Delta h_{fa}} (1 - Y_b) \quad (29)$$

Substituting this relation and the equality $\Delta hf_b - \Delta hf_a = \bar{c}_p(T_d - T'_s)$ in equation 25, we obtain

$$Y_b = \frac{T_b - T}{T_b - T'_s} \quad (30)$$

The reactant concentration is therefore still independent of the down-stream boundary, T_s . Similarly Y_c can be shown to be independent of T_c in the region between T_c and T_d .

The variation of the mass flux with the downstream boundary condition is therefore similar to that of the single flame. It is almost independent of the value of T_s as long as T_s does not approach T'_s . When this occurs, we can no longer

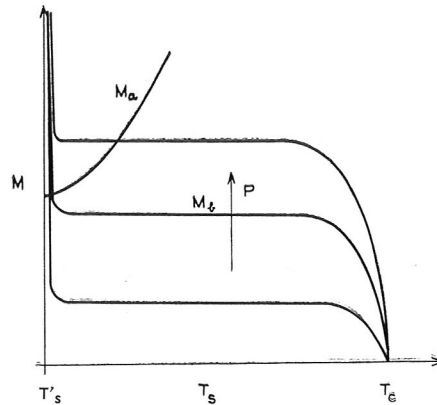


FIG. 8. Variation of mass flux and surface temperature of condensed phase with pressure for zero order-first order coupled system.

neglect the term $(T_c - T)dG_b$ in the solution of equation (21). The exact solution for M^2 indicates that it tends to infinity as $T_s \rightarrow T'_s$ in the same way as the single step flame illustrated in Fig. 7. The way in which the lower boundary condition and the mass flux are determined by the combustion pressure is illustrated in Fig. 8, where the mass fluxes for the solid phase and the first order gas phase reactions are plotted as functions of the surface temperature T_s . The mass flux for the coupled system, and the value of T_s , is determined by the intersection of the two curves. The solid phase curve is independent of the pressure but the curves for the first order gas reaction are shifted vertically upwards as the pressure increases, M_b being proportional to the square root of the pressures. Below a certain pressure, P^* , the intersection lies on the nearly vertical section of the M_b curve where $T_s \rightarrow T'_s$. The burning rate is effectively that of the adiabatic solid phase reaction. Above P^* the intersections occur on the section of the curve which is nearly parallel to the T_s axis, the burning rate is then determined by the gas phase reaction and will increase with the square root of the pressure. Because of the sharpness of the bend in the gas phase mass flux curve, the transition between the two conditions occurs over a narrow interval of burning

rate. A similar set of curves can be drawn for the conjunction of the two gas phase reactions.

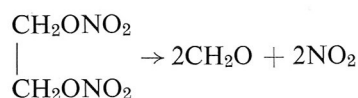
The variation of burning rate with pressure for this type of consecutive reaction scheme corresponds to a series of regions in which the pressure exponent is constant and identical to that of one particular step in the reaction sequence. This conclusion is quite different from that reached by Vilyunov who assumed that the fractional concentration of the gas phase reactant at the surface of the condensed phase was unity. He wrote the variation of concentration with temperature as $Y_b = (T_c - T)/(T_c - T_s)$. The reaction rate w_b is then a function of T_s . For a zero order solid phase decomposition and a first order gas phase reaction he calculated that the pressure exponent would increase continuously with the pressure and burning rate and was actually greater than that of the gas phase flame. Although his results agree roughly with the experimental behavior of simple double base propellants, his assumption is inconsistent with the correct solution of the diffusion equation derived in this paper and it is clear that a simple series of consecutive reactions of increasing reaction order is not an adequate model. If we require the pressure exponent to increase continuously, then we must either assume that the reaction order of the rate controlling step increases continuously or that effective heat of reaction associated with that step increases with pressure.

4. CHEMICAL REACTIONS IN THE BURNING OF NITRATE ESTER PROPELLANTS

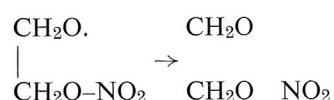
If we are to try to interpret the burning rate properties in terms of the rates and exothermicities of elementary chemical reactions, we need to identify these and to devise methods for determining the variation of rate with temperature and reactant concentration. For the complex decomposition and oxidation system involved in the combustion of even the simplest nitrate ester this is a formidable problem. In the last fifteen years there have been improvements in techniques of chemical identification and quantitative estimation which may make this objective possible, but it will be many years before it is achieved. At present much of the data that we have refers to the net result of a sequence of elementary reaction steps. Any one product of the reaction may be formed by several competing reaction sequences. This is particularly true at high temperatures where difference in the rates of elementary reactions caused by differences in activation energy become smaller.

For the purposes of this lecture it will be desirable to present a somewhat oversimplified picture of the mechanism of reaction but to draw attention to reactions which can be of importance in determining the flame properties even though they occur to a relatively minor extent. The primary process in the decomposition of organic nitrates is without doubt the splitting of the RO-NO₂ bond with an activation energy of approximately 40 kcal mole. When compared at a temperature of 200°C, the rates of decomposition increase with the complexity of the compound over a range of about 10⁻⁴ to 10⁻² sec⁻¹, increasing with increasing

complexity and being somewhat greater in the liquid phase than in the gas phase. Experimental activation energies for liquid phase decompositions are frequently quoted in the range 40–50 kcal/mole, the value increasing with increasing temperature. It appears that the decomposition is catalyzed by the retention of decomposition products. As the temperature and the rate of decomposition increases, the steady concentration of volatile products in the condensed phase increases, causing the apparent activation energy to exceed the true value for the primary step. The observed products of the decomposition depend upon the structure of the nitrate ester. Ethylene glycol dinitrate gives formaldehyde and nitrogen dioxide:

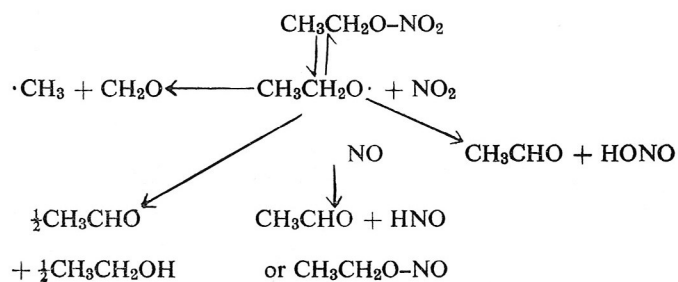


The breaking of one O—NO₂ bond gives a free radical which can decompose, probably without further activation, to formaldehyde and nitrogen dioxide:



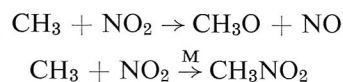
The rate of oxidation of formaldehyde by nitrogen dioxide has been studied [15] and is known to have an activation energy of about half that of the decomposition of the nitrate ester. In the pressure and temperature range of importance for rocket propellants it will be a slow reaction compared to the decomposition of the nitrate ester. Thus at 1000°K and a reactant partial pressure of 50 atm the life time of nitrogen dioxide will be about 300 times longer than that of the nitrate ester molecule.

Ethyl nitrate decomposes at about the same rate as the glycol dinitrate but the products formed are much more complex [16]. A major product is ethyl nitrite. The ethoxy radical produced by the breaking of the O—NO₂ bond cannot rearrange intramolecularly to give stable products. Its decomposition to an aldehyde will give yet another free radical or atom and will require some energy of activation. Thus the alkoxy radical can be destroyed only by reaction with another free radical or with nitrogen oxides, thus

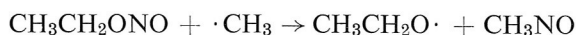


These reactions of alkoxy radicals with other radicals and with nitrogen oxides require little or no energy of activation and are therefore fast compared with the decomposition of the nitrate ester. The rate constants have recently [18] been reinvestigated and fall within the range 10^{10} – 10^{11} mole⁻¹ cc sec⁻¹. The reaction half life of the alkoxy radical in the presence of nitrogen oxides will be of the order of 10^{-6} P⁻¹ sec atm⁻¹ compared with 10^{-3} sec at 500°C for the nitrate ester.

The sequence of reactions in the ethyl nitrate flame has been studied by Hicks [19]. At a pressure of 35 mm Hg the flame is some 6 mm thick so that the variation of chemical composition with distance can be determined by gas sampling techniques. Figure 9 shows the results obtained. These show that the rate determining process is the decomposition of nitrate, the nitrogen dioxide being removed so rapidly by reactions with radicals that its concentration is too small to be estimated. The presence of the ethoxy radical can be inferred from the formation of ethyl nitrite, acetaldehyde and ethanol. In the high temperature zone of the flame we find a range of products containing one carbon atom which indicates that at higher temperatures the ethoxy radical pyrolyses rapidly to a methyl radical and a molecule of formaldehyde. This decomposition has an energy of activation of between 10 and 20 kcal/mole and would be expected to be significant relative to the other reactions of the radical in the hotter regions of the flame. The methyl radical reacts with nitrogen dioxide in the following reactions:



M being a third body which removes the energy of formation of the nitromethane. The methyl radical is most probably responsible for the rapid disappearance of ethyl nitrite which should be relatively stable compared with the nitrate at these temperatures. It is known [20] that a rapid exchange reaction can occur:



The nitrosomethane formed in this reaction was not detected but it is known to be unstable at these temperatures and to be the source of minor amounts of hydrogen cyanide,



and of nitrogen-containing polymers which are produced in the combustion of nitrate esters [21].

When ethyl nitrate is burned at atmospheric pressure, the final products show a similar pattern, but some 35 per cent of the nitric oxide is reduced to nitrogen and there is considerable decomposition of the aldehyde and alcohols formed in the primary reaction. The measured flame temperature is increased by some 300°C.

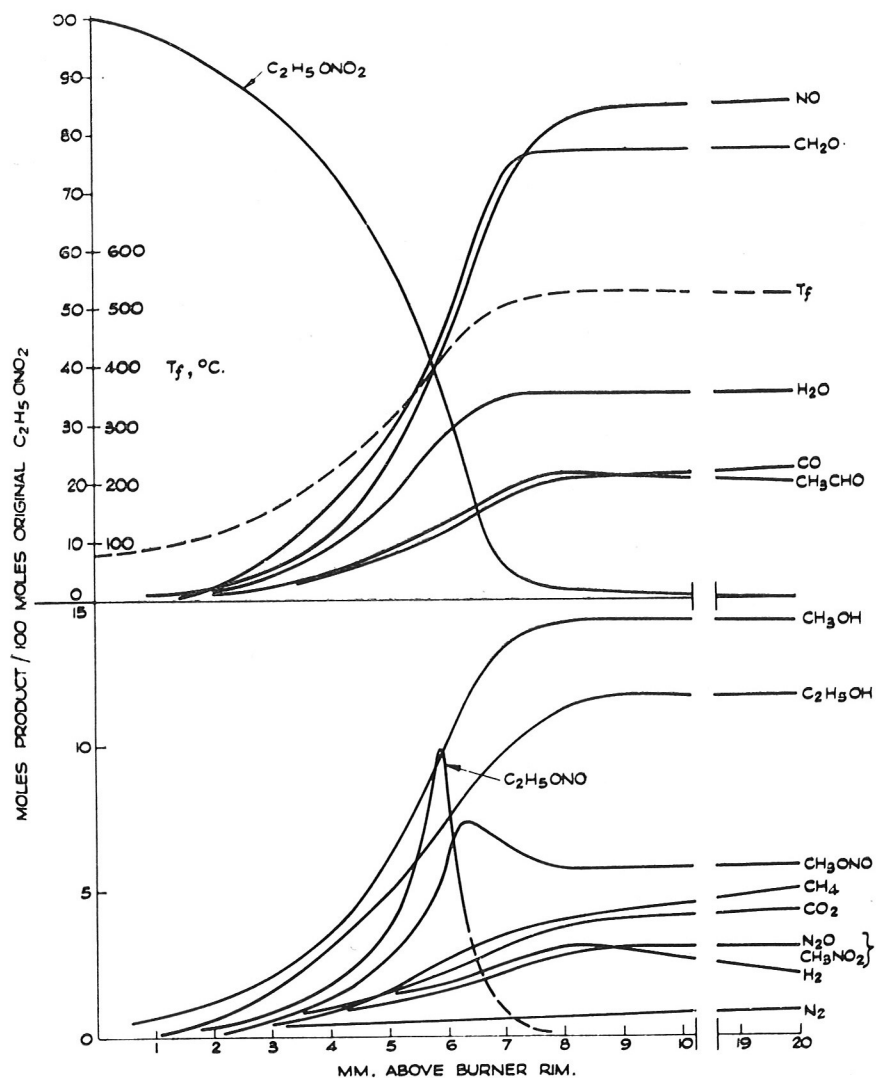
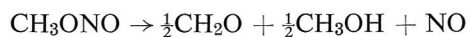


FIG. 9. Spatial variation of composition and temperature through ethyl nitrate flame at 35 mm Hg. (After Hicks [19].)

The flame temperature in nitric ester combustion is very sensitive to the degree of reduction of nitric oxide. The thermal decomposition of this molecule or the reaction with fuel molecules should be slow below 2000°C, but in fact significant amounts of nitrogen are almost always produced in the primary decomposition zones of nitrate esters burning at atmospheric pressure. The primary step in this reduction of nitric oxide appears to be the abstraction of a hydrogen atom from alkoxy radicals and molecules containing a reactive hydrogen to form the transient molecule HNO. It has been shown that methyl nitrite can sustain

combustion at flame temperatures of about 1000°K and at atmospheric pressure. The composition profiles have been studied by Powling [22], who found that the rate of reduction of nitric oxide was linked with the rate of pyrolysis of the primary decomposition products, formaldehyde and methanol:



This reaction is almost thermally neutral and extensive reduction of nitric oxide is essential for the propagation of a flame in this system. About half of the

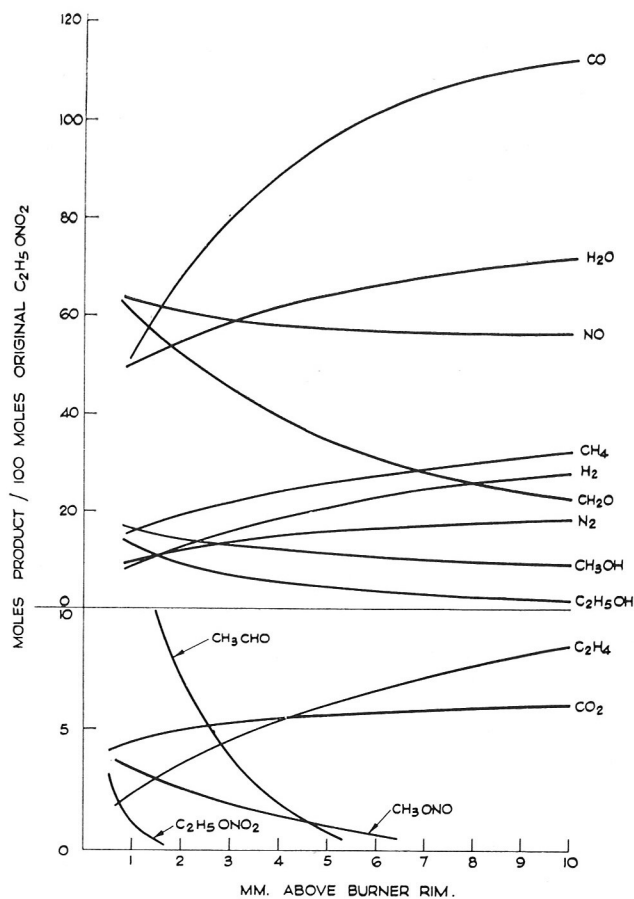


Fig. 10. Spatial variation of composition through ethyl nitrate flame at atmospheric pressure.

available nitric oxide is reduced to nitrogen; the reduction ceases when the formaldehyde and methanol have been completely oxidized or pyrolyzed (Fig. 11). It seems probable that in this flame the three reactions are linked by a common factor, the availability of reactive hydrogen from the methoxyl ($\text{CH}_3\text{O}\cdot$) or formyl ($\cdot\text{CHO}$) radicals or as free hydrogen atoms.

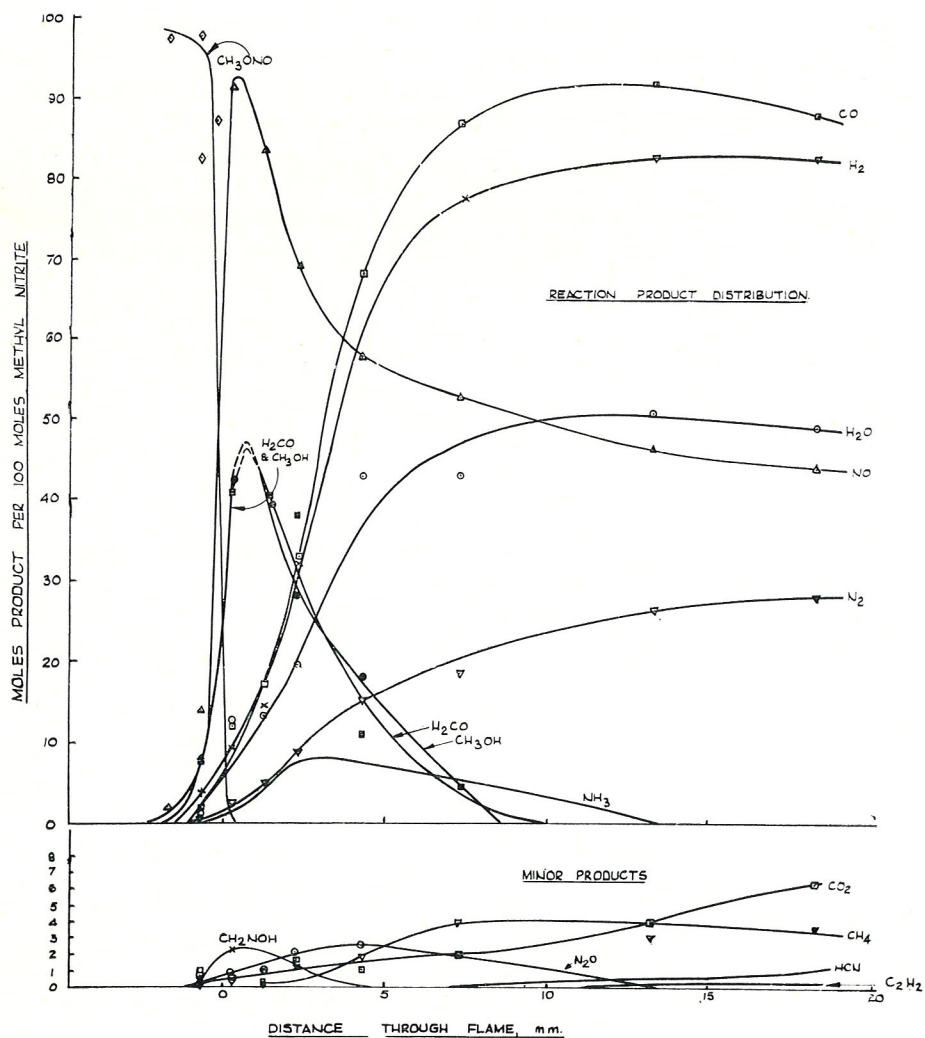


FIG. 11. Spatial variation of composition through methyl nitrite flame at atmospheric pressure. (After Powling [22].)

These reactions are relatively slow in the ethyl nitrate flame at pressures of 50 mm Hg and below. The rate determining step can be identified with the primary decomposition of the nitrate ester. The evidence for this is that the activation energy derived from the variation of flame speed with flame temperature is 38 kcal/mole, a value very close to the strength of the O-NO₂ bond. Furthermore the same value is found from the heat release profile obtained by differentiating the temperature-distance curve (Fig. 12). The ethyl nitrate concentration is seen to be a linear function of the temperature in the flame and to vanish at the maximum flame temperature. This not only confirms its identity as the rate-determining reactant but also indicates the degree of applicability

to such complex systems of the theoretical relationship obtained by setting the Lewis number equal to unity. When this concentration temperature relationship is used to determine the specific rate constant from the heat release distribution, the activation energy over the major portion of the heat release region is again 38 kcal/mole.

At pressures below 150 mm Hg, the flame speed is independent of pressure. This suggests that the decomposition reaction is controlled by the rate of collisional activation. At higher pressures the flame speed decreases with increasing pressure indicating a transition to first order unimolecular decomposition kinetics. The flame speed in the vapor has not been determined over a sufficient pressure range to enable the pressure exponent to be determined with

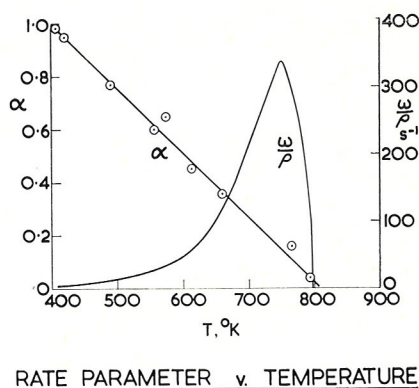
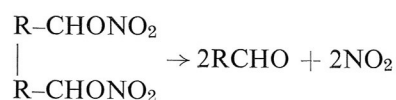


FIG. 12. Ethyl nitrate mass fraction α and decomposition rate ω/ϕ as function of temperature in flame. (After Hicks [19].)

any precision. Above one atmosphere pressure the flame can be stabilized on the surface of the liquid and the burning rate can be determined over a wide pressure range but the observed pressure exponent is nearer to unity than to the value of one-half expected for a first order reaction. However, the flame temperature is also found to be increasing with pressure due to the reduction of increasing amounts of nitric oxide. It appears that the reaction of nitric oxide with molecules such as those of aldehydes becomes increasingly important as the pressure is raised. The burning rate of liquid ethylene glycol dinitrate, which decomposes into formaldehyde and nitric oxide, is almost identical with that of ethyl nitrate in the pressure range 500 to 1000 psi. This tends to confirm the suggestion that this type of reaction is important in determining the burning rate and pressure exponent at high pressures.

The composition profiles of a number of other liquid nitric flames at atmospheric pressure have been studied by Powling [23-25]. Of particular interest are the dinitrates where spectrophotometric measurements have shown that

nitrogen dioxide is a major intermediate product. The dinitrate decomposes to produce equal amounts of aldehyde and nitrogen dioxide:



This reaction is about thermally neutral and the rate determining reaction in the flame is the oxidation reaction between nitrogen dioxide and the aldehyde

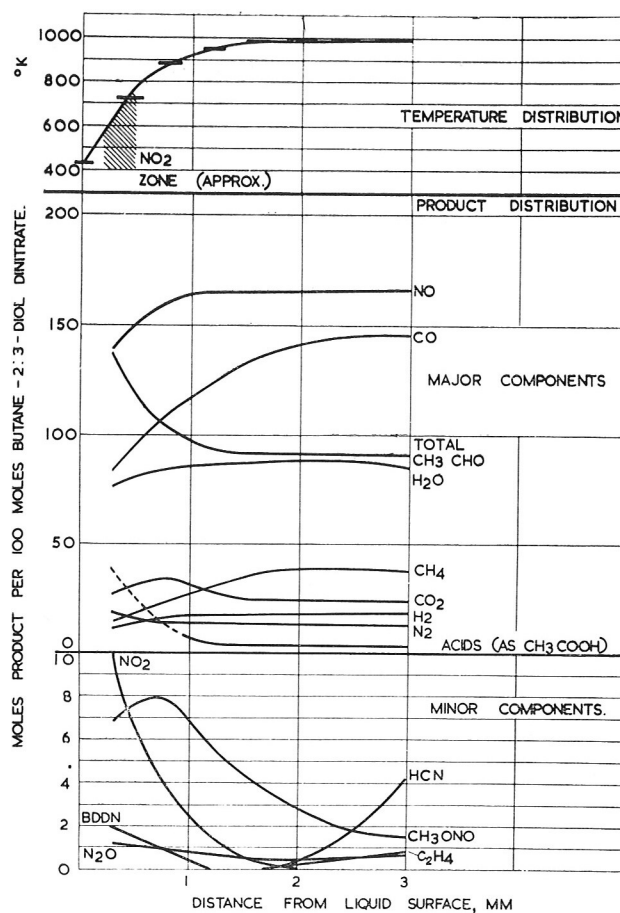


FIG. 13. Spatial variation of composition through butane-2,3-diol dinitrate flame. (After Powling [25].)

(Fig. 13). This is confirmed by the fact that the flame speeds for the combustion of dinitrates are identical with those of mixtures of nitrogen dioxide and the appropriate aldehyde. Figure 14 shows both the large difference between the flame speeds of different nitric esters at similar flame temperatures and pressures, and also the similarity between the speeds for the dinitrates and for mixtures

of nitrogen dioxide with the appropriate aldehyde. The equivalent flame speed of liquid ethylene glycol dinitrate (calculated with respect to the flame products so that, for identical products, we are comparing the mass burning rates) is identical with that of a formaldehyde-nitrogen dioxide mixture extrapolated

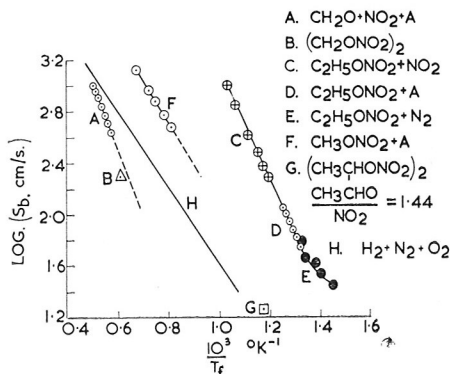
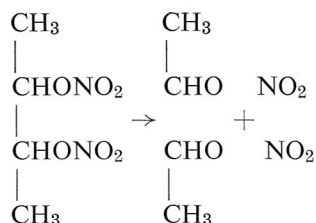


FIG. 14. Flame speed measured with respect to the products of combustion as a function of flame temperature for various nitrate esters and nitrogen dioxide mixtures.

to the same flame temperature. Similarly the flame consumption rate of 2,3-butane-diol dinitrate is identical with that of its primary decomposition products, acetaldehyde and nitrogen dioxide



We may conclude that at low pressures the burning rate of the mononitrate is controlled by the rate of decomposition of the nitric ester molecule which is slow compared with the oxidation of the resulting free radical. With the dinitrates, the rate controlling process is the oxidation of the aldehyde. The decomposition of the nitrate ester is relatively fast and is completed well below the final flame temperature.

At pressures above one atmosphere the properties of these flames are liable to be influenced by the reduction of nitric oxide to nitrogen which takes place within the primary reaction zone. This reaction is quite distinct from the visible flame reaction which is observed some distance from the primary zone at high pressure and which can be identified with the reaction of nitric oxide with the stable products carbon monoxide and hydrogen. It is clearly associated with reaction of the nitric oxide with free radicals produced in the decomposition of the nitrate ester and with intermediate products such as formaldehyde. The extent to which the reaction occurs depends upon the structure of the nitrate

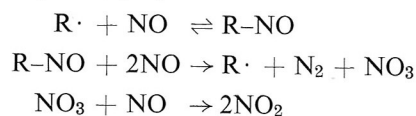
ester and its decomposition products and, unlike the visible flame, becomes more obvious as the energy of the system is reduced. Table 1 gives the percentage of reduction for a range of nitrate ester propellants at atmospheric pressure.

TABLE 1

Composition	Cal. val. cal/g	% NO Reduced
Methyl nitrate	1640	10
Ethylene glycol dinitrate	1740	4
Ethylene glycol mononitrate	920	50
Ethylene glycol dinitrate (70%) + Triacetin 30%	860	25
Ethyl nitrate	870	35
2-Methoxy ethyl nitrate	510	55
Isopropyl nitrate	515	10
Nitrocellulose (12.2% N)	912	15
Double base propellant	767	26

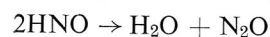
In some, although not all systems, the amount of reduction increases continuously in the range 1 to 40 atm pressure and the measured flame temperature increases as much as two-fold.

We know very little about the detailed kinetics of reduction reactions of nitric oxide. At low temperatures and pressures, and in the liquid phase, one type of reaction is known to involve the reaction of two molecules of nitric oxide with an unstable nitroso compound [26]:

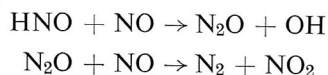


The rate of consumption of NO is second order in the nitric oxide concentration and may have a negative temperature coefficient due to the first equilibrium being displaced to the left by increasing temperature. This type of reaction is likely to be unimportant in the high temperature regions of the flame but may be significant where the primary decomposition and oxidation reactions occur in the condensed phase.

In the flame the formation of HNO by hydrogen abstraction from radicals and molecules with a weak C-H bond is likely to be more important. HNO can then lead to nitrogen formation through the relatively unstable nitrous oxide



or, at high temperatures,



The detailed mechanisms of the decomposition and combustion of the two main components of double base propellants, nitrocellulose and nitroglycerine are less well understood than those of the simple nitrates. Wolfram *et al.* have

made an extensive study of the products of ignition of nitrocellulose at sub-atmospheric pressures [27]. As one would expect from the possible variations in the individual chain segments in partially nitrated cellulose and the number of ways in which each segment can break down, the products form a complex mixture of partially denitrated and depolymerized fragments together with simple carbonyl compounds formed by oxidative pyrolysis of the glucopyranose rings. The gaseous products contain considerable fractions of molecular nitrogen and nitrous oxide. These are formed even in the slow isothermal decomposition of nitrocellulose so that the state of the intermediate decomposition products must favour ready reduction of the nitrogen oxides initially produced. When formed in a polymer chain, free radicals are restrained from undergoing mutual disproportionation reactions by reason of their immobility and may therefore be more readily available for reaction with nitrogen oxides.

Nitrogen dioxide has not been observed as a major intermediate in the combustion of double base propellants which tends to confirm the supposition that the mechanism is more nearly that corresponding to the mononitrates (rapid reduction of nitrogen dioxide by free radicals) than to that of the dinitrates.

The rate of pyrolysis of nitrocellulose has been reinvestigated in recent years by Phillips, Orlick and Steinberger by a spectrophotometric technique using thin films of nitrocellulose [28]. Their rate constants and temperature dependence can be used to estimate the temperature at which the primary decomposition reaches completion, a temperature which should correspond to the measured surface temperature.

From Section 3 the mass flux and the temperature are approximately related by the equation

$$M^2 = \frac{2\rho\lambda k}{\bar{c}_p(2T_s - T'_s - T_0)} \frac{RT^2}{E} \exp\left(\frac{-E}{RT_s}\right) \quad (20)$$

If we insert a measured value of the mass burning rate and the values of k and E given in reference [28], we can calculate a value for the surface temperature. The heat release of the solid phase reaction and therefore the adiabatic surface temperature T'_s are not known but the calculation is relatively insensitive to the possible variation in these parameters. We shall assume $T'_s - T_0$ equal to 250°C corresponding to a heat reaction in the solid phase of ~ 90 cal/g; if we had assumed zero heat of reaction the surface temperature, T_s , would be $\sim 10^\circ$ higher.

At atmospheric pressure the burning rate of a nitrocellulose strand is quoted by Powling [29] as 4.5×10^{-2} cm/sec. We use the values:

$$k = 3.54 \times 10^{18} \text{ sec}^{-1}$$

$$E = 45 \times 10^3 \text{ cal/mole}$$

$$R = 1.9866 \text{ cal/deg mole}$$

$$T_0 = 300^\circ\text{K}$$

and

$$\lambda/\bar{c}_p = 5 \times 10^{-4} \text{ cm}^2/\text{sec}$$

The last value is estimated from the known thermal diffusivities of organic liquids in an appropriate temperature range.

Solving equation (20) for T_s we obtain a value of 585°K which is not very different from the experimental value of $\sim 600^\circ\text{K}$ measured by Powling [29] using an infrared emission technique. At first sight these values appear surprisingly low in comparison with the temperature of the ethyl nitrate decomposition flame ($\sim 800^\circ\text{K}$). The difference arises not so much from the faster decomposition rate of the nitrocellulose at similar temperatures as from the higher density and thermal diffusivity of the condensed phase reaction zone. The measured gas temperature close to the burning surface is $\sim 870^\circ\text{K}$ at atmospheric pressure. The heat released in combustion at atmospheric pressure is a fraction of the thermochemical energy of the reaction to products in chemical equilibrium and is of the order of 200 cal/g. Since the calculated surface temperature is insensitive to the heat release assumed for the solid phase reaction, we cannot make any statement on the latter quantity other than that it cannot exceed a value of about 100 cal/g at atmospheric pressure. It may seem odd that a reduction in the assumed heat release in the solid phase leads to a slightly higher calculated surface temperature for a given mass flux. This arises because a decrease in the exothermicity increases the temperature gradient in the reaction zone and therefore decreases the thickness of the reaction zone. This must be compensated by a higher volumetric reaction rate and therefore by a higher surface temperature.

At higher pressures where the burning rate is greater than at atmospheric pressure, the surface temperature must increase. There are no reliable experimental measurements of the rate of increase of surface temperature with pressure.

The calculated surface temperature at a pressure of 600 psi where the burning rate is ten times its value at atmospheric pressure is 667°K , which is still considerably less than experimental values of the gas temperature of 1300°K adjacent to the surface at this pressure. Measurement of the temperature profile by the insertion of fine thermocouples into propellant strands so that they are overtaken by the combustion zone indicate that there is a further rapid temperature rise just upstream of the propellant surface. The rate of rise of temperature is too great at high pressures for the thermocouple method to give a reliable indication of the heat release profile or the surface temperature, but it is clear that a major proportion of the heat release takes place in the gas phase close to the solid surface. The amount of heat release in the gas phase is found to increase considerably with increasing pressure above atmospheric. This is associated with the reduction of increasing amounts of nitric oxide. What is not clear is what proportion of this heat release is effective in increasing the burning rate of the propellant and whether the rapid rise of gas temperature close to the solid surface is due to reduction of some fraction of the nitric oxide or to the reduction of nitrogen dioxide formed by the initial pyrolysis of the nitrate ester. The thermochemistry of the decomposition of nitrocellulose indicates that some reduction of nitric oxide is essential if the heat of decomposition is to reach values of 200 cal/g, but this amount depends very much on the extent of degradation of the glucopyranose ring structure.

Strictly the concept of a uniform regression of a surface at a uniform temperature is an over-simplification of the burning of double base propellants in this pressure range. It can be observed visually that the burning surface exhibits a wave-like mode of consumption. It appears as if glowing filaments of carbonaceous material periodically move over the surface consuming a thin layer of propellant. Ciné photography of the propellant surface shows that a smooth area on this surface appears to darken and to roughen. This area is then consumed by a wave of combustion which moves across the surface and leaves behind a network of carbon filaments which are blown off the surface by the steady evolution of gas. The edge or periphery of the surface wave is delineated by a glowing filament of carbonaceous product. This effect is related to the "foam" reaction observed by Crawford and Huggett [33] and to the intermittent nature of the burning of cordite first reported by Huffington [34].

The consumption of the reacting surface layer leaves a smooth surface which subsequently repeats this sequence. It seems probable that the overall, average rate of burning is the result of two components: a steady rate analogous to the burning of a liquid propellant and a surface or condensed phase reactive wave moving laterally across the surface. The enhanced temperature of the carbonaceous filaments appears to be due to their combustion in nitric oxide but it is not completely certain whether they are the cause or effect of the surface wave process. The fact that the burning rate of nitrocellulose and compositions containing it is some twice as fast as that of nitric esters of similar flame temperature with which the surface mode is not observed, suggests that it makes a substantial contribution to the average burning rate. We know that the production of a solid carbonaceous residue does not of itself cause high burning rates even though its formation would tend to increase the exothermicity of the solid phase decomposition as against the formation of simple gaseous products. This can be demonstrated by adding traces of flame-retardants such as phosphates which can be seen to promote the formation of carbonaceous products but inhibit their oxidation. These additives depress the burning rate by a factor of two. This suggests that the burning of the carbonaceous residue in nitric oxide can have a significant effect on the burning rate.

This reaction of a carbonaceous residue with nitric oxide has been suggested [31] as a possible cause of the "platonization" effect of lead compounds described by Preckel [6, 7]. The addition of lead compounds to cellulose esters can be observed to promote the formation of solid carbonaceous residues on pyrolysis as do many other inorganic compounds. Lead also catalyzes the oxidation of this carbonaceous residue by nitric oxide [32]. Visual and photographic observation on the burning of propellant strands show that additions of lead compounds increase the number and extent of the incandescent regions on the burning surface which are associated with the formation of carbonaceous products and that these "hot spots" disappear when the pressure is increased to values at which the catalysis of the burning rate vanishes. There appears to be a correlation between the occurrence of incandescent regions on the propellant surface and the promotion of the burning rate.

Qualitatively it is easier to understand why a strongly exothermic, heterogeneous reaction on the propellant surface should increase the burning rate than to explain why this effect vanishes with increasing pressure. There is some evidence that an active agent in the action of lead compounds is lead oxide produced by their pyrolysis. When lead oxide itself is added to the propellant composition it has been observed that the smaller the amount of added oxide the higher is the pressure at which the rate promoting effect vanishes. This conforms with the observation that the more stable aromatic lead salts are more effective in promoting the burning rate at high pressure than the easily pyrolyzed aliphatic lead compounds [7]. It appears that lead oxide can catalyze some rate-promoting reaction but can also eliminate, as the combustion pressure is increased, some intermediate responsible for this reaction. If the intermediate is supposed to be a carbonaceous residue, the effect might be explained on the basis of a lead catalyzed reduction of nitric oxide on a carbonaceous product, coupled with the destructive oxidation of such a product by lead oxide [31].

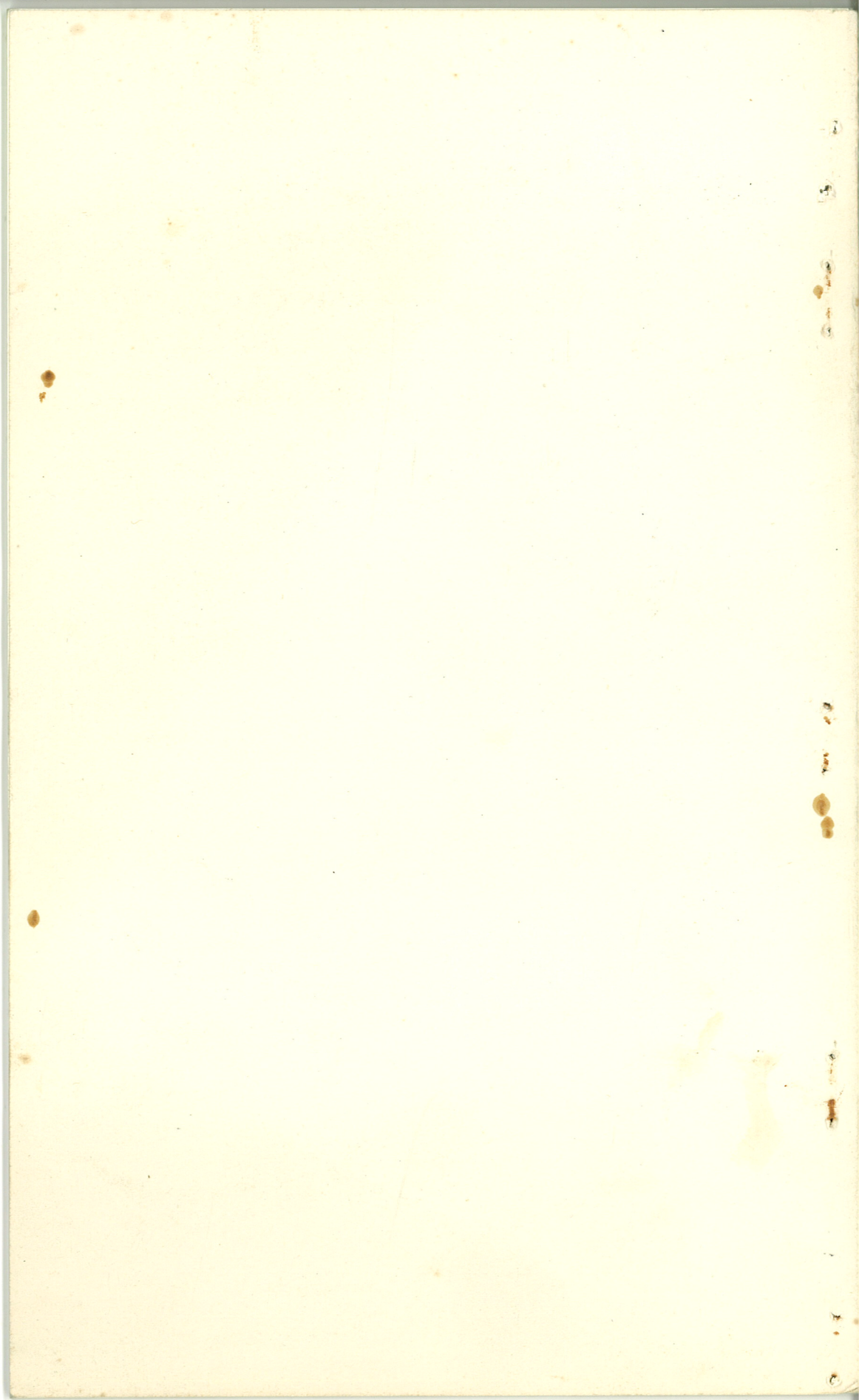
It is, however, difficult to see why the oxidation of a carbonaceous residue by lead oxide should be inactive in promoting the burning rate when oxidation by nitric oxide is assumed to be effective. Both reactions will be strongly exothermic and an increase in pressure should favour the reaction with the gas phase species rather than that with the solid oxide. There appears to be no evidence of any major change in the gaseous products of combustion on addition of lead compounds although there is an indication of a slight increase in the amount of nitrogen formed and a consequent small increase in the temperature of the products of the primary reaction zone. On the other hand, it has been observed that lead tetramethyl added to ethyl nitrate decreases the burning rate [35] and completely inhibits the formation of nitrogen in the products of combustion at atmospheric pressure, resulting in a fall in the measured flame temperature of some 200°C.

We must conclude that the action of lead compounds in nitrate ester combustion is no less complex than is their role in hydrocarbon combustion.

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Metrication

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Computer "print outs" for the conversion of inches to millimetres and psi to MN/m^2 can be obtained on application to Mr. M.J. Harper (Ext. 419). In addition a computer program is available which will enable other conversions to be planned as required. It is to be noted that in the course of time centimetres will probably become obsolete, as the recommended multiplying prefixes are limited to 10^{+3} .

As a result of decisions in the last ISO meeting, the following non-SI units are likely to persist in metric mensuration and may be used in conjunction with SI if so desired.

Plane angle degree ($^{\circ}$), minute ($'$), second ($''$).

Length micron

The symbol for a micron is μm , not μ as in BS. A millimicron is, therefore, represented by nm.

Volume litre (l), millilitre (ml)

The word 'litre' is used as a special name for the cubic decimetre (dm^3), but is not to be used to express the result of precise measurements.

Time minute (min), hour (h), day (d), week, month, year

It is to be noted that the abbreviation for hour is h not hr, and in this connection that the SI abbreviation for second is s not sec.

Mass tonne or metric ton (t)

The equivalent value in SI units is Mg.

Density kg/l (kg/dm^3), g/ml (g/cm^3), g/l (kg/m^3)

The equivalent SI units are shown in brackets. (See also remarks under Volume.) cc is no longer used having being replaced by cm^3 .

Pressure bar (b)

Viscosity Dynamic poise (P) (10^{-1} N s/m^2)

centipoise (cP) (10^{-3} N s/m^2)

Kinematic stokes (St) ($10^{-4} \text{ m}^2/\text{s}$)

centistokes (cSt) ($10^{-6} \text{ m}^2/\text{s}$)

Abbreviations and equivalent SI values are shown in brackets.

Energy, work kilowatt hour (kW h) (3.6 MJ)

electron volt (eV) ($1.6021 \times 10^{-19} \text{ J}$)

Symbols and equivalent SI units are shown in brackets.

/In

In addition to the above the following non-SI units are in common use:

Temperature degree Celsius ($^{\circ}\text{C}$)

This is the practical unit of temperature formerly called Centigrade. The change of name was made partly on account of the fact that in France 1 Centigrade means 1/10 000 right angle. Temperature intervals may be referred to in either of two ways e.g., degC or $^{\circ}\text{C}$. In texts where degF is not included, deg is recommended instead of degC.

Radioactivity curie (Ci)

Strictly, the SI unit of activity of radionuclides is 1 per second (s^{-1}), but the above unit (1 Ci equals $3.7 \times 10^{10} \text{ s}^{-1}$) was accepted because of its widely established use.

Rotational frequency rev/min, rev/s

In connection with the use of gramme as the elementary unit of mass, the spelling is as shown and not 'gram', and the abbreviation is g not gm.

In the presentation of results the following points should be noted:

- (i) The multiplication of symbols is indicated by a gap between them, e.g. $\text{kJ/m}^2 \text{ s degC}$ not $\text{kJ/m}^2 \cdot \text{s} \cdot \text{degC}$ or $\text{kJ/m}^2 \times \text{s} \times \text{degC}$.
- (ii) In many countries the comma (,) is employed in numerical values where in the UK a decimal ('full') point is used, either on the line or above it. In the UK the comma is often used to separate the digits of large numbers into groups of three.

To avoid confusion the digits of large numbers are often separated by gaps into groups of three starting from the decimal point. This should be adopted for SI values although a slight variation is permissible for four digits as shown in the following examples:

	1 000 or 1000
	10 000
	1 000 000
	0.001 3 or 0.0013
but	0.001 35
and	0.001 356

- (iii) Abbreviations and symbols do not take a full stop, e.g. mm not mm. and V not V.. In addition they do not take 's' in the plural, e.g. cm not cms. Digressing somewhat, it is now the Ministry policy that full stops be eliminated as far as possible where clarity is not affected, e.g. ERDE, RDX, PVC, etc.

Reference to the above and other SI details are to be found in the following:

- (i) Pamela Anderton and P.H. Bigg, Ministry of Technology, National Physical Laboratory. Changing to the Metric System. Conversion Factors Symbols and Definitions. Second Edition. 1967.
- (ii) The Royal Society, Conference of Editors. Metrication in Scientific Journals. January 1968 (Reprinted March 1968).
- (iii) BSI PD 5686. The Use of SI Units. April 1967.
- (iv) BS 3763 : 1964. The International System (SI) Units.

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CONFERENCE ON NITROCELLULOSE CHARACTERISATION
AND
DOUBLE-BASE PROPELLANT STRUCTURE

7, 8 and 9 MAY, 1980

ABSTRACTS

PROCUREMENT EXECUTIVE,
MINISTRY OF DEFENCE,
PROPELLANTS, EXPLOSIVES AND ROCKET MOTOR
ESTABLISHMENT,
WALTHAM ABBEY, ESSEX, ENGLAND

INTRODUCTORY PAPER

T J LEWIS
PERME (WA)

An overall picture is given of the more fundamental aspects of the UK government-sponsored research programme on nitrocellulose and nitrocellulose propellants.

Areas of particular interest are identified. These include (1) the characterisation of a material in which morphological factors may be as important as molecular or chemical properties (2) the effect of molecular weight distribution on processability (3) the non-Fickian interaction with plasticisers (4) the relationship between molecular relaxation phenomena and measurable mechanical properties, and (5) the structure and properties of doughs.

Some new instrumentational techniques show promise, but there is also much scope for the application of classical methods supported by our present greater understanding of the structure of polymers and gels.

A SIMPLE VISCOMETRIC TEST FOR NUMBER AVERAGE AND WEIGHT AVERAGE MOLECULAR WEIGHT OF 12.6% N PYRO NITROCELLULOSE

D J BULLOCK, J D COSGROVE, B C HEAD and T J LEWIS
PERME (WA)

D J MARSHALL and D WASON
NEC Ltd., Stevenston, Ayrshire, Scotland

and

B M WATSON
Organics Division, ICI, Stevenston, Ayrshire, Scotland

The viscosity of a 3 per cent solution of 12.6% N pyro nitrocellulose in acetone/ethanol solvent is found to be related to the geometric mean of the number average and weight average molecular weights. The fractional increase in the viscosity of such a solution on the addition of lead β resorcyate is a function only of number average molecular weight. Once calibration has been made against osmotic pressure measurements and intrinsic viscosity, both number and weight average may be measured rapidly with an accuracy which is no less than that of the osmotic pressure and intrinsic viscosity measurements themselves. The role played by the molecular weight distribution of nitrocellulose in the production of propellant doughs is discussed.

GPC MEASUREMENTS ON CELLULOSE SOLUTIONS

J O WARWICKER
Shirley Inst., Manchester

A method of finding the molecular weight distribution in cellulose samples was put forward by Pettersson et al (B.A. Pettersson and E Treiber, Das Papier 1969, 23 139) in which cellulose is dissolved in Carboxen and gel permeation chromatography carried out on agarose gels. This method has been investigated in relation to cotton linters used for propellant manufacture. It is shown that cellulose samples with closely similar fluidity values can have significantly different molecular weight distributions to have effects on the properties of propellants derived from them. The control of the molecular weight distribution in samples of cellulose used for propellants is therefore important. To explore the methods of control of this molecular weight distribution cotton linters at different stages of purification were investigated by this method of GPC. The consequences of applying these chemical methods used in the purification of linters to the structure, molecular weight distribution and properties of cellulose will be discussed.

GEL PERMEATION CHROMATOGRAPHY OF NITROCELLULOSE

A F CUNNINGHAM, C HEATHCOTE, D E HILLMAN, J I PAUL
MQAD, Woolwich

This paper reviews the problems found in the gel permeation chromatography of nitro-cellulose. The influence of concentration, calibration method, choice of column exclusion limits and the degree of nitration is discussed, together with problems due to the presence of microgel.

The change in molecular weight distribution at different stages during the industrial preparation of propellant grade nitrocellulose is described.

ELECTROCHEMICAL DETECTOR STUDY FOR GEL PERMEATION CHROMATOGRAPHY OF CELLULOSE NITRATE

M PAINDAVOINE and M STEPHAN
S.N.P.E., Le Bouchet, France

A method to determine both molecular weight and nitrogen content distribution would be useful in characterising industrial cellulose nitrate samples.

Molecular weight distribution is generally evaluated by Gel Permeation Chromatography using a refractive index detector. A second detector is needed in order to measure continuously nitrate concentration. For this purpose an electrochemical detector working on the differential pulse voltammetric principle was developed and its characteristic parameters were investigated.

Electrochemical behaviour of cellulose nitrates in THF and THF-DMSO solvents was studied.

Response of the detector is dependent on hydrodynamic volume of eluted species. Hence, nitrocellulose standards were prepared by preparative Gel Permeation Chromatography to calibrate the detector.

CELLULOSE SOURCE AND NITRATION PROCESS EFFECTS ON NITROCELLULOSE

R A STRECKER and E V TURNGREN
ARRADCOM, Dover, N.J., USA

A variety of sulfite and sulfate woodpulp were studied in order to identify pulp variables which had an effect on the properties of nitrocellulose. Cotton linters nitrocellulose was studied to determine the effect of nitration process, continuous versus batch nitration, and the condition of the linters, baled versus sheeted, on the molecular weight distribution of nitrocellulose.

Pulp variables evaluated were percent alpha-cellulose, viscosity, pentosan content, crystallinity, pulping process, and density. The nitrocellulose properties monitored were percent nitrogen, viscosity, stability, and molecular weight distribution. The study showed that the following pulp variables affected nitrocellulose properties: sheet density; degree of polymerization; pulping process; and cellulose crystal lattice type.

A study of cotton linters nitrocellulose prepared from baled and sheeted linters shows that the baled linters produce a nitrocellulose with a greater fraction of high molecular weight material. The continuous nitration process produces a nitrocellulose with a different molecular weight distribution than the batch nitration process.

CHARACTERIZATION OF WOOD AND COTTON NITROCELLULOSES

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One cotton nitrocellulose (NC) and three wood NC samples were characterized at 25°C by viscometry, Gel Permeation Chromatography (GPC) and Light Scattering (LS). In all methods investigated, the results varied according to the technique used to clarify the solutions. The Huggins parameter computed from the viscosity measurements was practically constant in THF but was about 40% higher in the case of Cotton NC than it was for wood NC in Acetone and Ethyl Acetate. GPC measurements were carried out in THF, a concentration effect was observed and molecular averages were extrapolated to zero concentration. The absolute molecular weight averages were determined using the Universal Calibration method and an empirical relation that took into account the high polydispersity of the samples ($M_w/M_n = 6-10$). LS measurements were carried out in THF and Ethyl Acetate at two different wavelengths: 546 and 436 nm. NC in solution consisted of a molecularly dispersed portion and a microgel portion that could be reduced by centrifugation and by lowering the solution concentration. The refractive index increment (dn/dc) was generally lower when the solution was centrifuged. The presence of microgels in the filtered solutions produced distortions in Zimm plots that appeared as a marked curvature in the angular dependence of scattering and a deviation from linearity in the concentration dependence. The centrifuged solutions yielded Zimm plots which exhibited a downward curvature at low concentration only for some wood NC samples in some solvents but not for Cotton NC. The data at high angles yielded M_w and chain dimensions of the NC molecularly dispersed component.

VISCOMETRIC STUDIES OF NITROCELLULOSE SOLUTIONS

J D COSGROVE
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Although dilute solution viscosity is generally regarded as satisfactory for molecular weight comparisons of polymers, propellant nitrocelluloses fall within a narrow viscosity range and great care is needed both in measurement and interpretation of results. However viscosity has proved to be reliable and a sensitive indicator of pyro nitrocellulose origin and behaviour. Viscosity coupled with osmotic pressure tests on pyro nitrocellulose fractionated by precipitation have yielded MW distribution data and with several different samples the major part (80% or over) appears to have a degree of polymerisation between 150 and 600.

Partial cellulose degradation probably occurs during industrial cellulose nitration but proceeds much further during stabilisation (boiling) of the nitrocellulose. A study of the boiling process has shown that nitrocellulose degradation is slow in acid solution but 10 times faster at pH 9.2. Viscosity measurements have proved capable of giving a quantitative kinetic interpretation of the reaction and the observed changes can be interpreted as a constant rate chain scission mechanisms. The chain scission may be random but it is possible that the nitrated cellulose molecules break only at weaknesses occurring at intervals of approximately 150 glucose units.

OSMOTIC STUDIES OF NITROCELLULOSE SOLUTIONS

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Number average weights, \bar{M}_n , of six nitrocellulose fractions isolated from mechanical Pyro (12.6%N) have been estimated by dynamic equilibrium osmometry. Molecular weights in the range $2.5 \times 10^4 \leq \bar{M}_n \leq 2.1 \times 10^5$ obtained using Selectron RC51 membranes showed no dependence on either of the two good solvents ethyl acetate or tetrahydrofuran.

Comparative osmotic data are presented for corresponding measurements to the unfractionated polymer using Selectron RC51 and Sartorius SM115 regenerated cellulose membranes for which equal mean pore diameters (<5mm) are claimed by their manufacturers. In contrast to the behaviour of SM115 membranes, osmotic pressures developed with RC51 membranes showed some solvent dependence, consistently lower molecular weights, \bar{M}_n , being obtained in tetrahydrofuran. These observations are discussed in terms of reduced polymer diffusion in this system.

Examination of 32 different samples of Pyro, using the less retentive system RG51/ethyl acetate, suggests that despite the occurrence of limited polymer diffusion, qualitatively useful estimates of \bar{M}_n are obtainable for these materials when adequate measures are taken to standardise membrane permeability.

HIGH RESOLUTION NMR SPECTRUM OF CELLULOSE NITRATE

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The structure of cellulose nitrate was studied by Nuclear Magnetic Resonance. The resolution enhancement technique applied to very low polymerisation degree cellulose nitrate samples provided high resolution spectra. Thus assignation of all the lines of the spectrum was possible and coupling constants were determined.

Solvent effect on proton chemical shift was studied in order to class each proton according to its acidity.

ESCA STUDIES OF THE NITRATION AND DENITRATION OF CELLULOSE MATERIALS

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Univ. of Durham

Many of the important properties of nitrocellulose based formulations may be expected to depend on surface phenomena and it is perhaps surprising that so little attention has previously been directed at this aspect of the chemistry of nitrocelluloses. Since the initial reaction with any nitrating medium of cellulose fibrils is at the surface, and since it is the surface which interfaces with the surroundings, the question of the mechanism of synthesis, of initial burn rate, and of denitration etc. are circumscribed by details of structure and bonding in not only the bulk but also in the outermost few tens of Angstroms of the surface. The paucity of data on details of structure and bonding in the surface regions of nitrocelluloses can be traced to the lack of any convenient technique for monitoring surface chemistry and the change therein consequent upon chemical reactions initiated at the surface. The advent of ESCA (XPS) over the past decade as a powerful tool for elaborating details of structure and bonding in polymeric systems means that direct investigation of surface nitration and denitration of cellulose are a realistic possibility. In this paper we review detailed studies of the kinetics and mechanism of the surface nitration and denitration of celluloses using the wide range of information levels available from ESCA. Comparison with bulk data provides considerable new insight into this important area which has been of interest to both science and technology for well over a century.

PULSED NMR STUDIES OF THE NC/NG SYSTEM

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Pulsed NMR studies (at 40 MHz) are reported for the nitrocellulose/nitroglycerine system. Proton spin-lattice (T_1) and spin-spin (T_2) relaxation times have been measured for a range of NG contents (from 0 to 60%) covering a temperature range from -50 to 110°C. Over most of the temperature range the T_2 measurements show two component decays, a longer decay which is attributed to mobile NG and a shorter (rigid-lattice) decay associated with NG and immobile NG. The fraction of mobile NG measured by NMR increases with increasing temperature which is indicative of a distribution of motional frequencies, and hence environments, for the NG. The results provide evidence for the existence of strongly bound NG (approximately 12%) with the remainder being in a more loosely bound state.

The spin-lattice relaxation is describable by a single relaxation time over the whole temperature range suggesting that the whole spin system is relaxed by the mobile NG via the spin-diffusion process. A T_1 minimum is observed around 20°C which is a high frequency manifestation of the NG motions which cause the changes in the spin-spin relaxation at lower temperatures. The motional frequencies determined by NMR are consistent with those obtained from dielectric and dynamic mechanical measurements.

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ESCA STUDIES ON NITROCELLULOSE AND NITROCELLULOSE/NITROGLYCERINE PASTES

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Univ. of Durham

and

F S BAKER
PERME (WA)

X-ray photoelectron spectroscopy has been used to study the solid state chemistry of nitrocellulose and nitrocellulose/nitroglycerine pastes.

Examination of the spectra of commercially prepared nitrocellulose has shown that, apart from the expected components, a nitrite ester was present and that some samples contained native carbon.

Pastes have given spectra very similar to those obtained for nitrocellulose. Nitroglycerine was not detected, but quite often a NI(s) peak at 409 eV was detected. This peak is about 1eV higher in energy than that due to the NI(s) electron in the nitrate group.

Both thermal and photo degradation of nitrocellulose and pastes have been monitored. These investigations show that in these environments, paste is less stable than nitrocellulose.

DIELECTRIC RELAXATION OF PROPELLANT PASTES

F S BAKER
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Dielectric studies have been made on rolled and unrolled nitrocellulose/nitroglycerine pastes containing one per cent by weight of carbamate.

Both interfacial and dipole orientation relaxations have been found, the former occurring at about 10^{-3} Hz and the latter in the 10 MHz region at room temperature. It is thought that the high frequency relaxation is predominately associated with the movement of the nitroglycerine molecules in the matrix. Its position is a function of temperature and nitroglycerine concentration. There is some evidence that the peak position is dependant on the processing of the paste, and also that there may be a low frequency (0.1 to 1.0 Hz) relaxation present at room temperature.

SECOND ORDER TRANSITIONS IN NITROCELLULOSE
ENERGETIC PLASTICIZERS SYSTEMS

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Structural changes corresponding to second order transitions in polymeric systems cause important changes of their mechanical properties. Different nitrocellulose - energetic plasticizers (TEGDN, TMETN, NG, NG-TA) mixtures have been studied by differential scanning calorimetry, and in some cases by thermomechanical analysis, with the object of improving mechanical properties of double-base propellants.

A second-order transition, unmodified by thermal history, appears at low temperature. Its temperature is lowered down to the plasticizer transition temperature when the amount of plasticizer is increased. The evolution of the characteristics of this transition (T, 1/T, amplitude) with the amount of plasticizer, was studied.

The results obtained allow some assumptions on the nitrocellulose - plasticizer interactions.

An intricate phenomenon, modified by thermal history, appears at temperatures above ambient.

DYNAMIC MECHANICAL ANALYSIS OF NC/NG SAMPLES

D TOWNEND
AMTE, Holton Heath, Dorset

A range of materials have been analysed using a DuPont 980 DMA. Results show high and low temperature peaks in the $\tan \delta$ curves. Attempts are being made to relate the structure of the materials to the positions and movements of these two peaks.

MECHANICAL RELAXATION STUDIES ON DOUBLE-BASE PROPELLANTS

R STENSON
PERME (WA)

Force torsional oscillatory tests of solid rods and rectangular bars in the frequency range 0.1 Hz to 10 Hz have been investigated to characterise accurate values of storage modulus G^1 , loss modulus G^{11} and loss angle δ over a temperature range from -100°C to $+70^\circ\text{C}$ for a series of standard double-base propellants and synthetic nitrocellulose/nitroglycerine matrices.

The effects of plasticiser content on the glassy and transition regions and on the size and position of peaks in the $\tan \delta$ /temperature curve have been investigated. Particular interactions between constituents in some systems at intermediate temperatures are suggested from changes in mechanical damping with temperature. G^{11} shows a sharp low temperature peak which in general polymer experience would be regarded as a glass transition temperature T_g . Comparison with uniaxial tensile data determined at a constant rate of strain^g shows that at this critical temperature strain to failure becomes very low (1 per cent or less).

The contributions of crystalline fillers to dynamic properties have been measured, including the effects of the shape of the particles employed.

TMA STUDIES ON THE NC/NG SYSTEM

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The thermal expansion of a series of nitroglycerine-nitrocellulose compounds has been measured over the temperature range -150° to $+100^\circ\text{C}$. A change in expansion coefficient corresponding to a second order transition occurs below 0°C . The transition temperature and the width of the transition increase with decreasing nitroglycerine content. Above 0° the expansion for most compounds deviated from linearity. Possible causes for this deviation will be discussed.

DIELECTRIC STUDIES OF SOME CELLULOSE DERIVATIVES

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Dielectric measurements are reported for cellulose, methyl cellulose, ethyl cellulose and cellulose acetate over a temperature range 193 to 323K at a frequency of 1 kHz as a function of the water content. These studies reveal that the way in which water interacts with the polymer matrix is influenced by the nature of the side group substituent. In ethyl cellulose the position of the water relaxation is essentially coincident with that of the side chain motion, whereas in the case of cellulose acetate the two peaks are well resolved. These observations will be discussed in terms of the nature of the molecular interactions which occur in the system.

THE DETERMINATION OF MOISTURE TRANSITIONS IN CELLULOSE NITRATES USING DIFFERENTIAL SCANNING CALORIMETRY

Mlle RAT
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Differential scanning calorimetry has been applied to characterize moisture transitions in cellulose nitrates. The determination of the enthalpic heat of melting of the freezable water using the area under the endothermic curve and the determination of the melting temperature allows the calculation of the total bound water content and the free water content. Thus specific transitions for these materials have been identified including free water incorporation point, total bound water and fiber saturation point.

The influence of some characteristics of nitrocelluloses (nitrogen content, polymerisation degree, ...) has been studied.

NETWORKS OF NITROCELLULOSE

M MAYEN

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The residual hydroxyl functions of the nitrocellulose (NC) are used for reacting with a diisocyanate and for crosslinking. Plastisol nitrocellulose (microspheres) is blended with nitrated esters and diisocyanates.

The crosslinking agent - plasticizer mixture moves into the microspheres during the curing process. There is a competition between the diffusion of the crosslinking agent and the chemical reaction of the isocyanate. The structure and the mechanical properties of the final product depend on the relative kinetics of these different processes. The plasticized and cured NC is a rubber, and follows the fundamental laws of the rubber-like elasticity. Hence, it is possible to determine the crosslink density by swelling. Different parameters governing the network formation are described, as:

- nature of the isocyanate
- nature of the plasticizer
- ratio isocyanate/alcohol
- ratio NC/plasticizer
- crosslinking catalyst.

SYNTHESIS AND PROPERTIES OF INTERNALLY-PLASTICIZED ETHYL CELLULOSE AND CELLULOSE ACETATE

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PERME(WA)

Ethyl cellulose and cellulose acetate polymers have been modified by attaching flexible side chains to the base polymer. A variety of chemically-linked plasticizing groups have been introduced using techniques, such as radiation polymerization and condensation polymerization, under conditions which preclude cross-linking of the base polymer. The modified polymers have been characterized by IR, GPC, NMR and their mechanical and physical properties have been determined. The chemically modified polymers have lower glass transition temperatures than polymers modified using normal plasticizers and are more easily fabricated. By linking the plasticizer to the base polymer, losses and migration of plasticizer on storage have been prevented. Furthermore the chemically modified polymers are more resistant to nitroglycerine uptake.

THE DIFFUSION OF ACETONE AND ISO-PROPYL NITRATE INTO NITROCELLULOSE AND NITROCELLULOSE/NITROGLYCERINE FILMS

J D COSGROVE, T G HURDLEY and T J LEWIS
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Diffusion into glassy polymers is almost always non-Fickian in nature. Two limiting mechanisms have been recognised - Case II swelling, in which a sharp boundary between swollen and unswollen material moves at a uniform velocity through the polymer, and Case III swelling, in which rapid diffusion maintains a uniform concentration of diffusant throughout the polymer at all times. This concentration increases as the lattice expands, enabling more diffusant to be accommodated.

A recent paper (Polymer 1978, 19, 285) describes both Case II and Case III mechanisms in nitrocellulose films. Acetone shows Case II behaviour, but iso-propyl nitrate, although exhibiting Case II behaviour on the first sorption cycle, shows Case III on each subsequent sorption. This is because desorption is always incomplete, and the later sorptions are taking place into a polymer which is already uniformly plasticised with diffusant. This work has now been extended to the sorption of acetone and iso-propyl nitrate into nitrocellulose plasticised with nitroglycerine. On all occasions Case III behaviour is seen. This is characterised by the percentage uptake versus time curves being independent of film thickness. Most curves approximate to a linear relationship between uptake and $(\text{time})^{\frac{1}{2}}$, and had not variable film thickness been studied a Fickian mechanism would have been presumed. But with Case III, since the uptake at any particular time reflects the extent of chain disentanglement, a simple relationship with time or $(\text{time})^{\frac{1}{2}}$ is not to be expected. Any observed approximation to such a relationship is fortuitous.

SORPTION OF DIETHYL PHTHALATE BY NITROCELLULOSE FIBRES

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The manner in which diethyl phthalate (DEP) is absorbed into nitrocellulose (NC) fibres has been observed microscopically. The movement of pure DEP into dry fibres is overwhelmingly influenced by capillary motion up the lumen and through microcracks between fibrils. Attack spreads from these foci, and within the time-scale of the experiment there is little interaction with the outer wall of the fibre. If, however, the lumen and other capillary passages are blocked by water or other liquid, then attack proceeds evenly from the outer wall and a sharp boundary between swollen and unswollen material moves at a uniform speed towards the centre of the fibre and appears to be unaffected by the fibrillar structure (Case II swelling). If the supply of DEP to the surface is interrupted, this boundary becomes immobile, and the concentration of DEP in the swollen layers is that which is just sufficient to saturate residual un-nitrated hydroxyl groups on the NC. Reducing the activity of the DEP by admixture with benzene results in similar sharp boundaries, presumably because capillaries become blocked with spent diluent. Apart from capillary action, movement is always perpendicular to the fibre axis.

SCANNING ELECTRON MICROSCOPE STUDIES OF DOUBLE-BASE PROPELLANT

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A method has been developed, using the scanning electron microscope, which allows a detailed study of the internal and external morphology of double-base propellants. Various procedures are involved in the preparation and subsequent examination of these nitrocellulose/nitroglycerine compositions and a description will be given of the techniques involved.

The microscopy results obtained, which relate to the degree of material gelation as a function of fabrication parameters, will be discussed and possible future trends highlighted.

MECHANICS OF CRACK GROWTH IN DOUBLE-BASE PROPELLANTS

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If cracks develop in a propellant grain during storage or the ignition/burning phase then the extra and exposed surface will, when the propellant grain is ignited, burn and cause an unexpected rise in gas pressure. This may affect the ballistic performance and possibly result in the shell- or missile-case bursting. Thus there is an essential need for crack growth in such materials to be thoroughly understood and for pertinent failure criterion to be established. In this paper the crack growth in a nitrocellulose/nitroglycerine propellant has been studied employing a continuum fracture mechanics approach.

Values of the stress-intensity factor, K_{IC} , at the onset of crack growth have been measured and found to be a function of both test temperature and thickness of the specimen. These effects may be understood and predicted by modelling the measured value of K_{IC} as the sum of a plane-strain contribution, which is virtually temperature invariant, and a plane-stress contribution, which is usually greater in magnitude and highly temperature dependent. This temperature dependence reflects the viscoelastic and plastic energy dissipative mechanisms which occur at the crack tip. Indeed, correlations are established between the propellant's fracture behaviour and its viscoelastic and plastic flow behaviour, as ascertained from independent dynamic-mechanical and uniaxial-tensile tests.

Finally, the various failure criteria which have been identified are critically discussed and their application to improving and predicting the crack resistance of propellants considered.

MECHANICAL PROPERTIES OF GUN PROPELLANTS

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Interior ballistic problems associated with abnormal burning of propellant grains due to mechanical failure are under study. Compressive mechanical properties have been investigated as a function of temperature and strain rate for a "modified" double-base propellant (JA2) and comparison made with similar studies for triple-base propellants. Measurements were made at strain rates of 10 seconds^{-1} and $10^{-3} \text{ seconds}^{-1}$ and temperatures of 20°C and -45°C . At the higher strain rate the double-base propellant shows ductile behavior at 20°C and brittle failure at the low temperature. However, comparison with triple-base propellants indicates that this double-base propellant is much less brittle at the lower temperature. Considerably less fragmentation is observed for the double-base propellant. While the ductile to brittle transition can be related to a glass transition temperature, the difference in fragmentation is apparently related to composition and structure. The relationship of ductile and brittle failure to abnormal burning leading to unsafe gun firing conditions will be discussed.

THE EFFECT OF MICROSTRUCTURE ON THE PHYSICAL PROPERTIES OF THE NC/NG SYSTEM

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The microstructure of various nitrocellulose-nitroglycerine propellants has been observed with optical and scanning electron microscopy. Correlations between microstructure, thermal and mechanical properties of these propellants have been found. A model of propellant structure is proposed to explain some of the observed behaviour.

SOLID STATE REACTIONS IN THE THERMAL DECOMPOSITION OF NITROCELLULOSE AND THE INFLUENCE OF BALLISTIC MODIFIERS

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The pyrolysis process of neat nitrocellulose and of nitrocellulose contained in double-base matrices was investigated in an optical bomb and by thermal analysis instrumentation.

During the pyrolysis process characteristic carbonaceous fibers are formed through the action of ballistic modifiers in the solid phase. These fibers form a link to super-rate burning: it is observed only in the presence of these carbonaceous fibers.

The carbonaceous fibers are the product of the thermal decomposition of nitrocellulose catalyzed by ballistic modifiers. Catalysis can take place only if the modifiers are in close contact with the nitrocellulose.

The results support the hypothesis of Suh, Adams and Lenschitz.

DETERMINATION OF THE THERMAL DECOMPOSITION BEHAVIOUR OF NITROCELLULOSE AND GUN PROPELLANTS

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Usually the stability of nitrocelluloses and gun propellants is measured by tests conducted at temperatures far above 100°C. In many cases the results of these methods do not agree with the actual stability below 100°C. A 90°C weight loss test or the measurement of the stabilizer depletion rate would be much more appropriate to elucidate the real stability of propellants.

To get more information in this connection, gun propellants without and with different stabilizers have been aged at several temperatures between 95 and 65°C. The decomposition behaviour was determined by measuring the weight loss and the stabilizer depletion rate. The following results have been evaluated:

- . There is a straight line correlation between 95°C and lower temperatures.
- . The stabilizer depletion rate increases from acardite II (methyldiphenylurea), ethylcentralite to diphenylamine.
- . The rate of stabilizer consumption is closely connected with both the decomposition rate and the autocatalytic decomposition (safe life time) of the propellant.
- . A correlation based on these results enables the assessment of the safe life time of propellants in a much shorter time than by conducting weight loss tests.
- . Propellant instability can be recognized very soon.

CHEMILUMINESCENCE STUDIES OF PROPELLANT DECOMPOSITION

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A facility based on a chemiluminescence NO_x analyser has been developed to study aspects of the thermal decomposition of propellants. The NO_x evolution characteristics of a number of single, double and triple base propellants have been determined. Some of the results have been used to solve specific problems arising from traditional stability tests on propellants and their nitrate ester ingredients. The contribution of the chemiluminescence method to stability and compatibility testing will be highlighted. In addition its use in providing information to predict motor lifetime and for the identification of fundamental mechanisms of propellant decomposition will be evaluated.

COMPARISONS OF THERMAL STABILITY DATA FOR NITROCELLULOSE & PROPELLANTS

N J BLAY
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Experimental methods to measure quantitatively the rates of decomposition of nitrocellulose usually rely upon the analysis of nitrogen oxides in the gases evolved by the material when it is heated. Four such methods are considered and data from them compared. Most of the results appear consistent despite considerable differences in the temperatures and other conditions of the tests.

Stability information for nitrocellulose can be combined with that for nitroglycerine and used to predict stability parameters for propellants. However, these rarely correspond with observed propellant stability data which usually indicate much higher rates of decomposition, particularly if obtained from relatively low temperature storage tests. Possible causes contributing to these discrepancies are briefly discussed.

EXTRUSION PROPERTIES OF PROPELLANT DOUGHS

R E CARTER
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The behaviour during extrusion of double- and triple-base gun propellant solvent doughs will be discussed, with particular respect to the influence of the nitrocellulose/nitroglycerine matrix upon those properties. The effects of such parameters as extrusion temperature, solvent strength and solvent concentration upon the processability of propellant doughs containing nitrocellulose of different degrees of nitration and different nitroglycerine levels will be demonstrated. Also, the contribution of the matrix to the flow behaviour of filled gun propellants during processing will be considered.