

Fundamentals of Pyrotechnics

by

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Preface

This third edition of the book has been considerably revised and contains new material reflecting the achievements of pyrotechnics in recent years.

The general theoretical bases of pyrotechnics are expounded in the book, as well as contemporary methods of compiling and calculating pyrotechnic compositions, and information is given on the properties of various forms of pyrotechnic compositions.

The properties of components, fuels and oxidisers are described in more detail; greater attention is devoted to the physical nature of the processes of combustion under consideration. The properties of various types of pyrotechnic compositions are considered separately (illuminating, incendiary, solid rocket fuel, etc.).

The book is a textbook for students in VTUZ (Higher Technical Educational Institutions). It will also be of interest to scientific workers and industrial engineers working in pyrotechnics and in fields related to it (explosives, powder, rocket design, etc.).

Preface to this version

An English translation of the Third Edition of Shidlovsky's Fundamentals of Pyrotechnics (published in Russian in 1964) was published in 1964 by the U.S. Joint Publication Research Service (Technical Memorandum 1615, Feltman Research Laboratories, Picatinny Arsenal).

That was a valuable service because the book contains much interesting information. However, the translation contains some obscurities, and the practice of providing the translations to the numerous tables in the form of footnotes makes it somewhat inconvenient to use. This present version is in no sense a re-translation, but only a re-working of the American text, and a re-casting of the tables. It is intended to make this work easier to use for private research and as an introduction to the subject. The major changes involve the conversion of most of the physical quantities to S.I. units, and the Anglicisation of certain terms, particularly the distinction between sensitivity and sensitiveness.

N. Davies
1995

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INTRODUCTION

Since the second edition was published in 1954, very great changes have occurred in pyrotechnics due to new achievements in defence engineering.

Several new theoretical principles have been developed and new fields of application of pyrotechnic compositions have appeared, in particular in the national economy and in rocket engineering.

In writing this book the author has used the published works of Soviet and foreign specialists.

The course "Bases of Pyrotechnics" expounded in this book consists of two parts:

In Part One we give a classification of pyrotechnic compositions, information on the principles of their design, and we also consider the physico-chemical properties that are common to all types of such compositions.

In Part Two we describe the individual types of pyrotechnic compositions, their specific properties, and the requirements imposed upon them.

The description of pyrotechnic *devices* is given only in general terms, so far as this is necessary to explain the requirements placed upon the compositions.

In this book we also expound the bases of pyrotechnic technology and give a brief sketch of the history of the development of pyrotechnics in Russia.

Besides this, we give a considerable bibliography of contemporary literature on pyrotechnics and related branches of knowledge such as the physics and chemistry of combustion, thermochemistry, illumination engineering, the chemistry of oxidisers (mineral salts), powder metallurgy, polymer chemistry etc., with which specialists in pyrotechnics frequently come in contact.

The author expresses his gratitude for assistance in compiling this textbook to Candidate of Technical Sciences I.I. Vernidub who wrote Chapter XIV, Candidate of Technical Sciences Ye.S. Shakhidzhanov who wrote Chapter XX, and Engineer A.V. Smetana who wrote Chapter XXIII, Sections 6 and 7 of Chapter XIII and part of Section 2 of Chapter VIII.

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The author will be very grateful to readers who have any comments or who can indicate any specific shortcomings of this book.

Part One

Chapter I

General Concepts of Pyrotechnic Devices and Pyrotechnic Compositions

The word "pyrotechnics" is derived from the Greek - *πυρο* – fire and *τεχνι*- art.

Pyrotechnics is the science of methods of production of pyrotechnic compositions and products, and of their properties.

Pyrotechnic compositions when ignited (or exploded) give illuminating, thermal, smoke, sound, or mechanical effects, which are useful in military engineering and in the national economy (in industry, transport, agriculture, motion picture photography, etc.). Besides this, pyrotechnic compositions are used for making salutes and fireworks.

Manuals available on the fabrication of fireworks include those by Solodovnikov ⁶, Tsytoich ⁹², Izzo ¹², and Weingart ¹⁵; the products of fireworks pyrotechnics are not considered in this book.

Chapter XXII is devoted to the application of pyrotechnic compositions to the national economy.

Section 1. Classification of Pyrotechnic Devices and Compositions.

The following types of devices of military significance are filled with pyrotechnic compositions.

1. illuminating devices (cartridges, projectiles, bombs etc.) used for illuminating the terrain under night conditions;
2. photoflash devices (photobombs) used in night aerial photography;
3. tracer devices to make visible the trajectory of bullets and projectiles (and other moving objects) facilitating the range finding of rapidly moving airborne and ground targets;
4. night signal devices (cartridges, grenades, etc.) used for making signals at a distance;
5. daytime signalling devices (cartridges, grenades, etc.) used for the same purpose, except in daytime;
6. incendiary devices (bullets, bombs, projectiles, etc.) for the destruction of materiel, offensive weapons, and defences of the enemy; special incendiary agents are also used against enemy personnel;
7. screening devices (smoke pots, projectiles, etc.) used to make smoke screens;
8. rockets of various purposes and ranges; their motors are filled with rocket compositions (solid pyrotechnic fuel);
9. training and simulating devices used in manoeuvres, in training, and also in a battle situation; their effects imitate those of various types of ammunition (atomic bombs, high explosive projectiles and bombs, chemical warfare agents, etc.) or various phenomena occurring on the field of battle (the sound of gunshot, fire, etc.) and may thus may confuse the enemy observers;

10. target indicating devices (projectiles, bombs, etc.) to show air forces or artillery the enemy objectives that are to be attacked.

Pyrotechnic compositions can be divided into the following categories:

1. illuminating
2. photoflash (photomixture)
3. tracer
4. night signal flare
5. day signal smoke
6. incendiary
7. white, grey, and black screening smoke
8. solid pyrotechnic fuel
9. igniting (which are contained in small quantities in all pyrotechnic devices)
10. miscellaneous (simulating, whistling, etc.)

Many categories of compositions are used in the most diverse forms of devices. Thus, for example, illuminating compositions are frequently used in tracers; white and black smoke compositions may be used not only in screening devices but also in tracers, and in training and simulating devices, etc.

Pyrotechnic compositions may be classified in the following manner depending on the nature of the processes occurring during their combustion:

Flame Compositions

White Flame.

Used in rockets, illuminating, photoflash, tracer, training and simulating, target indicating and incendiary devices.

Coloured Flame.

Used in tracer, night signals, training and simulation, target indicating devices.

Thermite Compositions

Thermite Incendiary.

Used in incendiary devices.

Gasless (low gas).

Used in time fuses and exploders.

Smoke Compositions

White, grey, black Smoke.

Used in screening, tracer, training and simulation, target indicating devices.

Coloured Smoke.

Used in day signals, tracer, training and simulation, target indicating devices.

Substances and Mixtures burning in atmospheric oxygen

Metals and Alloys.

Used in incendiary and photoflash devices.

Phosphorus, its solutions and alloys.

Used in incendiary devices.

Petroleum mixtures.

Used in incendiary agents and in flame throwers.

Substances and Mixtures igniting in contact with water or air.

Used in incendiaries and special signal devices.

Section 2. Combustion of Compositions.

Highly exothermic chemical reactions may occur in the form of combustion. The formation of a flame or a glow is not an unfailing sign of combustion; thus, for example, a flame is usually not formed in the combustion of pyrotechnic smoke compositions, and no liberation of light is observed.

The basic criteria distinguishing the process of combustion from other forms in which chemical reactions may occur are:

1. The presence of a moving reaction zone of high temperature which separates the reaction products from substances which have not yet reacted.
2. The absence of a pressure jump in the reaction zone; in this essential respect, combustion differs from explosion.

The combustion of pyrotechnic reactions is an oxidation-reduction reaction in which the oxidation of some components of the composition - *fuels* - proceeds simultaneously with the reduction of other components of the same composition - *oxidisers*. Several forms of combustion are distinguished by the degree of homogeneity of the initial system.

Solid or liquid fuel burning in the oxygen of the air form an *heterogeneous* system (before the start of combustion).

Combustion of *homogeneous* systems is also known; such systems include explosive gaseous mixtures or specific explosives.

Pyrotechnic compositions, which are mechanical mixtures of several finely pulverised components, usually solid, have a degree of homogeneity intermediate between that of condensed fuel (burning in air) and specific explosives (or homogeneous mixtures).

The combustion of pyrotechnic mixtures results from heat transfer from the reaction zone to layers in which preparations for the process of combustion are proceeding.

The ignition of pyrotechnic compositions is also based on the principle of heat transfer. To initiate combustion, it is necessary to create a local increase in temperature in the pyrotechnic composition; this is usually achieved by the direct effect of hot gases arising from the powder, or by the application of specific igniting compositions.

When the pyrotechnic composition is activated by a firing stimulus and its combustion takes place unconfined, its rate of combustion is not great and, in the majority of cases, is measured in millimetres per second.

Sometimes an accelerated rate of combustion is observed when a large quantity of pyrotechnic is ignited without confinement.

The following basic operations must be performed to prepare pyrotechnic compositions and fill devices with them:

1. preparation of components (pulverisation and drying);
2. preparation of the powdered composition (mixing of components, granulation, and drying of composition);
3. compaction and forming of the composition (by pressing or some other method).

For the pyrotechnic composition to be most effective it is normally necessary for its components to be well pulverised and mixed uniformly with one another. In a well prepared composition, with the exception of thermite, the particles of individual components are indistinguishable to the naked eye.

By compacting the composition, the process of combustion is retarded, the volume occupied by the composition is decreased, and great mechanical strength is achieved. Compositions are pressed in most pyrotechnic devices. Photoflash compositions are exceptional as they are filled into photo bombs as powder, and some signal smoke compositions are filled as granules.

The preliminary preparation of the components is safe since both the fuels and the presently used oxidisers, taken separately, are in most cases insensitive to mechanical effects (shock, friction), and do not have explosive properties.

This cannot be said for the various forms of fuels scattered into the air as dust. For example, cases of violent explosions of aluminium dust are known. Other exceptions are found with certain oxidisers - ammonium perchlorate, ammonium nitrate, and the chlorates of certain metals, which even in the pure form without combustible substances in admixture, may explode if subjected to a sufficiently powerful stimulus.

Mixtures of oxidisers with fuels are sensitive to mechanical stimuli and may begin to burn when subjected to shock or friction. Sometimes sufficient shock or friction may bring a pyrotechnic mixture to explosion. Therefore, preparation and pressing pyrotechnic mixtures, during which the materials are unavoidably subjected to mechanical effects, are normally dangerous

Section 3. Requirements imposed upon pyrotechnic devices and compositions.

The basic requirement imposed upon pyrotechnic devices is that of obtaining the maximum special effect when they operate. Factors affecting the desired effect will be discussed in detail in the chapters dealing with particular types of composition. Here, we will give only a few examples as illustration.

For tracers, the special effect is the good visibility of the trajectory of the bullet or projectile. Visibility is predetermined by the luminosity of the tracer and depends also to a great degree upon the colour of the flame.

A good special effect of igniting devices - their unfailing ignition of the appropriate combustible material - is predetermined (if the ammunition is adequately designed) by the development of an adequately large region of combustion, high flame temperature, and adequate duration of the combustion of the composition, and by the quantity and properties of the residue from the combustion process.

For screening smoke devices, the special effect is the development of a smoke screen that is as dense and stable as possible.

The quality of rockets is determined by the range and accuracy of their flight, guaranteeing that they will reach the intended target. The range may be a direct function of the unit impulse I (kg s kg^{-1}) of the rocket composition, and increases with increasing ratio of the weight of composition to the total weight of the rocket.

All pyrotechnic devices must be safe for handling and storage. The effects obtained when they operate must not deteriorate after prolonged storage.

The materials used for the preparation of pyrotechnic devices must be readily available (i.e. must not be strategically scarce materials). The processes must be simple, safe, and must permit the mechanisation and automation of production for large scale manufacture.

Pyrotechnic compositions must have the following qualities:

1. they must give the maximum special effect with the minimum expenditure of composition[†];
2. they must burn uniformly at a definite rate;
3. they must be chemically and physically stable during prolonged storage;
4. they must have as low a sensitiveness to mechanical impulse as possible;
5. they must not be excessively sensitive to heat effects (ie must not ignite after a small temperature rise, etc.);
6. they must have minimum explosive properties; rare cases in which explosive properties are required in a composition will be mentioned below;
7. they must not produce poisonous combustion products which may hamper fire fighting during production;
8. they must have a simple manufacturing process;
9. they must not contain scarce ingredients;
10. they must not contain ingredients toxic to humans.

Products formed from pyrotechnic compositions must have adequate mechanical strength to satisfy the operational requirements.

[†] The efficiency of the effect is determined not only by the recipe of the composition, but also by the design of the product, manufacturing technology of the composition, and the external conditions such as pressure and temperature under which its combustion occurs.

In order to produce pyrotechnic compositions which satisfy the above requirements, it is necessary in each case to select carefully the fuel and oxidiser and to calculate the ratio of their quantities. The physico-chemical characteristics of the fuel and oxidiser must be considered using published data on the mixtures and their ingredients.

The development of compositions and the calculation of the ratios of components is complicated considerably by the fact that a binary mixture (fuel plus oxidant) is frequently inadequate, and other components must be added to perform particular functions.

Section 4. Designation of Ingredients of a composition.

The ingredients of a pyrotechnic composition may be divided into the following categories:

1. fuels
2. oxidisers
3. binders
4. combustion accelerators and retarders
5. phlegmatisers (additives which decrease the sensitiveness of the composition to friction)
6. substances used for production purposes (lubricants, solvents for the organic polymers introduced into the composition, etc.)

Further, substances to colour the flame are introduced into the compositions for signal flares, and smoke forming substances into smoke compositions.

In some cases, a particular ingredient may perform different functions in the same composition:

Binding agents always act as a fuel, and sometimes also as a combustion inhibitor.

Strontium nitrate is both an oxidant and a source of flame colour in red signalling compositions.

The following authors deal with the problems considered in Sections 1-4 in this Chapter: Budnikov, Levkovich, Bystrov, et al.¹, Bystrov², Gorst³, Zhirov⁵, Shilling¹⁵⁶, and Ellern⁹.

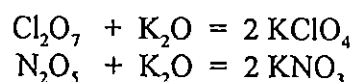
Section 5. Possible highly exothermic reactions.

Any chemical reaction occurs with disruption of the bonds between the atoms and the formation of other new bonds. If the energy liberated in forming the new bonds is greater than that expended in breaking the old bonds, then the reaction is *exothermic*. Obviously, the greatest amount of heat will be liberated when the bonds being broken are weak, and those being formed are very strong.

The strongest bonds are formed between those elements which are most different in their properties, i.e. between typical metals and typical non-metals such as fluorine and oxygen. Such reactions form ionic compounds. Reactions between non-metals (elements of groups V-VII of the periodic table) give covalent compositions with low bond energies.

Frequently, fuels such as aluminium and magnesium are used in pyrotechnics. Fluorine and oxygen are gases under ordinary conditions, and this considerably hampers their applications to pyrotechnic systems. Therefore, we try to use as oxidants compounds in which oxygen or fluorine are bonded weakly to other non-metals. However, most such compounds are either gases or liquids with low boiling points. For example ClF_3 , OF_2 , NF_3 , N_2F_4 , SF_6 , Cl_2O_7 , ClO_2 , NO_2 , N_2O_4 etc. This fact, and also their toxicity and excessive chemical reactivity hampers their practical application.

These properties disappear largely when we react the oxides of non-metals (anhydrides) with the oxides of metals (thus reducing the available energy), e.g:



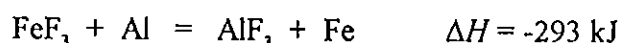
Solid salts are formed which are very suitable for use in pyrotechnics. They are less reactive chemically, their powders may be mixed with ordinary fuels at an ordinary temperature, and these mixtures are adequately stable thermally.

Oxidisers which are ordinarily used in pyrotechnics include: KClO_4 , KNO_3 , $\text{Ba}(\text{NO}_3)_2$ which are convenient to use, but are, of course, considerably less favourable energetically than elemental oxygen.

Another type of oxidiser used in pyrotechnics is the oxides of metals of low reactivity. Obviously, reactions involving their replacement by more active metals will occur with liberation of heat. Such, for example, is the combustion reaction of ferroaluminium thermite:



By analogy, we would expect an active metal to displace a less reactive metal from its fluorine compound, for example:

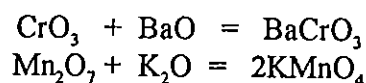


This heat corresponds to 0.20 kJ g^{-1} of the mixture. Now the fluorine content of the earth's crust is not great (0.03%), and it occurs most commonly as the extraordinarily stable compound fluorspar, which is the usual source of other compounds of the element.

Besides economic considerations, the use of fluorides as oxidants in pyrotechnics is also limited by the fact that fluorine (an extremely reactive element) forms very few solid compounds with weak bonds; consequently, it would be difficult to formulate a high energy mixture based on fluorides. The nature of the combustion of the mixture $\text{FeF}_3 + \text{Al}$ will be entirely different from that of $\text{Fe}_2\text{O}_3 + 2 \text{Al}$ because AlF_3 sublimes at 1260°C .

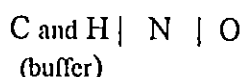
In principle, the use of the higher oxides of certain metals, such as Mn_2O_7 , and CrO_3 as oxidants would be possible, but the physico-chemical properties of these compounds do not favour their use: Mn_2O_7 is a liquid of low chemical stability, CrO_3 is highly hygroscopic.

Reaction of these oxides with the oxides of the alkali or alkaline earth metals leads to materials which are acceptable as practical oxidants for pyrotechnics use, for example:



The peroxide is superior to the oxide of the same metal as far as oxygen content is concerned, but many of them have little thermal stability (e.g. CaO_2) or react with water (e.g. Na_2O_2). In practice, the only peroxides used in pyrotechnics are barium peroxide BaO_2 , and in rare cases strontium peroxide SrO_2 ⁹.

Now we will turn to a consideration of fuels. Besides metals, hydrogen forms strong bonds with fluorine and oxygen; oxygen also forms adequately strong bonds with boron, carbon, silicon and phosphorus. This means that these elements and also certain compounds of them (boranes, hydrocarbons, etc.) may be used in pyrotechnics as fuels. But then the thought involuntarily arises: since many non-metals (nitrogen and chlorine) have weak bonds with oxygen, and also with carbon and hydrogen, why should we not combine atoms of these elements in a molecule in such a manner that the nitrogen (or chlorine) would perform in it the role of a buffer, separating the C and H from the oxygen:



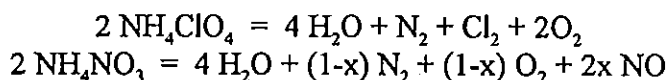
Application of external energy to such a molecule would displace the buffer and allow combination of the C and H with oxygen, with the formation of CO_2 and H_2O and the liberation of a great amount of heat. Such intramolecular combustion reactions may be very energetic. This thought is valid, and was realised many years ago. The buffers (nitrogen or chlorine) in a molecule between C and H on the one hand, and O on the other, have been long known: they are the nitrocompounds or esters of nitric (or perchloric) acid. These substances are capable of intramolecular combustion, but they have one essential shortcoming from the standpoint of pyrotechnics: the absence of heterogeneity, and the short distance between the atoms in the molecule can lead to decomposition at high velocity (an explosion) when the molecule receives an adequate stimulus. In other words, these compounds are high explosives.

The application of intramolecular combustion of high explosives to pyrotechnics is possible, but it is accompanied with considerable risk in many cases: in the disruption of the combustion regime (see later in Chapter XI), a transition from combustion to explosion may occur.

Incidentally, between the two extremes of heterogeneous systems (pyrotechnic compositions) on the one hand, and homogeneous systems (explosives) on the other hand, an intermediate stage is possible. If, in the molecule of some substance containing a nitrogen buffer, there are *few* atoms of the combustible elements and an *excess* of oxygen atoms (up to a certain limit, of course), the substance will be capable of an intramolecular combustion reaction, but the heat of the reaction

will be small, the temperature of combustion will be low, and the probability of a transition from combustion to explosion will be considerably lower.

Precisely such substances are the ammonium salts of certain acids containing oxygen, such as ammonium nitrate and ammonium perchlorate. Combustion of these substances liberates free oxygen, and the combustion heat and temperature are comparatively low:



However, it is easy to correct the energetics of these reactions by adding the calculated quantity of fuel (such as an organic binding agent), in order to use entirely the free oxygen in these substances. If a considerable quantity of fuel is added, and the homogeneity of the system is disrupted, then the danger of a transition from combustion to explosion will be reduced.

A further variation uses substances with a nitrogen buffer and containing *few* atoms of oxygen, and *an excess* of atoms of C and H. Such substances also are capable of an intramolecular combustion reaction, but the heat and temperature of the reaction will be low, and there will also be small probability of a transition from combustion to explosion. Such substances include nitroguanidine $\text{CN}_4\text{H}_4\text{O}_2$, dinitrotoluene $\text{C}_7\text{H}_6\text{N}_2\text{O}_4$, polynitrourethanes, polyvinyl nitrate, and others.

It is easy to correct the energetics of these substances too, by adding a certain quantity of oxidiser that is incapable of exothermic decomposition. In this case the homogeneity is disrupted, and the possibility of an explosion occurring is reduced considerably.

Everything stated above may be illustrated in Table 1.1.

Serial	System	Physical State	Explosive Properties
1	1. fuel 2. oxidiser	heterogeneous	low
2	1. fuel including a little N(buffer) and a little O 2. additional oxidiser	heterogeneous	average
3	1. oxidiser including a little N (buffer) and a little H and C 2. additional fuel	heterogeneous	average
4	explosive substance: contains N (buffer), and C + H in stoichiometric ratios	homogeneous	high

Table 1.1 Degree of Heterogeneity and Explosive Properties of Pyrotechnic Compositions.

Section 6. Ability of various substances and mixtures to burn.

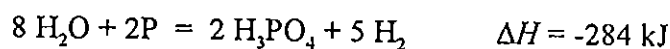
Pyrotechnics is a young science, and it is developing rapidly. New problems are arising, new requirements are being advanced, and new compositions, and even new forms of compositions are being developed to meet them.

A pyrotechnists must be able to estimate the *possibility* of some chemical reaction or other occurring as a combustion. In accordance with Berthelot's principle (which is undoubtedly valid for highly exothermic reactions occurring at room temperature) any chemical system in which an exothermic reaction may occur, may, with the appropriate selection of external conditions, be capable of propagating a combustion reaction within itself.

By working from this principle the author of this book studied and experimentally proved the ability of the system $\text{H}_2\text{O} + \text{Mg}$ to support combustion ³⁹, as well as a number of inorganic salts of ammonium ²³⁷, hydrazine salts, and also hydroxylamine sulphate.

Undoubtedly, combustion reactions are possible in mixtures of magnesium with many organic substances containing oxygen - such as alcohols, aldehydes, carbohydrates, etc.; such processes are more easily realised with solids, and less easily with liquids.

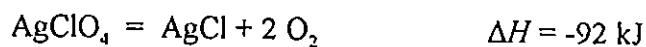
A combustion reaction in the system $3 \text{H}_2\text{O} + 2 \text{Al}$ is quite possible. We have also given calculations of the exothermicity of reactions in systems $3 \text{H}_2\text{O} + 2 \text{B}$; $2 \text{H}_2\text{O} + \text{Si}$; and $4 \text{H}_2\text{O} + \text{P}$ ^{119 page 540}. In the latter system, in our opinion, the reaction with white phosphorus may be:



which corresponds to 1.4 kJ g^{-1} of the mixture of reactants.

In some cases estimates of the exothermicity of the reaction are made for another purpose - that of estimating the fire (or explosion) hazard of the system.

The explosion hazard of silver perchlorate, which was recently established experimentally by accident ⁴⁴, could have been predicted from the thermochemical calculation:



Substances or mixtures which in practice are not capable of combustion (or explosion) at room temperature, since their heat of decomposition is too small, may become capable of explosion when the energy reserve in them is increased by raising the temperature.

An example of this is the great explosion of molten potassium chlorate (Liverpool 1899). The addition of small quantities of fuel (1% iditol + 5% MnO_2 catalyst) to potassium chlorate makes it capable of combustion at room temperature. Extensive material on the problem of unexpected fires and explosions is available in the articles by Langhans ¹⁵⁹, and by Tomlinson and Audrieth ¹²².

Chapter II

Oxidisers

A mixture of fuel and oxidant forms the basis of all pyrotechnic compositions.

It would appear that adequate heat to produce the desired special effect could be produced by burning the fuel in the oxygen of the air. But the burning of fuels under such conditions usually occurs much more slowly than combustion with the oxygen of an oxidising agent and therefore for pyrotechnic purposes mixtures which do not themselves contain an oxidiser (see Chapter XVII, Sections 6-8) are used more rarely than compositions with oxidiser[†].

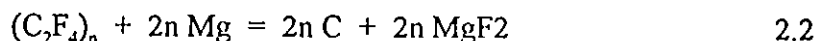
Most frequently we use oxygen compounds as oxidisers in pyrotechnic mixtures, but we sometimes encounter oxidisers that do not contain oxygen. As an example of a combustion reaction not involving oxygen:



The oxidiser in the above equation is hexachloroethane.

Many active metals (such as aluminium and magnesium) liberate more heat when combining with fluorine than with oxygen. We may therefore imagine compositions in which organofluorine compounds will serve as oxidisers.

Thus, for example, a mixture of magnesium with polytetrafluoroethene ("Teflon") will be capable of combustion^{††}.



The heat of reaction is calculated to be about 9.6 kJ g⁻¹.

In this chapter we will consider only oxidisers within the narrow meaning of the word, i.e., substances whose oxidising effect is due to the oxygen contained in them, which is consumed during combustion of the fuel.

Section 1. Selection of Oxidisers and their Classification

An oxidiser must be a solid with a melting point not lower than 50-60°C, and must have the following properties:

1. it must contain as much oxygen as possible;
2. it must release oxygen readily during the combustion reaction;

† The only exception is where there is a large surface area for contact between the fuel and the air, i.e., when the fuel is present as a finely dispersed powder in the air.

†† The ability of $(\text{C}_2\text{F}_4)_n + \text{Na}$ to sustain combustion has been shown in Ref 233, Volume 1, page 592.

3. it must be chemically stable over the temperature range -60°C to $+60^{\circ}\text{C}$, and must not be decomposed by water;
4. it must be non-hygroscopic;
5. it must not be scarce, or difficult to obtain;
6. it must not be toxic to humans.

However, oxidisers presently used in pyrotechnic compositions do not necessarily have all the desirable properties listed above. For example, NaNO_3 and NaClO_4 are hygroscopic, and lead salts are toxic.

We must often accept the disadvantageous characteristics of individual oxidisers and seek to minimise them by the production process, for example, by hermetic sealing.

Particular attention should be paid to the sensitiveness of the composition to mechanical stimuli, and to its explosiveness.

When an oxidiser is selected for flame compositions, we must also consider the spectral radiation of its decomposition products. Therefore, in signal flare compositions, we must not use oxidisers which change the colour of the flame (e.g. sodium salts must not be used for red, green or blue flare compositions).

The following compounds are most frequently used as pyrotechnic oxidisers:

Salts

1. nitrates - NaNO_3 , KNO_3 , $\text{Sr}(\text{NO}_3)_2$, $\text{Ba}(\text{NO}_3)_2$;
2. chlorates - KClO_3 ;
3. perchlorates - KClO_4 , NaClO_4 .

Peroxides

1. barium - BaO_2

Oxides

1. iron - Fe_3O_4 and Fe_2O_3 ;
2. manganese - MnO_2 ;
3. lead - Pb_3O_4 , PbO_2 .

Besides the above materials, we should also consider the possibility of using oxidants such as:

chromates and dichromates	- BaCrO_4 , PbCrO_4 , $\text{K}_2\text{Cr}_2\text{O}_7$;
potassium permanganate	- KMnO_4 ;
chlorates	- NaClO_3 , $\text{Ba}(\text{ClO}_3)_2$;
lead nitrate	- $\text{Pb}(\text{NO}_3)_2$;
sulphates	- CaSO_4 , SrSO_4 , BaSO_4 ;
certain oxides and peroxides	- CuO , SiO_2 , SrO_2 .

Potassium dichromate is used in some match (i.e., fuse) compositions, but in little else because it liberates 16% by weight oxygen; it decomposes comparatively readily, since the first stage of decomposition absorbs a small quantity of heat:



We must also consider that potassium dichromate and potassium permanganate exert a strong irritant or even corrosive effect on human mucous membranes.

Explosive (and semi-explosive) substances capable of intramolecular combustion are also used as oxidisers in pyrotechnic mixtures. For example:

1. polynitro compounds - trinitrotoluene (tritol, TNT), hexogen, hexanitroethane, etc..
2. ammonium salts - perchlorate NH_4ClO_4 , and nitrate NH_4NO_3 ;

However, their use often increases considerably the composition's explosive properties and its sensitiveness to mechanical stimuli.

Recent research ¹⁵⁵ has established that water can act as an oxidiser in compositions containing such fuels as magnesium or aluminium. These investigations have a practical significance in view of the use of certain oxidisers containing water of crystallisation.[†]

The oxides of several metals - chromium, vanadium, etc., - are used as oxidisers in pyrometallurgical processes to obtain pure metals.

Ellern ⁹ notes that oxides such as Cu_2O , Bi_2O_3 and WO_3 are occasionally used in pyrotechnics, and that among the peroxides, sodium peroxide, Na_2O_2 is used, and even silver peroxide, Ag_2O_2 , which has little thermal stability, and which decomposes at slightly elevated temperature. He also indicates the possibility of using other oxidising salts such as bromates, iodates, periodates and ferrates, which are as yet of only theoretical interest. However, it is known that lead iodate, $\text{Pb}(\text{IO}_3)_2$, may be used in anti-hail compounds (see Chapter XXII) to obtain PbI_2 .

Section 2. Physico-Chemical Properties of Oxidisers.

The most important quantitative properties of oxidants are:

1. density (at room temperature);
2. melting point;
3. temperature of rapid decomposition;
4. the thermal decomposition reaction;
5. the heat of thermal decomposition;
6. the percentage content of active oxygen (calculated on the basis of 4.);
7. hygroscopicity;
8. toxicity;
9. melting points and boiling points of the decomposition products.

† See Ref 41 for the use of hydrated salts.

The melting point of an oxidiser is of pyrotechnic interest because most oxidants decompose rapidly only at or above this temperature.

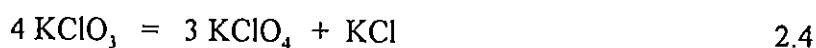
The "temperature of rapid decomposition" mentioned in many articles is ill-defined. It *should* be quantified as the temperature at which the partial pressure of oxygen above the oxidiser achieves some definite value (e.g. 5 or 50 mm Hg), but, unfortunately, such data are not yet available for the majority of oxidisers.

Equations for the thermal decomposition of oxidisers are given in many text books. However, it must be remembered that the reaction under the conditions of combustion (high temperature) may be different, and the extent of decomposition is likely to be more complete since all (or almost all) the oxygen in the oxidiser is used to sustain the combustion. The heat of the decomposition reaction, if the equation is known, is calculated by Hess's law (see Chapter VI).

Quantitative estimation of hygroscopicity will be discussed later in this chapter.

The properties of those oxidisers most frequently used in pyrotechnics are given in Table 2.1. The equation in column 5 of this table is that of the decomposition reaction most likely under the conditions of the pyrotechnic reaction. (The properties of NH_4ClO_4 and NH_4NO_3 , used primarily in rocket compositions, are considered in Chapter XX).

At low temperatures, potassium chlorate decomposes to form the perchlorate:



Under combustion conditions, however, its products are only potassium chloride and oxygen:



Potassium chlorate decomposes rapidly only above its melting point (270°C) but the decomposition temperature may be reduced sharply by the addition of catalysts. The most pronounced catalytic effects are shown by manganese dioxide MnO_2 , and by cobalt oxide Co_2O_3 .

Alekseyenko¹⁶ considered the relative thermal stabilities of the chlorates of the various metals and concluded that decomposition is favoured by cations with large charge and small radius. A sharp decrease in the thermal stability of chlorates (and also of nitrates) is observed in the series: Na, Mg, Al and Ca, Mg, Be.

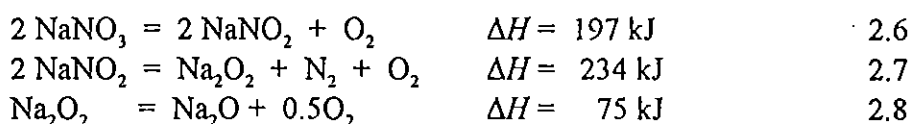
Potassium perchlorate and sodium perchlorate decompose when strongly heated ($500\text{-}600^\circ\text{C}$) into the metal chloride and oxygen. (see Table 2.1).

According to Gmelin (42, No 22), the decomposition of KClO_4 is accelerated by compounds of Fe, Co, Ni, and W. The addition of copper salts has a particularly marked effect.

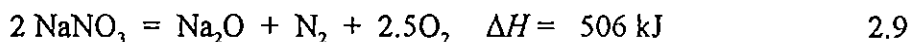
The decomposition of the alkali metal or alkaline earth nitrates proceeds by stages⁴⁷, for example:

Formula	MW	Density Mg m ⁻³	MP °C	Decomposition Reaction	Heat of Formation kJ mol ⁻¹		Heat of Decomposition Reaction kJ mol ⁻¹	Active Oxygen %	Oxidant liberating 1g oxygen g	Compositions in which used
					Oxidiser	Combustion products				
KClO ₃	123	2,300	360	2KClO ₃ = 2KCl + 3O ₂	401	443	41.8	39	2.55	smoke and match. Rarely in signal flare.
KClO ₄	139	2,500	ca.610	2KClO ₄ = 2KCl + 4O ₂	433	436	5.0	46	2.17	Incendiary, rocket. Rarely in signal flare.
NaClO ₄	122	2,500	ca.482	2NaClO ₄ = 2NaCl + 4O ₂	385	410	46	52	1.9	Illuminating. Hygroscopic.
NaNO ₃	85	2,200	308	2NaNO ₃ = Na ₂ O + N ₂ + 2.5O ₂	464	422	-506	47	2.13	Illuminating. Yellow flare. Hygroscopic.
KNO ₃	101	2,100	336	2KNO ₃ = K ₂ O + N ₂ + 2.5O ₂	498	364	-631	40	2.53	Igniting.
Sr(NO ₃) ₂	212	2,900	645	Sr(NO ₃) ₂ = SrO + N ₂ + 2.5O ₂	966	594	-372	38	2.65	Tracer and red flare.
Ba(NO ₃) ₂	261	3,200	592	Ba(NO ₃) ₂ = BaO + N ₂ + 2.5O ₂	991	556	-435	30	3.27	Illuminating. Tracer, green flare, incendiary.
Fe ₂ O ₃	232	5,200	1,527	Fe ₂ O ₃ = 3Fe + 2O ₂	1112	0	-1112	28	3.34	Thermite, incendiary.
MnO ₂	83	5,000	(>530)	MnO ₂ = Mn + O ₂	523	0	-523	37	2.72	Thermite,
				MnO ₂ = MnO + 0.5O ₂	523	389	-134	18	5.44	incendiary.
BaO ₂	169	5,000	(700)	BaO ₂ = BaO + 0.5O ₂	627	556	-71	9	10.6	Igniting.

Table 2.1 Properties of Oxidisers.



Adding (2.6), (2.7), (2.8) we obtain:



When non-metals, such as carbon, sulphur, phosphorus, or organic materials are used as fuels, the nitrates decompose to the metal oxides (Na₂O in the example). In these cases, where the combustion temperature is low, the combustion products contain a considerable proportion of nitrites; this is the case when sodium nitrate reacts with lactose. We should note in this context that the nitrites of the alkali and alkaline earth metals are less stable thermally than the corresponding nitrates (see Voskresenskaya and Berul²³). When high energy reducing agents such as aluminium or magnesium are used as fuels, more extensive decomposition of the nitrates is likely to occur. Thus the combustion of a mixture of magnesium and barium nitrate may be expressed:



We should note that the reaction of magnesium with barium oxide is accompanied by the liberation of a small quantity of heat:



Considerably more heat is liberated by the reaction of magnesium with sodium oxide:

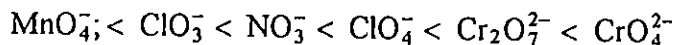


The formation of metallic sodium during combustion of $\text{NaNO}_3 + \text{Mg}$ mixtures containing more than 60% magnesium has been established experimentally by ignition of these mixtures in a calorimetric bomb.

Shargorodskiy and Shor ³⁸ have obtained thermograms for the decomposition of the nitrates of Be, Ca, Sr, and Ba, from which the decomposition temperatures were established as: $\text{Be(NO}_3)_2$ 175-200°C, $\text{Ca(NO}_3)_2$ 480-500°C, $\text{Sr(NO}_3)_2$ 580-600°C, and $\text{Ba(NO}_3)_2$ 555-600°C.

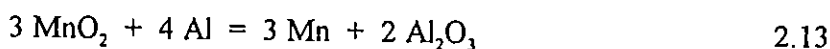
Hogan, Gordon, and Campbell report ⁴⁵ that a mixture of equivalent parts of $\text{Ba(NO}_3)_2$ and KClO_4 melts at 520°C.

From Ellern ⁹ it follows that, with a constant cation, the decomposition temperature of oxidising salts increases in the order:



For a given anion, the decomposition temperature of the sodium salt is lower than that of the potassium salt.

Free metals are formed during the combustion of ferroaluminium and manganese-aluminium thermites:



But during combustion of compositions not containing active metals (Mg, Al), manganese dioxide releases only half of the oxygen contained in it (see Table 2.1).

Barium peroxide BaO_2 readily releases only half of its oxygen and is converted to BaO .

In Table 2.1, columns 6 and 7 give data on the heat of formation of the oxidisers and their decomposition products. Column 8 gives the essential characteristic of the oxidiser: the quantity of heat released or absorbed during its decomposition.

To obtain the greatest quantity of heat from combustion of a composition it is, of course, advantageous to use oxidisers which require the minimum heat to decompose. But we must note that such compositions are usually the most sensitive to mechanical effects. Chlorate compositions are especially sensitive to mechanical effects and have considerable explosive properties, since decomposition of a chlorate liberates a very perceptible quantity of heat.

Thus, for example, the heat that is liberated during the decomposition of KClO_3 is adequate to heat the salt from room temperature to its melting point, i.e., to 370°C .

The processes of decomposition of sodium chlorate and especially barium chlorate are even more exothermic:



Compositions containing barium chlorate are little used at the present time because of their great sensitiveness to friction and their considerable explosive properties (see also Chapter XVI).

Oxidisers which decompose with the liberation of heat may, under certain circumstances, have explosive properties themselves, even when not mixed with fuels. For example, the molten chlorates of potassium, sodium or barium can be exploded by a heavy blow.

Potassium perchlorate KClO_4 has no explosive properties on its own because decomposition occurs with the liberation of only a small quantity of heat, 2.5 kJ mol^{-1} †, which corresponds to 17 kJ kg^{-1} .

Sodium perchlorate should be considered more dangerous than potassium perchlorate because it liberates more heat on decomposition:



From Table 2.1 it is apparent that the nitrates of the alkali metals normally require an absorption of heat for decomposition: this generally reduces the heat balance of the pyrotechnic composition made from them.

The heat consumption in the decomposition of an oxidiser is even more important for the oxides of iron and manganese.

Heat expenditure on the decomposition of peroxide (barium peroxide is given in Table 2.1) is comparatively low. But the oxygen content of BaO_2 is small (see Table 2.1) and this strongly reduces its value as an oxidiser.

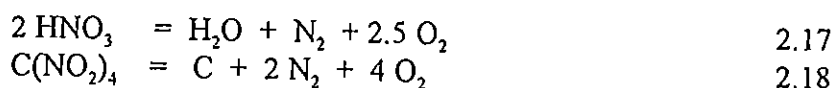
† Skuratov et al.,^{22,33} report 10.5 kJ mol^{-1} for the decomposition of KClO_4 , but this does not agree with the figures from other investigators.

The ease with which oxygen can be liberated from an oxidiser, and the heat needed to decompose the oxidiser are closely linked. Thus, chlorates liberate oxygen more readily during the combustion of a pyrotechnic composition (at lower temperature) than do nitrates; the latter, however, may liberate it more readily than many oxides. We should note that oxides have been used so far only when mixed with magnesium, aluminium, and certain other substances which liberate a great quantity of heat on combustion.

Table 2.1 Column 9 gives the percentage of active oxygen in the oxidiser; i.e., the number of grammes of oxygen released during decomposition of 100 grammes of the oxidant. The numerical data in this column are calculated on the basis of the decomposition reactions of the oxidiser given in Column 5. We should note that it is not the total amount of oxygen contained in the oxidiser that is of the greatest interest, but that quantity of oxygen which participates actively in the reaction and which is expended directly on the oxidation of the fuel; these figures are also shown in Column 9.

As is apparent from Table 2.1, the quantity of oxygen liberated from oxidisers is not more than 52% of the weight of the compound.

It is interesting at this stage to make a comparison with liquid oxidisers such as nitric acid and tetranitromethane (TNM). According to the equations below the active oxygen content of HNO_3 is 63%, and of TNM is 65%



The total oxygen content of hydrogen peroxide is very great - 94% - but the active oxygen content is 47%.

The figures from Column 10 are used for the calculation of the percentage content of the component in binary mixtures (see Chapter V).

Table 2.2 contains data on the melting and boiling points of certain decomposition products of

Substance	KCl	NaCl	SrO	BaO	Fe	Mn	MnO
MP /°C	768	800	2,450	2,190	1,527	1,242	1,785
BP /°C	1,415	1,165	-	-	2,710	1,900	-

Table 2.2 Properties of Decomposition Products of Oxidisers.

oxidisers. From these data we may form some ideas about the presence or absence of a gaseous phase and liquid residue on combustion, the quality of smoke formation, etc.

The oxides of the alkali metals Na_2O and K_2O melt at red heat, i.e., at approximately 800°C.

Section 3. Hygroscopicity of Oxidisers.

Many salts which satisfy most of the requirements for oxidisers are very hygroscopic. The readily soluble salts of magnesium, calcium, sodium, and ammonium are especially hygroscopic.

The quantity of water absorbed by the salts depends upon the humidity and temperature of the air, upon the individual properties of the salt, and the area of contact between the salt and the moist air.

If the relative humidity of the air in contact with the salt is greater than the relative humidity of air over a saturated solution of the salt, then the salt will absorb moisture from the air to form a saturated solution. If salt crystals are spread in the air, and the air has a lower relative humidity than the air over a saturated solution of the salt, then the salt will dry out. It is even possible to lose the water of crystallisation from certain crystalline hydrates.

Thus sodium nitrate absorbs water from air of relative humidity greater than 77%.

The relative humidity of the air over a saturated solution of a salt may be calculated by dividing the vapour pressure over the saturated solution of the salt (p) by the vapour pressure over pure water (p_0) at the same temperature. The vapour pressure is usually expressed in mm Hg. The relative humidity over a saturated solution of sodium nitrate at 20°C is hence:

$$\frac{p}{p_0} = \frac{13.5}{17.5} = 0.77$$

Literature values of "hygroscopic points" of oxidiser salts at a temperature of 20°C are given in Table 2.3.

In those cases where there are no data available on the vapour pressure over a saturated salt solution, the hygroscopicity of the salt may be judged by the degree of solubility of the salt in water. Although it is inaccurate, we may judge that the hygroscopicity of the salt is proportional to its solubility in water.

From Table 2.3 it is apparent that the least hygroscopic salts are $\text{Ba}(\text{NO}_3)_2$, KClO_4 , KClO_3 , and then NH_4ClO_4 , $\text{Ba}(\text{ClO}_3)_2$, $\text{Pb}(\text{NO}_3)_2$, and KNO_3 .

Salts above which the vapour pressure is less than that above a saturated solution of potassium nitrate are considered to be hygroscopic.

In practice, it is difficult to work with salts which have saturated solutions giving less than 75-80% relative humidity.

$\text{Mg}(\text{NO}_3)_2$, $\text{Ca}(\text{NO}_3)_2$, $\text{Al}(\text{NO}_3)_3$, $\text{Sr}(\text{ClO}_3)_2$, and $\text{Ba}(\text{ClO}_4)_2$ are not used at all in pyrotechnics as oxidisers because of their great hygroscopicity.

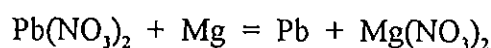
For the same reason, NaNO_3 is used only where the composition can be reliably sealed from the air. Strontium nitrate is used in pyrotechnic mixtures only in the absence of salts of magnesium

and calcium which raise the hygroscopicity. Useful information on the hygroscopicity of salts is published by Pestov ²⁹.

Oxidiser	100 p/p ₀ when t = 20°C	Solubility of anhydrous salt in water g/100g solution			
		0°C	20°C	50°C	100°C
<u>Chlorates</u>					
KClO ₃	97	3	7	17	36
Ba(ClO ₃) ₂	94	17	26	37	51
NaClO ₃	74	45	50	59	67
<u>Perchlorates</u>					
KClO ₄	94	0.7	1.7	5	18
NH ₄ ClO ₄	96	11	18	30	
NaClO ₄	69-73	-	66	71	75
<u>Nitrates</u>					
Ba(NO ₃) ₂	99	4.8	8	15	25
KNO ₃	92.5	12	24	46	71
Pb(NO ₃) ₂	94	27	34	44	56
Sr(NO ₃) ₂	86	28	42	18	50
NaNO ₃	77	42	47		63
NH ₄ NO ₃	67	54	64	78	94

Table 2.3 Hygroscopicity and Solubility of Oxidisers.

The salts of heavy metals are seldom used as oxidisers in pyrotechnics for several reasons: they are scarce; the proportion of oxygen contained in them is relatively low; exchange reactions may occur with metals such as magnesium and zinc to produce hygroscopic salts e.g.,



Electrode	E ₀ /V	Electrode	E ₀ /V	Electrode	E ₀ /V
Li/Li ⁺	+3.01	Mn/Mn ²⁺	+1.05	Cu/Cu ⁺	-0.51
K/K ⁺	+2.92	Zn/Zn ²⁺	+0.76	Hg/Hg ⁺	-0.80
Ba/Ba ²⁺	+2.92	Fe/Fe ²⁺	+0.44	Hg/Hg ²⁺	-0.80
Sr/Sr ²⁺	+2.89	Tl/Tl ⁺	+0.34	Ag/Ag ⁺	-0.80
Ca/Ca ²⁺	+2.84	Sn/Sn ²⁺	+0.14	Au/Au ⁺	-1.70
Na/Na ⁺	+2.71	Pb/Pb ²⁺	+0.13	Pt(F ⁻)/F ₂	-2.80
Mg/Mg ²⁺	+2.38	Pt(H ₂)/H ⁺	0		
Al/Al ³⁺	+1.66	Cu/Cu ²⁺	-0.34		

Table 2.4 Electrode Potentials E₀ at 25°C (voltage series)

Generally speaking, if a pyrotechnic composition contains active metal powders (magnesium, zinc, etc.), we must select the oxidiser from salts of metals lying above these in the voltage series (see Table 2.4).

In those compositions which include magnesium, of those metals that have suitable voltages, and whose salts could be considered acceptable, lithium salts are costly, calcium salts are too hygroscopic, and therefore only potassium, barium, strontium and sodium salts can be considered in practice.

Section 4. Technical Requirements imposed upon Oxidisers

The following requirements are imposed upon the purity of oxidisers used in pyrotechnics:

1. Maximum content of specified material (usually not less than 98-99%.)
2. Minimum moisture content (usually not more than a few tenths per cent.)
3. Minimum contamination by hygroscopic salts and salts of heavy metals.
4. Neutral reaction of aqueous solution.
5. Absence of combustible or solid (e.g., sand, glass) impurities which would increase the sensitiveness of the composition to mechanical stimuli.
6. Absence of contaminants which would reduce the chemical stability of the composition in storage (e.g., bromate impurities in chlorates), or which would reduce the desired effect of the composition.

Besides this, the oxidiser must have the necessary particle size.

As an example, we give the technical specification for barium nitrate[†].

1 Pure $\text{Ba}(\text{NO}_3)_2$	not less than 99%
2 Moisture	not more than 0.5%
3 Residues insoluble in water	not more than 0.25%
4 Chlorides expressed as BaCl_2	not more than 0.1%
5 Reaction of aqueous solution (to litmus)	neutral
6 External appearance and colour	small crystals of white to light-yellow colour

Chlorides are undesirable contaminants in oxidisers since they are quite hygroscopic, as shown by the following data on "hygroscopic points" (percent at 20°C):

KCl - 86; NaCl - 77; NH_4Cl - 80; $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ - 33

[†] GOST (All-Union State Standard) 1713-53

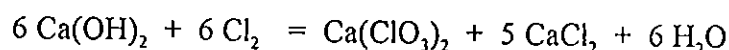
We may see how the addition of chlorides affects the hygroscopicity of the salt from the following data:

	KClO ₃		
	Chemically pure	+ 0.05% KCl	+ 0.1% KCl
Moisture content of salt after storage for a day at 15-20°C (%)	0.1	0.3	0.9

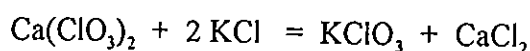
Section 5. Production of Oxidisers

Chlorates. At the present time chlorates are produced both by electrochemical and by purely chemical methods.

Potassium and sodium chlorates have the greatest industrial significance. The chemical method of producing potassium chlorate consists of a reaction between slaked lime, chlorine, and potassium chloride in solution:



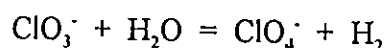
and



The solution is cooled, the crystalline potassium chlorate separates, and is filtered off and dried. The essential shortcoming of the process is the great quantity of waste: about 3 tonnes CaCl₂ per 1 tonne of KClO₃.

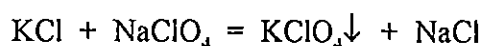
The advantage of the electrochemical process for the production of chlorates lies in the absence of wastes and in its simplicity. It involves the electrolysis, in cells without diaphragms, of a naturally occurring chloride. The chlorine that is liberated at the anode reacts with the alkali formed at the cathode to form the chlorate. In the case of the preparation of potassium chlorate from potassium chloride, the process is continued until the concentration of KClO₃ reaches 0.2 kg l⁻¹ when it is cooled to precipitate crystals of the chlorate. Potassium chloride is added to the mother liquor and the process is continued.

Perchlorates. These are obtained by electrochemical oxidation of chlorates according to the summary equation:



Sodium perchlorate is usually prepared by this method.

Potassium perchlorate, which is much less soluble in water than sodium perchlorate, is obtained by an exchange reaction:



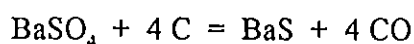
Nitrates. Sodium nitrate was previously mined from saltpetre bearing earth in Chile from where it was exported to all countries for use as fertiliser. Now, sodium nitrate is obtained almost exclusively by synthetic means - the reaction between nitric oxides and a solution of soda.

Potassium nitrate is encountered naturally in very small quantities. It is obtained from potassium chloride by an exchange reaction with sodium nitrate.

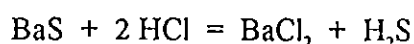
The nitrates of strontium and barium may be obtained by dissolving the natural minerals *strontianite* (SrCO_3) or *witherite* (BaCO_3) in nitric acid.

A more complex process for obtaining the nitrates of strontium and barium is from their sulphate minerals *barytes* (BaSO_4), and *celestine* (SrSO_4). The chemistry of this process is indicated below using barium as an example.

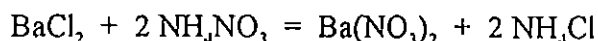
When a mixture of barytes and coal is calcined in flame furnaces, the following reaction occurs:



The sulphide is then treated with hydrochloric acid:



The barium chloride is converted to the nitrate by an exchange reaction with a solution of ammonium nitrate:



Barium nitrate has limited solubility in cold water, and is easily separated.

Detailed descriptions of the preparation of the salts listed here have been published by Vol'fkovich ²¹, Pozin ³⁰, Billiter ¹⁸, Shraybman ⁴⁰, Minnovich ²⁶, and Smirnov ³⁴.

Barium peroxide BaO_2 is obtained by heating the porous oxide of barium BaO in a current of hot air at about 500°C . The barium oxide is obtained by roasting barium carbonate or barium nitrate. Barium peroxide forms the octahydrate $\text{BaO}_2 \cdot 8\text{H}_2\text{O}$.

Iron slag Fe_3O_4 occurs naturally in enormous quantities as the mineral *magnetite*. It is roasted at $400\text{-}500^\circ\text{C}$ to remove moisture and organic contaminants, and then pulverised.

Manganese dioxide MnO_2 is encountered in nature as the mineral *pyrolusite*. It may also be prepared from manganese salts or from potassium permanganate.

Chapter III

Fuels

In this chapter we consider the properties of combustible substances which do not act just as binders in pyrotechnic compositions. A description of binders is given in the next chapter (Chapter IV).

Section 1. Selection and Classification of Fuels

In the selection of a fuel for a pyrotechnic composition it is necessary to consider all the requirements imposed upon the composition, and one of these factors is the way in which best to achieve the desired pyrotechnic effect.

The best effect for incendiary, illuminating, tracer and photoflash compositions is achieved with a high temperature of combustion; in this case, high-energy fuels must be used.

High-energy fuels must also be used for solid pyrotechnic propellants.

For smoke compositions, a high temperature of combustion is usually undesirable; frequently we either chose a fuel with an average heat of combustion, or we arrange for incomplete combustion (for example, the combustion of carbon to CO) to occur.

The physico-chemical properties of the products of a fuel's oxidation products also play an important part in the selection of the fuel. First it is necessary to know the aggregate state of the combustion products at room temperature and at the temperature of the combustion of the composition. For illuminating compositions, it is important to observe a certain optimum ratio between the quantity of gaseous products, which has a strong effect on the dimensions of the flame (and consequently on the size of the luminous area), and the concentration (density) in the flame of solid and liquid particles of radiators. Either an excess or a deficiency of gaseous products cause a decrease in the light power.

In the combustion products of rocket compositions (solid pyrotechnic fuel), there must be a maximum quantity of gas, and a minimum quantity of solid matter (see Chapter XX, section 1 for more details).

In smoke compositions, the quantity of gases formed on combustion must be very significant, because this ensures the timely ejection of smoke-forming particles into the atmosphere.

The products of combustion of thermite must remain liquid for some time otherwise the required incendiary effect would not be achieved.

For flame compositions, selection of the fuel requires consideration of the intensity of the light radiated by its oxidation products, and also the distribution of this radiated energy throughout the spectrum.

The ease with which the fuel may be oxidised also plays an important part in its selection. For example, silicon and graphite are oxidised only with difficulty, even by the most energetic oxidisers (pure oxygen or chlorates), and consequently have limited application as pyrotechnic fuels.

Aluminium, as a sufficiently fine powder, burns adequately energetically both with the oxygen from an oxidiser, and with the oxygen of the air (when the metal powder is suspended in air).

Magnesium, which is very readily oxidised even if not finely powdered, may be burned completely in atmospheric oxygen. The ability to burn in atmospheric oxygen is a very desirable property of a pyrotechnic fuel.

Some fuels are readily oxidised, and compositions containing them are consequently excessively sensitive to shock and friction, or have too low an ignition temperature. For example, white phosphorus cannot be mixed with any oxidiser, and it cannot even be stored in air without self-ignition. The use of red phosphorus in mixtures with oxidants is also very limited: mixtures with chlorates are almost unavoidably subject to self-ignition, and mixtures with other oxidisers (with nitrates, for example), have an excessively great sensitivity to shock and friction.

It is desirable that as little oxygen as possible is required for the combustion of a unit weight of the fuel, since it is a disadvantage to have a high proportion of oxidiser in the mixture: it leads to a reduction in the amount of fuel, and to a reduction in the quantity of heat liberated.

In addition, the choice of fuel is influenced by the need for adequate chemical stability of the composition during storage. We would consider, for example, mixtures containing a chlorate and sulphur to be inadequately stable chemically.

Therefore, the fuels used in pyrotechnic compositions must satisfy the following basic requirements. They must:

1. have a heat of combustion which is matched to the required effect;
2. be sufficiently readily oxidised, either by the oxygen in the oxidiser, or by the oxygen in the air;
3. have products of combustion which assist the required effect;
4. require the minimum quantity of oxygen for their combustion;
5. be chemically and physically stable over the temperature range -60°C to $+60^{\circ}\text{C}$, and be as stable as possible to the effects of weak solutions of acids and alkalies;
6. be non-hygroscopic;
7. be easily pulverised;
8. not be toxic to humans;
9. be readily obtainable materials that are not in critical short supply.

The fuels used for the manufacture of pyrotechnic compositions may be divided into the following categories:

Inorganic Fuels

1. High-energy metals: magnesium, aluminium; zirconium and titanium are used considerably more rarely.
2. Alloys of magnesium and aluminium: aluminium - silicon (AM), magnesium - silicon, aluminium - silicon, and others.
3. Metals of average heat of oxidation: zinc, iron, antimony, and others.
4. Non-metals: phosphorus, carbon (as carbon black or charcoal), sulphur.
5. Inorganic compounds: a) sulphides: sesquisulphide (P_4S_3), antimony sulphide (Sb_2S_3), pyrites (FeS_2), and others.
b) other inorganic compounds: phosphides, silicides, carbides, and others.

Organic Fuels

1. hydrocarbons: benzene, toluene, naphthalene, and others.
2. Mixtures of aliphatic and carbocyclic hydrocarbons: gasoline, kerosene, petroleum, black fuel oil, paraffin, and others.
3. Carbohydrates: starch, sugar (milk, beet), sawdust.
4. Organic substances of other classes: urotropine, stearic acid (stearine), dicyanamide, metaldehyde, and others.

Section 2. High-Energy Fuels

The greatest quantity of heat during combustion, both in atmospheric oxygen and with oxygen from an oxidiser, is liberated by the following 12 elements:

<u>metals:</u>	lithium, beryllium, magnesium, calcium, aluminium, titanium, zirconium [†] .
<u>non-metals</u>	hydrogen, boron, carbon, silicon, and phosphorus.

The quantities of heat liberated during combustion of these elements are given in Table 3.1.

The quantities Q_1 , Q_2 , and Q_3 serve as a characteristic of the heat of reaction of the elements.

The quantity of heat Q_1 liberated in the combustion of 1 kg of the element to oxides may serve as a standard of the heat of the fuel under the conditions of atmospheric oxidation. Q_1 is calculated by dividing the kilogramme-molecular heat of formation of the oxide (Q) by the product of the atomic weight (A) and the number of atoms (n) of the element in the molecule of the oxide.

The quantity of heat Q_2 liberated in the formation of 1 kg of the oxide may serve to some degree as a standard of the heat of the composition, in which some fuel or other undergoes combustion with the oxygen of the oxidiser.

In Fig 3.1 we show how the value of Q_2 for oxides varies with the position of the element in the periodic table.

[†] We should also consider niobium, vanadium, scandium, and yttrium as high-energy metals, but, in our opinion it is premature to consider them as pyrotechnic fuels. Ellern⁹ gives recipes for "exotic" compositions including niobium and tantalum.

The quantity of heat Q_3 , obtained by dividing the gramme-molecular heat of formation of the oxide (Q) by the number of atoms of the element in a molecule of the oxide (n), makes it possible to judge to some degree the combustion temperature of the element since, to a first approximation, the combustion temperature is proportional to the quantity of heat per gramme-atom, i.e., it is proportional to Q_3 .

Element Atomic Weight	Oxides		Heat of formation /kJ			
	Formula	Molecular Weight	per mol of oxide	$Q_1 = \frac{Q}{m.A}$	$Q_2 = \frac{Q}{M}$	$Q_3 = \frac{Q}{n}$
<u>Metals</u>						
7	Li ₂ O	30	598	43	20	199
9	BeO	25	594	66	24	297
24	MgO	40	602	25	15	201
27	Al ₂ O ₃	102	1,673	31	16	335
40	CaO	56	636	16	11	212
48	TiO ₂	80	937	20	12	312
91	ZrO ₂	123	1,087	12	9	362
<u>Non-metals</u>						
1	H ₂ O	18	286	143	16	95
12	CO ₂	44	393	33	9	131
11	B ₂ O ₃	70	1,263	57	18	253
28	SiO ₂	60	870	31	14	290
31	P ₂ O ₅	142	1,535	25	11	219

Table 3.1 Heat of Formation of Oxides^{98,94}

The highest temperature is developed by combustion of metals: zirconium, aluminium, magnesium, and calcium.

Hydrogen, carbon, phosphorus, and lithium have a considerably lower combustion temperature.

At the present time, only aluminium and magnesium are used on the large scale, and phosphorus and carbon to a lesser degree.

Aluminium should be considered to be the basic high-energy pyrotechnic fuel - the metal forms a large fraction of the earth's crust (8.8%), and it is mined in very great quantities: in 1960 the world production of aluminium exceeded 4,000,000 tons.

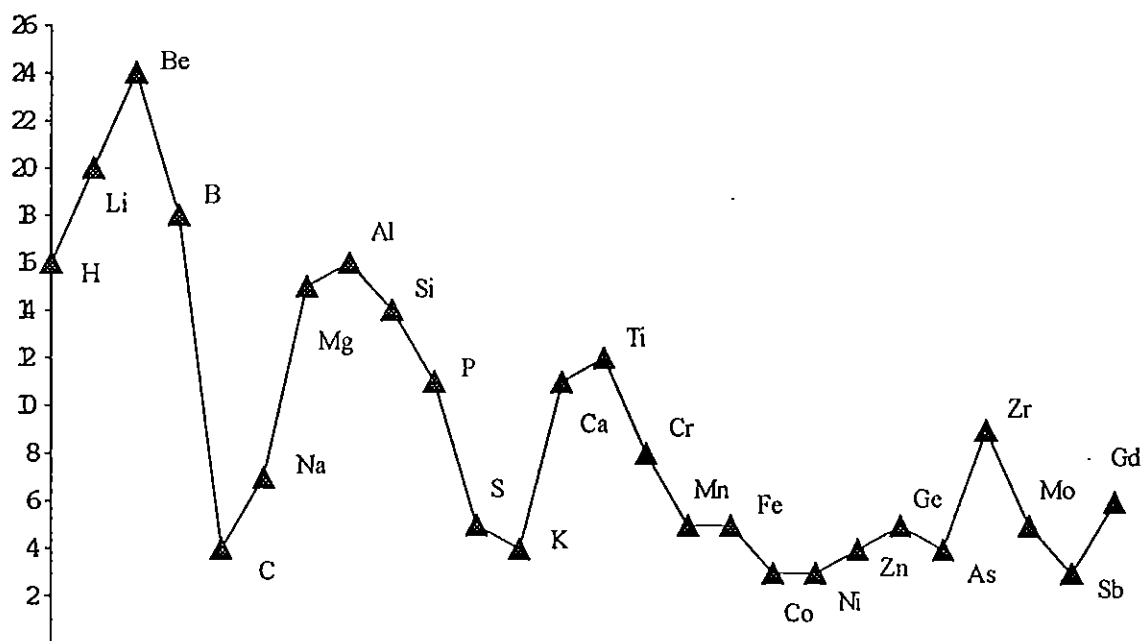


Fig 3.1 Dependence of heat of formation of an oxide (MJ kg^{-1}) upon the atomic number of the element.

Magnesium occupies the second place. World production in 1944 (during the war) was about 210,000 tons; in 1958 it was about 110,000 tons. In recent years the USSR has occupied the first place in the world for magnesium production. The ever increasing demand for magnesium alloys which are used in aircraft construction and rocket engineering has a great influence on the growth of the magnesium industry: alloys of magnesium with Al, Zr, Mn, and Zr are of technical significance; magnesium is also used in the production of metallic titanium⁶⁸.

Beryllium is a comparatively rare element in the Earth's crust (0.0006%); production of its ore *beryl* did not exceed 10,000 tons in 1959. Beryllium has still been little studied as a pyrotechnic fuel: a great obstacle to its use is its very significant toxicity⁶⁹, particularly in a finely divided state. The high boiling point of beryllium (about 2400°C) makes it difficult to vaporise during combustion. Beryllium is among the fuels that are difficult to burn. The properties of beryllium have been collected⁶⁹.

Zirconium⁶² is an expensive and strategically critical material; its abundance in the Earth's crust is not great (0.02%). Compositions containing zirconium have a high temperature and a high rate of combustion. At the present time zirconium is used only in gasless delays and igniting compositions (see Chapter XXI for more details), in products of small dimensions. The advantages of zirconium include the small quantity of oxygen consumed in its combustion, and its great resistance to corrosion.

The combustion of zirconium is discussed by Harrison¹⁰⁸.

Titanium reacts readily at 400-600°C not only with the oxygen, but also with the nitrogen of the air. The titanium content of the earth's crust is significant (0.6%). In the USA titanium is known

as the "war baby" (1941-1945). World titanium production in 1956 amounted to about 20,000 tons. As yet, titanium is still costly, but the prospects for the development of the titanium industry are great ^{53, 63}.

Patents have been secured for the use of titanium in pyrotechnic compositions. For example, a composition for a smoke mixture: Ti - 14%; C_2Cl_6 - 43%; ZnO - 43% (Patent DBR 1,063,507).

In US patent 2,929,697 (1960), a rocket powder composition is recommended containing $KClO_4$, graphite, Ti powder (8%), and an organic bonding agent.

Calcium is not expensive and is not in strategically short supply. It is an important constituent of the Earth's crust (3.6%) but it is produced in smaller quantities than magnesium because it has fewer uses.

Powdered calcium is difficult to use as a fuel because it reacts energetically with the moisture and the oxygen of the air. Calcium can be used in the form of alloys with other metals.

Lithium occurs in only small quantities in the Earth's crust (0.006%). The use of lithium, or even of alloys containing a considerable percentage of lithium, is difficult because of the extraordinary reactivity of the metal with the moisture and oxygen of the air ⁶⁴.

Hydrogen is used only in compounds, as organic fuels. The use of hydrides in pyrotechnics is problematical because of the low chemical stability of these compounds ⁷⁰, and because of their low density.

Boron is not a common element in the Earth's crust (0.001%), but the world production of borates and boric acid amounts to hundreds of thousands of tons annually. At one time, the use of boranes, which have a higher energy than ordinary hydrocarbon fuels, was widely advertised in US rocketry. However, in 1959 it was reported that their production had ceased because of their high toxicity (c.f., Maxwell and Young ²²⁷).

The use of elemental boron in pyrotechnic compositions is associated with certain difficulties: the high melting point (2050°C) and boiling point (2550°C) of boron, and the low softening point of boric oxide B_2O_3 . The melting and vaporisation of the latter prevent to some extent the attainment of high temperatures on combustion.

There are indications in the literature that crystalline boron is capable of rapid oxidation, but these do not give us complete confidence that boron will find practical application in pyrotechnic compositions. The rate of oxidation of boron ^{82, 228} depends to a great degree on the extent to which the oxide film can be removed. Samsonov ⁶⁵ has published details.

The use of elementary silicon in pyrotechnics is hampered by the difficulty with which it oxidises; it may give acceptable results in, for example, illuminating compositions, in the form of alloys with magnesium, aluminium, and other metals. Silicon has been used as an additive to explosives ⁸¹.

In pyrotechnics, the quantity of heat liberated on combustion of unit volume of fuel (Q_4 , MJ m⁻³) is of great significance. Such data have been given ⁹, and are shown somewhat differently in Table 3.2. It is apparent that with respect to heat per unit volume, boron occupies first place (density 2.3 Mg m⁻³), the heavy metals Zr, Nb, Mo, Ta, and W are comparable to aluminium, and

Substance	Q_1 kJ kg ⁻¹	Q_4 MJ m ⁻³	Substance	Q_1 kJ kg ⁻¹	Q_4 MJ m ⁻³
Be	66	121	Nb	10.5	87
Al	31	83	Mo	8	79
Mg	25	42	Fe	8	59
Ca	16	25	Mn	7	50
Ti	20	84	Ce	7	46
Zr	12	75	Ta	6	96
B	59	138	Zn	5	38
Si	31	75	W	5	88
P (white)	25	46	Ni	4	38

Table 3.2 Heat liberated on combustion of 1 kg (Q_1) and 1 m³ (Q_4) of certain fuels

considerably more energetic than magnesium. The physico-chemical properties of these elements are given in Table 3.3.

The ignition temperature of metal powders depends to a great degree on the dimensions and shape of the particles of the powder, and also on the quality of the oxide film covering them. The greater the state of division, the lower the temperature of ignition.

Schlichter ¹⁶¹ has surveyed foreign literature and indicates that the ignition temperature of titanium powder may vary within the limits of 300 to 600°C, and that some specimens of finely divided zirconium powder may ignite at room temperature. He also reports that moistened zirconium powder burns more fiercely than dry powder (the system 2 H₂O + Zr is capable of combustion and explosion), and burning zirconium can be extinguished only by smothering it with powdered CaF₂ or CaO, since H₂O, CCl₄, CO₂, and even CaCO₃ react violently with it.

Ellern ⁹ indicates that a number of serious accidents have occurred while working with finely divided titanium (2-5 μm).

It is noted that the ignition temperature of finely divided zirconium powder is about 85°C. It is transported under water, and is also processed under water as far as possible. Coarser fractions of Zr powders have ignition temperatures of the order of 180-200°C. Zirconium alloys always contain traces of hydrogen, and its ignition temperature is lower if there is less hydrogen in it.

Fuels						Oxides		
Symbol	Density Mg m ⁻³	Ignition Temperature of Powder in Air °C	Temperature (°C)		Mass of Fuel reacting with 1 kg oxygen (kg)	Formula	Temperature (°C)	
			Melting Point	Boiling Point			Melting Point	Boiling Point
Metals								
Li	0.5	150	181	1370	0.87	Li ₂ O	1,430	(2,600)
Be	2	>800	1284	(2,460)	0.56	BeO	2,530	(4,120)
Mg	2	550	650	1103	1.52	MgO	~2,800	-
Al	3	>800	660	~2,500	1.12	Al ₂ O ₃	2,030	~3,000
Ca	2	~600	850	1420	2.50	CaO	2,600	(3,500)
Ti	5	600-800	1660	(3,260)	1.50	TiO ₂	1,920	~3,000
Zr	7	180-200	1568	(4,750)	2.85	ZrO ₂	2,700	(4,300)
Non-Metals								
H	0.7	-	-259	-253	0.12	H ₂ O	0	100
C	2	-	>3,600		0.38	CO ₂	-78	sublimes
B	2	>900	2,050	(2,550)	0.45	B ₂ O ₃	~150	(1,500)
Si	2	>900	1430	2600	0.88	SiO ₂	1743	(~2,500)
P (red)	2	260	590	sublimes	0.78	P ₂ O ₅	580	605

Table 3.3 Physico-Chemical Properties of Fuels and their Oxides^{95, 25, 27}

Zirconium powders with particles of 10 µm or more are considered ⁹ to be relatively safe to handle.

Hydrogen requires the greatest quantity of oxygen for its oxidation, and is followed by carbon burning to CO₂ (see Table 3.3). It follows that compositions in which the fuels are organic substances must contain a very great amount of oxidiser and accordingly very little fuel.

The comparative thermal stability of high melting oxides (data from Ref⁵⁸) is shown in Fig 3.2: the most thermally stable oxides are CaO, Y₂O₃, La₂O₃, and ThO₂. The numbers of the groups of the periodic table to which the elements belong are indicated in the figure by Roman numerals. The lines connect oxides having the same values of heats of formation calculated as kg equivalents (at 25 °C). The wide linear cross hatching shows comparatively low stability; the heaviest cross-hatching shows the region of greatest stability.

One of the basic factors determining the chemical stability of metals is the normal electrode potential. Values are given in Table 2.4.

The ease with which metals oxidise is governed by the quality of the oxide film covering the metal. According to the rule formulated by Pilling and Bedworth^{80, 170 page 43}, if the volume of the oxide formed is less than the volume of the metal replaced by it, the oxide film has a friable,

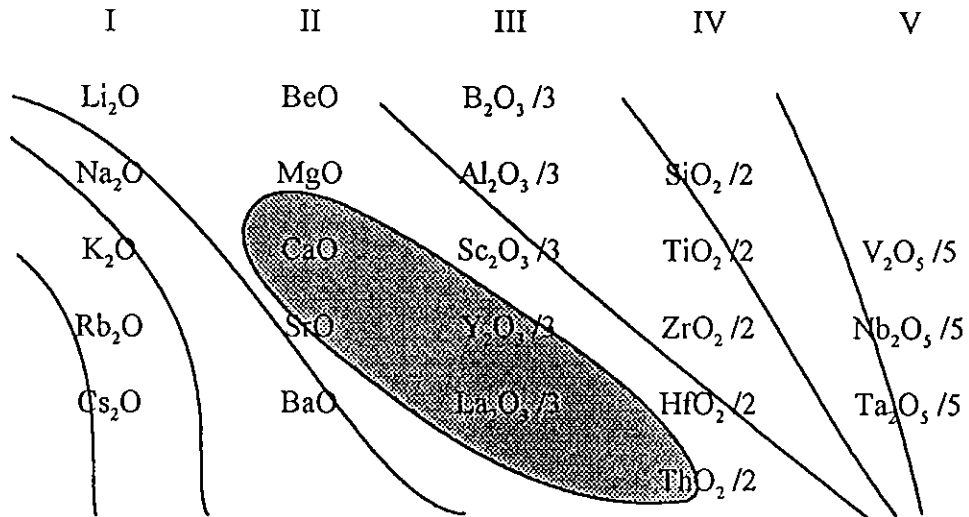


Fig 3.2 Comparative thermal stability of high melting oxides.

porous structure, and cannot protect the metal reliably against further oxidation. If the ratio of the volume of the oxide to the volume of the metal is greater than one, the oxide film formed has a compact, solid structure, reliably insulates the metal from the effects of gaseous oxygen, and consequently hampers further oxidation of the metal. The coefficient α as formulated by Pilling and Bedworth is calculated by the formula:

$$\alpha = \frac{M_{ox} \cdot D_{me}}{D_{ox} \cdot A_{me} \cdot n}$$

where M_{ox} is the molecular weight of the oxide,
 D_{ox} is the density of the oxide,
 D_{me} is the density of the metal,
 A_{me} is the atomic weight of the metal,
 n is the number of atoms of the metal in the formula for the oxide.

The values of α for various metals and for silicon are given ^{242, 80} in Table 3.4. As is apparent from the Table, $\alpha > 1$ for non-ferrous metals, alkali metals, alkaline earth metals and aluminium. As Pilling and Bedworth indicate, the value of α determines the behaviour of the metal on high temperature oxidation: if $\alpha < 1$, the metal corrodes easily and rapidly. The low value of α for magnesium (0.81) is apparently one of the factors determining the great rate of combustion of magnesium compositions.

Samsonov and Portnoy ⁶⁶ note that at very large values of α , the oxide layer is subject to considerable internal stresses; it cracks and loses its protective properties, and therefore the layers for which α does not exceed 1 very significantly have the greatest protective properties.

K	0	Sr	1	Pb	1	Al	1	Ni	2	Si	2	Co	2
Li	1	Ba	1	Cd	1	Zr	1	Cu	2	Fe	2	Cr	4
Ca	1	Mg	1	Sn	1	Zn	2	Ti	2	Mn	2		

Table 3.4 Ratio of Volume of Oxide to Volume of Metal
(α) after Pilling and Bedworth ²⁴²

The physico-chemical properties of two metals magnesium and aluminium are of the greatest importance for pyrotechnists.

Magnesium ^{56, 68, 79}. The heats of fusion and vaporisation of magnesium are, respectively 8.8 and 128 MJ kg-atom⁻¹ (see Table 3.3 for the melting and boiling points). The heat of sublimation at the boiling point is 142 ± 6 MJ kg-atom⁻¹. The atomic heat constant is 24.5 kJ kg-atom⁻¹ K⁻¹ at 0°C, 28 at 300°C, 31.7 at 650°C; for liquid magnesium it is 33.9,; and for vaporised magnesium it is 20.8. The thermal conductivity is 154 W m⁻¹ K⁻¹ at 100°C. The saturated vapour pressure in mm Hg is: 1 at 622°C, 5 at 702°C, 20 at 750°C, and 100 at 909°C ⁷³.

Magnesium is very reactive chemically, but is protected to some degree against oxidation to about 350°C by the oxide film (see Makolkin and Vernidub ⁶¹). At 500°C the rate of oxidation of magnesium is 5.2 g m⁻² hour⁻¹ according to Pilling and Bedworth ⁸⁰. Magnesium in the form of large pieces and plates ignites in air at 600-650°C, and powdered magnesium at about 550°C. During combustion in air, magnesium forms magnesium oxide MgO and certain amounts of magnesium nitride Mg₃N₂.

Coffin ¹⁴³ and Kirschfeld ¹⁴⁶ have published studies of the combustion of magnesium strip in oxygen, in air, and in other oxygen-containing gaseous mixtures. Delaveau has indicated that addition of 1% SiF₄ or BF₃ by volume to the air is sufficient to extinguish the flame of burning magnesium.

Magnesium oxide is a light white powder (density 3.6 Mg m⁻³); when well roasted, it loses its capacity to combine with water or to dissolve in acids.

MgO is noticeably volatile at 2000°C; its melting point is about 2800°C. Its boiling point has been established experimentally to exceed 2800°C; most literature values lie between 3000 and 3600°C. Since the melting and boiling points increase along the homologous series Ba, Sr, Ca, and Mg ^{7, page 36}, and the boiling point of CaO is 2850°C, then the boiling point of MgO cannot be less than 3100°C. The latent heat of sublimation of MgO is estimated ⁶⁸ to be 627 kJ mol⁻¹.

Magnesium oxide is widely used in the production of refractory materials.

Magnesium nitride Mg₃N₂ is a grey green solid readily soluble in water: the reaction of magnesium and nitrogen liberates considerably less heat than that of magnesium and oxygen. The heat of formation of Mg₃N₂ from the elements is 481 kJ mol⁻¹ (for 3 MgO it is 1810 kJ).

Aluminium ^{201, 55}. The heats of fusion and boiling of aluminium are 10.5 and 291 kJ kg-atom⁻¹ respectively. The atomic heat content is 25 J mol⁻¹ K⁻¹ at 0°C, 30.8 at 660°C; that of liquid aluminium is 30.1 at 1000°C; the vapour pressure in mm Hg is 2×10^{-5} at 660°C, 1 at 1284°C, 5 at 1421°C, 20 at 1555°C, and 100 at 1749°C ⁷³. The thermal conductivity is 217 W m⁻¹ K⁻¹ at 20°C. Aluminium is chemically active, but under ordinary conditions (including as a powder), its oxidation is hampered by the thin but strong oxide film covering its surface. When heated, powdered aluminium burns violently in the air. At a red heat it combines actively with sulphur forming Al₂S₃. Aluminium combines with nitrogen at 800°C to form white crystals of the nitride AlN which melts at 2200°C (under a nitrogen pressure of 4 atmospheres).

Aluminium is trivalent in its compounds, but monovalent aluminium compounds exist at high temperatures (see Chapter XVII and Belyayev and Firsanova ¹⁹⁶).

Aluminium oxide is a white powder having a density of 3.9 Mg m⁻³ (α-Al₂O₃, *corundum*) or 3.4 Mg m⁻³ (γ-Al₂O₃, *alumina*). The dependence of the molar specific heat on the temperature over the range 100-1400°C may be expressed: $C_p = 99.78 + 0.0281t$ J mol⁻¹. The melting point of Al₂O₃ is 2050°C. At high temperature (around 3000°C), Al₂O₃ dissociates to a considerable extent forming AlO, or in a reducing atmosphere Al₂O, so that the published values of the boiling point of Al₂O₃ depends on the conditions.

Of the alloys used in pyrotechnics, those of magnesium and aluminium deserve special mention (Fig 3.3). The intermetallic compound Mg₂Al₃ (54% Mg by weight) has a heat of formation of - 205 kJ mol⁻¹, its density is 2.15 Mg m⁻³; and its melting point is 463°C. This alloy has advantages over the corresponding mixture of magnesium and aluminium because it is less likely to corrode and because it is friable and can be readily powdered. It is recognised that intermetallic compounds in general tend to be brittle, and that they tend also to be harder than the constituents. Alloys of magnesium and aluminium containing 85-90% magnesium are called "elektron" alloys ¹. More details are given by Portnoy et al[†].

A phase diagram for magnesium - silicon alloys is given in Fig 3.4.

Section 3. Technical Requirements imposed on powdered metals.

The following requirements are usually imposed upon powdered metals for use in pyrotechnics:

1. Maximum content of active (unoxidised) metal (ranging from 90 to 98% depending on the metal and grade of powder).
2. Not more than tenths percent content of iron and silicon as impurities (with the exception of alloys containing these elements as constituents).
3. Minimal quantities (usually only traces) of heavy metals (copper, lead).
4. Not more than tenths per cent of fat; in some cases no fat is permitted at all.
5. Moisture content not more than tenths percent.
6. Standardised degree of size.

† Portnoy and Lebedev, *Magniyevyye splavy* (Magnesium alloys), Metallurgizdat (Metallurgical Publishing House), 1952.

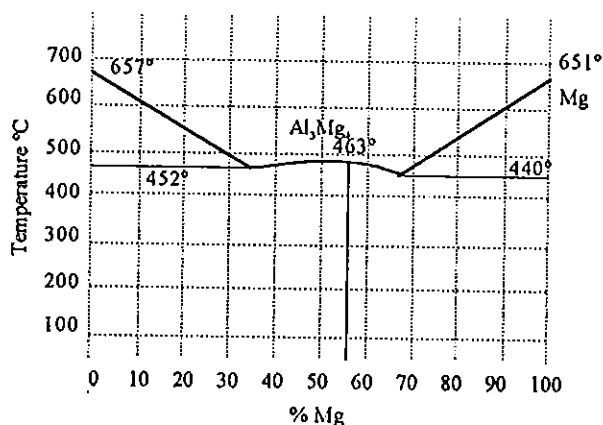


Fig 3.3 Phase diagram of Mg-Al alloys

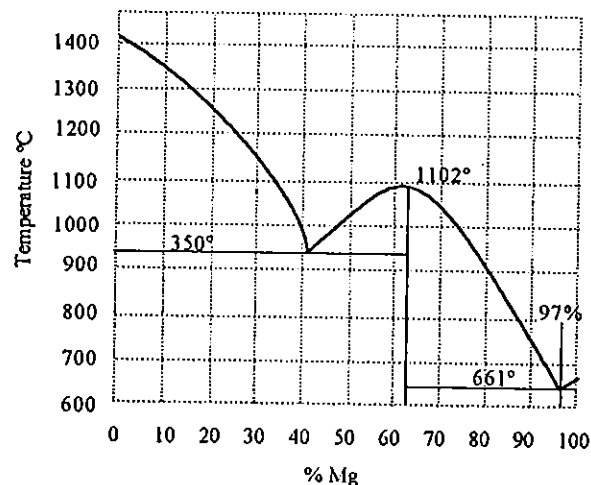


Fig 3.4 Phase diagram for Mg-Si

An admixture of silicon is dangerous if it is in the form of compounds (sand, glass) which can increase the sensitiveness of the compositions.

The presence of copper, lead, or iron in a metal powder (especially the first two) may facilitate the formation of a galvanic couple in a moistened composition, which will undoubtedly accelerate its decomposition on storage.

A high fat content retards the process of combustion and may increase the tendency to sparking.

The requirements for aluminium powder with respect to active metal content and impurities are:

Active aluminium	not less than 96%
Aluminium oxides	not more than 3%
Admixtures of iron	not more than 0.8%
Admixtures of silicon	not more than 0.6%
Admixtures of copper and lead	traces
Fats	not more than 0.5%
Moisture	not more than 0.2%

The requirements imposed upon magnesium powder with respect to the content of active metal and impurities are:

Active metal	not less than 98%
Magnesium oxides	not more than 1%
Iron	not more than 0.35%
Silicon	not more than 0.1%
Moisture	not more than 0.15%
Copper	not permitted
Chlorides	traces
Fats	not permitted

Particle size (holes per linear cm.)

Pass No 30 sieve

100%

Pass No 60 sieve

not more than 10%

Section 4. Production of Metal Powders.

Several methods are used to obtain metal powders:

1. mechanical pulverisation
2. spraying the liquid metal
3. reduction of oxides
4. electrolysis

Mechanical pulverisation is carried out in ball or hammer mills. This method is most convenient for brittle metals and alloys.

Spraying molten metal (a very economical method) is used to obtain powders of comparatively low melting metals including aluminium and zinc. Several variations of this method exist: a) atomisation by compressed air or gas, b) centrifugal spraying, c) granulation by pouring molten metal into water.

Thermal reduction of oxides is used, for example, to make powdered titanium and niobium.

The electrolysis of fused materials can be used to obtain powdered refractory metals such as zirconium.

The shape of the particles depends upon the method of preparing them. Spraying molten metals produces drop-shaped or spherical particles; reduction of metal oxides yields porous, friable particles; electrolytic methods produce irregular and dendritic structures. The sizes of the particles depend upon the method for obtaining them, and they vary within wide limits - from 500 μm (coarse powders), 50-20 μm (fine powders), to 5-2 μm (superfine powders). Of course, the finer the metal powder, the greater its reactivity, and the less its density when poured or shaken.

Magnesium readily undergoes chemical reactions, and magnesium powder is therefore usually obtained by pulverisation. Magnesium ingots are turned into fine shavings (chips) by milling and further pulverisation is conducted under an inert atmosphere in special milling machines. The production of magnesium powder is dangerous because of its great reactivity. Another method of obtaining powder is by the condensation of magnesium vapour.

Aluminium powder is obtained by means of spraying the molten metal with compressed air, or by centrifugal spraying³⁴. Aluminium dust is obtained by pulverising aluminium powder (or sheets of foil) in ball or hammer mills. This last process, which results in a considerable increase in the surface area of the aluminium, is accompanied by the risk of oxidation. To avoid this, about 1% fatty additives (stearin and paraffin) are added to the aluminium powder before pulverisation, and are subsequently removed by extraction or by heating in a vacuum.

Production of aluminium in Germany between 1939 and 1945 was about 25,000 tons annually and of magnesium and magnesium alloys about 10,000 tons annually ⁵⁴.

Information on the preparation of metal powders has been published by Bal'shin ⁸⁴, Eisenkolb ⁵⁴, Edwards and Wray ⁷⁶.

Methods of determining the particle size of powders are described by Deryagin ⁵⁷, Tovarov ⁷⁴, Entelis ⁷⁵, Orr and Delavalle ⁷⁸.

Section 5. Inorganic Fuels of Average Heat Content.

When a great liberation of heat and a high combustion temperature are not required, such as, in smoke compositions, then zinc, antimony, iron, manganese, sulphur, and perhaps other elements, or inorganic compounds may be used as fuels.

The heat of formation of the oxides of certain elements of comparatively low heat content (see Q_1 and Q_2) are given in Table 3.5.

Not only simple substances (elements) or alloys of metals, but also inorganic compounds may be used as fuels in pyrotechnics.

Obviously, other things being equal, the heat of combustion of a compound will be greater if its heat of formation is lower. Thus, we will describe the principle of selection: compounds of elements given in Tables 3.1 and 3.5 having a low heat of formation (Q_2) may be used as pyrotechnic fuels.

Covalently bonded compounds usually have a low heat of formation. Compounds that merit evaluation for pyrotechnic purposes include those of metals with non-metals of groups III, IV, V, and VI - i.e., the borides, carbides, silicides, phosphides, and sulphides.

Many of these compounds still have not been tested by pyrotechnists, others are not suitable because of other properties, being too easily oxidised (many phosphides), or too difficult to oxidise (the silicides of certain metals).

Of the binary inorganic compounds we use in practice: sulphides FeS_2 , *pyrites*, Sb_2S_3 , and certain others. Their properties are given in Table 3.6.

Section 6 Organic Fuels

Liquid hydrocarbons (petrol, kerosene, crude oil, and others) are used in incendiary mixtures, reacting with the oxygen of the air. The characteristics of various petroleum products are given in Table 3.7 and later on in the text. The quantity of heat Q_1 liberated by combustion of 1 kg of the product is 46.8 MJ for petrol, 45.2 for crude oil, and 41.8 for benzene. Petrol and kerosene freeze below -80°C , and benzene freezes at $+6^\circ\text{C}$. The hydrogen content of petrol is 14-15%, and of benzene is 7.7%.

Elements		Oxides		Heat of Formation (kJ)			
Symbol	A	Formula	M	Q	$Q_1 = \frac{Q}{m \cdot A}$	$Q_2 = \frac{Q}{M}$	$Q_3 = \frac{Q}{n}$
Na	23	Na ₂ O	62	414	9	7	138
K	39	K ₂ O	94	355	5	4	118
Cr	52	Cr ₂ O ₃	152	1,142	11	8	228
Mn	55	MnO	71	389	7	5	194
Fe	56	Fe ₂ O ₃	160	815	7	5	163
Co	59	CoO	75	155	3	2	77
Ni	59	NiO	75	243	4	3	121
Zn	65	ZnO	81	347	5	4	174
Gd	70	Gd ₂ O ₃	187	1,071	8	6	214
Ge	73	GeO ₂	105	535	7	5	178
As	75	As ₂ O ₃	230	916	6	4	131
Mo	96	MoO ₃	144	753	8	5	188
Sb	122	Sb ₂ O ₃	324	962	4	3	137
S	32	SO ₂	64	297	9	5	99
C	12	CO	28	109	9	4	54

Table 3.5 Heat of Formation of Oxides

Formula	Molecular Weight	Density	Temperature °C		Colour	Heat of Formation	Combustion prods. (other than SO ₂)	Heat of combustion of 1kg of substance	Wt fuel burning with 1kg oxygen
		Mg m ⁻³	Melting	Boiling		kJ mol ⁻¹		kJ	kg
P ₄ S ₃	220	1,300	172	407	yellow	322	P ₂ O ₃	16	0.86
FeS ₂	120	5,000			gray	360	Fe ₂ O ₃	7	1.36
As ₂ S ₃	214	3,500	320	505	orange	79	As ₂ O ₃	5	1.92
As ₂ S ₅	246	3,500	340	507	yellow	84	As ₂ O ₃	6	1.71
Sb ₂ S ₃	340	4,600	548		black	151	Sb ₂ O ₃	6	2.36

Table 3.6 Physico-chemical properties of sulphides.

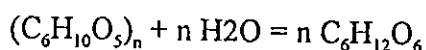
Turpentine is obtained from the resinous secretions of coniferous trees; its main constituent is the unsaturated hydrocarbon pinene, C₁₀H₁₆. Turpentine differs from saturated hydrocarbons in the greater ease with which it is oxidised; it readily ignites on contact with concentrated nitric acid.

Where the liberation of a large quantity of heat would degrade the desired pyrotechnic effect, various carbohydrates may be used as fuels. Properties of certain carbohydrates are given below.

Petroleum Products	Density Mg m ⁻³	Temperature °C	
		Boiling Point	Flash Point
petroleum ether	0.64-0.67	50-60	-58
petrol light	0.67-0.72	60-100	
heavy	0.72-0.76	100-120	
ligroin		120-160	+5 to +15
kerosine light	0.78-0.84	150-300	+28 to +45
heavy	0.80-0.87		
pironaft (high-temp kerosine for light house lamps)		270	100
spindle oil	0.88-0.89		160
machine and cylinder oil	0.90-0.92		180-220
black fuel oil	0.91	300	100-140
crude oil	0.78-0.792		30-90
benzene	0.88	80	-12 to +10

Table 3.7 Properties of Petroleum Products

Starch. $(C_6H_{10}O_5)_n$, $[C_6H_7O_2(OH)_3]_n$. Its heat of formation is -6.48 MJ kg^{-1} , its density is 1600 Mg m^{-3} . It is almost insoluble in cold water, but much more so in hot. Starch hydrolyses grape sugar in an acid medium to:



Milk sugar.(Lactose) $C_{12}H_{22}O_{11} \cdot H_2O$. Its density is 1.1 Mg m^{-3} . The water is removed only above 125°C ; the sugar melts at about 200°C . At room temperature, 17 g of sugar dissolve in 100 g of water, and the solubility increases markedly with increasing temperature. It is very slightly soluble in ethanol. The heat of formation is $-2718 \text{ kJ kmol}^{-1}$.

Beet sugar. $C_{12}H_{22}O_{11}$. Its density is 1.1 Mg m^{-3} . It melts with some decomposition at 160°C . At room temperature 190 g sugar dissolves in 100 g of water. It is slightly soluble in ethanol.

Wood. consists chiefly of cellulose $(C_6H_{10}O_5)_n$, which may amount to $2/3$ the weight of dry wood. The heat of formation of cellulose is -6.48 MJ kg^{-1} ; air dried wood gives about $12.5\text{-}14.6 \text{ MJ kg}^{-1}$ on combustion, and cellulose 17.6 MJ kg^{-1} .

Of the other organic fuels, we should make specific mention of stearin, naphthalene, paraffin, urotropine, and dicyandiamide.

Stearin or Stearic Acid. $C_{17}H_{35}COOH$. In a manual on pyrotechnics published at the end of the 19th century[†] it is recorded that: "stearin (acidulum stearinicum) is one of the components of tallow. It is used in a scraped form because it is very difficult to powder it. Stearin cinders are used for this purpose. Stearin must not smell of tallow or soil the hands. It is used in certain flare compositions."

The melting point of stearic acid is 71°C; its boiling point is 359-383°C at atmospheric pressure, and its density is 0.94 Mg m⁻³. Stearic acid is classed as a surfactant, and is stably absorbed on the surface of powders of the components of a composition. The heat of formation of stearic acid from the elements^{III} is -936 kJ mol⁻¹.

At present, stearin is used to prepare consolidated fuels, and as a fuel and plasticiser in many flame compositions (illuminating, rocket, and others).

Technical stearin is a mixture of stearic and palmitic acids. The melting point of palmitic acid $C_{16}H_{32}O_2$ is 62°C and its boiling point is 268°C.

Naphthalene $C_{10}H_8$. Its melting point is 80°C, its boiling point is 218°C, density 1.16 Mg m⁻³. The specific heat of solid naphthalene at 20°C is 1.25 kJ kg⁻¹ K⁻¹, and of liquid naphthalene at 87°C is 1.67 kJ kg⁻¹ K⁻¹; the latent heat of melting is 145 kJ kg⁻¹, and the latent heat of vaporisation is 315 kJ kg⁻¹. The heat of formation of naphthalene from the elements is -67 kJ mol⁻¹. Naphthalene is used as a fuel in flame compositions; in white smoke compositions having a low combustion temperature it partly burns and partly sublimes, acting as an additional smoke producing agent.

Paraffin is a mixture of saturated hydrocarbons. In stoichiometric calculations we use the formula $C_{26}H_{54}$. It is a white or slightly yellowish mass without taste or odour. It is obtained by processing certain grades of crude oil, lignite, or peat. Its melting point is 44-58°C, its density 0.88-0.91 Mg m⁻³. Chemically it is less reactive than naphthalene or stearin. The heat of combustion of paraffin with a melting point of 52.5-53°C^{III} is 46.8 MJ kg⁻¹.

Urotropine (hexamethylenetetramine), $C_6H_{12}N_4$. It is obtained by the condensation of formaldehyde with ammonia. It contains much nitrogen, and therefore gives a colourless, almost smokeless flame during combustion; this property is particularly valuable when it is used in signal flares compositions.

Urotropine is the main component of the briquettes of "solid alcohol" used domestically for heating water, food etc. It dissolves readily in water: 167 g urotropine dissolves in 100 g water at room temperature; it is slightly soluble in absolute ethanol, and even less in benzene. It

† PF Simonenko, Pyrotekhnika (Pyrotechnics), St Petersburg, 1894.

decomposes when treated with acids. It is thermally stable - it sublimes in a vacuum at 230-270°C with little decomposition.

Urotropine is an endothermic compound; its heat of formation from the elements is +125 kJ mol⁻¹. It is widely used in medicine, and it serves as the raw material for the manufacture of the powerful explosive - hexogen (RDX).

Dicyandiamide or DCDA, C₂N₄H₄. It is used as a fuel and flame suppressant in smoke compositions. It is obtained by the dimerisation of cyanamide in the presence of ammonia. Its melting point is 209°C, its density is 1.4 Mg m⁻³. It is slightly soluble in cold water (2.2 g in 100 g water), and is non-hygroscopic. It dissolves readily in acetone, hot water, and hot alcohol, and is insoluble in benzene. When it is heated above 180°C it releases ammonia and forms melamine C₃N₃(NH₂)₃. The heat of formation from the elements ¹¹¹ is -18.8 kJ mol⁻¹.

During World War II DCDA was added as a flash suppressant to artillery powder charges Ref ⁵¹ Vol 5, page 827. In industry, DCDA is used for making aminoplasts.

Chapter IV

Methods of Filling Compositions and Testing the Strength of Pellets.

Binders: Organic Polymers

Section 1. Methods of Filling Compositions. Purpose of Bonding Agents.

The filling and forming of pyrotechnic compositions may be carried out by different methods: pressing, screw-feeding, casting, and in certain cases even filling by hand.

Screw-feed filling is accomplished with an Archimedian screw, also called a worm screw which feeds the composition into the case and consolidates it. Consolidation is achieved by applying a constant force in the direction opposite to that in which the material is being fed to prevent the movement of the composition from the screw up to a certain limit, while the screw is operating ¹⁵⁶.

Screw feeding is an efficient method of filling. However, its application to pyrotechnic materials is difficult because of the sensitiveness of the compositions to mechanical stimuli. It is also hampered by the fact that many pyrotechnic compositions do not have the degree of plasticity required for this method of filling.

Certain screening smoke compositions (see Chapter XVIII) are less sensitive mechanically, and are adequately plastic; the screw feeding method is acceptable for them.

The casting (pouring) method is used when working with yellow phosphorus, its alloys, and its solutions. Incendiary compositions with liquid, condensed, or solidified fuels (TG (solid propellant), napalm, and others), are also filled only by casting.

In recent years, the casting method has been used for mixed powders containing at least 20% organic substance (see Chapter XX). The main obstacle to filling other pyrotechnic compositions by this method is the high melting point of the basic components of the compositions - inorganic oxidants and metallic fuels.

Pyrotechnic compositions containing an oxidiser seldom have a low-melting component (with a melting point of less than 120-150°C) in excess of 10-15%. It is therefore seldom possible to use this method of suspending high melting components in a liquid medium, which is used, for example, in casting high percentage amatols (60/40).

The most frequently used method of filling pyrotechnic compositions is by cold pressing, using either an hydraulic or a mechanical press.

Pressing at elevated temperature (60-100°C) might improve the quality of filling, but this would be too dangerous, because the sensitiveness of pyrotechnic compositions to impact and friction increases sharply with increasing temperature.

As we have already indicated, it is necessary to consolidate a composition to make its combustion slower and more uniform. The consolidated composition must have a high mechanical strength. This is especially necessary in those cases when the products (flares, pellets, segments, and others), are subjected to considerable destructive mechanical stresses at the moment of their use in battle conditions. A product made of pressed pyrotechnic compositions must have such a high mechanical strength that neither when it is fired, nor when it is burning, is there any cracking, splitting, or separation of individual pieces of the composition.

It is not always possible or feasible to achieve a high strength of pressed composition simply by the use of high pressures during pressing. In order to increase the strength of pyrotechnic products, binders (also called cementing agents) are frequently introduced into the compositions [†].

Artificial and natural resins, rubber, and certain other organic substances are most frequently used as binders, but in some cases inorganic substances such as sulphur are also used.

In certain special cases the binding agent is necessary to give the necessary strength to consolidated compositions (? for uncased transport?).

Section 2. Testing and Strength of Pellets.

In most cases pyrotechnic compositions are pressed into the required shape before filling into the munitions.

At the present time, the most frequently used method of testing the strength of pressed pyrotechnic compositions is to measure the force needed to crush an experimental pellet. This is done in special testing machines (Fig 4.1).

The IM-4R machine is an example of the type that has a mechanical drive and a lever-pendulum displacement measuring mechanism. It automatically records the load - deformation curves during the test ^{††}. A special attachment - a reversing gear - is used with the IM-4R machine; it is not necessary with the IM-4A machine.

The specimen of pressed composition under test (usually a pellet of diameter 20 mm and height 30 mm) is placed between two small plates which are pressed together slowly at a constant rate. The force needed to break the pellet is found.

Such machines give us the opportunity of determining accurately the force required to destroy the pellet; most importantly, they provide constancy of rate of increase of the load, and they make it possible to record the curve reflecting the nature of the deformation of the pellet with increasing load.

The yield point in compression, σ of the sample being tested, is calculated from:

[†] Organic binders act simultaneously as fuels; they also retard the combustion and improve the chemical stability of many compositions.

^{††} For more details on the design and operation of test machines see Ref 83, pp 49-56.

$$\sigma_1 = \frac{P_{\max}}{S} \text{ kg m}^{-2}$$

where $P_{\max}$ is the force in kg needed for the total destruction of a pellet of cross sectional area $S \text{ m}^2$.

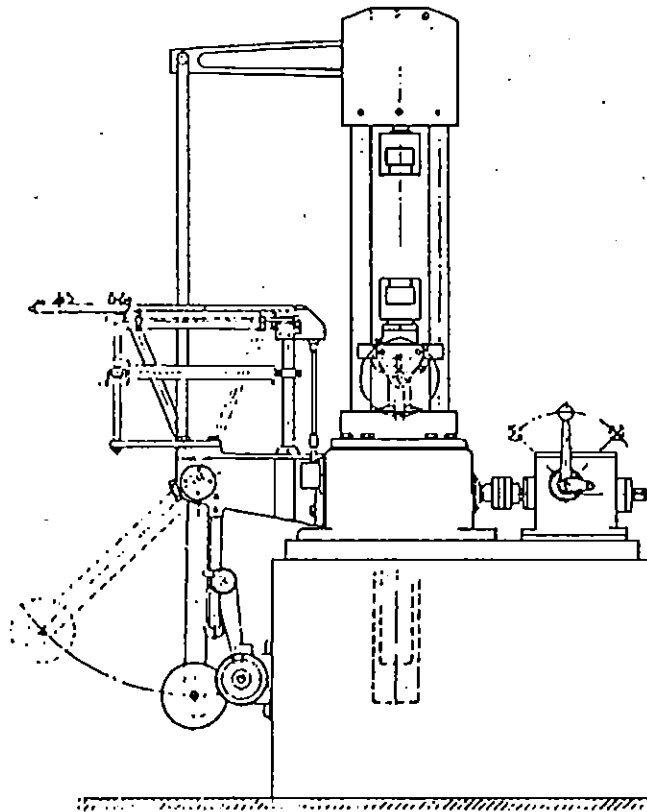


Fig 4.1 IM-4R testing machine

Section 3. Factors affecting the strength of pressed compositions.

The strength of the pressed composition depends upon:

1. the properties of the basic oxidiser-fuel mixture;
2. the properties of the binding agent, and the quantity of it in the composition;
3. the particle size of the components and the method of manufacture of the composition (sequence of mixing components, duration of mixing, type of mixing equipment, etc.);
4. the method of introducing the binding agent, etc.;
5. the concentration of the solution of the binding agent, etc.;
6. the consolidation pressure and dwell time;
7. the height of the increment, the pressing area, and the ratio of these quantities.

Undoubtedly, the crystal system and the hardness of the crystals in the composition have a great influence upon the strength of the pressed product. Compositions consisting of very hard ingredients yield poorly on pressing and, other things being equal, give relatively weak products.

The strength of the product increases with increasing compaction pressure¹, see Table 4.1, although certain compositions exhibit the phenomenon of "over pressing", that is, the yield strength decreases at high compaction loads. The yield point σ of the product under compression usually does not exceed 20-25% of the compaction pressure.

Composition		Compacting Pressure, P (Mg m^{-2})	Yield point under compression	
			σ (Mg m)	$\sigma \times 100/P$
Ba(NO ₃) ₂	80	10,000	800	8.0
Al dust	20	20,000	1760	8.8
		30,000	23	9.6
Ba(NO ₃) ₂	55	10,000	2160	21.6
Al dust	45	20,000	384	19.2
		30,000	633	24.4

Table 4.1 Dependence of strength of pellet upon compacting pressure (Pellets 20 mm diam x 20 mm long).

With single end pressing (i.e. pressure applied from one end only), the height of the column of composition being pressed in one operation must not exceed the diameter of the pellet by a factor of 1.5 - 2. If it does, the pressure is not adequately transmitted from layer to layer, and the lower parts of the column will be inadequately pressed. The ratio may be increased considerably by the use of double end pressing.

The pressure p_h at distance h from the drift may be calculated⁸⁴.

$$p_h = p \cdot \exp(-A \cdot h)$$

where p is the pressure on the drift

A is a constant, determined experimentally, and approximately inversely proportional to the diameter of the die.

In some cases we succeed in obtaining adequate strength of a pressed product even without the addition of a special binding agent, but usually we must use one.

Binders also increase the plasticity of the composition. The density and strength of compositions containing binders decrease less markedly when the pressure is reduced than is the case for compositions containing no such agents.

Section 4. Classification of Binders. Their physico-chemical properties[†].

The following binders are those most frequently used in the manufacture of pyrotechnic compositions[†].

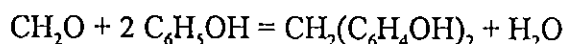
1. artificial resins - iditol, Bakelite, and others;
2. natural resins, and products obtained by processing them: rosin, resinsates, and shellac;
3. drying oils - boiled linseed or hempseed oil;
4. glue - dextrine.

Besides these, various asphalts and bitumens may also be used as bonding agents. In some cases, solutions of nitrocellulose and rubber in the appropriate solvents are used. For nitrocellulose, an alcohol-ether mixture or acetone may serve as solvent; for rubber, benzene or petrol, etc..

The characteristics of rubbers are:

1. insolubility in water;
2. solubility in organic solvents;
3. ability to form a film when the solution dries;
4. adhesiveness of the solutions;
5. complete resistance to decay (in distinction from glues of animal origin).

Iditol is an artificial resin (of the "lacquer resin" type), obtained by condensing an excess of phenol with formaldehyde in the presence of an acid catalyst (such as HCl). The initial stage of the condensation reaction is:



The initial product of condensation is dioxydiphenylmethane which polymerises to a resin when heated.

The formula $\text{C}_{13}\text{H}_{12}\text{O}_2$ is used for iditol in pyrotechnics calculations.

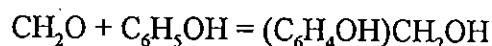
The heat of formation of technical iditol, derived from its heat of combustion, is -3.09 MJ kg^{-1} ; its density is $1.25\text{-}1.30 \text{ Mg m}^{-3}$. Iditol dissolves readily in ethanol.

The lacquer resins dissolve readily in alcohols, and are almost insoluble in hydrocarbons and in mineral oils. They are stable to water, acids, ammonia, and weak alkali solutions, but decomposes in a strong basic solution.

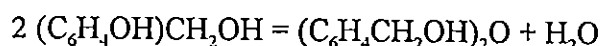
Specimens of technical iditol always contain some free phenol which accounts for their reddish colour. The technical requirements imposed on iditol reduce basically to standardisation of its softening temperature (not lower than $90\text{-}97^\circ\text{C}$, depending upon grade), establishment of the phenol content ($0.1\text{-}3.0\%$, depending upon grade), and testing for the absence of rosin.

[†] The properties of binders used in the manufacture of rocket compositions are given in Chapter XX.

Bakelite is an artificial resin obtained by the condensation of phenol with an excess of formaldehyde in the presence of a basic catalyst such as ammonia. The reaction proceeds initially:



On heating, condensation occurs with the formation of Bakelite A:



Bakelite A, $\text{C}_{14}\text{H}_{14}\text{O}_3$, has a softening point of 75-100°C, and dissolves readily in ethanol. Heating to higher temperatures leads to the formation of Bakelite B usually given the formula $\text{C}_{43}\text{H}_{38}\text{O}_7$. When Bakelite B is heated further, it polymerises to Bakelite C.

Bakelite C softens, but does not melt when heated; it is insoluble in the usual organic solvents; it is very resistant to chemical attack, and has a high mechanical strength.

Bakelite A is usually formed at a temperature below 100°C. The transition from Bakelite A through Bakelite B to Bakelite C is achieved at a higher temperature of 120-150°C or even up to 180°C.

Bakelite A is usually added to pyrotechnic compositions (particularly thermite incendiary compositions) as a powder or in the form of an alcohol lacquer; the conversion of Bakelite A to Bakelite C (Bakelisation) is achieved by heating the pressed composition to about 150°C¹. The density of Bakelite (C ?) is 1.20-1.29 Mg m⁻³.

The conventional formula $\text{C}_{12}\text{H}_{11}\text{O}_2$ is used in calculations for convenience; this more or less corresponds to the formula $\text{C}_{43}\text{H}_{38}\text{O}_7$.

Shellac is a natural resin obtained from trees growing in South Asia. Its empirical formula is $\text{C}_{16}\text{H}_{24}\text{O}_5$; its density is 1.05-1.20 Mg m⁻³. Shellac dissolves readily in ethanol, and it is almost insoluble in petrol. It is imported and may be replaced by agents of domestic origin in pyrotechnic compositions.

Rosin is obtained from the resins of coniferous trees. The main constituents of rosin are the unsaturated abietic and pimaric acids. Both acids have the formula $\text{C}_{20}\text{H}_{30}\text{O}_2$.

The density of rosin is 1.0-1.1 Mg m⁻³; its softening point must be not less than 65°C. Rosin is soluble in ethanol, ether, benzene and its homologues, and to some degree in petrol. When heated, it dissolves in drying oil.

Products formed by the reaction of rosin with hydrates of the oxides or salts of the appropriate metals are called resinates. Calcium resinate is obtained by melting rosin with slaked lime at 230-240°C. However, this reaction does not go to completion, as is apparent by the definite acid value of the product (not more than 80), although this is considerably less than that for rosin

(160-180). The softening point of calcium resinate is 120-150°C; its composition is approximately $(C_{19}H_{29}COO)_2Ca$.

Petrol, or a 1:1 mixture of petrol and alcohol are used as solvents for calcium resinate.

Of the other metal resins strontium resinate has possible applications, as it has some advantages for the production of red flame.

Ellern ⁹ indicates that the following monomers might be used in pyrotechnic compositions, and would become binders after polymerisation; the materials and the heats of polymerisation are quoted as:

methyl methacrylate	54.3	MJ kg-mol ⁻¹ of monomer.
vinylidene chloride	60.2	
styrene	67.3	
acrylonitrile	72.3	
vinyl acetate.	89.1	

These values correspond to 544-1360 MJ kg⁻¹ of substance.

Information on the properties of artificial resins and organic polymers is published by Losev and Petrov ⁸⁷, Petrov and Levin ⁸⁹ Losev and Trostyanskaya ⁸⁸, Lazarev and Sorokin ⁸⁶, in the collection *Novyye materialy v tekhnike* (New materials in Engineering) ⁹⁰, and also in the second edition of our book ⁷ page 53.

Of the organic binders not included in the class of resins, we should mention drying oil and dextrin.

Natural drying oil (GOST[†] 7931-56) is a product of the polymerisation and partial oxidation of linseed or hempseed oil, and is a viscous liquid of light yellow or light-brown colour. Its density (γ_4^{20}) lies within the limits 0.930-0.938 Mg m⁻³ depending upon the grade; its viscosity measured by the VU viscometer at 20°C is 12-16°C (?). Drying oil is obtained by blowing air through linseed or hempseed oil heated to 160°C. To expedite the drying of the drying oil, siccatives (dessicants) or "driers" are added to it - these are substances which accelerate the process of drying. Usually the resins or linoleates of manganese, lead or cobalt are used as siccatives. In pyrotechnics, the better grades of drying oils are used, without siccatives; sometimes, a solution of rosin in drying oil is used as a binder. The properties of drying oil have been published ⁸⁵.

Dextrin is a vegetable glue obtained by heating starch and treating it with acids. Its formula is $(C_6H_{10}O_5)_x$; its density is 1.04 Mg m⁻³. Dextrin dissolves readily in cold and hot water.

Some physico-chemical properties of certain organic fuels, both those which have, and those which do not have binding properties, are given in Table 4.3. For simplicity of calculations, Table

† All-Union State Standard.

4.3 gives the conventional empirical formula obtained from elementary analysis of compounds of high molecular weight; these formula have only this practical significance.

The data in this section are used for calculating the content of components of binary mixtures (see Chapter V). The elementary composition of organic fuels and, in particular, their oxygen content, plays an important part in the selection of a fuel for flame compositions.

Sulphur is sometimes used as an inorganic binding agent. It has little effect on the strength of cold-pressed compositions. When hot pressed close to its melting point, however, it increases the strength of the composition.

Section 5 Quantity of Binder used in a Composition.

It is advisable to add a binder to a pyrotechnic composition (other than rocket compositions) in quantities not exceeding 10-12%.

We should remember that all organic binders act simultaneously as a fuel and consequently require the consumption of a corresponding amount of oxidiser for their combustion. The addition of a binding agent, particularly rosin or calcium resinate, greatly retards the combustion process. To obtain a composition of the required combustion rate, we may in practice sometimes introduce more than 10-12% of the binding agent into the basic mixture of metal and oxidant.

The dependence of the strength of a compressed compound, pressed at 294 MPa, upon the quantity of added binding agent, is shown in Table 4.2. The strength of the product increases slightly if the amount of binding agent is increased above 10-12%.

Organic binders have the greatest influence on the strength of the composition when they are added as a solution in an appropriate solvent (as a lacquer).

Composition %			Yield point σ under compression MPa
Ba(NO ₃) ₂	Al dust	iditol	
80	20	0	28
78	20	2	40
76	20	4	45
74	20	6	52
72	20	8	55

Table 4.2 Effect of quantity of binding agent on strength of pellet 20 mm x 20 mm.

Name and Formula of Substance		Density (Mg m ⁻³)	Conventional Molecular Weight	Mass of Substance combusting with 1 kg oxygen (kg)		Composition (%)		
				to CO and H ₂ O	to CO ₂ and H ₂ O	C	H	O
Iditol	C ₁₃ H ₁₂ O ₂	1,300	200	0.74	0.42	79	6	15
Bakelite	C ₁₂ H ₁₁ O ₂	1,300	187	0.75	0.42	78	5	17
Shellac	C ₁₆ H ₂₄ O ₅	1,100	269	0.8	0.47	65	8	27
Rosin	C ₂₀ H ₃₀ O ₂	1,100	302	0.57	0.36	79	10	11
Calcium resinate	(C ₂₀ H ₂₉ O ₂) ₂ Ca	1,200	643	0.61	0.38	75	9	10
Drying oil	C ₁₆ H ₂₆ O ₂	930	250	0.58	0.36	77	10	13
Starch	(C ₆ H ₁₀ O ₅) _x	1,600	162	1.69	0.85	45	6	49
Lactose	C ₁₂ H ₂₄ O ₁₂	1,500	360	1.88	0.94	40	7	53
Paraffin	C ₂₆ H ₅₄	910	366	0.43	0.29	86	14	0
Stearin	C ₁₈ H ₃₆ O ₂	940	284	0.52	0.34	76	13	11
Naphthalene	C ₁₀ H ₁₈	1,140	128	0.57	0.33	94	6	0
Dicyandiamide	C ₂ N ₄ H ₄	1,400	84	1.31	0.88	29	4	0
Urotropine	C ₆ N ₁₂ N ₄		140	0.73	0.48	51	9	0
Charcoal	C ₆ H ₂ O	1,500- 1,700	90	0.94	0.48	81	2	17
Graphite	C	2,200	12	0.75	0.38	100	-	-
<u>Salts colouring flames</u>								
sodium oxalate	Na ₂ C ₂ O ₄	2,300	134	-	8.37	18	-	48
strontium oxalate	SrC ₂ O ₄	-	176	-	10.98	14	-	36

Table 4.3 Physico-chemical properties of organic fuels.

Chapter V

Principles of Formulation and Calculation of

Pyrotechnic Compositions.

After selecting the constituents, it is necessary to decide on the weight ratios to be used in the composition.

The basic principles for the calculation of binary and multi-component mixtures were found in the second half of the 19th Century by the Russian pyrotechnist P.S. Tsytovich ⁹². He assumed in his calculations that all the fuel in binary mixtures reacts with the oxygen of the oxidiser; he did not consider that atmospheric oxygen would participate in the combustion process. He considered ternary and multi-component mixtures to consist of two or more individual binary mixtures. The ratio of binary mixtures forming a multi-component composition was optimised by means of many experiments.

Section 1. Calculation of binary mixtures.

To determine the formulation of a binary mixture, we must write the equation for the combustion reaction, and calculate from it the weight ratio of the fuel and oxidiser.

Example 1. The combustion reaction of a binary mixture of potassium perchlorate and magnesium may be expressed by the equation:



For 139 g of potassium perchlorate, we must have $24.3 \times 4 = 97.2$ (say 97 g in round numbers) of magnesium. Having added the numbers obtained: $139 + 97 = 236$ g, we obtain the total quantity of the composition in grams. Hence, it is not difficult to find that the content of 100 g of the composition will be:

$$\text{KClO}_4; \frac{139 \times 100}{236} = 58.9 \text{ g} \quad \text{Mg}; \frac{97 \times 100}{236} = 41.1 \text{ g}$$

Rounding the figures obtained, we have the recipe for the composition:



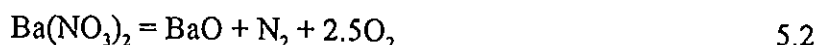
But even for binary mixtures, we often do not have complete confidence that the equation corresponds with reality. We may have this confidence only when we have data from a chemical analysis of the products of combustion; if we do not have them, we may speak only of the probable equation for the combustion reaction.

Because of this, we should speak of the most probable equation for the decomposition of the oxidiser in a specific case, and of the most probable equation for the combustion of the fuel.

The most probable equations for the decomposition of oxidisers are given in Table 2.1, and for the oxidation of fuels in Table 3.3. By using them, we may be able in many cases to write the probable equation of the combustion reaction of a binary mixture and find the formulation for the composition.

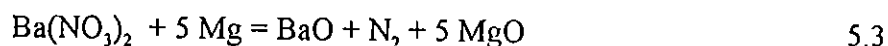
Example 2. Let us work out the equation for the combustion, and find the formulation of a binary mixture of barium nitrate and magnesium.

We find the equation for the decomposition of the oxidiser in Table 2.1:



The oxidation product of magnesium is MgO (Table 3.3).

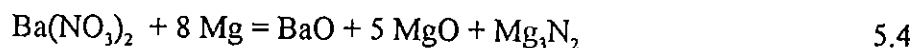
By using the oxygen liberated during the decomposition of the oxidiser for the oxidation of the magnesium, we obtain the equation for the reaction:



which corresponds to: barium nitrate 68%, magnesium 32%.

This composition may be used as a photoflash mixture.

It is well known that with a deficiency of oxygen, magnesium may also react with nitrogen, and therefore another equation may be written (without the participation of the oxygen of the air):



which corresponds to: barium nitrate 57%, magnesium 43%.

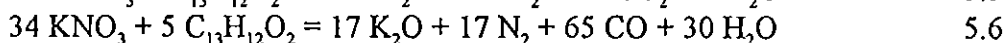
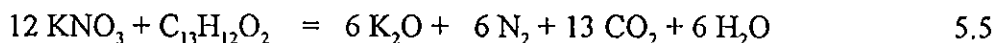
We should be guided by thermochemical considerations when performing the calculations and writing the equations for the proposed combustion reaction. Thus, for example, in the present case, we should consider that the heat liberated by the reaction of magnesium with nitrogen is about one third that liberated by the reaction of magnesium with oxygen, and that it is therefore not always advantageous to direct the reaction towards the formation of nitrides¹. A considerable gain in the quantity of heat is obtained when the Mg_3N_2 formed can be oxidised in the flame by the oxygen of the air to MgO.

Tsytoovich indicated that when working out the equations of combustion of compositions containing charcoal or organic oxidisers, we may perform the calculations: 1) for the complete

combustion of the fuel with the formation of water and carbon dioxide, or 2) with a reduced amount of oxidiser, with the formation of water and carbon monoxide.

Example 3. Work out the equation for the combustion reaction of mixtures of potassium nitrate and iditol.

Assuming that iditol has the simplified formula $C_{13}H_{12}O_2$, we obtain for the two equations:



	For (5.5)	For (5.6)
potassium nitrate	86%	77%
iditol	14%	23%

Equations (5.5) and (5.6) are only approximations to reality. It is known that some quantities of potassium nitrite and potassium peroxide are also formed on combustion of potassium nitrate with organic fuels, and that potassium carbonate is formed by the reaction of potassium oxide and carbon dioxide.

The selection of the coefficients in the calculation of these mixtures (especially with organic fuels) requires much time, and Demidov ⁹¹ has proposed the use of tables indicating the weight of oxidiser required for the liberation of 1 g of oxygen, and the quantity of fuel which can be oxidised by 1 g of oxygen.

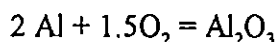
These tables are compiled in the following manner.

It is known that under combustion conditions potassium perchlorate decomposes according to the equation:



It follows that 1 g of oxygen is obtained from $139/64 = 2.17$ g $KClO_4$.

The oxidation of aluminium occurs according to the equation:



Consequently, 1 g of oxygen will oxidise $54/48 = 1.12$ g aluminium.

Tables 2.1, 3.3, and 4.2 give such data for oxidisers and fuels.

Example 4. Find the recipe for the composition containing potassium nitrate and iditol which forms carbon dioxide and water.

In Table 2.1 we find the number 2.17 for potassium perchlorate, and in Table 4.2 column 4, we find 0.42 for iditol. These numbers represent the parts by weight of the constituents in the mixture:

KClO ₄	2.17	which corresponds to	83.8%
iditol	<u>0.42</u>		16.2%
total	2.59		

Section 2. Compilation and calculation of ternary and multi-component mixtures.

In many cases, ternary mixtures may be considered as two binary mixtures containing the same oxidiser.

But sometimes the presence of two different fuels in the composition sharply changes the direction of the reaction, and then this approach is not applicable. For example, in a composition containing aluminium, sulphur and barium nitrate, a reaction occurs between the aluminium and the sulphur with the formation of aluminium sulphide Al₂S₃, which may then be converted to Al₂O₃ and SO₂.

Among the products of combustion of such a composition may be BaO, Al₂O₃, Ba(AlO₂)₂, BaS, BaSO₄, Al₂S₃, SO₂, N₂, and others.

The combustion products depend not only on the ratio of the constituents in the composition, but upon the combustion conditions: the surrounding pressure, the initial temperature, the density of the composition, the diameter of the flare, etc.

The following method may be used for the tentative calculation of a ternary mixture consisting of an oxidiser, a metallic fuel, and an organic fuel (binder).

Example 5. Find the recipe for a ternary mixture of barium nitrate, magnesium and iditol, which completely converts the iditol into carbon dioxide and water.

From the equations or from Demidov's tables we establish the compositions of the two binary mixtures:

barium nitrate - 68%,	magnesium - 32%
barium nitrate - 88%,	iditol - 12%.

Recognising that 4% iditol provides adequate mechanical strength for an illuminating star, we select a 2:1 ratio of the two binary mixtures.

On this assumption, the proportions of the ingredients may be calculated readily:

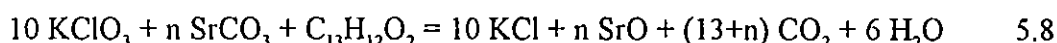
$$\begin{array}{lcl}
 \text{barium nitrate} & \frac{68.2}{3} + \frac{88.1}{1} & = 75\% \\
 \text{magnesium} & \frac{32.2}{3} = ; & 21\% \\
 \text{iditol} & \frac{12.4}{3} = & 4\%
 \end{array}$$

Obviously, the ratio between the two binary mixtures selected by chance is not the optimum one, and the recipe is tentative, and should be refined experimentally with due consideration of the special requirements for illuminating compositions.

In some signal flare compositions, the salt which colours the flame (in a formal approach which does not consider the intermediate products of combustion) does not participate in the combustion process.

Example 6. Find the recipe for a red flare composition containing potassium chlorate, strontium carbonate, and iditol.

The combustion reaction is given approximately by the equation:



Experience shows that 20-25% strontium carbonate is sufficient to produce a good red flame, and the remaining 80-75% may be distributed between the potassium chlorate and the iditol on the basis of the above equation.

With 25% strontium carbonate, we obtain the composition:

potassium chlorate	64.4%
strontium carbonate	25.0%
iditol	10.6%

Section 3. Calculation of compositions with negative oxygen balance.

In many cases the special effect of the pyrotechnic is increases rather than decreased if the combustion of the fuel involves not only the oxygen of the oxidiser, but that of the air. This is so, because for very many forms of compositions (illuminating, incendiary, and others), the desired effect increases as the heat of combustion of the composition increases. The heat of combustion of the composition, other things being equal, will be greater if the content of fuel in it that can be completely oxidised (even with atmospheric oxygen) increases.

Compositions containing an excess of fuel usually give a good special effect when the fuel is an easily oxidised substance capable of reacting partially with the oxygen of the air. The quantity of fuel that can react with the oxygen of the air should be determined experimentally.

Pyrotechnic compositions having an excess of oxidiser over that required for complete combustion of the fuel are said to have a *positive oxidation balance*. An excess of oxidiser which does not actively participate in the combustion process is undoubtedly harmful in all cases. Compositions with positive oxygen balance[†] are practically never used in pyrotechnics[†].

† Compositions for "oxygen candles" are an exception. See Ref 294 and Chapter XXII.

Compositions containing the quantity of oxidiser required for complete combustion of all the fuel or fuels in them are called compositions with a *zero oxygen balance*.

Compositions containing an inadequate quantity of oxidiser for complete combustion of all the fuel in them are called compositions with a *negative oxygen balance*.

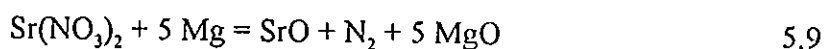
Most pyrotechnic compositions used at the present time have a negative oxygen balance. The efficiency of the effect of such compositions depends largely on the extent to which the oxygen of the air may, in practice, participate in the process of combustion.

By the term "*oxygen balance (n) of a composition*" we understand that quantity of oxygen, in grams, which must be added to achieve the complete oxidation of all the fuels in 100 g of composition.

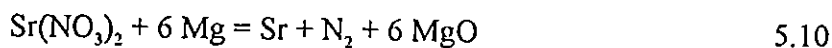
The ratio of the quantity of oxidiser contained in the composition to the quantity of oxidiser required for complete combustion of all the fuel is called the *use factor (k)*.

The oxygen balance which gives the best special effect is called the *optimum oxygen balance*.

In calculations of binary mixtures of aluminium or magnesium with the nitrates of alkali or alkaline earth elements, the concept of "*active*" and "*complete*" oxygen balances are used. By "*active*" oxygen balance we refer to that oxygen which is not firmly bound within the oxidiser, the so called "*active oxygen*", such as, for example:



In the case of complete oxygen balance, the calculation assumes that all the oxygen in the oxidiser is used in the reaction, and at least in the flame zone the metal of the oxidiser is obtained in its free form. For example:



Compositions with a complete oxygen balance are, of course, compositions with a negative oxygen balance.

Some examples of calculations of compositions with a negative oxygen balance are given below. The required oxygen balance (in grams) is indicated.

Example 7. Calculate a binary mixture of potassium chlorate and magnesium on the assumption that its oxygen balance is -20 g oxygen.

Tables 2.1 and 3.3 give for potassium chlorate and magnesium 2.55 and 1.52 respectively. So 20 g oxygen will oxidise $20 \times 1.52 = 30.4$ g magnesium.

The remaining 69.6 g of composition must be calculated in the usual way for a zero oxygen balance.

The potassium chlorate content is: $\frac{2.55 \times 69.6}{2.55 + 1.52} = 43.6\%$
 and the magnesium content is: $100 - 43.6 = 56.4\%$.

During combustion the oxygen of the oxidiser will react with $56.4 - 30.4 = 26.0\%$ of the magnesium.

The use factor (k) of the oxidiser in this case is: $26.0/56.4 = 0.46$.

Similar calculations may be made for multi-component mixtures.

In many cases it is necessary to determine by calculation the rationale for a composition already developed. The calculation of the oxygen balance n and the use factor k in particular allow us to judge how necessary is contact of the composition with atmospheric oxygen at the time of combustion. These quantities allow us to determine the cause of, for example, sparking of the composition.

The calculation of n and k is shown in the following example.

Example 8. Calculate n and k for a yellow flare composition: potassium chlorate 60%, sodium oxalate 25%, and shellac 15%.

From Tables 4.2 and 2.1 we find that for combustion to carbon dioxide and water, 0.47 g of shellac or 8.37 g sodium oxalate require 2.55 g potassium chlorate. Therefore, for combustion, 15 g shellac require $(2.55 \times 15)/0.47 = 81.5$ g potassium chlorate, and 25 g sodium oxalate require $(2.55 \times 25)/8.37 = 7.6$ g potassium chlorate.

Hence, the use factor may be calculated:

$$k = \frac{60}{81.5 + 7.6} = 0.67$$

and the oxygen balance:

$$n = \frac{60 - (81.5 + 7.6)}{2.55} = -11.4 \text{ g O}_2$$

Section 4. Calculation of metal - chloride compositions.

In metal - chloride compositions, an organochlorine compound acts as the oxidiser, and the powdered active metal as the fuel.

The oxidiser must provide sufficient chlorine for complete oxidation of the metal. Thus, for example, for each kg-atom of zinc, it is necessary to take as much oxidiser as contains 2 kg-atoms of chlorine.

Hence, the equation for the reaction between hexachloroethane and zinc must be written:



For simplification in calculations, we may use Table 5.1 which indicates the quantity of oxidant which releases 1 kg chlorine on decomposition, and the weight of metal reacting with 1 kg chlorine.

Organochlorine compound (oxidiser)	Molecular Weight	Weight of oxidiser releasing 1 kg chlorine	Fuel (metal)	Atomic Weight	Weight of metal reacting with 1 kg chlorine
carbon tetrachloride CCl_4	154	1.08	zinc	65.4	0.92
hexachloroethane C_2Cl_6	237	1.11	aluminium	27.0	0.27
hexachlorobenzene C_6Cl_6	285	1.34	magnesium	24.3	0.34
hexachlorocyclohexane $\text{C}_6\text{H}_6\text{Cl}_6$	291	1.37	zirconium	91.2	0.64
polyvinylchloride $(\text{C}_2\text{H}_3\text{Cl})_n$	60.5	1.76	iron	55.8	0.53 (forms FeCl_3) 0.79 (forms FeCl_2)

Table 5.1 Chlorine content of oxidisers.

Example 9. Calculate the percentage content of a binary mixture of hexachloroethane and aluminium.

From Table 5.1:	hexachloroethane	1.11 g
	aluminium	<u>0.27 g</u>
	total mixture	1.38 g

i.e.	hexachloroethane	80.5%
	aluminium	19.5%

The calculation of ternary mixtures containing organochlorine compounds is more complex.

Example 10. Calculate a green flare composition containing barium nitrate, hexachloroethane, and magnesium.

Experience indicates that to obtain a red or green flame with a good colour index, compositions containing nitrate oxidisers must have not less than 15% of organochlorine

compounds. Hence, a further condition is derived: the composition must contain 15% hexachloroethane, the carbon of which must be oxidised to CO at least.

Table 5.1 shows that 1.11 g C_2Cl_6 releases 1 g chlorine, and that 0.34 g magnesium react with 1 g chlorine. Hence, a composition with 15% C_2Cl_6 requires $(15 \times 0.34)/1.11 = 4.6\%$ magnesium.

On decomposition, the hexachloroethane forms $(15 \times 24)/237 = 1.5\%$ carbon, which must be oxidised to CO. From Table 4.2 we find that 0.75 g charcoal react with 1 g oxygen to form carbon monoxide; from Table 2.1 we find that 3.27 g $Ba(NO_3)_2$ liberate 1 g oxygen; Hence, $(1.5 \times 3.27)/0.75 = 6.5\%$ $Ba(NO_3)_2$ is required to oxidise the carbon.

Now we know that in 100 g composition there must be :

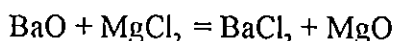
$$15 \text{ g } C_2Cl_6 + 4.6 \text{ g Mg} + 6.5 \text{ g } Ba(NO_3)_2 \quad 5.12$$

We determine how many grams of the composition are contained in the binary mixture $Ba(NO_3)_2 + Mg$: $z = 100 - 15 - 4.6 - 6.5 = 73.9 \text{ g}$.

From Table 2.1, 3.27 g $Ba(NO_3)_2$ liberate 1 g oxygen, and from Table 3.3, 1.52 g Mg react with 1 g oxygen. Hence, 3.27 g $Ba(NO_3)_2$ react with 1.52 g Mg and 73.9 g of the binary mixture contains $(3.27 \times 73.9)/(3.27 + 1.52) = 50.4 \text{ g } Ba(NO_3)_2$ and $(73.9 - 50.4) = 23.5\%$ Mg.

Summarising these calculations:	barium nitrate	$50.4 + 6.5 = 56.9\%$
	hexachloroethane	15.0%
	magnesium	$23.5 + 4.6 = 28.1\%$

The solid products of combustion of this composition will be MgO , BaO , and $MgCl_2$; but as the result of a reversible exchange reaction which occurs in the flame, barium chloride is formed which colours the flame green.:



If we introduce an organic binder - iditol - into the composition, we obtain the recipe ^{7 page 62}:

barium nitrate	59.5%
hexachloroethane	15.0%
magnesium	20.5%
iditol	5.0%

Section 5. Calculation of compositions with a fluorine balance.

This type of calculation is similar in principle to the calculation of metal - chloride compositions.

Here, fluorine compounds (fluorides of low-energy metals or organofluorine compounds) play the part of oxidiser, and powders of active metals act as fuels. Sufficient oxidiser must be used to oxidise the metal completely.

Table 5.2 may be used to simplify the calculations: it gives the quantity of oxidiser which releases 1 kg fluorine on decomposition, and the quantity of fuel reacting with 1 kg fluorine.

Example 11. Calculate the binary mixture of teflon with zirconium.

From Table 5.2, we find that 1.32 g teflon react with 1.20 g zirconium.

teflon 52.4%
zirconium 47.6%

Oxidiser Fluorine Compound	Molecular Weight	Weight of oxidiser releasing 1 kg fluorine	Fuel	Atomic Weight	Weight of fuel reacting with 1 kg fluorine
CaF ₂	102	2.74	Be	9.0	0.24
AgF	127	6.68	Mg	24.3	0.64
PbF ₂	245	6.45	Al	27.0	0.47
(C ₂ F ₄) _n teflon	100	1.32	Zr	91.2	1.20
XeF ₄	207	2.72			

Table 5.2 Properties of some fluorine oxidisers

The combustion of compositions containing an excess of oxidiser may be accompanied by the liberation of fluorine. The formation of free fluorine is most likely when fluorides of metals with variable valency are used as oxidisers, such as CoF₃, MnF₃, and PbF₄.

The properties of fluorine compounds are described by Simons ²⁰⁵, Ryss ²⁰¹, Knunyants and Fokin ²⁰⁰, and in Section 9 of Chapter XVII in this book.

Chapter VI

Heat of Combustion of Pyrotechnic Compositions

The special effect of a pyrotechnic composition is affected to a considerable degree by the quantity of heat liberated by the combustion. The heat of combustion of pyrotechnic compositions may be determined by two methods:

1. by calculation using Hess's Law.
2. experimentally by burning the composition in a calorimeter.

Section 1. Calculation of heat of combustion.

Hess's Law may be formulated: the quantity of heat liberated in a chemical reaction depends only on the initial and final states of the system, and does not depend upon the way in which the reaction occurs.

For the purpose of calculation, another formulation of this law may be used: if a system moves once from state 1 to state 3 directly, and a second time via a number of intermediate states, the heat of the direct transformation will be equal to the sum of the heats of the intermediate reactions.

In other words:

$$Q_{1,3} = Q_{1,2} + Q_{2,3}$$

where $Q_{1,3}$ is the quantity of heat liberated when the system moves from state 1 to state 3, etc.

It follows from Hess's Law that the heat of formation of the products of combustion of a pyrotechnic composition from the elements is equal to the sum of the heats of formation of the components of the composition plus the heat of the combustion reaction. Consequently the heat of a combustion reaction is determined by the difference between the heat of formation of the products of combustion and the heat of formation of the components of the composition:

The combustion of pyrotechnic compositions usually occurs at a comparatively low rate, and for

$Q_{2,3}$	=	$Q_{1,3}$	-	$Q_{1,2}$
heat of combustion of pyrotechnic composition		heat of formation of products of combustion		heat of formation of components of composition

the greater part under conditions of venting. We may therefore consider that combustion occurs at constant pressure. Since thermodynamic tables usually give the heats of formation of compounds at constant pressure, the heat of reaction calculated as above is the heat at constant pressure, Q_p .

The calculation of the heat of combustion of a pyrotechnic composition differs from the calculation of the heat of explosion of an explosive, which is taken to be the heat of reaction at constant volume, Q_v . The relationship between Q_p and Q_v is:

$$Q_v = Q_p + 2.38 n \quad \text{kJ mol}^{-1}$$

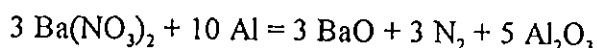
where n is the number of moles of gases formed during reaction.
(see also reference ^{7 page 64}).

For the calculations, standard heats of formation of substances from the elements ($-\Delta H_{298}$) are given by Rossini ⁹⁸, Britske, Kapustinskiy, et al ⁹³, Karapet'yants ⁹⁴, Glushko (editor) ²³³, Kubashevskiy and Evans ⁹⁵. A summary of the heats of formation of many substance is published by Andreyev and Belyayev ¹¹¹ from works by Medart.

Values of the heats of formation of components of pyrotechnic compositions, and certain of their reaction products, are given in Table 6.1.

Heats of formation of certain oxidisers and their decomposition products are given in Table 2.1; the heat of formation of oxides is given in Tables 3.1 and 3.5.

As an example, we will calculate the heat of combustion of the mixture:



The published heat of formation of the products of combustion ⁹⁸ is:

5 Al_2O_3	5 x 1674 =	8370	
3 BaO	3 x 557 =	<u>1671</u>	
		10,041 kJ	($Q_{1,3}$)

The heat of formation of the components of the composition is:

3 $\text{Ba(NO}_3)_2$	3 x 991 =	2973 kJ	($Q_{1,2}$)
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The heat of the combustion reaction is:

$$Q_{2,3} = 10,032 - 2973 = 7059 \text{ kJ}$$

The sum of the $\text{Ba(NO}_3)_2$ and the Al by weight is:

$$M = 261.4 \times 3 + 27.0 \times 10 = 1054$$

The heat of combustion of the composition is:

$$q = \frac{7059}{1054} = 6.71 \text{ kJ g}^{-1}$$

Such a method of calculation is adequately accurate, but it gives no indication of the separate contributions of the fuel and the oxidant to the general heat balance of the composition. Such an

$$q = 8.0 - 1.13 = 6.87 \text{ kJ g}^{-1}$$

In this particular case, decomposition of the oxidiser requires $1.13/8 \times 100 = 14\%$ of the heat liberated on combustion of the magnesium.

A similar calculation for the ferroaluminium thermite Fe_3O_4 75%, Al 25% gives a heat balance:

$$q = 7.61 - 3.60 = 4.01 \text{ kJ g}^{-1}$$

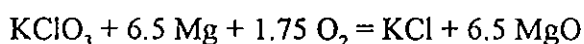
That is, 47% of the heat liberated on combustion of the aluminium is expended on the decomposition of the oxidiser.

Table 6.2 contains data on the heat of combustion of certain pyrotechnic compositions; the components are in stoichiometric ratios, and the heat of combustion was calculated from Hess's law.

If we ignore substances whose combustion consists of reaction with the oxygen of the air, such as the magnesium alloy "elektron", the greatest heat of combustion is possessed by photoflash compositions, followed by illuminating, tracer, and rocket compositions; signal flares liberate comparatively little heat, and smoke compositions the least of all. Recipes for incendiary compositions are so numerous, and the components so diverse, that the heat of combustion varies very widely.

If atmospheric oxygen participates in the combustion process, then compositions of negative oxygen balance give more heat than compositions of the same components in stoichiometric ratios.

As an example, consider a composition KClO_3 44%, and Mg 56% with an oxygen balance of $n = -20 \text{ g O}_2$. The combustion reaction may be represented by the equation:



The heat of combustion of this composition is equal to

$$q = \frac{602 \times 6.5 + 443 - 401}{123 + 24.3 \times 6.5} = 14.1 \text{ kJ g}^{-1}$$

Compared with the value in Table 6.2 for the stoichiometric composition, the heat of reaction has been increased by 50%.

Section 2 Experimental determination of heat of combustion.

The heat of combustion of a pyrotechnic composition is determined experimentally by burning a known weight of it in a calorimetric bomb. The quantity of heat liberated is given by the product of the heat capacity of the system (water + apparatus) multiplied by the difference between the

Compound	Heat of Formation kJ mole ⁻¹	Compound	Heat of Formation kJ mole ⁻¹	Compound	Heat of Formation kJ mole ⁻¹
NaF	569	SrO ₂	644	starch	C ₆ H ₁₂ O ₆ 949
Na ₃ AlF ₆	3,170	Sr ₃ N ₂	385	lactose	C ₁₂ H ₂₄ O ₁₂ 2,722
Na ₂ SiF ₆	2,798	SrSO ₄	1,430	ethanol	C ₂ H ₅ OH (l) 280
NaHCO ₃	945	SrCl ₂	828	ether	C ₄ H ₁₀ O (l) 272
Na ₂ CO ₃	1,133	BaCO ₃	1,192	shellac	C ₁₆ H ₂₄ O ₃ 949
Na ₂ C ₂ O ₄	1,317	Ba ₃ N ₂	376	iditol	C ₁₃ H ₁₂ O ₂ 623
NaNO ₂	368	ZnCl ₂	414	TNT	C ₇ H ₅ N ₃ O ₆ 67
Na ₂ SO ₄	1,388	AlN	314	RDX	C ₃ H ₆ N ₆ O ₆ -100
K ₂ CO ₃	1,179	AlCl ₃	698	urotropine	C ₆ H ₁₂ N ₄ -125
K ₂ SO ₄	1,430	Al ₂ S ₃	585	C ₂ Cl ₆	226
Cu(OH) ₂	447	Pb(NO ₃) ₂	447	CS ₂	-88
CuCO ₃	598	FeCl ₃	393	pyroxylin (13%N)	?
CuCNS	-42	NH ₃ (g)	46	C ₂₄ H ₂₉ (ONO ₂) ₁₁ O ₉	
CuCl	134	NH ₄ Cl	314	collodion cotton	?
CuCl ₂	222	HCl (g)	92	C ₂₄ H ₃₁ (ONO ₂) ₉ O ₁₁	
MgCO ₃	1,117	CCl ₄ (l)	105		
Mg ₃ N ₂	481	CH ₄ (g)	75		
MgS	351	C ₆ H ₆ (l)	-54		
MgCl ₂	640	naphthalene C ₁₀ H ₈	-67		
MgF ₂	1,104	anthracene C ₁₄ H ₁₀	-134		
SrCO ₃	1,213				
SrC ₂ O ₄	1,204				

Table 6.1 Heat of Formation ($-\Delta H_{298}$) of pyrotechnic ingredients and certain combustion products.

analysis may be made by other methods. We will show this using the example of a mixture of Ba(NO₃)₂ and Mg.

Calculations[†] show that stoichiometry occurs at Ba(NO₃)₂ 68%, Mg 32%. From Table 3.1 we find that 0.32 g Mg liberates $0.32 \times 25 = 8.0$ kJ. From Table 2.1 we find that 435 kJ are required for the decomposition of 261 g Ba(NO₃)₂, and so 1.13 kJ are required to decompose 0.68 g. Comparing these data, we obtain the heat of combustion of the mixture:

[†] See Chapter V, Example 5.

Formulation (%)				Heat of Combustion (MJ kg ⁻¹)		Type of Composition	
KClO ₄	83	Be	17		13	Not used in practice	
KClO ₄	60	Mg	40		9	Photoflash mixture	
KClO ₃	63	Mg	37		10	Photoflash mixture	
Ba(NO ₃) ₂	75	Mg	32		7	Photoflash mixture	
KClO ₄	66	Al	34		10	Incendiary	
NaNO ₃	60	Al	40		8	Illuminating (without binder)	
Fe ₂ O ₃	75	Al	25		4	Thermite	
Ba(NO ₃) ₂	75	Mg	24	iditol	4	5	Illuminating
Ba(NO ₃) ₂	63	Al	27	sulphur	10	6	Illuminating
Sr(NO ₃) ₂	69	Mg	25	Ca resinate	6	6	Tracer
NG - collodion powder					5	Rocket fuel	
mixed powder ²²⁸						Rocket fuel	
NH ₄ ClO ₄	90	resin	10		5	Rocket fuel	
NH ₄ ClO ₄	80	resin	20		4	Rocket fuel	
Ba(ClO ₃) ₂ ·H ₂ O	88	iditol	12		4	Green signal flare	
KClO ₃	57	SrCO ₃	25	shellac	18	3	Red signal flare
C ₂ Cl ₆	81	Al	19		4	Screening smoke	
C ₂ Cl ₆	17	KClO ₄	21	Zn	61	2	Screening smoke
KClO ₃	35	lactose	25	rhodamine red	40	2	Red smoke
KNO ₃	75	carbon	15	sulphur	10	3	Gunpowder
Mg	90	Al	10		26	"Elektron" alloy (reacts with air)	

Table 6.2 Heat of combustion of pyrotechnic compositions and solid rocket fuel

final and initial temperatures of the water in which the bomb is submerged. The heat capacity of the system, also called the "water number" of the calorimeter, is determined by particular experiments; substances such as benzoic acid, with a known heat of combustion, are burned in the bomb.

The volume of the bomb is usually 300 - 400 cm³, and the weight of water (weighed to an accuracy of up to 1 g) is about 3 kg.

A pyrotechnic composition usually burns in air, and more rarely in an atmosphere of nitrogen or argon. There is no point in burning a pyrotechnic composition in an atmosphere of oxygen, since

the heat of complete combustion may always be calculated with adequate accuracy from Hess's law.

If the heat of combustion in air is required of a composition with negative oxygen balance, we should provide in the bomb the maximum quantity of air per unit weight of composition, which is achieved by reducing the weight of composition to the least amount consistent with adequate accuracy of determination. Usually, the weight is about 0.5 - 1 g, but the heat rise should not be less than 0.3°C. Consider that a bomb of volume 300 cm³ filled with air at atmospheric pressure contains 0.1 g oxygen which is adequate for the oxidation of only 0.5 g of a composition with an oxygen balance $n = -20$ g O₂.

There is much experimental evidence to indicate that atmospheric oxygen participates in the process of combustion of compositions with negative oxygen balance.

Only certain smoke compositions are burned in an atmosphere of nitrogen, because atmospheric oxygen would partially or even completely oxidise the smoke producing substance and distort the results of the determination. Nitrogen is not an inert gas as far as aluminium and magnesium are concerned, since these metals react to form nitrides AlN and Mg₃N₂. If it is necessary to eliminate entirely the effect of an atmosphere on the combustion of compositions containing magnesium or aluminium, then the combustion should be undertaken in an inert atmosphere such as argon.

Contact with a red-hot, fine nichrome (an alloy of nickel, chromium and iron) wire is adequate to ignite most compositions. If this is not adequate, the composition is covered with a small quantity (some hundredths of a gram) of an igniting composition whose heat of combustion must be determined in advance. Addition of such an igniting composition reduces the accuracy of the determination because of the possibility of a chemical reaction between the products of combustion of the composition being tested and of the igniting composition. The igniting composition should therefore be used only as a last resort.

Popov⁹⁷ has published the methodology of calorimetric determinations.

Section 3. Connection between the type of composition and the heat of combustion.

From calculated data such as Table 6.2, and from experimental determinations, we may establish a relationship between the type of composition and the quantity of heat liberated during combustion. (Table 6.3)

Type of composition	Heat of combustion MJ kg ⁻¹
Photoflash mixture	7.1 - 12.5
Illuminating and tracer	6.3 - 8.4
Rocket (without complete combustion in air)	
colloidal nitroglycerine - powder	3.3 - 5.4
mixed powders (tentative data)	4.2 - 6.3
Incendiary (with oxidiser)	3.3 - 12.5
Night signal compositions	2.5 - 5.0
Screening smokes	1.7 - 4.2
Coloured signal smokes	1.3 - 2.5

Table 6.3 Relation between the type of composition and its heat of combustion

Chapter VII

Gaseous Reaction Products of Pyrotechnic Reactions

Almost all pyrotechnic compositions form some gaseous products during their combustion reaction. Of all the commonly used compositions only ferroaluminium thermite does not appear to give any gaseous combustion products[†].

For illuminating, tracer, and signal flare compositions the formation of gaseous substances on combustion is necessary to obtain a flame and so increase the quantity of light energy being radiated. It is necessary that solid pyrotechnic fuels form gaseous reaction products on combustion to provide the necessary thrust for the rocket motor. Smoke compositions require gaseous products to eject the particles of various smoke forming substances from the reaction zone into the atmosphere. Gaseous products are also desirable from the combustion of incendiary compositions, because this helps spread the fire.

The combustion of pyrotechnic compositions produces a certain quantity of solid, as well as gaseous products. Solid pyrotechnic composition is an exception, as are certain combustible compounds or mixtures of them which react with atmospheric oxygen. Thus liquid hydrocarbons - petrol, kerosene, petroleum, and others, used in pyrotechnic incendiary agents, produce very few solid products on combustion.

The ratio between the quantities of gaseous and solid products of the combustion reaction depends upon the purpose of the composition, and the design requirements placed upon it. For example, illuminating and tracer compositions produce gaseous compositions amounting to 15 - 25% of the weight of composition, while smoke compositions produce a great quantity of gaseous products.

The quantity of gaseous products obtained as a result of the combustion of 1 g of pyrotechnic composition is generally not expressed by weight, but by the volume occupied under normal conditions (0°C and 760 mmHg). This volume of gaseous product is the specific volume, v_0 .

In calculations, the volume occupied under normal conditions by the water vapour is added to the volume occupied by the gases formed in the process (CO_2 , CO , and others).

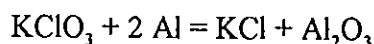
If the volume v_0 is known, the volume v_t of the gaseous products at the temperature of the combustion reaction are calculated in accordance with the well known law of Gay-Lussac:

$$v_t = v_0 (1 + 0.00366t)$$

In the calculation of v_t we should consider not only the true gases and water vapour, but all the substances which are vapours at the temperature of the combustion reaction.

† However, at the temperature of the reaction (ca. 2400°C) a comparatively small part of the intermediates and reaction products are in the vapour state.

As an example, consider the reaction between potassium chlorate and aluminium, which proceeds according to:



Since the combustion temperature of this mixture is about 3000°C, the potassium chloride, which boils at 1415°C, will be entirely in the vapour state. This explains why in certain cases the combustion of this mixture may occur at a rate approaching that of an explosion.

The gaseous products of a combustion reaction are formed essentially from the oxidation or decomposition of constituents containing hydrogen, carbon, nitrogen, sulphur, and chlorine. The first two elements are constituents of organic ingredients of pyrotechnic compositions.

Nitrogen is contained in organic nitro- or amino- compounds, and also in nitrates, which are the most commonly used oxidisers in pyrotechnics. Sulphur is used in the form of sulphides (Sb_2S_3 , pyrites, and others), and is also sometimes used in pyrotechnic compounds as the element. Chlorine is contained in organochlorine compounds. Free chlorine and hydrogen chloride are formed in the combustion of compositions containing ammonium perchlorate NH_4ClO_4 .

As a result of the oxidation and decomposition of compounds containing the elements mentioned, H_2O , CO_2 , CO , N_2 , SO_2 , H_2 , Cl_2 , and HCl are formed, and in certain cases the oxides of nitrogen, NO and NO_2 , as well.

The volume occupied under normal conditions by 1 kg of certain gases is given in Table 7.1.

Gas	1 kg ⁻¹	Gas	1 kg ⁻¹
H_2	11,200	HCl	614
H_2O	1,247	CO_2	509
CO	800	SO_2	350
N_2	800	Cl_2	315

Table 7.1 Volume of gas under normal conditions
(litres per kg)

As is apparent from Table 7.1, at equal weights in the gaseous state, hydrogen occupies the greatest volume, followed by water and carbon monoxide. We may conclude that if we wish to obtain a great volume of gaseous products it is important to use organic substances as the fuel since they contain much hydrogen; the quantity of oxidiser should be calculated to give H_2O and CO only or, if it is dictated by thermochemical considerations, to H_2O and CO_2 . Paraffin and stearin are amongst the solid fuels which contain much hydrogen.

The specific volume of gaseous products of the reaction may be determined by two methods

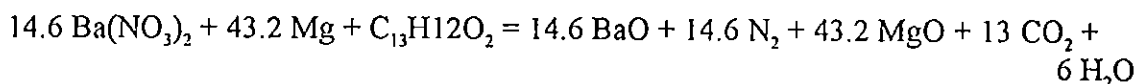
1. Experimentally - by burning the pyrotechnic composition in a calorimetric bomb. The gaseous products are transferred to a gas meter for measurement ¹⁵⁴. Alternatively, the

pressure of the gases in the bomb may be measured with a mercury manometer and the quantity obtained after correction for temperature. We should consider that the composition of the gases after cooling differs from that at the moment of combustion. This may distort the results of the determination. For example, on combustion of perchlorates, metal chlorides are formed which condense on cooling; CO_2 may react with metal oxides to form carbonates. All these processes lead to a decrease in the value of v_0 . Note that the experimental determination does not include the value for the water vapour.

2. Calculation - on the basis of the equation of the combustion reaction, which may be hypothetical, or (more accurately) supported by the known process occurring with similar compositions. The specific volume is calculated as: $v_0 = \frac{22.4 \cdot n \cdot 1000}{m}$ where n is the number of moles of gaseous products liberated during the combustion reaction (the sum of the coefficients of the gaseous substances on the right hand side of the equation for the reaction); and m is the weight of the composition in grams.

Example 1. Calculate v_0 for an illuminating composition 71% barium nitrate, 21% magnesium, 4% iditol.

The combustion may be expressed approximately by the equation:



hence:
$$v_0 = \frac{22.4(14.6 + 13 + 6) \cdot 1000}{14.6 \times 6.261 + 43.2 \times 24.3 + 200} = 149 \text{ m}^3\text{Mg}^{-1}$$

Table 7.2 lists values of v_0 for various compositions of recipes given in Table 6

We may establish a certain connection between the type of composition and the specific volume of its combustion products (see Table 7.2). The numerical data in Table 7.3 should be considered tentative because of the inadequacy of available experimental material.

We should note that the specific volume of gaseous products for the presently used pyrotechnics, with the exception of solid rocket fuel, is considerably less than for basic explosives for which some v_0 values are: RDX 908, tetryl 750, and TNT 688.

In conclusion, we should mention that for solid rocket fuel, other, more accurate methods are used to calculate the quantity of gaseous reaction products (see Chapter XX).

Composition type	Formulation						Gaseous products of combustion	v_0 (l kg ⁻¹)	Weight of gases as % weight of composition
photoflash mixture	Ba(NO ₃) ₂	68	Mg	32			N ₂	58	7
	Ba(NO ₃) ₂	74	Al	26			N ₂	61	8
thermite	Fe ₂ O ₄	75	Al	25				0	0
illuminating	Ba(NO ₃) ₂	75	Mg	21	iditol	4	N ₂ , CO ₂ , H ₂ O	144	21
green signal flare	Ba(ClO ₃) ₂ ·H ₂ O				iditol	12	CO ₂ , H ₂ O	330	43
		88							
red signal flare	KClO ₄	57	SrCO ₃	25	shellac	18	CO, H ₂ O	375	40
red smoke	KClO ₄	35	lactose	25	rhodamine	40	CO, H ₂ O	365	39
gun powder	KNO ₃	75	charcoal	15	sulphur	10	CO, CO ₂ , H ₂ O, N ₂	280	

Table 7.2 Volume of gaseous combustion products of certain compositions

Type of Composition	v_0 (l kg ⁻¹)
photoflash	50 - 100
illuminating and tracer	100 - 300
night signals	300 - 450
smoke (except metal - chloride mixtures)	300 - 500
incendiary (containing oxidiser)	0 - 300
solid rocket fuel	600 - 850

Table 7.3 Relationship between type of composition and the specific volume v_0 .

Chapter VIII

Combustion Temperature of Pyrotechnic Compositions

The determination of the combustion temperature of pyrotechnic compositions is of great significance because it gives us a criterion for the evaluation of existing compositions and facilitates the development of new, improved recipes.

The combustion temperature of pyrotechnic compositions may be determined by two methods:

1. Calculation - in accordance with formula 8.7 which uses the well known principle that the temperature of reaction is equal to the heat of reaction divided by the total heat content of the reaction products. Losses to the surroundings are not considered; in particular the radiation losses, which are quite significant for pyrotechnic flames, are ignored.
2. Measurement - by means of optical pyrometers or thermocouples.

Section 1. Calculation of combustion temperature of compositions.

We should indicate from the very beginning that a flame has different temperatures in different zones. Calculation yields only the upper limits of the possible temperature. Calculation of combustion temperatures is hampered by the absence of accurate numerical data for the heat capacities of many compounds at high temperatures (above 2000°C). Also, the latent heats of fusion and boiling for many compounds have not been determined, or have been determined only with inadequate accuracy.

The calculated temperature is the upper limit, which is unattainable in practice, since the combustion temperature is lowered considerably because of the expenditure of heat on thermal dissociation of the products of combustion, and because of heat losses to the surroundings.

Calculation of combustion temperature from formula 8.7 is satisfactorily accurate for temperatures which do not exceed 2000-2500°C. Otherwise, the results are only tentative - for example, calculations of the combustion temperature of compositions containing more than 10-15% magnesium, aluminium, or other high-energy fuel.

Since the gaseous combustion products are usually able to expand, the specific heat at constant pressure, c_p , is used. The molar specific heats at constant pressure and at constant volume, c_v , are related:

$$c_p = c_v + R \quad 8.1$$

where R is the gas constant, 8.28 J mole⁻¹ K⁻¹.

The molar specific heat at constant volume is:

$$c_v = iR/2 \quad 8.2$$

where $i =$ 3 for monatomic gases
 5 for diatomic gases
 6 for polyatomic gases.

From formulae 8.1 and 8.2 we obtain the values of c_p :

20.7 J mole⁻¹ K⁻¹ for monatomic gases
 29.0 for diatomic gases
 31.9 for polyatomic gases.

Temperature Interval °C	N ₂ , O ₂ , CO	H ₂	H ₂ O	CO ₂
0- 100	29.3	28.9	33.5	38.1
0 - 500	29.7	29.3	34.7	43.1
0-1000	30.5	29.7	36.8	47.3
0-1500	31.4	30.9	39.7	49.8
0-2000	32.2	31.8	43.1	51.4
0-2500	32.6	32.2	47.7	52.3
0-3000	33.5	32.6	53.5	53.1

Table 8.1 Average molecular heat content c_p for gases (J mole⁻¹ K⁻¹)

Experimental data do not always agree for diatomic gases, and particularly not for polyatomic gases. Experimental values of c_p are given in Table 8.1.

For simple substances at high temperature (1000°C and above) in the solid state, we may apply the law of Dulong and Petit, that the kg-atom weight is constant, and equal to approximately 26.8 kJ K⁻¹.

For solid compounds at high temperatures the Neumann-Kopp law, that the molecular specific heat is equal to the sum of the atomic specific heats, is a valid approximation.

The experimental values of specific heats for certain substances of interest to pyrotechnists are given in Table 8.2.

The difference between c_p and c_v is very small for solids, and may be ignored in practice.

It is difficult to give any definite relationships for the specific heat of liquids at high temperature (above 1000°C). We can only note that the specific heat of a molten substance is higher than that

Substance	Temperature (°C)	c_p (J mole ⁻¹ K ⁻¹)	Substance	Temperature (°C)	c_p (J mole ⁻¹ K ⁻¹)
Fe	0- 100	25.9	NaCl	600	57.7
	20-1500	40.1	Al ₂ O ₃	30- 300	96.2
Cu	20- 100	24.7		30-1100	115.8
	20-1500	39.3		30-1500	117.5
NaCl	20- 785	56.9		20-2030	119.2
MgO	20-1735	50.6		570- 600	123.0
	20-2370	58.5		965- 973	138.8
	20-2780	59.8	BaCl ₂	100	82.0
KCl	400	55.6	BaCO ₃	1000	133.0

Table 8.2 Specific heat c_p of solids

of the solid: sometimes the approximation is used that c_p for a liquid is 1.3 times the value for the solid.

Richards and Crompton have found the following relationship between the latent heats of fusion and the melting point for the majority of simple substances:

$$\frac{Q_s}{T_s} = 0.008 - 0.013 \quad 8.3$$

where Q_s is the latent heat of fusion in kJ g-atom⁻¹
 T_s is the melting point in K.

This relationship has not been validated with adequate accuracy for many simple substances.

The latent heat of fusion may be calculated, in our opinion, by the approximation:

$$\frac{Q_s}{T_s} = 0.008n \quad 8.4$$

where n is the number of atoms in the molecule of the compound.

The value of the latent heat of vaporisation depends upon the temperature: it decreases as the vaporisation temperature increases. Thus for water, the molar latent heat of vaporisation is 45.2 kJ at 0°C, and 40.6 kJ at 100°C.

The latent heat of boiling of liquids at high temperature can be very great. The dependence of the heat of boiling and the boiling point of the liquid at 760 mmHg is given by Trouton's rule.

$$\frac{Q_k}{T_k} = 0.08 \quad 8.5$$

where Q_k is the heat of vaporisation at the boiling point,
kJ kg-mole⁻¹

T_k is the boiling point of the liquid at 760 mmHg. K.

For many inorganic compounds (especially high-boiling compounds), the latent heat of vaporisation, in our opinion, may be calculated according to the following empirical formula with greater accuracy than with Trouton's formula:

$$\frac{Q_k}{T_k} = 0.046n \quad 8.6$$

where n is the number of atoms in the compound.

Obviously, the latent heat of vaporisation of compounds is considerably greater than that of fusion. Q_k and Q_s must be allowed for in calculations involving high-melting and high-boiling inorganic compounds.

$$t = \frac{Q - \sum (Q_s + Q_k)}{\sum c_p} \quad 8.7$$

The maximum combustion temperature is calculated by the formula:

where Q is the quantity of heat liberated in the combustion reaction

$\sum c_p$ is the sum of the heat contents of the reaction products

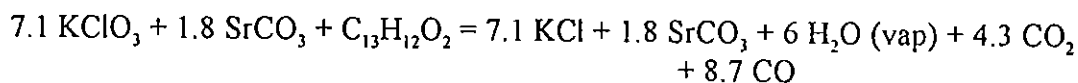
$\sum (Q_s + Q_k)$ is the sum of the latent heats of fusion and vaporisation of the combustion products

t is the combustion temperature.

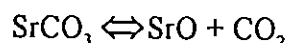
Two examples follow on the calculation of combustion temperature by this formula.

Example 1. Calculate the combustion temperature of a red flare composition consisting of 65% KClO_3 , 20% SrCO_3 , and 15% iditol ($\text{C}_{13}\text{H}_{12}\text{O}_2$).

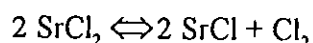
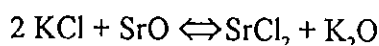
The combustion reaction is approximately:



In this case there is an inaccuracy due to the occurrence of certain reactions in the flame: the dissociation reaction:



and the reactions (see Chapter XVI):



The heat of combustion is calculated from Hess's law, and the heat of formation of iditol is assumed to be 3.09 MJ kg^{-1} :

for H_2O (vap) $6 \times 240 = 1440$ CO_2 $4.3 \times 381 = 1638$ CO $8.7 \times 109 = 948$ KCl $7.1 \times 443 = \underline{3145}$ 7171 MJ	for KClO_3 $7.1 \times 401 = 2847$ $\text{C}_{13}\text{H}_{12}\text{O}_2$ $3.09 \times 200 = \underline{618}$ 3465 MJ
--	--

The quantity of heat liberated in the reaction is:

$$Q = 7171 - 3465 = 3706 \text{ MJ}$$

We assume that the combustion temperature will be about 1500°C , and we therefore take into consideration the latent heats of melting and boiling of KCl.

From published data ⁹⁸:

$$Q_{s, \text{KCl}} = 26.3 \text{ MJ at } 768^\circ\text{C}$$

$$S_{k, \text{KCl}} = 167 \text{ MJ at } 1415^\circ\text{C}$$

Hence

$$\Sigma(Q_s + Q_k) = 193.3 \times 7.1 = 1372 \text{ MJ}$$

$$Q - \Sigma(Q_s + Q_k) = 3706 - 1372 = 2334 \text{ MJ}$$

The heat content for the gases and water vapour in the temperature interval $0 - 1500^\circ\text{C}$ (from Table 8.1):

for H_2O	$6 \times 39.7 = 238$
CO_2	$4.3 \times 49.8 = 214$
CO	$8.7 \times 31.4 = \underline{273}$
	725 MJ

The heat content of KCl and SrCO_3 is assumed, in accordance with the Neumann-Kopp law, to be 53.5 and $134 \text{ kJ K}^{-1} \text{ kg-mole}^{-1}$ respectively.

Hence

$$53.5 \times 7.1 = 380$$

$$134 \times 1.8 = \underline{241}$$

621 MJ

and finally

$$\Sigma c_p = 725 + 621 = 1346 \text{ kJ K}^{-1}.$$

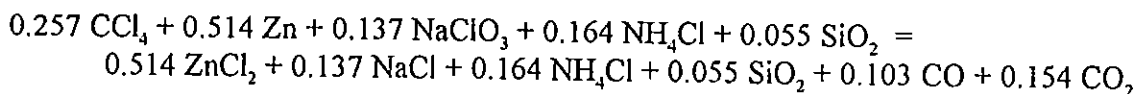
Hence

$$t = \frac{2334 \times 1000}{1346} = 1734^\circ\text{C}$$

If we had considered the thermal dissociation $\text{SrCO}_3 \rightleftharpoons \text{SrO} + \text{CO}_2$ for which $\Delta H = 226 \text{ MJ}$, which proceeds to some extent in the flame, then the calculated temperature would have dropped to about 1600°C .

Example 2. Calculate the combustion temperature of a smoke composition having the composition: 39% CCl_4 , 34% Zn, 15% NaClO_3 , 9% NH_4Cl , 3% SiO_2 (kieselguhr).

Compiling the equation for the combustion reaction:



Kieselguhr (diatomaceous earth) acts as an absorbent for the liquid CCl_4 , and does not participate in the combustion reaction. $Q = 197.4 \text{ MJ}$.

$$\begin{array}{ll} \text{For } \text{ZnCl}_2 & t_s = 365^\circ\text{C}; \quad t_k = 732^\circ\text{C} \\ \text{NaCl} & t_s = 800^\circ\text{C}; \quad t_k = 1440^\circ\text{C} \\ \text{SiO}_2 & t_s = 1470^\circ\text{C} \end{array}$$

For NH_4Cl sublimation point is 335°C .

The combustion temperature of smoke compositions rarely exceeds 1000°C , therefore the latent heat of vaporisation of NaCl and the heat of fusion of SiO_2 are not taken into consideration.

$$\begin{array}{ll} \text{Now,} & Q_{s \text{ ZnCl}_2} = 16 \text{ MJ kg-mole}^{-1} \text{ (from Formula 8.4:)} \\ & Q_{s \text{ NaCl}} = 30 \text{ MJ kg-mole}^{-1} \\ & Q_{k \text{ ZnCl}_2} = 138 \text{ MJ kg-mole}^{-1} \\ & Q_{\text{sublimation NH}_4\text{Cl}} = 163 \text{ MJ kg-mole}^{-1} \end{array}$$

$$\text{Hence:} \quad \Sigma(Q_s + Q_k) = 0.514(16 + 138) + 0.137 \times 30 + 0.164 \times 163 \\ = 110 \text{ MJ}$$

$$Q - \Sigma(Q_s + Q_k) = 87.4 \text{ MJ}$$

Calculate the heat content:

$$\begin{array}{ll} \text{ZnCl}_2 & 0.514 \times 83.6 = 43.0 \\ \text{NaCl} & 0.137 \times 56.9 = 7.8 \\ \text{NH}_4\text{Cl} & 0.164 \times 151 = 24.8 \\ \text{SiO}_2 & 0.055 \times 75.3 = 4.1 \\ \text{CO} & 0.103 \times 30.5 = 3.1 \\ \text{CO}_2 & 0.154 \times 47.3 = 7.3 \end{array}$$

$$\begin{array}{ll} \Sigma c_p & = 90.1 \text{ MJ} \\ t & = \frac{87.4 \times 1000}{90.1} = 970^\circ\text{C} \end{array}$$

In 1953 Venturini¹⁰⁹ introduced certain changes to the method of calculating the combustion temperature of aluminium. He calculated a temperature of 3500K (3227°C), for ordinary ferroaluminium, which does not agree with experiment (see below). At first impression, Ventorini's calculations seem valid, but his error lies, as he himself indicated, in ignoring the vaporisation of the combustion products. This vaporisation occurs in aluminium combustion

processes, and this is the reason, in our opinion, why Ventorini's results differ so much from the experimental values.

We must again comment that if the combustion temperature exceeds 2000 - 2500°C, the data calculated from Formula 8.7 reflect only the order of magnitude, and are therefore useful only in comparing different compositions.

For rocket fuels, a very high degree of accuracy is required in the calculation of combustion temperature, and more information on the combustion products is required. In this case, very labour intensive calculations are performed, in which the processes of thermal dissociation and vaporisation of the combustion products are considered. The starting data for such calculations have been published ²³³.

Section 2. Experimental determination of combustion temperature.

The combustion temperature of most flame pyrotechnic compositions lies within the limits 2000 - 3000°C. The flame temperature of such compositions is usually measured by optical methods. The basis for these methods is the assumption that the radiation of the pyrotechnic flame obeys (at least approximately), the laws of radiation of a black body.

That is, the radiation is in accordance with:

1. the Stefan-Boltzmann law $E = c \cdot T^4$

where E is the total radiated energy
 c is a constant equal to $5.73 \cdot 10^{-8} \text{ W} \cdot \text{m}^{-2} \cdot \text{K}^{-4}$
 T is the absolute temperature, K.

2. Wien's radiation shift law $\lambda_{\max} \cdot T = 2884$

where $\lambda_{\max}$ is measured in μm .

3. Planck's radiation law $E_{\lambda} = c_1 \lambda^{-5} (e^{c_2/\lambda T} - 1)^{-1}$

where c_1 is $1.19 \cdot 10^{-16} \text{ W m}^2 \text{ sr}^{-1}$
 c_2 is $1.44 \cdot 10^{-2} \text{ m K}$

In fact, the radiation from a pyrotechnic flame differs to a certain degree from that of a black body.

A black body has a continuous spectrum.

In a flame, incandescent solid or liquid particles give a continuous spectrum, but certain gaseous substances give a non-continuous spectrum with lines or bands. The spectrum of the flame from a pyrotechnic composition therefore consists usually of a continuous spectrum with a non-continuous spectrum from the gases superimposed on it. The relative intensities of the

continuous and non-continuous spectra depend upon many factors including, primarily, the temperature of the flame and the quantitative ratio of the solid and gaseous phases.

From what has been said, it follows that the measurement by optical methods gives only an approximation to the flame temperature which, for white flames, may be in error by ± 50 to $\pm 100^\circ\text{C}$.

Measurement of the luminance and the colour temperature of the flame are the most readily accessible methods.

The luminance temperature T_{lu} is the temperature of a black body which has the same brightness at a wavelength of $0.665 \mu\text{m}$.

The colour temperature T_{∞} is the temperature of a black body which has the same colour as the flame. In this case, the ratio of the intensities of the radiation of a black body at two different wavelengths λ_1 and λ_2 is equal to the ratio of the intensities of the radiation of the given physical body at the same wavelengths. The experimental determination of the colour temperature of the body reduces to the determination of the ratio of the radiation intensity for the two different wavelengths $K = E_{\lambda_1}/E_{\lambda_2}$ and the determination from tables of the temperature at which a black body has the same value of K for the same wavelengths.

Types of Optical Pyrometers.

Optical pyrometer with disappearing filament. (Fig 8.1)

This is a visual pyrometer in which the brightness of the light radiated by the body (flame) being investigated is measured by comparing it with that of a standard incandescent body (the filament of a lamp), at the same wavelength ($\lambda = 0.665 \mu\text{m}$).

The incandescent lamp filament is placed at the focus of the objective lens which, together with the eyepiece, forms the optical system, and its image is matched with that of the flame. By varying the voltage to the lamp the brightness of the filament is varied until it equals that of the flame. This equality is perceived by the observer as the disappearance of the incandescent filament in the background of the flame. He reads the scale of the rheostat which is marked in degrees of luminance temperature. The pyrometer type OPPIR-017 produced by industry has two measurement scales which allow measurement of temperature over the ranges $1500 - 2500^\circ\text{C}$ and $2200 - 6000^\circ\text{C}$.

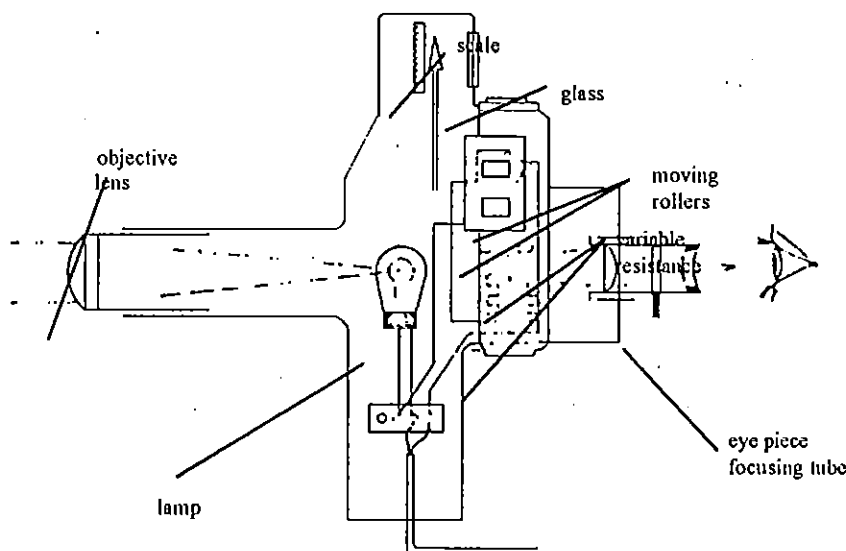


Fig 8.1 Optical pyrometer with disappearing filament

Motion Picture pyrometer. (Fig 8.2)

This is an ordinary cine camera equipped with a red light filter ($\lambda = 0.665\mu\text{m}$) and a series of ribbon lamps installed alongside the object being measured. The basis of this method of measuring temperature is the principle of photographing the flame in its own light and comparing the amount of fogging s of the photographic film with that produced by the lamps. By photographing ribbon lamps of known temperature simultaneously with the flame we can construct for the region of normal densities a calibrated curve $s = f(1/T)$. Hence, the temperature can be determined. This technique is of particular interest for the pyrotechnist because it allows determination of the temperature of different parts of the flame, and of the variations with time. Typical results are shown in Fig 8.3.

The photoelectric pyrometer

FEP-0.65 is a variation of the optical pyrometer developed specially for measuring the temperature of pyrotechnic flames with the data being recorded on an oscillograph. The FEP-0.65 measures the mean luminance temperature of the flame, and its emissivity (the energy radiated at a definite wavelength from the surface of the body, in unit time, at a specified temperature ¹⁰¹ i.e., E_λ in $\text{J m}^{-2} \text{s}^{-1}$).

The emissivity is measured by positioning a ribbon lamp and lens behind the flame (Fig 8.4) so that the image of the lamp filament is projected onto the part of the flame being investigated. Between the lamp and the lens is placed a rotating screen (modulator), periodically covering the light of the lamp with a frequency of 10 Hz. The oscillograph records first the photocurrent i_l from the lamp alone. When combustion is underway, the record shows alternately the photocurrents i_n from the flame alone, i_{l+n} from the combination of lamp and flame.

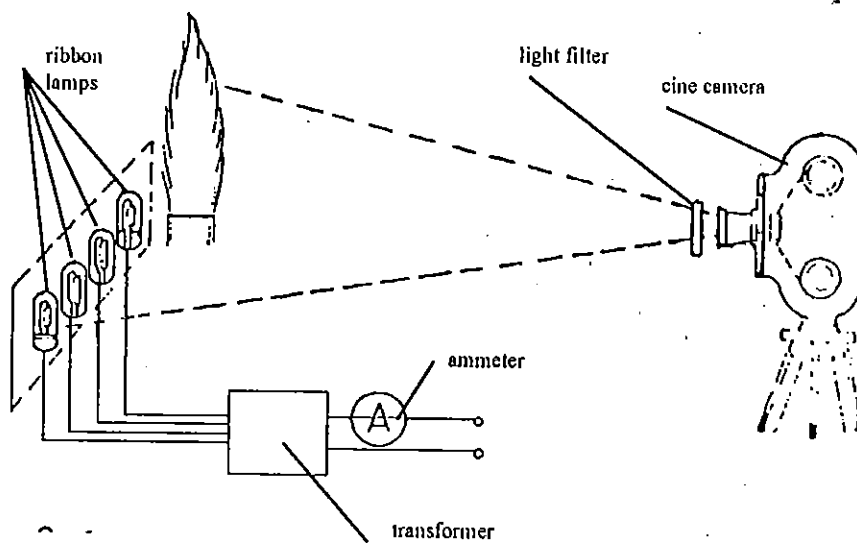


Fig 8.2 Diagram of a cine pyrometer

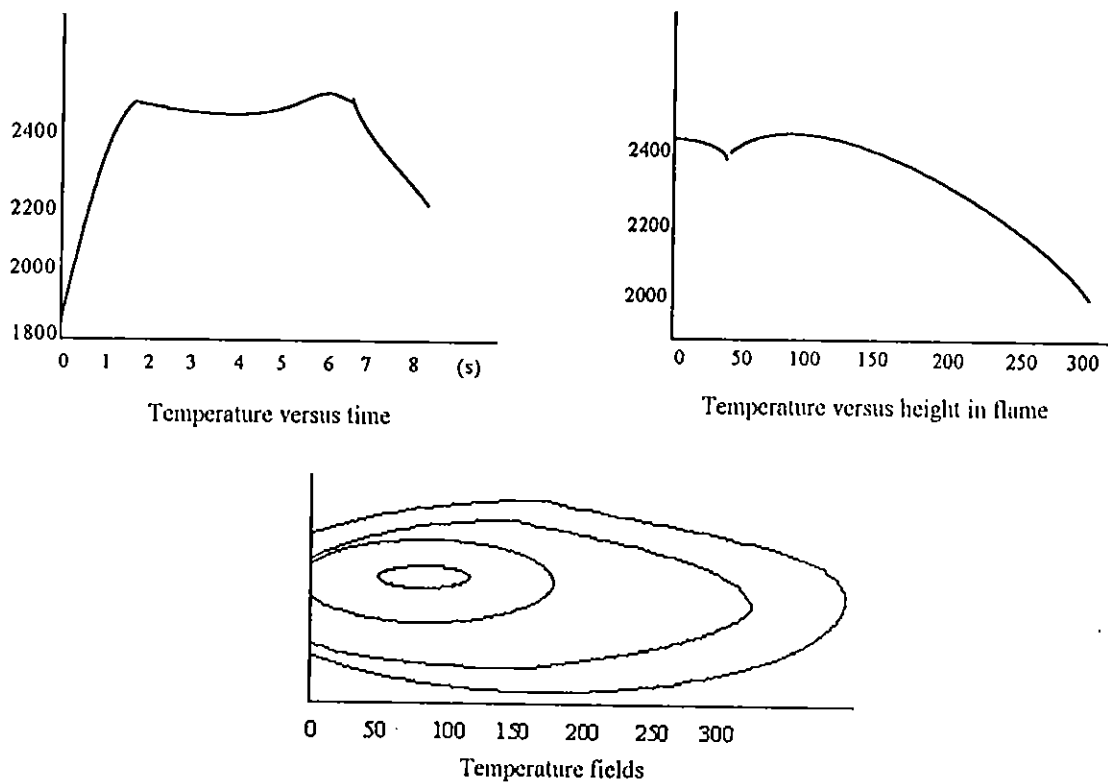


Fig 8.3 Results from motion picture pyrometer

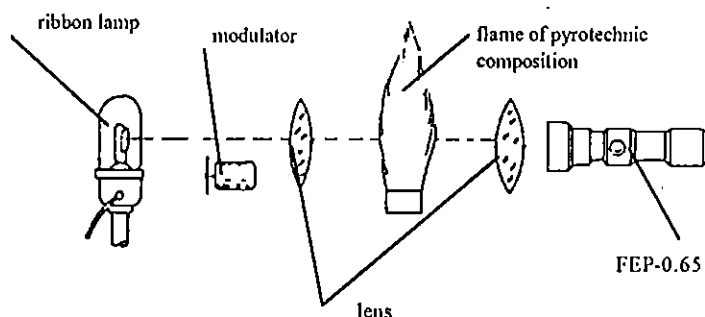
The transmission factor of the flame is calculated:

$$\tau_{\lambda} = \frac{i_{\lambda} i_{\text{fl}} - i_{\text{fl}}}{i_{\text{fl}}}$$

and the absorption factor of the flame:

$$\alpha_{\lambda} = 1 - \tau_{\lambda}$$

By Kirchhoff's law, the absorption factor is equal to the emissivity of the flame E_{λ} .



8.4 Measurement of emissivity of flame

Colour pyrometer (red-blue ratio).

This is a recording lux meter which measures simultaneously the radiation intensity in the red and blue regions of the spectrum. The most common design (Fig 8.5) is a block consisting of two photoelements in front of which is installed a rotating disc with two rows of holes. On one row of holes are fixed red and blue filters. (red $0.685 \mu\text{m}$, blue $0.456 \mu\text{m}$). The photoelements are installed such that the rays fall simultaneously on both. The photoelement without the light filter allows a correction to be introduced for variation in light flux during the movement of the filters.

The colour temperature may also be determined from the spectrum of the solid constituents using that portion with no superimposed lines. Descriptions of methods for measuring flame temperature are given in the books of Kadyshevich ¹⁰¹, Kirillin and Scheyndlin ¹⁰², and Dean ¹⁰⁵, and in articles by Bokhil ¹⁰³, and Sobolev ¹⁰⁴.

The optical pyrometer determines the temperature of the incandescent solid or liquid residue of combustion considerably more accurately than the temperature of the flame.

Wartenberg ^{7 page 8} determines the temperature of a spraying jet of ferroaluminium thermite by the optical method and found it to be equal to $2400 \pm 50^\circ\text{C}$.

Eggert, Eder, and Jinobek ^{7 page 87} have measured the intensity of the radiation of magnesium flames in various parts of the spectrum and have calculated the "colour temperature" of the flame: for combustion of magnesium in oxygen it is $\sim 3700^\circ\text{C}$; in air $\sim 3400^\circ\text{C}$. The colour temperature of the flame in a photoflash mixture $\text{Th}(\text{NO}_3)_2 + \text{Mg}$ is $\sim 3100^\circ\text{C}$.

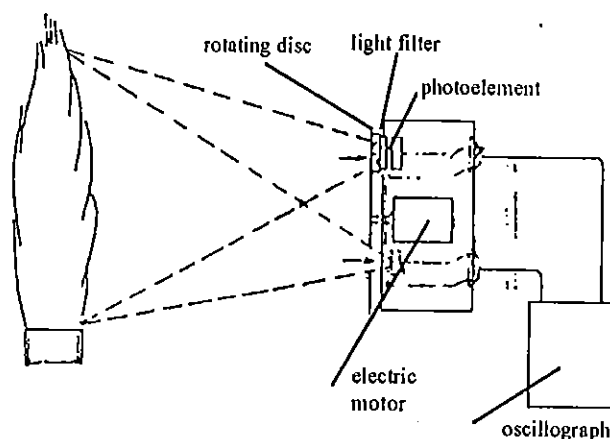


Fig 8.5 Colour pyrometer

The combustion temperature of aluminium in oxygen was measured by Cuelleron and Scartazzini as $\sim 3000\text{--}3200^\circ\text{C}$ using a luminance pyrometer.

From this, it follows that the combustion of magnesium and aluminium powders can give a temperature if the order of $3000\text{--}3500^\circ\text{C}$. The great expenditure of heat on the vaporisation and partial decomposition of the oxides of these metals prevents higher temperatures being attained.

The highest temperature in the combustion of metallic powders is obtained with zirconium in oxygen. The temperature, estimated from thermochemical calculations ¹⁰⁶ is 4930K . The temperature limit is set by the boiling point at 1 atm of the oxide ZrO_2 (see Table 3.3).

Consequently, the attainment of very high temperatures is limited not only by the high heat content of the fuel, but by the maximum possible boiling point and chemical stability of the combustion products (oxides of metals).

A gaseous mixture $\text{H}_2 + \text{F}_2$ has an even higher combustion temperature (5400°C)^{223 page 139}.

Harrison ¹⁰⁸ has estimated that the combustion of titanium in oxygen is within the limits $2950\text{--}3500^\circ\text{C}$.

The variation of the combustion temperature of elements in oxygen with the atomic number is shown in Fig 8.6.

Using an optical luminance pyrometer, Arditti ^{7 page 88} obtained temperatures of $1400\text{--}1500^\circ\text{C}$ for the combustion temperature of match compositions containing about 40% potassium chlorate.

In conclusion, we remark again that the temperature in a flame varies from zone to zone, and when we speak of the temperature of a flame, we usually understand the temperature of the hottest zone.

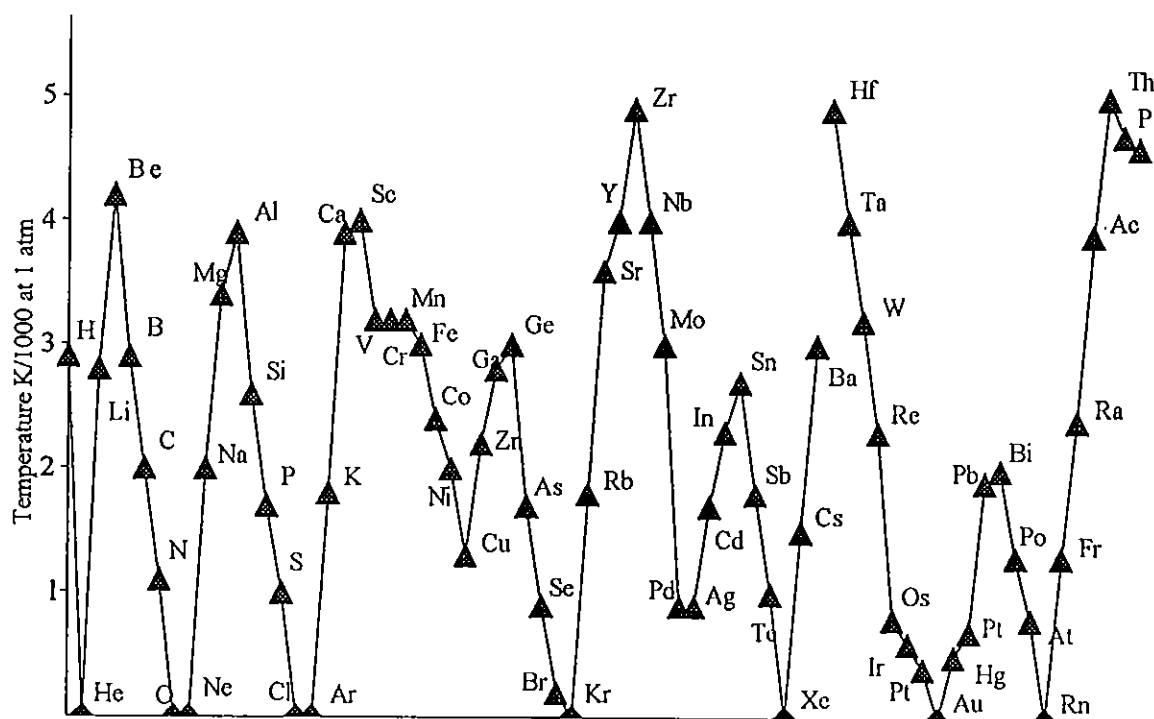


Fig 8.6 Combustion temperatures of elements in oxygen ²⁴³

The combustion temperature of certain slow burning smoke compositions which lies in the region 360-600°C may be measured using pressurised mercury in quartz thermometers. A low combustion rate is necessary to allow the bulb of the mercury thermometer to heat up adequately and provide a temperature close to actual.

A chromel-alumel thermocouple may serve to measure temperatures up to 1300°C. For higher temperatures, up to 1600°C (?), a thermocouple may be used which has one wire of platinum, and one of a platinum alloy containing 10-15% rhodium (platinum melts at 1771°C).

W-Ir and W-Re thermocouples may be used for temperatures up to 2100°C and 2700°C respectively, but they are of little use in pyrotechnics because they must be used in a reducing or inert atmosphere.

An Ir-Rh/Ir thermocouple (40% Ir) is graduated and used up to 2100°C with an accuracy of 10°. It may be used in air for short periods.

When using a thermocouple to measure temperatures, special attention must be paid to its thermal lag, and attempts made to reduce it. Results close to reality can be obtained only if the wire of the thermocouple is unalloyed metal with a diameter not exceeding 0.05-0.1 mm or is a ribbon of the same thickness. The inertia of the recording instrument - a millivoltmeter - must also be as low as possible.

The following results obtained for a red signal smoke composition (containing rhodamine) show the effect of the diameter of the (unalloyed) wires of the thermocouple:

diameter of wires	(mm)	0.5	0.2	0.1
maximum reaction temperature	(°C)	338	697	837

Obviously the reaction temperature in this case is somewhat more than 837°C, and a further reduction in the diameter of the wire may improve the measured result.

The temperature of combustion of two different smoke compositions was measured using a iron-constantan (an alloy of nickel and copper) thermocouple with a wire of diameter 0.1 mm, and also calculated. The results were:

	Temperature °C	
	measured	calculated
mixture No 1	1080	1262
mixture No 2	1000	1070

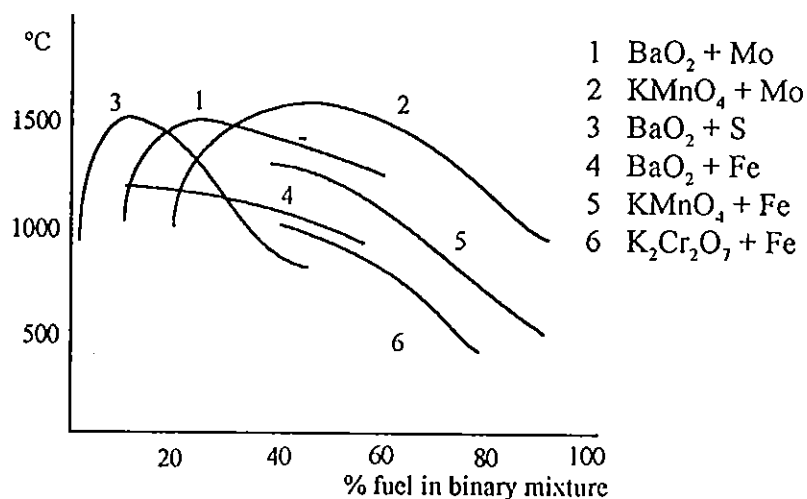


Fig 8.7 Maximum temperature of combustion

Hill and Sutton used thermocouples to investigate the variation of combustion temperature of binary mixtures as the ratio between them was varied. The results are shown in Fig 8.7.

Section 3. Relation between type of composition and its maximum combustion temperature.

Published experimental evidence indicates that there is a definite relationship between the type of composition and the maximum temperature in the combustion zone (Table 8.3).

Composition	Maximum flame temperature (°C)
Photoilluminating	2500-3500
Illuminating and tracer	2000-2500
Incendiary (containing oxidiser)	2000-3500
Solid rocket fuel	2000-2900
Night signal flare	1200-2000
Smoke compositions	400-1200

Table 8.3 Type of composition and maximum temperature

Chapter IX

Sensitivity and Sensitiveness of Pyrotechnic Compositions[†]

The minimum quantity of energy needed for initiation of a combustion reaction (or explosion) in a pyrotechnic composition may be called the "initiator stimulus". The lower this quantity of energy, the more sensitive the pyrotechnic composition is to external effects. We may initiate a fast reaction in a pyrotechnic composition by using various forms of energy: thermal, mechanical, electrical, radiant, etc., but the actual mechanism of the process may be different in each case. The normal mode of reaction of a pyrotechnic is initiated by a thermal initiator stimulus (flame, quick match or priming composition); only with photoflash and certain incendiary compositions do we use an explosive charge (i.e., a combined mechanical and thermal impulse) as the initiator stimulus and deliberately cause an explosion in the pyrotechnic composition.

The sensitiveness and sensitivity of pyrotechnic compositions must be established to ensure:

1. correct methods of manufacturing and storage to avoid ignitions (i.e., sufficiently low sensitiveness).
2. correct methods of ignition to provide the desired special effect (i.e., an adequate sensitivity).

Sensitiveness tests for pyrotechnics include:

1. self-ignition temperature (spontaneous combustion).
2. ignition by flame
3. shock
4. friction

Tests performed more rarely include:

1. ignition from special priming compositions (n.b., a sensitivity test).
2. bullet attack (ordinary ball incendiary bullets).

Every pyrotechnist must understand the likely sensitiveness/sensitivity of compositions that he is developing, and be guided in his choice of ingredients. In many cases the characteristics can be predicted before the tests are carried out.

Section 1. Determination of the thermal sensitiveness

The determination of the thermal sensitiveness of pyrotechnic compositions is essentially the determination of their ignition temperature, and their reaction to a flame.

† The US translation uses "sensitivity" throughout. In the rather more precise English usage, "sensitivity" refers to the readiness with which the composition reacts to the design stimulus; this is different from "sensitiveness" which reflects the ease with which the composition can be ignited by an accidentally applied stimulus. Both characteristics are important: sensitivity is a design parameter, sensitiveness is a safety characteristic. Here, I have used whichever word seems more appropriate. There are many ambiguities in the translation, and some freedom of interpretation has been assumed.

Determination of self-ignition temperature.

A pyrotechnic composition may undergo a slow decomposition reaction at a temperature below its ignition temperature. The lowest temperature to which a composition must be heated to attain self-combustion, accompanied by a clearly perceptible light, sound or smoke effect, is termed the ignition temperature.

According to modern concepts, the essence of the phenomenon of self-ignition lies in the following. At a low temperature, the rate of the exothermic reaction in the composition is low, and all the heat liberated is readily transmitted to the surrounding medium. As the temperature rises, the rate of reaction, and the rate of heat production increase rapidly, and at a certain moment the rate of heat production begins to exceed the rate of heat dissipation; the temperature rises due to self-heating and the rate of heat production rises still further. The result is the ignition of the composition.

The ignition temperature of a composition is not entirely constant, but depends to a considerable extent on the conditions of heat input and heat transfer prevailing during the determination. In practice, the quantity of material and the experimental conditions (method and time of heating) are strictly controlled.

One of the various methods of determining the ignition temperature is as follows: Three glass test tubes are immersed to one third their length in molten Wood's alloy in a special iron bath; the central tube is furnished with a thermometer. The bath is heated to a temperature close to the anticipated ignition temperature of the composition, and 0.1 g of the composition is added to each of the two empty test tubes. The time to ignition is recorded, or if no event occurs within five minutes, the result is recorded as "failed to ignite". Several such experiments with fresh weighed samples of composition performed at various temperatures allow us to establish with an accuracy of up to 5°C the minimum temperature at which self-ignition does not occur during the 5 minute test. This temperature is accepted as the self-ignition temperature. If required, the results of the test may be supplemented by compiling a graph showing the dependence of the induction time (ignition delay time) upon the test temperature.

An electric furnace rather than a bath is used for compositions whose ignition temperature is above 400-450°C. In this case it is adequate to determine the ignition temperature to within 10°C.

Data obtained by the above method on binary mixtures are given in tables 9.1 and 9.2. In general the ignition temperatures of binary mixtures containing chlorates as oxidisers are considerably lower than those of mixtures containing perchlorates or nitrates. Exceptions to this rule are binary mixtures with powdered metals as fuels.

Ellern⁹ divides pyrotechnic fuels into three groups depending on the value of their flash point:

1. Flash point 200-350°C
2. Flash point 350-600°C
3. Flash point >700°C

In the first group he places Zr, Ti, red phosphorus, S, Th, and perhaps Nb, and Ta. In the second group he places Mg (520-540°C), Mn (492°C), the sulphides of antimony and arsenic, and possibly zinc and calcium silicide. Only aluminium, according to Ellern, belongs to the third group. We must therefore conclude that the lower the flash point of the fuel, the lower will be the ignition temperature of the pyrotechnic composition containing it.

Oxidant	Fuel				
	sulphur	lactose	charcoal	magnesium powder	aluminium powder
	Ignition temperature °C				
KClO ₃	220	195	335	540	785
KClO ₄	560	315	460	460	765
KNO ₃	440	390	415	565	>890

Table 9.1 Ignition temperature of stoichiometric binary mixtures

Fuel	Ignition temperature °C	Fuel	Ignition temperature °C
shallac	250	antimony	295
iditol	345	graphite	890
rosin	335		

Table 9.2 Ignition temperature of binary mixtures of potassium chlorate

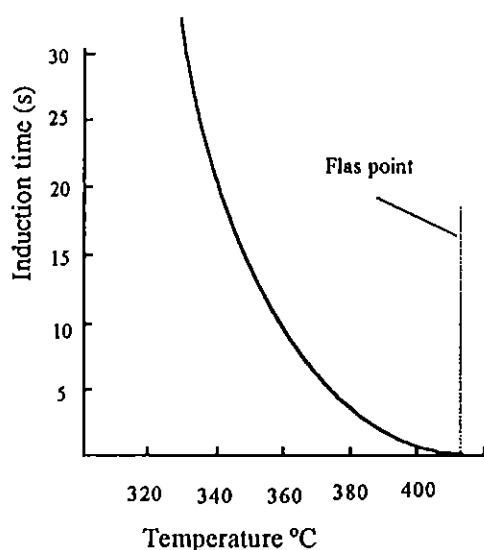


Fig 9.1 Determination of flash point

In 1943 Zhiron developed and standardised a new method (GOST 2040-43) for determining the ignition temperature of pyrotechnic compositions using an electric furnace, the temperature of which is measured with a thermocouple connected to a millivoltmeter. By this method the ignition temperature, the induction time and also the flash point of the composition are measured. The flash point is the temperature at which the induction time for ignition is zero. The value of the flash point is determined by extrapolation of the graph (Fig 9.1).

Zhiron's method, which is accepted at the present time as the standard, is more complex and labour consuming than earlier methods because of the number of parallel determinations. However, for

compositions that are difficult to ignite (incendiary compositions and others), where the purpose of the measurement is the selection of the appropriate igniter for the composition being tested, Zhiron's method has undoubted advantages over the older ones.

For many compositions, the flash point according to GOST 2040-43 is considerably higher than the corresponding ignition temperature determined by the older methods using a bath, and there is inadequate comparison of the two methods. Table 9.3.

Mixture					Ignition Temperature (in a bath) (°C)	Flash Point (GOST 2040-43) (°C)
KClO ₃	86	iditol	14		345	540
KNO ₃	86	iditol	14		460	570
KClO ₃	63	Mg	37		540	670
KNO ₃	63	Mg	37		565	670
NaNO ₃	65	Mg	35		-	640
Ba(NO ₃) ₂	68	Mg	32		510	660
NaNO ₃	66	Al (dust)	34		-	800
gunpowder					310	480
KNO ₃	75	Mg	10	iditol 15	445	555

Table 9.3 Ignition temperature and flash point of mixtures

Determination of Sensitivity to a Flame

The determination of the sensitivity of a pyrotechnic to a firing stimulus facilitates the selection of a reliable ignition composition for it. In addition, the test results indicate the degree of flammability of the composition and the risk of accidental ignition by a spark (i.e. its sensitiveness to ignition by spark).

A Bickford fuze, cut straight, is used as the test stimulus. The sensitivity of the composition is characterised by the greatest distance between the cut end and the surface of the composition at which ignition still occurs. Zhiron proposes that the sensitivity of a composition to a flame is characterised by:

1. the upper limit of sensitivity: i.e., the least distance between the cut end of the Bickford fuze and the surface of the composition at which 100% ignition occurs.
2. the lower limit of sensitivity: i.e., the least distance between the cut end of the Bickford fuze and the surface of the composition at which 100% failure to ignite occurs.

3. the guarantee factor, i.e., the tangent of the angle between a straight line connecting the experimentally determined points, when the abscissa is the distance between the Bickford fuze and the composition, and the ordinate is the percentage of ignition.

The relevant results for certain compositions are given in Table 9.4. The method suffers from a lack of reproducibility, and must be improved. The Bickford fuze might be replaced by an igniting cap.

Test methods based on the prolonged effect of a flame from a gas burner on the surface of the composition are less suitable for the practical determination of a composition's flammability.

Compositions that are not ignited by a Bickford fuze are subjected to other tests, not yet standard, which assess the ignitability of the composition from a series of igniting compositions of increasing effectiveness.

At this moment, unfortunately, no method has been developed for determining the sensitivity of compositions to the effect of radiant heating; see reference ¹¹⁹ page 27.

Composition	Upper limit mm	Lower limit mm	Guarantee factor
gunpowder, Grade No 1	20	150	0.7
Igniter composition	30	130	0.8
Red flare composition	0	20	3.0
Illuminating composition	0	30	1.0

Table 9.4 Sensitivity of compositions to ignition by flame
(after Vernidub and Sukhikh)

Section 2. Determination of the Sensitiveness/Sensitivity of compositions to mechanical effects.

During manufacture and filling pyrotechnic compositions are inevitably subjected to certain mechanical effects, no matter how carefully the processes are performed. The effects are most frequently frictional, but impact and shock cannot be excluded. The possibility of shock during transport of pyrotechnic products must also be considered.

When artillery projectiles are fired, considerable inertial forces originate at the moment of firing. These forces may cause movement of the pyrotechnic and other elements in the projectile and lead to considerable friction. Because of this, the study of the sensitiveness of compositions to mechanical stimuli is of great significance. Tests are usually made for sensitiveness to impact[†] and to friction.

[†] The usual English usage is "impact" rather than shock, and this is used throughout.

We should note that sometimes pyrotechnic compositions that are more sensitive to friction are also more sensitive to impact, but there is no complete correspondence between these characteristics, and there is no correspondence between the flash point of the compositions and their sensitiveness to impact and friction. This is due to the fact that different compositions have different capabilities for absorbing energy in a particular form. This capability depends upon the physical properties of the composition, and on the conditions under which the effect is produced. See reference ¹¹¹ page 266.

Determination of the sensitivity to impact.

The same apparatus is used as for the similar testing of explosives: i.e., drop hammers and roller appliances (sic) (Fig 9.2). Before use, drop hammers and roller appliances must undergo technical acceptance inspections in accordance with GOST 4545-48.

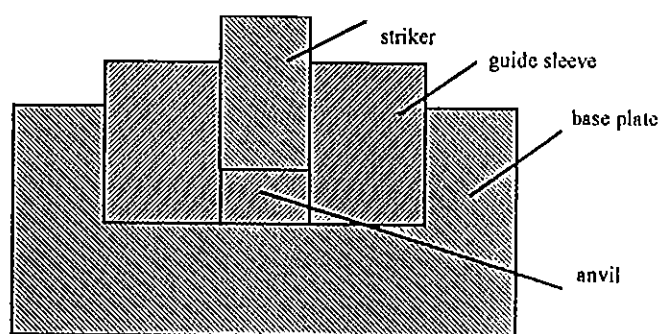


Fig 9.2 Roller appliance

For drop hammer testing of pyrotechnic compositions in accordance with GOST 2039-43, a 10 kg weight is used, or a 5 kg weight for more sensitive compositions. A weighed 0.05 g portion of composition is subjected to a blow over an area of 0.5 cm².

Two quantities are indicated in the GOST as characteristics for the sensitiveness to impact of the pyrotechnic composition.

1. lowest drop height of the weight that produces $95 \pm 5\%$ explosions in 25 parallel tests, called the upper sensitiveness limit, and,
2. the greatest drop height at which 100% misfires occur, called the lower sensitiveness limit.

Standard compositions are tested simultaneously under similar conditions, and the results of tests of experimental and standard compositions are compared with one another.

In especially critical tests, a great number of tests are performed with the weight dropping from various heights, and a graph is plotted to show the number of explosions that occurred as a percentage (from 0 to 100), as a function of the drop height (Fig 9.3).

If the sensitiveness curve is found to be symmetrical, the drop height of the weight at which 50% explosions result may be found, and then the sensitiveness to impact may be expressed by the

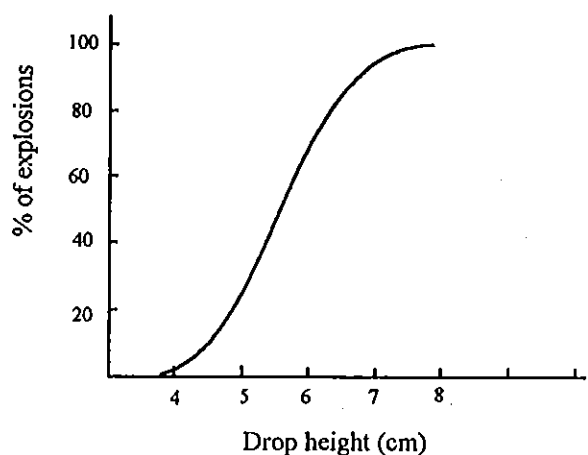


Fig 9.3 Percent explosions as a function of drop height

amount of work (in kg-f.m) per unit area of the composition through which the shock is propagated:

$$A = \frac{p \cdot h}{S} \cdot \frac{\text{kg-f.m}}{\text{cm}^2}$$

where p is the testing weight, kg,
 h is the drop height, metres,
 S is the roller cross-section, cm^2

Some data on the sensitiveness to impact obtained by this method for certain stoichiometric binary mixtures are given in Tables 9.5 and 9.6.

Many works have been published on possible mathematical expressions for the impact sensitiveness of various substances. Opinions have repeatedly been expressed that we must consider the height of rebound of the weight (h') and estimate the sensitiveness of the substance or mixture by the magnitude of the energy actually absorbed during the impact ($A = p(h-h')/S$).

Oxidiser	Fuel				
	sulphur	lactose	charcoal	Mg powder	Al dust
KClO ₃	1.1	1.8	3.2	1.5	4.5
KClO ₄	1.2	2.9	4.2	4.4	5.0
KNO ₃	3.6	5.0	5.0	1.6	5.0

Table 9.5 Impact (kg.m.cm^{-2}) for binary pyrotechnic mixtures

It has been indicated as well that the percentage of explosions for the same amount of work on impact depends to a great degree upon the final velocity of the weight and thus, for example, a higher percentage of explosions is obtained when a 2 kg weight is dropped from a height of 0.5 m, than when a 5 kg weight falls from a height of 0.2 m.

At various times, new designs have been proposed for drop hammers and test rigs for the determination of a composition's sensitiveness to impact. However, most of these have been complex designs which have not come into widespread use.

We should mention specially the work of Kholevo who developed a new design of rig which he called "Appliance No 2" (see Fig 9.4). The distinguishing feature of this apparatus, apparent in the figure, is the presence of an annular groove cut from the inside of the die. This feature allows the composition being tested to be squeezed from under the drift into the groove at the moment of impact.

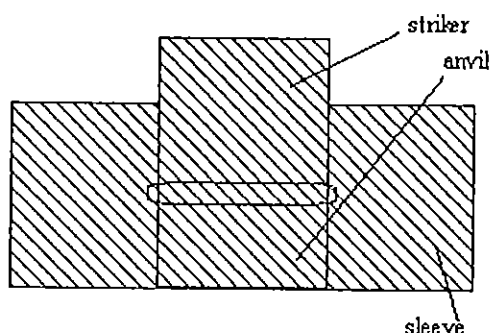
Fuel	Impact energy kg.m.cm ⁻²	Fuel	Impact energy kg.m.cm ⁻²
KCNS	0.5	naphthalene	1.3
As ₂ S ₂	0.6	K ₄ Fe(CN) ₆ .H ₂ O	2.2
paraffin	1.1	Sb ₂ S ₃	3.5
sulphur	1.1	graphite	10.0

Table 9.6 Impact sensitiveness of binary mixtures containing KClO₃

This new design introduces a combined test in which both impact and friction are present.

In recent years several works have appeared on the mechanism of the origin of explosions in explosives, and on methods of estimating the sensitiveness of an explosive to mechanical effects: for example Kholevo, Andreyev et al.^{111, 119}, and Bowden¹¹⁶. Some of these conclusions may be carried over to pyrotechnic compositions.

In particular, Andreyev^{119, page 92} concludes that "testing with the drop hammer variants (Instrument No 1 according to GOST 4545-48, and Instrument No 2), has the principal disadvantage that it characterises the probability of initiation of reaction, and not the propagation". He also says that



"in combination with flammability determinations, the results of Kozlov's pendulum instrument (see below) may characterise the danger of the explosive under test better than other methods." This assertion does not signify that testing for impact sensitiveness with the drop hammer is not necessary, but reflects the opinion that the drop hammer does not adequately model the conditions that arise during practical work with explosives.

Fig 9.4 Appliance No 2

Determination of Sensitiveness to Friction

Some indication of the friction sensitiveness of a composition may be gained by crushing it in an unglazed porcelain mortar. The mortar is usually 10 cm in diameter and 6 cm height; a sample of composition no greater than 0.02-0.03 g is placed in it on the tip of a spatula and ground with an unglazed porcelain pestle. The operator must wear protective goggles (made of organic glass). The test may be performed simply and quickly, but of course it is subjective - it depends upon the method of grinding and on the strength of the experimenter.

It is obviously possible in principle to develop an instrument capable of providing a defined rotary and vibratory motion to the pestle in the mortar. In 1938 Dobrysh developed an instrument for

determining the friction sensitiveness of explosives and pyrotechnic compositions. The composition is ground between two parallel steel surfaces, the lower of which (the die) is fixed, while the upper (the ram) rotates at a rate of 150 rpm. A pressure of up to $2,000 \text{ kg cm}^{-2}$ may be applied to the ram. A 0.02 g sample of composition is used to which 0.002 g fine quartz sand is added to increase the friction. The duration of the normal test is 10 seconds. The friction sensitiveness is estimated quantitatively by the minimum pressure required to obtain ignition of the specimen during crushing. Six tests are performed for each load, and parallel determinations with samples of known sensitiveness are carried out.

However, the method needs improvement; after repeated experiments it has been established that there are many compositions which do not explode, even under $2,000 \text{ kg cm}^{-2}$ pressure. The friction sensitiveness of certain stoichiometric binary mixtures determined with Dobrysh's instrument are given in Table 9.7.

Fuel	Friction sensitiveness kg cm^{-3}	Fuel	Friction sensitiveness kg cm^{-3}
$\text{K}_3\text{Fe}(\text{CN})_6$	8	sulphur	65
KCNS	22	$\text{K}_4\text{Fe}(\text{CN})_6 \cdot \text{H}_2\text{O}$	85
lactose	60	antimony sulphide	90

Table 9.7 Friction sensitiveness of binary mixtures containing potassium chlorate.

Bowden and Garton^{111, page 322} have developed a machine for the determination of the friction sensitiveness of explosives. In this instrument, the specimen of explosive is compressed between two horizontal parallel steel surfaces (a roller and a rod). Under the effect of the lateral impact, the steel rod shifts in a horizontal direction, and in this shift the explosive is subjected to heavy friction.

Kozlov has improved this instrument. In the Bowden - Kozlov instrument (Fig 9.5), the sample of explosive is compressed between two drifts of 10 mm diameter. The impact of the pendulum is transmitted to the upper moving drift which moves horizontally between the fixed support above it, and the lower drift fastened in a sleeve. The sensitiveness of the explosive is determined by the change in the probability of explosion as the compression pressure varies. The instrument is capable of providing up to $8,000 - 10,000 \text{ kg cm}^{-3}$. TNT gives explosions in this instrument at pressures above about $5,000 \text{ kg cm}^{-3}$. Since some skewing of the roller occurs during testing, we are not dealing purely with friction, but with a combination of friction and a sliding impact.

Section 3. Factors influencing the sensitiveness of compositions to stimuli.

The quantity of energy that must be imparted to a system to produce a fast chemical reaction in it is determined by the internal resistance of the system, and by the possibility of its developing its

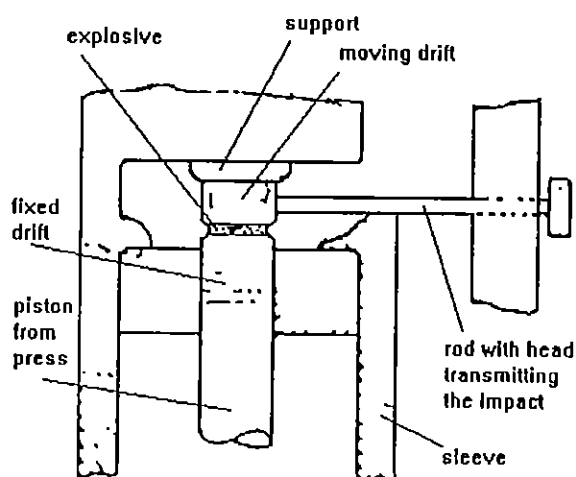


Fig 9.5 Part of the Bowden - Kozlov instrument for determining friction sensitiveness of explosives

own energy. The influence of the energy factor is shown in a reaction that has begun in a small volume due to an external stimulus, which develops due to the energy liberated as the reaction progresses. The stronger is this tendency to spontaneous development of the reaction, the greater will be the probability of the propagation of the reaction, even with comparatively weak initiatory stimulus.

Semenov wrote "In order to make a chemical reaction occur, it is necessary to break existing chemical bonds and form new ones." The internal resistance of the system is determined by that quantity of energy that is needed for breaking the bonds; this quantity is customarily called the activation energy of the process.

The quantity of energy liberated by the time the process has been completed is determined by the difference between the quantities of energy liberated in the formation of new bonds and the energy needed to break the original bonds.

By ignoring for the time being the influence of external physical factors, we may say that the sensitiveness of a chemical system to initiatory stimuli is determined primarily by the magnitude of the activation energy and the magnitude of the heat of reaction. Both these quantities have the dimensions - kJ/kg-molecule (or kJ/mole).

But, in many cases, this unquestionably correct general principle does not allow us to predict the sensitivity or sensitiveness of individual substances (explosives) in practice. The basic difficulties in this case are:

1. the real activation energy of the process has very little in common with the activation energy of thermal decompositions.
2. the effect of various physical factors associated with different rates of absorption of energy arriving from outside.

The situation becomes even more difficult when we are considering a system such as a pyrotechnic composition, which is a multi-component and, more particularly, a heterogeneous system.

To determine properly the likelihood of initiating a reaction in a pyrotechnic compound, we must first of all consider the ease with which the individual "elementary" processes are accomplished: the decomposition process of the oxidiser and then the oxidation process of the fuel.

Again, the activation energy and the reaction heat of the process must be determined by the characteristics of these simpler, but in essence still highly complex, processes. But, in practice, we are obliged in the majority of cases to limit ourselves to a consideration of the reaction heat of the process, and instead of the activation energy we must consider the values of the decomposition temperature of the oxidiser, or the flash point or decomposition temperature of the fuel. The appropriate numerical material for various components of the composition may be found in the tables in Chapters II and III.

Other things being equal (primarily for the same fuel), the less energy that is required to decompose the oxidiser, and the lower its decomposition temperature may be, the more sensitive the composition will be to initiatory stimuli (see Tables 9.1 and 9.5).

From a comparison of the properties of compositions with three different oxidisers - potassium chlorate, potassium perchlorate, and potassium nitrate - we see that the chlorate compositions are most sensitive, since the decomposition process of the potassium chlorate occurs at a comparatively low temperature of $\sim 350^{\circ}\text{C}$ and, which is most important, unlike the decomposition processes of the majority of other oxidisers, is accompanied by the liberation of a perceptible quantity of heat.

Mixtures containing potassium perchlorate as an oxidiser are somewhat less sensitive and mixtures with a potassium nitrate oxidiser have a considerably lower sensitiveness (see Table 2.1 for the heats of decomposition). Such metal oxides as ferric oxide, ferroso-ferric oxide, etc., decompose with the greatest difficulty and at the highest temperatures.

Obviously, compositions containing these latter materials will have the lowest sensitiveness to all forms of initiatory stimuli. We will note, in particular, that iron-aluminium thermite has very little sensitiveness to impact or friction, has an ignition point of about 1300°C , and does not ignite even when heated with a gas burner flame, not to mention the tongue of flame from a Bickford fuze.

The variation of the sensitivity of compositions with the same oxidiser but different fuels is considerably more complex. Compositions with only low-energy fuels, with as an oxidiser that requires a great quantity of heat for its decomposition, have low sensitiveness. Such compositions include, for example, binary mixtures of nitrates and sulphur. Compositions containing only fuels that are difficult to oxidise, with a very high ignition point, such as graphite or iron, for example, have low sensitiveness.

The individual physical properties of the fuel are of very great importance in considering the sensitiveness of compositions; these properties include melting and boiling points, thermal conductivity, plasticity (ductility), hardness, etc.

Among the binary mixtures, we should note the extremely high sensitiveness of mixtures of potassium chlorate and phosphorus; they explode even when rubbed slightly with a rubber stopper or when subjected to the slightest jar.

Mixtures of chlorates with sulphur, selenium, metallic arsenic, and the sulphides of phosphorus, arsenic, and antimony, are highly sensitive to impact and friction. Mixtures of chlorates with thiocyanates, ferricyanides, and ferrocyanides are particularly sensitive to impact and friction as may be seen from Table 9.6 and 9.7. Mixtures of chlorates with various organic fuels, such as hydrocarbons, resins, etc., have a considerable sensitiveness to friction.

Binary mixtures of chlorates with metal powders (magnesium or aluminium) are sensitive to friction and are very dangerous to handle. Because of the great danger of explosion, in certain countries it is prohibited to make a mixture of $\text{KClO}_3 + \text{Al}$ ⁸.

Among the binary mixtures containing the nitrates, significant sensitiveness to impact and friction is found only with powders of highly active metals such as magnesium, aluminium, zirconium, and others, if we do not consider the very sensitive mixtures with phosphorus and sesquisulphide.

The sensitiveness of mixtures of nitrates with organic fuels is not great in most cases.

The self-ignition point of aluminium is considerably higher than that of magnesium and therefore the self-ignition temperatures of aluminium compositions are considerably higher than those of magnesium compositions. Because of this, we must use igniting compositions having higher combustion temperatures for ignition of compositions containing aluminium.

As a rule, it is easier to ignite compositions having a lower flash point with a tongue of flame or a Bickford fuze.

Gunpowder is ignited without difficulty by a tongue of flame, as are binary mixtures of potassium nitrate with carbon or iditol, and the majority of the chlorate compositions.

As a rule, compositions are considerably less susceptible to the tongue of flame when pressed than they are in a powder form.

The sensitiveness of compositions to a tongue of flame increases as the particle size of the components decreases, and therefore the most dangerous compositions from the fire hazard standpoint are those from components that have been ground to a "dust".

On the basis of available experimental material, we may conclude that those compositions in which the components are in stoichiometric proportions, or have a small deficiency of fuel are the most sensitive; compositions with a large excess of fuel, as a rule, are less sensitive to initiatory stimuli.

We should note the degree of pulverisation (particle size) of the components among the factors of a physical nature. In considering this problem from the theoretical standpoint, we should note that finer pulverisation of the components entering into the composition must facilitate a closer contact between them, and consequently also facilitate the initiation of the combustion reaction.

Actually, as was already indicated, the sensitivity of formulations to a tongue of flame increases when the particle size of the components of the composition is reduced; the particle size has a lesser influence on the spontaneous ignition temperature. Note, however, that in those cases when the particle size of the fuel is very small (on the order of a micrometre or less), a very great increase in the surface of the substance occurs, which leads to a considerable reduction of the spontaneous ignition temperature of the fuel. Thus, for example, sublimed magnesium, precipitated on the walls of a test tube in the form of the finest crystals, ignites spontaneously upon contact with the air, even at room temperature. The effect of component pulverisation on the sensitiveness of compositions to friction has been studied but little; it is known that in individual cases the presence of large grains of a solid oxidiser may somewhat increase the sensitiveness of the composition to friction.

An increase in the density of a composition lowers its sensitiveness to initiatory stimuli (except for the spontaneous ignition temperature), since when the density is higher, the same quantity of energy is expended in a larger mass of the composition, and the efficiency of the effect on individual particles of the composition is lower.

When the initial temperature increases, the sensitiveness of pyrotechnic compositions to mechanical effects and to a tongue of flame increases, and therefore when drying pyrotechnical compositions the appropriate precautionary measures must be taken.

The introduction of various additives to pyrotechnic compositions has a great influence, in many cases, on their sensitivity to mechanical and thermal impulses.

The addition of phlegmatizers - soft plastic substances such as paraffin, vaseline, stearin, and various oils - to pyrotechnic compositions reduces their sensitivity to friction and to a tongue of flame. Sensitiveness to friction decreases in this case as a consequence of the distribution of the force of friction over a larger mass of the composition. Sensitiveness to a tongue of flame decreases as a consequence of the fact that the phlegmatizer covers the individual particles of the composition with a film and thus inhibits the penetration of heat to them; the phlegmatizer itself, in the majority of cases, is a substance of low activity that is difficult to ignite.

The introduction of organic phlegmatizers has only an insignificant effect on sensitiveness to impact, and sometimes when paraffin or a similar substance to it is added to a composition, the sensitiveness to impact increases, which, for example, is observed in a mixture of potassium chlorate and magnesium.

If inert substances not participating actively in the combustion process are introduced into the composition in large quantities, they are non-specific phlegmatizers, reducing the sensitivity of the composition to all forms of initiatory stimulus. Such materials include magnesium oxide, magnesium fluoride, barium fluoride, and others as well as carbonates, oxalates, etc., when there are no free metals in the composition.

Thus, for example, in a red flare composition containing potassium chlorate, strontium carbonate, and iditol, the strontium carbonate plays the part of a phlegmatizer; iditol cannot be called a

phlegmatiser in this case, although it is a soft plastic substance. In the composition given, iditol is a basic fuel and participates actively in the combustion process.

Admixture of sand, glass, and other solids considerably increases the sensitiveness of pyrotechnic compositions to mechanical effects and makes them very dangerous to handle. In some cases, an increase in sensitiveness of the composition to impact and friction also occurs when solid metal powders (such as ferro-silicon, for example) or solid crystals of certain oxidisers are added to them. Values of the Moh hardness of many substances may be found in the handbooks or determined experimentally. When a very hard substance is added to the composition, mechanical stresses (shocks, friction) are concentrated on these particles. This local concentration of energy leads to an increase in the sensitivity of the composition.

Information available in the literature concerning the sensitiveness of pyrotechnic compositions is very scanty, and the facts are scattered in supplements or appendices in individual articles in the periodical literature.

Among the communications devoted basically to the sensitiveness of pyrotechnic compositions, we must mention the articles by Blinov ¹¹⁴, Tomlinson and Audrieth ¹²², and Langhans ¹⁵⁹. Essential information is also available in Ellern's work on pyrotechnics ⁹, as he, remarking on the special danger of chlorate mixtures, also mentions the great sensitiveness of mixtures in which the oxidisers are the perchlorates of ammonia and the alkali metals, and certain oxygen compounds of lead, especially PbO_2 . He also writes that the danger of accidental initiation by static electricity is great in the presence of fine powders (units of a micrometre) of such metals as Zr, Mg, and Al.

Chapter X

The Combustion Mechanism of Pyrotechnic Compositions and Factors Affecting their Combustion Rate

Section 1. Combustion Mechanisms of Compositions.

The combustion process of pyrotechnic compositions may be divided into three individual stages: ignition, inflammation, and combustion.

The ignition of the composition is usually accomplished by means of a heat stimulus which is imparted only to a limited part of the surface of the pyrotechnic composition.

Inflammation of the composition is the term ordinarily used for the propagation of combustion across the entire surface of the composition.

Combustion proper is the propagation of the process into the interior of the composition.

The inflammation rate of pyrotechnic compositions is many times greater than the rate of combustion; a similar relationship is also observed for powders (both black powders and smokeless powders).

For a composition, the inflammation rate depends upon the following factors:

1. The degree of pulverisation of the components: the finer the components are pulverised, the greater the total surface area of the composition will be, and the easier and more rapidly inflammation will proceed.
2. The density of the composition: the higher this density is, the less its total surface will be (the number of pores in the composition is reduced and its inflammation will proceed with greater difficulty and more slowly).
3. The initial temperature of the composition: the higher it is, the more easily and rapidly the process of inflammation will occur.
4. The external pressure: when the external pressure rises, the rate of inflammation increases rapidly; this may be explained by the fact that the compressed gases transfer more heat in a unit of time to the surface of the condensed system that they are igniting, than the same gases would at atmospheric pressure.
5. The composition of the gaseous phase and, in particular, oxygen content in it, since the oxygen actively participates in the processes of the inflammation of many pyrotechnic compositions (see reference ¹¹¹ page 154).

The highest inflammation rate is observed for loosely packed photomixtures and for gunpowder; the inflammation rate of gunpowder trains in an open space amounts to about 3.5 m/sec.

We should note that the inflammation processes of both pyrotechnic compositions, and of powders and explosives have not yet been adequately studied, and one of our tasks in the

immediate future must be the accumulation of experimental material and its use as a basis for a complete theory of inflammation.

The combustion process of pyrotechnic compositions is extraordinarily complex. Comparatively little attention has been devoted to a study of it so far. On the other hand, in the Soviet literature in the past 10 or 15 years, a great quantity of work has been published on the combustion mechanism of explosives and powders.

Of course, the combustion process of pyrotechnic compositions has a great number of specific features which differ from those of explosives or powders, but there are many quantitative similarities which have been demonstrated experimentally. Therefore, in further expositions in certain cases we will give analogies between the quantitative relationships of the combustion of pyrotechnic compositions on the one hand, and the quantitative relationships of the combustion of explosives and powders on the other.

The combustion process of pyrotechnic compositions is a result of many exothermic and endothermic chemical processes, and the physical process of heat transfer. If, making a rough division, we separate the process of combustion into two stages, we should indicate that it begins in a condensed (solid) phase and ends in a gaseous phase (in a flame).

The processes occurring in the condensed phase should be considered, as a whole, as endothermic or weakly exothermic; the degree of exothermicity of the reaction in the condensed phase depends both upon the recipe of the composition and upon the conditions of its combustion (external pressure). The processes occurring in the gaseous phase (the flame) tend to be exothermic. In many cases the processes occurring in the condensed phase can be affected only by the heat entering it from the flame.

This principle is confirmed by the observation that all pyrotechnic compositions investigated up to this time become incapable of combustion at sufficiently low pressures (say, less than 1 mm of mercury).

The ratio of the quantity of heat liberated in the condensed and in the gaseous phases must be considered individually for each type of composition. As yet no quantitative data on this problem are available.

According to Andreyev, in the combustion of certain explosives at low pressures, the principal exothermic reaction is in the condensed phase, and at high pressures in the flame. Obviously, this principle is applicable also to the combustion process of pyrotechnic compositions. An indispensable condition for the accomplishment of normal uniform combustion is an equality of the heat influx and the heat output in all the reaction zones. If this equality is disrupted, combustion either dies down or becomes non-uniform - a pulsation arises (see the works of Andreyev¹¹⁰ for more information on pulsating combustion)

But the division of the process into only two stages is a first approximation, and a very rough approximation at that. In making a more detailed analysis of the combustion mechanism of pyrotechnic compositions, we should note that the essential difference between explosives, on the

one hand, and pyrotechnic compositions on the other hand, lies in the fact that the pyrotechnic compositions are heterogeneous systems.

For a high-speed reaction to be achieved in a heterogeneous system, it is necessary to ensure close molecular contact between the reactants. This cannot occur in the solid state and reactions between solids therefore occur very slowly, as we know, even at very high temperatures; the fact that "low-gas" compositions can burn quite rapidly does not contradict this principle, since it is very probable that the basic oxidation reaction of the fuels for these compositions occurs in the liquid or in the gaseous phase, which is present at the temperature of combustion.

A high-speed reaction between two components in a pyrotechnic composition can begin only when at least one of them is in a liquid or a gaseous state.

If we differentiate the processes by the physical state of the reagents, two types of processes are possible in the condensed phase: liquid + solid; liquid + liquid.

The components of compositions frequently have melting points that differ sharply from each other, and also boiling points or thermal decomposition temperatures that are equally different. We may therefore understand why in many cases the reactions between components (or between the products of their decomposition) occur at the surface of discontinuity between the condensed and gaseous phases; in this case the following variations are possible: gas + solid; gas + liquid.

The likelihood of chemical reactions occurring will be determined to a great degree by the rate of gaseous (and liquid) diffusion, and also by the possibility of rapid removal of the products of combustion from the reaction zone.

Finally, in the zone of the highest temperature, all the substances reacting will be in a gaseous state, and here the reaction will occur in a gas + gas system, i.e., in a homogeneous gaseous system.

In many cases the oxygen of the air participates heavily in this last stage of combustion of a pyrotechnic composition. We should note that the temperature in the flame of many pyrotechnic compositions is considerably higher than the temperature in the flame of a powder or a nitro compound burning at atmospheric pressure.

All that has been said above about the combustion mechanism of pyrotechnic compositions can be illustrated clearly by a diagram very similar to the combustion diagram of powder, proposed by Zeldovich (Fig. 10.1).

An increase in the temperature in the condensed-phase reaction zone may occur either because of the heat transferred from the gaseous phase or from the boundary between the phases, and sometimes also because of the heat of the reaction occurring in the condensed phase itself.

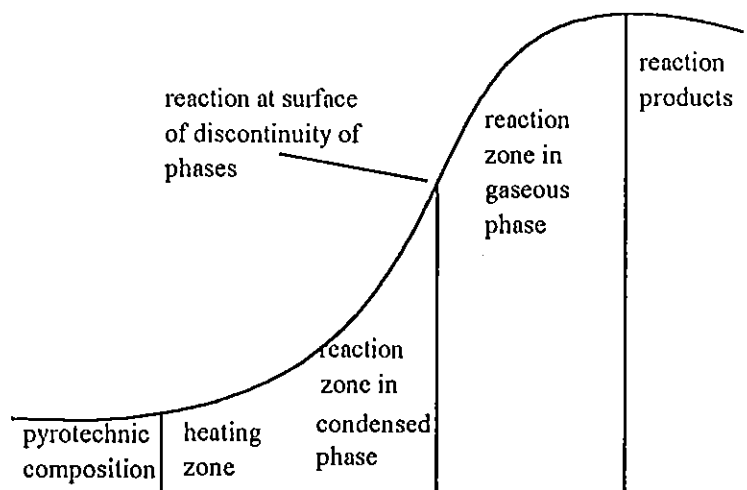


Fig 10.1 Combustion of a pyrotechnic composition

A study of the dependence of the rate of combustion upon the pressure of the surrounding medium may help indicate which processes, in the condensed phase or in the gaseous phase, dominate in the combustion of any specific pyrotechnic composition.

The more dependent the rate of combustion is upon pressure, the greater will be the "specific weight" of the reactions occurring in the gaseous phase or at the boundary between the gaseous and condensed phases.

However, the combustion scheme of pyrotechnic compositions described above is oversimplified and does not correspond entirely to reality.

At the present time it has been proven experimentally that in the combustion of pyrotechnic compositions at atmospheric pressure, just as in the combustion of low-volatility explosives^{111, page 171}, a dispersion of the particles of the unreacted components of the composition occurs, primarily the particles of the metal powders, magnesium or aluminium, and also drops of fused oxidiser (nitrate).

This discharge of unreacted particles into the gaseous phase is caused by uneven reaction in the layer of the condensed phase close to the surface and by the fact that the gaseous products formed in the condensed phase escape and carry solid (and liquid) particles of the components with them into the flame. Consequently, in many cases the gaseous phase is heterogeneous and the flame zone closest to the condensed phase should be called a smoke-gas flame zone. Those particles that move further into the flame react eventually in it.

In individual cases, consideration of the properties of the components of the composition help establish the combustion mechanism.

As an example we may consider the combustion mechanism of a composition of potassium chlorate and magnesium.

We will note the melting point of the oxidiser and the melting point and boiling point of the fuel. Potassium chlorate melts at 360°C with comparatively little decomposition¹. However, additives such as MnO₂, Co₂O₃, and others catalyse the decomposition of the potassium chlorate which will occur in the region 200-250°C. Magnesium melts at the higher temperature of 650°C, and boils at atmospheric pressure at 1100°C.

Working from these facts, the reaction process of these two substances may be represented in the following manner:

1. In the condensed phase:
 - a) $\text{KClO}_3 \text{ (liquid)} + \text{Mg (solid)} \longrightarrow$
 - b) $\text{KClO}_3 \text{ (liquid)} \longrightarrow \text{KCl} + \text{oxygen}$
2. At the boundary between the condensed and gaseous phases and in the smoke-gas flame zone:
 - a) $\text{Mg (solid)} + \text{oxygen} \longrightarrow$
 - b) $\text{Mg (liquid)} + \text{oxygen} \longrightarrow$
3. In the gaseous phase (in the flame):
 - a) $\text{Mg (vapour)} + \text{oxygen} \longrightarrow$
 - b) $\text{Mg (vapour)} + \text{oxygen of the air} \longrightarrow$

Section 2. Factors affecting the rate of combustion of pyrotechnic compositions.

Rates of combustion may be expressed in two ways: we may calculate the linear rate of combustion u in mm/sec, but we also may calculate the mass rate of combustion u_m expressed in g cm⁻² s⁻¹; u_m defines the quantity of the composition burning in 1 sec from unit area of burning surface. Knowing the linear rate of combustion and the density of the composition, we may calculate the mass rate of combustion from the formula:

$$u_m = 0.1 u.d$$

where d is the cubic density of the composition, in g cm⁻³.

As has already been indicated, the combustion process occurs uniformly only in an adequately compacted composition. However, to judge the degree of compaction of the composition, it is not only necessary to know its density d , but also to calculate the compaction coefficient K , by dividing the density obtained by the limiting density of the composition $d_{\max}$ calculated from the densities of the components.

$$K = \frac{d}{d_{\max}}; \quad d_{\max} = \frac{100}{\frac{a}{d_1} + \frac{b}{d_2} + \dots + \frac{n}{d_n}}$$

where $d_1, d_2, \dots, d_n$ represent the density of the components in the composition; and $a, b, \dots, n$ are the percentage proportions of these components in the composition.

For the majority of pressed compositions, the compaction coefficient ranges from 0.7 to 0.9¹. The porosity of the composition is characterised by the value of $(1 - K)$, and consequently, the porosity of pressed compositions varies from 0.3 to 0.1. For powdered compositions, the so called "loose density" amounts to 40-50% of $d_{\max}$.

For pyrotechnic compositions of various formulations the linear rate of combustion varies quite significantly from tenths of a mm/sec (for smoke compositions) to 20-30 mm/sec (for quick-burning illuminating compositions).

Upon what factors does the rate of combustion of these compositions depend? The rate of combustion, which is a most complex physico-chemical process, is determined by the rate of the individual (elementary) chemical reactions and the heat-transfer conditions from one reaction zone to another. The conditions of heat transfer, at constant external pressure and initial temperature, depend upon the density of the composition and the particle size of its components, and also to a considerable degree on the temperature differences between the various reaction zones.

It has been established experimentally that, as a rule, compositions having the highest flame temperature are those that burn fastest. However, the many departures and exceptions from this rule show that a high temperature in the flame is only one of the factors determining the rate of combustion of the composition.

The rate of combustion depends strongly upon the absence or presence of low-melting or easily volatilised components in the composition. When low-melting or volatile substances are present in the compositions, the heat that under other conditions would cause a sharp rise of the temperature in the reaction zone and consequently a sharp acceleration of many chemical processes, is expended in converting these substances from one physical state to another.

It is precisely this latter circumstance that, in our opinion, explains why such low-melting organic substances as resins, paraffin, stearin, and others, when added to binary mixtures (oxidiser + metal) sharply reduce their rates of combustion. The rates of the individual (elementary) chemical reactions have an even more decisive effect on the rate of the combustion process.

Highly exothermic (flame) reactions will be the leading reactions in the combustion process. However, the rate of a complex, multistage process will be determined, as a whole, by that minimum rate with which the stage of the process that is most difficult and proceeds most slowly occurs. Endothermic chemical reactions occur most slowly and with the greatest difficulty.

Therefore, in many cases the rate of combustion of compositions is determined precisely by the rate of the process of decomposition of the oxidiser.

An objective index characterising the ease with which an oxidiser decomposes is the partial pressure of oxygen above an oxidiser at various temperatures. The oxides of metals, which are used in thermite-type incendiary compositions, appear to have the simplest decomposition mechanisms.

As is well known, the rate constant, K , of a chemical reaction increases exceedingly rapidly when the temperature rises according to the law

$$K = B \cdot e^{-\frac{E}{RT}}$$

where B is a proportionality factor (pre-exponential multiplier)

E is the activation energy, kJ/mole

R is the gas constant

However, even a knowledge of the maximum temperature and activation energy of a process does not give us a complete opportunity for preliminary calculation of the rate, since "all combustion phenomena are related to the rate of the chemical reactions taking place under conditions other than isothermal" ¹³⁷.

Without a doubt, a knowledge of all these intermediate stages through which the combustion process passes is very important. However, to establish the compositions of the intermediate products of a reaction, it is necessary in most cases to perform very complex experimental investigations; at the present time, these data are unfortunately not available for most combustion reactions of pyrotechnic compositions.

Turning to a consideration of the factual material accumulated up to the present time, we should note that the rate of combustion of pyrotechnic compositions is determined both by the recipe of the composition (the chemical factor), and by the conditions under which the compositions burn (physical factors).

From a consideration of data on the rate of combustion of densely compacted compositions (compacting coefficient $K \geq 0.85$), under conditions of atmospheric pressure and standard temperatures (ca. 20°C), it follows that some of the fastest burning compositions are the binary mixtures of alkali (or alkaline earth) nitrates with magnesium, containing 50-60% magnesium. Also, compositions containing zirconium and titanium burn very rapidly.

Compositions containing aluminium burn considerably more slowly than compositions containing magnesium with the same particle size. Compositions containing beryllium, boron, or silicon as the main fuel burn slowly. The higher the ignition point of a fuel, the lower is the rate of combustion of the composition with that fuel, other things being equal. It is possible that there is also a mutual connection between the rate of combustion of the composition and the Pilling and Bedworth number for the metal contained in the compositions (and also for B and Si). For fast-burning metals such as Mg and Zr these numbers are, respectively, 0.81 and 1.45; for Be, Si, and B these numbers are greater and are equal, respectively, to 1.75, 2.04, and 4.08 (see also Table 3.4).

The rate of combustion of binary mixtures of an oxidiser and a metal increases rapidly as the content of the metallic fuel increases in the composition (up to a certain limit, of course); for magnesium this limit is 60-70%; such an increase in the rate of combustion is connected to a certain degree with the increase in the thermal conductivity of the composition as its metal content increases.

With the same metal content, binary mixtures of the nitrates of alkali metals and magnesium burn more slowly than mixtures of the chlorates of alkali metals and magnesium. It is possible that the reason for this is the exothermic reaction of the fused nitrate with the magnesium in the condensed phase; for more details on the oxidation of magnesium powder at increased temperatures, see the works of Makolkin and Vernidub ⁶¹.

Composition	Rate of combustion at atmospheric pressure and $K \geq 0.85$ (mm s ⁻¹)
illuminating	1 - 10
tracer	2 - 40
signal flares	1 - 3
thermite incendiaries	1 - 3
smoke	0.5 - 2

Table 10.1 Typical burning rates for pyrotechnic compositions

Among the mixtures that do not contain metallic fuels, only chlorate mixtures and gunpowder burn rapidly. In recent times the works of Belyayev have appeared in which the effect of sulphur on the rate of combustion of gunpowder was considered ^{127,128}, and also a work by Benture and others ¹⁴⁰ concerning the effect of various organic additives on the rate of combustion of powder.

Mixtures of potassium nitrate with carbon or iditol burn at moderate rates.

Data on the rate of combustion of various forms of multi-component pyrotechnic compositions are given in Table 10.1.

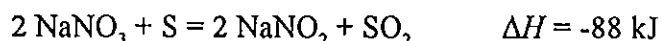
Fuel	Oxidiser			
	KClO ₃	KNO ₃	NaNO ₃	Ba(NO ₃) ₂
sulphur	2	does not burn	does not burn	-
charcoal	6	2	1	0.3
sugar	2.5	1	0.5	0.1
shellac	1	1	1	0.8
drying oil	0.5	-	-	-

Table 10.2 Linear burning rate of stoichiometric binary mixtures

Nitrate compositions that do not contain metallic fuels burn slowly and usually at low intensity. Comparative data on rates of combustion of certain chlorate and nitrate binary mixtures which do not contain metallic fuels are given in Table 10.2. The value of K is 0.5 to 0.6, and the compositions were burned in cardboard tubes of 16 mm diameter. As is apparent from the Table, mixtures of chlorates with sulphur burn quite vigorously; mixtures of sodium nitrate or potassium nitrate with sulphur at standard temperatures are difficult to ignite and their combustion has little stability. This is apparently explained by the fact that the quantity of heat liberated in the combustion of the sulphur is inadequate to cause a decomposition of the nitrate or even to heat up adjacent layers of the composition.

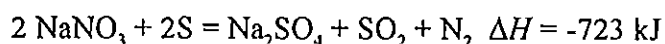
The introduction of drying oil or rosin into multi-component compositions greatly inhibits the process of their combustion.

At a temperature of up to 300-350°C, the decomposition reaction of the nitrates occurs with the formation of nitrites and the hypothetical reaction between sodium nitrate and sulphur may be expressed by the equation:



In this case the heat liberated is 0.4 kJ per 1 g of the composition, and this is inadequate for independent propagation of the reaction.

However, in the presence of a strong initiatory stimulus, combustion is possible, since complete reduction of the nitrate the reaction is accompanied by a more significant liberation of heat:



which corresponds to 2.9 kJ g⁻¹ of composition.

In 1941 Molchanov succeeded in igniting the composition NaNO₃ 68%, S 32%, at standard temperature and $p = 1$ atmosphere, in a cardboard tube with a diameter of 16 mm. The rate of combustion of the composition was ca. 0.4 mm/sec.

It is easier to ignite compositions containing an excess of sulphur and a low percentage of sodium nitrate (17 percent); a great part of the sulphur in such compositions react with the oxygen of the air; such compositions, developed by Sidorov have found application in the national economy (see Chapter XXII).

Among the physical factors affecting the rate of combustion we should mention the following:

An increase in the density of the composition greatly reduces the rate of combustion of most compositions. The effect of the density is especially strongly noted in the combustion of photomixtures: 1 kg of a photomixture in a powdered state burns in tenths of a second, and the combustion time of the same quantity of photomixture compacted under a pressure of the order of 1000 kg cm⁻² is several dozen seconds.

The dependence of the rate of combustion of one illuminating composition upon the specific pressure used in compaction is expressed by the following figures:

Compacting pressure,	kg cm ⁻²	1000	2000	3000	4000
Rate of combustion of composition	mm s ⁻¹	5.0	4.2	3.8	3.6

An increase in compacting pressure above 3000 kg cm⁻² has only a comparatively small further effect on the density of the composition and, consequently, on its rate of combustion.

The effect of the density of a composition on the rate of combustion is explained by the fact that as the density of the composition increases, the possibility of the penetration of hot gases within the composition is reduced, and thus the process of the heating and inflammation of deeper layers is inhibited.

In connection with this, it would be interesting to study the gas permeability of compacted pyrotechnic compositions; this investigation should be performed under conditions of increased temperature, while striving if possible to reconstruct the real combustion conditions of the compositions.

For compositions not containing a metallic fuel and having a lower flame temperature, the rate of combustion varies little when the density of the composition is changed. Andreyev ^{119, page 95} gives details on the dependence of the rate of combustion of explosives upon density

We should note that low-gas compositions also exist in which an increase in density facilitates heat transfer in the condensed phase, and therefore their rates of combustion even increase slightly as the density is increased; the establishment of the dependence of the rate of combustion upon the density of the compositions may help greatly in understanding how great a role the processes occurring in the condensed phase play in the combustion of the composition.

Finer pulverisation of the components also affects the rate of combustion of the compositions to a considerable degree. The smaller the size of the particles of the components of the composition, the greater will be the rate of combustion of the composition. The degree of pulverisation and the shape of aluminium particles entering into compositions have an especially strong effect on the rate of combustion. Compositions based on aluminium powder burn at only a fraction of the rate of compositions based on aluminium dust.

Two important factors affecting the rate of combustion of pyrotechnic compositions are temperature and pressure. When the initial temperature of the compositions is raised, the rate of their combustion increases; this becomes understandable if we consider that at a higher initial temperature of the composition a smaller quantity of heat from the flame zone to the condensed phase is required for the combustion reaction to occur ². As the initial temperature of the composition rises the flame temperature also increases, although not in a well-defined manner.

According to Andreyev ^{119, page 406}, the temperature coefficient of the rate of combustion is an inverse function of the flame temperature (combustion temperature), and of the pressure at which the combustion occurs. The temperature coefficient for a composition, at constant pressure is not constant, but increases when the initial temperature of the composition is increased ^{226, page 269}.

A low value of the temperature coefficient is shown by mixed rocket powders (see Chapter XX) having a high surface temperature of the condensed phase ^{223, page 269}.

Apparently, substances or mixtures having a high self-ignition temperature have a lower temperature coefficient.

The following formula ¹²⁸ is used to calculate the temperature coefficient α of the rate of combustion:

$$\alpha = \frac{1}{u} \cdot \frac{du}{dt}$$

For individual explosives, α usually varies from $3 \cdot 10^{-3}$ to $8 \cdot 10^{-3}$; this signifies that when the temperature changes by 1°C the rate of combustion changes by 0.3-0.8%. For JPN nitroglycerine colloidal powder, over the range $20\text{-}60^\circ\text{C}$, $\alpha = 4\text{-}5 \cdot 10^{-3}$.

The temperature coefficient of the rate of combustion of pyrotechnic compositions is less than for explosives or colloidal powders.

From Baum's data ¹¹³ we may calculate that from -30° to $+44^\circ\text{C}$ the temperature coefficient for gunpowder $\alpha = 0.65 \cdot 10^{-3}$. According to our measurements, the temperature coefficient of gunpowder from 0° to 100°C , when $p = 1$ atmosphere, is $(1.5 \pm 0.4) \cdot 10^{-3}$.

The temperature coefficient for all pyrotechnic compositions investigated from this standpoint does not exceed $3 \cdot 10^{-3}$ (at a maximum initial temperature of 100°C). Andreyev ^{110, page 166} gives the temperature coefficient as the ratio of U_{100° to U_0 . Working from this, he gives values of the temperature coefficient for a number of explosives and powders, including 2.9 for nitroglycerine powders, and 1.15 for gunpowder.

According to Andreyev, the physical cause of the effect of pressure on the rate of combustion lies in the fact that at a high pressure the rate of the reaction in the gaseous phase (in the flame) is higher, and the zone of high temperature is closer to the surface of the condensed phase. Accordingly, the quantity of heat transferred in a unit of time from the gaseous phase to the condensed phase also increases. Therefore, as the external pressure increases, the rate of combustion of pyrotechnic compositions increases. On the other hand, pyrotechnic compositions burn more slowly at reduced pressure than at atmospheric pressure, at a sufficiently low pressure (some mm Hg) entirely lose the capability of propagating combustion.

As Andreyev notes ¹²⁴, "the existence of a minimum pressure below which combustion is not propagated should be explained by the fact that as the pressure decreases, the rate of the reaction in the gaseous phase also decreases, and accordingly there is a decrease in the quantity of heat imparted to the condensed phase from the gases". Since the rate of heat dissipation throughout the condensed phase does not depend upon the pressure, when the latter decreases it becomes greater than the rate of heat influx, and the combustion process dies out.

Compositions containing a large excess of fuel over the stoichiometric ratio, or compositions with fuels which are difficult to oxidise, lose their capability of combustion more rapidly than others when the pressure is reduced.

For powders and explosives, the dependence of the rate of combustion on the pressure is frequently expressed by the formula:

$$u = A + Bp^\nu \quad 10.1$$

where A , B , and ν are constants
 u is the burning rate in $\text{g cm}^{-2} \text{ s}^{-1}$
 p is the pressure in kg cm^{-2}

Andreyev ^{119, page 408} has proposed on the basis of experimental evidence that $\nu=1$ for a number of explosives.

If u and p are in the above units, the pressure coefficient B for high explosives lies between 0.0071 for TNT and 0.031 for jelled nitroglycerine 97:3.

For modern nitroglycerine powders, the exponent is close to 0.7 ^{111 page 190}.

Belyayev ¹²⁷ indicates that the value of ν lies within limits 0.5 - 1.0 for most powders and explosives.

If we characterise the dependence of the rate of combustion of pyrotechnic compositions by formula (10.1), for all compositions the exponent ν (in distinction from explosives) will be considerably less than one.

However, examples are also known among explosives and among powders where the dependence $u = f(p)$ changes essentially when the pressure varies; for example, for potassium picrate ^{111, page 172}, or for gunpowder ¹²⁷.

The use of constant values of B and ν over a wide range of pressures does not always lead to the correct results.

The weak dependence of the rate of combustion upon pressure shows that exothermic reactions occur in the condensed phase to a considerable degree.

According to Baum's data ¹¹³, the exponent ν in formula (10.1) for tubular-grain powders is a direct function of the volume of the gaseous products of combustion v_0 per unit weight of the powder.

According to Andreyev ^{110, 123}, the dependence of the rate of combustion of gunpowder on pressure in the interval 2 to 30 atmospheres, is expressed by the formula $u = 1.21.p^{0.24}$, where p is the pressure in atmospheres, and u is the rate of combustion in cm/sec . Andreyev has established the fact that gunpowder still burns stably at a pressure of 0.1 kg cm^{-2} .

Belyayev ¹²⁷ describes $u = f(p)$ for gunpowder by two formulae:

$$\begin{aligned} u &= 0.88p^{0.5} & (p < 5 \text{ atmospheres}) \\ u &= 1.5 + 0.2p^{0.47} & (p > 5 \text{ atmospheres,}) \end{aligned}$$

It would appear that for gas-free compositions the rate of combustion need not depend upon the external pressure at all. But it has been established by the experiments of Belyayev and

Komkova ¹²⁶ that the rate of combustion of aluminium and magnesium thermites nevertheless increases as the pressure increases, although not sharply.

Thus, for the thermite compositions $\text{Fe}_2\text{O}_3 + \text{Al}$, $\text{MnO}_2 + \text{Al}$, and $\text{Cr}_2\text{O}_3 + \text{Mg}$, the rate of combustion increases by a factor of 3 - 4 when the pressure is increased from 1 to 150 atmosphere. This establishes beyond a doubt the fact that in the combustion these compositions reactions occur (possibly the oxidation of the aluminium by the oxygen formed in the decomposition of the ferric oxide) in the gas phase or at the boundary between the phases. Together with this, Belyayev's experiment demonstrated that compositions also exist for which the rate of combustion does not depend upon pressure: thus, the thermite composition $\text{Cr}_2\text{O}_3 + \text{Al}$ burns at a uniform rate of 2.4 mm s^{-1} both at 1 atmosphere and at 100 atmospheres. Apparently from this we should conclude that in this case the combustion reaction occurs in the condensed phase from beginning to end.

When compositions producing a large quantity of gases burn in a closed or semi-enclosed space, a high pressure is developed; the rate of combustion increases considerably and the combustion may shift to an explosion. Such progressive acceleration of combustion ending in an explosion is observed most frequently for chlorate compositions containing a large quantity (80 -90 percent) of chlorate, such as, for example, the green flare composition: $\text{Ba}(\text{ClO}_3)_2 + \text{resin}$ (for more details concerning the transition of combustion, to explosion, see Chapter XI).

The intensity of heat transfer to the surrounding medium is also reflected in the rate of combustion of these compositions. In connection with this, the rate of combustion of compositions in narrow tubes should be somewhat less but in narrow tubes the outflow of gases is hampered to a greater degree, and excess pressure is developed, especially in a case of fast-burning compositions, and therefore, in practice, a decrease in the rate of combustion is not always observed. At very small diameters, the heat losses to the surrounding space become so great that a composition loses entirely its capability to propagate combustion.

The limiting tube diameter at which stable combustion of the composition still occurs depends upon a great number of factors: recipe of the composition, initial temperature, material and thickness of the tube walls, and the density of the composition. As a rule, the more heat that is liberated in the combustion of the composition in unit time, i.e., the faster the composition burns, the less is the minimum diameter for it.

In connection with heat losses to the surrounding space, we also should consider the question of the minimum possible rate of combustion of a composition.

At normal conditions of temperature and pressure, it is impossible to achieve a combustion process having a very low rate (such as 0.001 mm s^{-1} , for example), for the reason that as a consequence of the slow heat influx per unit of time and the relatively great heat losses to the surrounding space we do not succeed in developing that significant difference between the temperature in the gaseous phase and the condensed phase which is one of the most characteristic features of the combustion process.

One of the slowest-burning mixtures is that consisting of 96% NH_4NO_3 and 4% charcoal, which burns at $p = 1$ atmosphere and $t = 20^\circ\text{C}$ ($d = 0.94 \text{ g cm}^{-3}$) at a rate $u = 0.08 \text{ mm s}^{-1}$. Assuming, in approximation, that the volume of gases formed as the mixture burns $v_g = 700 \text{ cm}^3 \text{ g}^{-1}$ and the combustion temperature $T = 900\text{K}$, we obtain the exhaust velocity of the gases in the flame, and consequently also the rate of their combustion:

$$u' = 0.008 \times 700 \times \frac{900}{293} = 17 \text{ cm s}^{-1}$$

This figure is close to the rate of combustion of the slowest-burning gaseous mixtures. Zel'dovich¹³⁰ indicates that the minimum possible rate of combustion of the gaseous mixture $\text{CO} + \text{O}_2$ at normal conditions, must be about 2 cm s^{-1} .

Up to this time, the problem of catalysis in the combustion of pyrotechnic compositions has not been adequately solved.

In practice, catalysts are used in solid rocket fuels containing ammonium nitrate as an oxidiser (see Chapter XX); in this case, the chromates and dichromates of potassium or ammonium, or sometimes Prussian blue are used as additives.

For the effect of catalytic additives on the dependence $u = f(p)$ for colloidal powders, see reference^{111 page 191}. The introduction of catalysts into chlorate compositions, according to Volodina's data, increases the rate of combustion of binary mixtures consisting of KClO_3 + an organic fuel (when $p = 1$ atmosphere); chlorate compositions with a low percentage of fuel (2-4 percent) are not capable of combustion at $p = 1$ atmosphere but acquire this capability under the same conditions with the addition of a catalyst (such as MnO_2 , for example).

Chapter XI

The explosive properties of pyrotechnic compositions.

To acquaint the reader with the mechanism of the origin and propagation of an explosion and methods of investigating explosive processes, we may recommend the relevant sections in the courses on explosives^{111, 1, 154, 156, 148, 152A}.

Most pyrotechnic compositions are intended for uniform combustion and therefore it is desirable that such compositions possess minimal explosive properties or none at all.

The production of compositions having a high sensitiveness to shock and friction, together with a considerable rate and force of explosion, is a very dangerous process. The method of production of pyrotechnic compositions is determined largely by the explosive properties of the composition which dictate also the quantity of the composition that can be kept in the shop, what distances must be established between separate shops, the type and construction of production buildings (thickness of walls, presence of windows and blow-out ceilings, compartment sizes, the necessity of providing fenced-off yards, etc.); the selection of apparatus (type, size and capacity of mixers, type of presses, methods of mass-production compaction of products, etc.).

Besides this, it is necessary to have a clear conception of the conditions under which an ignition reaction may become an explosion.

The laboratory tests which are conducted to ascertain the explosive properties of pyrotechnic compositions differ essentially from the comparable tests of explosives.

1. Explosives are tested to obtain the characteristics of the force of their explosion, and to compare explosives to each other with respect to their efficiency.
2. Pyrotechnic compositions are tested firstly to establish whether an explosion can be established and propagated at the specified density. Only in those cases when it has been established that the composition is capable of a stable explosive propagation does it become advisable to conduct further tests to determine the rate of propagation of the explosion and to determine the effect of this explosion.

When testing a pyrotechnic under laboratory conditions, we should use the most severe conditions to guard against unexpected manifestation of previously unestablished explosive properties of the composition during production. This is absolutely necessary, since, except for chlorate mixtures and solid rocket fuel with an NH_4ClO_4 oxidiser, an explosion of pyrotechnic compositions is considerably more difficult to initiate than that of ordinary secondary explosives.

The severity of the test conditions reduces to the following:

1. Use of the heaviest possible charges of the compositions being tested (not less than 50-100 g) in a powdered form.

2. Use of a powerful initiatory stimulus (a supplementary tetryl booster weighing not less than 8 g.
3. Placing the charge under test in a strong casing (iron tubing, or, even better, a thick-walled lead shell).

In practice, tests may be conducted in a Trauzl lead block, with the hole increased to 40 mm diameter. An explosion in the composition (a weighed powder specimen of 50 g) is witnessed by a considerable expansion (ca. 100 cm³) of the hole in the lead block after the test.

Elongated charges with a diameter of not less than 40 mm and a length of not less than 15-20 cm should be used to test the ability of a pyrotechnic composition to support stable propagation of an explosion. To create the severe test conditions a supplementary detonator should be used, and the composition enclosed in a strong casing.

A lead column (with a diameter of 40 mm) as used in the Hess (?) Test, or a sheet of 2 mm tin plate is a suitable witness for the propagation of explosion from one end of the specimen to the other.

The D'Autriche method may be used to determine the detonation rate of compounds capable of stable explosive propagation. The rate of detonation is determined more accurately with a photo-recorder with a mirror sweep ¹¹¹. In conducting all these tests we must bear in mind that in most compositions the ease of initiation and stable propagation of an explosion is reduced as the density of the composition increases. In compacted pyrotechnic compositions, explosive decomposition is very difficult to excite, and once it has been excited, it dies out easily and quickly.

Therefore, the most dangerous operations in the preparation of pyrotechnic compositions are those in which the composition is in an uncompacted form.

We should again emphasise the fact that tests used for explosives, such as the brisance test, the Trauzl-block test (in the usual formulation of the test), and determination of the rate of detonation, are not very characteristic of pyrotechnic compositions and they should be performed only in those cases when we are confident that the given pyrotechnic composition is capable of the stable propagation of explosive decomposition. As experiments have demonstrated, explosive decomposition is easily excited and propagates reliably only in chlorate pyrotechnic compositions (containing not less than 60 percent chlorate), solid rocket fuel with a NH_4ClO_4 oxidiser, (see Chapter XX) or in compositions containing explosive additives.

Mixtures of chlorates with magnesium or aluminium develop very high temperatures during explosion, but they also produce a comparatively small quantity of gases. This may be explained by the fact that mixtures of chlorates with magnesium or aluminium have lower explosive properties than mixtures of the same oxidisers with organic substances.

The explosive properties of certain chlorate mixtures are given in Tables 11.1, 11.2, and 11.3.

Composition (%)	Expansion in Trauzl Block (cm ³)	Detonation Velocity (m s ⁻¹)
Ba(ClO ₃) ₂ 81 resin 19	155	1600 - 2000
Chloratite 3 KClO ₃ 91 kerosene 9	255	3,600
TNT 100	285	6,700

Table 11.1 Explosive properties of green flare composition and explosives chloratite-3 and TNT

Fuel	Fuel content in mixture (%)	Trauzl Block test		Detonation velocity (m s ⁻¹)
		Quantity of mixture (g)	Expansion (cm ³)	
wood dust	25	10	220	2,600
powdered sugar	10	13	105	-
carbon black	10	13	160	-
aluminium	25	10	160	1500 ¹
¹ ignition by gunpowder				

Table 11.2 Explosive properties of mixtures of potassium chlorate with various fuels

Fuel	Fuel content in mixture (%)	Rate of combustion	
		Density of composition	Detonation velocity (m s ⁻¹)
charcoal	13	1.27	1,620
graphite	13	1.44	500
sulphur	28	1.36	1,600

Table 11.3 Velocity of detonation of potassium chlorate with various fuels

For a mixture of 69% potassium chlorate and 31% aluminium, the Hess test for brisance is conducted with an upsetting (?) of the lead cylinders of 7 mm.

The introduction of a large quantity of inert additives into chlorate compositions sharply reduces their explosive properties. Thus, compositions for screening and coloured signal smokes containing large quantities of low-activity substances such as NH_4Cl and organic pigments, and a comparatively small quantity of KClO_3 (not more than 40 - 45%) are almost incapable of explosive decomposition. Oxalates or carbonates of alkali or alkaline earth metals in quantities of 20 - 30% also have a strong phlegmatising effect on coloured signal-flare compositions based on chlorates.

A necessary but occasionally still inadequate condition for the initiation of an explosion is the formation of a considerable quantity of gaseous products as a result of the reaction. Therefore, gasless compositions, or those that produce very little gas at the temperature of the reaction will not have explosive properties in practice, or will have them to a very minimal degree.

Ferroaluminum thermite forms almost no gaseous phase on combustion, and therefore has no explosive properties. The sputtering of individual particles in the combustion of thermite is caused only by the air included in them, which expands as the temperature rises.

In the combustion of incendiary compositions that contain in addition to thermites other components such as barium nitrate or potassium nitrate, for example, as well as organic binders, a small but definite quantity of gas is formed, and therefore the given composition may possess explosive properties. But in practice, it is extraordinarily difficult to induce an explosive decomposition in preparations containing more than 50 - 60% ferroaluminium thermite; for this, the presence of a strong casing is needed, and a very powerful initiatory impulse (a considerable quantity of some explosive), and nevertheless the result of the experiment is still doubtful.

A second necessary, but not sufficient, condition for a system to have explosive properties is that the reaction is highly exothermic.

Since the rate of a chemical reaction depends greatly upon temperature, an explosive decomposition reaction can be achieved only when the temperature developed is no lower than 500-600°C.

Almost all pyrotechnic compositions satisfy this condition ($t \geq 500\text{-}600^\circ\text{C}$), with the exception only of certain screening smoke compositions containing 40 - 50% of such low-activity substances as NH_4Cl .

A third condition determining the ability of a system to initiate and develop processes of explosive decomposition in itself is homogeneity of the system - a property that pyrotechnic compositions possess only to a small degree.

As is pointed out in courses on the theory of explosives, solid explosive mixtures not containing detonation conductors - specific explosives - have a very low brisance, and the process of explosion is initiated and propagated in them only with great difficulty. Note that the situation is different with mixed liquids, which form solutions. Here, dispersion occurs at the molecular level

and therefore the explosion waves can propagate unimpeded. An example of such a mixture is gunpowder. Pyrotechnic compositions are solid mixtures. They can possess strongly expressed explosive properties only when they contain an explosion (detonation) conductor - a specific substance capable of an exothermic spontaneous decomposition reaction.

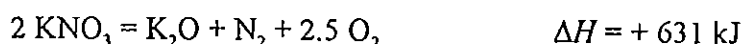
In chlorate pyrotechnic compositions, potassium chlorate is such a conductor, as an influx of heat from outside is not required for its decomposition, and in solid rocket fuel (composite propellant) ammonium perchlorate (or ammonium nitrate) serves as the conductor.

Potassium perchlorate decomposes with the liberation of a very small quantity of heat:



and therefore explosive decomposition should occur in compositions containing KClO_4 and be propagated therein with greater difficulty than in chlorate compositions.

Nitrates (except NH_4NO_3) require a very large heat influx from outside for their decomposition:



and therefore the process of explosive decomposition in nitrate compositions (except compositions containing NH_4NO_3) is initiated only with great difficulty and, on the other hand, dies out quickly and readily.

Nitrate mixtures possess considerably lower explosive properties than chlorate mixtures.

A powerful stimulus is required to initiate explosive decomposition in illuminating compositions containing barium nitrate as an oxidiser and aluminium powder or dust as the basic fuel.

Comparative data on the explosive properties of mixtures of potassium perchlorate or barium nitrate with aluminium dust are given in Table 11.4.

Oxidiser	Content of oxidiser in composition (%)	Expansion of Trauzl block (cm ³)	Test for rate of detonation	
			Density of composition	Velocity of detonation ¹ (m s ⁻¹)
KClO_4	66	172	1.2	760
$\text{Ba}(\text{NO}_3)_2$	73	34	1.4	misfire

¹ VoD measured in iron tubes 30 mm diameter and 250 mm long; initiated by No 8 detonator and a 10 g tetryl booster.

Table 11.4 Explosive properties of binary mixtures of potassium perchlorate and barium nitrate with aluminium

The process of explosive decomposition is initiated somewhat more easily in nitrate illuminating compositions containing magnesium. But the rate of explosive decomposition of nitrate illuminating compositions, in the majority of cases, does not exceed 1000 m s^{-1} ; the rate of explosive decomposition of gunpowder, which also may be considered as a nitrate pyrotechnic mixture, does not exceed 400 m s^{-1} .

Explosive decomposition of uncompact binary mixtures of nitrates with magnesium or aluminium-magnesium alloy is initiated readily not only from a detonating cap, but also from a flame (gunpowder or quick match), if the mixtures are used in adequate quantities (more than 50-100 g). As a consequence, such mixtures must be regarded as being among the most dangerous pyrotechnic compositions and should be handled with great caution.

Because of this, it is useful to note that the high combustion temperature facilitates the transition of combustion to explosion both in a case of pyrotechnic compositions and in the case of explosives.

Andreyev indicates that the burning gases penetrating into the pores of the charge ignite the particles of explosive more easily if the temperature of the gases is higher. In this case, an increase in the combustion surface and the rise in pressure associated with it lead to the formation of a detonation wave.

That TEN (tetraethyl nitrate [sic]) and hexogen undergo transition from combustion to explosion more easily than other secondary explosives, is explained by their high combustion temperature ¹⁵¹. ^{119 page 411}. The combustion of ammonium perchlorate does not shift to an explosion under conditions in which the transition occurs easily in TEN. If, however, a little finely dispersed aluminium is added to the ammonium perchlorate, a transition from combustion of the mixture to an explosion occurs with increasing temperature just as easily as for TEN or hexogen ¹⁵¹. The effect of the aluminium is to raise the temperature of the products of combustion: the hotter gases ignite its particles more easily as they penetrate into the porous powder.

Let us now consider the behaviour of these compositions when various forms of initiatory stimulus act on them. Shock (or friction) applied to an individual section of the surface of a pyrotechnic composition, in the absence of conditions allowing a rise in pressure during combustion, usually causes only a local explosion of the composition; the remaining mass of the composition burns normally, as in the effect of an ordinary heat impulse.

If a bullet with considerable velocity strikes pyrotechnic products, in many cases it will often cause pyrotechnics to burst into flame, and if the composition is strongly confined, it may even cause an explosion of the composition.

In an enclosed space (such as, for example, when sparking occurs during compacting in a steel die) and in all those cases when the composition is enclosed in a very strong metallic case, a rise in pressure causes an increase in the rate of combustion, and in many cases the process ends with an explosion, even when ordinary firing devices are used to provide the initial impulse.

The same rise in pressure, causing a transition of combustion to explosive decomposition, originates in some cases from the simultaneous ignition of a large quantity (10 kg or more) of fast-burning powdered composition.

Andreyev has designed a very simple device for establishing the possibility of a transition of the

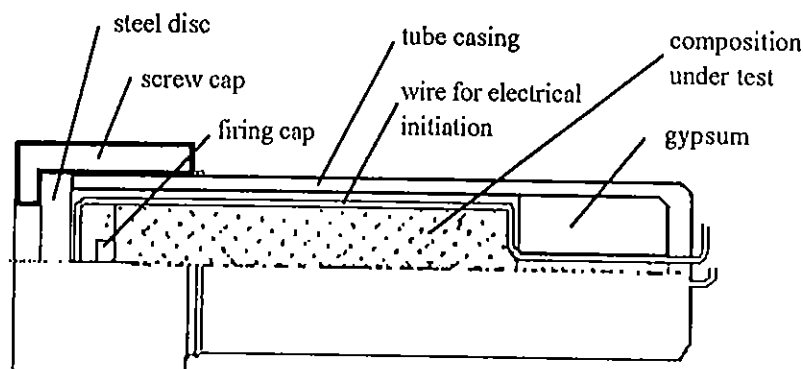


Fig 11.1 Tube designed by Andreyev to investigate the transition from combustion to explosion

combustion of an explosive in an enclosed volume to an explosion ^{153 page 59}. This device is a strong iron tube with a length of 200 mm and a internal diameter of 40 mm, closed on all sides, which is partially filled with explosive (50 g); the explosive is then ignited by a cap of igniter composition

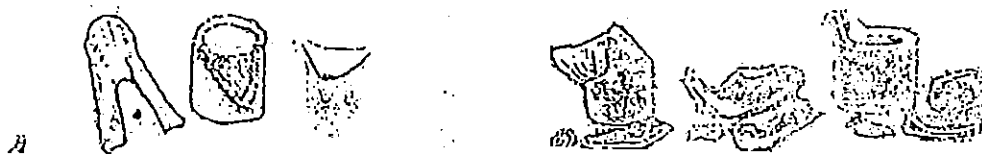


Fig 11.2 Nature of deformation of test pipes designed by Andreyev during combustion (left) and in a transition from combustion to explosion (right)

which is ignited by a thin wire heated by electric current (Fig. 11.1).

The shattering of the tube (pipe) into a large number of fragments (five to six or more) indicates that the combustion undergoes a transition to explosion (Fig. 11.2).

The tendency for pyrotechnic compositions to undergo a transition from combustion to explosion in an enclosed volume may be determined in the same manner. If desired, this test may be supplemented by weighing the fragments and calculating the average weight of a fragment.

Andreyev and his co-workers ¹⁴⁹ have recently developed a test to demonstrate the ability of small charges of explosives to undergo a transition from combustion to explosion by igniting them in a manometric bomb; in this case the charges are compressed in Plexiglass beakers, the initiator is

gunpowder, and the change in pressure is recorded on the oscillograph film. This method allows us to use the manometric curve to trace the entire process, while Andreyev's pipe testing device records only the final results.

The shortcomings of this new method, in our opinion, are the small samples (a few grammes) of the substance being tested and the fact that the charge burns only from the end. This makes the test conditions somewhat unrepresentative of the conditions under which the combustion of explosives (or pyrotechnic compositions) may occur in practice.

In some cases, it is of interest to trace the behaviour of the composition as it burns in a semi-enclosed volume, i.e., with severe restriction of venting of the gases. Andreyev's iron pipe may be used for this purpose if a hole of the appropriate diameter (from 2 to 12 mm) is first drilled in the steel disk that encloses one of the ends of the pipe.

The Trauzl block test, with a small charge of gunpowder instead of a detonating cap for the initiatory stimulus, similarly investigates the behaviour of a pyrotechnic composition during combustion in a semi-enclosed volume.

Sequence Number	Composition (Uncompacted) (%)		Expansion for 20 g composition (cm ³)	
			Bickford fuze	No 8 detonator
1	KClO ₄	85	198	318
	charcoal	15		
2	KClO ₄	59	49	88
	magnesium	41		
3	Ba(NO ₃) ₂	89	0	120
	iditol	11		
4	TNT (pressed, for comparison)		-	718

Table 11.5 Influence of initiation on the Trauzl Block Expansion

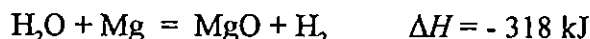
As is apparent from Table 11.5, when a flame serves as the initial stimulus, the expansion in the Trauzl block is approximately 50% of the normal, while for low-sensitivity compositions (composition 3) combustion does not shift to explosion at all and no expansion of the passage is obtained.

In conclusion, we should note that in certain cases the danger of explosion is not excluded even when handling individual components used in preparing the compositions.

Thus, for example, an explosion may result when there are large concentrations of aluminium powder dust in the air, or finely pulverised magnesium powder, powdered aluminium/magnesium alloy, powders of zirconium and titanium, or even the dust of certain combustible substances

such as, for example, carbon, hydrocarbons, the powders of resins, etc. For more details, see Godzhello ¹⁵², and also reference ^{111 page 152}. In particular, it has been found that the lower limit of an explosive capability of aluminium dust (with a particle size of 0.1-0.3 μm) corresponds to a concentration of 40 mg of it per litre of air; the corresponding figure for magnesium powder is 25 mg per litre of air.

The powders of many metals have explosive properties under certain conditions when wetted with water. The reaction of magnesium or aluminium with water occurs with a very great liberation of heat, and the formation of considerable quantities of gases:



This corresponds to 7.61 kJ g^{-1} , while the quantity of the gas is equal to 530 $\text{cm}^3 \text{g}^{-1}$. Thus all conditions needed for initiation of an explosion are present. Explosion may be achieved if a sufficiently powerful initiatory stimulus is applied ¹⁵⁵ (Fig. 11.3).

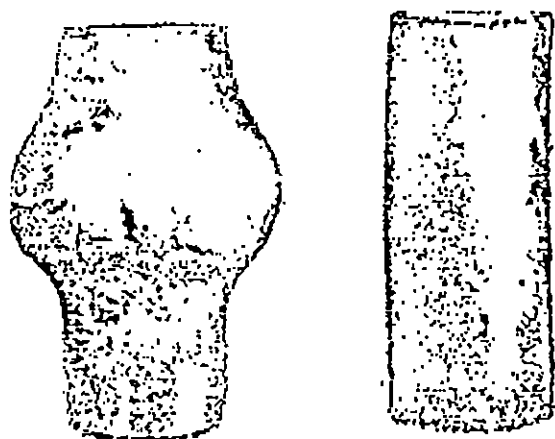


Fig 11.3 Thick-walled lead cylinder before (right) and after (left) explosion in it of 50 g $\text{H}_2\text{O} + \text{Mg}$ in stoichiometric proportions. Detonator No 8.

However, the absence of molecular contact between the particles of the oxidiser (water) and the fuel, i.e., the non-homogeneity of the mixture, prevents stable propagation of the explosion, as demonstrated by this experiment ¹⁶⁰ even though the system allows its initiation.

For the possibility of water oxidising non-metals (B, Si, and P) and the lower oxides of the elements, see reference ^{119 page 540}.

Explosion of an individual component - such as potassium chlorate - having a great destructive force (high brisance) may occur only if significant additives of fuels are present in it (more than 1%).

The quantity of heat liberated on decomposition of a pure salt (without admixtures), at room temperature, is small (0.33 kJ g^{-1}); therefore,

even if an explosive decomposition of KClO_3 occurs because of a very powerful initiatory stimulus, nevertheless the destructive effect of the explosion will be insignificant.

See Chapter XX for the explosive properties of the oxidisers ammonium perchlorate and ammonium nitrate.

Chapter XII

Physical and Chemical Stability of Pyrotechnic Compositions

By the term "stability of pyrotechnic compositions" we mean their ability to preserve their properties when stored for a prolonged period of time.

Section 1. Changes Occurring in Compositions During Storage

Physical and chemical changes occur in pyrotechnic compositions during storage of pyrotechnic products. These changes can be so significant that the products can become unsuitable for use, and sometimes even dangerous to handle. Therefore, in each case, we should establish the nature of the changes in the composition and also the effect of various factors on the rate of the of the decomposition processes of the composition.

Such investigations establish storage conditions under which the processes of decomposition are minimised, and permissible durations of storage for individual types of pyrotechnic products.

Physical changes occurring in a composition during storage are most frequently caused by absorption of moisture by the composition. In this case, a partial solution of the components of the composition occurs, and the density and shape of the compacted (pressed) charge occurs.

More rarely the cause of the deformation of a charge (a flare or grain) results from mechanical effects or the variation in the temperature of the surrounding medium.

We should especially note the changes in the composition caused by sublimation of the volatile components such as, for example, naphthalene, hexachloroethane, and others.

The hygroscopicity of a composition depends basically upon the hygroscopicity of its components, and also upon the density and state of the surface of the composition subjected to the effect of moist air. As a rule, compositions attract moisture from the air to a considerably lesser degree when they are in a pressed (compacted) state than when they are in the form of powder. Hygroscopicity of a composition in storage, other conditions being the same, increases as a function of the subdivision of its components.

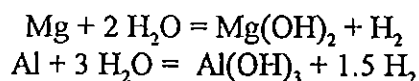
To protect the composition from absorbing moisture from the air when, for some reason, it is not possible to seal the product completely, the particles of the composition or particles of the individual components are coated with a protective film of some plastic organic substance. Mineral oils, stearin, and the stearates of various metals are most frequently used for this purpose, as well as paraffin, lacquers based on various artificial and natural resins, drying oil, and others.

The protective effect of resins is especially marked when they are used as lacquers; in a dry form (powder) they offer considerably less protection against the penetration of moisture.

Chemical changes occurring in the compositions may be very diverse, as the result of the extraordinarily great variety of components used in their manufacture. But some general principles may be established nevertheless.

Compositions containing metal powders and inorganic oxidisers

Magnesium or aluminium powders are used as fuels in many pyrotechnic compositions. The decomposition of these compositions begins with the corrosion of these powders in the presence of moisture in the composition:



The reaction of magnesium with water occurs much more vigorously than that of aluminium with water. The oxide film of the magnesium is porous and not very strong, so that it is an inadequate protection against further corrosion of the metal. Aluminium powder (or dust) usually oxidises only at the surface, and the dense oxide film formed on its surface reliably protects the film from further oxidation.

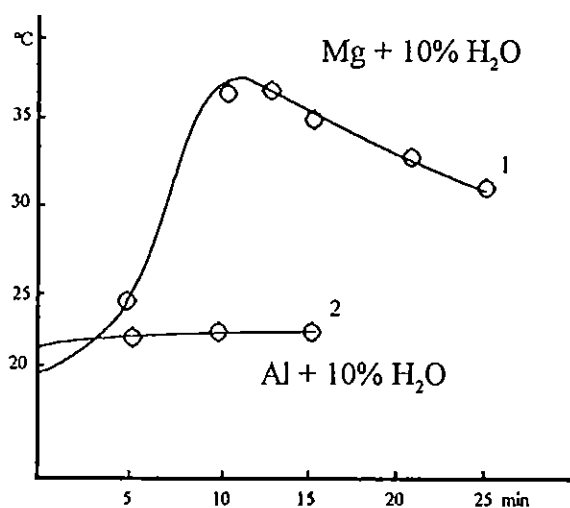


Fig 12.1 Temperature rise when water is added to mixture

Fig. 12.1 shows a graph of the change of temperature with time when 10% water is added to magnesium or aluminium powder. Since the reaction of aluminium or magnesium with water releases a considerable amount of heat, heating, or if the mass is sufficient (a kilogram), or if the composition is chemically unstable (see below) spontaneous ignition may even occur if binary mixtures with oxidisers (such as nitrates) are made wet.

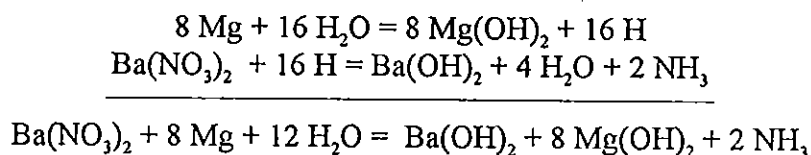
The corrosion of metal powders depends upon the same quantitative relationships as the corrosion of the massive metals, but it occurs much more rapidly because of the very high specific surface of the powders.

It is generally known that magnesium corrodes extensively in acid medium, but that the metal is stable in alkali. This is explained by the properties of the magnesium oxide film which dissolves readily in acids, but is insoluble in bases.

The oxide film on aluminium dissolves in acids and in alkalis. Aluminium is characterised by its ready corrosion in a highly basic medium. If the oxidisers present in the composition produce an acid or basic medium when moistened, then the presence of that oxidiser will obviously increase the rate of corrosion of the metal powder.

The nitrates of the alkali and alkaline earth metals are reduced to ammonia by the hydrogen formed by the corrosion of the metal.

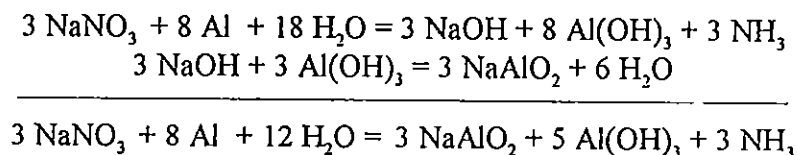
The decomposition of a moist mixture of $\text{Ba}(\text{NO}_3)_2 + \text{Mg}$ may be expressed by the equations:



In this case the products are basic, and the reaction is retarded.

Experience over many years shows that compositions containing magnesium and the nitrates of alkaline earth or alkali metals are stable in storage, particularly if they contain a few percent of an organic binder.

The decomposition of a moist mixture of $\text{NaNO}_3 + \text{Al}$ may be expressed by the equations:



In this case the sodium hydroxide formed as a result of the decomposition of the NaNO_3 considerably accelerates the corrosion of the aluminium powder. A mixture of $\text{NaNO}_3 + \text{Al}$ has a low chemical stability, and may be used only if it can be reliably protected against the moisture of the air by lubricating [sic] additives or by hermetic sealing of the product.

The stability of nitrate compositions containing metal powders depends strongly upon the presence of moisture in the composition and, consequently, upon the hygroscopicity of the oxidiser. From this we may conclude that under the same storage conditions, the least significant chemical changes will occur in compositions containing the least hygroscopic salts - barium nitrate - as an oxidiser.

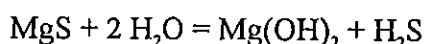
Compositions containing aluminium, except with the nitrates of the alkali metals, are undoubtedly more chemically stable than the corresponding compositions with magnesium powder. This is valid even when a coarse magnesium powder and a finely pulverised aluminium dust are compared.

As was stated previously, the presence of an organic binder considerably hampers the access of moisture to the particles of the composition. Therefore, illuminating and tracer compositions with organic binders will be more chemically stable than the corresponding binary compositions of the photomixture type, in the absence of reliable hermetic sealing of the product.

The addition of sulphur does not reduce the chemical stability of a mixture of barium nitrate and aluminium dust or powder. According to the literature, aluminium does not react with sulphur even when the sulphur is molten. Mixtures of barium nitrate, aluminium and sulphur are among the most stable pyrotechnic compositions when in storage.

Mixtures of sulphur with magnesium are chemically unstable, as was noted as early as the 19th century by the Russian pyrotechnics experts Matyukeviches and Ordynskiy.

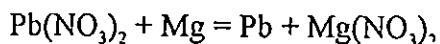
Mendeleev^{165, Chapter 20} notes the effect of high pressures on the ability of solids to form chemical bonds with each other. "At a pressure of 6000 atmospheres," he writes, "sulphur is capable of bonding with many metals at room temperature"; see also reference¹⁶⁴. When a mixture of magnesium and sulphur, which already contains MgS, is moistened, the following reaction occurs:



Mixtures containing both magnesium and aluminium powders are more sensitive to the effect of moisture than similar compositions containing only one of these metals. Thus, when a composition containing the powders of both metals is moistened, it heats up much more strongly than a composition containing magnesium alone. This is explained by the formation of microscopic galvanic elements (metal - salt solution - other metal) in the moist composition, which considerably accelerate the corrosion of the magnesium.

Compositions containing the powders of AlMg alloys are considerably more chemically stable than compositions containing a mixture of the powders of these two metals. This occurs because the particles of the alloy are coated with a dense protective film of aluminium oxide.

Mixtures of the nitrates of heavy metals $\text{Pb}(\text{NO}_3)_2$ or $\text{Cu}(\text{NO}_3)_2$ with magnesium are not chemically stable when wetted because of exchange reactions, such as:



There are indications that in the mixture $\text{Pb}(\text{NO}_3)_2 + \text{Al}$ the aluminium is coated with a layer of the basic lead nitrate which protects it against further effects of the solution.

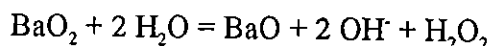
Mixtures of chlorates with metal powders. Mixtures of potassium chlorate with magnesium powder show significant chemical changes under conditions of increased humidity, and therefore cannot be recommended for prolonged storage.

It is possible that the rapid oxidation of magnesium when mixed with KClO_3 occurs principally because of the catalytic effect of the oxidiser, in spite of the low hygroscopicity of potassium chlorate which makes this salt a bad transmitter of moisture from the air to the magnesium powder.

A sound-producing composition of potassium chlorate with aluminium is considerably more chemically stable than a mixture of that oxidant with magnesium.

Mixtures of metallic powders with potassium permanganate are reported to have a low chemical stability.

Mixtures of barium peroxide with metal powders. When anhydrous barium peroxide comes in contact with water, it is hydrated, forming $\text{BaO}_2 \cdot 8\text{H}_2\text{O}$. On its own, barium peroxide is only slightly decomposed by water at room temperature; at 0°C the equilibrium constant of the reaction in solution is $18 \cdot 10^{-12}$.

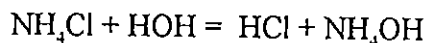


When moist barium peroxide is mixed with aluminium powder, the OH^- ions are consumed by reaction with the oxide film on the aluminium, the equilibrium of the decomposition reaction is shifted to the right, and the process of decomposition of the composition occurs very violently.

Experiments have shown that when mixtures of $\text{BaO}_2 + \text{Al}$ are moistened, their temperatures rise, depending upon the grade of aluminium used, by $60\text{-}100^\circ\text{C}$.

Ferroaluminium thermite and thermite compositions are very stable chemically. The oxidiser contained in them is not capable of decomposition at low temperatures. Very coarse aluminium powder is used for thermite compositions, which does not react significantly with moisture at normal temperatures.

Effect of ammonium salts. The addition of ammonium salts, particularly ammonium chloride, to compositions containing magnesium is undesirable because ammonium salts are very hygroscopic, and the aqueous solutions of its salts of strong acids are acidic because of hydrolysis; e.g. a 10% solution of NH_4Cl has a pH of approximately 5:



The strong acid formed by hydrolysis reacts with the oxide film on the particles of the metal powder and the freed magnesium corrodes rapidly in the acid solution.

It is possible that corrosion of magnesium will occur more slowly in a solution of NH_4NO_3 than in a solution of NH_4Cl , since the Cl^- ion is a promoter of corrosion.

The corrosion of aluminium powder is only slightly accelerated when ammonium salts are added to the compositions ^{167A}. Aluminium shavings covered with a concentrated solution of NH_4NO_3 produced a gas, very slowly at room temperature, but considerably more rapidly (more than $1 \text{ cm}^3 \text{ hr}^{-1}$) at 60°C , which contained 6-13% hydrogen and 45-60% nitrous oxide ¹⁶².

We should also avoid adding any salts whose aqueous solutions hydrolyse to give an acidic reaction to compositions containing metal powders, especially magnesium powder. The corrosion of magnesium proceeds somewhat more rapidly in a neutral aqueous solution of potassium chloride than in water, but only a fraction as fast as in solutions of ammonium salts.

The corrosion of aluminium powder is highly accelerated in the presence of copper and especially in the presence of mercury, as well as in the presence of soluble salts of these metals, and therefore adding them to the compositions is absolutely intolerable.

In some cases, chemical changes occur more rapidly in compacted (pressed) compositions because the components are in close contact with one another, than in powdered compositions, even though compositions are more hygroscopic in a powdered form.

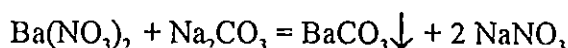
The monographs of Evans ¹⁷⁰, Akimov ¹⁶³, and Tomashov ¹⁶⁸ may be recommended for problems on the corrosion of metals (including the corrosion of metal powders).

Compositions containing powdered metallic iron are chemically unstable in most cases since the process of the oxidation of finely pulverised iron in the presence of moisture occurs very rapidly. For fireworks compositions, the iron filings are first subjected to a browning operation - treatment with hot linseed oil - to prevent their oxidation before they are incorporated in the composition ⁶.

Compositions not containing Metal Powders.

In most cases no significant chemical changes occur on moistening such compositions. An exception is found in mixtures in which two soluble salts are present, which are capable of entering into a double-decomposition reaction in solution, with the formation of a precipitate.

Exchange reactions. An example of such an undesirable combination of salts is a yellow flare composition which includes a mixture of barium nitrate with sodium sulphate, sodium carbonate, or sodium oxalate. Exchange reactions occur when such mixtures are moistened with the formation of barium salts that are almost insoluble, for example:

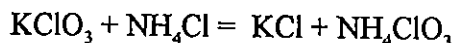


The formation of the hygroscopic salt NaNO_3 results in further moistening of the composition and in some cases the reaction can go almost to completion.

Signal flare compositions not containing metal powders or hygroscopic salts (or combinations of salts capable of double decomposition) usually do not undergo important chemical or physical changes in storage. A red flare composition such as: potassium chlorate, strontium carbonate, and resin is an example of a composition that is very stable in storage: .

Signal smoke compositions containing potassium chlorate, sugar or starch, and some organic pigment are quite hygroscopic, but do not undergo any essential chemical changes in storage. The same thing is also observed in many cases for screening smoke compositions which do not contain metallic powders.

Formation of an unstable salt - ammonium chlorate. When screening smoke compositions containing a smoke-forming substance such as ammonium chloride together with potassium chlorate, are moistened, the following exchange reaction is theoretically possible:



Ammonium chlorate is capable of spontaneous decomposition and even spontaneous explosion at a slightly elevated temperature (30-60°C). Nevertheless, in practice, screening smoke compositions containing a great quantity of naphthalene or anthracene together with potassium chlorate and ammonium chloride (such as Yershov's mixture), are quite stable in storage²¹. Cases of spontaneous combustion of smoke mixtures similar to Yershov's mixture have not been noted up to the present time.

Because of the danger of an exchange reaction with the formation of ammonium chlorate, the use of ammonium nitrate in chlorate compositions is not permissible. A combined use of ammonium nitrate and chlorates is prohibited also in explosive mixtures. According to literature sources, a mixture of potassium chlorate with a stoichiometric quantity of ammonium nitrate explodes at the low temperature of 120°C.

See reference ⁷ page 133 for information on chlorite compositions containing NH_4NO_3 , copper salts, and metal powders, which are hypergolic due to the effect of water.

Unstable mixtures of chlorates and sulphur. These mixtures are not used at all for filling products intended for long-term storage. The possibility of spontaneous ignition of mixtures of $\text{KClO}_3 + \text{S}$ is especially great if the sulphur contains traces of sulphuric acid. The addition of carbonates (such as, for example, chalk, or CaCO_3) to such mixtures to neutralise the traces of acid reduces, but apparently does not entirely eliminate, the probability of spontaneous ignitions.

Among the hypergolic mixtures that react very rapidly are a mixture of glycerin with finely pulverised potassium permanganate, which ignites spontaneously 10-20 seconds after the mixing of the components.

A mixture of potassium chlorate with red phosphorus, as we have already indicated, is so sensitive that it explodes even when it is rubbed gently with a rubber stopper. Even if this mixture is prepared with great caution, apparently it may ignite spontaneously after a short period of time, without any sort of external stimulus. The rate of oxidation of pure red phosphorus increases as the temperature of the surrounding medium rises; the oxidation of red phosphorus is inhibited considerably when its particles are treated with an iditol (or shellac) lacquer.

Section 2. Methods of determining the hygroscopicity and chemical stability of compositions.

Under ordinary storage conditions for pyrotechnic products, i.e., with an air humidity of not more than 80 percent and a temperature corresponding to the climate of the given locality (we have in mind a dry, unheated warehouse), the moistening of the compositions occurs very slowly; under these conditions, the processes of chemical decomposition of these preparations also occurs slowly in most cases.

Under such conditions, noticeable chemical changes in stable pyrotechnic compositions occur only over a number of years. In order to cause these changes artificially in the laboratory in a

comparatively short period of time, the composition is stored for a definite time at an increased humidity, and sometimes simultaneously at an increased temperature.

The term "test of pyrotechnic compositions for chemical stability" usually means holding the composition in artificially created "severe" conditions and studying the changes occurring in it (by weighing, chemical analysis, measuring the pressures of the gases over it, etc.).

It is extremely difficult to establish a definite quantitative relationship between the nature and magnitude of the changes occurring in pyrotechnic compositions and the changes in the storage conditions. We cannot predict the interval of time over which pyrotechnic products stored under ordinary warehouse conditions will change to the same extent as those tested in the laboratory in accordance with the "test for chemical stability" over a much shorter interval of time.

Usually the chemical changes observed in a composition after its testing "according to sample" are compared to the changes occurring in testing with the same "sample" in a chemically stable composition. The composition being investigated is considered chemically stable and is released for production if the test data "according to sample" do not exceed the variations of the chemically stable composition, i.e., a composition that has already been proved in practice.

However, a final judgement of the chemical stability of compositions may and must be made only on the basis of observations of the changes occurring on long-term storage under real conditions of products filled with it.

The hygroscopicity of compositions is usually determined in hygrometers, i.e., instruments in which a definite air humidity is constantly maintained. The most frequently used type of hygrometer is a desiccator, on the bottom of which is poured water or a saturated salt solution. The composition being tested is placed on the desiccator platform in open vessels or small crystallisation pans.

The essential shortcoming of such a hygrometer is that the absolute humidity within the instrument may vary widely because of changes in the temperature of the surroundings, and actually only the relative humidity remains invariable. This test will be better if the hygrometer is placed in a thermostat.

To obtain a definite air humidity within the hygrometer either water (for a test at 100% relative humidity) or a salt solution is poured into its bottom. A relative humidity of 92.5% is obtained at 20°C over a saturated solution of potassium nitrate, and of 77.5% over a saturated solution of sodium chloride at the same temperature.

If the hygroscopicity test is being conducted with a powdered composition, a definite weighed sample of the composition (say 10 g, for example) is placed in an open beaker on the desiccator platform; sometimes pellets or even completely filled small pyrotechnic products are tested in hygrometers.

In comparative testing of many compositions, it is mandatory that the surface of the source of moisture be maintained constant (by the use of beakers of standard dimensions), and also that the

thickness of the layer of composition under test be kept small; for a sample of 10 g, the diameter of the beaker must not be less than 50 mm.

The composition is weighed periodically during tests. The total duration of hygroscopicity testing of a composition at room temperature (20°C), is usually less than 30 days.

Upon completion of the experiment, a graph is plotted (Fig. 12.2), showing the change of the composition's weight, as a function of the time it was kept in the hygostat. On the abscissa we plot the time in days, and on the ordinate the relative increase in the weight of the composition in percentages of the initial weight.

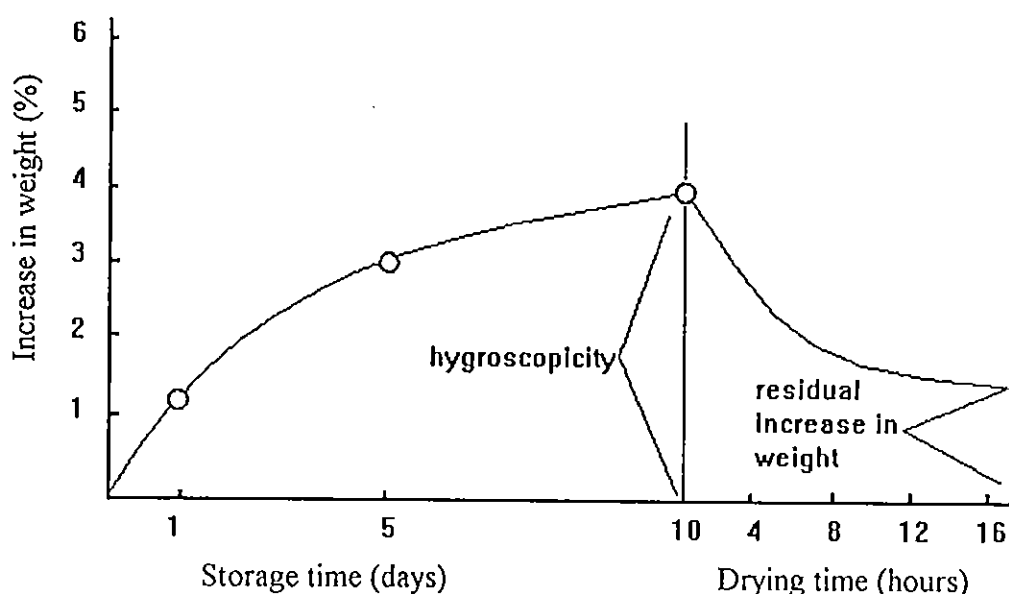


Fig 12.2 Change in composition's weight at increased humidity and on subsequent drying

Norms exist for the increase in composition weight after 10 days of testing in a hygostat at $t = 20^{\circ}\text{C}$ and at 100% relative humidity: the result of the test is considered entirely satisfactory if the composition's increase in weight does not exceed 2%.

For gunpowder, the increase in weight after it is kept at room temperature in 92.5% relative humidity for one day must not exceed 1.75%.

We should note that testing compositions by keeping them at an increased relative humidity cannot be called only a test of the hygroscopicity of the composition, since under these conditions, according to the given method, a number of parameters characterising the chemical stability of the composition are determined simultaneously.

The chemical stability of pyrotechnic compositions may be determined by various methods.

Pyrotechnic compositions are frequently divided into three categories with respect to their chemical stability, :

1. compositions containing metal powders and inorganic oxidisers;
2. compositions containing metal powders and organic oxidisers containing chlorine;
3. compositions not containing metal powders.

In most test methods for chemical stability used at the present time, the effect of moisture is determined in some manner or other.

Usually the compositions are kept in hygrometers at an increased relative humidity for not less than 30 days. The composition is sampled after 10, 20, and 30 days. If it contains a metal powder (Mg or Al), the change in the activity of the metal is determined, as well as the increase in weight (see below), and a graph plotted of the dependence of these quantities upon the time that the composition is kept under the test conditions.

Since the weight of a metal powder increases during oxidation because of its reaction with water, a composition subjected to the effect of moisture usually does not return to its initial weight after drying. In order to determine the stability of illuminating and similar compounds containing metal powders, it is adequate to know only the increase in weight of the composition after the test (see Fig. 12.2).

Together with this, we must remark that the residual weight gain cannot be used as a measure of the chemical stability of a pyrotechnic composition which contains volatile components.

The pressure developed by gaseous products of the decomposition reaction of the moistened composition is measured comparatively rarely; this method of checking the chemical stability of a composition has not been considered reliable up to the present time, since the hydrogen liberated in the decomposition of many compositions may be partially consumed in the reduction of the oxidisers (nitrates and others).

A complete analysis of the compositions¹ is usually not performed when testing for chemical stability not only because a great expenditure of time is required, but also for the reason that in most cases existing methods of analysis do not give results which are easy to relate to the actual changes in the compositions. Methods of analysing pyrotechnic compositions are given by Danner and Goldenson¹⁷¹, and in the first edition of our book (1943).

Section 3. Decrease in the efficiency of compositions during storage and their permissible storage lives.

Moistening pyrotechnic compositions usually leads to a decline in the special effect. Moist compositions burn more slowly, develop a lower temperature during combustion, and radiate a lesser quantity of light. A decrease in the "activity" of metals as a consequence of decomposition processes occurring in illuminating, tracer, and other compositions leads to the same results (see Table 12.1).

Therefore, for pyrotechnic products we must establish the maximum permissible storage life during which they may be used. This period, which depends upon the recipe of the composition

Activity of the metal powder (%)	Indices obtained on ignition of the composition	
	Intensity of light (k candlepower)	Combustion time (s)
95	56	5.6
88	35	6.4

Table 12.1 Efficiency of the effect of a composition
Ba(NO₃)₂ 64%; Mg 24%; Iditol 12%

and the thoroughness with which the product is sealed, may vary from one or two years to several decades.

A period of 10 years or more is considered as a normal storage life for pyrotechnic products.

The most stable compositions include signal flare compositions not containing metal powders. Among the illuminating and incendiary compositions the most chemically stable are those containing only aluminium as the basic fuel and barium nitrate as the oxidiser.

The addition of magnesium to such compositions reduces their chemical stability and reduces the possible storage lives of the pyrotechnic products containing them. Since compositions are more subject to the effect of moisture when powdered than when pressed, other things being equal, possible storage lives for photomixtures should be considered as somewhat shorter than those for other forms of pyrotechnic compositions.

If the product is tightly sealed, the permissible storage life may be very significant in most cases, running into decades.

In individual cases, after the permissible storage life has expired, pyrotechnic products may be subjected to tests for the efficiency of their effect and for the chemical stability of the composition. If the test results are satisfactory, the storage life of these products may be extended for a certain interval of time.

