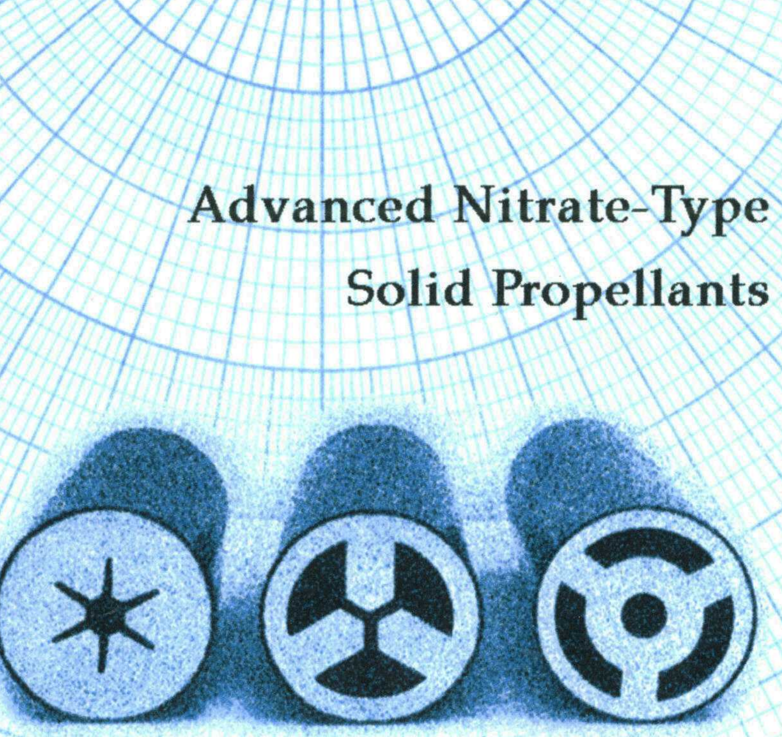
Solid Propellant Engineering

Volume 2

Advanced Nitrate-Type Solid Propellants



Solid Propellant Engineering

Volume 2: *Advanced Nitrate-Type Solid Propellants*

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SOLID PROPELLENT AND EXOTHERMIC COMPOSITIONS

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By

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PREFACE

THE greater part of my working life has been occupied in the Explosives Industry in devising chemical compositions of one sort or another for providing energy to carry out various jobs, ranging from the winning of coal to the dispersion of insecticides. To me at least there has been a common theme or purpose throughout this work and there has been considerable satisfaction in working on safer explosives for use in fiery mines or in designing compositions for starting jet engines. The purpose has been to use chemicals as a source of energy to replace human effort and to tame explosives, as it were, in order to carry out a large number of operations for which they are specially fitted. The theme has been developed in various talks I have given, particularly in Christmas Lectures to Children, on " Explosives in the Service of Man ", and over the years has developed into the wider field of exothermic reactions in the solid state as sources of energy for a multitude of operations and purposes. I have worked to some extent on liquid and gas reactions, but the explosives industry is largely concerned with solid compositions and specifically with those which " burn " with oxygen contained in their own compositions and therefore need no assistance from outside air.

Therefore, when the publishers asked me to write a book on chemicals as a source of energy, I welcomed the opportunity of developing the theme for the first time along broad lines, though I realised the serious limitations which were inherent in such a presentation with the material which I had available. I have tried in this book to give a picture of the wide range of chemical compositions which have been developed as sources of energy for various applications and also to describe the applications. The material is largely derived from work which has been carried out in the Nobel Division Laboratories of Imperial Chemical Industries over the last thirty years and on which I and many of my colleagues in the Research Department were engaged, but it is supplemented by information from other published work. The presentation is unfortunately uneven, both in nature and technical content, for a variety of reasons. Most of the investigations were carried out for immediate practical applications and much of the work lacks basal scientific treatment. They were technical rather than scientific investigations. Further, a great deal of the subject matter is still of a secret or classified nature and is not available for publication and it has been necessary to restrict the contents to material which either has been freely published or is contained in patent specifications. Again, as there is already a number of works dealing fully with many aspects of explosives, explosive accessories and propellants, I have, in such cases, dealt only with various points which I have considered necessary for the general theme of the book or because they have not been fully covered in recent books.

There is much fundamental work which could be profitably done in this field and if the present book stimulates interest it will have fulfilled its purpose.

In writing this book I have been greatly assisted by various colleagues in I.C.I., particularly by members of the Nobel Division Research Department, and I have drawn freely on the published work of many of them and on some of their internal reports.

I am particularly grateful to Mr. E. Whitworth and Mr. E. G. Cooke who have helpfully criticised the manuscript, made many useful suggestions and corrections and provided a considerable amount of information; to Dr. P. F. Gay who undertook the checking of literature references; to Mr. R. Tulip who supplied much of the material for Chapter 2; to Dr. T. C. Owen who provided the matter on the mechanism of burning of colloidal propellants for Chapter 5; to Mr. R. D. Smith for his help on the treatment of the decomposition of ammonium nitrate; to Mr. R. Wark for his assistance in connection with the treatment of power cartridges; to Dr. G. P. Sillitto who supplied me with Chapter 8 on Rocket Motors; to Mr. R. A. W. Hill for his assistance on Gasless Reactions; to my son J. S. Taylor for assistance in preparing the sections on Pyrotechnics and on Gasless Reactions; to Dr. R. J. Doyle for his assistance on Cap Compositions, and to Dr. T. R. Paterson who supplied me with so much of the patent information. I am most indebted to Miss J. M. Davidson who has carried out the onerous task of checking up and recalculating most of the thermochemical data for the book ; to Miss A. M. Wylie who has performed the difficult task of typing the manuscript and preparing it for publication, and to Dr. J. G. Cockburn for correcting proofs and preparing the index.

I would like to thank the Editors of various journals for their kind permission to reproduce or make use of material previously published in them: the Clarendon Press, Oxford, for permission to reproduce the data in Table 1 of the book *Detonation in Condensed Explosives*; Butterworth Scientific Publications Limited for the use of some of the material from the paper " Advances in British Commercial High Explosives ", *Research*, **1**, No. 2, 1947; the

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I am also indebted to the Ministry of Supply for allowing me to use two of their photographs (Plate 5) to illustrate the book; to the Temple Cox Development Company Limited for permission to use their drawing for Fig. 18, and to the Plessey Company for permission to use Plate 10.

J. T.

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CHAPTER I

SELF-SUSTAINED EXOTHERMIC CHEMICAL REACTIONS

THE standard of living which man has been able to achieve has been governed ultimately by what he can wrest from reluctant Nature. This is largely determined by the energy that can be made available per unit of population. The energy available from the unaided physical efforts of the human being is very restricted and the standard of living corresponding to this would be pitifully low. It has, of course, been possible to raise the standard of the few by forcibly marshalling the energies of the many, as in slave societies and feudal states. Such practices do not of themselves raise the average of the whole community.

Advances of civilisation have been brought about by men learning to harness sources of energy outside themselves, such as air, fire and water. Fire is, of course, derived from chemical energy. The history of the utilisation of chemical energy to supplement and replace human effort is one of the most fascinating of stories, and it is one aspect of this story with which we shall be concerned in the following pages.

Until the advent of nuclear power the available sources of energy were derived exclusively, for all practical purposes, directly or indirectly from solar radiation. The human species in its primeval state obtained its energy solely from the food it gathered, which comprised chemical substances synthesised by sunlight. It is the oxidation of the carbon and hydrogen in the food by oxygen from the air which people breathe that provides the source and store of energy which is used by each human being. So too, in the case of conventional fuels like wood and coal, the oxygen required for the chemical reaction is derived from the air.

Combustion with air is by far the most important reaction used to produce energy for the needs of human beings and has culminated in such developments as our great power stations, our internal combustion engines, our jet-propelled planes; but there is another class of chemical reaction which sophisticated man has harnessed to supplement human effort in which the fuel and oxygen are condensed together, as it were, ready to react when suitably initiated. Some of these chemical reactions give rise to gaseous products at very high pressure and temperature and are thus capable of doing mechanical work by expansion, others produce large quantities of heat with little or no gaseous products (like thermite). All are sources of energy which can be directed by human ingenuity to perform useful operations. These reactions cover an extraordinary range of speeds of the chemical reactions involved and this is responsible for the spectacular and wide scope of their applications. Thus high explosives detonate at linear speeds up to about 9,000 metres per second, and at the other end of the scale there are compositions which react at only a fraction of an inch in a second. They offer a field of exploitation, therefore, ranging from operations which take place in a few microseconds to those lasting for hours. They are not efficient methods of providing energy because they have to carry their own oxygen instead of getting it gratis from the air. Thus 1 gm. of coal takes roughly 2 gm. of oxygen from the air for complete combustion and gives about 8,000 calories; 1 gm. of cordite, on the other hand, only yields 1,000 calories. Nevertheless, for providing high power for short intervals of time, or for use under conditions when atmospheric oxygen is not available, these compositions provide simple and convenient sources of power.

In recent years, for example, a great deal of attention has been given to using cordite and other propellants as controlled energy sources, for doing mechanical operations. This is called the " power cartridge field " and it includes cartridges for starting aeroplane engines, for the ejection of pilots from high-speed aircraft —in an emergency, of course—for operating fire extinguishers and a whole variety of similar purposes. The " philosophy "—as the Americans would say—of carrying out " non-military " operations by exothermic solid chemical reactions has been established.

SELF-SUSTAINED EXOTHERMIC REACTIONS

In this book we shall restrict our considerations to one facet of these chemical reactions in which the fuel and oxygen are included together in the compositions, namely, compositions which are self-sustained or self-propagating when initiated or ignited at a local point. Much has been written about gaseous reactions of this type, as, for example, mixtures of vaporised fuels like petrol with air, universally employed in modern internal combustion engines: we shall not be concerned with such reactions, but with those which occur in the condensed state, namely, as solids or liquids and, indeed, our attention will be largely confined to reactions in the solid state.

An early example of this type of reaction was gunpowder, which is an intimate mixture of charcoal, sulphur and potassium nitrate. As everyone knows from experience of fireworks, once a train of gunpowder is ignited by a flame, however small, it will continue to burn or deflagrate in a chain reaction. Such reactions require no oxygen from the air, they are diverse in chemical nature and character, but they all have the common property that the process involved in the chemical transformation characterising the process is exothermic. Many chemical substances or mixtures which fulfil this criterion are not self-propagating and consequently can only be used in applications where heating of the fuel occurs before spontaneous decomposition takes place as in the case of monofuels, like isopropyl nitrate used in engine starters. Our primary object in the present work is to deal with self-propagating compositions and their applications, but some reference will be made to certain others, particularly liquids, which have achieved practical applications.

Some of these reactions are very violent in nature and constitute " high " or detonating explosives. Others, like cordite, are slower and the rate of reaction depends on the pressure of operation. In such cases these compositions are propellants which are used in guns and for other propulsive purposes, or pyrotechnic compositions of the familiar type used in fireworks. Another class is almost gasless, like thermite, and such are employed as convenient sources of heat for special purposes like welding.

Self-sustained reactions are initiated by the local application of energy from some outside source. The energy applied is either in the form of heat or of a mechanical blow.

Propellants like cordite, or incendiary mixtures like thermite, in fact, all the so-called " deflagrating " or " burning " compositions are initiated by heat, generally by a flame. Thermal ignition of this sort may be achieved via a flame, an electrically heated wire, by friction or impact, or by chemical reaction.

In the case of high explosives, like dynamite or TNT, initiation is obtained by a local intense shock or blow which sets up a shock wave of high intensity in the explosive and causes the onset of detonation. The shock is usually supplied by a detonator (see Chapter 4).

Initiation of any self-sustained reaction in practice is normally through an orderly sequence of events, for example, in the case of a shotgun cartridge, the pressing of the trigger releases a strong spring which drives the firing pin with considerable energy against the cap. This blow ignites the cap composition which provides a flame which in turn ignites the propellent charge in the cartridge.

It is, of course, obvious that explosives would be quite ineffective if they were not self-propagating reactions when suitably initiated.

Until comparatively recently such compositions as were used in practical applications were very highly exothermic, and in the cases of non-detonating or propellent compositions of this type it was not surprising that the heat liberated was adequate to heat the adjacent undecomposed material to bring about its " combustion " and make the reaction self-sustained. Thus the heat liberated per gm. is about 700 calories for gunpowder compared with nearly 1,000 calories for British cordite.

The bulk of the compositions derive their energy from an oxidation process of carbon or hydrogen with oxygen, both being included in the composition itself, either in a single molecule as in nitrocotton or in the form of a fuel mixed with metallic nitrates, chlorates or perchlorates. The basal oxidation processes involved are of high exothermicity and temperature, and in a sense we can regard such reactions as " brute-force " reactions, the energy liberation being more than adequate to force the unreacted molecules over the energy thresholds by temperature alone.

Whilst the established type of composition was satisfactory for a great number of practical applications it was not suitable, for example, for use in blasting devices in " fiery " coal mines where methane/air explosive mixtures were likely to occur, or for mechanical operations where the " ironmongery " could not withstand high gas temperatures.

Consequently, a need became manifest for low-temperature exothermic gas-producing, self-sustained compositions for technical application, and in the early nineteen-thirties the author took up the task of investigating the problem. Subsequent researches have disclosed a fascinating field of self-sustained low-temperature combustion reactions in the solid state which has been uncovered largely by empirical investigations in the last two decades or so and which it is considered would well repay fundamental investigations. These compositions are now achieving important applications in coal mining, jet propulsion and dispersion of insecticides, and it is one of the objects of the present work to describe these compositions, their properties and uses.

Lastly, mention should be made of the whole range of energy- and gas-producing liquids like hydrogen peroxide and its mixtures, methyl nitrate and other alkyl nitrates, the applications of which to rockets and guided projectiles made great progress under the duress of war. Some of these liquid reactions are self-sustained, but others are promoted by the heating of the fuel in the combustion chamber. In the present work we shall be largely concerned with reactions in the solid state and liquid propellants will only be mentioned incidentally.

The property of a reaction being self-propagating or self-sustaining is not so simple as it appears at first sight. For example, TNT is not ignited by a small flame and is not a self-sustained propellant. Nevertheless, it is detonated by the blow from a detonator and the chemical decomposition is then propagated at very high speed. Furthermore, if TNT is confined in a steel tube it can be made to propagate from a source of thermal ignition and the same is true if there is a large enough bulk of TNT and a sufficient volume is heated up.

Again, there are exothermic compositions such as intimate mixtures of ammonium nitrate with small amounts of mineral oil which, whilst incapable of being self-sustained at normal pressures become self-sustained at pressures of the order of a few hundred pounds per square inch. So, too, many compositions which are not self-propagating at ordinary temperature become so at elevated temperatures.

The chemical reactions which we are considering and which we term self-sustained exothermic reactions in the solid state are thus not as clear-cut and definitive as the terms might suggest. So long as our considerations refer to use under normal conditions, however, there is little ambiguity and the selection of reactions which fulfil the necessary conditions by simple tests is relatively easy.

It may be well to stress in this introduction that the words " burn ", " combustion ", " deflagration ", etc., are generally used in discussing the self-sustained decomposition reactions of propellants and the various chemical compositions with which we shall be concerned, but it must be understood that their use in this context is an extension of their everyday meanings and is adopted simply because of convenience and established use.

THE ENERGY BASES OF EXOTHERMIC COMPOSITIONS

The chemical substances which can be used alone or in admixture to provide energy on reaction, are extremely numerous.

If we consider a substance or a mixture in a certain state and it is then transformed into some other state, there will be a difference in intrinsic energy between the first and last states. If the energy of the last state is less than the first the reaction is exothermic and energy will be produced, normally as heat. This heat, in theory at least, is available to do useful work or perform some service.

Some transformations are very simple and involve no chemical change as in latent heat transformations such as condensation of steam or freezing of water. Latent heat transformations are not of high exothermicity and most exothermic compositions rely for their energy supply on chemical reactions.

The chemical reaction used as energy base may be one occurring within a single chemical substance or in a mixture. It is not necessary that the chemical reaction shall be itself self-sustained, but if it is not self-sustained then some means of forcing it through or catalysing it must be provided. This is analogous to starting off the combustion of coke with a mixture of the more sensitive coal.

Similarly the base of a self-sustained exothermic composition may be a single chemical substance or it may be a mixture of two or more substances themselves not propagating. We shall discuss these in more detail later on.

SINGLE CHEMICAL SUBSTANCES

Most single-substance explosives of practical significance derive their energy from reaction between oxygen contained in molecules, and fuels, carbon or hydrogen, also constituents of the molecule. There are explosive substances which contain no oxygen such as nitrogen trichloride NCl_3, which breaks down readily with explosive violence, as follows:

$$2NCl_3 \rightarrow N_2 + 3Cl_2 \qquad (1.1)$$

The heavy metal azides are other examples: lead azide, for example, is used as an initiating explosive in detonators, but apart from special applications, there is no great outlet for such substances.

The oxygen of the single-substance explosive is usually contained in the nitrate (ONO_2) groups of nitric esters as in nitroglycerine or in nitro (NO_2) groups as in TNT. On explosion the nitrogen is transformed into free nitrogen (apart from some minor production of oxides of nitrogen) which contributes to the gas volume and the capacity of the explosive to do work.

Single substances like RDX, PETN and TNT and nitroglycerine (when 8 per cent. nitrocellulose is mixed with it to produce blasting gelatine) are themselves perfectly satisfactory explosives for many purposes, acting both as their own sensitiser and energy base.

Fundamentally, and ignoring any non-explosive ingredients present, modern propellants are in the same picture, the main oxidising group in colloidal powders being the (ONO_2) group of a nitric ester while the fuel is the organic residue, e.g., cellulose or glycerine to which it is attached, together with such non-explosives present as are oxidisable.

In addition to the single-substance explosives there are others containing large proportions of the lighter elements, usually hydrogen, nitrogen, carbon and oxygen, which can undergo exothermic reaction but are non-explosive, and in some cases do not even of themselves provide a self-sustained reaction. These substances are used in modern compositions for providing bases for mechanical operations and for jet propulsion, and will be dealt with in more detail later on. They include ammonium nitrate, guanidine nitrate, nitroguanidine, urea nitrate and similar compounds. There is also a number of liquids in this class, such as isopropyl nitrate, which will be dealt with briefly later in this chapter.

Whilst single-substance explosives are very suitable for such purposes as defence where economic considerations are not paramount, there are many practical uses as in commercial blasting, for example, where economic considerations predominate and these substances are too expensive for use alone. They are therefore " stretched " by using cheaper energy-producing bases of which the chemical reactions can be forced through by the action of the dearer single explosive constituent.

These energy-producing bases include a substance which can provide oxygen to sustain the combustion in admixture with another substance which provides the fuel.

OXYGEN-PROVIDING CONSTITUENTS FOR ENERGY BASES

The possible oxygen-providing substances or oxidising agents are numerous and comprise both solids and liquids. The most commonly used have been nitrates, notably potassium and sodium nitrates and later ammonium nitrate, which latter, however, unlike the metallic nitrates, contains some combustible fuel in its own molecule. Heavy nitrates, like barium and calcium nitrates and even lead nitrate, have been used on occasion.

Other widely used constituents have been chlorates and perchlorates, including ammonium perchlorate. Permanganates, chromates, peroxides and metallic oxides can also be used to provide oxygen to react with suitable fuels in special compositions.

Among liquids, liquid oxygen is an efficient oxygen provider, whilst nitrogen peroxide, strong nitric acid and hydrogen peroxide have found uses. Chromic acid and perchloric acid are also possibilities in this field, but their use has been rather as oxidising agents in chemical reactions than in compositions for practical application.

To provide " gasless " reactions oxidising agents consisting of metallic oxides like iron oxide Fe_3O_4, titanium dioxide TiO_2 and manganese dioxide MnO_2, are widely used.

FUEL CONSTITUENTS FOR ENERGY BASES

The substance which provides the " fuel ", or reducing agent, can also be selected from a wide range, both solid and liquid, but so far as cheap energy-producing chemical compositions are concerned, the choice has been largely restricted to charcoal and sawdust (cellulose), to mineral oils and jellies and to a few organic compounds containing part of the oxygen required for their own combustion, like dinitrotoluene or nitrobenzene. For special purposes, however, many sorts of organic chemicals are used, such as lactose, salicylic acid and asphalt. Sulphur is also employed.

For certain purposes such as to increase the power of commercial blasting explosives, powdered or granular aluminium and calcium silicide are utilised and fine metallic powders are widely used in " gasless " compositions as fuels.

Again, for specific applications, phosphorus and phosphorus compounds are employed. For example, one of the commonest and most useful applications of self-sustained compositions is the ordinary match.

The match-head of the common or non-safety match is a rather complicated mixture of which the principal ingredients are P_4S_3 phosphorus sulphide and potassium chlorate bound with a glue. When rubbed on a rough surface such as a strip of sandpaper, heat is generated locally by the friction and ignition occurs.

The mixture on " safety-matches " is also a composite one, consisting principally of sulphur, manganese dioxide, potassium chlorate and potassium dichromate. The " strip " on the box is coated with a mixture of antimony trisulphide, red phosphorus and powdered glass and the " safety-match " ignites when rubbed along this strip.

The energy bases of commercial explosives are of a specialised nature and will be dealt with in Chapter 3. They mainly comprise mixtures of nitrates with sawdust and the reaction of the non-explosive base is forced through by the explosion of the explosive constituent. Such detonating reactions are propagated at 2,000 or 3,000 metres per second. Deflagrating or propellent type reactions are, however, much slower, being of the order of a few inches per second only and consequently many mixtures of fuels with oxygen-containing chemicals provide self-sustained propellent reactions without sensitisation. The classical example of this type is, of course, gunpowder, and if the sulphur is removed from the gunpowder composition the resultant mixture is still self-sustained, and in fact is used in practice under the name of sulphurless gunpowder. We may select such a finely milled mixture of potassium nitrate and charcoal as illustration. Neglecting the hydrogen in the charcoal, the reaction to produce fully oxidised products is:

$$4KNO_3 + 5C \longrightarrow 2K_2CO_3 + 2N_2 + 3CO_2 \qquad (1.2)$$

Thus 4 molecules of potassium nitrate of weight 404·4 react with 5 atoms of carbon of weight 60, or 87·1 per cent. by weight of potassium nitrate with 12·9 per cent. carbon. The heat liberated by the reaction is 779 cal./gm. at 25° C. (constant volume), and the gas comprises nitrogen and carbon dioxide with a total production of 240 cm.^{3}/gm. The temperature of the reaction is about 2,700° C. (constant volume). The reaction gives rise to a large amount of solid product, namely, potassium carbonate. This is a typical example of a mixture of two substances, neither of which is an explosive or capable of exothermic decomposition itself which together form a self-propagating reaction. It is in fact one stage before gunpowder.

The reaction between potassium nitrate and sawdust or woodmeal can be considered in a similar way to that of the mixture with charcoal. It is a rather cooler reaction (see Table 1).

Perchlorate reactions are hotter and more energetic as will be seen from the reaction of potassium perchlorate and cellulose, namely:

$$3KClO_4 + C_6H_{10}O_5 \longrightarrow 3KCl + 5H_2O + 6CO_2 \qquad (1.3)$$

Here the heat liberated is 1,090 cal./gm. at 25° C. and constant volume, water vapour, the gas volume 426 cm.^{3}/gm. and the temperature nearly 3,200° C. Table 1 summarises the thermochemical data for a number of typical oxidation reactions based on inorganic nitrates and perchlorates.

Instead of using conventional fuels containing hydrogen and carbon it is possible to use finely divided metals. A notable example is aluminium which has a very high heat of oxidation. Aluminium powder has, in fact, been used for several decades in certain TNT/ammonium nitrate commercial explosives (e.g. the Ammonals), as an additional " fuel " to increase the power and gas volume. Aluminised military explosives came into prominence in the Second World War. The reaction in such cases can be represented as:

$$2Al + NH_4NO_3 \longrightarrow Al_2O_3 + 2H_2 + N_2 \qquad (1.4)$$

The heat liberated is 2,350 cal./gm. at 25° C. and constant volume, the gas volume 502 cm.^{3}/gm. and the temperature 5,400° C.

According to the oxygen balance * of the composition the hydrogen may, or may not, be oxidised to steam.

Magnesium powder in admixture with potassium nitrate also forms a very vigorous, sensitive self-propagating mixture of which the reaction may be depicted as:

$$5Mg + 2KNO_3 \longrightarrow 5MgO + K_2O + N_2 \qquad (1.5)$$

The heat liberated is 1,760 cal./gm. at 25° C. and constant volume, and the gas volume 69 cm.^{3}/gm.

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* For definition of oxygen balance see p. 12.

TABLE 1

THERMOCHEMICAL DATA AND GAS VOLUMES FOR A NUMBER OF OXIDATION REACTIONS

Reaction	Heat Liberated at 25° C. CV : WG cal./gm.	Gas Volume WG cm.^{3}/gm.	Temperature of Reaction °C.
$2NH_4NO_3 + C \longrightarrow 2N_2 + 4H_2O + CO_2$	900	912	2,620
$12NH_4NO_3 + C_6H_{10}O_5 \longrightarrow 12N_2 \rightarrow 29H_2O + 6CO_2$	882	939	2,500
$4KNO_3 + 5C \longrightarrow 2K_2CO_3 + 2N_2 + 3CO_2$	779	240	2,700
$24KNO_3 + 5C_6H_{10}O_5 \longrightarrow 12K_2CO_3 + 12N_2 + 18CO_2 + 25H_2O$	765	381	2,430
$4NaNO_3 + 5C \longrightarrow 2Na_2CO_3 + 2N_2 + 3CO_2$	949	280	2,780
$3KClO_4 + C_6H_{10}O_5 \longrightarrow 3KCl + 5H_2O + 6CO_2$	1,090	426	3,200

It will be observed that these reactions with metals yield metallic oxides which are solid at high temperature and are thus poor gas producers. Going a stage further, we arrive at the so-called gasless compositions.

Some of the exothermic self-sustained reactions between finely pulverised metals and metallic oxides and oxygen-containing compounds are practically gasless, like thermite, and have found special applications which are dealt with in Chapter 11.

So far we have considered as fuels either substances like charcoal and cellulose, or powdered metals. In all these cases the heat produced on oxidation is high and the compositions derived from them react at high temperature, frequently with much flame. As has already been pointed out, for many applications, this is a disadvantage and needs arose for solid chemical energy bases characterised by lower temperatures of reaction. For this purpose certain salts containing partially oxidised constituents are attractive and energy bases produced in this fashion by salt pairs have been used in certain safety blasting explosives, together with normal fuels like woodmeal.

Examples of such pairs are stoichiometric mixtures of sodium nitrate and ammonium chloride or ammonium sulphate which can be regarded as reacting thus:

$$NaNO_3 + NH_4Cl \longrightarrow NaCl + NH_4NO_3 \qquad (1.6)$$

$$2NaNO_3 + (NH_4)_2SO_4 \longrightarrow Na_2SO_4 + 2NH_4NO_3 \qquad (1.7)$$

The "transient" ammonium nitrate can then be regarded as reacting forthwith with cellulose in the normal manner, thus:

$$12NaNO_3 + 12NH_4Cl + C_6H_{10}O_5 \longrightarrow 12NaCl + 12N_2 + 29H_2O + 6CO_2 \qquad (1.8)$$

The heat liberated is 534 cal./gm. at 25° C. and constant volume, water vapour, the gas volume 578 $cm.^3/gm.$, and the temperature 1,680° C.

This reaction is very much cooler than the direct oxidation of cellulose by ammonium nitrate and can be used as the basis for safety blasting explosives.

Such reactions are not self-sustained and must be forced through by the energy produced either by general heating or by including an explosive in the composition.

The free oxygen in the nitrate molecule also constitutes a disadvantage for some purposes as it does not yield fully oxidised non-acid gases without conventional fuel additions. The extra atom of oxygen can be avoided by using, for example, sodium nitrite instead of sodium nitrate, and as we shall see later the resultant salt pair actually undergoes a low-temperature self-sustained reaction which has been put to a number of practical uses, thus:

$$NaNO_2 + NH_4Cl \longrightarrow NaCl + N_2 + 2H_2O \qquad (1.9)$$

That such substances as ammonium chloride and sulphate are combustibles or fuels can readily be demonstrated by dropping pieces into a dish of heated molten sodium nitrite or nitrate. The piece of chloride or sulphate swims round the dish on the surface of the liquid burning vigorously.

Ammonium nitrate is also an attractive substance as an energy base for use in low-temperature gas-producing compositions. This subject is dealt with fully in Chapter 7.

OXYGEN BALANCE

Explosives like guncotton which produce gases containing H_2 and CO because they have not enough oxygen in their molecules to oxidise to H_2O and CO_2 are called *oxygen negative* explosives.

Explosives, on the other hand, which have more than enough oxygen to produce fully oxidised products are called *oxygen positive*. Such an explosive is nitroglycerine of which the explosion may be regarded as:

$$2C_3H_5N_3O_9 \longrightarrow 6CO_2 + 5H_2O + 3N_2 + \tfrac{1}{2}O_2 \qquad (1.10)$$

Thus two molecules of nitroglycerine yield one atom of available free oxygen on explosion.

The oxygen surplus or deficit of an explosive or propellent composition is referred to as its oxygen balance and is important in technical applications of propellants and high explosives, on the one hand, because it enables a considerable control of the calorimetric value and gas volume of compositions to be achieved, and, on the other hand, because it can lead to corrosion and many ill effects when compositions are used to operate mechanical devices or can be detrimental to workers in blasting practice. Actually, the importance of achieving compositions which, on detonation, would yield approximately oxygen-balanced products and thus ensure non-toxic detonation products or " fume", was not sufficiently appreciated in the early days, and compositions highly oxygen-positive or highly oxygen-negative in their constituents were manufactured and used, especially in attempts to produce safer explosives for coal mines by reducing the temperature of explosion. In this connection it has been stated that, towards the end of the last century, many shotfirers in the country were suffering from anæmia, due to nitric oxide poisoning from using oxygen-positive explosives, and others were suffering from carbon monoxide poisoning from using oxygen-negative explosives. The rational design of blasting explosives of oxygen-balance, such as will give non-toxic detonation products, has largely developed during the present century and depends upon a careful balance between the oxygen-providing and fuel constituents of the composition.

STABILITY OF EXPLOSIVES

Whilst the function of explosives is to yield large quantities of energy in a violent manner, obviously they must do so only when required, and they must normally be stable. The same applies to propellants and to all ingredients of exothermic compositions of practical use. Further, they must be capable of being stored, often for many years under adverse conditions of storage without becoming unstable or decomposing spontaneously. For this reason, many chemicals must be excluded so far as practical use is concerned. Anything which becomes unstable at moderately high temperatures such as are likely to be encountered in practice or which is unduly sensitive to friction or blow is unsuitable for normal use. Modern explosives, and particularly those used in Service stores, may be subjected to very severe storage conditions and they must be able to withstand these satisfactorily for prolonged periods. Contrary, therefore, to common opinion, practical explosives are not treacherous unstable compounds, but are characterised by high stability until initiated by the correct and appropriate means. It will be understood then that unstable or extremely sensitive explosives like nitrogen trichloride, silver acetylide or hydrazoic acid (of which even solutions in water can detonate readily) are not used in practice. Certain combinations, such as chlorate mixtures containing sulphur, as a result of numerous accidents, have been prohibited and made illegal (1894). Mixtures of chlorates with phosphorus are also particularly dangerous.

The stability of an explosive is for obvious reasons a matter of prime importance both to the manufacturer and the user. All explosives are subjected to stability tests to determine their suitability for practical use.

There is no evidence to suggest that the initial step in the decomposition of an explosive is in any way different from that of a non-explosive of a similar chemical class. It is only the large free energy of the molecule, the rapidity of its release, and the accelerating effects of the decomposition products which produce an explosive reaction. Stability as in the case of other substances can therefore be considered in the light of an activation energy.

Before any chemical reaction can proceed, a minimum amount of energy per molecule must be supplied to the system. This activation energy, or energy barrier, will have a characteristic value for a given substance. In a mass of the substance it is to be expected on statistical grounds that a small number of the molecules will have an energy content greater than the value characteristic of the substance. In other words, the mass will contain some molecules which are more reactive than the majority. Stability tests are designed to estimate the relative number of these molecules with lower activation energy and to show how their number may be expected to increase with the age of the substance. Since thermal energy is so convenient, it is not surprising that all stability tests consist of measurements of thermal decomposition products.

The most widely applied stability test in Britain is the Abel Heat Test,[1, 2] which is a rigidly standardised extremely sensitive qualitative stability test. The test is designed to detect by means of starch iodide paper minute traces of nitrogen peroxide when a sample of explosive is heated in a test tube. The paper turns blue due to formation of iodide of starch. Another important stability test is the S.15 test developed in the laboratories of the Government Chemist by Farmer in 1920.[3] This test consists of heating a weighed amount of explosive in an evacuated apparatus and estimating the volume of gas evolved after a given time at constant pressure. Many other tests have been devised and applied in various countries.[2]

The isothermal decomposition of explosives is well dealt with in a recent paper by Cook.[4]

LITERATURE ON EXPLOSIVES

In a short monograph of the present type it is necessary to restrict the range of the subject matter to keep the size of the volume within bounds. The study of conventional explosives has been covered fairly fully in other publications and a short list of books on the subject of explosives and propellants is given.[5]

REFERENCES

1. First Report of the Departmental Committee on the Heat Test as Applied to Explosives. (H.M.S.O., London, 1914.)
2. Farmer, R. C. *Manufacture and Uses of Explosives.* (Pitman, 1921.)
3. Farmer, R. C. *J. Chem. Soc.* (1920), **117,** 1432, 1603.
4. Cook, M. A. *Industr. Engng. Chem.* (Industr.) (1956), **48,** 1090–95.
5. Read, J. *Explosives.* (Penguin Books Ltd., 1942.)

Marshall, A. *Explosives, Their History, Manufacture, Properties and Tests.* (J. and A. Churchill, 1917–32.)

Davis, T. L. *The Chemistry of Powder and Explosives.* (J. Wiley & Sons, 1943.)

Muraour, Henri. *Poudres et Explosifs.* (Presses Universitaires de France, 1947.)

Farmer, R. C. *Manufacture and Uses of Explosives.* (Pitman, 1921.)

Encyclopedia of Chemical Technology, Vol. 6, Explosives. (Interscience Encyclopedia, Inc., New York, 1951.)

Taylor, J. *Detonation in Condensed Explosives.* (Oxford University Press, 1952.)

Taylor, J., and Gay, P. F. *British Coal Mining Explosives.* (Newnes, 1958.)

CHAPTER 2

GUNPOWDER AND PYROTECHNICS

THE forerunner of modern explosives was gunpowder, or blackpowder, as it is now called. Gunpowder was remarkable in that it enabled large quantities of energy to be released in extremely short intervals of time and by it spectacular destructive effects could be achieved. It was inevitably applied to the art of warfare and a long time elapsed before it was adapted to the winning of coal and stone and to civil engineering purposes.

The origin of gunpowder is obscure and it has been attributed to the Chinese, the Hindus and the Arabs. It is possible that its antecedent was Greek Fire, a mixture of sulphur, pitch, resin, etc., used as an incendiary material in battles long before gunpowder was known.

So far as the application of gunpowder in Europe is concerned, the pioneers are considered to be Roger Bacon in England and Berthold Schwarz in Germany,[1, 2] and it appears that mixtures of saltpetre, charcoal and sulphur were first made and used for propellent purposes in the early part of the fourteenth century. These early powders consisted of approximately 40 per cent. saltpetre, 30 per cent. charcoal and 30 per cent. sulphur.

MANUFACTURE

The earliest method of preparation was to grind the ingredients separately in a mortar and mix them by hand to yield a fine dry powder. This method was replaced by stamp mills but they proved to be very dangerous and were forbidden by law in England in 1772, and they in turn were replaced by " edge runner mills ". The methods of manufacture have not materially altered in the last 100 years. The modern process consists of milling the ingredients together in a suspended runner mill, small amounts of water being added to the charge to improve milling and increase the safety of the operation. The resultant millcake is pressed between brass plates in a hydraulic press to yield compact cakes which are broken down by passing through breaker rolls, and the lumps produced are then corned in a corning machine to the size required. The resultant granules are glazed with small amounts of graphite to produce free-flowing grains.[2]

COMPOSITION OF BLACKPOWDER

A normal modern composition comprises 75 per cent. potassium nitrate, 15 per cent. charcoal and 10 per cent. sulphur. The composition, however, varies according to the special use for which the powder is intended, for example, according to whether it is a blasting powder or a fuse powder. In recent years, cheaper powders have been produced for purposes such as blasting in which the potassium nitrate is replaced by sodium nitrate. Such powders are, of course, cheaper, but they suffer from the defect that they are much more hygroscopic than potassium nitrate powders. Both types of blasting powder are manufactured in the form of grain and also in the form of compressed cylindrical pellets with a central hole. The pellets are more convenient for use in horizontal or rising shotholes than grain and as these burn more slowly than grain their action in blasting is less violent and they are used in places where great fragmentation would be undesirable.

There are also special types of gunpowder containing no sulphur, termed *sulphurless powders*. They are used where any corrosion due to sulphur is undesirable. Powders for pyrotechnic devices (e.g. incendiary bombs, Very lights and flares) are often, but not exclusively, of the sulphurless variety.

The granulation of gunpowder not only enables it to flow freely, which is desirable for many uses, but it also allows penetration of flame and uniform and rapid ignition when it is used in guns and as blasting charges. The compression to form pellets, referred to above, is sufficient to yield coherent cylinders, but not enough to prevent penetration of the hot gas flame, thus ensuring correct and rapid burning.

Special powders are also prepared for safety fuse and time ring fuse

Safety fuse powders are usually compounded from birch charcoal and in Britain they are of two types: (1) high nitrate and (2) low nitrate. The low nitrate powders are of such composition that when incorporated into safety fuse they burn with less production of " smoke " than that produced by conventional high nitrate powders. Fuse powders are made with a variety of burning speeds to meet various requirements.

Fuse powders are a special case of the general type of powders used in delays. Delay powders are also manufactured with a variety of speeds such as the very fast delays required in time rings in shells and the slower burning powders required in aircraft bombs.

BURNING SPEED

The burning speed of blackpowder varies with its composition and with the type of charcoal used in its manufacture.

The burning speed may be estimated in a variety of ways such as the time for burning the time ring as used in shells, or from the pressure and muzzle velocity when it is used as a charge for a gun. The two most important methods nowadays are the determination of the burning time of a length of lead tube filled with the powder and drawn down to a narrow diameter, and of the pressure-time curve of a charge fired in a closed vessel.[3]

The effect of pressure on the burning speed of blackpowder has been studied by a number of investigators and a general law deduced,[4] namely,

$$R = \beta P^{a} \tag{2.1}$$

where R is the linear rate of burning, P is the circumambient pressure (in the closed vessel, for example) and a and β are constants.

The most recent work of Blackwood and Bowden[5] yielded figures of the order of 0·4 cm./sec. for the rate of burning of grains of gunpowder and a rate of propagation along a line of grains of the order of 60 cm./sec. at atmospheric pressure. By reduction of pressure they found that both the rate of burning and propagation were greatly reduced and at about a quarter of an atmosphere the powder failed to burn.

The burning of the powder grains was from the surface inwards without disintegration and propagation from grain to grain is probably due to an emission of a fine spray of hot molten potassium salts projected from one grain to another.

THERMOCHEMISTRY OF GUNPOWDER

Noble and Abel carried out experiments on the explosion of gunpowder and described their work in two papers which are now historical.[6, 7]

Extensive experiments were carried out in steel explosion vessels with various loading densities from 0·1 to 0·9 gm./cm³. The pressures were measured by crusher gauges, the permanent gases were collected in a special gas holder and measured, and the solid residue was removed from the vessel and analysed.

Noble and Abel determined the heat of reaction of the powders with which they worked and also the permanent gases. Table 2 summarises the results.

The explosion pressures developed at various loading densities within a closed vessel were also measured. The results showed that when the charge completely fills the vessel the pressure is about 42 tons per sq. in.

From this work they also developed their well-known pressure-

TABLE 2

HEATS OF REACTION AND GAS VOLUMES GENERATED BY POWDERS TESTED BY NOBLE AND ABEL

	Heat of Explosion Q cal./gm.	Permanent Gas Volume V cm.^{3}
Pebble	721·4	278·3
Rifle large grain . . .	725·7	274·2
Fine grain	738·3	263·1
Spanish spherical . . .	767·3	234·2
Curtis and Harvey No. 6 . .	764·4	241·0
Blasting	516·8	360·3

loading density equation, namely:

$$P = P_0 \frac{(1 - \alpha\delta_0)}{\delta_0} \quad \frac{\alpha}{(1 - \delta)} \tag{2.2}$$

where P is the pressure developed, δ is the ratio of the bulk volume of powder to the volume of the vessel, P_0 and δ_0 are known corresponding values of P and δ, and α is the ratio of the volume of liquid residue just after explosion to that of the powder = 0·6.

They also estimated the temperature of explosion as about 2,200° C. Explosion temperatures and thermochemical pressures

TABLE 3

THERMOCHEMICAL PROPERTIES OF GUNPOWDER

	Loading Density gm./ml.	Experimental heat of explosion cal./gm.	Gas Volume N.T.P. cm.^{3}/gm.	Estimated Temperature °C.	Thermochemical tons./sq. in.
Blasting powder .	0·1	509	360	1,860	2·0
Pebble powder .	0·1	715	289	2,800	2·3
Rifle large grain	0·1	718	275	2,780	2·3
Fine grain.	0·1	727	286	2,880	2·2

calculated more recently by Thomas at the Research Department of the Nobel Division of I.C.I. for the compositions considered by Noble and Abel are summarised in Table 3. The explosion pressures are of the order of magnitude as quoted by Noble and Abel.

Determinations of the calorimetric values of both normal gunpowder G.12 and sulphurless gunpowder S.F.G.12 have been made recently in the Research Department of the Nobel Division of I.C.I. using their standard calorimetric bomb technique.*

The determinations were made in a bomb calorimeter under a pressure of 20 atmospheres of nitrogen in order to ensure effective reaction at pressure. The results obtained were as follows:

1. *Normal Gunpowder G.*12.

Analysis:		
	Potassium nitrate	75·3 per cent.
	Charcoal	14·4 per cent.
	Sulphur	10·3 per cent.

Calorimetric value 735 ± 15 cal./gm. (moisture content = 0·85 per cent.)
= 740 ± 15 cal./gm. (dry powder)

2. *Sulphurless Gunpowder S.F.G.*12.

Analysis:		
	Potassium nitrate	70·0 per cent.
	Charcoal	30·0 per cent.

Calorimetric value 650 ± 20 cal./gm. (moisture content = 2·73 per cent.)
= 670 ± 20 cal./gm. (dry powder)

THE NATURE OF THE PRODUCTS OF THE EXPLOSION OF GUNPOWDER

The composition of the gases and solid products formed on explosion of gunpowder has been the subject of many investigations dating back to the beginning of the eighteenth century.[9] There has been much controversy on the subject. Débus[10] summarised the products of combustion as follows:

(*a*) Chief products—K_2CO_3, K_2SO_4, K_2S_2, CO_2, N_2.
(*b*) By-products—H_2, H_2S, CH_4, NH_3, H_2O, KCNS.
(*c*) Constituents of powder not burnt—KNO_3, C and S.

It should be noted that the charcoal of the gunpowder contains, besides carbon, also oxygen, hydrogen, ash and moisture and that these add to the complexity of the explosion products. Indeed, the suitability of low carbon content charcoals (ca. 70 per cent. carbon) is considered by Blackwood and Bowden[5] to be related to the quantity of organic materials present in the charcoal.

CHEMISTRY OF THE DECOMPOSITION PROCESS

Much work has been done on the nature of the chemical processes involved in the decomposition of gunpowder and this too has been the subject of considerable controversy.

The main decomposition reaction, ignoring the " by-products ",

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* The values were communicated to the author privately. The apparatus used is described in Ref. 8.

is represented by the following equation according to Débus.[10]

$$4KNO_3+7C+2S \longrightarrow K_2CO_3+K_2S_2+3CO_2+3CO+2N_2 \qquad (2.3)$$

and this may be taken as giving a general indication, although oversimplified, of the process.

The initiation and subsequent early stages of thermal decomposition of gunpowder have been investigated by Blackwood and Bowden.[5] They summarise their view of the reactions occurring in the initiation of gunpowder as follows. The first reaction is the formation of hydrogen sulphide.

$$S + \text{organic material in the charcoal} \longrightarrow H_2S$$

and at the same time a reaction occurs between the organic material and the nitrate with the production of nitrogen dioxide.

$$KNO_3 + \text{organic} \longrightarrow NO_2$$
$$KNO_3 + 2NO \longrightarrow KNO_2 + NO + NO_2$$

The nitrogen dioxide then reacts with hydrogen sulphide to give nitric oxide and sulphur.

$$H_2S + NO_2 \longrightarrow H_2O + S + NO$$

and thus explains the disappearance of the hydrogen sulphide and apparent cessation of gas evolution as observed by Blackwood and Bowden.[5] The latter reaction proceeds until all the hydrogen sulphide is used up and then nitrogen dioxide appears and reacts with sulphur to produce nitrogen and sulphur dioxide.

$$2NO_2 + 2S \longrightarrow 2SO_2 + N_2$$

The sulphur dioxide then reacts with potassium nitrate to give potassium sulphate

$$2KNO_3 + SO_2 \longrightarrow K_2SO_4 + 2NO_2$$

The latter reaction is strongly exothermic and produces the heat necessary for continued decomposition leading finally to the explosion of the powder in which the principal reactions are the oxidation of carbon and sulphur by the potassium nitrate.

Hofmann [11] as well as Blackwood and Bowden [5] have considered the difference between normal gunpowder and sulphurless gunpowder which is slower in speed and less readily ignited than the normal powder. From the results it appears that sulphur reduces the ignition point of the powder and sulphur-free powders are more difficult to ignite because the latent heat of fusion of the potassium nitrate must first be supplied.

So far as practical application is concerned it should be noted that normal gunpowder is not only more readily ignited but is accompanied by a considerably higher energy yield per unit weight than sulphurless powder. Normal gunpowder has a calorimetric value of about 740 cal./gm. whereas sulphurless has 670 cal./gm. (see p. 20). This greater heat of the reaction accounts for the fact that the normal gunpowder is faster than sulphurless. Sulphurless gunpowder is normally only used in applications where the presence of sulphur dioxide and other sulphur compounds are likely to produce corrosion or other ill-effects.

APPLICATIONS OF GUNPOWDER

During its long life gunpowder has been used for many applications, more in fact than any other explosive. The main uses to which it has been, and is applied, are as a propellant, a blasting explosive and a delay ignition agent.

Gunpowder was probably used originally by the Chinese as an incendiary material for warfare, and it was not until the turn of the fourteenth century that its use as a propellant for guns was established. From that time it was the only propellant in use in artillery until 1884 when cordite was introduced as the British Service powder. The performance of gunpowder in ordnance was investigated very fully by Noble and Abel in their historical researches to which reference has already been made.[6, 7, 12] In 1861 Rodman [13] invented perforated pressed gunpowder and prismatic powder which may be regarded as the earlier exponents of the geometrical forms used in modern colloidal powders.

Although gunpowder has been used for a very long time as a propelling charge for rockets it is a poor performer because of its low specific impulse*, 40–80 seconds, compared with 200 seconds for modern rocket compositions.

As a blasting explosive gunpowder was first used in military land mines early in the fifteenth century. Its application in industrial blasting was described in a historical paper communicated to the Royal Society in 1665 entitled " A Way to Break Easily and Speedily the Hardest Rocks ".[14] Gunpowder was used to demolish buildings damaged in the Great Fire of London until the public complained and its use was stopped.[15]

The first recorded instance of its use in other engineering works was in 1696 when it was utilised to widen a road in Switzerland. From that time it was applied in increasing amounts in all sorts of blasting operations until the end of the nineteenth century when it was gradually displaced by dynamite and other high explosives. Nevertheless, substantial quantities are still used where a relatively " gentle " type of blasting or breaking action is required.

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* For definition of specific impulse, see p. 95.

One of the greatest difficulties with blackpowder as a blasting charge was to ensure its proper ignition. The method of blasting is to bore a cylindrical hole in the coal or rock to be blasted, introduce the explosive charge and then stem or close up the hole with a resistant tamping like sand or sand/clay. If this is not done the high pressure gases from the explosion of the blackpowder will simply blow out of the shothole and little or no work on the coal or rock will be done. The difficulty is to ignite the charge through the stemming and allow sufficient time for the shotfirer to retire to a safe place. Various methods, such as straws filled with gunpowder and touch paper, were used, but it was not until William Bickford invented safety fuse in 1831 that a really safe and reliable method of ignition became available. At a much later date electric ignition was introduced and is still utilised to some small extent. In this method a blackpowder electric fuse is used comprising a stout paper tube of about ¼ in. diameter, sealed at one end and filled with 5 grains of a fine gunpowder. The other end of the tube has sealed into it an electric fusehead with electric leading wires (see Chapter 4). The electric powder fuse is ignited by passing a current through the leading wires from a battery or " exploder " and this sets off the main blackpowder charge into which the fuse is inserted.

It is in its application to safety fuse and other delay ignition systems that blackpowder probably has no equal and its success in this field is due to two properties it possesses, namely, it is capable of burning regularly in the form of a compressed pellet or a thin-sheathed continuous train and it is capable of igniting other deflagrating compositions, such as cordite, etc.

Probably about 60 per cent. or more of the blackpowder manufactured to-day is used in safety fuse or ignition systems.

These properties are used in a great many delay systems such as the time rings in shell fuses and the delays in aircraft bombs. In these types of delay the powder has to be modified in order to obtain the very fast or very slow speeds required. Blackpowder is also employed in guns as an igniter for the very material which replaced it as a propellant. One of the advantages of blackpowder in this application is the fact that it burns more rapidly than cordite at low pressures and therefore it pressurises the system thus enabling the cordite to burn more efficiently.

The most important application of blackpowder in a delay ignition system, however, is in safety fuse. Safety fuse consists of a train of blackpowder around which are entwined several strands of jute fibre. The " semi-fuse " so formed is then covered with one or more bitumen varnishes and other waterproofing media such as gutta-percha and plastics to produce a fuse which will stand up to severe weather conditions and still be capable of burning continuously along its length. By using powders of different compositions it is possible to vary the burning speed of the finished fuse to meet various requirements. Such fuse is used in igniting blackpowder charges and, in conjunction with detonators, high explosives, and this application has grown to such an extent that about 50 per cent. of the blackpowder produced in this country is utilised in safety fuse manufacture.

Among the many other miscellaneous uses of blackpowder we may also mention saluting charges, spotting charges for aircraft bombs and base charges in shrapnel shells.

Another interesting application of gunpowder which is worthy of recording was its use to prove alcohol. In this test alcohol was poured upon a small heap of gunpowder or " proof powder " and a light was then applied. If the mixture burnt with explosion it was overproof, if it did not burn, or with difficulty, there was too much water in the alcohol and it was underproof, and if it burnt with " slight " explosion it was proof spirit (containing about 49 per cent. alcohol by weight).[16]

PYROTECHNICS

FIREWORKS

A discussion on gunpowder would not be complete without a brief reference to fireworks which were used for military and recreational purposes long before gunpowder was known. Philostratus described the resistance of some villagers to Alexander the Great in 326 B.C. The General's Indian campaign was hindered by " lightning and thunder " which Brock [17] considers to have been " Greek Fire ". Pyrotechnics spent its youth in the East, but came to Europe sometime during the fourth century A.D. Later, it became inextricably bound up with the production of gunpowder, and books on the subject dwelt on the military applications of the art.[18]

Fireworks became part and parcel of any celebration in spite of restrictions by an Order in Council in 1685. In 1860, the Gunpowder Act legalised them and laid down rules for their manufacture. This Act was amplified by the Explosives Act of 1875.

The commonest ingredient of fireworks mixtures is mealed powder, which is ungranulated gunpowder; variations on the theme are obtained by mixing the meal with charcoal, saltpetre, and sulphur in various proportions, and colours are obtained from other additions. The added charcoal is roughly ground when a good spark trail is required.

Coloured fire is obtained by using chemicals in which the metal gives the appropriate flame test of simple analytical chemistry. A few are given in Table 4.

When coloured fireworks were first produced the only way to raise the temperature of combustion sufficiently to volatilise these metallic salts was to incorporate the appropriate metal chlorate into the mixture. Such mixtures are very sensitive to friction when sulphur is present, and because of many accidents, sulphur-chlorate mixtures were prohibited by an Order in Council in 1894. For similar reasons, the sulphides of antimony, arsenic and copper, and elementary phosphorus are not mixed with chlorates.

Of the two oldest forms of fireworks, rockets and crackers, the former are the most important. The case is usually made of cardboard or rolled paper. A conical former is inserted at the vent end and the fuel then packed round it and up to about one and a half times the bore of the tube from the closed end. A clay plug is then inserted and a piece of touch-paper is pushed through a hole in the middle of the plug. The head of the rocket is then filled with the same, or a different composition, and the end is sealed. The fuel is often mealed powder, sulphur, charcoal and saltpetre, and the total proportions of the last three are normally 9–16 per cent., 16–35 per cent. and 57–58 per cent. respectively.[19]

TABLE 4

METAL INGREDIENTS FOR COLOURED FIRES

Colour	Salt Required
Yellow . . .	Sodium
Red . . .	Strontium
Blue . . .	Copper or lead
Green . . .	Copper or barium

Crackers are made by filling paper cases with gunpowder and then rolling them flat. The flattened cases are then folded " concertina-wise " and tied together. Fountains are derived from the rocket by mixing in metal filings, but if magnesium or aluminium powders are used very intense white light is produced.

Roman candles and their spiral relations, Catherine-wheels, are plain paper tubes filled with rocket-like mixtures. Farmer [20] gives four suitable formulæ, shown in Table 5.

TABLE 5

COMPOSITIONS FOR ROMAN CANDLES AND CATHERINE-WHEELS

Ingredient	I	II	III	IV
Sulphur . . .	3	2	1	4
Charcoal . . .	1	3	2	1
Saltpetre . . .	4	2	4	5
Mealed Powder . .	5	8	3	4

The stars which appear when a rocket explodes are compressed pills of chlorate mixtures combined with mealed powder to make ignition easier, and bound together with shellac. These pills are placed in the head of the rocket or with the ordinary mixture in Roman candles. Again, aluminium or magnesium powders give very bright stars.

Whistling fireworks used to be popular. They are usually small thick cases which are filled with either potassium picrate and saltpetre, or potassium chlorate and gallic acid in the proportions 3 : 1.[21]

MILITARY PYROTECHNICS

Pyrotechnics have been applied to military arts from the earliest times for incendiary purposes, as rockets and in recent times for coloured signal lights, smoke screens and a wide variety of uses. Military pyrotechnics up to the First World War are dealt with exhaustively by Faber in an official publication of the U.S. Government.[22] In his first volume he describes the history and development of pyrotechnics from the earliest times, in Volume 2 he deals with the manufacture of pyrotechnics, and Volume 3 comprises a study of the chemicals used in their manufacture.

Compositions for military pyrotechnics are similar to those for civil use, but the requirements are wider and the specifications very stringent. They are prepared by mixing the finely divided ingredients either dry or wet and are usually consolidated in cylindrical cases of paper or metal. In the case of smoke and photoflash compositions, they are loaded as loose powders. A short description of compositions used in various applications is contained in Ref. 23. They comprise basally mixtures of oxidising agents and fuels with additives designed to give special effects or properties, for example, binders, colour intensifiers, and the like.

Rockets have been used for military purposes as incendiaries, and with solid iron and high-explosive warheads as alternatives to firearm propelled projectiles. Signal rockets containing one or more coloured stars in their heads are frequently used.

From rocket star signals it is a short step to Very lights which are fired from a pistol and produce single stars of green or red colour.

Flares are utilised for numerous purposes. One type of flare is made by placing an aluminium powder/barium nitrate star in the head of a rocket and equipping it with a parachute so that it falls to the ground slowly. Flares are also used by aircraft for illuminating enemy targets and as a landing aid in rain or fog, and at night.

Smoke bombs were developed in the First World War and have been extensively used since. Some were filled with mixtures such as saltpetre, sulphur, borax, pitch and black lead, and often contained volatile dye additions to produce coloured smokes for signalling. For the production of dense black smoke, hexachlorethane is widely used as a source of free carbon in conjunction with a reducing agent. Such a composition, for example, is made by mixing hexachlorethane, aluminium powder and zinc oxide.

Tracer ammunition is produced in large quantities both for small arms and for artillery. The purpose is to see the trajectory and assist in the direction of fire. In the rifle tracer bullet, for example, the rear of the bullet has a cylindrical cavity bored in it, into which is loaded a tracer and igniter composition. More complicated tracer elements are designed for shell.

CIVIL APPLICATIONS

The saving of life must be the most satisfying use of any discovery or invention and, in this cause, pyrotechnics have been remarkably successful. In 1808 Henry Trengrouse adapted a large rocket to carry a line from shore to ship, or *vice versa*, and to-day the Schermuly apparatus is basically the same. The steel-cased rocket is fired from a large pistol to give greater range and aiming accuracy. It is estimated that 20,000 lives were saved by this method alone up to 1949.[21]

Railway fog signals fired by percussion caps set off by locomotive wheels are well-known.

REFERENCES

1. Guttman, Oscar. *Monumenta Pulveris Pyrii.* (Artisto Press, London, 1906.)
2. A General Account of the Manufacture and History of Gunpowder will be found in *The Manufacture of Explosives,* Guttman, Oscar. (Whittaker & Co., London, 1895.)
3. Douillet, A. *Mem. Poud.* (1955), **37,** 167.
   Fenning, R. W. Aeronautical Research Committee Report No. 902 (H.M.S.O., London, 1924) and Report No. 998 (H.M.S.O., London, 1926).
4. Vieille, P. *Mem. Poud.* (1893), **6,** 256.
5. Blackwood, J. D., and Bowden, F. P. *Proc. Roy. Soc.*, Series A (1952), **213,** 285.
6. Noble, A., and Abel, F. A. *Phil. Trans.* (1875), **165,** 49.
7. Noble, A., and Abel, F. A. *Phil. Trans.* (1880), **171,** 203.
8. Taylor, J., and Hall, C. R. L. *J. Phys. Chem.* (1947), **51,** 593.
9. Bunsen, and Schischkoff. *Ann. Phys., Lpz.* (1857), **102,** 321.
   Linck, J. *Liebig's Ann.* (1859), **109,** 55.
   Karolyi, L. von. *Phil. Mag.*, Series 4 (1863), **26,** 266.
   See also Refs. 6, 7 and 10.
10. Débus, H., *Liebigs Ann.* (1882), **212,** 257 and **213,** 15; *Phil. Trans.* (1882), **173,** 525.
11. Hofmann, K. A., S. B. *Preuss. Akad. Wiss.* (Phys. & Maths. Section) (1929), **25,** 509.
12. Noble, A. *Artillery and Explosives.* (John Murray, London, 1906.)
13. Rodman, Capt. T. J. *Properties of Metals for Cannon and the Qualities of Cannon Powder.* (C. H. Crosby, Boston, 1861.)
14. Moray, Sir R. *Phil. Trans.* (1665), No. 5, 82.
15. Wren, C. *Parentalia or Memoirs of the Family of the Wrens.* (London, 1750.)
16. Tate, Francis G. G. *Alcoholometry*, p. 33. (H.M.S.O., London, 1930.)
17. Brock, A. St. H. *Pyrotechnics.* (Daniel O'Connor, London, 1922.)
18. E.g. Graceous, M. *Liber Ignium and Hostes Comburendos.* (ca. 1300.)
19. Marshall, A. *Explosives*, Vol. II. (J. and A. Churchill, London, 1917.)
20. Farmer, R. C. *The Manufacture and Uses of Explosives.* (Pitman, London, 1921.)
21. Brock, A., St. H. *A History of Fireworks.* (Harrap, London, 1949.)
22. Faber, H. B. *Military Pyrotechnics,* Vols. 1–3. (Government Printing Office, Washington, 1919.)
23. Encyclopedia of Chemical Technology, Vol. 11, p. 322.

CHAPTER 3

EXPLOSIVES

GUNPOWDER held the field until the latter half of the nineteenth century when a great advance occurred by the development of detonating explosives, like guncotton ($C_6H_7N_3O_{11}$), nitroglycerine ($C_3H_5(NO_3)_3$) and TNT ($C_7H_5N_3O_6$). Gunpowder deflagrates or burns with the oxygen contained in its composition and is relatively slow in action. The pressure which it can build up to do work, even in the best circumstances when it is closely confined, is only of the order of 40 tons per sq. in. Detonating explosives, however, when suitably initiated are tremendously fast and pressures of the order of 1,000 tons per sq. in. are realisable. The nature of the reaction in such cases is quite different from that of gunpowder, the chemical reaction being initiated and sustained by a mechanical shock wave which passes at very high speed through the explosive. The velocity of this shock wave, which is akin to a sound wave, is extremely high, in some cases 9,000 metres per second. Combustion reactions produce relatively little damage to nearby objects other than by burning or scorching. On the other hand, the shock wave which is set up in a detonating explosive is capable of causing considerable damage even when the explosive is unconfined.

The difference in effect between gunpowder and a detonating explosive can be illustrated by firing charges of these explosives on ¼ in. thick steel plates. The results of such an experiment are shown in the photograph (Plate 1). It will be seen that the plate on which the gunpowder has been fired has suffered no damage at all while the second plate on which a charge of blasting gelatine was fired has a hole punched through, the metal is splayed out at the back, and most of the steel removed is recovered almost entire in the dished disc.

Recent years have seen a great amount of investigation on the theory of detonation in condensed explosives and it has now been placed on a quantitative basis by the development of the hydrodynamic theory of detonation, thereby enabling the velocity of detonation, detonation pressure and the other detonation parameters to be calculated.[1]

Detonating explosives are widely used both for civil and military purposes. They are vital to the production of coal, limestone and other minerals, and have been one of the greatest boons to man in cutting out a tremendous amount of human sweat and toil.

Gunpowder is still used for blasting, where a " gentler " action than that given by high explosives is required, such as in slate quarrying.

The use of explosives for civil purposes has not only diminished the time required for many civil engineering works, but has also enabled man to undertake projects which were previously considered impossible. For example, in the old days of pick-axe, hammer and wedge, it took 150 years to drive a tunnel five miles long in the Harz Mountains. By modern methods using explosives this could readily be done in two or three years.

An interesting and forceful example of the saving in time and labour can be obtained from the Glenmoriston Hydroelectric Scheme. One of the tunnels in this scheme was just over three miles long and took 105 men exactly eleven months to complete. In the first century A.D. a tunnel was driven to drain Lake Fucino. This tunnel was just over three miles long, but it took eleven years to complete and 30,000 labourers were employed to dig it.

Very few people realise the extent to which they are indebted to explosives in their everyday life. Our roads are built with road-metal blasted from quarries; railway cuttings are excavated with the help of explosives; the hydroelectric schemes have been made possible only by the use of explosives for driving tunnels and for blasting the foundations for dams. The development of the electrical industry was largely dependent on large supplies of copper being made available—without explosives it would not have been possible to blast out the enormous quantities of copper ore required.

The oil industry uses large amounts of explosive, both for prospecting for new oil fields and for increasing the yield in existing oil wells.

In agriculture, explosives are used for removing tree stumps, for ditching in wet marshy ground and for breaking up sub-soil.

Chimneys, old buildings, disused bridges, etc., are readily and safely demolished using explosives—and there is a host of other examples such as plaster shooting and " shaped " or " coned " charges for attacking concrete, armour plate or piercing oil well casing.[1]

By far the greatest use of explosives in Britain, however, is for the winning of coal.

The great industrialisation which occurred in Great Britain during last century was founded on coal and the rapidly increasing quantities required for industry created an urgent need for blasting explosives of increased safety. Gunpowder never provided any real safety in coal mines where it was used to blast the coal, because methane/air mixtures, which occur in fiery mines, are readily ignited by the flame from gunpowder. With the advent of detonating explosives, chemists had a wonderful new opportunity and were able to develop explosives containing cooling materials which can, in fact, be fired into methane/air mixtures or even fired when suspended directly in such mixtures without causing ignitions, provided the charges are restricted in size. These discoveries have brought about an important advance in safety in coal mining and constitute one of the most important developments in the present century.

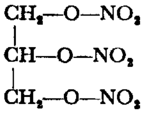
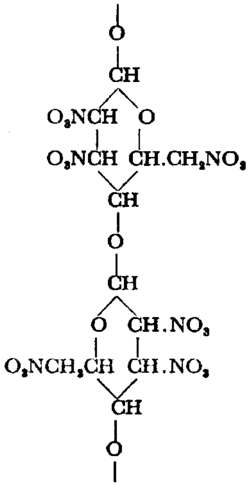
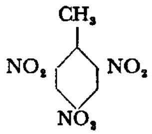
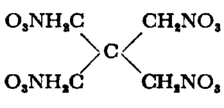
CATEGORIES OF EXPLOSIVES

Explosives are conveniently divided into two main categories, the high explosive or detonating explosive, and the low explosive or non-detonating explosive which is used as a propellant. As we have seen, the fundamental process of detonation is quite different from that of combustion though many explosives can be made to enter into detonation or combustion according to the means of initiation.

High explosives are normally initiated by a blow from a detonator which is the only practical method of providing a shock of sufficient intensity to initiate the severe processes of detonation. Such a blow is provided as a rule by what are known as initiating explosives or primary explosives. These are a special category of detonating explosive which, when ignited by a flame or by friction, pass extremely rapidly from the combustion phase to the detonation phase. This sequence of build-up to full detonation of a detonating charge is extremely important and it was not until the sequence could be carried out in a reliable manner and with certainty that the era of modern commercial blasting explosives began. It was the discoveries of Alfred Nobel which brought this about. Nobel was concerned with the utilisation of the powerful and dangerous nitroglycerine, which chemically is the trinitrate of glycerine. It is a liquid of density 1·6 gm./cm^3. It is difficult to use it in practice in the liquid form and indeed after many accidents in its transport and use, the use of the liquid itself was prohibited by law in the United Kingdom. Nobel's researches were aimed not only at finding means reliably of initiating nitroglycerine, but also at putting it into a form more suitable for practical application. This he achieved in two ways, the one by absorbing the explosive liquid in kieselguhr (70 per cent. nitroglycerine absorbed in 30 per cent. kieselguhr), and the other by "gelatinising" or making a stiff permanent jelly of nitroglycerine by mixing it with 8 per cent. of

TABLE 6

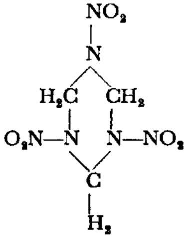
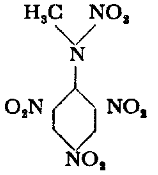
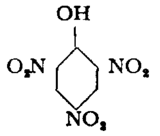
A SELECTION OF SINGLE-SUBSTANCE EXPLOSIVES*

Name	Formula	Structural Formula	Uses
Nitroglycerine (NG)	$C_3H_5N_3O_9$	 $\begin{array}{l} CH_2\text{—}O\text{—}NO_2 \\ \vert \\ CH\text{—}O\text{—}NO_2 \\ \vert \\ CH_2\text{—}O\text{—}NO_2 \end{array}$	Ingredient of civil and military explosives. Not used alone.
Nitrocellulose (NC)	$(C_6H_7N_3O_{11})_n$†		Ingredient of civil and military explosives. May be used as a primer or military explosive.
Trinitrotoluene (TNT)	$C_7H_5N_3O_6$		Ingredient of civil and military explosives. Used alone for military purposes (shell filling, etc.)
Pentaerythritol tetranitrate (PETN)	$C_5H_8N_4O_{12}$		Used alone or as an ingredient of military high ex-explosives. Filling for detonating fuse.

*† See page 33.

TABLE 6

A SELECTION OF SINGLE-SUBSTANCE EXPLOSIVES—*Continued.*

Name	Formula	Structural Formula	Uses
Cyclotrimethylene trinitramine (CTMTN or RDX)	$C_3H_6N_6O_6$		Military high explosive. May be used as ingredient of civil explosives.
Trinitrophenylmethyl nitramine (Tetryl)	$C_7H_5O_8N_5$		Used as a primer for high explosives.
Picric acid	$C_6H_3N_3O_7$		Military high explosive—now obsolete.

* Extracted from *Detonation in Condensed Explosives* by J. Taylor, Table, 1, p. 12.

† The formula given shows complete nitration. In nitrocellulose used for explosives the nitration is incomplete and the nitrate groups, which are not less in number than three-quarters of those shown in the formula, are distributed at random.

nitrocotton.[2] The first explosive was called dynamite and the second blasting gelatine.

Dynamite is practically never made nowadays. It is a very sensitive explosive and has to be mixed in small quantities by hand methods little suited to modern industrial methods and it has been superseded. Blasting gelatine was, and still is, the most powerful commercial explosive and is one of great merit. It is, however, expensive and is too powerful for all except the most severe tasks of blasting in very hard rock, and it has been largely displaced by cheaper and slower compositions more appropriate to the normal conditions of use. Most modern explosives are composite mixtures designed for special purposes as, for example, for safety in fiery mines or for seismographic prospecting.

High explosives have been dealt with adequately in other publications[3] and it is not necessary to deal with them in detail here, but a short discussion on initiating explosives will be given in Chapter 4.

Table 6 gives a selection of the most important single substance explosives which have emerged during the last century.

Propellants of the nitrocellulose and cordite type are classed as explosives, but our considerations at the moment are concerned with detonating explosives, and propellants will be dealt with in detail in Chapter 5.

The energy bases of modern commercial explosives merit some special consideration.

COMMERCIAL BLASTING EXPLOSIVES

In British commercial blasting explosives a process of development and simplification has led to the use of cheap energy-producing bases sensitised with a true explosive like nitroglycerine or TNT. In the compositions produced with nitroglycerine early in this century an energy base of potassium nitrate was used, which, as it is oxygen-positive, requires fuel to consume the extra oxygen in its molecule. Sawdust or woodmeal were favoured as such fuels. The stoichiometric formulation of the reaction can be regarded as:

$$24KNO_3+5C_6H_{10}O_5 \longrightarrow 12K_2CO_3+12N_2+18CO_2+25H_2O \quad (\mathbf{3}.1)$$

Table 1 gives the thermochemical data. The reaction itself is extremely slow and would be useless for an explosive, but when 15 per cent. or more of nitroglycerine is added to the mixture it detonates well.

Later on a similar base using the cheaper sodium nitrate, $NaNO_3$, together with the appropriate amount of fuel was employed, namely:

$$24NaNO_3+5C_6H_{10}O_5 \rightarrow 12Na_2CO_3+12N_2+18CO_2+25H_2O \quad (\mathbf{3}.2)$$

Sodium nitrate has the disadvantage that it is more hygroscopic than potassium nitrate. Consequently, explosives made with it require to be packed in well moisture-proofed cartridges.

The energy bases of (**3**.1) and (**3**.2) both have the defect that they produce large amounts of solid residues without adding to their capacity for doing work. Their usage is decreasing and the principal energy-gas producing base used nowadays is ammonium nitrate, which is made in very large quantities synthetically and is consequently cheap and readily available. It provides greater power and gas volume. Since it is also oxygen-positive, oxygen balance is usually achieved by the addition of cellulose (woodmeal), or for TNT explosives, TNT itself, since TNT is oxygen-negative.

The two main energy base reactions for modern blasting explosives are thus:

$$12NH_4NO_3 + C_6H_{10}O_5 \longrightarrow 12N_2 + 29H_2O + 6CO_2 \qquad (3.3)$$

and

$$21NH_4NO_3 + 2C_7H_5(NO_2)_3 \longrightarrow 24N_2 + 47H_2O + 14CO_2 \qquad (3.4)$$

The reactions are highly exothermic and produce large yields of non-toxic gases. These reactions are therefore ideally suited for use as gas producers in blasting explosives intended for underground work. Table 1 gives the thermochemical data for (3.3).

The reaction of the energy-producing base is forced through by the explosion of the nitroglycerine or TNT, whichever is used as sensitiser.

STABILITY OF EXPLOSIVES

We have touched on the subject of the stability of explosives in Chapter 1. Explosives in their normal condition are in a metastable state. Their free energy is considerably higher than that of their decomposition products, and the fact that they are effectively stable at ordinary temperatures depends on the high energy of activation of the possible decomposition reactions. Nevertheless, if the temperature is raised, and especially if suitable catalysts are added, the rate of thermal decomposition may become serious. In general, it is possible to write down several modes of decomposition, each of which results in a decrease in free energy, and which are therefore all potentially possible. Some of them are autocatalytic, in that they are catalysed by reaction products, usually nitric acid. Such autocatalytic reactions are especially dangerous, since they automatically accelerate until large quantities of gas and heat are evolved, leading to " fume-off ".

CHEMISTRY AND REACTION KINETICS OF THERMAL DECOMPOSITION

The chemistry and kinetics of thermal decomposition of explosives are difficult to study because of the complexity of the products. The particular case of nitroglycerine has been examined in many investigations.

The over-all decomposition may be written as:

$$4C_3H_5(ONO_2)_3 \longrightarrow 12CO_2+10H_2O+6N_2+O_2 \qquad (3.5)$$

Such a complete disruption of a molecule is unlikely to occur in an ordinary chemical reaction except as the result of a large number of individual stages. The mode of decomposition may well be operative on detonation, but it is unlikely to occur thermally on account of the large number of bonds which have to be broken simultaneously. The thermal decomposition of nitroglycerine has been studied by a considerable number of investigators, but the results are inconclusive and it will suffice here to give a few references to the original works.[4, 5, 6, 7, 8, 9] Nitrocotton, which is also a nitric ester, probably decomposes in a manner analogous to nitroglycerine. The nitrogen content of the nitrocotton gradually falls during storage. Moreover, probably on account of the oxidative reactions, the chains of the nitrocotton structure are gradually broken down, so that viscosity of the nitrocotton also falls. Such effects are marked only after considerable decomposition has occurred. The thermal decomposition of nitrocellulose is summarised in a recent book by Miles.[10]

Nitrobodies, such as TNT, fall in a different class since they are not nitric esters. They are not, as is nitroglycerine, subject to acid hydrolysis and are therefore stable under conditions of low *p*H. For this reason nitrobodies tend to have good thermal stability.

Recent work has shown that no simple scheme can confidently be put forward to describe the kinetics of explosive decomposition. No comprehensive analysis has been done on higher molecular weight nitrates, but recent work on nitrocellulose raises doubts about previous deductions without substituting satisfactory alternatives.[11]

In spite of the fact that the chemical reactions involved are unknown, it is possible to measure the rate of decomposition as a function of temperature. As an indication of reaction rate, use is made of loss of weight, evolution of gas (total, or of specific compounds such as nitrogen dioxide), or changes in acidity or composition. Calorimetric methods have also been used.

Thus Robertson [9] studied the thermal decomposition of nitroglycerine by passing carbon dioxide over the heated liquid and determining the rate of evolution of nitrogen dioxide by spectroscopic means. Robertson has also published figures for rates of reaction of a number of explosives.[12]

According to Roginsky[13] the decomposition of nitroglycerine follows the simple unimolecular law:

$$\frac{dx}{dt} = K(a - x) \text{ where } K = Be^{-E/RT} \qquad (3.6)$$

where x is the amount of substance decomposed, and a, B and E are constants. Semenoff[14] has collected values for E and B for a number of explosives (see Table 7).

TABLE 7

SEMENOFF'S VALUES FOR E AND B FOR THE THERMAL DECOMPOSITION RELATION (3.6) FOR VARIOUS EXPLOSIVES

Explosive	Temperature Range °C	E, cals.	Log$_{10}B$
Nitroglycerine . . .	90–125	42·6	18·0
Nitroglycerine . . .	125–150	45·0	19·2
Nitroglycerine . . .	150–190	50·0	23·5
Nitrocellulose . . .	90–135	49·0	21·0
Nitrocellulose . . .	140–155	48·0	20·0
Nitrocellulose . . .	155–175	56·0	24·0
Tetryl, liquid . . .		60·0	27·5
Tetryl, liquid . . .		55·0	24·5
Tetryl, solid . . .		52·0	22·5
Picric acid . . .		58·6	22·5
Trinitrotoluene . .		53·0	19·0

The application of Semenoff's theory to solid explosives would appear to be doubtful; the considerable difficulties in the way of applying chain reaction theory to explosives are clear from a discussion by Macdonald.[15]

STABILISERS

It has been suggested that the most important decomposition reaction of nitric esters is a hydrolysis catalysed by nitric acid, itself produced in the reaction. To prevent the reaction from being autocatalytic and to reduce the initial rate of decomposition, it is customary to add a stabiliser, which will maintain a suitable neutrality by combining preferentially with the nitric acid. A strong base cannot be used for this purpose, since it would itself catalyse the decomposition reactions.

For gelignite blasting explosives, which contain soluble salts and a certain amount of moisture, direct *p*H control is possible by addition, for example, of diammonium phosphate,[15] which gives a buffer mixture of diammonium and monoammonium phosphates. Such additions are effective only in the presence of moisture, since *p*H control depends on solution of the buffer salts.

It is not usual to add stabilisers to explosives based on nitrobodies, on account of the higher intrinsic stability of such compounds.

THE LAW IN RELATION TO EXPLOSIVES

The manufacture, transport and use of explosives is regulated by law. The Explosives Act of 1875 lays down regulations for the manufacture, storage, transport and sale of explosives. This is supplemented by various subsequent Orders in Council and Orders of Secretary of State. The provisions of the Act are dealt with fully by Thomson[16] and Watts[17] and a recent Government publication deals fully with carriage by sea.[18]

A recent article by Weston and Wardle deals comprehensively with the safety aspects of the Explosives Industry.[19] It describes the effects of explosions and the consequent necessity of having adequate safety distances between buildings. (These are laid down by law.) The Table of Safety Distances is given and the safety principles involved in the explosive manufacturing operations and the organisation of staff to ensure that these are carried out are described.

The use of explosives in coal mines is controlled by Section 61 of the 1911 Act under which Coal Mines Orders have been made from time to time. These Orders have recently been reviewed and revised.[20]

THE INITIATION OF EXPLOSION

We have seen that propellent or deflagrating explosives are initiated by thermal means such as a flame and that high explosives are initiated by a blow, in practice provided by a detonator which contains a special type of explosive known as an initiating explosive. There are many means of bringing about explosion and considerable advances have been made in recent years in the understanding of the underlying processes. Bowden and his school have studied the initiation and growth of explosion in liquids and solids[21] and made a number of important contributions to the subject. Especially important is the hypothesis of initiation by hot spots produced by adiabatic compression of small air pockets.

Since these researches have been adequately written up it is not proposed to deal with them here, but it is deemed useful to consider shortly various practical initiating explosives and their application to detonators and this is done in the following chapter.

REFERENCES

1. Taylor, J. *Detonation in Condensed Explosives.* (Oxford University Press, 1952.)
2. " Alfred Nobel ", Dynamite King, Architect of Peace. Herta E. Pauli. p. 90, *History of Nobel's Explosive Company,* 1871–1926, London, 1938.
3. The following is a list of books on Explosives and Propellants to which the reader is referred for fuller information.
   Read, J. *Explosives.* (Penguin Books Ltd., London, 1942.)
   Marshall, A. *Explosives, Their History, Manufacture, Properties and Tests.* (J. and A. Churchill, London, 1917–32.)
   Davis, T. L. *The Chemistry of Powder and Explosives.* (John Wiley & Sons, New York, 1943.)
   Muraour, H. *Poudres et Explosifs.* (Presses Universitaires de France, 1947.)
   Farmer, R. C. *Manufacture and Uses of Explosives.* (Pitman, 1921.)
   Taylor, J. *Detonation in Condensed Explosives.* (Oxford University Press, 1952.)
   Miles, F. D. *Cellulose Nitrate.* (Published for Imperial Chemical Industries by Oliver and Boyd, 1955.)
   Taylor, J., and Gay, P. F. *British Coal Mining Explosives.* (Newnes, 1958.)
4. Berthelot, M. *C.R. Acad. Sci.*, Paris (1900), **131,** 519.
5. Klason, P., and Carlson, T. *Ber. Dtsch. Chem. Ges.* 1906), **39,** 2752.
6. Lowry, T. M., Browning, K. C., and Farmery, J. W. *J. Chem. Soc.* (1920), **117,** 552.
7. Farmer, R. C. *J. Chem. Soc.* (1920), **117,** 806.
8. Muraour, H. *Chim. et Industr.* (1928), **20,** 610.
9. Robertson, R. *J. Chem. Soc.* (1909), **95,** 1241.
10. Miles, F. D. *Cellulose Nitrate,* Chapter 7. (Published for Imperial Chemical Industries by Oliver and Boyd, 1955.)
11. Gelernter, G., Browning, L. C., Harris, S. R., and Mason, C. G. *J. Phys. Chem.*, **60,** 1260 (1956).
    Phillips, R. W., Orlick, C. A., and Steinberger, R. *J. Phys. Chem.*, (1956) **50,** 1034.
    Wolfrom, M. L., *et al.* (10 authors). *J.A.C.S.*, (1955) **77,** 6573.
    Wolfrom, M. L., *et al.* *J.A.C.S.*, (1956) **78,** 4695.
12. Robertson, R. *J. Chem. Soc.* (1921), **119,** 1.
13. Roginsky, S. *Phys. Z. Sowjet* (1932), **1,** 640.
14. Semenoff, N. *Chemical Kinetics and Chain Reactions.* (Oxford University Press, 1935.)
15. Macdonald, J. Y. *Trans. Faraday Soc.* (1938), **34,** 977.
16. Thomson, J. H. *Guide to the Explosives Act,* 1875. (H.M.S.O., 1941.)
17. Watts, H. E. *The Law Relating to Explosives.* (Charles Griffen & Co. Ltd., London.)
18. *Rules for the Packing, Stowage and Labelling of Explosives for Carriage by Sea.* H.M. Stationery Office, 1957.)
19. Weston, B. A., and Wardle, T. *Chem. and Ind.* (1958), 239.
20. Coal Mines (Explosives) Order, 1951, No. 1675. (H.M.S.O., 1951.)
21. Bowden, F. P., and Yoffe, A. D. *The Initiation and Growth of Explosion in Liquids and Solids.* (Cambridge University Press, 1952.)

CHAPTER 4

INITIATING EXPLOSIVES

SOME materials on being heated or subjected to shock enter the detonation régime directly and when used in relatively small quantity are capable of communicating their detonation to high explosives; those substances are called initiating explosives. This phenomenon of initiation was discovered by Alfred Nobel and its discovery forms the prelude to the development of modern explosives. The embodiment of the idea in the detonator is fundamental in the explosives art.

Initiating explosives are used mainly in copper or aluminium tubes termed detonators and the most important tests employed to determine the efficiency of the material are based upon this type of assembly. Thus the suitability of a substance as an initiator is related ultimately to its performance under these conditions.

The ability of an initiating explosive to function correctly in a detonator is, however, only one of a number of requirements that have to be satisfied. The substance must be readily and conveniently made so as to be available at a reasonable price. It must not be too sensitive to be handled in quantity during manufacture and use. Its physical form has to be favourable for multiple loading into detonators, that is, it should exhibit free-flowing behaviour. Compatibility with the metal of the containing tube is essential, and also with the materials composing the ignition system. Further, the stability of the substance should be so high that it retains its efficiency almost indefinitely in normal storage and for long periods under adverse conditions of temperature and humidity.

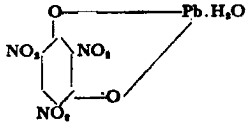
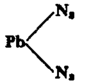
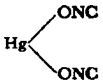
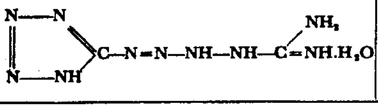
A very large number of substances has been examined as initiating explosives, but only very few fulfil the stringent requirements enumerated above. It seems as well, therefore, to deal with the most important initiators and incidentally to review briefly the types of materials that have been examined as initiating explosives. In Table 8 the main initiating explosives and their formulæ and uses are displayed.

MERCURY FULMINATE

Mercury fulminate has the historic distinction of being the first

TABLE 8

THE PRINCIPAL INITIATING EXPLOSIVES

Lead trinitro-resorcinate hydrate (Lead styphnate)	$C_6H_3N_3O_9Pb$		Used to facilitate the ignition of lead azide in detonators.
Lead azide	PbN_6		Initiating explosive. Used widely as initiating charge in detonators.
Mercury fulminate	$C_2N_2O_2Hg$		Initiating explosive. Used widely as a filling for detonators in admixture with potassium chlorate.
Tetrazene	$C_2H_8ON_{10}$		Not a true initiator but used as a sensitiser in percussion compositions.

Largely from *Detonation in Condensed Explosives* by J. Taylor; Table I, Page 12.

initiating explosive to be used in a detonator, and thus constituting the original Nobel invention. At the present time, however, it is only used to a limited extent for this purpose, and has been largely superseded by other substances.

During recent years the price of mercury has fluctuated violently, and moreover in time of war the supply is likely to be uncertain. The process of manufacture is not a convenient one and does not lend itself readily to large batch production of high quality material. As a consequence, investigations were directed towards alternative initiators and finally fulminate was largely displaced by lead azide.

Investigations of the structure of mercury fulminate have been made over many years. It has been concluded that fulminic acid is the oxime of carbon monoxide and best represented as containing a divalent carbon atom.

$$C = NOH$$

Mercury fulminate $Hg(CNO)_2$ is the salt of this acid. Its specific gravity is 4·45, but the packing density in detonators is about 2·5 gm./cm.^{3} Its ignition temperature, that is the temperature at which it explodes on heating has been determined by a number of methods and some of the values obtained for the material and other initiating explosives[1] are given in Table 9. The materials were in the form of microcrystalline powders compressed into pellets of 0·02 gm. The temperature at which explosion occurred within 5 seconds was recorded.

Mercury fulminate and other initiating explosives are very sensitive to friction and blow. The percussion sensitiveness is determined by the so-called " fall-hammer " method, for example, by dropping a steel ball on to the material confined within two steel cylinders.[2]

Another essential test conducted on initiating explosives is the determination of the smallest amount necessary to cause detonation of high explosives; the result is called the minimum value. The

TABLE 9

IGNITION TEMPERATURE OF VARIOUS INITIATING EXPLOSIVES

Initiating Explosive	Ignition Temperature °C.
Mercury fulminate . .	215
Silver fulminate . . .	170
Copper fulminate . . .	205
Cadmium fulminate . .	215
Sodium fulminate . . .	215
Potassium fulminate . .	225
Thallium fulminate . .	120
Cobalt azide. . . .	148
Barium azide . . .	152
Calcium azide . . .	158
Strontium azide . . .	169
Cuprous azide . . .	174
Nickel azide	200
Manganese azide . . .	203
Lithium azide . . .	245
Mercurous azide . . .	281
Zinc azide	289
Cadmium azide . . .	291
Silver azide	297
Lead azide	327

TABLE 10

MINIMUM VALUE OF SOME INITIATING EXPLOSIVES

Initiating Explosive	Minimum Value (gm.) for Initiation of		
	Tetryl	Picric Acid	TNT
Mercury fulminate	0·29	0·30	0·36
Silver fulminate	0·02	0·05	0·095
Cadmium fulminate	0·008	0·05	0·11
Copper fulminate	0·025	0·08	0·15
Thallium fulminate	0·30	0·43	
Lead azide	0·025	0·025	0·09
Silver azide	0·02	0·035	0·07
Cadmium azide	0·01	0·02	0·04
Cuprous azide	0·025	0·045	0·095
Mercurous azide	0·045	0·075	0·145
Thallium azide	0·07	0·115	0·335

test is performed in a detonator, charged first with the high explosive (base charge or secondary initiator) such as tetryl or TNT and surmounted with the initiating explosive (primary initiator). The minimum value obtained depends on the mode of assembly and the base charge. Some results obtained for fulminate and other initiating explosives are given in Table 10.[3]

The velocity of detonation of mercury fulminate and other initiating explosives has been determined in detonators, and the values obtained for various densities are given in Table 11.[4]

Summarising the position of mercury fulminate as an initiating explosive, it may be said that it has rendered invaluable service over

TABLE 11

VELOCITY OF DETONATION OF SOME INITIATING EXPLOSIVES

Initiating Explosive	Density	Velocity of Detonation m./sec.
Mercury fulminate	2·5 3·3	3,600 4,490
Mercury fulminate/potassium chlorate (85/15)	3·1	4,550
Lead azide	3·8	4,500
Lead styphnate	2·6	4,900
Cyanuric triazide	1·15	5,545

a long period. Judged by modern standards, however, it is a relatively weak initiator and it is not sufficiently resistant to adverse storage. For these reasons it is no longer used for the assembly of detonators in the U.K.

LEAD AZIDE

The principal initiating explosive that has replaced mercury fulminate is lead azide.

The study of the methods of preparation of lead azide revealed that two types of crystal could be formed, the normal orthorhombic or alpha form, and a supersensitive monoclinic, or beta form[5], which may be spontaneously explosive in course of preparation. Later work suggests that there may not be a difference in sensitivity between the two forms after isolation.[6] It is not surprising that in the early days of the use of crystalline lead azide a number of explosions occurred and these seemed to be associated with sensitive forms of the azide. Detailed study of the lead azide reaction led to the devising of methods of precipitating the lead azide in the presence of small amounts of colloids, notably dextrine, whereby the lead azide precipitated was free from crystal facets and formed rounded particles (see Plate 2) not unduly sensitive. Such " dextrinated " lead azide is now used widely in commercial detonators.[5]

Lead azide PbN_6 is characterised by a density of 4·7 for the alpha form and 4·9 for the beta form. It is a much more brisant explosive than mercury fulminate but is relatively insensitive to ignition by flame. This disadvantage is usually overcome in practice by using mixtures with more sensitive ignition agents like lead styphnate.

Hydrazoic acid itself, as mentioned before, is a treacherous and powerful explosive and can be initiated even in dilute solution.[7] The acid and azides are also toxic.

Silver azide has also been used in some types of detonators.

It should be remarked that lead azide when stored under adverse conditions of high humidity may undergo hydrolysis yielding hydrazoic acid.[8] If the lead azide is stored in copper tubes as in the case of some detonators the liberated hydrazoic acid may react with the copper producing copper azide which is sensitive and may be dangerous. Such a danger is overcome in practice by using detonator assemblies hermetically sealed. No plain open detonators with lead azide in copper tubes are issued, such being restricted to aluminium tube type.

LEAD STYPHNATE

As mentioned previously, lead styphnate is used in conjunction with lead azide in order to sensitise the mixture to ignition by flame. It is also used as an ingredient in certain cap mixtures for rifle cartridges, etc.

Lead styphnate, that is, lead trinitroresorcinate

$$C_6H(NO_2)_3O_2Pb.H_2O$$

has a density of 3·08 gm/cm^3. The molecule of water is tenaciously held. The material is highly sensitive to friction and to electrostatic discharge and is never used alone, but in admixture with other substances usually with lead azide.

TETRAZENE

Tetrazene is not a true initiator, but has been used as an ignition agent with lead azide in the same way as lead styphnate.

Its chief use, however, is as a sensitiser in percussion compositions. The name is a shortened form of 1-guanyl-4-nitrosoaminoguanyl tetrazene which is of considerable interest chemically on account of its mode of formation and structure.[9] It has recently been shown to be a tetrazole derivative.

Tetrazene, $C_2H_8ON_{10}$, has a specific gravity of 1·65–1·70. It is very sensitive to percussion and friction, being more sensitive than most primary initiating explosives.

Its use with lead azide in explosive rivets is described in a patent.[10] The incorporation of as little as 2 per cent. results in improved performance of percussion compositions.[11]

OTHER INITIATING COMPOUNDS

We have described the initiating compounds most widely used in the U.K. Other substances, for example the aromatic diazo-compounds, have been a much favoured field of investigation in the search for fresh initiating explosives, but have been found to have various disadvantages. Dinitrodiazophenol[12] is a more powerful initiating explosive than mercury fulminate, but less powerful than lead azide.

Trinitrotriazidobenzene[13] is an initiating explosive proposed for use in a thermoplastic explosive detonator.

Cyanuric triazide is an initiating explosive which has also been much investigated,[14] whilst hexamethylenetriperoxide-diamine (H.M.T.D.) is an example of an organic peroxide, many of which have these explosive properties.[15]

Another tetrazole derivative of interest is nitrotetrazole, which is capable of serving as a primary initiator.

REACTION KINETICS

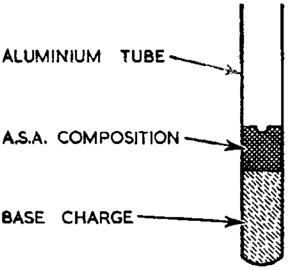
The thermal decomposition of initiating explosives has been investigated in detail, especially by Garner and his co-workers. In general, single crystals were studied, both kinetically and microscopically. A review of the subject of reaction kinetics in solids which includes initiating explosives, has been provided recently by Garner in the work *Chemistry of the Solid State.*[16] In this publication the slow and rapid decomposition of explosives are dealt with and the analysis of pressure-time curves and nucleation of the products are treated in detail.

The initiation of metal azides has recently received further attention by Gray and Waddington, Sawkill and Yoffe and Evans, who are accumulating data on which to explain sensitivity in terms of electron theory.[17]

DETONATORS

It has already been mentioned that the normal means of initiating or detonating a charge of blasting explosive is a detonator.

Detonators[18] comprise tubes either of copper or aluminium which are loaded usually with a pressed base charge of an explosive such as tetryl or PETN (see Table 6), on top of which is pressed a suitable initiating charge such as mixture of lead azide and lead styphnate (see Table 8). A diagrammatic representation of such a detonator, termed a plain detonator, is given in Fig. 1. Plain detonators are themselves initiated by means of safety fuse (see Chapter 2).



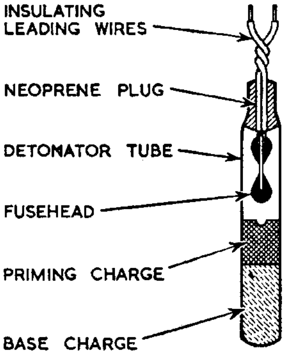


Fig. 1. (*above*) Plain detonator.
Fig. 2. (*right*) Electric detonator.

Electric detonators are also widely used for initiating blasting charges, and indeed are compulsory for use in safety light coal mines.

Electric detonators comprise the normal plain detonator into which an electric fuse with insulated leading wires has been sealed. A diagrammatic representation of an electric detonator is given in Fig. 2. It is fired by a current passed from a suitable source via its leading wires.

FUSEHEADS

The electric fuse employed to fire a detonator comprises a match-head in which a very fine nichrome wire is embedded and which on being subjected to the passage of the firing current heats up and fires the match-head composition which in turn ignites the initiating charge of the detonator. The match-head composition may be of various materials, but a commonly used one nowadays is a mixture of lead mononitroresorcinate and potassium chlorate together with a little nitrocellulose as binder. They are designed to give a hot and vigorous flame in order to ensure ignition of the detonator.[18] Fig. 3 gives a diagrammatic representation of a fusehead. The ignition characteristic of electric fuseheads has been investigated in detail by E. Jones and others.[19]

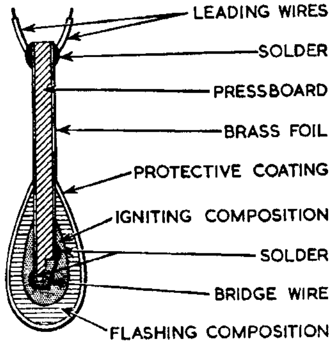


FIG. 3. Low-tension electric fusehead.

For delay detonators special "gasless" fuseheads are used (see Chapter 11).

PERCUSSION PRIMERS

One important use of initiating explosives is to provide means for igniting firearm cartridges in a reliable manner and with sufficiently short time delays to ensure repeatable and accurate ballistics.

In the case of centre fire cartridges the initiator comprises a brass cap which is loaded with a composition such that when the cap is struck by the centre pin of the firearm it will be ignited by the percussive blow.

Forsyth invented ignition of firearm charges via the percussion of fulminate in 1805 and it was adopted by the British Army in 1836.[20] It was a great advance on the old method of ignition via a fire channel in the breech of the gun, filled with gunpowder, and initiated by a flint lock. Fig. 4 illustrates a modern cap and shows the " Anvil " which is driven into the cap composition and initiates it when the firing pin hits and drives in the base. The composition must be suitably sensitive to blow and friction and ground glass is often added to achieve this. A typical example is 10 per cent. mercury fulminate, 37 per cent. potassium chlorate, 40 per cent. antimony sulphide, 13 per cent. ground glass.[21] The compositions are hazardous to mix and the operation is carried out using very small quantities. Formerly mixing was carried out using dry ingredients, but there has been a considerable change-over to wet mixing which is safer. In the case of rim-fire cartridges such as are used for ·22 rifles the composition is " spun " into the rim of the cartridge itself so that when the rim is struck by the off-centre firing pin it ignites.

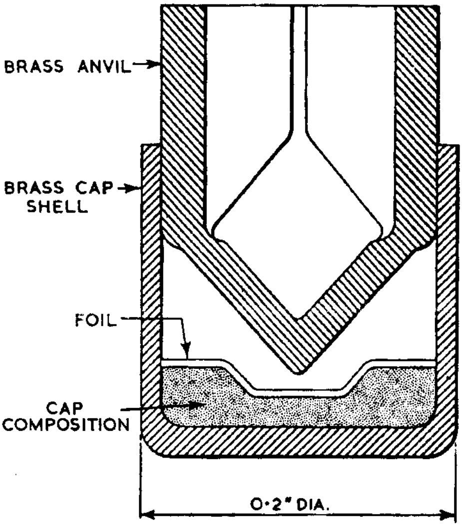


Fig. 4. Percussion cap.

Percussion primers for small arm cartridges are usually called " caps " in Britain. Whilst caps are used for most small arms cartridges, electric primers are employed for large calibre firing.

The firing of the cap if the composition contains chlorine compounds, as chlorates, which yield chlorides on reaction, may give rise to barrel corrosion in small arms or shotguns. Non-corrosive or rust-free caps containing no compounds of chlorine and yielding alkaline non-corrosive decomposition products have been devised and are now in use. An example of such a composition is 40 per cent. mercury fulminate, 25 per cent. antimony sulphide, 25 per cent. barium nitrate, 6 per cent. barium carbonate, 4 per cent. powdered glass.[21]

EXPLOSIVE RIVETS

In the fabrication of machines, such as aeroplanes and tanks, it is often required to use rivets where it is impossible for someone to " back-up " the rivet in order to form a head. In 1937, the German firm of Heinkel invented a partly hollow rivet, containing an explosive which detonated at about 130° C., in an attempt to solve this problem.[22, 23, 24] The rivet was heated and the resulting detonation of the explosive expanded the end of the rivet, giving a watertight joint. The explosive used varied, but usually consisted of mixtures of aluminium powder, tetrazene and nitromannitol.[25] These rivets were widely used during the Second World War for the construction of bombers, etc. Since the war, improved explosive rivets have been described,[26] in which the cavity extends along practically the whole length of the rivet. It is claimed that a more uniform effect is produced by this means.

REFERENCES

1. Wöhler, L., and Martin, F. *Z. Angew. Chem.* (1917), **30**, 33.
2. Marshall, A. *Explosives,* Second Ed., 423–428. (J. and A. Churchill, London, 1917.)
3. Wöhler, L., and Martin, F. *Z. ges. Schiess-u. Sprengstoffw.* (1917), **12**, 18.
4. Kast, H., and Haid, A. *Z. Angew. Chem.* (1925), **38**, 45.
5. Miles, F. D. *Phil. Trans.* Series A (1936), **235**, 125.
6. Gray, P., and Waddington, T. C. *Nature, Lond.* (1955) **176**, 653.
7. Annual Report of Inspectors of Explosives, 1927. (H.M.S.O., London, 1928.)
8. Cirulis, A. *Z. ges. Schiess-u. Sprengstoffw.* (1943), **38**, 42.
9. Stettbacher, A. *Nitrocellulose* (1941), **12**, 83.
   Hofmann, K. A., and Roth, R. *Ber. dtsch. chem. Ges.* (1910), **43**, 682.
   Patinkin, L. H., Horvitz, J. P., and Lieber, E. *J. Amer. Chem. Soc.* (1955), **77**, 562.
10. U.S. Patent 2,080,220.
11. U.S. Patent 2,009,556.
    Owens, R. D. J. Private communication.
12. Griess, P. *Proc. Roy. Soc.* (1857–9), **9**, 594.
13. Davis Tenney, L. *The Chemistry of Powders and Explosives,* Vol. 2, 436–458. (John Wiley & Sons, Inc., New York, 1943.)
14. Kast, H., and Haid, A. *Z. Angew. Chem.* (1925, **38**, 43. U.S. Bureau of Mines Report of Investigations 2513 (August 1923.)
15. Taylor, C. A., and Rinkenbach, W. H. *Army Ordnance* (1925), **5**, 463.
16. Garner, W. E. *Chemistry of the Solid State.* (Butterworth's Scientific Publications, 1955.)
17. Gray, P., and Waddington, T. C. *Proc. Roy. Soc.,* Series A (1956), **235**, 106.
    Gray, P., and Waddington, T. C. *Proc. Roy. Soc.,* Series A (1956), **235**, 481.
    Gray, P., and Waddington, T. C., *Chem. & Ind.* (1955), 1255.
    Evans, B. L., and Yoffe, A. D. *Proc. Roy. Soc.,* Series A (1957), **238**, 568.
    Sawkill, J. *Proc. Roy. Soc.,* Series A (1955), **229**, 135.
    Yoffe, A. D., Evans, B. L., and Deb, S. K. *Nature, Lond.* (1957), **180**, 294.
18. Taylor, J., and Gay, P. F. *British Coal Mining Explosives,* Chapter 7. (Newnes, 1958.)
19. Jones, E. *Proc. Roy. Soc.,* Series A (1949), **198**, 523.
    Stout, H. P., and Jones, E. Third Symposium on Combustion, Flame and Explosion Phenomena. Paper No. 35, p. 329. (The Williams & Wilkins Company, Baltimore, 1949.)
20. *Text Book of Small Arms.* (H.M.S.O., 1929.)
21. Davis Tenney, L. *The Chemistry of Powders and Explosives,* Vol. 2, p. 455 (John Wiley & Sons, Inc., New York, 1943.)
    Davis Tenney, L. *Ibid.,* p. 458.
22. U.K. Patents 467,514 and 467,515.
23. German Patent 648,842.
24. Luftfahrtforschung, Butler, K. 1938, Band 15, Lfg 1/2, 91.
25. Report on a visit to the D.A.G. Small Arms Factory at Stedeln, near Nürnberg, Combined Intelligence Objectives Sub-committee, London. (H.M.S.O.)
26. U.S. Patent 2,556,465.

CHAPTER 5

PROPELLANTS

GUNPOWDER was the only propellant for cannon and small arms until towards the end of the last century[1] when it was superseded by cordite, and was the only filling for rockets until the Second World War. Many people think that jet propulsion is a very recent invention, but that is not so. Gunpowder war rockets were used well over a century ago ; in fact, the British Fleet bombarded Boulogne in 1806 and Copenhagen in 1807 with war rockets.

Improved rockets using cordite instead of gunpowder were introduced during the Second World War.

MODERN GUN PROPELLANTS

In order that any chemical substance or composition shall be used successfully as a propellant it is obvious that it must deflagrate in a controlled, repeatable and predictable manner. The performance of modern guns, for example, in regard to accuracy is extraordinarily good and is only obtained by the use of propellent charges which behave identically in every round.

Until the end of last century gunpowder was the only propellant which gave satisfactory results in guns. Its reliability was based on meticulous arts of manufacture which had developed over many centuries. Essentially break-up and " running away " of charge in the gun was prevented by using compressed pellets of powder of carefully selected geometrical size and form and compressing the composition so hard that it was no longer porous to the penetration of the hot gases. If the pressing of the pellets is insufficient the hot gases produced from the burning charge enter the interstices between the particles of composition and produce progressive build up of reaction which can finally go out of control.

After guncotton was discovered by Schönbein in 1846 its high energy and large gas production made it potentially attractive as a gun charge. Experiments showed that even in compressed pellet form this " cottonwool " material was too dangerous for guns. Its combustion was too rapid and uncontrolled and it was liable to detonate and shatter the firearm.

Guncotton is produced by treating cottonwool with a mixture of strong nitric and sulphuric acids and is then thoroughly washed in water and dried. Its appearance and physical form remain precisely the same as cottonwool although the cotton has undergone chemical reaction to form guncotton which is really a cellulose nitrate. The dried guncotton is a very sensitive explosive that will burn extremely rapidly if it is ignited by a flame, because of its enormous surface area and it also detonates very readily.

The reaction which takes place is strongly exothermic and produces hot gases.

It was found that guncotton would dissolve in acetone and if such solutions were evaporated a horn-like substance remained which burned in a slower and more controlled fashion.

It is possible to react cellulose with nitric acid so that there are fewer hydroxy groups substituted by the nitrate groups, indeed, a wide range of products can be obtained, and the fewer the nitrate groups the less the energy content and calorimetric value of the product. Nitrocottons in practice are characterised by their nitrogen content and the practical nitrocottons vary between 11 per cent. and 14 per cent. nitrogen. Cellulose trinitrate $C_6H_7O_2(NO_3)_3$ contains 14·15 per cent. N_2.[2]

The nitrocottons of lower nitrogen content are more readily soluble than guncotton and will dissolve in such solvents as mixtures of alcohol and ether. By making mixtures of guncotton and the soluble nitrocottons and macerating with alcohol/acetone mixtures the French produced doughs which could be extruded in the form of strips and tubes and then dried to free from solvent to form colloidal propellants. More recently, such powders have been produced, particularly by the Americans, in the form of multi-perforated cylinders. Propellants made from nitrocottons alone are termed single-base propellants to distinguish them from double-base propellants which are colloidal propellants made from mixtures of nitrocotton and nitroglycerine.[2]

The first double-base propellant was Ballistite, which was devised by Alfred Nobel. It was a colloid formed by working together nitrocellulose and nitroglycerine in the proportions of about 60/40 and was produced in the form of flat rectangular plates of various dimensions according to the gun in which it was to be fired.

Shortly afterwards, cordite, a gelatinised mixture of 58 per cent. nitroglycerine, 37 per cent. guncotton and 5 per cent. mineral jelly, was produced for the British Government and used in the form of cylinders as gun charges. The first cordite (Mk. 1) proved to be too hot and erosive and produced too much erosion and wear in guns and was superseded by a similar, but cooler, type of composition 65 per cent. guncotton, 30 per cent. nitroglycerine and 5 per cent. mineral jelly, called M.D. Cordite. It was used in the form of cylinders or tubes.

Colloidal powders were originally manufactured, as we have seen, by macerating the ingredients with solvents. In the case of single-base powders the solvent was a mixture of ether and alcohol, but for cordites acetone was used. The doughs were pressed through suitable dies in a hydraulic press in the form of strips, cylinders or tubes and emerged very like macaroni in appearance. These had to be dried in suitable stoves to remove the solvent as far as possible. The process of drying was extremely slow and in the case of thick tubes or cords took weeks. It was not possible by such methods to produce cylinders or tubes of diameter more than a fraction of an inch or so.

For large-calibre guns, powders of greater web thickness were needed and the production of such powders was enormously simplified by the Germans round 1912 when they introduced a process in which the compositions were manufactured by a solventless process. British powders were developed on similar lines and the solventless cordite of composition 41 per cent. (by weight) nitroglycerine, 50 per cent. nitrocellulose, 9 per cent. carbamite (diethyl diphenyl urea) was widely used.

The method of manufacture has been described by Wheeler, Whittaker and Pike.[3]

Until the thirties, solventless cordite was made in relatively small diameter sizes for guns, but the method of manufacture was suitable for powders of increased web thickness, such as were required for rockets, aeroplane take-offs and the like. During the Second World War cordites of 2 in., 3 in. and 4·3 in. nominal diameter were manufactured[3] and development work on larger sizes still has proceeded. Similar cordites were used by Germany. Such large diameter cordites could be used to supply gas steadily for operating and powering devices for substantial periods, for example, 3 or 4 seconds' duration.

These modern colloidal propellants are substantially impermeable to the circumambient hot gases which they produce (unless specially so designed), and burn uniformly from the surface inwards without penetration of hot gases. Consequently, the deflagration is controlled, repeatable and predictable, and does not " run away " by fissuring, desquamation or other defects of the colloid. Propellants used for guns are all in the form of grains of various geometrical forms. Notwithstanding this, they are always referred to as powders. Such powders derive their energy from the chemical reactions occurring during the deflagration of the nitrocellulose and/or nitroglycerine constituents. They produce gases, comprising hydrogen, carbon monoxide, carbon dioxide, nitrogen and steam, at high temperature which are used to propel the projectile along the bore of the gun. The thermochemical constants of propellants are consequently widely used for ballistic calculations and control of manufacture and it is of importance to be able to calculate them for any composition and to predict the effect of any change of constituent.

THERMOCHEMISTRY OF PROPELLANTS

The normal method of determining the heat of combustion of an organic substance is, of course, to burn it with gaseous oxygen in a suitable calorimetric bomb. In the case of explosive substances, such as cordite and propellent powders, and various other deflagrating compositions, in which exothermic reaction can be brought about without supplying any free oxygen, it is the usual practice to explode them in special calorimetric bombs capable of withstanding high pressures,[4] and to measure directly the heat produced by the explosion. At the same time the total gas volume and the permanent gas volume produced by the reaction can be determined. The heat produced per gram of composition is termed the *calorimetric value*.

Modern propellants largely consist of colloidal mixtures of nitroglycerine and nitrocotton, with the addition of various organic compounds as stabilisers and coolers.

Such propellants contain insufficient oxygen in their constitution to oxidise fully the carbon and hydrogen, and it is established that the reactions occurring in their gaseous products are governed primarily by the water-gas reaction:

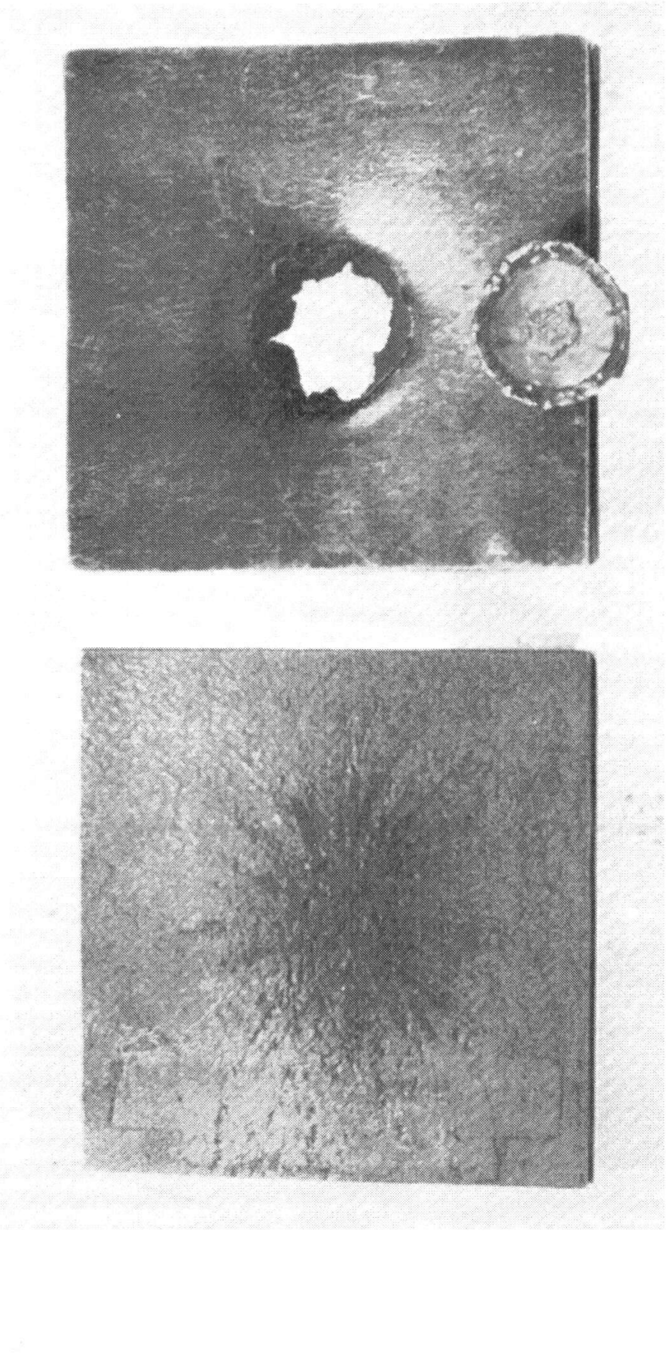
$$CO_2 + H_2 \rightleftarrows CO + H_2O \qquad (5.1)$$

Thus, the gaseous products can be regarded as consisting almost entirely of carbon monoxide, carbon dioxide, hydrogen, water and nitrogen, the relative concentrations of the first four gases being determined by the water-gas equilibrium constant corresponding to the " freezing-out " temperature. Since the water-gas reaction involves no change in volume then the volume of gas produced per gm. of composition will be independent of the exact nature of the gaseous products and is thus readily calculated. For example, considering for a moment cellulose dinitrate $C_6H_8O_3(NO_3)_2$, the breakdown on deflagration can be regarded arbitrarily as:

$$C_6H_8O_3(NO_3)_2 \rightarrow 4CO + 2CO_2 + H_2O + 3H_2 + N_2 \quad (5.2)$$

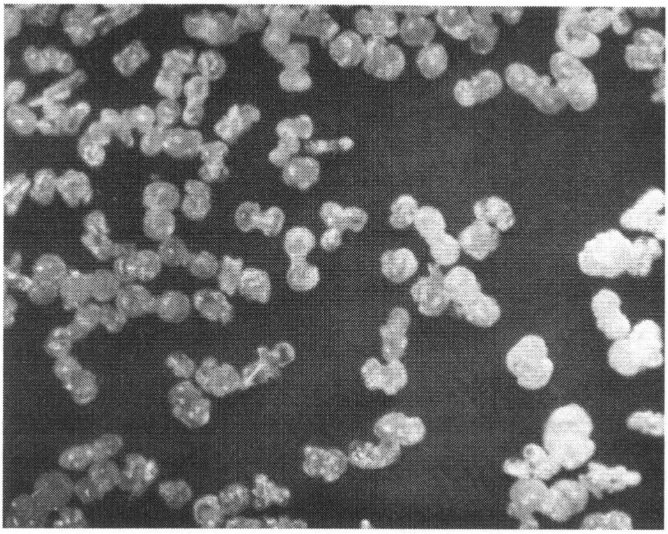
The formula weight $C_6H_8O_3(NO_3)_2$ is 252 gm. and the moles of gas produced are 11, being independent of the real distribution of

PLATE 1

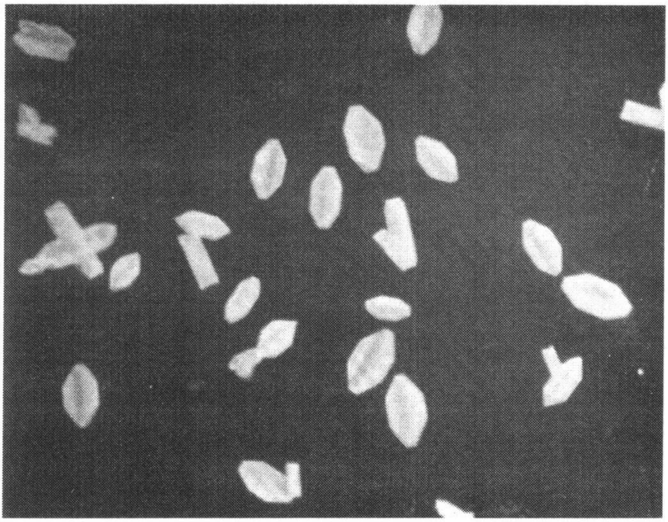


Firing gunpowder (*left*) and blasting gelatine on steel plates.

PLATE 2

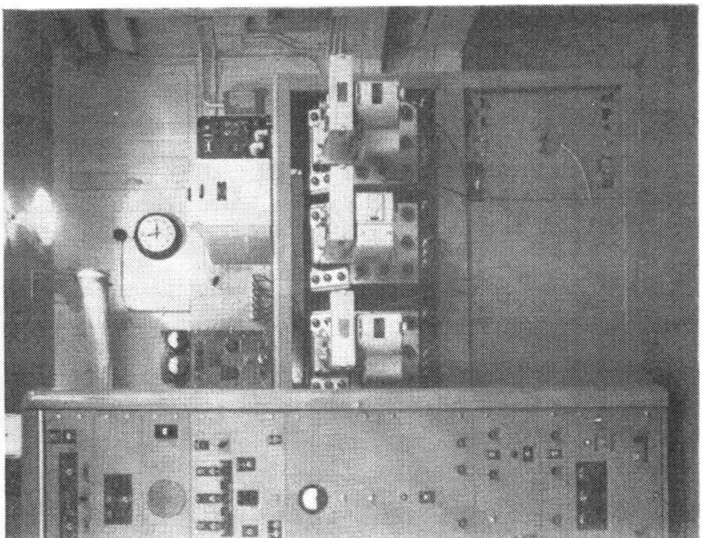


Lead azide (dextrinated) x 75.



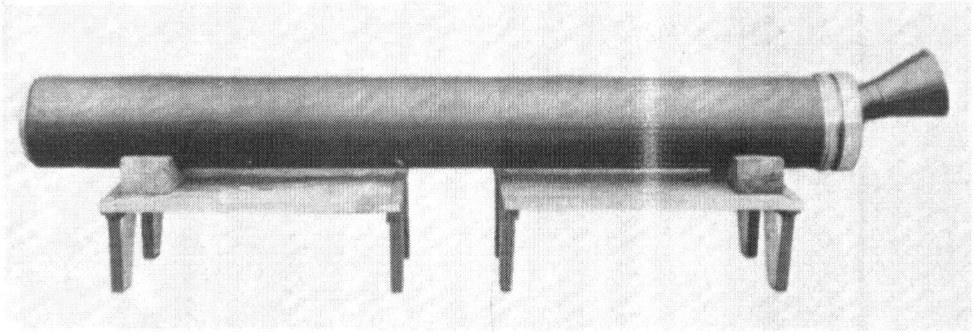
Lead azide (crystalline) x 85.

PLATE 3

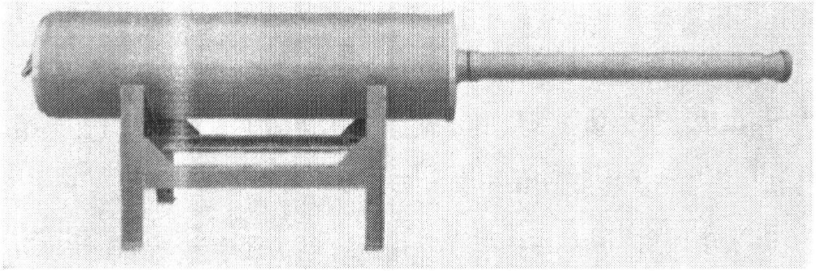


Instrumentation panel in a modern rocket-testing establishment.

PLATE 4



(*a*) Typical guided-missile boost-rocket motor. Canting the nozzle enables the thrust from each boost motor to be directed through the centre of gravity of the missile when two or more boost motors are attached to the missile.



(*b*) Typical guided-missile sustainer-rocket motor. The location of the sustainer motor in the missile is such that its centre of gravity is close to the centre of gravity of the missile, so that the burning of the propellant does not affect the " trim " of the missile. The propellant gases are ducted by means of the tube to the nozzle, which is at the aft end of the missile.

CO, CO_2, H_2O and H_2. The volume of gas per gm. of the guncotton is consequently:

$$\frac{11 \times 22{\cdot}4 \times 1000}{252} \text{ or approximately } 980 \text{ cm}^3.$$

By extending the considerations it can be shown that the calorimetric value at constant volume and 33° C. (water liquid) of such propellants is also unaffected by any reaction which may be brought about among the gaseous molecules according to the water-gas reaction.[5]

The theorems described above have enabled simple methods of calculating the calorimetric values and gas volumes of propellants to be developed and these have been in extensive use for many years.[5]

Values for typical colloidal propellants are given in Table 12.

TABLE 12

CALORIMETRIC VALUE, GAS VOLUME AND RATE OF BURNING OF TYPICAL GUN PROPELLANTS

Propellant	Calorimetric value, water liquid (cal./gm.)	Total Gas volume (water vapour) (cm.^{3}/gm.)	Linear coefficient for rate of burning from one surface (in./sec./t.s.i.)
Cordite M.D. . . .	1,025	940	0·595
Cordite W.M. . . .	1,013	934	0·575
Cordite S.C. . . .	970	957	0·500
Cordite N.Q. . . .	880	1,001	0·375
Cordite N.	765	1,058	0·315
N/C Pyro Cannon Powder .	875	955	0·40
N/C NH Cannon Powder .	765	978	0·380
N/C FNH Cannon Powder .	740	1,005	0·355

THE MECHANISM OF BURNING OF COLLOIDAL PROPELLANTS

The mechanism of burning of colloidal propellants (cordites and nitrocellulose powders) has proved to be an extremely complex problem, a real understanding of which is only currently being obtained. Fundamentally, and ignoring any non-explosive ingredients present, burning involves a rearrangement of the atoms within molecules containing both oxidising groups and fuel in a condition which may be considered as one of metastable equilibrium. The main oxidising group in colloidal propellants is the NO_3 group of a nitric ester while the fuel is the organic residue, e.g. cellulose or glycerine to which it is attached, together with such non-explosives present as are oxidisable. The main final products of complete equilibrium as we have seen are nitrogen, carbon monoxide, carbon dioxide, hydrogen and water in proportions as required by the water-gas equilibrium at the adiabatic flame temperature.

The most important characteristic of the burning of propellants, from the point of view of practical application, is the linear burning rate. The two laws governing this, Piobert's law of burning by parallel layers,[6] and de Saint Robert's first formulated connection between the rate R, and the applied pressure, p,[7]

$$R = ap^n \tag{5.3}$$

where a and n are constants, were first enunciated from a consideration of the properties of blackpowder. Their application to colloidal propellants was first demonstrated by Vieille,[8] with whom the scientific treatment of the problems attending the combustion of colloidal propellants may be said to have originated.

During the next forty-five years the study of burning appears to have been considered mainly in respect to its direct ballistic application in guns. Under the high pressures involved, it was shown that de Saint Robert's law could be replaced by a simpler relationship:

$$R = A + Bp \tag{5.4}$$

where A and B are constants.

A further major advance was the appreciation of the relationship between the linear rate of burning and the heat of explosion or, better, the temperature of explosion for a given propellant. Muraour,[9] from the relationship

$$\text{Log}\, R = 1{\cdot}405 + 0{\cdot}26\frac{T}{(1000)} \tag{5.5}$$

later[10] modified to

$$\text{Log}\, R = 1{\cdot}37 + 0{\cdot}27\frac{T}{(1000)} \tag{5.6}$$

T being the temperature of explosion, obtained fairly wide and accurate agreement with experimental results. The effect of the temperature of the propellant on its burning rate was appreciated, as was the fact that the surrounding gas in closed bomb experiments affects the burning rate only by virtue of its pressure and not its temperature.

The application of colloidal propellants in rockets and for other purposes involving relatively low pressures (500–2,000 lb. per sq. in.) during and since the Second World War and the immense effort expended on investigations of these applications necessitated the study of the mechanisms of the reactions involved. It is to be expected that a large amount of this work remains unpublished in open literature, but sufficient work has been published to give a fairly clear picture of the trends of recent thought in this direction and the broad outlines of the reaction scheme involved.

OBSERVATIONS ON FLAME STRUCTURE

The burning mechanism involves three distinct zones of reaction, the foam, fizz and flame zones,[11] as shown in Fig. 5.

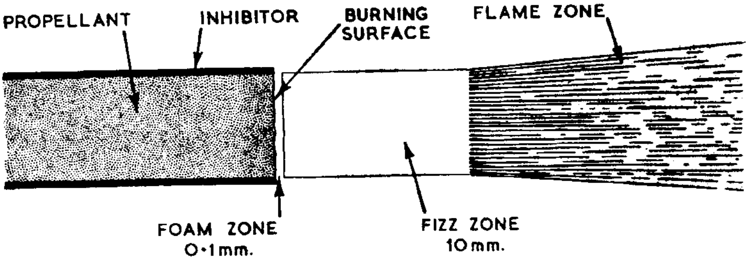


Fig. 5. Diagrammatic representation of stick of propellant burning on one face only at about 300 lb. per sq. in.

THE FOAM REACTION

The foam reaction involves first-order breaking of the O-N bond of the nitric ester group and occurs at, or immediately above or below the actual propellant surface. The energy of activation of this reaction is about 45,000 cal./mole. The temperature within this zone has been both estimated and determined as being between 200° and 700° C., with a figure close to the former probably bearing more weight. Other experiments[12] indicate a temperature of at least 1,000° C. in the outer burning surface layer.

THE FIZZ ZONE

When cordite is ignited in an inert atmosphere at low pressures no luminous flame is apparent, while the process of decomposition is observed from the " melting " and steady regression of the surface. As the pressure increases, a luminous flame appears some distance from the decomposing surface and, with further increase in pressure, the flame approaches the surface at a rate which is accurately represented by the relationship:

$$S = \frac{C}{P^3} \qquad (5.7)$$

where S is the distance of the flame from the burning surface, P the pressure and C is a constant.

At 1,000 lb. per sq. in. the luminous flame is about 0·25 mm. from the surface. The intermediate zone, known as the fizz zone, is non-luminous, but is a region of intense chemical reaction where something under half of the total heat of explosion and final flame temperature are developed. The reaction is that between the NO_2 and the organic fragments produced by the primary decomposition in the foam reaction and is approximately bimolecular. The reaction products are nitric oxide (NO) and glyoxal and other small organic fragments mainly of an aldehydic nature. The temperature developed is probably between 1,300° and 1,500° C. Huffington[13] has investigated the unstable burning of propellants at low pressure, where the fizz zone is of primary importance as little or no luminous flame occurs. When the propellant is ignited at a low pressure in a vented vessel it undergoes an oscillatory mode of burning known as " chuffing ", with the development alternately of pressure peaks and troughs. A luminosity builds up in the vessel from the end remote from the nozzle during the low pressure troughs and travels towards the nozzle end with each pressure peak. As the pressure increases, the luminosity becomes more uniform and intense, the period of oscillation decreases, and the condition of steady burning is approached. Frank-Kamenetzky[14] has shown that in a slab of explosive undergoing spontaneous self-heating there is for a given thickness a critical temperature above which explosion occurs. This theory has been applied to cordite under conditions of unstable burning.[13, 15]

THE FLAME ZONE

In the flame zone, at pressures at which it appears, nitric oxide and organic fragments react together and the gas composition required by the water-gas equilibrium at the adiabatic flame temperature (about 3,000° C.) is established.

Rice and Ginell[16] consider that in the fizz burning zone there develops a concentration of active particles which at a certain definite concentration and distance from the surface cause the gas to undergo reaction, giving rise to luminous flame. Similar phenomena involving induction periods and the build up of a concentration of active particles are observed in branching chain explosions in ordinary reaction vessels. Applying the law of steady heat flow developed by Boys and Corner[17] that the heat crossing any plane per unit time is equal to that crossing any other plane at a steady state of burning of the propellant, Rice develops a theory of fizz burning covering the effect of diffusion, the pressure and temperature coefficients and the effect of the flame. This picture contrasts somewhat with that of Boys and Corner.[17]

As soon as the pressure at which the propellant burns becomes high enough to cause the luminous flame to approach the burning surface, radiation from the flame plays a great part in controlling the burning characteristics. It has been shown that the surface pitting and " worm-holing " of large charges, particularly of hot burning rocket propellants, and especially with inorganic salts present, is due to absorption of such radiation followed by local ignition below the surface. The thermal conductivity of double-base propellant is very poor and Avery[18] has shown that insufficient heat can be transferred by conduction to produce this effect, but that radiation could cause it.

OTHER OBSERVATIONS ON THE BURNING OF PROPELLANTS

Steinberger and Carder[19] examined the burning of liquid nitric esters in glass tubes as having surfaces more easily seen as reference points than would be possible with solid-propellant samples. Temperature profiles from fine thermocouples inserted into the burning liquid give a relatively low temperature gradient from 0° C. up to 300° C. over about 0·2 mm. from the burning surface and an abrupt rise to 1,458° C. beyond this for triethylene glycol dinitrate at 800 lb. per sq. in. The most probable agent causing surface decomposition below 300° C. is thought to be free radicals from the flame zone. It is shown that data derived from this hypothesis fit the experimental data given above. Hildenbrand[20] disputed this conclusion and showed that an evaporation mechanism could not be ruled out.

Klein[21] *et al.* similarly determined the thermal structure of the burning of a solid propellant by means of thermocouples and found at pressures from 350 lb. per sq. in. to 700 lb. per sq. in. a rapid rise in temperature to about 1,200° C. followed by a slower rise. The total burning range was about 0·6 mm. From data obtained they considered the surface temperature to be about 250° C.

The general picture of the burning of propellant is one, therefore, of a foam zone in which the unimolecular decomposition of the nitric esters of which the propellant is composed occurs, this decomposition being dependent on the energy received in all forms from the fizz and flame zones. This picture has been developed from various standpoints by several workers.

DEVELOPMENT OF BURNING THEORIES

Crawford *et al.*[22] consider that exothermic reactions within the foam zone contribute significantly to the energy necessary to decompose the surface, while little energy gets back to it from the luminous flame at low pressures. They show that propellants composed solely of nitrocellulose and nitroglycerine will not burn below about 200 lb. per sq. in., while at pressures slightly above this the gas given off by non-luminous reaction when mixed with air burns with a luminous flame having a spectrum similar to that of the luminous flame normally observed at high pressures. They consider that at low pressures the rate of burning is controlled by reactions associated with the non-luminous reaction close to and within the surface. They show that the adiabatic flame temperature and the heat of explosion remain at a fairly constant low value of about half of the theoretical between atmospheric pressure and about 300–400 lb. per sq. in. Above this, over the pressure range where the fizz zone length is decreasing rapidly, the values of both these parameters increase sharply, clearly indicating an added energy derived from the luminous flame. Both the older formulæ for the dependence of the rate of burning on the pressure are considered to give reasonable values at high pressure, while

$$R = a + bp^n \tag{5.8}$$

a, b and n being constants, is more reliable between atmospheric pressure and 6,500 lb. per sq. in. These workers associated the pressure independent term a with the solid (surface) phase reaction (foam reaction) and the pressure dependent b with transfer of energy back from the gas phase reactions, although it is stressed that this represents an undoubted over-simplification. The linear relationship between the heat of explosion or, better, the temperature of explosion, and the rate of burning is verified, with the reservation that this relation cannot be expected to hold at lower pressures. These workers present a qualitative picture of surface layer decomposition into volatile fragments which pass into the gaseous flame region. The energy required is derived partially from exothermic reaction within the surface, and partially by transfer from the hotter flame. The surface temperature is probably about 300° C. before decomposition is complete. The rate of volatilisation, i.e. the rate of burning, is itself governed by the rate of supply of energy to the surface from all sources. The fizz zone is where the primary decomposition products react to give nitric oxide and further oxidised organic fragments, together with some nitrogen, water, carbon monoxide and carbon dioxide, about half the total heat of decomposition being developed and a temperature of 1,500° K. being attained. In the luminous reaction, nitric oxide reacts with the partially oxidised organic fragments with attainment of thermodynamic equilibrium at about 3,000° K. Little energy is transferred back from the flame reaction at low pressures, as this is too remote from the foam zone at these pressures and radiation is of minor importance compared with conduction. At higher pressures, however, heat transfer from the flame zone becomes controlling. Additives favouring the exothermic fizz reaction increase the rate of burning, e.g. ethyl centralite, diphenylamine and especially *p*-phenylenediamine. Cooling by additives which decompose with absorption of energy, at about 200° C., e.g. paraformaldehyde, has the opposite effect and reduces the burning rate.

Wilfong *et al.*[12] derive an expression for the rate of burning from the activation energy required to rupture the O-N bond of the nitric ester molecule, assuming a perfectly smooth plane propellant surface at a temperature of 1,000° C.

Parr and Crawford[23] have carried out a mathematical treatment of a model, considering the foam and fizz reactions to be of first and second order respectively. Their treatment is similar to that of Rice and Ginell[16] but allows the foam reaction to take place in a zone of finite instead of infinitesimal width. Good agreement with the experimental observations is obtained and it is considered that the low pressure drop off in the rate of burning is satisfactorily accounted for on the basis of a solid phase reaction zone of finite thickness.

Saenger[24] treats the problem by considering that the heat absorbed in the foam and fizz zones is converted into chemiluminescence of the combustion gases. A formula is developed which expresses the linear rate of combustion of the powder as a function of the fraction of luminescent moles in the combustion gases, the lifetime of the excited state and the corresponding radiation wavelength.

STABILITY OF PROPELLANTS

We have already touched upon the stability of explosives in Chapters 1 and 3. Propellants pose special problems in that they are stored for very long periods and often under adverse conditions.

Double-base propellent powders, and blasting gelatine, unlike many other compositions, cannot be stabilised adequately with inorganic buffer salts. A wide variety of stabilisers has been suggested and tested for such explosives following in general the principle of adding an easily nitrated organic compound. Mineral jelly was at one time widely used, since some of its components are capable of ready nitration,[25] but it has now been replaced by readily nitrated aromatic compounds, especially centralite (symmetrical diethyldiphenylurea), also known as carbamite. The dimethyl derivative is also used. Centralite has basic properties, and thus tends to accelerate hydrolysis, but this disadvantage is more than balanced by its extreme efficacy in removing nitric acid and preventing autocatalysis. The reaction probably proceeds by nitration of the centralite, followed by a breaking down to derivatives of ethylaniline.

In the absence of nitroglycerine, as for example in nitrocellulose propellants, more basic compounds may be tolerated, and the usual stabiliser is diphenylamine, which is converted during storage to nitroso- and then nitro-derivatives, at least up to the trinitro compound.[26]

APPLICATION

As we have already seen, the modern colloidal propellant burns on the surface only. The rate of production of gas from a powder charge must therefore be directly proportional to the surface of the powder charge and the rate of consumption or deflagration of the charge must also be directly proportional to the surface of the charge. The rate of burning of such propellants, that is to say, the linear amount of the grain burnt through per second, depends on the calorimetric value of the propellant, being higher the greater the calorimetric value, and it also depends on the pressure of the gases produced in the reaction. Most guns operate at pressures of the order of 5–20 tons per sq. in. chamber pressure, and in this range of pressures the rate of burning of colloidal powders has been determined directly by firing samples of propellants in closed vessels provided with suitable pressure gauges for determining the pressure time curve of the propellent charge burning.[27]

It has been determined that in such cases the linear rate of burning is directly proportional to the pressure. In other words, the constant A in relationship (5.4) is negligibly small compared with the term Bp and the simplified form:

$$R = Bp \tag{5.9}$$

is obtained, where R is the linear rate of burning, p is the pressure and B is a constant characteristic of the composition. B is usually of the order of an inch or two per ton pressure. Table 12 gives some data for the rates of burning of typical propellants.

We can readily combine the above laws for surface and pressure and obtain the formula for the rate of consumption of any powder charge, namely:

$$\frac{dx}{dt} = \rho BSp \tag{5.10}$$

where x is the weight of the charge at the time t, ρ is the absolute density of the propellant, and S is the area undergoing deflagration.

The shortest thickness in a propellant grain to be burnt through is called the web thickness and is a very characteristic magnitude. It will be realised that, in a rifle, for example, where the time during which the bullet is propelled along the bore is about one-thousandth of a second, the web thickness of the powder required will be very much smaller than that for a big gun in which the projectile may take one or two hundredth parts of a second to travel along the much longer barrel. Consequently, a tubular cordite used for a rifle cartridge charge is very much smaller than a similar powder used for a gun. The web thickness of powders for some typical cases are given in Table 13.

TABLE 13

WEB THICKNESS OF TYPICAL GUN PROPELLANTS

Propellant	Gun or Rifle	Web Thickness
Cordite C.D. T 5/2 . .	·303 in.	0·014 (annulus)
Cordite N/S . . .	3·7 in.	0·058 (annulus)
Cordite S.C. . . .	6 in. Mk. 23	0·150 (cord diam.)
Cordite S.C. . . .	14 in.	0·300 (cord diam.)

In the case of rockets, the charge, unlike that for a gun which contains a large number of grains, comprises a single grain. Rocket motors have achieved such importance in recent years that they merit a chapter to themselves (Chapter 8).

REFERENCES

1. Taylor, J. *Detonation in Condensed Explosives.* (Oxford University Press, 1952.)
2. Miles, F. D. *Cellulose Nitrate,* Chapter 1. (Oliver and Boyd, Edinburgh, 1955.)
3. Wheeler, W. H., Whittaker, H., and Pike, H. H. M. *J. Inst. Fuel* (1947), **20,** 137.
4. Taylor, J., and Hall, C. R. L. *J. Phys. Chem.* (1947), **51,** 593.
   De Bruin, G., and De Pauw,. P. F. M. Communiqué de la Societé Anonyme *Fabriques Neerlandaises d'Explosifs,* Nos. 8 and 9, 1928–29.
5. De Pauw, P. F. M. *Z. ges. Schiess-u. Sprengstoffw.* (1937), **32,** 10, 36 and 60.
   Taylor, J., Hall, C. R. L. and Thomas H., *J. Phys. Chem.* (1947), **51,** 580.
6. Piobert. *Traité d'Artillerie* (1839).
7. Berthelot. *Sur la force Matières Explosives,* Vol. 1, p. 85 (1885).
8. Vieille, P. *Mémor. Poud.* (1893), **6,** 256.
9. *Inter. al.* Muraour, M. H. *Mémor. Artill. fr.* (1938), **17,** 831, and earlier papers.
10. Muraour, H., and Aunis, G. *Chim. et Industr.* (1952), **67,** 920.
11. Symposium on Kinetics of Propellants. *J. Phys. Chem.* (1950), **54,** 847 *et seq.*
12. Wilfong, R. E., Penner, S. S., and Daniels, F. *J. Phys. Chem.* (1950), **54,** 863.
13. Huffington, J. D. *Trans. Faraday Soc.* (1954), **50,** 942.
14. Frank-Kamenetzky, D. A. *J. Phys. Chem. Moscow* (1939), **18,** 738.
    Frank-Kamenetzky, D. A. *C. R. Acad. Sci. U.R.S.S.* (1938), **18,** 413.
    Frank-Kamenetzky, D. A. *Acta. Phys. Chem. U.R.S.S.* (1939), **10,** 365.
15. Huffington, J. D. *Nature, Lond.* (1950), **165,** 840.
16. Rice, O. K., and Ginell, R. *J. Phys. Chem.* (1950), **54,** 885.
17. Boys, S. F., and Corner. *J. Proc. Roy. Soc.,* Series A (1949), **197,** 90.
18. Avery, W. H. *J. Phys. Chem.* (1950), **54,** 917.
19. Steinberger, R., and Carder, K. E. *J. Phys. Chem.* (1955), **59,** 255.
20. Hildenbrand, D. L. *J. Phys. Chem.* (1955), **59,** 672.
21. Klein, R., Menster, M., von Elbe, G., and Lewis, B. *J. Phys. Chem.* (1950), **54,** 877.
22. Crawford, B. L., Huggett, C., and McBrady, J. J. *J. Phys. Chem.* (1950), **54,** 854.
23. Parr, R. G., and Crawford, B. L. *J. Phys. Chem.* (1950), **54,** 929.
24. Saenger, E. *Z. Naturf.* (1950), **5a,** 467.
25. Robertson, R. *J. Chem. Soc.* (1921), **119,** 1.
26. Dalbert, R. *Mémor. Poud.* (1938), **28,** 119, 127.
27. Crow, A. D., and Grimshaw, W. E. *Phil. Trans.,* Series A (1932), **230,** 39.
    Taylor, J., and Wark, R. *J. Sci. Instrum.* (1946), **25,** 115.

CHAPTER 6

LOW-TEMPERATURE GAS-PRODUCING REACTIONS BASED ON NITRITES, AND THE "HYDROX" BLASTING DEVICE

In any investigations which have as their objective the production of compositions capable of yielding large quantities of non-toxic gases such as steam, carbon dioxide or nitrogen at low temperature it was natural that attention should be turned to reactions based on nitrites. The author began such investigations in 1932 as part of a general exploratory effort on low-temperature gas-producing reactions.

It was known that certain nitrites, notably ammonium nitrite,[1] are readily decomposable at low temperature. Ammonium nitrite also possesses the great advantage of decomposing into nitrogen and water without yielding excess oxygen to be burned as does ammonium nitrate. Thus:

$$NH_4NO_2 \longrightarrow N_2 + 2H_2O$$

Ammonium nitrite was found to be too unstable for practical use, the results confirming previous experimental work in this respect.[2] Furthermore, the reaction is of high exothermicity and would not provide a low temperature gas-producing composition in any case. Thermochemical calculations indicated, nevertheless, that the " indirect preparation " of ammonium nitrite from stoichiometric mixtures of a metallic nitrite with an ammonium salt was of potential promise and practical investigations were initiated.

The researches were directed towards the use of the readily available sodium nitrite and ammonium salts like the chloride or sulphate, and it was soon established that dry intimate mixtures of these components could be made over a wide range of compositional limits which were self-sustained when initiated at a local point by a hot wire or fusee. The composition most suitable for practical application was the stoichiometric mixture of sodium nitrite and ammonium chloride for which the self-sustained reaction can be depicted as:

$$NaNO_2 + NH_4Cl \longrightarrow NaCl + NH_4NO_2 \longrightarrow NaCl + N_2 + 2H_2O \qquad (6.1)$$

A possible alternative reaction mechanism is also:

$$NaNO_2 + NH_4Cl \longrightarrow NH_3 + HCl + NaNO_2 \longrightarrow NaCl + HONO + NH_3 \longrightarrow NaCl + N_2 + 2H_2O \quad (6.2)$$

At atmospheric pressure the gases do smell of ammonia and have a brownish tint, indicating that ammonia and oxides of nitrogen are being evolved separately. This appears to be a side reaction which arises from the thermal dissociation of ammonium chloride, followed by decomposition of sodium nitrite by the hydrochloric acid so formed. This reaction becomes negligible when the gases are produced under pressure, however, and the above equation is then applicable.[3]

STABILITY

Literature examination disclosed the fact that such a mixture had been used technically[4] by the rubber industry for the inflation of hollow rubber articles during the vulcanising process. It had been appreciated that the mixtures were not intrinsically stable and required the inclusion of a stabiliser and means of maintaining them in a dry condition if they were to be stored. The stabiliser chosen had been soda ash (2 per cent.).

Experimental work was undertaken to ascertain the underlying causes of lack of stability with a view to producing mixtures suitable for practical application. It was found that moisture is the primary cause of instability. The relation between moisture content and the stability of the mixtures in a modified S.15 Test[5] at 60° was found to follow the law:

$$y = Kx^2 \quad (6.3)$$

where y = total gas evolution, after time t from the commencement of a test, from a mixture of initial moisture content x. Since moisture cannot be eliminated completely, the mixtures slowly decompose and produce more moisture and the rate of decomposition increases. Acid was found to increase still further the rate and alkali to diminish it. This led to investigations of the effect of pH value on stability. Stability was found to increase with pH value. At 60° C., 20 per cent. solutions of the mixture were apparently completely stable at a pH value of 8·2–8·4 or greater, while at normal temperatures, what was apparently complete stability was obtained at a pH value of 7·0 or greater. Thus alkalinity and dryness are factors which greatly aid stability. The use of anhydrous sodium carbonate can produce both of these conditions and its effectiveness is thereby explained.

It was realised as the work continued that the stabilising properties of soda ash were primarily due to the fact that it was an alkaline substance rather than to its dehydrating properties. The dehydrating effect is only temporary because the soda ash reacts with the ammonium chloride forming ammonium carbonate and salt, thus:

$$2NH_4Cl + Na_2CO_3 \longrightarrow (NH_4)_2CO_3 + 2NaCl \quad (6.4)$$

$$2NH_4Cl + Na_2CO_3.10H_2O \rightarrow (NH_4)_2CO_3 + 2NaCl + 10H_2O \quad (6.5)$$

and consequently the moisture which is absorbed by the soda ash is thrown back into the mixture as the decomposition proceeds. Moreover, as the decomposition progresses ammonium carbonate is formed which has a fairly high vapour pressure and consequently evaporates from the powder.

Soda ash and ammonium carbonate are both excellent stabilisers if they can be kept in the powder. It is their transience which is the difficulty.

It appears that nitrous acid is the accelerator of the decomposition and that it can readily be formed from the sodium nitrite if the mixture is even mildly acidic in the presence of moisture. It is evident, therefore, that alkaline substances, drying agents and nitric oxide absorbers will be stabilisers of the mixture. If a substance which combines alkalinity with drying properties can be used it ought to be a better stabiliser than one which possesses only one of these properties. On this basis, it could be expected that substances like magnesium oxide would be excellent stabilisers.

A further property of importance is the permanence of the stabiliser. The stabilising action as stated above appears to arise from the formation of ammonium carbonate by metathesis of ammonium chloride and the stabiliser. In the case of sodium carbonate this metathesis occurs fairly rapidly and there is much more ammonium carbonate formed than is necessary for stabilising purposes. The ammonium carbonate disappears and the stabiliser is thus gradually lost. With the insoluble carbonates and magnesium oxide this metathesis occurs very slowly and, whilst it is adequate to ensure stabilisation, it is slow enough to ensure long life of the stabiliser. Experimental investigations fully supported and confirmed these views and showed that magnesium oxide, particularly, was an excellent stabiliser. It was therefore adopted for practical purposes and 2 per cent. was used as stabiliser for the powders.[6]

The stability of the powder depends, in addition, on the degree of intimacy of mixing, a milled powder being less stable than a mechanical mixture of fairly coarse grist size. This is, of course, due to the fact that the constituents in the former case are in much more intimate contact and the surface area at which reaction can occur is much greater.

" HYDROX " POWDER

The stoichiometric mixture of sodium nitrite and ammonium chloride stabilised with soda ash or with magnesium oxide was developed for use with steel tube blasting devices for use in fiery mines.[7,8] The device itself, which is described later in the chapter, was called " Hydrox " and the powder " Hydrox " Powder. For practical use it was much more convenient to have the charge in granular form and consequently the " Hydrox " powder was compressed and then broken up into suitably sized granules.

Thermochemical data for "Hydrox" powder are given in Table 14.

TABLE 14

THERMOCHEMISTRY OF "HYDROX" POWDER STABILISED WITH 2 PER CENT. SODA ASH

State of Water	Condition	Heat Liberated at 25° C. (cal./gm.)	Temperature of Reaction °C.	Gas Volume ($cm.^3/gm.$)
Vapour .	Constant Pressure . .	420	1,120	537
Liquid .	Constant Pressure . .	589	1,120	
Vapour .	Constant Volume . .	435	1,310	537
Liquid .	Constant Volume . .	594	1,310	

Products of complete reaction: NaCl, 46·7 per cent.; N_2, 22·4 per cent.; H_2O, 28·8 per cent.; Na_2CO_3, 2·1 per cent.; all by weight.

The total gaseous products comprise 51·2 per cent. by weight of all products.

ALTERNATIVE MIXTURES

Stoichiometrical mixtures of sodium nitrite with other ammonium salts such as ammonium sulphate, phosphate and the like, also yield self-sustained mixtures and so do certain other nitrites, like potassium nitrite. These mixtures have no advantages over sodium nitrite and ammonium chloride, substances which are cheap and readily obtained, and it is not considered worth while to describe them in any detail here.

THE INITIATION OF " HYDROX " POWDER BY ACIDIC SUBSTANCES

The normal method of initiating the self-sustained reaction in sodium nitrite/ammonium chloride mixtures is to heat the powder at a point by a fusee, by a heated piece of metal or, if the mixture is enclosed in a container, by a gunpowder igniter (see p. 71). It was found during the stability investigations that initiation could be brought about by an entirely different method simply by placing a few drops of solution of certain acid substances on the powder, in which case, after a period of relative quiescence the self-sustained reaction set in. The time for this to happen depended on the nature of the solutions and the concentration as well as on the nature and amount of the stabiliser in the powder.[9] This method of initiation is so novel and interesting that it merits further description.

When strong acids were poured on to " Hydrox " powders it was observed that violent reactions with copious emission of brown fumes occurred, the brown fume production becoming less as the concentration of the acid was diminished. Neither hydrochloric nor nitric acid initiated a self-sustained reaction in powders stabilised with soda ash or magnesium oxide. When, however, 0·2 cm.^{3} of a solution of 100 gm. chromic anhydride in 100 gm. of water were poured on to " Hydrox " powder stabilised with 2 per cent. soda ash in a tube, self-sustained reaction occurred in 10 seconds. Similarly 8 cm.^{3} of a solution of phosphoric acid (19 gm. in 100 cm.^{3} water) initiated the powder after 2½ minutes, 5 cm.^{3} nitric acid (20 per cent. strength) initiated in ¾ minute and 5 cm.^{3} acetic acid (10 per cent. strength) initiated in 2½ minutes.

As mentioned previously 20 per cent. solutions of $NaNO_2$-AmCl were found to be stable at a *p*H of approximately 7, but they were spontaneously decomposable at about *p*H 5.

It is to be expected therefore that an acid poured on to " Hydrox " powder will initiate a self-sustained reaction if it can neutralise the stabiliser and force the *p*H of the acid-powder interface to a figure of round about 5. Why cannot hydrochloric acid and nitric acid accomplish this? It is considered that they are destroyed too rapidly by direct action on the nitrite and that the nitric oxide reaction is largely responsible for this destruction.

This reaction appears to be of the following types:

$$3NaNO_2 + 3HCl \longrightarrow 3NaCl + HNO_3 + 2NO + H_2O \qquad (6.6)$$

for sodium nitrite, and for the mixtures

$$3NaNO_2 + 2HCl + NH_4Cl \rightarrow 3NaCl + NH_4NO_3 + 2NO + H_2O \qquad (6.7)$$

These reactions destroy acid and increase the *p*H values.

It is assumed that when acid is poured on to " Hydrox " powder these reactions occur in addition to the main reaction which it is desired to promote, namely:

$$NaNO_2 + NH_4Cl \longrightarrow NaCl + N_2 + 2H_2O \qquad (6.8)$$

(An alternative reaction mechanism is (6.2).)

Reactions (6.6) and/or (6.7) become increasingly important as the concentration of the acid is increased and with strong acid destruction of the nitrite occurs very rapidly.

Summarising the action of a strong acid on " Hydrox " powder—it violently attacks the sodium nitrite with production of nitric oxide. This reaction destroys the acid. By this side reaction the acid reservoir is reduced until it is incapable of neutralising the alkali stabiliser to an extent sufficient to maintain the *p*H value sufficiently low to initiate the self-sustained reaction.

On this theory, if there is no stabiliser to neutralise, then weak acid should initiate the self-sustained reaction, though strong acid is incapable of doing so.

Experiments on hydrochloric and nitric acids confirmed this.

CONDITIONS NECESSARY FOR INITIATING A SELF-SUSTAINED REACTION IN " HYDROX " POWDER BY MEANS OF ACIDIC SOLUTIONS

Sodium nitrite/ammonium chloride mixtures (of approximately molecular proportions) become unstable provided the *p*H value of the solution in contact with them is maintained at a sufficiently low value. As soon as instability sets in, exothermic decomposition is initiated, the rate of decomposition depending on the *p*H value and on the temperature. This exothermic decomposition raises the temperature of the mixture locally, and if in any volume of the powder a condition arises in which the rate of accumulation of heat in that volume is continuously greater than the rate of loss of heat from that volume, a self-sustained reaction will be induced.

The necessary conditions for effective operation by a solution is therefore that it should provide sufficient hydrogen ions to neutralise the effect of any stabiliser and maintain in addition a *p*H value, at least locally in the mixture, sufficiently low, and for a sufficiently long time for the rate of accumulation of heat due to decomposition in some volume of the powder to be greater than the rate of loss of heat from that same volume. If the side reaction (6.7) is not to be severe it is necessary that the reservoir of acid shall be available at a fairly low hydrogen ion concentration, that is at a fairly high *p*H value. On this basis promising solutions would be those of acids of low dissociation constants, acid salts, and salts of weak bases and strong acids, which are strongly hydrolysed.

The experimental results, some of which were quoted above, gave general support to the above explanation.

This method of initiating self-sustained exothermic low-temperature reaction is an interesting one because it offers quite a number of novel possibilities, for example, the devising of a blasting device which will be set off by a weak acid without the intervention at any point of a flame or high temperature which could conceivably be dangerous in fiery mines.[9]

THE " HYDROX " BLASTING DEVICE[7, 8]

The purpose of the " Hydrox " device is to provide a means of blasting coal, which is safer than ordinary permitted explosives, and yet is more effective and practical than alternative devices such as hydraulic and pneumatic coal-bursters, wedges, etc.

In its operation " Hydrox " may be regarded as a modification of the Cardox system in which liquid carbon dioxide, contained in a stout steel tube, is heated above its critical temperature by an electrically initiated chemical heater, and thus builds up sufficient pressure to burst a disc, whereupon the carbon dioxide gas issues from the tube and can be used for blasting purposes. The blasting equipment is similar in most respects for both Cardox and " Hydrox ", but the " Hydrox " charge is a granular solid, supplied in tins, and is loaded into the tubes simply by pouring it in. Although non-explosive, the powder is capable of a self-sustained gas-producing reaction when initiated locally by heating, and in the tube the gases formed on initiation build up pressure to burst a disc as in the case of Cardox. Various initiators have been used. The first type which has seen much service was a blackpowder electric fuse containing 30 grains of gunpowder. Alternative fuses which would not be able to ignite methane/air mixtures, such as special detonators[7] and gasless hot tube igniters[10] (see Chapter 11) have been proposed.

As compared with explosives, shotfiring with Cardox and " Hydrox " is somewhat more expensive; and as the charge is of a definite size confined in a fairly heavy steel tube, there is not the same ease of handling, and adjustability of charge weight to the work to be done, as in ordinary shotfiring. A certain flexibility exists, in that the size of tube and charge, and thickness of bursting disc can be varied within limits to suit requirements at different collieries; it is not practicable to use these variations from shothole to shothole as the tubes have to be loaded outside the coal mine. There is, however, a gain in safety; and this is officially recognised in that shotfiring with " Hydrox " and Cardox is permitted under certain conditions in which the Regulations forbid the use of explosives. In general, Cardox and " Hydrox " have been found to favour production of coal in relatively large pieces, without shattering, which is desirable for certain markets.

DESCRIPTION OF THE " HYDROX " DEVICE

One form of the B.37 " Hydrox " tube and equipment is illustrated in Fig. 6. A steel tube contains the charge and the igniter, and is closed at one end by a " firing head ", which carries contacts

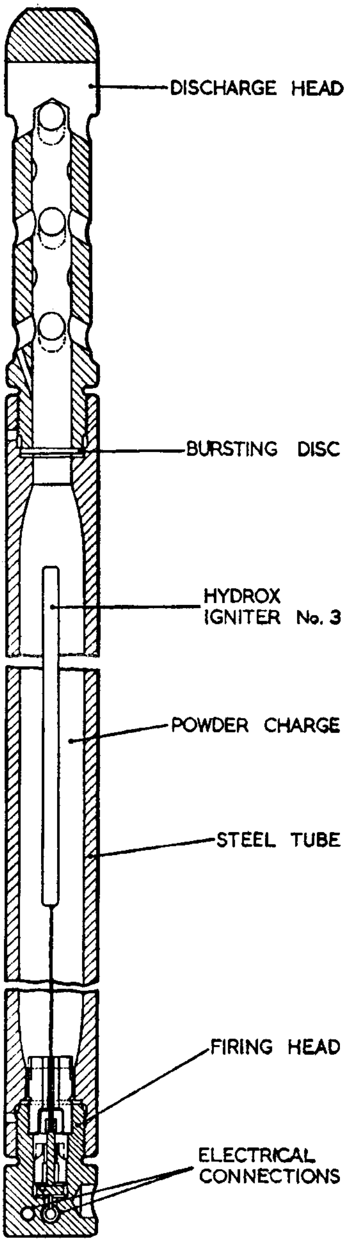


FIG. 6. "Hydrox" blasting cartridge.

for the wires from the shotfiring exploder, and at the other by a bursting disc which is clamped between the tube and the " discharge head " which screws into the tube. Appropriate washers, etc., are used to make the tube gas-tight.

In order to load the tube, the discharge head and firing head are unscrewed, and the remains of the bursting disc from the previous shot are removed. An igniter is fitted to the firing head, inserted in the tube, the firing head screwed home, and the continuity of the circuit is tested. The charge of " Hydrox " powder is then loaded into the tube using a metal funnel, a new bursting disc is inserted, and the " discharge head " is screwed home. After again testing the continuity of the electrical circuit, the tube is now ready for firing.

The tube is then loaded into the borehole, discharge head first, and connected to the firing circuit. It is not essential to use stemming, though it is usually preferable. A wooden sprag should be so placed as to prevent the tube from being driven violently out of the borehole by the discharging gases. This rarely occurs nowadays since the discharge head is either designed to vent the gas in such a direction that the tube is thrust inwards into the hole, or carries lugs which grip the walls of the borehole.

On firing, the igniter initiates a flameless gas-producing reaction in the powder, and the gas pressure in the tube increases until the bursting disc yields at a pressure of about 12 tons per sq. in. The gases are suddenly released into the borehole when the disc bursts, and their energy is available for blasting.

SPECIFICATIONS

The precise specifications of the forms of the device which are allowed to be used in coal mines, are detailed in the current C. & H. Permits made under the Coal Mines (Cardox and " Hydrox ") Order, 1941.

IMPROVED DEVICES

Improved types of " Hydrox " device have been developed in the last year or two. They are not based on nitrites, but as they are the successors of the original " Hydrox " it is appropriate to mention them here. In the most recent form[11] the sodium nitrite/ammonium chloride mixture has been replaced by a mixture of ammonium nitrate with one of the hydrated nitrates of such a metal as magnesium and a fuel such as sawdust. Lewis and Watts have recently given a detailed description of the development of the new " Hydrox " device suitable for underground loading.[12] The main charge has the composition:

Ammonium Nitrate	47·5–50·5 per cent.
Magnesium Nitrate Hexahydrate	33·0–36·0 per cent.
Woodmeal	14·0–16·0 per cent.

Its reaction corresponds to the following:

$$4C_6H_{10}O_5+23NH_4NO_3+5Mg(NO_3)_2.6H_2O \rightarrow 24CO_2+96H_2O+28N_2+5MgO \quad (6.9)$$

The products are non-toxic and non-inflammable and the total solid residue is very much less than with the original " Hydrox ". The main charge is initiated by a special primer composed mainly of guanidine nitrate and ammonium persulphate.[12]

DISPERSION OF PESTICIDES

Mixtures based on " Hydrox " powders have also been examined for the dispersion of pesticides as alternatives to compositions based on ammonium nitrate catalysed mixtures described in Chapter 7.

REFERENCES

1. Mellor, J. W. *A Comprehensive Treatise on Inorganic and Theoretical Chemistry*, Vol. 8, p. 470. (Longmans, Green & Co. Ltd., London, 1928.)
2. Kast, H. *Z. ges. Schiess-u. Sprengstoffw.* (1926), **21,** 205.
3. Taylor, J. *Industr. Chem. Mfr.* (1948), **24,** 289.
4. U.K. Patent 185,089.
5. Farmer, R. C. *J. Chem. Soc.* (1920), **117,** 1451, 1603.
   Cook, M. A., and Abegg, M. T. *Industr. Engng. Chem.* (*Industr.*) (1956), **48,** 1090.
6. U.K. Patent 461,647.
7. U.K. Patent 431,935.
8. Taylor, J., and Gay, P. F. *British Coal Mining Explosives*, Chapter 12, p. 127. (Newnes, 1958.)
9. U.K. Patent 507,328.
10. U.K. Patent 430,750.
11. U.K. Patents 758,563 and 767,238.
12. Lewis, I. O., and Watts, R. *Trans. Inst. Min. Eng.* (1958), **117,** 6, 419.

CHAPTER 7

AMMONIUM NITRATE, GUANIDINE NITRATE AND NITROGUANIDINE COMPOSITIONS

In the early 1930s a need became manifest for low-temperature exothermic gas-producing self-sustained compositions for technical applications, and the author took up the question of investigating the problem. Whilst the established types of compositions were adequate for a great number of applications they were not suitable, for example, for use as blasting agents in " fiery " coal mines where methane/air explosive mixtures were likely to occur, or for mechanical operations where the " ironmongery " could not withstand high gas temperatures.[1]

The initial objective was to produce a composition which would provide adequate gas and energy for blasting coal, but which would be flameless and would not ignite methane/air explosive mixtures such as occur in coal mines. This objective necessitated too that the product gases should be non-toxic.

The second aim was to produce low-temperature compositions suitable for carrying out mechanical operations.

SAFETY COMPOSITIONS FOR BLASTING

The first objective may be defined as the production of a safety composition for blasting.

One of the most attractive substances for use in a safety composition is ammonium nitrate which is the principal energy gas-producing substance in the commercial explosives industry. Its molecule is over-oxygenated and it is necessary for the application under consideration that this excess oxygen shall be " burned " to give non-toxic products like water or carbon dioxide.

The direct oxidation by ammonium nitrate of charcoal, cellulose, or the like gives too hot a reaction for the purposes in view (see Table 1), but it was recognised that it was a promising subject as a constituent of salt pairs.

Thermochemical examination showed that the reactions of ammonium nitrate with ammonium bicarbonate or ammonium oxalate were of considerable promise from the point of view of providing large gas yields at relatively low temperatures.

These reactions may be depicted as:

$$3NH_4NO_3+2NH_4HCO_3 \longrightarrow 11H_2O+4N_2+2CO_2 \quad (7.1)$$

The heat liberated is 414 cal./gm. at 25° C. (constant volume, water vapour), the gas volume 957 cm.^{3}/gm. and the temperature 1,310° C.

$$4NH_4NO_3+(NH_4)_2C_2O_4.H_2O \rightarrow 13H_2O+5N_2+2CO_2 \quad (7.2)$$

The heat liberated is 566 cal./gm., the gas volume 970 cm^3/gm. and the temperature 1,690° C.

These temperatures compare with 2,620° C. and 2,500° C. for the balanced reactions with charcoal and cellulose respectively.

Mixtures of the above type are, however, not self-sustained and can only be made to proceed by means of a general heating, preferably at high pressure.

In order to carry through such reactions a method was devised[2] in which a mixture of coarse granules of the ammonium nitrate and bicarbonate composition together with coarse gunpowder was loaded into a steel tube which could be vented when a sufficiently high pressure was achieved (this device is described in Chapter 6). The granules of gunpowder were ignited by an ordinary type of electric powder fuse. They burned rapidly, but did not provide enough pressure to cause venting of the steel tube. The heat provided by the gunpowder was sufficient to cause decomposition of the ammonium nitrate/ammonium bicarbonate mixture according to the equation (7.1) above.

This reaction provided both gas and heat and was of relatively low temperature. Consequently, the products of the gunpowder explosion were damped down and cooled, and when the pressure built up so that the steel tube vented, the products were cool enough to give no danger of ignition if they came into contact with inflammable methane/air mixtures. Similar results were obtained with ammonium nitrate/ammonium oxalate mixtures, but the reaction was hotter than that of the corresponding bicarbonate mixtures (cp. equations (7.1) and (7.2)).

The bicarbonate mixtures were not practicable because of the evanescent nature of this salt and the fact that the ammonia in it tended to form Diver's liquid with the ammonium nitrate and give a wet product unsuitable for storage.

The investigations were extended to include many other chemicals such as guanidine nitrate, nitroguanidine, urea nitrate and others, and yielded data which proved very useful for later work. It was concluded after experience of these sorts of mixtures that they, containing as they did, granules of gunpowder, were potentially hazardous in practice and should be abandoned for truly self-sustained compositions of low reaction temperature.

The devices had, however, been tested out practically in the blasting of coal and found to be efficient, so that it was clear that, if a suitable composition could be found, the fact that its rate of reaction proved too slow to be used directly in the shothole no longer precluded its use, as it could be employed in a vented steel tube device in which a relatively slow rate of reaction would not be an insuperable obstacle. Further, there was in existence a practical steel tube blasting device already employed for the getting of coal, based on the use of liquid carbon dioxide which was immediately available for application (see Chapter 6).

The net was cast fairly widely for likely chemicals and one possibility soon presented itself as worth pursuing, namely, nitrite compositions, which are dealt with in Chapter 6. Investigations in this field were pursued vigorously and finally led to the production of practical compositions and to the steel tube blasting device known as " Hydrox ". In view of the success of nitrite compositions the use of salt pairs based on ammonium nitrate was abandoned.

There remained, however, the possibility of producing self-sustained reactions of ammonium nitrate without forcing them through thermally by gunpowder or such means, and investigations to this end were pursued.

It had, of course, been realised for a considerable time that ammonium nitrate in particular provided a cheap, readily obtainable oxygen-provider capable of yielding gaseous products at low temperature and, indeed, proposals to utilise ammonium nitrate in the liquid form with ammonia (Diver's liquid) were patented as long ago as 1905.[3]

As far as is known such liquids have not yet achieved practical applications, but methods of using ammonium nitrate in the solid state as a mono-propellant and in some cases as one component of a bi-propellent system have been worked out during the past two decades.

THE DECOMPOSITION OF AMMONIUM NITRATE INTO PRODUCT GASES

Ammonium nitrate, as we have already mentioned, is an oxygen-positive molecule containing one atom of oxygen per molecule in excess of what is required for fully oxidised products. It is thus evident that, in principle, it can be used as a fuel in several ways, either alone, since its decomposition can be exothermic, in which case the product gases will be cool, but may contain oxides of nitrogen and be acidic; or with fuels which will consume the extra oxygen available and in this case the product gases will usually be hot but non-corrosive.

Various modes of decomposition of ammonium nitrate itself have been postulated by various workers,[4, 5, 6] and a number are given in Table 15. Reactions 1–5 are those of Berthelot, 6 is from Saunders, and from Haid and Koenen, and 8 from Kaiser. The reaction 7 is favoured by some recent unpublished work by R. D. Smith in the laboratories of the Nobel Division of I.C.I. Smith's view is that reactions 2, 1 and 7 are the three fundamental decomposition routes of ammonium nitrate, 3 being a minor component. The equations are probably merely approximations to the complicated results when ammonium nitrate decomposes under quite narrowly defined conditions.

TABLE 15

Possible Modes of Decomposition of Ammonium Nitrate

1. $NH_4NO_3 \longrightarrow NH_3 + HNO_3$
2. $NH_4NO_3 \longrightarrow N_2O + 2H_2O$
3. $NH_4NO_3 \longrightarrow N_2 + 2H_2O + \frac{1}{2}O_2$
4. $2NH_4NO_3 \longrightarrow N_2 + 2NO + 4H_2O$
5. $4NH_4NO_3 \longrightarrow 3N_2 + 2NO_2 + 8H_2O$
6. $8NH_4NO_3 \longrightarrow 5N_2 + 4NO + 2NO_2 + 16H_2O$
7. $5NH_4NO_3 \longrightarrow 4N_2 + 2HNO_3 + 9H_2O$
8. $4NH_4NO_3 \longrightarrow 2NH_3 + N_2 + NO + 3NO_2 + 5H_2O$

Reactions 1 to 5 from Berthelot, M., "Sur la force des Matières Explosives," Paris, 1883.

Reaction 6 from Saunders, H.L., *J. Chem. Soc.* (1922), **121**, 702.

Reaction 7 from Smith, R. D., unpublished reference.

Reaction 8 from Kaiser, R., *Angewandte Chemie* (1935), **48**, 149.

Reaction 6 also from Haid, A., and Koenen, H., *Chemiker Zeitung* (1952), **76**, 471.

Table 16 gives thermochemical data for the reactions.

It will be seen that all the decompositions are of low calorific value and the product gases are of low temperature compared with most normal propellent or fuel reactions. Ammonium nitrate, however, does not itself burn from a local ignition; indeed, thermal decomposition does not normally occur to any considerable degree until the temperature is well above the melting point (169° C.).[5]

The main reaction characterising the decomposition of the pure salt above its melting point is:

$$NH_4NO_3 \longrightarrow 2H_2O + N_2O \qquad (7.3)$$

This is a very attractive reaction as the product gases are non-acidic

TABLE 16

THERMOCHEMICAL DATA FOR THE DECOMPOSITION OF AMMONIUM NITRATE

Reaction	Heat liberated, at 25° C. constant volume, water vapour (where present, (cal./gm.)	Gas volume water vapour (where present) (cm.^{3}/gm.)	Temperature of reaction (° K.)
1 . . .	−538	560	Endothermic
2 . . .	133	840	770
3 . . .	380	981	1,560
4 . . .	110	981	720
5 . . .	328	910	1,390
6 . . .	219	946	1,080
7 . . .	392	840	1,470
8 . . .	−240	840	Endothermic

and clean, but there is, however, a wide range of possible modes of decomposition as outlined in Table 15 and which may occur to some degree.

Since none of the reactions is self-sustained in normal circumstances and all are characterised by very low energy releases it was decided that the only method of promoting them would be to find a suitable catalyst. Therefore, when investigations were undertaken in 1933 the object was to find a catalyst which when mixed with ammonium nitrate would promote its decomposition so that it would " burn " or undergo combustion with its own oxygen when ignited locally, yielding relatively low-temperature product gases. Mention of chemicals which promoted the catalytic decomposition of ammonium nitrate to some extent in the molten state was later found in the literature,[7] but there was no indication of the existence of any substance which when mixed with solid ammonium nitrate would promote rapid decomposition.

Preliminary experimental investigations disclosed a number of chemical substances which had some effect and others which had none. Among the most successful were copper, manganese and chromium compounds, and the immediate research was then restricted to these, and in a short time centred on chromium compounds which proved to be the most successful. After carrying out a considerable number of experimental investigations it was ascertained that flameless decomposition of ammonium nitrate could be induced by mixing intimately with potassium chromate or ammonium dichromate in proportion of the order of 3 per cent. or more.[8]

THE NATURE OF THE CHROMATE-INDUCED DECOMPOSITION

If an intimate mixture of ammonium nitrate and potassium chromate, in powder form, is heated at a point in it by a flame or hot wire, the ammonium nitrate begins to decompose at that point and this decomposition spreads slowly and smoothly throughout the mixture until all the ammonium nitrate has been consumed. There is no flame or glow, but the decomposition of the ammonium nitrate produces volumes of gas coloured brown by nitrogen dioxide. The potassium chromate remains at the end of the reaction, some of it having changed into potassium dichromate, the excess potassium being present as nitrate. Essentially, however, the potassium chromate obeys the criterion of a catalyst, of being unchanged by the reaction. By arranging the experiment so that a column of ammonium nitrate has resting on it an ammonium nitrate/potassium chromate mixture, and causing this to react, the potassium chromate will gradually pass down through the column of ammonium nitrate, causing it all to react. Thus the reaction is definitely one of catalysis by the potassium chromate.

If ammonium dichromate is used instead of potassium chromate in admixture with ammonium nitrate, it not only brings about decomposition of the latter, but as it itself decomposes in a self-sustained manner when locally initiated evolving nitrogen and steam and leaving a voluminous green mass of chromic oxide, according to the reaction:

$$(NH_4)_2Cr_2O_7 \longrightarrow 4H_2O + N_2 + Cr_2O_3$$

the heat released is considerable and this assists the reaction of the ammonium nitrate thermally, so that the reaction is not solely catalytic. Nevertheless, this is not a case of thermal decomposition of the ammonium nitrate sustained by the heat of this reaction, since on the one hand the proportion of ammonium dichromate need not be sufficient to supply the heat requisite even to melt all the ammonium nitrate and, on the other hand, if a mixture of potassium nitrate, ammonium nitrate and ammonium dichromate is used, the chromium remains after the reaction in the form of potassium chromate and dichromate, indicating that the reaction between potassium nitrate and ammonium dichromate has preference, as it were, over the self-sustained thermal decomposition of the ammonium dichromate.

This catalytic aspect of the decomposition of ammonium nitrate differentiates it rather sharply from the combustion of cordite or blackpowder, which are by comparison high-temperature reactions, in which the energy released is sufficient to activate the molecules over the energy thresholds without the assistance of a catalyst.

The catalytic action is characteristic of some, but not all, compounds in which the chromate ion occurs. It does not appear, at any rate, to a useful degree, in chromic oxide or salts of chromium. The really effective catalytic chromates are those which are soluble in water; thus potassium, sodium and ammonium chromates or dichromates are active, but lead, barium, or chromium chromates are not so active. Some complex cobalt salts containing the chromate or dichromate group are active.

It is known that chromium compounds, if present as impurity in ammonium nitrate used for the manufacture of nitrous oxide by thermal decomposition (reaction 2 of Table 15) lead to the presence in the gas of nitrogen peroxide. It thus appears likely that the effect of the chromate catalyst is to promote reaction 5 of Table 15. It may be noted that this is one of the more energetic decomposition reactions of ammonium nitrate, thus favouring the process of decomposition. Substances like potassium chloride which have been claimed to assist catalytically the decomposition of ammonium nitrate into nitrous oxide and water, do not appreciably assist the self-sustained decomposition of solid ammonium nitrate. The product gases from the flameless combustion of ammonium nitrate compositions of the type described are not in practice found to be defined by any single reaction as given in Table 15. They comprise a mixture of them and the resultant products also depend on the prevailing conditions of pressure and temperature. As a general indication it may be said that the gases contain about 63 per cent. of water vapour, about 10 per cent. of nitrous oxide, up to about 20 per cent. of nitrogen and the remainder nitric oxide and nitrogen dioxide in varying proportions. A simple mixture of 90 per cent. of ammonium nitrate and 10 per cent. of potassium chromate yields approximately 8 per cent. by volume of nitric oxide and nitrogen peroxide in the products of its reaction.

The temperature of the product gases depends, of course, on the relative incidence of the various reactions and in many cases it increases with the operating pressure. The temperature of the reaction of a 90 per cent. ammonium nitrate, 10 per cent. potassium chromate mixture at atmospheric pressure is approximately 370° C. By the inclusion of an easily oxidised fuel, as, for example, starch, the composition of the product gases may be modified and their temperature increased.

Whilst it is considered that the study of the product gases from simple catalysed ammonium nitrate mixtures would be most instructive and illuminating, the mixtures employed in most practical applications usually contain additional components and the simplest cases have, therefore, not been much investigated.

Later investigations have led to the discovery of other catalysts and promoters,[9] but, in the opinion of the author, the chromates are still outstanding. Among the possible alternatives may be mentioned sodium, potassium and barium hypophosphites, manganese dioxide, ammonium thiosulphate, copper chromate and nickel chromite.

So far we have indicated how the decomposition of ammonium nitrate itself may be achieved in a self-sustained manner and this forms the basis for its use as a fuel. There are many other considerations to be observed, however, before practical application is possible and these will be considered later.

BLASTING DEVICES USING CHROMATE COMPOSITIONS

Work was carried out with the object of using ammonium nitrate chromate-catalysed compositions in the " Hydrox " steel tube blasting device. One of the great defects was the production by such compositions of product gases containing nitric oxide and nitric acid which are toxic and corrosive. The excess oxygen can be " burned " by using an igniter in the steel tube blasting device which is highly oxygen-negative[10] or oxygen-negative materials in granular form may be mixed with the self-sustained charge as, for example, granules of ammonium oxalate. Such devices have not, to date, proved as convenient in use as the " Hydrox " devices. The compositions have, nevertheless, been widely applied in other fields.

PROPULSIVE PURPOSES

Apart from providing charges for blasting devices there was the objective of producing compositions for carrying out mechanical operations, for providing gases at moderate temperatures for long periods of time, and for jet propulsion.

These investigations were in a number of directions, but one was the direct use of catalysed composition pressed into steel tubes, the intention being that they should burn in " cigar " fashion and give a source of gas to drive a motor, or for jet propulsion purposes. The initial experiments were carried out in steel tubes about 1¼ in. internal diameter, and the powders were stemmed in by hand pressure. Such columns reacted fairly satisfactorily when the tubes vented freely to atmosphere, but as soon as ever the escape of gas was restricted or controlled, gas penetration into the mixture occurred, and the volume in combustion became progressively greater until the tube blew up or some safety device operated. Such results were not really surprising and were overcome by compressing the powdered compositions, by suitable incremental loading in a press, to high densities so that gas penetration at the operative pressure could not occur. This proved fairly satisfactory with low temperature compositions, but when the calorific value was raised slightly " blow ups " were again experienced, especially when thin-walled steel tubes of diameters of the order of 2 in. were used. This proved to be due to heat conduction down the sides of the tube, the tube walls being heated in advance of the reacting composition surface and heating the pressed composition above its decomposition temperature, thus causing a progressively larger surface to react. In order to avoid this it was necessary to insulate the inside of the steel containing tube and this was conveniently done by sheets of insulating material of the type used for steam and other high temperature joints.[11] This, however, did not get rid of all troubles.

Ammonium nitrate is a very hygroscopic chemical and this necessitated special packaging and storage precautions to avoid the composition becoming damp, but, even with such precautions, the trouble of volume change on temperature cycling, so well known in the ammonium nitrate trade, was still encountered.

Compacted ammonium nitrate compositions tend to crack and sometimes even to break up when they are subjected to temperature variations which cause them to pass up and down through the transition point (32° C.) at which the crystal form of the ammonium nitrate changes from modification IV to modification III. The work of Jänecke[12] suggested a method of overcoming the volume change which occurs at the transition temperature by using mixed crystals of ammonium and potassium nitrates. The application of this method in another field of investigation had shown the technique of using potassium nitrate (in a proportion of about 10 per cent. of the ammonium nitrate) to be effective[13] in suppressing the tendency to crack or break up and it was applied in an improved and simplified form for preparing compacted ammonium nitrate compositions of the present type.[11]

Certain applications require not relatively " cool " product gases but much higher temperature gases characterised by high energy content and thrust constant (if used for jet propulsion). In such cases it is frequently most convenient to incorporate directly into the composition a fuel which will consume the extra oxygen available in the ammonium nitrate. The fuel may be chosen from a wide variety of substances, depending on circumstances, such as charcoal, starch, ammonium oxalate, guanidine nitrate and nitroguanidine.

OTHER COMPOSITIONS

Guanidine nitrate and nitroguanidine are both exothermic materials capable of producing large gas volumes and catalysts and sensitisers to promote their decomposition were also sought.

The reactions may be represented approximately as:

$$CH_6N_4O_3 \longrightarrow 2H_2O + CO + H_2 + 2N_2 \qquad (7.4)$$

and

$$CH_4N_4O_2 \longrightarrow H_2O + CO + H_2 + 2N_2 \qquad (7.5)$$

Table 17 gives thermochemical data for reactions (7.4) and (7.5).

TABLE 17

THERMOCHEMISTRY OF GUANIDINE NITRATE, NITROGUANIDINE AND BALANCED MIXTURES WITH AMMONIUM NITRATE

Substance or Mixture	Reaction	Heat Liberated at 25° C. (CV:WG) (cal./gm.)	Temperature of Reaction °C.	Gas Volume (cm.³/gm.)
Guanidine Nitrate	$CH_6N_4O_3 \rightarrow CO + 2H_2O + H_2 + 2N_2$	441	1,450	1,102
Nitroguanidine	$CH_4N_4O_2 \rightarrow CO + H_2O + H_2 + 2N_2$	624	2,010	1,077
Ammonium Nitrate + Guanidine Nitrate	$2NH_4NO_3 + CH_6N_4O_3 \rightarrow CO_2 + 7H_2O + 4N_2$	851	2,480	953
Ammonium Nitrate + Nitroguanidine	$2NH_4NO_3 + CH_4N_4O_2 \rightarrow CO_2 + 6H_2O + 4N_2$	949	2,780	933

In practical cases there will also be CO_2 in the product gases and the relative proportions of H_2O, CO, CO_2 and H_2 will be determined by the water gas equilibrium constant at the " freezing-out " temperature. As shown in Chapter 5, this will not effect the gas volume per gm. of composition or the calorimetric value (water liquid). There will also, of course, be small quantities of other more complex products, and NH_3.

Investigations showed that self-sustained reactions could be initiated in these substances by various additives.

As sensitisers for nitroguanidine or guanidine nitrate there may be used, for instance, chromic oxide; a chromate, dichromate or polychromate of the alkali metals or ammonium; hypophosphites of ammonium, of alkali metals or barium[14]; copper powder and a number of copper compounds, as, for instance, cuprous oxide, cuprous chloride, cuprous oxalate, cupric chloride, cupric oxide; a number of nickel, silver, tin, selenium and vanadium compounds.

As further sensitisers of the thermal decomposition available in the case of nitroguanidine there may be mentioned, for example, a number of salts of the alkali metals, e.g. potassium nitrite, sodium nitrite, potassium carbonate, sodium carbonate (salts of potassium being more active than those of sodium); a number of aluminium compounds, e.g. aluminium chloride, aluminium oxide; various compounds of lead, molybdenum or zinc, for instance, lead nitrate, molybdic acid, zinc metal, zinc oxide and zinc carbonate, the two last mentioned compounds being especially active sensitisers.

For dicyandiamidine nitrate and nitrodicyandiamidine nitrate the sensitiser may be, for instance, a dichromate or a hypophosphite of an alkali metal or ammonium.

It will be understood that combinations of different sensitisers are often desirable to use, while also it may be advantageous to use mixtures of the nitrates and/or nitrocompounds.

As in the case of sensitised ammonium nitrate, the temperatures at which the sensitised nitrates and nitro-derivatives of the organic nitrogen bases burn are substantially lower than those yielded by the burning of black powder-like compositions or smokeless powder; but whereas ammonium nitrate is oxygen-positive these organic nitrogen compounds are oxygen-negative. Mixtures of guanidine nitrate or nitroguanidine with ammonium nitrate to give oxygen-balanced compositions can be used. Thermochemical data for some of these are given in Table 17.

The inclusion of additional oxygen-negative organic compounds tends to lower the temperature at which the gases are produced from these organic nitrogen compounds. Thus, with sensitised nitroguanidine further reduction of the temperature of the gases evolved on the progressive reaction of the mass can be achieved by including up to 10 per cent. of dimethyl diphenyl urea which is of high carbon content (70 per cent.) and low oxygen content (8·5 per cent.). Other suitable additions by way of example are starch or cellulosic compounds. Although the rate of combustion is slowed down by the addition of dimethyl diphenyl urea, the stability of the mass during its burning is much improved and steady burning without the breaking up of the charge is obtained at burning pressures up to at least 220 lb. per sq. in.

THE BURNING LAWS OF AMMONIUM NITRATE, GUANIDINE NITRATE AND NITROGUANIDINE COMPOSITIONS

Compacted charges of ammonium nitrate, guanidine nitrate and nitroguanidine compositions have been found to burn stably from atmospheric pressure up to at least several hundred pounds per square inch, and indeed quite a number up to a few thousand pounds. The rate of burning is capable of adjustment over a wide range by the inclusion of various substances which act as moderants of the combustion. For any specific application it is, of course, necessary to determine the rate of combustion of the charge it is proposed to use. Modern testing rigs are very elaborate and highly instrumented, but a simple technique was evolved for ammonium nitrate and similar compositions which merits description.[5] In this method the composition is consolidated to the required density by pressing into a steel tube container closed at one end and lined, as previously described, with a heat-insulating material to prevent conduction of heat along the walls of the steel tube. The open end of the tube is finally closed by a screwed fitting which contains a jet of preselected throat diameter (see Fig. 7). When the compacted charge is ignited at the free face it burns " cigar " fashion with a uniform area of burning and at a constant pressure which is determined by the size of the jet throat. The theory is given in Chapter 8. If the time of burning of a measured length of the column is determined, then it is obvious that the linear rate of reaction per second at the operating pressure is readily determined. The measured length is fairly simply provided by interpolating very thin layers of " fast " reacting material at a known linear distance apart. The passage across these " fast " layers is indicated by a momentary pressure " kick " in the recording instrument.

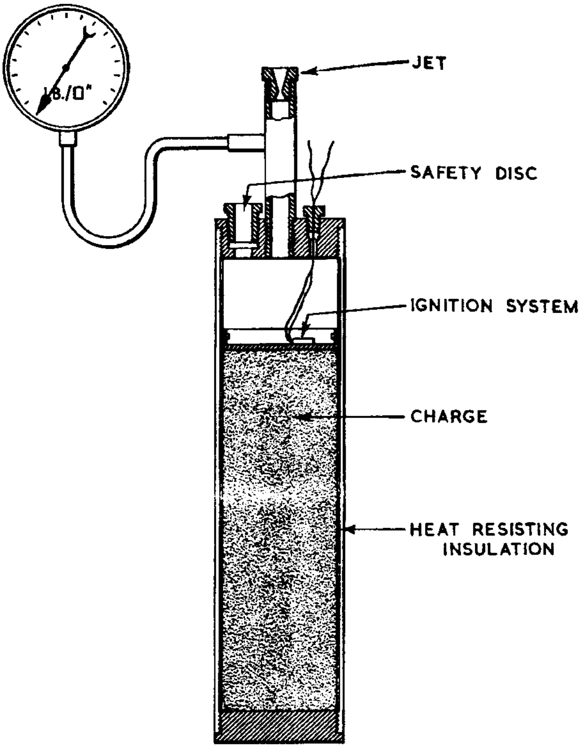


Fig. 7. Apparatus for measuring the rate of burning of pressed compositions.

The temperature of the gases immediately before their passage through the jet may also be measured by means of suitable thermocouples. Most of the compositions investigated have been found to obey fairly simple laws so far as rate of burning is concerned, of the type well established for other deflagrating compositions as shown in equation (5.3), Chapter 5. The pressure index for these compositions is fractional and has been found to be as high as 0·8 for some cast compositions and as low as 0·13 for some pressed charges.

The pressure-rate relationship for many pressed charges cannot be expressed satisfactorily by equation (5.3) because the value of n varies with the pressure. In such cases an equation of the form given in (5.4) has been found to fit the experimental results much better.

The rate of burning may be made very slow indeed by including suitable retardants in the composition but the maximum rate is, of course, restricted and is of the order of one or two tenths of an inch per second at pressures around 100 lb. per sq. in.

SMOKE GENERATORS FOR THE DISPERSION OF PESTICIDES

An interesting application of low-temperature gas-producing compositions based on ammonium nitrate, guanidine nitrate or nitroguanidine, is for dispersing pesticides in domestic, horticultural and industrial buildings with the object of producing toxic deposits on the walls and surfaces by smoke dispersion. One aspect of this, namely, the use of low-temperature self-sustained gas-producing mixtures, has been the subject of investigations in the I.C.I. Nobel Division Laboratories since 1946. Marke and Lilly[15] have published an account of the work.

Finely divided organic pesticide was mixed with a gas-producing base and the mixture on reaction volatilised and dispersed the pesticide. It was hoped that by using sufficiently low-temperature compositions uniform dispersion of the pesticide would be brought about without substantial thermal decomposition of the pesticide.

By using ammonium nitrate, guanidine nitrate or nitroguanidine, sensitised with potassium chromate or ammonium dichromate, mixtures with up to about 50 per cent. of benzene hexachloride (B.H.C.) or D.D.T. could be made which were self-sustained and effective in dispersing the pesticides.

The volatilised pesticides carried in these smokes condensed on surfaces and were shown to be toxic. Laboratory methods for the biological assessment of the deposits were developed in which the smoke was allowed to settle under standardised conditions on paper to which house-flies were subsequently exposed in a suitable container and the percentage fatalities determined. The particle size, persistence and settling time of the smoke deposits, their distribution over horizontal, inverted horizontal and vertical surfaces, and the relative toxicity of different types of surfaces were studied.

Experiments were carried out to ascertain the optimum proportions of gas-producing component, sensitiser and pesticide to give ready ignition, complete propagation and high volatilisation efficiency.

The compositions can be used either in the form of powders in tins or other suitable containers, or as pressed pellets. Pelleted compositions are readily initiated directly from a match, and the loose composition by inserting in it a wad consisting of a piece of woodpulp impregnated with potassium nitrate, which itself is initiated directly from a match.

The method is applicable to a wide range of pesticides including azobenzene and Parathion.

Such generators can be used in control of the bed-bug for public health purposes, insect infestation in grain stores, fleas on poultry farms, pests in greenhouses and against the common fly in all sorts of buildings, and in a variety of other applications.

REFERENCES

1. Taylor, J. *Industr. Chem. Mfr.* (1948), **24**, 289.
2. U.K. Patent 430, 258.
3. U.K. Patent 15,852.
   U.S. Patent 2,393,594.
   U.K. Patent 597,717.
4. Whetstone, J., and Holmes, A. W. *Industr. Chem. Mfr.* (1947), **23**, 717.
5. Taylor, J., and Sillitto, G. P. The Third Symposium on Combustion, Flame and Explosion Phenomena, Paper No. 73, p. 572. (Williams & Wilkins Co., 1949.)
6. Berthelot, M. *C. R. Acad. Sci., Paris* (1876), **82**, 932.
   Veley, V. H. *J. Chem. Soc.* (1883), **43**, 370.
   Saunders, H. L. *J. Chem. Soc.* (1922), **121**, 698.
   Shah, M. S., and Osa, T. M. *J. Chem. Soc.* (1932), 725.
   Kretzschmar, W. *Z. Anorg. Chem.* (1934), **219**, 29.
7. Tramm, H., and Velde, H. *Z. Angew. Chem.* (1934), **47**, 782.
8. U.S. Patent 2,159,234.
   U.K. Patent 453,210.
9. U.K. Patents 479,773 and 631,114.
10. U.K. Patent 454,091.
11. U.K. Patent 627,727.
12. Jänecke, E., Hannacher, H., and Rohlfs, E. *Z. Anorg. Chem.* (1932), **206**, 357.
13. U.K. Patent 573,147. Campbell, A. N., and Campbell, A. Jean R. *Canad. J. Res.* (1946), **24B**, 93.
14. U.K. Patent 583,986.
15. Marke, D. J. B., and Lilly, C. H. *J. Sci. Fd. Agric.* (1951), **2**, 56.

CHAPTER 8

ROCKET MOTORS

ROCKETS or rocket motors[1] utilise the principle of jet propulsion. This is the application of Newton's famous third law that " action and reaction are equal and opposite ". If a fluid is ejected from a vessel through a nozzle at high velocity, then the force causing it to be ejected results in an equal force in the opposite direction propelling the vessel in the opposite direction to the issuing fluid.

A fire hose or garden hose, if the water pressure is sufficiently high, is an everyday example of this. It has also been pointed out frequently that the principle is used in nature by certain kinds of cuttlefish which eject water forcibly, thereby " jet propelling " themselves in the opposite direction at high speed.

Although ships have been designed to operate by jet propulsion using water as the jet fluid, the modern developments of the principle, such as the gas-turbine jet engine, and all rocket motors, use gases as the jet fluid. A great deal of attention has been focused during recent years on special fuels for various forms of jet propulsion, more especially those devices which achieved military significance in Germany during the last war and their successors, and in the various rockets developed by the Allies.

ROCKETS AND ROCKET MOTORS

The rocket motor is distinguished from such other jet propulsion engines as the gas-turbine jet engine and the ramjet engine by the fact that it produces the whole of its jet gases within itself, whereas the others all depend upon taking in air, compressing and heating it by burning fuel in it, and then expelling it at higher velocity through the jet. The amount of fuel which has to be carried by the rocket is very much greater, to do the same amount of propulsion work. The other difference is that just because a rocket motor is quite independent of external air for its operation it can be used where no air is present; for instance, at heights where the earth's atmosphere is too thin to allow the operation of engines which depend upon air, or under water. It must be borne in mind, however, that rockets, particularly solid-propellant rockets, frequently are chosen for use in preference to air-using engines where these could be used, because of their relative simplicity and consequently low cost; this is especially the case when, as in guided missiles of war, the use is a " one-shot " one which will entail the loss or destruction of the engine when it is used.

Utilisation of fuels which obtain all the oxygen required for their combustion and transformation into hot gases from the air, is usually the most economical proposition, particularly for applications of long time duration, but there are exceptions to this. Some operations must be carried out in circumstances where atmospheric oxygen is not available, and there are others of which the duration is very short, or the thrust required very high over a short period. In the first case it is essential to use systems providing or carrying their own oxygen and in the other cases it is often less complicated and cheaper to operate with propellants which themselves contain the oxygen required for their reaction. Such propellants may be either mono- or bi-fuel propellent systems. Solid and liquid propellants of this type have achieved a position of great importance and, whilst the majority of applications have been made under the duress of war, there are no doubt many useful peace-time applications which either have been, or will be developed in the future. Such solid and liquid propellants have been reviewed in a paper to the Institute of Fuel.[2]

Liquid propellants have the advantage that their supply can be controlled by mechanically operated valves, and the combustion providing the hot gaseous products is therefore capable of being regulated over a wide range or even stopped altogether at will. On the other hand, solid propellants are not controllable in this manner and once reaction has started the combustion proceeds to completion; the rate of production of gas being determined purely by the nature of the propellant, its geometrical form and the venting area of the combustion vessel in which it is contained. Solid propellants have, however, an advantage over liquid propellants in that they require less complicated means of storage and normally no additional gear for control of supply.[3]

The term *rocket* is nowadays used to refer to the complete flying object, whilst the actual device in which chemical energy is transformed into energy of motion is called the *rocket motor*. In modern developments, the complete rocket may contain a variety of equipment and components besides the rocket motor, notably the " payload " or item which it is desired to project and which depends upon the purpose for which the rocket is fired, and instrumentation and equipment for enabling the rocket to follow some path, and sometimes to enable it to choose a particular path in response to an external stimulus such as the motion of some other object, for example, an aeroplane. The transformation of rockets from the phase of display fireworks, or signalling rockets requiring little in the way of reproducibility of speed or trajectory, into vehicles capable of launching an earth satellite, or of being used as weapons of war surpassing guns in effectiveness, has involved scientific progress over a very wide field indeed. Our understanding of the principles of rocket propulsion and the techniques of design of rocket motors has shared in this progress.

THE PRINCIPLES OF ROCKET MOTOR OPERATION

We turn now to consider in more detail the principles of rocket motor operation; beginning with the principles of the jet nozzle as a means of converting the energy of a hot compressed gas into energy of motion, and following with the physics and chemistry of the processes of production of such gases.

It can be shown that the thrust F produced by a jet of gas in which $\dot{w}$ lb. of gas are issuing per second with average velocity $\bar{v}_e$ through the exit plane of a nozzle at which the pressure is p_e, is

$$F = \bar{v}_e \dot{w}/g + (p_e - p_a)A_e \tag{8.1}$$

where p_a is the pressure of the atmosphere and A_e is the area of the nozzle exit plane, and g is the acceleration of gravity. The first term on the right-hand side of the equation is the contribution due to the momentum of the gas, while the second one represents the effect of the difference between the exit pressure and the external pressure.

In this expression $\bar{v}_e$, p_e and A_e are interdependent quantities, and their relations depend upon the theory of the motion of gases through nozzles. However, taking these three quantities for the

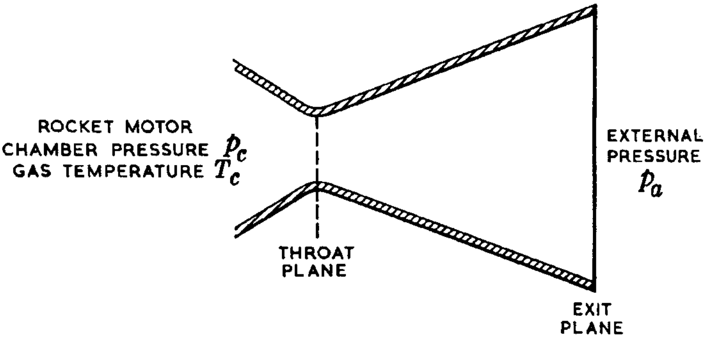


FIG. 8. Diagram of convergent-divergent nozzle.

moment as given, it is evident that the thrust is independent of the velocity of the rocket ($\bar{v}_e$ in the above expression is the velocity of the gas relative to the nozzle exit plane), and increases as the atmospheric pressure falls. This increase becomes significant in the designing of rockets to operate at great heights.

We now consider a nozzle comprising a convergent approach region, and a divergent exit section, so that where these join there is a cross-section of minimum area called the throat. Such a nozzle is illustrated in Fig. 8. Then assuming that the gas is perfect, which is close to the truth for hot rocket gases, it can be shown from the ordinary gas laws and laws of conservation of mass and energy that the following relations hold, provided that the ratio of the pressure upstream of the throat to the external pressure is greater than a certain rather small critical ratio.

$$\dot{w} = A_t p_c \sqrt{\frac{g\gamma}{RT_c}\left(\frac{2}{\gamma+1}\right)^{(\gamma+1)/(\gamma-1)}} \tag{8.2}$$

$$v_t = \sqrt{2g\gamma RT_c/(\gamma+1)} = \sqrt{g\gamma RT_t} \tag{8.3}$$

$$v_2 = v_t \sqrt{\left(\frac{\gamma+1}{\gamma-1}\right)\left\{1-\left(\frac{p_2}{p_c}\right)^{(\gamma-1)/\gamma}\right\}} \tag{8.4}$$

$$A_2 = A_t \left(\frac{2}{\gamma+1}\right)^{\frac{1}{\gamma-1}} \left(\frac{p_c}{p_2}\right)^{\frac{1}{\gamma}} \sqrt{\frac{v_t}{v_2}} \tag{8.5}$$

where

$\dot{w}$	denotes the mass rate of gas flow.
A_t	denotes the area of the throat cross-section.
p_c	denotes the rocket chamber pressure, i.e. the pressure upstream from the nozzle throat.
T_c	denotes the rocket chamber gas temperature.
T_t	denotes the gas temperature in the throat cross-section.
v_t	denotes the gas velocity in the throat cross-section.
v_2 p_2 A_2	denote the gas velocity, pressure, and cross-section area of the nozzle at any plane between the throat and the exit plane.
γ	denotes the ratio of specific heat at constant pressure to specific heat at constant volume for the gas.
R	denotes the gas constant, and
g	denotes the acceleration of gravity.

From these equations, a number of interesting features is immediately evident. From equation (8.2) it can be seen that for a given gas composition and temperature in the rocket chamber, the mass rate of flow through the nozzle is directly proportional to the nozzle throat area and the pressure in the chamber,

$$\dot{w} = \text{const} \times A_t p_c \tag{8.6}$$

The velocity of the gas through the throat cross-section, v_t, is exactly the velocity of sound in the gas at the temperature ruling there. This implies that the conditions of the gas in the chamber are quite independent of anything which may be happening to the gas downstream of the throat; for instance, the conditions of the chamber gas are unaffected by the surrounding atmospheric pressure. From equation (8.4) it can be seen that v_2 is greater than v_t, i.e. the gas velocity in the nozzle at any place downstream from the throat is supersonic, and in a diverging nozzle (i.e. one in which p_2 decreases as one travels downstream) the gas velocity increases as it travels downstream. By considering the plane of p_2, v_2 and A_2 to be the exit plane of the nozzle, we obtain from (8.4) and (8.5) the conditions p_e, v_e and A_e there. In relation to equation (8.1), however, we have to observe that v_e from equation (8.4) is rather different from $\bar{v}_e$ in equation (8.1), since the gas stream-lines are diverging and v_e refers to the velocity along a stream-line whereas $\bar{v}_e$ is the average of the components of v_e along the line of the axis of the nozzle.

It has been shown that $\bar{v}_e = \lambda v_e$ where λ depends only on the angle of divergence of the exit cone of the nozzle so that (8.1) can be written:

$$F = \lambda v_e \dot{w}/g + (p_e - p_a)A_e \tag{8.1'}$$

and now by using the relations between p_e, v_e and A_e afforded by (8.4) and (8.5) it can be shown that the thrust is a maximum if $p_e = p_a$, i.e. if the exit cross-section of the nozzle is such that the gas pressure there is just equal to the external atmospheric pressure.

The nozzle theory of which we have given the outline shows that if we attach a nozzle to a chamber in which there is gas under pressure, the jet of gas issuing through the nozzle will produce a thrust force, and gives quantitative relations between this force and the properties of the gas. It should be mentioned that the theory outlined is an idealised one, corresponding approximately to the theory of the compressible but non-viscous fluid of classical hydrodynamics. In order to get a more realistic picture, it is necessary to study the aerodynamic conditions, which introduce the boundary layer at the surface of the solid bounding the gas stream, and the possibility of velocity losses, and therefore thrust losses, due to shock waves in the supersonic gas. However, since it is found that provided certain rather simple precautions are taken, such as avoiding gross roughness and sharp changes of section inside the nozzle, the idealised theory is a very good approximation, and since also in practice there are other departures from theory which we have not taken into account, such as heat losses from the gas to the nozzle material, it is usual to subsume most of these departures from ideal conditions into experimental-determined correction factors. At this stage, therefore, we can leave the theory of the nozzle, and turn to consider the processes of production of the high-pressure gases in the rocket chamber.

In practice, the substances used to provide the rocket motor chamber gases are either liquids or solids, which are capable of decomposing smoothly and continuously into main gaseous products within the rocket motor chamber. Before considering individual substances of this kind and the ways of using them, it is advantageous to consider some criteria of performance. Intuitively one can expect that a substance will be a " good " one for the purpose if its use at a rate of $\dot{w}$ lb. per second gives a high thrust, and in fact the ratio:

$$I_s = \frac{F}{\dot{w}} \tag{8.7}$$

is called the *specific impulse* of the rocket propellant (the chemical substance whose decomposition provides the gases), and is widely used. If the rocket in which the propellant is used has a nozzle which expands the gases down to atmospheric pressure it follows from (8.1′) that

$$I_s = \frac{\lambda}{g} v_e \tag{8.8}$$

and hence from (8.3) and (8.4) that

$$I_s = \frac{\lambda}{g} \sqrt{\frac{2g\gamma R T_c}{\gamma - 1} \left\{ 1 - \left(\frac{p_e}{p_c} \right)^{\frac{\gamma - 1}{\gamma}} \right\}} \tag{8.9}$$

Now replace the gas constant R by the universal gas constant $R^1 = MR$ where M is the mean molecular weight of the gases

$$I_s = \frac{\lambda}{g} \sqrt{\frac{2g\gamma R^1 T_c}{(\gamma - 1)M} \left\{ 1 - \left(\frac{p_e}{p_c} \right)^{\frac{\gamma - 1}{\gamma}} \right\}} \tag{8.10}$$

From this expression it can be seen that if a propellant reacts under defined rocket chamber and nozzle conditions, its specific impulse is proportional to the square root of the temperature produced in the chamber by its reaction, and inversely proportional to the square root of the mean molecular weight of the gases produced, while also depending in a complicated way on the ratio of specific heats of the gases. The specific impulse as thus defined is therefore calculable by thermochemical methods for defined conditions of operation. The chamber gas temperature T_c is also nearly proportional, for a given gas composition, to the heat produced in the chemical reaction.

An efficient propellant will therefore be one which has a high heat of reaction, and produces gases of low average molecular weight. Now since in most high-temperature reactions (e.g. flame reactions) of commonly used substances the products of reaction are simple substances of relatively low molecular weight such as nitrogen, water vapour and oxides of carbon, the preponderating influence in most practical cases is the temperature due to, and hence the energy produced by, the chemical reaction.

So far we have considered a criterion for the efficiency of the propellent substance alone. The rocket motor, however, also contains such hardware as the nozzle, rocket motor chamber, with any thermal insulating material provided, means for retaining the propellant in place in a solid-propellant rocket, or in the case of liquid propellants equipment for holding them and for driving them into the chamber. It is natural, therefore, to look for a criterion of efficiency of the rocket motor as a whole. Returning to equation (8.7) for the moment, we see that if the thrust and the rate of consumption of the propellant are constant throughout the time t of operation of the rocket motor

$$I_s = \frac{Ft}{wt} \tag{8.11}$$

The product (Ft) of the thrust and the time for which it acts is called the total impulse, and wt is the total weight of propellant consumed. Under conditions of constant thrust, therefore, we may write

$$I_s = \frac{\text{Total Impulse}}{\text{Propellant Weight}}$$

and this can be generalised to cover cases when the thrust is not constant. It is then natural to consider as a criterion of efficiency of the rocket motor as a whole, the ratio of the total impulse to the weight of the whole rocket motor, a ratio sometimes called the *over-all specific impulse* of the rocket motor. It is evident that clever engineering design of the hardware to keep its weight as low as possible, as well as propellant of high specific impulse, contribute to raise the over-all specific impulse. It will also be appreciated that very high propellent specific impulse, entailing as is evident from equation (8.10) a very high temperature and high pressure of operation, tends to demand more insulation or other means of keeping the chamber and nozzle temperatures within safe limits, and greater thicknesses and therefore weights of material to contain the pressure, so that it aggravates the difficulties of designing the hardware to low weight.

We are now in a position to consider the substances to be used as propellants and their reaction in the rocket motor. In practice, either liquids or solid substances capable of energetic chemical reaction in a self-sustained manner may be used.

LIQUID PROPELLANTS

Liquid propellants may be incorporated in either mono- or bi-fuel systems.[3]

The best-known liquid monopropellant is concentrated hydrogen peroxide H.T.P. (80–85 per cent. H_2O_2). It is spontaneously decomposable into steam and oxygen when catalysed by various substances, notably permanganates.[4]

$$2H_2O_2 \longrightarrow 2H_2O + O_2 \qquad (8.12)$$

It was used, for example, in the launching device for the V-1 and the turbine-driven pump system of the V-2. It is also used in submarine propulsion and in aeroplane take-off units.

Usually hydrogen peroxide is utilised in bi-fuel propellent systems with fuels such as alcohols in order to use up the free oxygen and increase the energy release.

Other bi-propellent systems include liquid oxygen with alcohol as used in the V-2, and concentrated nitric acid and aniline as used in a number of aeroplane take-off units.

If the oxidising agent and the fuel are stored separately until they meet in the combustion chamber, then many of the difficulties of using two liquids are overcome and quite cheap simple liquid pairs can then be found which provide energetic reactions, such as concentrated nitric acid and kerosene, or liquid oxygen and a variety of combustible liquids.

Another monopropellant is methyl nitrate (CH_3NO_3), which is a powerful explosive and very dangerous in use. Possible liquid propellants include nitromethane (CH_3NO_2), nitroethane ($C_2H_5NO_2$), ethyl nitrate ($C_2H_5NO_3$), and more recently normal

TABLE 18
THERMOCHEMICAL DATA FOR SOME LIQUID MONOFUELS

	Formula	Heat of Combustion CV:WL cal./gm.	Calorimetric Value		Gas Temperature under C.P.W.V. conditions (° C.)	Calculated Decomposition Equation for C.P.W.V. conditions	Remarks
			CV:WL cal./gm.	CP:WV cal./gm.			
Hydrogen peroxide (100 per cent.)	H_2O_2	—	699	381	1,010	$H_2O_2 \longrightarrow H_2O + \frac{1}{2}O_2$	
Hydrogen peroxide (90 per cent.)	H_2O_2	—	629	234	760	$H_2O_2 + 0{\cdot}21\ H_2O$ $\longrightarrow 1{\cdot}21\ H_2O + \frac{1}{2}O_2$	
Hydrogen peroxide (80 per cent.)	H_2O_2		560	189	520	$H_2O_2 + 0{\cdot}47\ H_2O$ $\longrightarrow 1{\cdot}47\ H_2O + \frac{1}{2}O_2$	
Nitromethane	CH_3NO_2	2,880	1,220	1,060	2,400	$CH_3NO_2 \longrightarrow 0{\cdot}178\ CO_2$ $+ 0{\cdot}822\ CO + 0{\cdot}678\ H_2$ $+ 0{\cdot}822\ H_2O + 0{\cdot}5\ N_2$	
Nitroethane	$C_2H_5NO_2$	4,390	344	304	660	$C_2H_5NO_2 \longrightarrow 2CO + 2{\cdot}5H_2$ $+ 0{\cdot}5\ N_2$	In practice a higher decomposition temperature (900° C.) has been observed. This is probably due to formation of hydrocarbons and carbon.
Methyl nitrate	CH_3NO_3	2,080	1,640	1,430	3,500	$CH_3NO_3 \longrightarrow 0{\cdot}57\ CO_2 + 0{\cdot}43\ CO$ $+ 1{\cdot}43\ H_2O + 0{\cdot}07\ H_2 + 0{\cdot}5\ N_2$	
Ethyl nitrate	$C_2H_5NO_3$	3,450	857	739	1,650	$C_2H_5NO_3 \longrightarrow 0{\cdot}22\ CO_2$ $+ 1{\cdot}78\ CO + 1{\cdot}72\ H_2$ $+ 0{\cdot}78\ H_2O + 0{\cdot}5\ N_2$	

and isopropyl nitrate ($C_3H_7NO_3$), which is finding extensive application in starters for jet aeroplane engines.

The liquid fuel field is a large and expanding one and it is impossible to give more than these few brief remarks to it here. A few useful literature references are, however, appended.[5]

Some thermochemical data for a number of liquid monopropellants are given in Table 18.

It may be remarked that liquid-propellant rocket motors turn out in practice to be rather complicated devices involving considerable engineering, with their liquid tanks, pumps and metering devices, and reaction chambers complicated by the need to effect first-class mixing of the propellent liquids. The result is that, like gas-turbine engines, they tend to become costly for short-range, single-shot applications, besides usually entailing the transport and handling of rather unpleasant and dangerous liquids like concentrated nitric acid, hydrogen peroxide and liquid oxygen. Consequent upon the advances in solid-propellant rocketry made since the war, liquid-propellant rockets are tending to be designed for cases when repeated use is possible (e.g. to provide a take-off boost for aircraft) or for very long-range rockets. The fact that in America it is now proposed to use solid-propellant rocket motors for a Fleet Ballistic Missile gives some indication of the range (800–1,500 miles) up to which they are beginning to be preferred to liquid-propellant rocket motors. It should not be thought, however, that liquid-propellant rockets have expended their development potential and must now wait passively to be overtaken by solid-propellant rockets. This is certainly not the case, and indeed the prospects of a dramatic increase in performance from the present level are potentially great in the field of liquid propellants.

SOLID-PROPELLANT MOTORS

An outline sketch of a solid-propellant rocket motor is shown in Fig. 9. The propellant is arranged to burn on all the surfaces except its external cylindrical one, which is shown as bonded to the wall of the rocket motor tube, and thus unable to burn on this surface. An alternative arrangement is to have the propellent charge as a separate entity, but with its external cylindrical surface prevented from burning by an " inhibitor " coating of suitable material which does not burn to any appreciable extent during the burning of the propellent material.

Solid charges for rocket motors are dealt with in detail in Chapter 9.

For a material to be useful as a solid propellant for rockets, it must burn in a " layer-by-layer " fashion, so that if the conditions are uniform over the whole surface of the propellant, that surface regresses at a uniform speed into the propellant during burning. This rate of regression, as we saw in Chapter 5, is called the *rate of burning* under those conditions and is one of the most important parameters relating to a solid-propellant composition. For propellants in general, it is a function of the pressure at which the reaction is taking place, the temperature of the propellent material, and the rate of flow parallel to the propellent surface of the gases produced in the burning. If the conditions of burning are such that the last-mentioned effect can be neglected, then over the range of pressure of practical interest for rocket motors the dependence of rate of burning on pressure can usually be expressed by a law of the form (cp. Chapter 5)

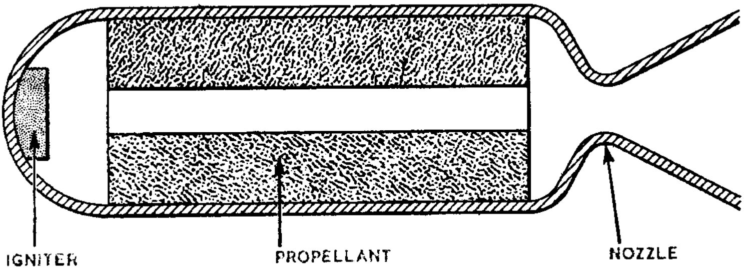


FIG. 9. Diagram of solid-propellant rocket motor.

$$r = ap_c^n \tag{8.13}$$

where r is the rate of regression of the burning surface when the rocket motor chamber pressure is p_c, a is a constant and n is another constant called the *rate of burning index*. Because of the form of this law, the relation between pressure and rate of burning yields a straight line of slope n when plotted on log-paper, and it is also found that the effect of temperature on the propellant is practically wholly an effect on the constant a. Thus the effects of charge temperature and chamber pressure on the rate of burning can be exhibited by a graph of the type shown in Fig. 10.

The magnitude of the rate of burning index n is of considerable importance in determining whether a propellant is capable of being used in practice as a rocket propellant. If ρ is the density of the

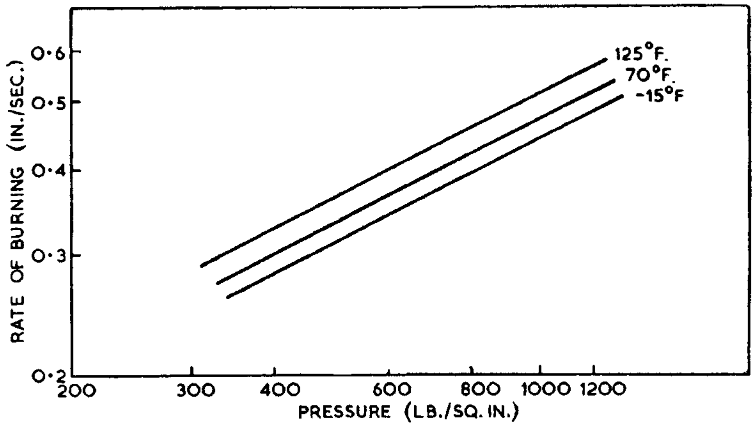


FIG. 10. Effects of rocket-chamber pressure and charge temperature on the rate of burning of a solid propellant.

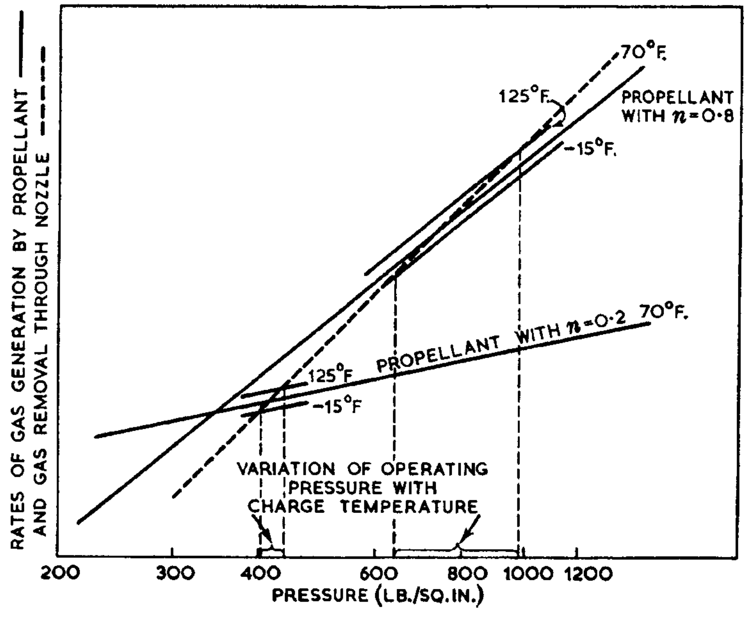


FIG. 11. Effect of propellant rate-of-burning index *n* on conditions and stability of operation of a solid-propellant rocket motor.

propellant and S is the surface area exposed to burning, then the mass rate of gas production by the propellant is $Sr\rho$, and hence using the rate of burning law

$$\text{Mass rate of gas production in rocket motor} = aS\rho p_c^n \quad (8.14)$$

while from equation (8.2) it can be seen that the mass rate of discharge through the nozzle of the rocket is proportional only to the pressure (the other quantities in the equation being determined by the rocket and its nozzle) and so can be written

$$\text{Mass rate of gas removal from rocket motor} = bp_c \quad (8.15)$$

For stable operation, the rates of production and removal of the gas must obviously be equal. Now let us assume that such a condition has been achieved and then imagine that some irregularity momentarily raises the chamber pressure by a small increment δp_c. Then the mass rate of gas production becomes, to the first order of the small quantity $\delta p_c/p_c$,

$$a\delta\rho p_c^n \left(1 + n\frac{\delta p_c}{p_c}\right) \quad (8.16)$$

while the same rate of discharge becomes

$$bp_c \left(1 + \frac{\delta p_c}{p_c}\right) \quad (8.17)$$

Hence the ratio of rate of production to rate of removal of gas is now altered by the factor

$$\frac{1 + n\dfrac{\delta p_c}{p_c}}{1 + \dfrac{\delta p_c}{p_c}} \quad (8.18)$$

and it is obvious that if $n > 1$, the rate of gas production will have increased faster than the rate of removal. This will entail a further increment of pressure rise, which by the same argument will entail another, and so on until the rocket chamber bursts. If n is less than 1, the increase in rate of gas production caused by the disturbance is less than the increase in rate of removal of gas, so that the pressure settles down again to its original level.

It is therefore essential that n should be less than 1 for a propellant to be capable of use in a rocket, and a further analysis shows that the smaller n is the better for this purpose.

An equivalent argument leading to the same conclusions can be conducted in graphical terms using the type of graph shown in Fig. 10, if we re-label the ordinates as in Fig. 11 which we are

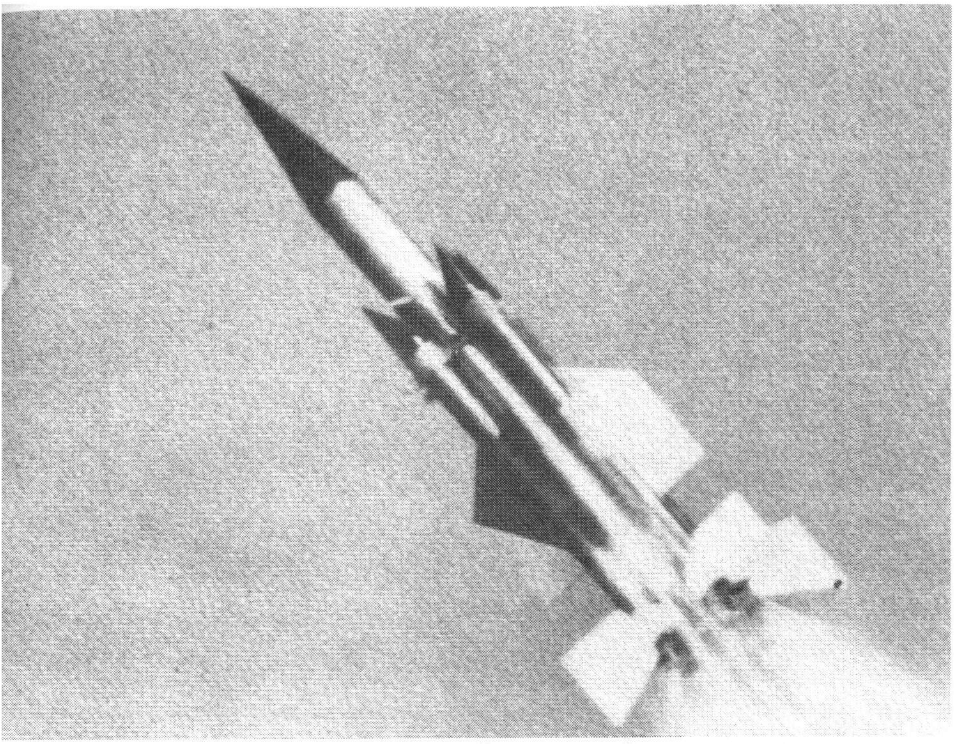
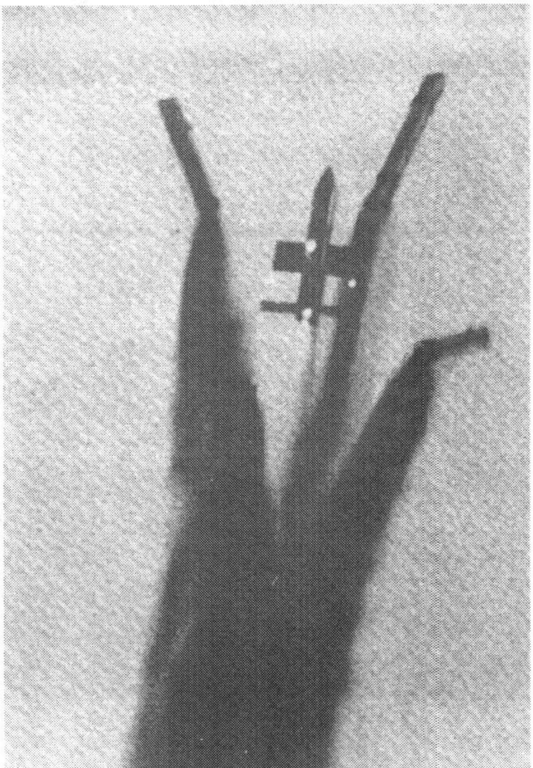


PLATE 5

(*above*) Ground-to-air guided missile (Red Shoes) in flight.



Motor test vehicle at separation.

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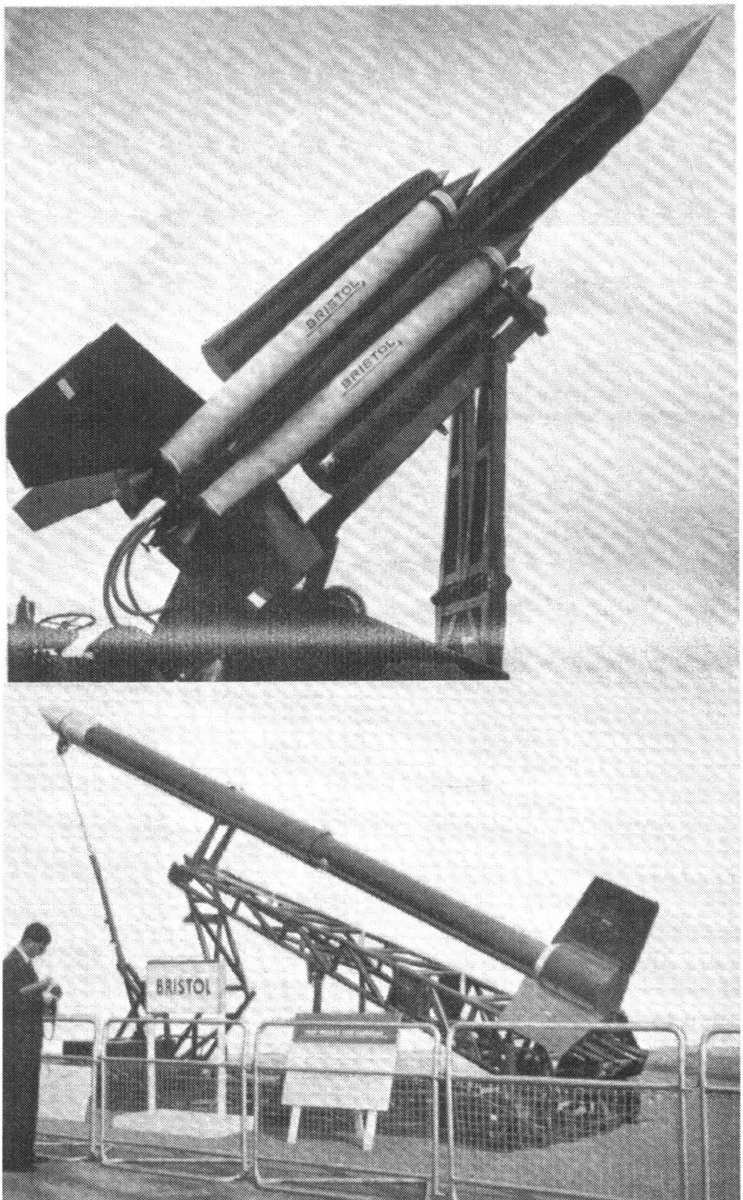
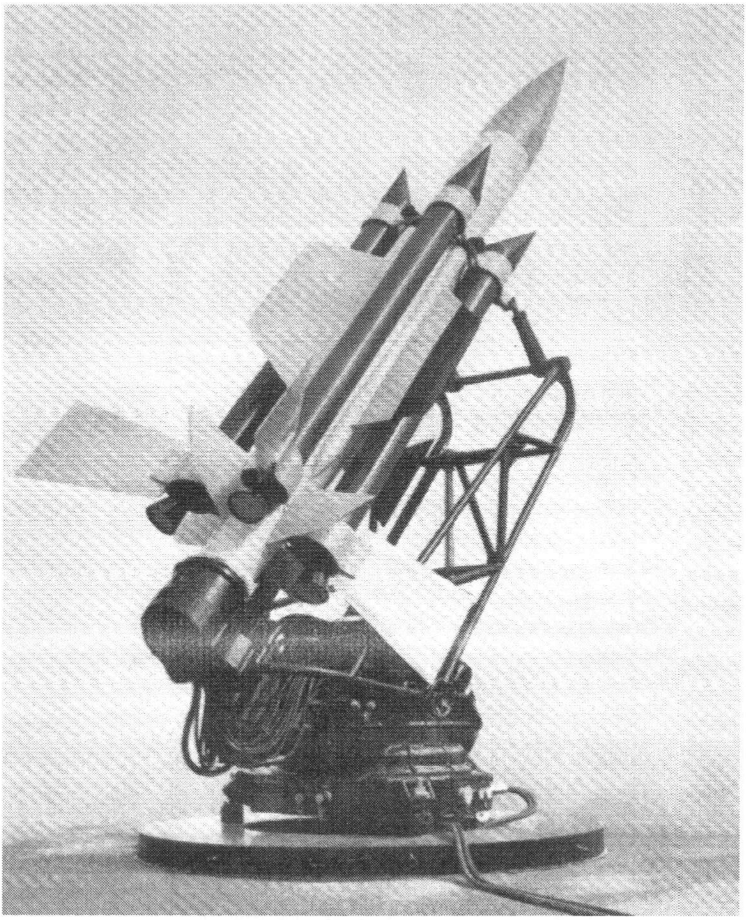
PLATE 6



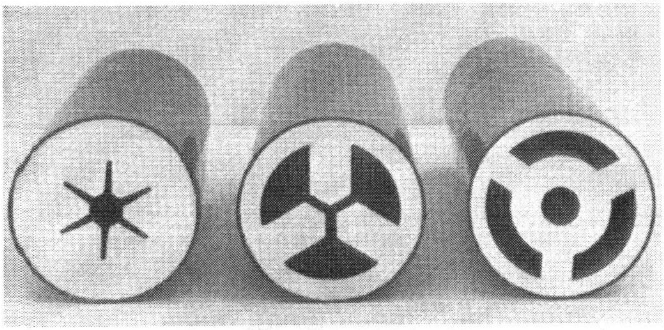


English Electric Thunderbird surface-to-air guided weapon.

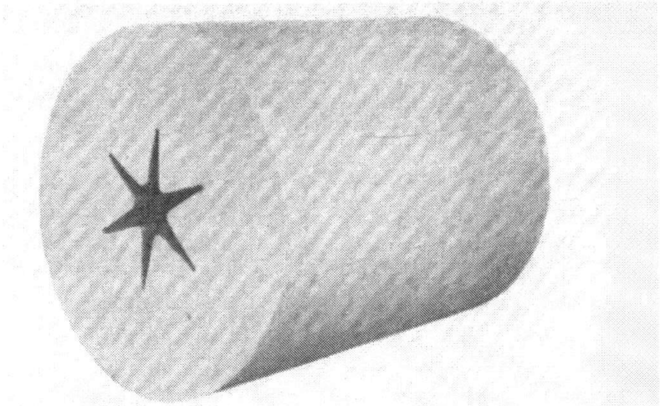
(*top left*) Bristol/Ferranti Bloodhound surface-to-air guided weapon.

(*bottom left*) Thirteen-inch diameter boost-rocket motor.

PLATE 8



(*a*) Typical designs of externally-inhibited propellant charges. Designs such as these maintain an almost constant area of burning during the burning of the propellant.



(*b*) Pressed ammonium nitrate propellant. The external surfaces are inhibited by a layer of inert pressed powder.

entitled to do so long as the burning surface S is constant. The curves of Fig. 10 then become curves showing the relation between pressure and rate of gas production and we can superimpose on these a line showing the relation between pressure and rate of removal of gas by the nozzle.

If n is less than 1, the " production " and " removal " lines cross as in Fig. 11 and the rocket operates at the pressure corresponding to the point of intersection. A disturbance of the operating pressure upwards is at once seen to increase the rate of removal of gas more than it does the rate of production, and the operating pressure settles back to the point of intersection. If n were greater than 1, as in Fig. 12, an upward pressure disturbance would lead to gas being produced faster than it is removed, or a downward disturbance would lead to the gas being removed faster than it is produced, and the rocket would burst or cease burning according to the direction of the disturbance.

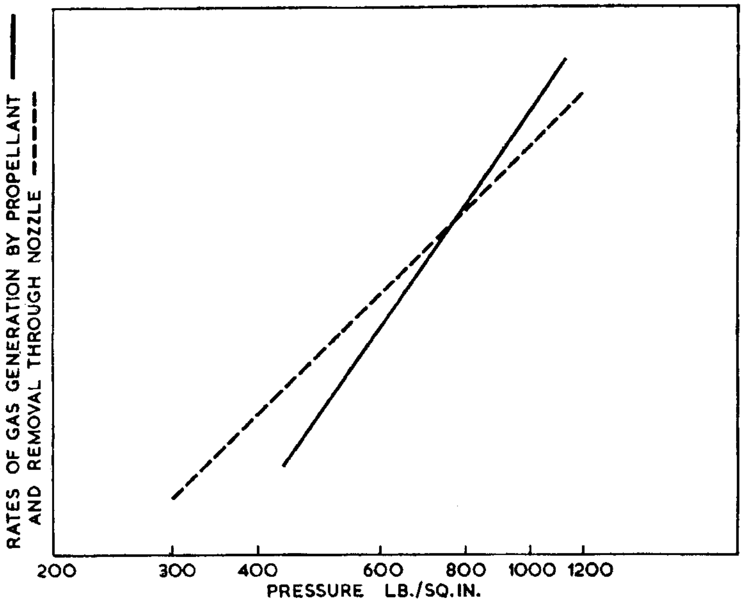


FIG. 12. Unstable condition of operation if the rate-of-burning index of the propellant is larger than unity.

Fig. 11 shows another advantage of a low value of n, namely that the operating pressure varies less with the charge temperature, other things being equal, because of the greater angle of intersection of the gas-production and gas-removal lines. This is of some importance in designing high-performance rocket motors to operate over a wide temperature range, because the extra strength built into the rocket motor case to withstand the operating pressure at the highest temperature is just a penalty at lower temperatures, and the ideal would be a propellant which would not change its operating pressure with temperature.

THE TESTING OF SOLID-PROPELLANT ROCKET MOTORS

Having designed and made a solid-propellant rocket motor, it is of course necessary to perform tests to establish that it will reliably meet the requirements for which it was designed. Clearly there will be a considerable number of tests which can be classed as " inspection checks ", whose object is to verify that the propellent charge, the motor body, and all the other components do in fact accord with the requirements of the design. Many of these are of a general nature such as would be applied to objects of their kind, whether or not they were to be used in rockets; e.g. chemical analysis of the propellant, hardness tests on metal components to check their strength, etc. A hydraulic pressure test of the motor body, to ensure that it has the required strength and is free from leaks, is a common practice in the case of large motor bodies. Since, as we have seen, the basis of the propellent charge design is that of layer-by-layer burning of the propellant so that its surface area at any instant during burning is calculable, it is important also to be able to check that the charge is a dense compact mass, without adventitious gaps or inclusions of air, since any bubble or internal crack provides additional and undesigned surfaces on which burning will take place. Particularly with large and expensive rocket motors, designed to be used to propel still larger and more expensive missiles, the direct cost of a failure of any kind is very high, and the importance of the development and application of thorough inspection techniques cannot be over-stressed.

Finally, however, the verification of the design can only be effected by measuring the performance of the rocket motor, which entails measuring its thrust during the period of burning. In order to do this, it is usually mounted on a stand which leaves some freedom of movement in its axial direction only, but with its forward end bearing against a thrust-measuring device. It is usual, during such a test, to measure also the pressure inside the rocket chamber, by means of a suitable tapping from the chamber which is connected to a pressure-measuring device. In addition, the opportunity of such tests is frequently taken, to measure the temperature at various regions of the nozzle and the motor body, since the strength of such components usually depends upon their temperature and it is important to know that the temperatures attained during the functioning of the rocket will not reduce their strength below the design figures.

In modern practice, the instruments for measuring thrust, pressure and temperature are usually devices for converting these quantities into an electrical analogue, such as voltage or frequency. The information in electrical form is conducted to a recording station and is there recorded in permanent form, for example, on photographic film via the agency of cathode-ray oscilloscopes, or on magnetic tape. For example, the thrust can be used to compress a rod or tube of metal, to which is attached a strain-gauge (an element of fine wire whose electrical resistance changes when it is extended). If the strain gauge is included in a resistance bridge circuit, the effect of the thrust is to unbalance the bridge. Similarly, pressure can be measured by strain gauges attached to a metal tube designed to deform when pressure is applied inside it. Temperature can be measured by thermocouples or thermistors applied to the motor body or nozzle. It is, of course, important to record also the time from some convenient datum instant, such as the instant of application of the firing current to the igniter of the rocket. It is also important that the various recording devices be suitably calibrated, so that the information recorded in photographic or magnetic form can be reconverted into terms of thrust, pressure or temperature.

The cost of a single firing of a large modern rocket motor is by no means inconsiderable, and it is important that all the intended records be obtained. Hence, in modern practice it is usual to duplicate all the recording gear in case any one information channel should accidentally fail. Further, it is quite frequent to have some degree of automation in the firing, so that, for example, a single pressing of a button sets in operation a sequence of relays which check that all the channels are operating, and apply appropriate calibration signals to the recording medium; and only if all this has been done correctly is the rocket igniter current applied by a further relay. Experience shows that this is far quicker and more reliable than having these operations done by human agency. Plate 3 shows the instrumentation in a modern rocket-testing establishment.

Such " static " tests, so-called because the rocket is not free to fly, are done not only at ambient temperature, but also at the highest and lowest temperatures at which the rocket motor may be used; and during development work they are also made after subjecting the motor to various other conditions which may occur in practice, for example, after long storage, storage under conditions of alternating high and low temperature, after rough-handling tests to simulate vibration and jolting during transport, or dropping during handling.

The final tests usually comprise actual flight tests, in course of which the pressure in the rocket chamber is transmitted by radio to a ground station, while the thrust is evaluated from the actual trajectory flown by the flight test vehicle in which the rocket motor is mounted. Such flight tests serve to confirm that the accelerations experienced by the rocket and its components during flight do not upset its performance.

APPLICATIONS

The principal application for which rocket motor development work has been carried out in an intensely active phase since the war is, of course, for the propulsion of guided missiles. Fig. 13 gives an outline sketch of a typical ground-to-air guided missile.[6] Such a missile is usually propelled from its launcher on the ground and accelerated to its designed operating speed, which is supersonic, by means of " boost " rocket motors which burn for only a few seconds, but during this time deliver a thrust numerically equal to several times the weight of the missile, and often several times as much as that of the largest jet engines. Having fulfilled their function, the boost motors then separate from the missile, while a " sustainer " rocket motor inside the missile starts burning, and delivers during a much longer time a thrust sufficient to maintain the missile at its operating speed while it manœuvres in pursuit of its target. Fig. 14 gives an outline sketch of the missile with its booster rockets.[6] Plate 4 shows a typical boost rocket motor and sustainer rocket motor for such a missile. Plate 5 shows a large ground-to-air guided missile in flight with its booster still in place and the separation of the boosts from the missile in flight. Plates 6 and 7 are photographs of static exhibits of guided weapons taken at the Farnborough Flying Display and Exhibition, 1957.

In this chapter on rocket motors it has not been possible to do more than to outline the scientific principles which underlie the transformation of the chemical energy of the rocket propellant into energy of motion. The problems of putting these principles into practice, which range over the chemistry of propellants and their combustion reactions, the internal ballistics of the gas motion inside the rocket, the engineering design and the metallurgy of the rocket motor case, the heat transfer problems in safely handling high-pressure gases whose temperature exceeds the melting point of the

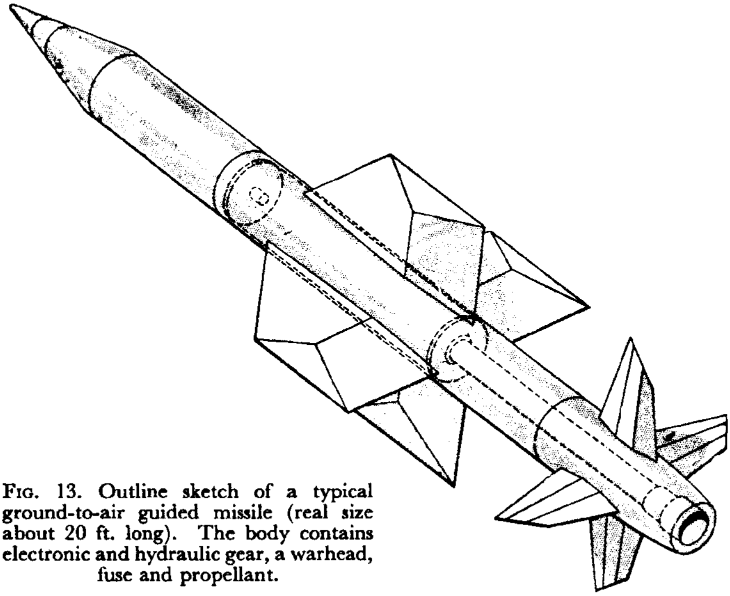


FIG. 13. Outline sketch of a typical ground-to-air guided missile (real size about 20 ft. long). The body contains electronic and hydraulic gear, a warhead, fuse and propellant.

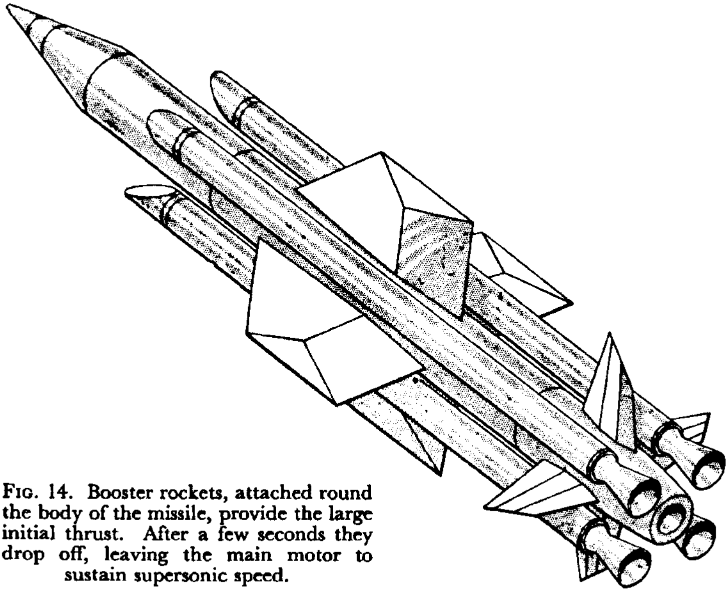


FIG. 14. Booster rockets, attached round the body of the missile, provide the large initial thrust. After a few seconds they drop off, leaving the main motor to sustain supersonic speed.

rocket motor case materials, and the instrumentation required for testing rocket motors and propellants in development and manufacture, are of great interest and offer high-class challenges to the scientists engaged in such work, but would require a book, rather than a chapter, to discuss them adequately.

The launching of the Russian satellites, particularly the famous " Sputnik," has aroused great interest throughout the world in space flight. Beard and Rotherham have recently written a book, *Space Flight and Satellite Vehicles* which contains much interesting information on this theme.[7]

REFERENCES

1. A Comprehensive Bibliography of Literature on Solid Propellants and Solid-propellant Rockets has been given recently by:
ZAEHRINGER, A. J. *Jet Propulsion* (1957), **27**, 900.
The reader may also be recommended to the following recently published books which, besides giving a fuller treatment of the subject of this chapter, contain extensive literature references:
SUTTON, G. P. *Rocket Propulsion Elements*, Second Edition. (John Wiley & Sons, New York, 1956.)
BONNEY, E. A., ZUCROW, M. J., and BESSERER, C. W. *Aerodynamics—Propulsion—Structures and Design Practice.* (Nostrand, 1956.)
2. WHEELER, W. H., WHITTAKER, H., and PIKE, H. H. M. *J. Inst. Fuel* (1947), **20**, 137.
3. TAYLOR, J., and SILLITTO, G. P. The Third Symposium on Combustion, Flame and Explosion Phenomena, Paper No. 73, p. 572. (The Williams & Wilkins Company, Baltimore, 1949).
4. SCHUMB, W. C., SATTERFIELD, C. N., and WENTWORTH, R. L. *Hydrogen Peroxide.* (Am. Chem. Soc. Monograph No. 128, New York, 1955.)
5. SUTTON, G. P. *Rocket Propulsion Elements*, Second Edition. (John Wiley & Sons, New York, 1956.)
WHEELER, W. H., WHITTAKER, H., and PIKE, H. H. M. *J. Inst. Fuel* (1947), **20**, 137.
BRAUN, W. VON. *J. Brit. Interplan. Soc.* (1951), **10**
SEIFERT, H. S. *Jet Propulsion* (1955), **25**, 594.
6. SILLITTO, G. P. *I.C.I. Magazine* (1958), **36**, No. 256, 48.
7. BEARD, R. B., and ROTHERHAM, A. C. *Space Flight and Satellite Vehicles.* (Newnes, 1957.)

CHAPTER 9

SOLID CHARGES FOR ROCKETS AND PROPULSION

Following our consideration of rocket motors in Chapter 8, we are now in a position to discuss in greater detail the materials to use as solid propellants for rockets and propulsion purposes.

As we have seen, they must be capable of self-sustained reaction or " burning " in absence of air, in a layer-by-layer manner, with a rate-of-burning index less than unity and preferably as low as possible, and preferably also with a low temperature coefficient of rate of burning. They should also evolve as much heat energy as possible in reacting, and the products of reaction should preferably be gases of low molecular weight. In addition, of course, they must be reasonably safe to make, handle and use, and adequately stable chemically so that they can be safely stored for considerable periods of time.

The inherent simplicity of solid propellent charges has led to a considerable interest in their development and much effort is being devoted to them, especially for rocket applications.

For rocket motors and for most propulsive purposes, the solid charge, as we have seen, is required in a form which will yield product gases in specified and controlled amounts. It is usual to achieve this by utilising compacted geometrical forms of which the area in combustion will be just correct to supply the right amount of gas at the operating pressure.

There are several methods of producing impervious compacted masses. First of all there is the hard colloid charge like cordite, secondly the plastic-like charge which can be made by compounding asphalt and rubber-like fuels with oxidising salts, thirdly the cast charge which is poured in the molten condition into a mould where it sets, and lastly the pressed charge formed by compressing dry mixed compositions at high pressure in a suitable mould. In each case the technique must be adequate to produce large-size products which are not progressively penetrated by the product gases and consequently do not " run " out of control.

Blackpowder (see Chapter 2), the oldest known propellant, continues to be used in small " firework " rockets because it is cheap and easy to make, but it falls far short of modern propellants in energy output, while also its reaction gives a high proportion of solid products. Practically speaking, the propellants used nowadays are either of the cordite type (see Chapter 5), comprising nitroglycerine and nitrocellulose with stabilisers, and other ingredients to control the rate of burning, or the class of " composite " propellants consisting of ammonium or potassium perchlorate as oxidant with a combustible " binder " which serves as the fuel and usually consists of a natural or synthetic plastic or elastomeric (rubbery) material, or ammonium-nitrate-based " pressed charges " which use ammonium nitrate as the main gas-producing and oxidising material, with a proportion of combustible material as fuel, ammonium dichromate to catalyse the reaction of the ammonium nitrate, potassium nitrate to control its crystalline transitions, and small quantities of burning-rate-controlling substances (see Chapter 7).

All these types of propellant give satisfactory results, and none can be said to have major advantages over the others, for all types of rockets. All are undergoing active development with a view to extending their potential fields of application, and each advance in development of any one is accepted as a challenge by workers with the others, and often leads to similar or to countervailing advances in development of the others.

CORDITE AND CAST DOUBLE BASE CHARGES

The cordite type of propellant has a long history of manufacture, study and use. It was used on a considerable scale for rockets in the Second World War.

The size and shape of cordite charges which can be made by conventional methods is, however, restricted and for some applications very large charges are required.

The manufacture of rocket cordite has been described in some detail by Wheeler, Whittaker and Pike,[1] but most of the recent work of making such charges and their compositions is confidential. One important advance which has been made and which has been published is the so-called " cast double base propellant " process,[2] in which the rocket charge is made by loading a mould with granules of nitrocellulose powder, filling the interstices between the granules with nitroglycerine mixture, and causing the nitrocellulose powder to swell and gelatinise with the liquid to form a horny coherent solid by heating the mould. One advantage of the process over the older extrusion processes for cordite is that, as can be seen from this brief description, there is almost no limit to the making of very large charges with relatively inexpensive equipment and little labour cost.

A limited amount of information on cast double base charges has been published by G. P. Sutton.[2] Table 19 extracted from his book gives particulars of the composition and properties of typical charges, while Table 20 shows representative compositions both of extruded and cast double base propellants as used in U.S.A. Sutton indicates that a variety of compositions has been successfully used with various additives (5 to 30 per cent.) of which the object is to improve physical properties, assist in manufacture, confer better stability under various conditions of storage, suppress flash from the venturi exhaust of the rocket motors, and inhibit ignition by radiation of energy through the translucent grain. He states that an increase in the nitrocellulose content of the charge usually improves physical strength, whereas a high nitroglycerine content increases the performance (specific thrust) and rate of burning.

The cordite type of propellant is always used as a " discrete " charge, i.e. one which is completely made and then inserted into

TABLE 19

COMPOSITIONS AND PROPERTIES OF TYPICAL CAST DOUBLE BASE CHARGES *

Propellent Type Propellent System	Cast Double Base Nitrocellulose (NC) Nitroglycerine (NG) Plasticiser (P) Miscellaneous
Typical ingredient variation, per cent.	NC (45–55) NG (25–40) P (12–22) Misc. (1–2)
Adiabatic flame temperature, °F.	2,600–4,000
Average molecular weight, lb. per mole	22–28
Specific heat ratio	1·24–1·26
Typical sea level specific impulse, sec.	160–220
Characteristic velocity, ft./sec.	3,500–4,200
Burning rate at 1,000 psi and 70° F., in./sec.	0·22–0·37
Burning rate exponent, *n*	0·1–0·8
Specific weight, lb./in.^{3}	Average 0·057
Maximum volume impulse at 1,000 psi, lb.-sec./ft.^{3}	19,500
Temperature sensitivity of pressure (psi/psi °F.), per cent.	0·1–0·8
Lower combustion limit, psi	<500
Pressure limit, psi	$>5,000$
Probable allowable operating temperature limits, °F.	-30–140
Storage stability,† temperature/humidity	bad/fair
Smoke	none
Mechanical properties	hard and tough

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* Extract from *Rocket Propulsion Elements*, G. P. Sutton, 2nd Ed., p. 313, Table 9–1, Properties of Some Propellent Systems.

† Storage stability is rated bad if the propellant cannot be stored indefinitely at temperatures greater than 150° F.

TABLE 20

REPRESENTATIVE COMPOSITIONS OF EXTRUDED AND CAST DOUBLE BASE PROPELLANTS *

Ingredients	Extruded Ballistite (JPN)	Expl. Casting Propellant	Expl. Castable Propellant	German Extrusion World War 2
NC	51·5	47·0	59·9	64·7
NG	43·0	37·7	38·7	
Diethyl phthalate	3·25			
Ethyl centralite	1·0	1·0	0·9	
Potassium sulphate	1·25			
Carbon black or graphite	0·2	0·3	0·2	0·1
Candelilla wax	0·22			
Dimethyl phthalate		14·0		
Diethyleneglycol dinitrate				29·3
Phenyl urethanes				4·8
Arcardite				0·1
Barium sulphate and titanium dioxide				0·9
Diphenylamine			0·2	

* Furnished in part by C. E. Bartley, late of Grand Central Aircraft Company, and in part by U.S. Naval Ordnance Test Station, China Lake, California.

the rocket motor. Although in the older rockets it was made in various shapes such as tubes burning on both cylindrical surfaces, or cruciform shapes burning on their external surface, in the larger modern rockets " internal burning " charges are used and are inhibited on the outer cylindrical surface. The usually desirable feature of a nearly constant burning surface so as to give nearly constant pressure and thrust during the operation of the rocket motor is obtained by devising a suitable charge geometry, such as a star-shaped perforation. Charges of suitable shape are shown in Plate 8 (*a*), in which can also be seen the inhibitor on the external cylindrical surface.

COMPOSITE PROPELLANTS

The composite type of propellant covers a wide class, depending upon the type of binder (fuel) used. Some are plastic propellants of the consistency of plasticine, not thermosetting, but retaining their plastic properties throughout their life. In general, such compositions comprise 90 per cent. of solid ingredients milled with a binder to give the required degree of plasticity. Considerable development has also taken place, particularly in the U.S.A., in the preparation of a solid propellant consisting of a mixture of a finely ground oxygen provider, such as potassium perchlorate, well dispersed in asphalt. Such a fuel mixture can be cast in the rocket tube or motor.[1] Several members of this class lend themselves to " case-bonding ", that is to say, the charge is formed actually inside the rocket motor case and adheres to the internal surface of the case. Thus there is no non-burning inhibitor present and the rocket motor is filled to the highest degree possible with propellant; consequently the over-all specific impulse is as high as can be attained with the composition and rocket motor in question. Since the coefficient of thermal expansion of steel, which is normally used for rocket motor cases, is much less than that of propellent materials in general, it is evident that a case-bondable composition must be plastic or elastic over the whole temperature range which the rocket motor may encounter in storage or use, so that variation of temperature does not set up in the charge, or in the bond between the charge and the wall, stresses large enough to crack the charge or cause it to separate from the wall.

The value of composite propellants lies in their potential cheapness compared with those based on nitrocellulose and nitroglycerine. Consequently, much effort is being directed towards the production of a cheap composite propellant possessing low sensitiveness, flexibility of rates of burning and ability to withstand rough handling and the effects of climatic storage. Since major developments still remain as classified security information, information is scanty and the following outline derived from published material must of necessity be fragmentary.

A variety of oxidants has been employed including ammonium picrate and the nitrates and perchlorates of sodium, potassium and ammonium. The use of lithium perchlorate has been suggested[3] as one of the better oxidants from the point of view of performance, but it is very hygroscopic and its combustion products include solids.

Among the fuels examined have been organic polymers, asphalt, nitroguanidine, guanidine nitrate, synthetic rubbers, metallic powders, e.g. aluminium,[3] carbazole and hexanitrodiphenylamine. In most cases details of the exact nature of a fuel-binder are lacking although certain criteria have been suggested[4] for such polymers. These were that the polymer should be an elastomer with good low-temperature properties, and have resistance to flow at high temperatures and high fuel value. A number of methods of preparation of the charges has been employed, including casting, extrusion and consolidation under pressure.

The Calcit range of propellants[5] produced in association with Aerojet[6] used potassium perchlorate (75 per cent.) as oxidant, with asphalt (25 per cent.) containing a little oil as binder. An early example, Calcit 53, could only be fired at temperatures between 40° F. and 100° F. Potassium perchlorate was also the oxidant in a Thiokol-based propellant[7] prepared by casting.

Ammonium perchlorate has been used as the oxidant in an Aerojet formulation[8] which contains Texaco 18 asphalt (8 per cent.), cetyl acetamide (3 per cent.), dibutyl sebacate (5·5 per cent.), castor oil modified glycerol sebacate (3 per cent.), oxidant (73 per cent.) and chromium sesquioxide (2·5 per cent.). The use of a mixed catalyst (up to 4 per cent.) containing equal quantities of chromium sesquioxide and a metal oxide, from the group ZnO, Fe_3O_4, TiO_2, SnO_2, Al_2O_3 and CuO, was also investigated as a means of controlling rates of burning. The booster unit 15KS–1000 uses ammonium perchlorate together with a " plastic fuel ".

Nitroguanidine, carbazole, nitrocarbazoles and hexanitrodiphenylamine have been investigated[9] as fuels for certain oxidisers including the nitrates and perchlorates of sodium, potassium and ammonium and the chlorates of sodium and potassium. Guanidine nitrate and nitroguanidine in ammonium nitrate compositions are also the subject of a number of patents[10] relating among other aspects to their self-sustained decomposition, the decomposition of ammonium nitrate being sustained in the presence of chromates and dichromates of sodium, potassium and ammonium.

Potassium chlorate was the oxidant in a propellant formulated by Pigot-Moodie.[11] Its preparation involved potassium chlorate, manganese dioxide and a liquid hydrocarbon gelled by addition of stearic acid treated with hydrogen chloride in the presence of water.

A composite propellant of the NDRC class based on sodium nitrate (45 per cent.), ammonium picrate (45 per cent.) and a partially polymerised thermosetting resin (10 per cent.), e.g. phenol-formaldehyde, was fashioned into grains by a process of cold-moulding under pressure followed by a period of cure.[12]

The Phillips Petroleum Company appear to be producing, in large quantity, composite propellants containing ammonium nitrate, carbon black and a synthetic rubber. These M-15 rockets[13] are claimed to be capable of operation over the temperature range − 75° F. to 170° F.

The performance of some composite propellants, including for comparison blackpowder, used in signal rockets, is given in Table 21.

CAST CHARGES

A considerable amount of work has been done on the production of cast charges for propulsive purposes using ammonium nitrate as oxygen provider.

TABLE 21

PERFORMANCE OF SOME COMPOSITE PROPELLANTS, INCLUDING FOR COMPARISON BLACKPOWDER, USED IN SIGNAL ROCKETS

Propellant	Pressure Range	I sp.* sec.	n	r_b* in./sec.
Calcit Alt. 161 . . .	1,350–3,700	186	0·75	1·4–1·5
NDRC Type EJA 218B (Sod. nitrate, ammon. picrate, resin propellant as in Ref. 12)	600–1,000	180	0·45	0·2–1·0
Blackpowder . . .	100–1,000	70	0·5–0·8	0·1–0·5

*Source Zaehringer.[13]

In order to produce compositions which can be cast at temperatures sufficiently low to avoid thermal decomposition, it was necessary to use melting point depressants like sodium nitrate, magnesium nitrate, calcium nitrate or other salts of the same metals. To give a specific example used for a small rocket,[14] a tubular cast oxidising charge was prepared from a composition containing 72 per cent. ammonium nitrate, 16 per cent. sodium nitrate, 4 per cent. ammonium chloride and 8 per cent. ammonium dichromate as catalyser. In preparing the cast, all the ingredients except the chromate were fused at 115° to 120° C., and when the fusion was complete the melt was cooled to 110° C. and the finely ground ammonium dichromate was stirred into it. The mix was poured into a mould from which the cast was removed after it had solidified.

An example of a fully oxidised cast charge containing its own fuel may be quoted.[15] Fifty-eight parts of finely ground crystalline ammonium nitrate, 11·6 parts nitroguanidine and 7·2 parts dicyandiamide were fused together at a temperature of 105° C. and 8 parts of finely ground crystalline ammonium dichromate were then stirred into the melt. The melt was cast into cardboard moulds of the required form, from which the casts were removed completely cooled and solidified.

Using the methods described above, compositions can be devised to yield product gases at temperatures from about 360° to 2,000° C. by the addition of fuels in controlled quantities. The density of the charges produced can be as high as 1·7 gm./cm.^{3} and the gas yield is from 1,150 to 1,350 cm.^{3} per cm.^{3} of composition (at N.T.P.).

Cast charges of the above type are liable to set with cavities in them and it is impossible satisfactorily to make large charges by such techniques.

In order to overcome this trouble a method was devised[16] in which an air-cooled rotating mandrel dipped into the molten composition and built up a " cheese " by very thin layers which solidified as the mandrel rotated. This method was very successful in building up sound high-density charges, but it was too slow for bulk manufacture.

Another serious defect was found in the cast charges. On storage, if they passed through the 32° C. ammonium nitrate crystal form change they tended to crack. This work was done before the method of adding 10 per cent. of potassium nitrate to the ammonium nitrate (see Chapter 7) had been discovered and the compositions were consequently very liable to break up.

Another defect of cast charges was the difficulty of utilising whatever fuel was dictated by energy requirements. The method necessitated fuels soluble in ammonium nitrate or fuels which were suitable for suspension in the melt. Consequently, cast charges were abandoned after pressed compositions were developed.

PRESSED CHARGES

We have already described in Chapter 7 the investigations leading to the production of " cigar-burning " pressed charges of compositions containing ammonium nitrate in steel tube around 2 in. diameter. The success of these charges and their inherent simplicity and cheapness led to considerable developments, and extension of their application to various propulsive purposes. Most of the work in the U.K. has been carried out by the Nobel Division of I.C.I., and because of security requirements it is only possible to publish a limited account of the results, namely, what has appeared in the Patent Literature.

The charges have for the most part been based on ammonium nitrate and guanidine nitrate together with appropriate catalysts for their decomposition. These catalysts have already been discussed in Chapter 7. The charges are prepared by compressing a dry uniform mix of the constituents, including the catalyst, in a strong steel mould by means of a high-pressure hydraulic press, to the shape of the charge required, the compacting pressure being of the order of 5,000 to 10,000 lb. per sq. in. The finished charge is hard and rock-like in character.

Such pressed charges have been made in a range of sizes from ½ in. to 20 in. in diameter and have been used to operate reciprocating engines, turbo-starters for aircraft, starter motors for diesel engines, rocket motors and for a variety of other purposes.

There are certain properties common to these pressed charges which are of interest to describe before going into any details.

They provide a very wide range of gas temperatures from about 400° C. to 2,000° C. or so, according to the amount and nature of the fuel used. All types operate at pressures from atmospheric upwards and as the rate of burning is controlled by catalysts, sensitising agents and inhibitors, the rate of burning may be adjusted over a wide range. The form of pressed charges can be varied widely by a suitable configuration of moulds and pressing rams, or by machining and drilling.

Pressed charges, as do other charges, such as cordite, require to be inhibited on all surfaces which are not deliberately exposed for burning. This is done by means of a layer of an inert china clay mixture which is applied during the pressing of the charge and is compacted with it. It is called a " shirt " and provides a very effective means of protecting the surface from ignition and allowing controlled burning of a pre-selected geometric form to take place. Plate 8 (*b*) shows a pressed ammonium nitrate charge with a protecting " shirt ".

Another method of protecting the external surface of the charge is to press-load it into a container which is lined with a layer of heat-insulating material of a relatively non-combustible nature such as is used for gaskets for high-pressure steam joints. This effectively fulfils the function of preventing decomposition along the peripheral surface of the column of composition ahead of the burning surface, and allows steady " cigar " burning to take place.

A considerable amount of information on pressed charges, including detailed examples of applications, has been published in various patents [17] and we can do little better than quote from these. Strictly speaking, these are power cartridge applications, which are dealt with in Chapter 10, but it is considered logical and preferable to deal with a few examples in the present chapter.

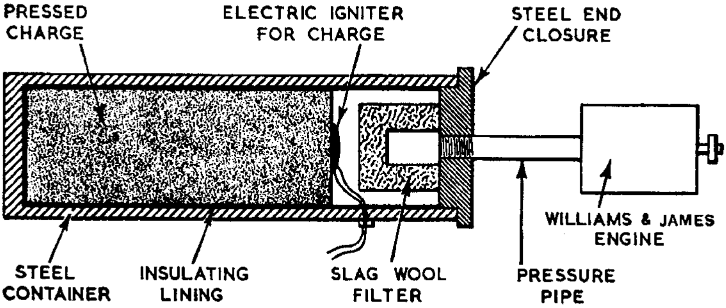


FIG. 15. Solid charge for actuating a small reciprocating engine.

CHARGE TO OPERATE A RECIPROCATING ENGINE

A solid charge for actuating a " William and James " motor, which is a four-cylinder reciprocating engine, has been described. The gas generator device is shown in Fig. 15. It comprised a strong-walled steel tube 4·7 in. internal diameter and 5 in. external diameter closed at one end and lined internally with a layer of " Hallite " steam jointing sheet material, into which was pressed a propellent composition in incremental charges under a pressure of 5,550 lb. per sq. in. forming a continuous column. The weight of the charge was 15 lb. It comprised a ball-milled powder of composition:

	PARTS BY WEIGHT
Ammonium nitrate	78·5
Potassium nitrate	9·0
Anhydrous ammonium oxalate	6·9
Ammonium bichromate	5·6
China clay	0·7

In order to test out the gas-generating device in conjunction with the motor the open end of the charge case was closed by a steel cap and coupled by a ⅜ in. steel pipe to a " William and James " motor designed for starting bus engines. The charge was about 15 in. long and was ignited at one end by means of an electric powder fuse comprising 5 grains of blackpowder together with a disc of blackpowder primed cambric. The gases from the charge were filtered through a slag wool filter in order to remove any solid particles. The combustion of the charge ran the engine for 3 minutes 20 seconds. The operating pressure rose to 280 lb. per sq. in. and the engine developed an average brake horse power of 3·3 and a maximum brake horse power of 4·1. The temperature of the gases leaving the device was 600° C., while the temperature at the inlet to the engine was 340° C., the drop in temperature being due to heat losses in the connecting tube. The engine ran smoothly throughout the test and when examined afterwards was found to be in good condition and free from corrosion. Fig. 16 shows a solid charge of similar composition to the previous example, but for a much larger engine. Composition (149 lb.) was pressed into a 17-in. diameter container lined on sides and base with " Hallite " jointing sheet. The charge was pressed in six equal increments at 12,000 lb. per sq. in. A charge of 8 lb. of china clay was spread evenly over the base of the container on top of the " Hallite " lining before loading the first increment. When pressed the china clay formed a firm incombustible layer bonded to the combustible charge thus ensuring even burning during the last stages of combustion.

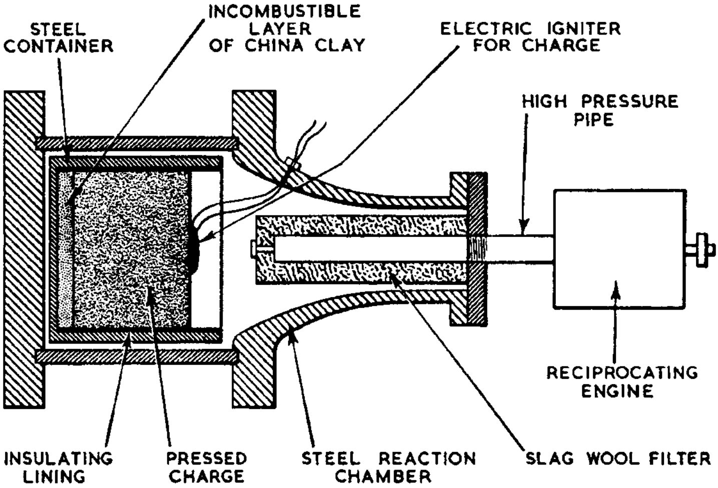


FIG. 16. Solid charge for actuating a large reciprocating engine.

The gases again were passed through a filter containing slag wool before being fed to the engine which was driven for 2 minutes at an average pressure of 530 lb. per sq. in. and developed an average power of 150 B.H.P.

Another charge was devised on the lines of that shown in Fig. 15 comprising 8 lb. of a powder composition pressed incrementally under a pressure of 6,000 lb. per sq. in. The charge was about 9 in. long and its composition was:

	PARTS BY WEIGHT
Nitroguanidine	56
Guanidine nitrate	28
Ammonium dichromate	8
Dimethyl diphenyl urea	4
Beech charcoal	4

The charge was connected in a similar manner to the previous example, but the gases were filtered through a steel wool filter instead of a slag wool filter. The " William and James " engine operated by this charge ran for 3 minutes 20 seconds at a pressure rising slowly from 100 to 190 lb. per sq. in. and developed 1 to 2 h.p. The gas temperature leaving the charge tube was 600° C., and that at the engine inlet 340° C. The engine ran smoothly and was free from corrosion after the run.

A similar charge for driving the " William and James " engine was made from a pressed composition of guanidine nitrate:

	Parts by Weight
Guanidine nitrate	94·5
Vanadium pentoxide	0·5
Cuprous oxide	5·0

This charge was ignited by several pieces of plastic sheet material made from a silicon/red lead/nitrocellulose mixture, covered by a sheet of primed cambric and fired by a 5-grain blackpowder igniter. The engine ran for 1 minute 50 seconds, the gas pressure rising to 135 lb. per sq. in., and the average brake horse power was 1·9 with a maximum of 3·2. The last two charges provide oxygen-negative gases which is an advantage for many applications.

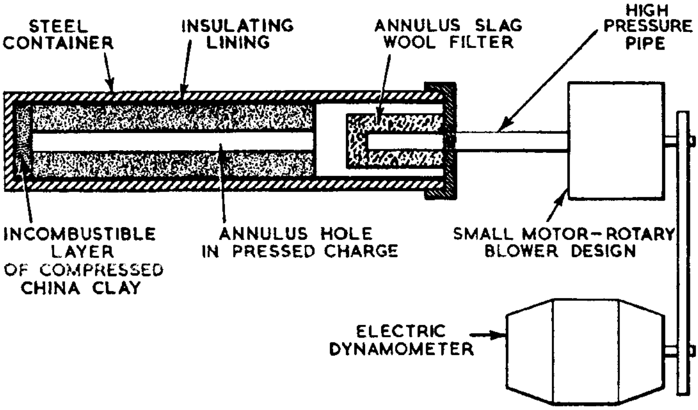


Fig. 17. Annular charge for driving a rotary blower motor.

CHARGE FOR ROTARY BLOWER MOTOR

Fig. 17 shows an annular charge for driving a rotary blower motor. Eight pounds of the charge was pressed in eight equal increments on a base of ½ lb. china clay in a 3½-in. internal diameter steel tube lined with " Hallite ". A 1-in. diameter hole was then drilled down the centre of the pressed composition to the china clay layer. The charge composition was:

	Parts by Weight
Ammonium nitrate	78·5
Potassium nitrate	9·0
Ammonium oxalate (anhydrous)	6·9
Ammonium dichromate	5·6
China clay	2·5

It was ignited in the central hole and on the top surface. The gases were filtered through an annular filter packed with slag wool. The charge was connected by means of a ½-in. diameter pipe to a small motor of rotary blower design coupled to an electric dynamometer. The pressure developed and the brake horse power figures are recorded in the following:

Time (seconds)	5	10	15	20	25
Pressure (lb. per sq. in.)	35	50	60	70	75
Brake horse power	4	6·5	10	11·5	13·5

REFERENCES

1. Wheeler, W. H., Whittaker, H., and Pike, H. H. M. *J. Inst. Fuel* (1947), **20**, 137.
2. Sutton, G. P. *Rocket Propulsion Elements*, Second Edition, pp. 313, 336 and 334. (John Wiley & Sons, Inc., New York, 1956.)
3. Bergaust, E. *American Aviation*, August 13, 1956, p. 36.
4. Arendale, W. F. *Ind. Eng. Chem.* (1956), **48**, 725.
5. Ley, W. *Rockets, Missiles and Space Travel*, p. 380. (Chapman & Hall, Ltd., London, 1951.)
   Scientific American, May 1949, p. 30.
6. U.K. Patent 608,125.
7. Humphries, J. *Rockets and Guided Missiles*, p. 27. (E. Benn, London, 1956.)
8. U.S. Patent 2,740,702.
9. U.K. Patent 681,095.
10. U.S. Patents 2,159,234; 2,604,391; 2,617,251; 2,637,274; 2,653,086; 2,682,461.
    French Patents 999,759; 1,007,437.
    U.K. Patent 453,210.
11. U.K. Patent 588,249.
12. U.S. Patent 2,742,672.
13. Zaehringer, A. J. *Aviation Age*, August, 1956, p. 50.
14. U.K. Patent 570,211.
15. U.K. Patent 570,075.
16. U.K. Patent 632,201.
17. U.K. Patent 627, 727.
    U.S. Patent 2,637,274.

CHAPTER 10

POWER CARTRIDGES

In Chapter 1 it was mentioned that in recent years there had been considerable developments in using cordite and other propellants as controlled energy sources for doing mechanical operations and that cartridges for such purposes were referred to conveniently as " power cartridges ".[1]

The propulsion of a bullet from a rifle or a projectile from a gun is certainly a mechanical operation—power is generated and work done by the cartridge, and the firearm is a machine for performing this work. All propellent cartridges are in this sense power cartridges, but in the conventional applications of propellent explosives in rifles and guns, the time of operation is of the order of a few thousandths or, in the case of the largest guns, a few hundredths of a second, and the maximum pressures are high—of the order of 5–20 tons per sq. in. To perform the operation of moving a piston, lifting a weight, or starting an engine at such a speed and operating pressure would be to impose disastrous strains on the apparatus, nor is such a speed of action necessary for correct functioning. Thus the new developments in power cartridges have been concerned with applications of gas pressure involving much longer times of operation applicable to the more normal engineering field, e.g. a few tenths of a second, a few seconds, or even 1 or 2 minutes. Whereas in rifles and guns there is usually no alternative to an explosive in some form or other owing to the rapid rate of gas development required, in this new field there is generally an alternative means of power available, e.g. compressed air, hydraulic pressure and so on. In this application, too, pressures are generally of a comparatively low order, up to a maximum of two or three thousand pounds per square inch. It is important to realise, therefore, that the use of a cartridge as a source of power in this field will justify itself, and therefore establish itself, only in so far as it shows advantages over other available means of power.

Strictly speaking, rockets should come into the power cartridge field, but by convention projectiles of whatever nature—except captive bolts—appear to have become excluded. In any case they are dealt with fully in Chapter 8.

CONDITIONS FOR USE OF PROPELLENT COMPOSITIONS

A solid propellant must possess certain characteristics to be capable of use for supplying hot gases to operate any specific device. These requirements, whilst simple, are not self-evident and are discussed shortly here.[2] The special case of rocket motors has been dealt with fully in Chapter 8.

First of all the propellant and the device, to be successful, must be matched for combustion.

Assuming that a propulsive or mechanical device, such, for example, as an engine, is accepting hot gas from a solid charge, it is obvious that the device will accept gas and use it in a manner depending on the operative pressure. In many cases, the law of acceptance, over the range of interest, can be denoted by:

$$Q_d = FP^m \qquad (\mathbf{10}.1)$$

where Q_d is the mass of propulsive gas used per second by the device and F and m are constants characteristic of the device.

Many, if not all, of the propellent compositions used, obey a rate-of-burning law of the form (**5**.3), and the mass of propulsive gas produced per second (due corrections being made for the solid " ash " produced), Q_m, will be

$$Q_m = C_1AP^n \qquad (\mathbf{10}.2)$$

where C_1 is a constant and A is the " burning area " of the charge. It is obvious that the propellant and device can be roughly matched for the pressure at which it is required to operate the device by making a charge of suitably large burning surface A, and by equating equations (**10**.1) and (**10**.2) with suitable values of the constants. Unless, however, the index of burning n for the propellant is less than the index of pressure acceptance m for the device, this matching or equilibrium will be unstable. If $m<n$ and a fortuitous rise of pressure occurs, then the operating pressure P will rise continuously until it is released either by a safety valve or disc or by failure of the cartridge container. If $m = n$ severe " hunting " will occur, but if $m>n$ conditions will adjust themselves to an operating equilibrium pressure given by:

$$P = \left(\frac{C_1A}{F}\right)^{\frac{1}{(m-n)}} \qquad (\mathbf{10}.3)$$

and the equilibrium will be stable and controlled and will reassert itself after any fortuitous pressure fluctuation.

Obviously, low values of the index n, in equation (**10**.2) will characterise greatest stability of performance and it will be readily appreciated that, since the pressure index is fractional for many compositions these will be adaptable for use in jet applications, such as rocket motors, where the pressure acceptance law is the first power (see Chapter 8). The index of acceptance for a considerable number of other devices is greater than unity and here again fractional index compositions are characterised by great stability.

SECTION 1 — CORDITE CARTRIDGES

THE DEVELOPMENT OF POWER CARTRIDGES

The development of the modern power cartridge goes back to the second half of the nineteenth century, but in the U.K. it had no "civil" use until just after the 1914–18 war, when Kynoch Limited (now I.C.I. Limited, Metals Division) developed a cartridge to operate the "humane cattle killer". In this, the pressure produced by a cartridge operates a captive bolt type pistol, thus eliminating the physical effort and skill required in the use of the poleaxe which, even in expert hands, was not always a dependable instrument. The "humane cattle killer" is now in widespread use throughout the country.

Another application, more closely allied to the employment of propellant in a gun, was the use of a cartridge to project a ball of refractory material into a hot gas retort for the purpose of sealing cracks in the lining, thereby saving the time that had previously been lost in allowing the retort to be cooled down for repair by hand.

An early development was the Cox submarine gun, used in salvaging operations. This will be described in some greater detail later on.[3]

Since the middle 1930 s considerable research and development has been carried out on the application of power cartridges and in various forms they are now being progressively utilised in a number of important fields. The Second World War gave a decided fillip to power cartridge developments. Thus a cartridge-powered cable-cutter was designed to safeguard allied aircraft against balloon barrage cables, and cartridge-operated starter motors were designed and used extensively.

Recent years have seen the extension of the applications to aviation, internal combustion engines of various types, jet engines, engineering and agriculture. To the engineer, it offers a handy source of power, the use of which can greatly simplify the design and reduce the manufacturing costs of many types of mechanical equipment.

The earlier applications were based on cordite, but some of the more recent developments in catalysed gas-producing compositions have promoted applications too.

GENERAL DESCRIPTION OF POWER CARTRIDGES

Most power cartridge applications to-day are operated by propellent explosives of the cordite type, and one type widely used is a range of special cordite compositions developed for the purpose and having the trade name " Mechanite ".

The usual method of translating the gas pressure produced by the cartridge into mechanical energy is by the movement of a piston along a cylinder, or by driving turbine blades.

Power cartridges in general use may be classified arbitrarily into two categories, the one for quick operations, comprising operating times less than about one second, the other for slow operations taking place in a time greater than one second. In the quick-burning class of operation, the maximum pressure developed is generally at least twice the average value, but cartridges designed for cycles in excess of about one second generate a steady pressure smoothly and peak pressures are not produced. Two means of achieving these results are available with cordite charges. For cartridges functioning relatively quickly the rate of burning of the propellant is controlled by its dimensions, that is its web thickness, and the pressure of operation (see Chapter 5).

For burning times of several seconds it is impossible to use a sufficiently large size of propellant within the limitation of the charge weight required, and a wrapped cordite charge has been introduced for the purpose.[4] In a wrapped charge the cordite rod is wholly or partly protected along its length and at one end by a relatively incombustible tape so that the cordite burns from one end only. Consequently, the burning time is determined by the length of the cordite stick instead of its diameter and is limited for practical considerations only by the size of the apparatus. This type of cordite stick charge is referred to as a " wrapped charge " and its functioning is appropriately designated as " cigar " or " cigarette " burning. Practical charges of this sort for operating various mechanical devices are produced by spiral winding of a stick of cordite with tape such as electrician's insulating tape.

The theoretical amount of work available in a typical " Mechanite " composition is approximately 2,000 ft. lb. per gm., but under normal conditions of operation the amount of effective work obtained is only approximately 15 per cent. of this owing to heat losses, while for types operated over a number of seconds the efficiency may drop to as low as 5–10 per cent. of the theoretical value.

SCOPE OF APPLICATION OF POWER CARTRIDGES

The great advantage of power cartridges over more conventional

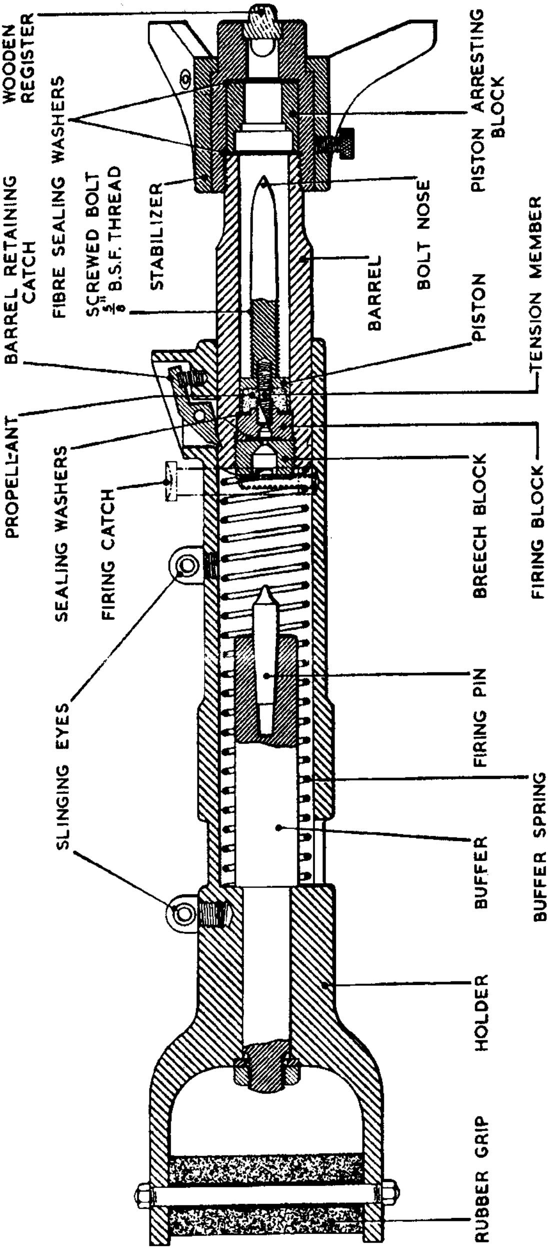


FIG. 18. Cox No. 2 submarine bolt driving gun. Complete assembly ready for firing the bolt.

forms of producing energy is the portability of the unit; this may be especially important, for example, for aircraft or large transport vehicles.

Heavy diesel engines are often started by compressed air and, consequently, require a separate expensive and cumbersome unit for starting purposes. Power cartridges are not intrinsically a cheap form of energy production, but the portability and elimination of expensive mechanism not infrequently swings the scales in their favour.

Since the burning characteristics of the power-cartridge propellants depend on the operating pressure it is necessary in each application envisaged to consider the strength and volume data of the apparatus proposed for the application, the pressures required and loads to be operated against and the time of the operation. The cartridge has to be exactly tailored to the operation.

APPLICATIONS OF CORDITE POWER CARTRIDGES

OPERATION TIMES OF LESS THAN ONE SECOND

Power cartridges may be ignited with a normal type of cartridge cap by a striker mechanism, or electrically ignited. In this Section we shall describe some applications in which the time of operation is less than about one second, and which require propellants of normal type such as are used in firearms.

THE COX SUBMARINE GUN

The Cox Submarine Gun[3] was developed primarily for use by divers in the recovery operations of salvaging the vessels of the German Fleet, sunk after the end of the First World War, in Scapa Flow.

The charge is contained in a special type of cartridge case and usually comprises about 40 grains of Superim propellant.

The gun is loaded with a pointed steel bolt before being lowered to the diver, who uses it to drive the bolt into the steel plates of sunken vessels in order to provide a means of lifting or alternatively by using hollow bolts to provide a means of forcing compressed air into compartments of the vessel to provide buoyancy. (Fig. 18 and Plate 9 illustrate the gun.) The gun can also be used for patching operations on ships and for cofferdam work.

RECOCKING OF SPRINGS

Some weapons are fitted with powerful springs to take up recoil. Such springs are normally cocked automatically on firing the weapon, but the first shot requires to be cocked by a hand-operated winch. A percussion-fired cartridge system which compresses a 1,600-lb. spring in about a tenth part of a second was developed[5] for this purpose and large numbers were used during the last war for Petard recoiling mortars.

DRENCHER OPERATIONS

In some of the manufacturing operations for solventless cordite the compositions are hot-rolled on heavy rolls to bring about correct gelatinisation. This operation is attended by the risk of spontaneous ignition of the sheets of cordite and at one time considerable damage was done by such fires. In certain factories, nowadays, an electrically primed cartridge is in routine use for the operation of water drencher systems which extinguish the fire in the event of an ignition. A photo-electric cell detects the first flash of light and the current produced, suitably amplified, fires the cartridge (2 gm. cordite) which lifts a 9-in. diameter water-release valve in about a quarter of a second. This device has proved extremely reliable and useful in practice.[6]

AEROPLANE ENGINE STARTER CARTRIDGES

The most important application of power cartridges to date has been for starters for aeroplane engines. One of the earliest of these applications was for the Coffman Engine Starter.[7] These starters, originally developed in the U.S.A., were adopted by the Royal Air Force and manufactured in the U.K. Large quantities of cartridges for these starters were supplied to the Air Force during the Second World War. Essentially, the starter comprises a mechanism whereby the horizontal motion of a piston is converted into the rotational motion of a dog which engages with the tail shaft of the engine. The time of operation is a few tenths of a second at maximum pressures between 1,000 and 2,000 lb. per sq. in.

It is interesting to record that in comparative tests by the R.A.F. throughout the winter of 1940, between squadrons fitted with

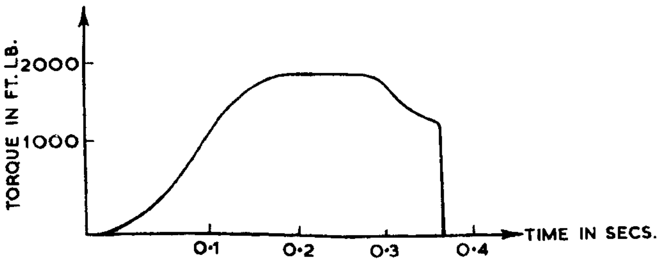


FIG. 19. Torque-time indicator diagram of Coffman starter.

cartridge starters and similar squadrons fitted with battery starters, the cartridge-operated machines were in the air more quickly than the others. (Fig. 19 shows an indicator diagram of the torque-time obtained from a typical Coffman starter. Plate 10 shows the multiple type breech assembly normally used with such starters and the starter unit.)

Power cartridges have also been developed for operating turbine starters. Such a starter is the British Thomson-Houston starter which also differs from the Coffman starter in that the working time is much longer and may be anything from 1 to 2 seconds. The torque is lower. Fig. 20 gives a torque-time indicator diagram for a typical B.T.H. starter cartridge.

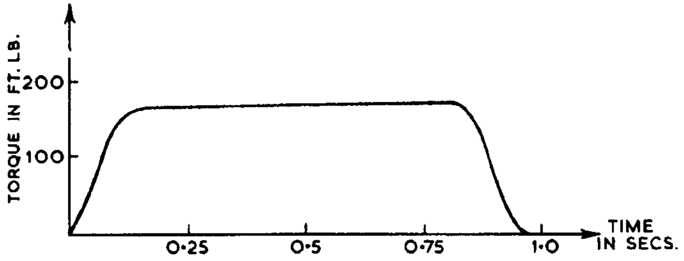


FIG. 20. Torque-time indicator diagram of B.T.H. turbine starter.

The Coffman and similar starters were used, of course, for piston-engined aircraft. More recently, cartridge-operated turbine starters have been developed for turbojet aircraft engines. The Rolls-Royce Avon turbojets, for example, are started by cartridge starter. B.T.H. triple-breech cartridge starters are used except on civil engines, which utilise Rotax electric starter motors.[8]

STARTING OF DIESEL ENGINES

Two methods have been developed for starting diesel engines by means of power cartridges.

1. Using a starter unit such as the Coffman engine starter;[9]
2. By direct injection of the powder gases into the cylinder head.[10]

The direct injection method is the simplest and is in current use for the Field Marshall Tractor two-stroke horizontal single-cylinder engine. This engine, which develops 20 h.p. on the drawbar has a 6½-in. bore cylinder and a piston stroke of 9 in. with a compression ratio of 16 : 1. The cartridge consists of a 12-bore case 2½ in. long fitted with a rust-free percussion cap and is fired in a combustion chamber, the breech of which incorporates a suitable powder trap. The charge consists of 12 gm. of a granular cordite. The gases produced are passed to the cylinder via a suitable pipe delivering to the half compression valve which is held open by means of the existing automatic gear worked from the flywheel. The cartridge is used in conjunction with the normal igniter wad which provides a " hot-spot " in the cylinder. Plate 11(*a*) is a photograph of the engine with the starter attached. A sharp blow on the firing pin fires the cartridge.

Both methods of engine starting have been applied to a five-cylinder 85-h.p. high-speed diesel engine which is normally started by compressed air. In the first method a Coffman starter (see Fig. 19 and Plate 10) engages with the main crank shaft of the engine, while in the second system the gas developed by the power cartridge is led directly into the reservoir normally used for compressed air and thence to four of the cylinders. The separate starter method is preferable on both technical and economic grounds for multi-cylinder engines.

OPERATION OF MODEL CATAPULT

A percussion-fired cartridge containing a 1-gm. charge of cordite was developed to operate a small catapult for the catapulting of model aircraft.[11] The time of extending the catapult is about half a second and the pressure a few hundred pounds per square inch. This application, it should be observed, is merely a small-scale adaptation of what has been done in practice for many years in the catapulting of naval aircraft. In this operation, the aircraft is hoisted on a trolley which is accelerated by a piston actuated by the gases from the combustion of suitably large-size cordite. This apparatus probably represents the earliest application of a power cartridge, albeit a very large cartridge.

TORPEDO LAUNCHING

A cartridge system has been developed for the launching of torpedoes from fast motor boats.[12]

Since the pressure to launch the torpedo at the required velocity of some 70 ft. per second is very low, it is necessary to burn the powder at a higher pressure and to vent the gases through a suitable nozzle into the torpedo tube. In this system no valves are employed between the low and high pressure sides.

OPERATION TIMES OF MORE THAN ONE SECOND

MOTOR CAR JACK

A cartridge unit for the operation of motor car jacks has been developed, the charge comprising a wrapped " Mechanite " charge giving the required burning time of 2 seconds.[13] The experiments were restricted to a system in which the jacks are kept extended by means of cold gas pressure from the cordite charge.

It is also feasible to operate oil hydraulic accumulator types of jack with non-return valves by means of power cartridges.

LOWERING OF AEROPLANE UNDERCARRIAGE AND ANCILLARY EQUIPMENT

Power cartridges have been developed for the emergency lowering of aeroplane undercarriages and ancillary equipment and are now in extensive use. The idea was patented by the late Mr. F. H. Hall and developed by the Nobel Division of I.C.I. Ltd. in collaboration with the Bristol Aeroplane Company.

The Ministry of Aircraft Production required two independent systems of lowering the undercarriage of a plane so that in the event of damage to, or failure of, the normal hydraulic system, the second system could be used. As a rule, the emergency system consists of a hand-operated pump, but the Bristol Aeroplane Company fitted a power-cartridge-operated emergency system to the Bristol Beaufort and to subsequent aircraft, which has proved very effective. The cartridge employs 73 gm. of a wrapped " Mechanite " charge contained in a 1½-in. signal case and has a time of operation of some 6 seconds. Six cartridges were employed per aircraft, namely, for main undercarriage, bomb door jacks and tailwheel.[14]

A larger cartridge fitted with electrically ignited primer and using a two-pounder brass case has also been developed.

OPERATION OF FIRE EXTINGUISHERS

The application of power cartridges to the expulsion of a liquid, e.g. water or methyl bromide from a fire extinguisher has been examined.

For example, a cartridge containing 20 gm. of a wrapped charge of " Mechanite " has been used for trials, with satisfying results. With this cartridge it is possible to empty a 2-gallon container in approximately 70 seconds, and on the whole its performance compares favourably with the normal soda/acid type of mechanism.[15]

SECTION 2 — CATALYSED COMPOSITIONS

The development of catalysed compositions and solid charges based on ammonium nitrate, guanidine nitrate and nitroguanidine are described in Chapters 7 and 9.

It was inevitable that such cartridges should be adopted for certain power-cartridge applications, and in 1934 work was commenced on the development of slow-burning pressed compositions containing one or more of the substances ammonium nitrate, guanidine nitrate, nitroguanidine, dicyandiamidine nitrate, urea nitrate, ammonium dichromate, usually bound with gelatinised nitrocotton. These compositions were pressed in the form of small pellets and were of low calorimetric value and rate of burning. Their behaviour at pressures up to 2,000 lb. per sq. in. was studied in a closed vessel. Such charges are described in the Patent Literature.[16]

During the Second World War a large amount of work on thermoplastic and cast catalysed propellants based on ammonium nitrate for rocketry and on pressed charges for driving torpedoes, gas-operated motors and various other purposes, was carried out.[17] The times of burning for such applications were 3 or more seconds, and for a large range of pressures from a few lb. per sq. in. to approximately 1,000 lb. per sq. in. It was found that in the case of ammonium nitrate pressed charges the inclusion of china clay raised the level of pressure at which stabilised burning took place and also controlled to a marked extent the rate of burning. Guanidine nitrate was found to be much superior to nitroguanidine in giving consolidation and was adopted for various applications. Fundamental improvement in performance was brought about by including 2 : 4-dinitroresorcinol as a sensitising agent, vanadium pentoxide as a gasifier and asbestos fibre to give a large surface for completion of the gaseous reaction in the presence of the vanadium pentoxide catalyst.[18] Such improvements led to the production of compositions which did not require filters to remove acidic or solid residues.

Whilst such compositions could be used in pressed cylindrical pellet form, unprotected, for small-scale operations, large charges required surface protection, either a thin inert " shirt " pressed on the outside of the charge[19] or an asbestos composition sheet liner between the container and the pressed charge which prevented burning along the sides[19] (see Chapter 9).

JET-PROPELLED MODELS

In 1945 Messrs. Wilmot Mansour requested I.C.I. Limited to look into the feasibility of producing charges for use in small reaction motors for various models. Compositions based on guanidine nitrate and 2 : 4-dinitroresorcinol which burned regularly and slowly at the low pressure of operation required and gave sufficiently low gas temperatures, were developed and a range of charges was designed for the various motors of interest.[20] A range of four charges designed in the form of cylindrical pellets, weighing from 3·3 gm. to 11·4 gm. and burning cigarette fashion was produced for loading into the motors. Plate 11 (*b*) shows a jet-propelled model helicopter operating on this principle.

INFLATING LIFE JACKETS

Gas-producing charges for inflating life jackets have also been developed.

STARTERS FOR RECIPROCATING ENGINES

In 1949 cartridges were designed for " Williams and James " reciprocating motor starters normally operated by compressed air. The largest cartridge consisted essentially of 5 perforated pellets of approximately 10 gm. of guanidine nitrate and up to 15 per cent. of 2 : 4-dinitroresorcinol composition of faster burning properties than usually used, loaded into a 1-in. bore percussion cartridge case with suitable ignition.[21] A nozzle and blow-off valve were incorporated in the breech equipment to assist in maintaining the desired pressure level. The time of operation of the starter was ultimately reduced from 4 seconds to 1 second.

It appears probable that the shorter burning time permissible could be better achieved by a cool clean-burning cordite propellant.[22]

FIRE EXTINGUISHERS

In 1949–50 a cartridge for the operation of a 2-gallon fire extinguisher was produced for the General Fire Appliance Company. The main charge consisted of three pellets of guanidine nitrate/2 : 4-dinitroresorcinol composition each weighing 12 gm. The pellets were contained in a suitable wrapping and arranged to burn cigarette fashion from one end. The expulsion time was about 1 minute.

A charge weighing 1·3 lb. was also developed for a 34-gallon extinguisher and successful tests carried out giving a 3-minute discharge.[23]

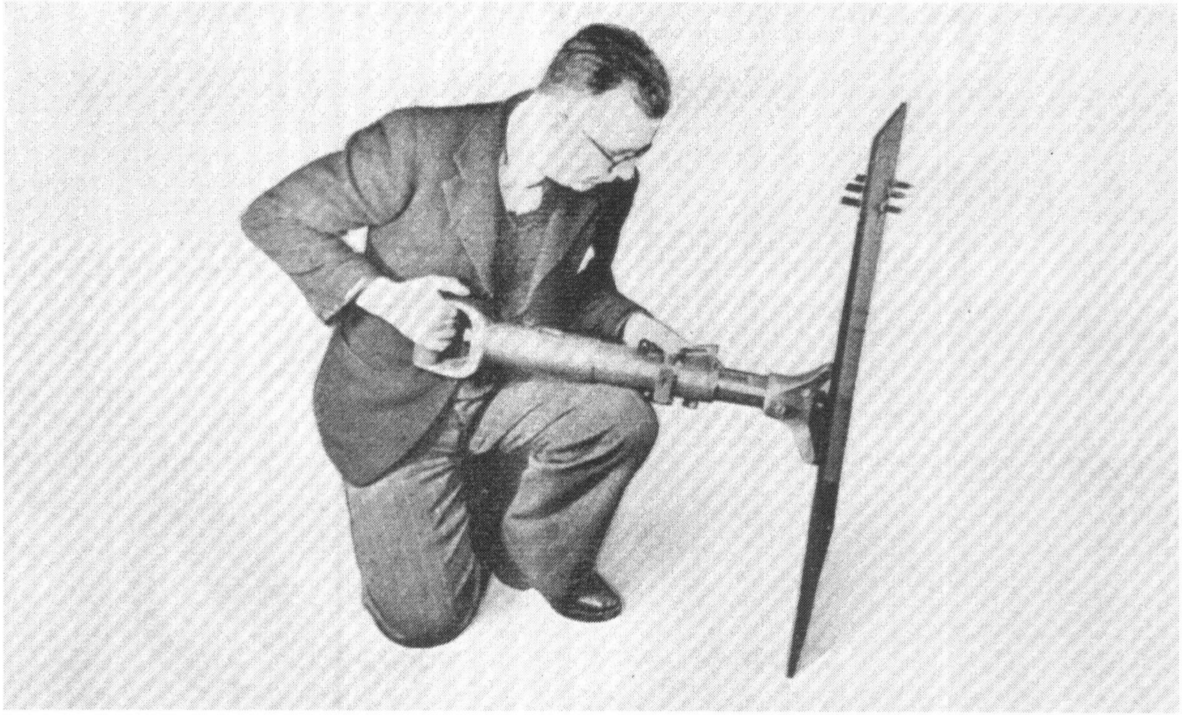
GAS TURBINE ENGINE STARTERS

Compositions of the ammonium nitrate/ammonium dichromate type and later guanidine nitrate/2 : 4-dinitroresorcinol type have been applied to the starting by turbo-starters of Armstrong Siddeley Sapphire turbojet engines. The charges are of the order of 5 lb. weight and are of the type protected on the outside surface, and burning on the ends and from the central hole. The time of operation is of the order of 10 seconds, and the operating pressure is 750 lb. per sq. in.[24]

REFERENCES

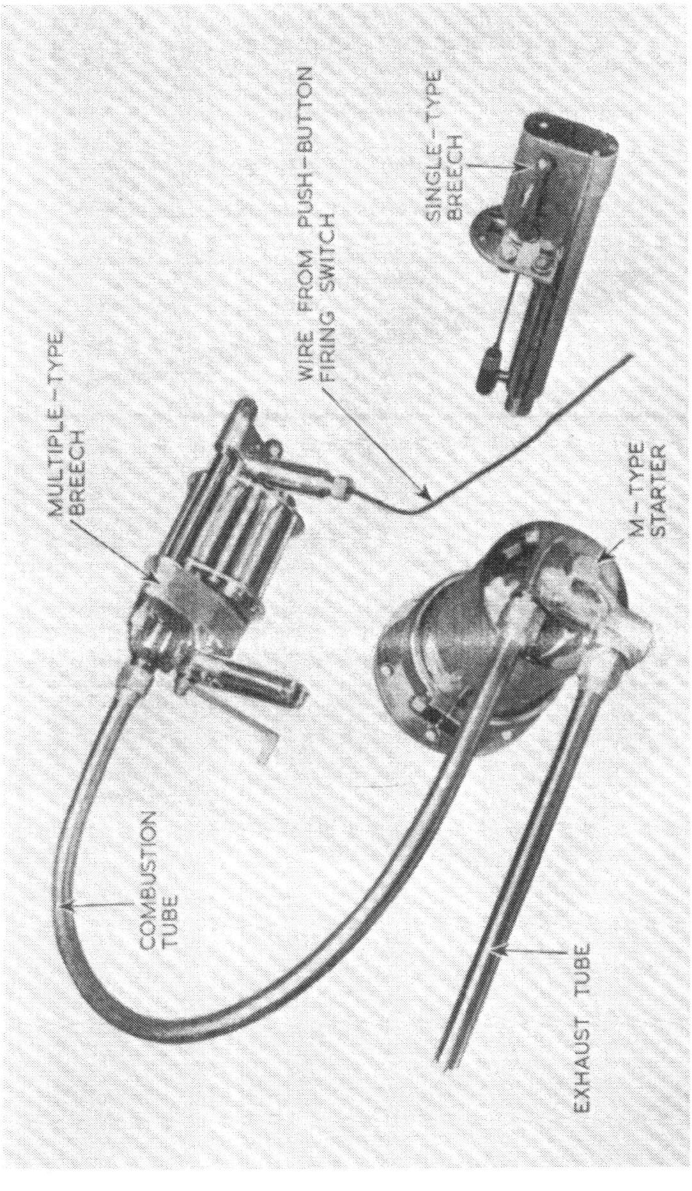
1. The following is a list of articles to which the reader is referred for full information on Power Cartridge Applications:
   "A Short History of the Development of Power Cartridges", *Times Trade Engineering Supplement*, 1948, IV.
   "Applications of Power Cartridges", *Engineering*, *Lond.* (1948), **165,** 296.
   "Recent Developments in Power Cartridges", *Chem. Trade J.* (1952), **131,** 1461.
   "Exhibition of Power Cartridges at Ardeer", *Chem. & Ind.* (1948), 219.
2. TAYLOR, J., and SILLITTO, G. P. Third Symposium on Combustion, Flame and Explosion Phenomena, Paper No. 73, p. 572. (Williams & Wilkins Co., Baltimore, 1949.)
3. *Engineering* (*Lond.*) (1948), **185,** 296.
4. U.K. Patent 489,297.
5. U.K. Patent 577,987.
6. *Engineer* (*Lond.*) (1948), **185,** 286.
7. U.K. Patents 521,743; 521,890; 549,232; 593,927; 604,489.
8. *Aeroplane* (1955), **89,** 950.
9. *Cartridge Starting.* Publication No. 352. The Plessey Co., Ilford, Essex.
10. U.K. Patent 674,899.
11. Brown Bros., Edinburgh.
12. U.K. Patent 577,036.
13. U.K. Patent 433,198.
14. U.K. Patent 482,474.
15. U.K. Patent 555,873.
16. U.K. Patents 454,091; 477,956.
17. U.K. Patents 570,210; 627,724; 627,727; 627,753.
18. U.K. Patents 645,897; 664,808.
19. U.K. Patent 627,727.
20. U.K. Patent 645,897.
21. U.K. Patent 664,674.
22. U.K. Patent 749,893.
23. U.K. Patent 664,808.
24. *Aeroplane* (1955), **89,** 580.

PLATE 9

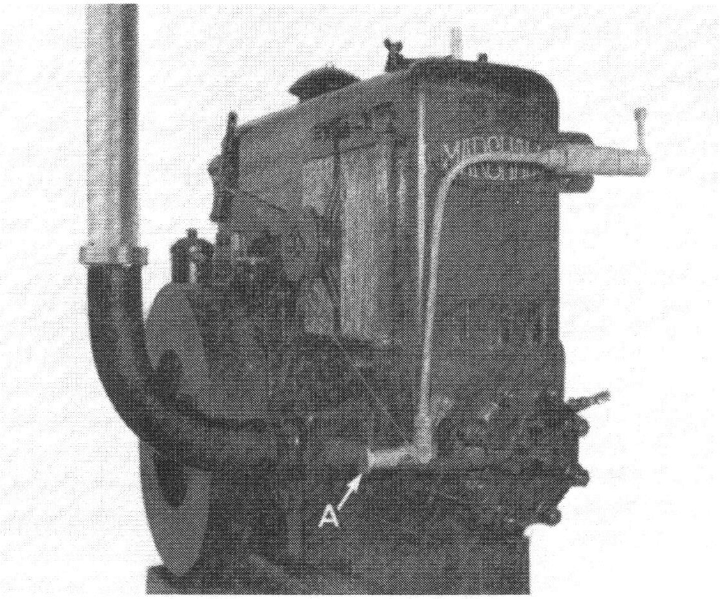


The Cox submarine gun. Driving a bolt through a half-inch steel plate.

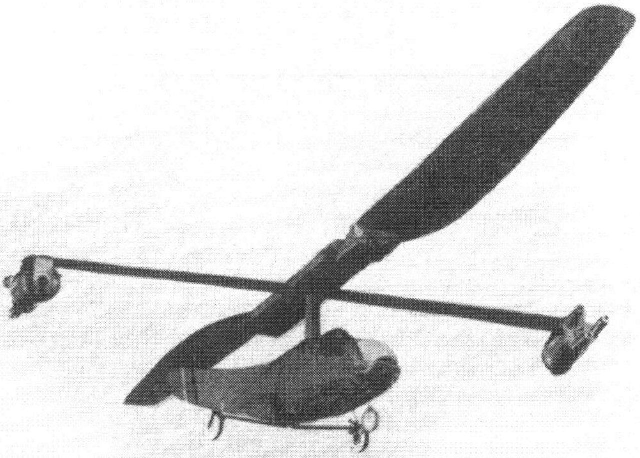
PLATE 10



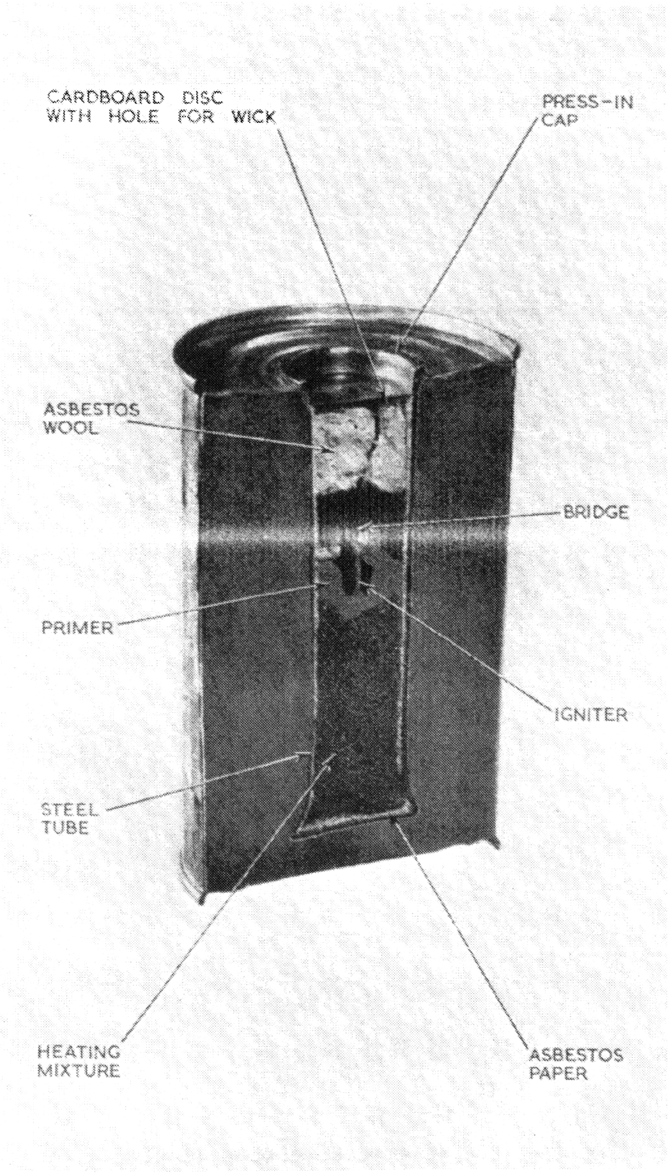
Coffman starter. Components of cartridge starter installation.



(*a*) Field Marshall single-cylinder diesel tractor engine with power cartridge starting. A sharp blow on the firing pin (shown at A) firees the cartridge.



(*b*) Model helicopter operated by jets.



Self-heating soup can.

CHAPTER 11

GASLESS REACTIONS

As we have seen in previous chapters, solid compositions containing large proportions of the lighter elements, usually hydrogen, nitrogen, carbon and oxygen, burn to give large volumes of permanent gas and are employed as sources of power and to do work by expansion. There are, however, certain compositions which contain heavier elements that give little or no permanent gas and are useful as sources of heat and light. Gasless compositions consist of finely powdered reducing agents and oxidising agents mixed together and often consolidated by compression. A self-sustained wave of reaction which can spread through an indefinitely large mass of reactant can be started by local heating.

The chemical processes involved are exothermic oxidation-reduction reactions, commonly involving transfer of oxygen from a metallic oxide or oxy-salt to a metal. Typically, titanium reacts with copper oxide to give copper and titanium dioxide:

$$Ti + 2CuO \rightarrow TiO_2 + 2Cu \qquad (\mathbf{11}.1)$$

It is not essential that oxygen-containing substances should be used. In certain cases, for example, sulphides are effective.

A great deal of empirical work has been done on such mixtures, but in recent years attempts at a more fundamental approach have been made by several investigators. Though these researches have disclosed the fundamental patterns of the reactions, the subject is very complex and much remains to be done.

Spice and Staveley[1] have carried out investigations on compressed mixtures of finely divided iron and barium peroxide, and iron and potassium dichromate, which undergo incandescent reaction when ignited. They found that in both of these systems a non-incandescent reaction, which they termed the pre-ignition reaction, set in at a measurable rate below the temperature of ignition. They concluded that this was a solid-solid reaction and investigated its kinetics and its significance in the propagation of the incandescent reaction. In a second paper[2] they described measurements which they made of the rate of burning (linear rate of self-propagation) of the reaction and of the heat of reaction (calorimetric value) in compressed binary solid mixtures. They studied eighteen systems using finely divided iron, manganese or molybdenum as reducing agents and barium peroxide, potassium permanganate and the nitrates of potassium, lead, strontium and barium as oxidising agents. Three other systems, iron/potassium dichromate, sulphur/barium peroxide and silicon/potassium dichromate were also studied. A range of proportions was investigated in all cases and the heat evolved in the reactions was measured.

TABLE 22

HEATS OF REACTION CORRESPONDING TO MAXIMUM RATES OF BURNING*

System	Max. R.B. (cm./sec.)	Heat Evolved for Max. R.B. (cal./gm.)
Fe/BaO_2 . . .	0·80	250
Mn/BaO_2 . . .	0·99	296
Mo/BaO_2 . . .	1·55	210
Fe/$KMnO_4$ . . .	1·06	350
Mn/$KMnO_4$. . .	8·0	735
Mo/$KMnO_4$ . .	0·75	212
Fe/KNO_3 . . .	0·50	382
Mn/KNO_3 . . .	0·98	312
Mo/KNO_3 . . .	0·73	145
Fe/$Sr(NO_3)_2$ . .	0·24	293
Mn/$Sr(NO_3)_2$ . .	1·10	708
Mo/$Sr(NO_3)_2$ . .	Will not burn	
Fe/$Ba(NO_3)_2$ . .	0·16	312
Mn/$Ba(NO_3)_2$ . .	0·72	588
Mo/$Ba(NO_3)_2$ . .	0·13	150
Fe/$Pb(NO_3)_2$ . .	0·39	285
Mn/$Pb(NO_3)_2$ . .	0·82	620
Mo/$Pb(NO_3)_2$ . .	0·32	340

* Extracted from: *The Propagation of Exothermic Reactions in Solid Systems,* Part II. Heats of Reaction and Rates of Burning," by J. E. Spice and L. A. K. Staveley. Table 4., *J.S.C.I.*, **68,** December 1949, p. 354.

Table 22 illustrates the results obtained. The thermochemical results were used to draw conclusions as to the most probable chemical reactions which occurred in the mixtures and to draw conclusions as to the dependence of the rate of reaction on the heat evolved.

In another paper, Hill, Sutton, Temple and White[3] used the same experimental studies with recorded temperature changes as the reaction passed any particular point. They concluded that the Mallard-Le Chatelier theory of propagation by thermal conduction is basally capable of explaining the behaviour of such reactions, but that it is somewhat inadequate in its simple form. Hill has continued basal investigations in recent years and has published a number of interesting papers.[4] In recent work he has investigated the kinetics of chemical reaction in $Fe/KMnO_4$ and $Mo/KMnO_4$ mixtures.

Reactions may be classified according to whether the products at the final temperature of combustion are solid, liquid or gaseous. If the temperature reached is less than about 1,000° C. the composition will probably be in the solid class, if greater than 2,000° C. in the gaseous class, and if between these temperatures in the liquid class. This guide is useful for mixtures of heavy metals and inorganic oxidising agents and is not, of course, satisfactory for allied compositions containing metalloids and non-metals which have low melting points and may give gaseous products. For example, low-temperature $Sb/KMnO_4$ compositions come into the liquid class because of the low melting point of antimony.

Though the mechanism and kinetics of gasless reactions have been the subject of a considerable number of recent studies it is a difficult subject for investigation. The practical applications are much further advanced.

THE GOLDSCHMIDT PROCESS

One of the best-known gasless reactions in everyday application is thermite, which comprises a mixture of aluminium powder and iron oxide, the reaction between the two substances producing aluminium oxide and metallic iron with a large emission of heat which raises the mass to a high temperature. The reaction may be depicted as:

$$3Fe_3O_4 + 8Al \longrightarrow 4Al_2O_3 + 9Fe \qquad (11.2)$$

The quantity of heat released by the reaction is about 850 cal./gm. and the temperature reached is enough to melt the iron and to permit it to separate from the molten slag of alumina.

The thermite mixture itself is not readily ignited and a fuse is used, often consisting of a ribbon of magnesium which ignites an intermediate exothermic primer comprising a mixture of aluminium powder and barium peroxide.[5] This process provides a purely chemical means of producing iron and various ferrous alloys and because of its simplicity and convenience it is used to a limited extent for such purposes. Chromium and manganese can also be produced from their oxides by the use of aluminium as a reducing agent. It has also been used for making a number of manganese-copper, manganese-zinc and ferro-titanium alloys.[5] The chemical reaction is rapid and may be of the order of a few minutes or even seconds.

The most widespread use is for welding. It can be employed for repairing a wide range of items, often *in situ.* It is necessary in use to form a mould around the part to be welded to contain the molten metal and the parts to be welded must be specially prepared and preheated.

Specific applications are repairing faulty heavy machinery castings, rail welding, forgings, stern frames of ships and large pump housings.[6]

The method was originally discovered and developed by Hans Goldschmidt (1861–1923).

INCENDIARIES

The thermite type of reaction is utilised in making incendiary bombs which played such a large part in the defeat of Germany and Japan in the last war. One of the most effective types of incendiary bomb is based on the heat of reaction produced by burning metals. The metallic incendiaries comprise two types, namely, those which get the oxygen for their combustion from the air and those which use an oxidising agent included in the composition.

TABLE 23

HEATS OF REACTION OF ALUMINIUM AND VARIOUS OXIDISING AGENTS

Material	Heat of Reaction (cal./gm.)
Al + O_2 (air)	7,000
Al + $KClO_4$	2,400
Al + KNO_3	1,800
Al + Fe_3O_4	800

The heat released per gm. of " incendiary " is, of course, much greater when the incendiary derives its oxygen from the air. Table 23, derived from the *Encyclopædia of Chemical Technology,*[7] illustrates this for aluminium and mixtures with it (see also Table 24). Table 23 also gives the heats of reaction of various incendiary mixtures.

Thermite itself is not an effective incendiary. The incendiary agent must heat the " target " it is to set on fire until the ignition temperature is reached. Usually at least four times the minimum heat required to do this must be supplied if ignition is to be certain. The thermite reaction is too rapid to allow the surroundings to attain the kindling temperature and the heat release is much less than that from metallic magnesium for example. Table 24, derived from Reference 7, shows the heats of combustion of various metals. Thermite is, however, used effectively as a mixture with additional aluminium powder, barium nitrate and sulphur as an igniting means for magnesium bombs.[7] Modern metallic incendiary bombs employ a casing of magnesium which can be ignited by a source of intense heat like the modified thermite mentioned above.

TABLE 24

HEATS OF COMBUSTION OF METALLIC SOLIDS

Material	Heat of Combustion (cal./gm.)	Material	Heat of Combustion (cal./gm.)
Aluminium .	7,000	Silicon . .	7,200
Beryllium .	15,000	Titanium . .	4,600
Boron . .	16,300	Zinc . .	1,500
Magnesium .	6,000	Zirconium. .	2,800

Typical incendiaries used in vast numbers in the Second World War were of hexagonal cross-section and were dropped in clusters. The casing was of magnesium alloy weighing about 1¼ lb. There was 10 oz. of igniting mixture to bring the magnesium alloy to ignition.

PHOTOFLASH MUNITIONS

Photoflash bombs comprising pyrotechnic compositions based on mixtures of finely divided magnesium and aluminium with an oxidising agent such as barium nitrate, akin to gasless compositions, but not actually gasless, were used widely in the Second World War to provide illumination for night aerial photography. Photoflash bombs for high-altitude aerial photography contained 25 lb. of photoflash powder and yielded the phenomenal peak intensity of 800,000,000 candles with a time duration of about 0·04 second.[7]

DELAY DETONATORS

One of the most useful and important applications of gasless compositions is for delay elements in electric detonators.

Modern conditions necessitate great speed in many civil blasting operations. It is essential in driving tunnels for hydro-electric schemes, in opening out underground roadways for coal mining and many other mining developments, or in constructing motor-way tunnels under rivers, and so on, that the rate of advance of the tunnel shall be a maximum. Speed is the essence of all such operations and industrial explosives technology has met the challenge by introducing new blasting techniques depending on electric delay detonators. These techniques require the firing of explosive shots at the advancing face of a tunnel in a definite sequence so that each shot may fire into the cavity created by an earlier shot. By use of modern delay detonators, closely controlled delay times can be obtained for sequence firing, and a series of detonators can be arranged to explode at definite intervals following a single passage of an electric current through the connecting wires.[8]

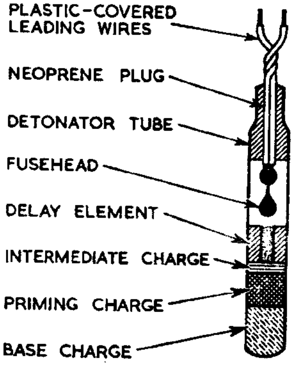


Fig. 21. Delay detonator.

Delay detonators have provided a novel means of controlled blasting which has not only speeded up blasting operations enormously, but has also reduced the hazards to workmen arising from frequent returns to the working face in the presence of toxic fumes and dangerous roofs.

The design of a typical present-day delay detonator is shown diagrammatically in Fig. 21. It consists essentially of an ordinary detonator with a tube longer than normal to accommodate a delay element, which is itself ignited by the flash from an electric fusehead similar to that for normal electric detonators (see Chapter 4), but made from a special gasless composition. The delay element is normally a gasless composition pressed into a metal sleeve, the length being chosen to provide the delay required. There are, however, other types of delay elements which will be described.

The delay sequences are frequently of ½-second intervals, but later types which are finding extended use have smaller interpolated delays of the order of 25 or 50 milliseconds and are called short or millisecond-delay detonators.[8] Owing to the fact that each detonator has to be hermetically sealed and waterproof, it is essential that the delay composition should evolve little or no gas, otherwise premature rupture of the detonator tube could occur due to build-up of gas pressure, or alternatively, the sealing plug could be ejected from the mouth of the tube resulting in a failure, an abnormally long delay period or a premature ignition of the blasting charge. All these must, of course, be avoided so it is necessary to use gasless compositions for the delay elements.

TABLE 25

SPEEDS OF FUSE FOR VARIOUS ZIRCONIUM/RED LEAD MIXTURES

Ratio of Zirconium to Red Lead by weight	Delay times in milliseconds per cm. length of fuse
20 : 80	50
30 : 70	23
40 : 60	20
50 : 50	22
60 : 40	32

GASLESS COMPOSITIONS FOR DELAY ELEMENTS

There is a vast amount of information in the patent literature on gasless compositions for delay elements and on the elements themselves. This literature is a mine of information on gasless reactions, though the approach is, of course, specific and empirical.

The most commonly used mixture has been antimony and potassium permanganate, which is practically gasless.

According to recent results a typical reaction in closed tubes is:

$$2Sb + 10/3KMnO_4 \longrightarrow 10/3MnO_2 + Sb_2O_5.5/3K_2O \qquad (11.3)$$

The heat liberation is 390 cal./gm. With smaller proportions of permanganate, or if there is a vent, Sb_2O_3 is produced instead of Sb_2O_5.

Many other compositions have been proposed for use and it is of interest to describe some of them and their special properties.

E. M. Patterson[9] described compositions for fast-burning delay fuses, such as are used for aerial bomb delays, comprising mixtures of finely powdered zirconium and red lead compressed into rigid tubes at pressures of 10 tons per sq. in.

Table 25 shows the speeds of different compositions.

I. O. Lewis[10] describes methods of preparing improved ventless delay electric detonators in which the delay fuse element consists of a length cut from a textile fuse comprising an unbroken continuously extruded core of thermoplastic composition of low gas evolution. This is an alternative to the metal sleeve filled with composition and resembles safety fuse (see Chapter 2) in which the gunpowder core is replaced by a plastic " gasless " composition. Actually, it is possible to use such fuses in long lengths as a replacement of ordinary safety fuse for normal blasting operations.

Canadian Industries Limited[11] have invented a short period delay detonator, or blasting cap as it is called in America, in which the delay composition is a homogeneous mixture of powdered Misch metal alloyed with aluminium to which is added an additional fuel such as silicon and an oxidising agent, such as red lead, yielding substantially gasless reduction products. An example of such a composition is:

70/30 Misch metal/aluminium	13·4 per cent.
Silicon	24·1 per cent.
Red Lead	62·5 per cent.

C.I.L.[12] also describe a delay detonator in which the delay composition is a fast and hot burning, relatively gasless homogeneous mixture of silicon metal powder and red lead to which may be added inert diluents, such as silica powder, to slow up and control the speed of the reaction. Millisecond-delays (50–1,525 milliseconds) were produced by this method. In a further Patent[13] they describe compositions, of which an example is 70 per cent. by weight of red lead with 18 per cent. of silicon and 12 per cent. diluent, of which the rate of reaction varies but little with change of internal pressure in the detonator.

An interesting variation in the construction of the delay element is described in an I.C.I. Patent.[14] The element is made by filling a lead tube of comparatively large diameter, for example 0·285 in. internal diameter, with a mixture of a composition comprising a mixture of red lead and silicon, in the proportions by weight of 70 to 30, for example, and drawing the lead tube down to an external diameter of 0·08 in. and an internal diameter of 0·05 in. The lead fuse is wrapped in paper or covered with a textile so as to be a good fit in the detonator tube. The element is cut to the length required for the chosen delay. Such delays are claimed to be safe for use in detonators for coal mines where inflammable mixtures of air and methane may be encountered.

An I.C.I. Patent[15] deals with delay compositions comprising mixtures of red lead and powdered titanium or zirconium which can be used for delays of 10–1,700 milliseconds. It is claimed that such compositions are insensitive to ignition by friction and are safe to manufacture. Potassium dichromate and potassium perchlorate were also used as the oxidising agents for such compositions.

GASLESS ELECTRIC FUSES FOR DELAY DETONATORS

In order to initiate the delay element it is necessary to use an electric fusehead which is also substantially gasless. Such fuseheads are described in the Patent Literature. In one form[16] the fuse, which consists of two pole pieces with the extremities connected by a fine bridge wire, is dipped in a suspension of a mixture of 50 parts of zirconium powder and 50 parts lead 2-mononitroresorcinate in a 5 per cent. solution of nitrocellulose in amyl acetate. The bead is dried and the assembly then completed. In a later invention[17] the bridge wire after being covered with a thin layer of 90 parts of lead mononitroresorcinate and 10 parts of potassium chlorate, to give easy ignition from the fuse wire, is then covered with a bead of cerium–magnesium alloy, lead dioxide, charcoal and aluminium powder mixture. Such fuseheads are not gasless, but the gas production is very small compared with ordinary fuseheads and is readily contained by the detonator assembly.

GASLESS IGNITERS

Another interesting application of gasless compositions is that of a hot tube safety igniter for initiating blasting devices of the " Hydrox " type (see Chapter 6).[18] A typical igniter of this type comprises a copper detonator tube 35 mm. long and 6 mm. internal diameter, of wall thickness 0·22 mm. Into this tube a charge of 0·75 gm. of a mixture containing 60 per cent. finely divided zinc and 40 per cent. potassium permanganate, pressed at 60 lb. per sq. in. is loaded. A gasless electric fusehead is positioned in the tube close to the composition, the free space being about 20 mm. and the fusehead assembly is crimped tightly into the copper tube. On initiating the fusehead by passing an electric current through the leading wires, the " gasless " charge reacts, but the products are contained by the tube and do not escape. The heat of the reaction is sufficient to raise the outside of the copper tube to about 300° C., enough to ignite Hydrox powder (or black-powder for that matter), but not high enough to ignite methane/air mixtures or coal dust/air mixtures, such as occur in fiery coal mines (temperatures of around 650° C. are required for this). Other compositions such as red lead and ferro-silicon, red lead and calcium silicide, or tin and lead peroxide, can also be used as the gasless filling charge.

SELF-HEATING FOOD CANS

A self-heating food can based on a gasless self-sustained composition was developed by Caldwell and Gillies during the Second World War. Several million cans were used by the British and American armed forces, especially Commando troops.

The idea of a self-heating can was not novel and there are a number of previous references in the literature, but none of these inventions appears to have reached the " production " stage.

TABLE 26

PRELIMINARY TESTS ON GASLESS HEATER COMPOSITIONS

Composition	Ratio	Remarks on Burning	Estimated Reaction Temperature, ° C.
$Pb_3O_4/CaSi_2$	70/30	Extremely fast, gives porous slag, fairly gasless.	800
$PbO_2/CaSi_2$	80/20	Almost instantaneous flash, much fume, little residue.	1,200
Pb_3O_4/Al	70/30	Almost instantaneous large flame, little residue.	1,400
$PbCrO_4/Si/Al$	88/11/1	Medium rate	800
Fe_2O_3/Al	75/25	Fairly fast; very hot flame appeared	1,400
$Fe_2O_3/CaSi_2$	50/50	Very slow; intensely hot slag, little fume; required primer to start.	1,500
$Fe_3O_4/CaSi_2$	50/50	Very slow; intensely hot, compact, slag; required primer to start.	1,500

Caldwell and Gillies have described the development of the self-heating can [19] and their analysis of the requirements for a practical solution. They conclude that for a self-heating can to be an acceptable commercial article it must be cheap, easily operated, free from the production of objectionable fumes, capable of heating up its foodstuffs content to a desirable temperature in a few minutes, and yet not be very much bulkier than an ordinary can containing approximately the same amount of foodstuff. On the basis of this appraisal, they selected gasless compositions as being the most promising for heating purposes. Table 26 summarises the results of their exploratory experiments and Table 27 gives calorimetric values, bulk densities, etc. of a number of promising compositions.

TABLE 27

BULK DENSITIES AND CALORIMETRIC VALUES OF HEATING MIXTURES
CALORIMETRIC VALUES DETERMINED IN BOMB CALORIMETER

Mixture	Ratio	Bulk Density at 25 lb./sq.in.	Bulk Density under Zero Pressure	Calorimetric Value cal./gm.	cal./cm.^{3} at 25 lb./sq. in.
$CaSi_2/Pb_3O_4$ . .	30/70	2·41	1·62	297	718
Fe_2O_3/Al . .	76/24	0·98	0·62	789	771
$CaSi_2/Pb_3O_4$/China Clay . . .	30/70/16	1·94	1·15	258	542
$CaSi_2/S/Pb_3O_4$.	25/75	2·47	1·51	307	760
$CaSi_2/Fe_3O_4$ . .	50/50	1·68	1·00	575	968
$CaSi_2Fe_2O_3$ . .	40/60	1·19	0·76	528	629
$CaSi_2Pb_3O_4/Fe_3O_4$.	50/25/25	1·88	1·12	389	730
$Fe_2O_3/Al/Pb_3O_4/$ $CaSi_2$/China Clay .	76/24/70/30/22	1·28	0·81	476	610

The heating mixture chosen as most suitable was the 50/50 mixture of finely powdered calcium silicide and hammerscale.

In order to ensure easy ignition of this heater mixture it was necessary to use a priming layer of 30/70 calcium silicide/red lead with the addition of 10 per cent. china clay to slow down the rate of reaction. The mixtures were loaded into a steel tube lined with asbestos paper and were ignited by a modified quickmatch.

Plate 12 shows a cross-sectional view of the self-heating-can assembly and gives a good idea of the final make-up.

REFERENCES

1. Spice, J. E., and Staveley, L. A. K. *J. Soc. Chem. Industr.* (1949), **68,** 348.
2. Spice, J. E., and Staveley, L. A. K. *J. Soc. Chem. Industr.* (1956), 692.
3. Hill, R. A. W., Sutton, L. E., Temple, R. B., and White, A. *Research* (1950), **3,** 569.
4. Hill, R. A. W. *Proc. Roy. Soc. A.* (1954), **226,** 455.
   Nature, Lond. (1952), **170,** 29. *Proc. Roy. Soc. A.* (1957), **476,** 239.
5. Kingzett. *Chemical Encyclopedia,* Eighth Edition, p. 1073. (Baillière, Tindall & Cox, London.)
6. Encyclopedia of Chemical Technology, Vol. 13, p. 940.
7. Encyclopedia of Chemical Technology, Vol. 7, pp. 798–9.
8. Taylor, J., and Gay, P. F. *British Coal Mining Explosives.* Chapter 8. (Newnes, 1958).
9. U.K. Patent 596,725.
10. U.K. Patent 638,454.
11. U.K. Patent 640,617.
12. U.K. Patent 651,552.
13. U.K. Patent 675,052.
14. U.K. Patent 716,909.
15. U.K. Patent 760,360.
16. U.K. Patent 428,872.
17. U.K. Patent 712,727.
18. U.K. Patent 430,750.
19. Caldwell, W. A., and Gillies, J. *Ind. Chemist.* (1950), **26,** 301.

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