

## Part Two

### Chapter XIII

#### Illuminating Compositions

##### Section 1. Special requirements imposed upon illuminating compositions.

The necessary information on optics and illumination engineering may be found in the books by Landsberg <sup>178</sup>, Meshkov <sup>182</sup>, and Gershun <sup>175</sup>.

Besides the general requirements placed upon compositions as indicated in the first part of this book, illuminating compositions must satisfy two additional special requirements.

1. The maximum quantity of luminous energy (measured in lumen-seconds) must be liberated during the combustion of a unit weight of illuminating composition. The light radiated, in addition to allowing adequate clarity of observations, must also permit the observer to distinguish colours correctly. Therefore, the radiation of an illuminating composition cannot be monochromatic - it must contain luminous energy in all parts of the spectrum.

For visual observation, it would be desirable to have a spectral distribution of radiation close to that of solar radiation to which the human eye is accustomed and adapted. The sensitivity of the human eye to light of various wavelengths is shown in Fig. 13.1.

However, we should indicate that although until recently the basic radiation detector has been the human eye, various physical radiant energy detectors such as photoelements, photoresistors, thermoelements, and others are now being used. Therefore, the spectral range of the radiation that is now required has expanded from 0.4 - 0.7  $\mu\text{m}$ , to 0.4 - 5  $\mu\text{m}$ .

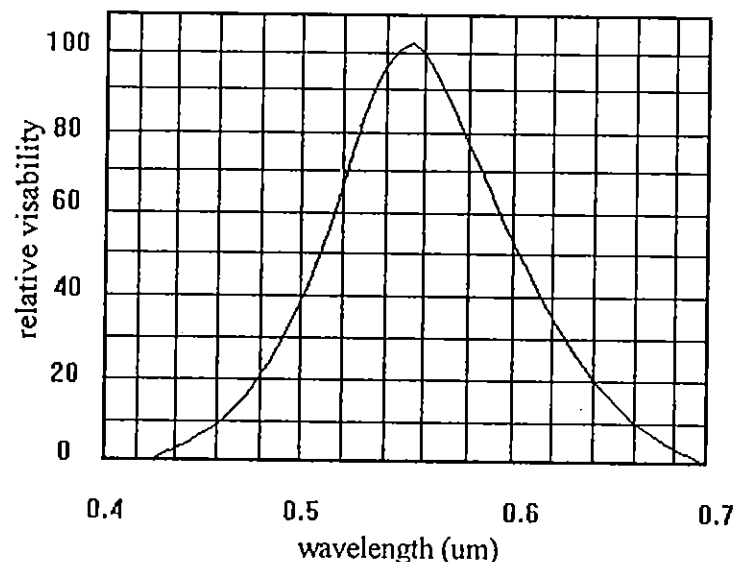


Fig 13.1 Visual acuity as a function of wavelength

2. The linear rate of combustion of compacted (pressed) illuminating compositions must be a few millimetres per second.

For large illuminating flares for illuminating bombs and projectiles, where an adequately long total time of combustion is required, special illuminating compositions are used having a rate of combustion in a compacted state of no more than  $1-2 \text{ mm s}^{-1}$ ; for small illuminating devices (illuminating stars for flare-pistol cartridges and rifle grenades), compositions are used which have a rate of combustion of  $5-10 \text{ mm s}^{-1}$  in a pressed state.

To fulfil the first requirement, it is necessary to select the components of the illuminating composition to provide the maximum quantity of heat as it burns. In practice, it has been shown that compositions should liberate at least  $6250 \text{ MJ kg}^{-1}$  on combustion to produce an adequately large quantity of radiant energy. This figure will serve as one of the selection criteria for components for an illuminating composition.

The luminous efficiency of an illuminating composition is a function of the quantity of thermal energy converted to luminous energy in the flame. The numerical value of the luminous efficiency obtained in the combustion of illuminating compositions is determined by many factors: the radiating ability of the products of combustion, the spectral composition of the radiation, the dimensions and optical properties of the flame, the rate of combustion of the composition, and so forth.

To obtain the greatest values of luminous efficiency we should select the appropriate recipe for the composition and a suitable design of the product to ensure that the flame formed on combustion of the composition has as high a temperature as possible, contains in itself an adequate quantity of solid or liquid particles that are good radiators of light when incandescent, and has the greatest possible radiation surface.

We should strive to increase the flame surface because the quantity of luminous energy radiated by a flame in unit time depends only upon the average brightness of the flame and upon the area of the radiating surface:

$$F(L) = \pi B.S$$

where  $F$  is the luminous energy in *lumens*

$B$  is the average brightness of the flame in *stilbs*

$S$  is the area of the radiating flame in  $\text{cm}^2$

This dependence is valid only to the first approximation since the radiation of the flame originates not just from the surface, but also from within. However, in many cases, at adequately large flame dimensions and with the large absorption of radiation which occurs in a flame which is typical of illuminating compositions, we should consider the sources as being surface radiation rather than volumetric radiation, since a considerable part of the radiation from the internal zones is absorbed by the outer layers of the flame.

Everything said above also refers to the power of the radiation flux beyond the spectral limits to which the human eye is sensitive. In this case, we should not speak of luminous efficiency, but of

radiation efficiency, indicating in each case the spectral interval of the radiation, which depends upon the radiation detector.

The radiant energy emitted by pyrotechnic flames is attenuated, in many cases, by the smokiness of the flame. The smoke is produced by finely dispersed particles of metal oxides which are cooled as they leave the flame. The presence of metal oxides ( $\text{MgO}$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{ZrO}_2$ , and others) in the flame is necessary, because they provide the bright glow of the flame. It is possible to reduce the smokiness of an illuminating composition, but not to free it entirely of smoke.

Because further explanations require the use of illuminating engineering terms, we will give below definitions of the basic illumination engineering units: the candlepower (or, more properly, candle), lumen, lux, and stilb.

1. The basic unit is an arbitrary one - the *new candle* (cp), equal to  $1/60$  of the intensity of light obtained from  $1 \text{ cm}^2$  of the surface of a black body at the temperature of the solidification point of platinum ( $2046.6\text{K}$ ), measured in a direction normal to this surface.
2. The unit of luminous flux is the *lumen* (L) - the flux radiated by a light source of 1 candle within a solid angle of 1 steradian. A source having an intensity of 1 candle in all directions is emitting a luminous flux of  $4\pi L = 12.5L$ .
3. The unit used for illumination is the *lux* - the illumination created by a luminous flux of 1 lumen uniformly distributed over an area of  $1 \text{ m}^2$ .
4. The *stilb* (sb) is used as a unit of brightness - it is the brightness of a uniformly bright surface in a normal direction emitting a light with an intensity of 1 candle from  $1 \text{ cm}^2$  in the same direction.

## Section 2. Thermal and luminescent radiation.

Each body continuously emits radiant energy if its temperature is above absolute zero. The process of conversion of thermal energy to radiant energy is called *thermal radiation*.

The origin of thermal radiation is the motion of the atoms and molecules in solids and liquids. A rise in the temperature of these bodies increases their energy because of the increase of the rate of motion (oscillatory and rotary) of the atoms or molecules.

Thermal radiation of solids and liquids is subject to the laws of radiation of a black body (see Section 2, Chapter VIII).

At high temperatures ( $500^\circ\text{C}$  or higher) thermal radiation increases, and produces a luminous radiation noticeable to the eye, i.e., the bodies begin to glow.

The presence of incandescent solid and liquid particles in the flame of an illuminating composition is unquestionably necessary, since the incandescent vapours and gases (without which no flame at all is possible) radiate themselves a comparatively small quantity of luminous energy. The glow of the solid and liquid particles present in the flame, as has already been said, obeys the laws of radiation of a black body.

Therefore the energy radiated by a flame rapidly increases as its temperature rises as indicated by the Stefan-Boltzmann law.

The brightness and luminous emission of a black body as a function of temperature are shown in

| Temperature<br>(K) | Brightness<br>(sb) | Luminous<br>emission<br>(L watt <sup>-1</sup> ) | Temperature<br>(K) | Brightness<br>(sb) | Luminous<br>emission<br>(L watt <sup>-1</sup> ) |
|--------------------|--------------------|-------------------------------------------------|--------------------|--------------------|-------------------------------------------------|
| 1,600              | 2                  | 0.2                                             | 2,800              | 1,552              | 13.9                                            |
| 2,600              | 44                 | 1.5                                             | 3,000              | 2,872              | 19.2                                            |
| 2,200              | 136                | 3.2                                             | 3,500              | 9,432              | 34.7                                            |
| 2,300              | 223                | 4.4                                             | 4,000              | $2.34 \cdot 10^4$  | 50.3                                            |
| 2,400              | 350                | 6.6                                             | 5,000              | $8.41 \cdot 10^4$  | 74                                              |
| 2,600              | 779                | 9.4                                             | 6,000              | $1.98 \cdot 10^5$  | 84                                              |

Table 13.1 Brightness and luminous emission of a black body at different temperatures

Table 13.1.

The spectral distribution of the radiation energy of a black body (at 3000K), the radiation from the flame of a typical illuminating composition, and a curve of visual acuity are shown in Fig 13.2.

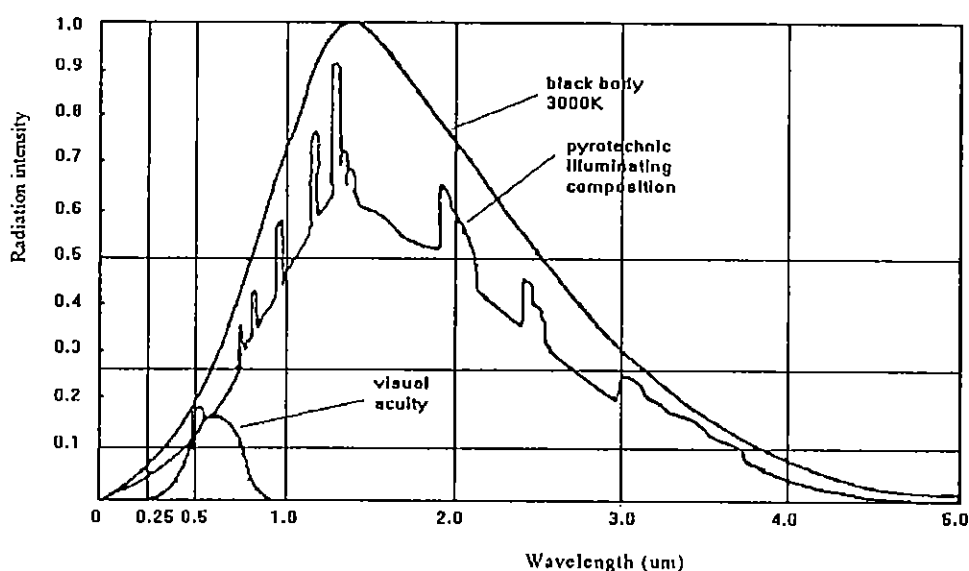


Fig 13.2 Distribution of energy throughout the spectrum

In general it is not advisable to use illuminating compositions with a flame temperature below 2000°C since the quantity of luminous energy emitted on burning is very small. At this temperature the luminous efficiency of a black body is only 0.7%.

Bodies that when heated give a spectral distribution similar to that of a black body of the same temperature, but with lower values of the ordinate are called *grey bodies*. Such radiators include carbon and certain ferrous-metal oxides. The total emissivity of graphite at 100 - 1500°C [sic] is 52% of the radiation of a black body at the same temperature.

The radiation spectrum of such white oxides as MgO or Al<sub>2</sub>O<sub>3</sub>, whose radiation is used in illuminating compositions, is continuous, like the spectrum of an black body; the energy radiated also increases rapidly as the temperature rises. The emissivity of white oxides, both monochromatic and total, is less than that of a black body.

| Oxide           | Formula                        | Temperature<br>(K) | Emissivity of oxides, as % emissivity of black body |     |     |     |     |     |     |
|-----------------|--------------------------------|--------------------|-----------------------------------------------------|-----|-----|-----|-----|-----|-----|
|                 |                                |                    | Wavelength (μm)                                     |     |     |     |     |     |     |
|                 |                                |                    | 750                                                 | 700 | 650 | 600 | 550 | 500 | 450 |
| aluminium oxide | Al <sub>2</sub> O <sub>3</sub> | 1,600              | 24                                                  | 25  | 31  | 40  | 53  | 81  | 90  |
| aluminium oxide | Al <sub>2</sub> O <sub>3</sub> | 1,900              | 31                                                  | 33  | 38  | 50  | 65  | 89  | 99  |
| magnesium oxide | MgO                            | 1,500              |                                                     | 23  |     | 35  | 45  | 65  |     |
| magnesium oxide | MgO                            | 1,900              | 37                                                  | 41  |     | 53  | 61  | 65  | 83  |
| thorium dioxide | ThO <sub>2</sub>               | 2,000              |                                                     | 47  |     | 48  | 49  | 49  | 50  |
| beryllium oxide | BeO                            | 1,700              | 6                                                   | 8   |     | 19  | 30  | 45  |     |
| chromic oxide   | Cr <sub>2</sub> O <sub>3</sub> | 1,500              |                                                     | 78  |     | 78  | 64  | 43  |     |

Table 13.2 Emissivity of metallic oxides

Some data on the emissivity (radiating capacity) of oxides at high temperatures are given in Table 13.2.

The oxides of magnesium and aluminium at high temperature radiate particularly intensely in the short wave region, where their radiation in certain cases becomes almost equal to that of a black body.

Luminescent radiation, as well as thermal radiation, is often observed in the flame of illuminating compositions. The origin of this luminescence is the change in the energy of the electrons in the atoms and molecules (excited as a result of the breaking or formation of chemical bonds).

The absence or presence of luminescent radiation in the flame of a pyrotechnic composition may be established by the Vavilov-Wideman criterion<sup>183</sup>, which sharply distinguishes between luminescence and other radiation processes. Vavilov considers luminescence as an excess over the thermal radiation of the body when this excess radiation has a finite duration considerably in excess of the period of the luminous oscillations.

The presence of individual lines and bands in the radiation spectra of flames of illuminating compositions cannot be considered an unquestionable proof that luminescence occurs since in any particular case the lines and bands may be due to thermal excitation of the atoms and molecules. The phenomenon of luminescence in the flame of illuminating compositions has still been little studied, and the effect of many "flame" additives on the luminous indices and the nature of the radiation of a flame still remains unclear in many respects.

### Section 3. Luminous characteristics of illuminating compositions.

The following quantities are determined experimentally in tests on illuminating stars or flares:

1. the weight of the burned composition  $m$ , grams;
2. the diameter  $d$  and height  $h$  of the star or flare burned;
3. the average luminous intensity (light intensity)  $I$ , candlepower;
4. the combustion time  $t$  of the star or flare, seconds;
5. sometimes the shape of the flame is recorded photographically, and the flame surface,  $\text{cm}^2$ , is calculated from the photograph.

We should note that neither the light intensity nor the combustion time can serve as characteristics for illuminating compositions; these quantities are characteristic of the complete device (flare, star) prepared from the illuminating compositions.

The illumination engineering characteristics referring directly to illuminating compositions are:

1. the specific integral quantity of light  $L_0$  (candle.s  $\text{g}^{-1}$ );
2. light output  $C$  (L/watt);
3. luminous efficiency  $K$  (in percent);
4. brightness of flame  $B$  (sb);
5. linear rate of combustion  $u$  ( $\text{mm s}^{-1}$ ) at a measured density of the compacted composition  $d$ .

In practice, the most important characteristics are the specific integral quantity of light and the linear rate of combustion.

Specific integral quantity of light. The quantity of luminous energy liberated in the combustion of 1 g of an illuminating composition is more properly expressed, of course, as lumen-seconds per gram ( $\text{L.s g}^{-1}$ ), but considering that in testing illuminating products it is not the luminous flux but the light intensity, in candlepower, that is measured, by the specific integral quantity of light we mean the quantity of candles per second obtained from 1 g of burnt composition:

$$L_0 = \frac{I \cdot t}{m} \text{ candle.s g}^{-1}$$

Example 1. Calculate the value of the specific integral quantity of light for an illuminating composition if a 50 g star pressed from it burns in 9 sec, developing a luminous intensity equal to 100,000 candlepower:

$$L_0 = \frac{100,000 \times 9}{50} = 18,000 \text{ candle.s g}^{-1}$$

The following formula is used to convert between lumens and candles:

$$F \text{ (lumens)} = 4\pi \cdot I \text{ (candles)}.$$

Light output. By light output  $C$  we mean the ratio of the total integral quantity of light  $L$  to the total energy  $Q$  expended to obtain the given quantity of light:

$$C = \frac{L}{Q} \text{ L/watt.}$$

The light output (luminous emission, light yield) is calculated from the experimental value of the luminous intensity with the formula:

$$C = \frac{I \cdot t}{m} \cdot \frac{4\pi}{q \cdot 1000} = \frac{I \cdot t \cdot 12.6}{m \cdot q \cdot 1000} \text{ lumen watt}^{-1}$$

where  $q$  is the quantity of heat, in kJ, liberated by 1 g of the illuminating composition during combustion.

Example 2. Calculate the light output for an illuminating composition if its specific integral quantity of light  $L_0$  is 18,000 candle-s g<sup>-1</sup>, and the heat of combustion  $q = 6.9$  kJ g<sup>-1</sup>.

$$C = \frac{18,000 \times 12.57}{6.9 \times 1000} = 32.8 \text{ lumen watt}^{-1}$$

Luminous efficiency. The luminous efficiency is a term used to denote the ratio of the light output of a given light source to the maximum light yield obtained in a 100% conversion of all the energy to luminous energy; for monochromatic light with a wavelength of 555 μm the latter quantity is equal to 621 L watt<sup>-1</sup>, from whence:

$$K = \frac{c \cdot 100}{621}$$

For a light source with a complex radiation spectrum, the calculation of luminous efficiency by such a formula is not possible. In this case, we must take into consideration the curve of visual acuity of the human eye (see Fig 13.2). As Zhiron indicates<sup>5</sup>, the luminous efficiency for white flames may be calculated, with some approximation, from the formula:

$$K = \frac{c \cdot 100}{248}$$

The average brightness of the flame is expressed in stilbs. It is calculated by dividing the intensity  $I$  of the light in candlepower, by the area  $S$  of the flame surface in cm<sup>2</sup>, as estimated from a photograph. This estimate is very approximate, since it is impossible to determine the true surface of the flame accurately; a flame has no true geometrical shape and its dimensions vary during combustion

$$B = \frac{I}{S} \text{ candle.s cm}^{-2}$$

The linear rate of combustion is expressed in  $\text{mm s}^{-1}$ . It is calculated by dividing the height of the flare or star being burned  $h$  in mm, by the duration of combustion  $t$  in seconds:

$$u = \frac{h}{t} \text{ mm s}^{-1}$$

The linear rate of combustion of a composition is not constant, but depends upon the density  $d$ ,

| Sequence | Type of Lamp | Light source                                                | Temperature (K) | Light output (L watt <sup>-1</sup> ) | Brightness (sb) |
|----------|--------------|-------------------------------------------------------------|-----------------|--------------------------------------|-----------------|
| 1        | filament     | gas-filled, 1 kw, incandescent lamp                         | 2,990           | 20                                   | 1,220           |
| 2        | filament     | gas-filled, 250w, special purpose, incandescent lamp        | 3,350           | 26                                   |                 |
| 3        | arc          | carbon arc                                                  | 4,200           | 12                                   | 70,000          |
| 4        | arc          | high intensity carbon arc                                   | 5,000           | 35                                   | 120,000         |
| 5        | vapour       | Na vapour; made by Svetotekhnik                             |                 | 50                                   | low             |
| 6        | vapour       | Super high pressure Hg lamp with water cooling, type SP-800 |                 | 62                                   | 91,000          |

Table 13.3 Some properties of electric lamps

and therefore the value of  $u$  should always be qualified "at (some specified) density of the composition".

Some characteristics of electric illumination sources are given in Table 13.3 to aid comparison of pyrotechnic and electrical sources.

The Table shows that the best light output is obtained from vapour lamps giving luminescent radiation.

#### Section 4. Compounding binary mixtures.

The basis of each illuminating composition is a binary mixture of fuel and oxidiser.

The total quantity of other components in an illuminating composition rarely exceeds 10-15%, and therefore the qualities of the composition are basically determined by the selection of the binary mixture of fuel and oxidiser. It is necessary to establish the best ratio in each case.

#### Selection of Fuel.

In the selection of fuels, we take into consideration the quantity of heat liberated on combustion, and also other physico-chemical properties both of the fuel itself and of its oxidation. For illuminating compositions we select elements for which the heat of formation  $Q_2$  of 1 g of oxide is not less than 8.4 kJ (2.0 kcal)..

From Table 3.1 it is apparent that such fuels include the following elements:

Li, Be, Mg, Al, Ca, Ti, Zr, H, C, B, Si, P.

In selecting a fuel we should consider that most, or a considerable part of the products of combustion of the composition must melt at a very high temperature and must not evaporate at the temperature of the combustion reaction, so that the flame will contain a considerable quantity of solid and liquid particles.

Therefore for illuminating compositions, it is necessary to select a fuel whose products of combustion would be high-melting substances that vaporise only with difficulty.

Hydrogen, carbon, and phosphorus do not satisfy this requirement, and therefore cannot be used as the basic fuel in illuminating compositions. We should note that the temperature developed on combustion of phosphorus in air does not exceed 1500°C.

All light sources based on the combustion of organic substances have very low light yields <sup>5</sup> (not more than 1 lumen watt<sup>-1</sup>). Elementary carbon gives a light yield of 1.9 L watt<sup>-1</sup> on combustion in an atmosphere of oxygen. In practice, it is scarcely possible to use beryllium or zirconium as fuels in illuminating compositions. As far as the quantity of energy liberated on combustion of these metals is concerned, only beryllium is of interest.

Data on the quantities of heat liberated in the combustion of certain compositions where the metals indicated are used as fuels and barium nitrate as an oxidiser, are given in Table 13.4.

A great quantity of luminous energy could be liberated on combustion of composition 2 only if the light yield for zirconium turned out to be considerably higher than for magnesium. Experience shows, however, that even under the most favourable conditions it is only slightly greater. Van Limpt indicates that in an atmosphere of oxygen the light output of zirconium is 36 L watt<sup>-1</sup>, while magnesium gives 28 L watt<sup>-1</sup>.

| No<br>of<br>composition | Composition<br>(%) |                                   | Heat of<br>combustion<br>(MJ kg <sup>-1</sup> ) |
|-------------------------|--------------------|-----------------------------------|-------------------------------------------------|
|                         | Fuel               | Ba(NO <sub>3</sub> ) <sub>2</sub> |                                                 |
| 1                       | Be 15              | 85                                | 8.11                                            |
| 2                       | Zr 46              | 54                                | 5.94                                            |
| 3                       | Mg 32              | 68                                | 6.94                                            |

Table 13.4 Heat of combustion of illuminants

Experiments by Bystrov on the photometry of illuminating compositions have shown that the specific luminous energy for these compositions is even smaller than might have been expected..

For a composition 49% Zr, 51% Ba(NO<sub>3</sub>)<sub>2</sub>,  $C = 20 \text{ L watt}^{-1}$ , which corresponds <sup>2</sup> to a specific integral light output  $L_0 = 7400 \text{ candle.s g}^{-1}$ .

So far, beryllium has not been tested as a fuel for illuminating compositions.

The remaining six elements Al, Mg, Ca, B, Si, and Ti are therefore the most promising for use as fuels in illuminating compositions. Certain of their characteristics are given in Table 13.5. As is apparent from the table, the greatest quantity of heat is obtained in the combustion of binary mixtures of barium nitrate with magnesium or aluminium. The oxides of these metals, moreover, have a good emissivity. All this, supports the preferential use of aluminium or magnesium, and their alloys or mixtures, as fuels in illuminating compositions.

| Binary mixture<br>(%) |                                   |    | Heat of<br>combustion<br>(MJ kg <sup>-1</sup> ) | Light<br>output<br>(L watt <sup>-1</sup> ) |
|-----------------------|-----------------------------------|----|-------------------------------------------------|--------------------------------------------|
| Fuel                  | Ba(NO <sub>3</sub> ) <sub>2</sub> |    |                                                 |                                            |
| Al                    | 26                                | 74 | 1.57                                            | 26                                         |
| Mg                    | 32                                | 68 | 1.65                                            | 28                                         |
| Ca                    | 43                                | 57 | 1.44                                            |                                            |
| B                     | 12                                | 88 | 1.37                                            |                                            |
| Si                    | 21                                | 79 | 1.28                                            |                                            |
| Ti                    | 31                                | 69 | 1.18                                            | 25                                         |

Table 13.5 Some characteristics of binary illuminating mixtures

The use of calcium or its alloys in illuminating compositions is not possible because of their ease of corrosion.

It is unlikely that any alloy containing a considerable quantity of boron or silicon will produce illuminating compositions with adequate light indices. Such alloys may only retard the combustion of illuminating compositions, which is necessary in certain cases.

The light output of titanium burnt in oxygen is found to be somewhat lower than that of magnesium and aluminium, under the same conditions (see Table 13.5). The quantity of

heat liberated in the combustion of titanium is also less than that from magnesium or aluminium. Therefore, there is no basis to expect good light indices from illuminating compositions made using metallic titanium or its alloys.

### Selection of Oxidiser

To obtain a high-energy illuminating composition, we should select for it an oxidiser requiring a minimum quantity of heat for its decomposition. Mixtures containing chlorates, however, are usually very sensitive to mechanical stimuli. Therefore, in spite of the fact that compositions prepared with these oxidisers liberate the greatest quantity of heat on combustion, they are seldom used as illuminating compositions. The same considerations also refer to a lesser degree to perchlorate oxidisers. Barium perchlorate, an extraordinarily hygroscopic substance, has not been used in pyrotechnics up to the present time.

In recent years indications have appeared in foreign literature (Tavernier <sup>185</sup>, Izzo <sup>12</sup>) of the possibility of using sodium perchlorate,  $\text{NaClO}_4$ , as an oxidiser in illuminating compositions. Actually, compositions based on this oxidiser may have high luminous indices; however  $\text{NaClO}_4$  is very hygroscopic (its hygroscopic point at room temperature is 69-73%), as a consequence of which reduced atmospheric humidity is necessary for the preparation of compositions to prevent their becoming moist. Izzo <sup>12</sup> gives a recipe for an illuminating composition for flares:  $\text{NaClO}_4$  65%, Al 30%, resin (gum arabic) 5%.

Nitrates are the most frequently oxidisers for illuminating compositions.

Stoichiometric mixtures of nitrates with magnesium or aluminium liberate from 6.3 to 8.4 MJ  $\text{kg}^{-1}$  heat on combustion.

| Oxidiser                   | Quantity of heat<br>required to liberate<br>1 g oxygen from the<br>oxidiser<br>(kJ) | Mg<br>(%) | Combustion reaction                                                               | Heat of<br>combustion<br>(kJ $\text{g}^{-1}$ ) |
|----------------------------|-------------------------------------------------------------------------------------|-----------|-----------------------------------------------------------------------------------|------------------------------------------------|
| $\text{Ba}(\text{NO}_3)_2$ | -5.0                                                                                | 32        | $\text{Ba}(\text{NO}_3)_2 + 5 \text{Mg} = \text{BaO} + 5 \text{MgO} + \text{N}_2$ | 7.1                                            |
| $\text{BaSO}_4$            | -15.5                                                                               | 23        | $\text{BaSO}_4 + 4 \text{Mg} = \text{BaS} + 4 \text{MgO}$                         | 5.0                                            |
| $\text{BaO}_2$             | -2.9                                                                                | 13        | $\text{BaO}_2 + \text{Mg} = \text{BaO} + \text{MgO}$                              | 2.9                                            |

Table 13.6 Thermochemical characteristics of binary mixtures

Of the nitrates, the two most frequently used in illuminating compositions are: barium nitrate, which is non-hygroscopic, and sodium nitrate, which is hygroscopic, but which has the advantage that it produces an intense radiation in the yellow part of the spectrum.

Mixtures of fuels with sulphates give less heat on combustion than do mixtures of nitrates with the same metals. Neither sulphates nor peroxides are advised as oxidisers in ordinary illuminating compositions.

Comparative characteristics of different barium compounds, and their heats of combustion with magnesium are given in Table 13.6.

As a general rule for the selection of oxidisers for illuminating composition, other things being equal, we should select salts of metals having low atomic weight, since they contain a great quantity of oxygen, and compositions prepared with them liberate a great quantity of heat on combustion.

| Composition of binary mixture<br>(%) |    |    |    | Density of<br>mixture<br>(Mg m <sup>-3</sup> ) | Compaction<br>factor | Linear<br>combustion<br>rate<br>(mm s <sup>-1</sup> ) | Specific<br>integral of<br>light<br>(candle.s g <sup>-1</sup> ) |
|--------------------------------------|----|----|----|------------------------------------------------|----------------------|-------------------------------------------------------|-----------------------------------------------------------------|
| Ba(NO <sub>3</sub> ) <sub>2</sub>    | 60 | Mg | 40 | 1.94                                           | 0.80                 | 8.0                                                   | 13,000                                                          |
| NaNO <sub>3</sub>                    | 60 | Mg | 40 | 1.71                                           | 0.85                 | 11.0                                                  | 15,200                                                          |
| KNO <sub>3</sub>                     | 60 | Mg | 40 | 1.69                                           | 0.87                 | 8.7                                                   | 10,600                                                          |
| NH <sub>4</sub> NO <sub>3</sub>      | 60 | Mg | 40 | 1.72                                           | 0.99                 | 1.8                                                   | 5,600                                                           |
| Ba(NO <sub>3</sub> ) <sub>2</sub>    | 60 | Al | 40 | 2.70                                           | 0.90                 | 4.9                                                   | 15,600                                                          |
| NaNO <sub>3</sub>                    | 60 | Al | 40 | 2.17                                           | 0.89                 | 2.6                                                   | 15,300                                                          |
| KNO <sub>3</sub>                     | 60 | Al | 40 | 2.18                                           | 0.94                 | 0.8                                                   | 1,300                                                           |
| NH <sub>4</sub> NO <sub>3</sub>      | 60 | Al | 40 | 2.02                                           | 1.00                 | 1.6                                                   | 800                                                             |

Table 13.7 Illuminating indices of binary mixtures with various oxidisers (24 mm diameter star in cardboard tube)

The undesirability of using the salts of heavy metals such as Pb(NO<sub>3</sub>)<sub>2</sub> as oxidisers has already been indicated. We also should mention that it is also undesirable to use potassium salts as oxidisers in illuminating compositions because of the low illumination indices of such compositions (see Table 13.7).

The use of sodium salts in illuminating compositions, on the contrary, increases their illumination indices. Sodium nitrate is one of the best oxidisers for high illumination indices of these compositions (see Table 13.7).

Barium and strontium salts as oxidisers give similar values of the specific integral quantity of light of compositions, and these values are quite high. Barium salts give the flame a slightly greenish tint, and strontium salts impart a pale rose colour to the flame. Strontium nitrate is rarely used as an oxidiser in illuminating compositions because it is more hygroscopic than barium nitrate.

#### Establishing the Quantitative Proportions of Oxidiser and Fuel in a Binary Mixture

Illuminating compositions are either stoichiometric or fuel rich to allow the excess fuel to oxidise in atmospheric oxygen. Thus, for example, the content of magnesium or Al alloy in ordinary mixtures for illuminating compositions may reach 50-60 percent in some cases.

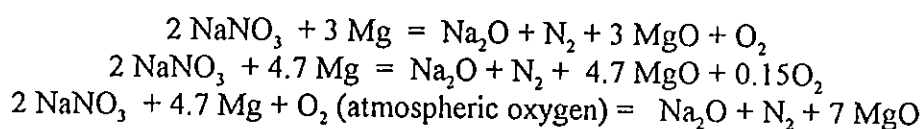
However, it is not always possible to use binary mixtures with a high content of metallic powders, since the rate of combustion of illuminating compositions increases considerably as the content of metallic fuel in them increases.

The illumination characteristics of certain binary mixtures containing magnesium powder are given in Table 13.8.

| Number of composition | Composition       |    | Density<br>(Mg m <sup>3</sup> ) | Linear combustion rate<br>(mm s <sup>-1</sup> ) | Specific integral quantity of light<br>(candle.s g <sup>-1</sup> ) | Heat of combustion<br>(kJ kg <sup>-1</sup> ) | Light output<br>(L watt <sup>-1</sup> ) |
|-----------------------|-------------------|----|---------------------------------|-------------------------------------------------|--------------------------------------------------------------------|----------------------------------------------|-----------------------------------------|
|                       | (%)               |    |                                 |                                                 |                                                                    |                                              |                                         |
|                       | NaNO <sub>3</sub> | Mg |                                 |                                                 |                                                                    |                                              |                                         |
| 1                     | 70                | 30 | 1.9                             | 4.7                                             | 9,800                                                              | 1.3                                          | 22.6                                    |
| 2                     | 60                | 40 | 1.7                             | 11.0                                            | 15,200                                                             | 2.0                                          | 25.0                                    |
| 3                     | 50                | 50 | 1.7                             | 14.3                                            | 20,000                                                             | 2.6                                          | 23.0                                    |

Table 13.8 Illumination characteristics of binary mixtures containing magnesium (24 mm cardboard cases)

The combustion reaction of the mixtures whose characteristics are included in Table 13.8 may be represented, approximately, by the equations:

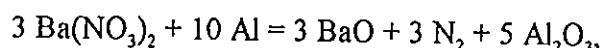


The average brightness of the flame during combustion of mixture 3 in Table 13.8 amounts to about 600 sb according to our calculations.

The light output of pyrotechnic compositions, expressed in L watt<sup>-1</sup>, is of the same order as for incandescent electric lamps (see Tables 13.8 and 13.3).

Data showing the dependence of the illumination indices of binary mixtures as a function of their aluminium content when burned as 24mm stars in cardboard sheaths are given in Table 13.9.

The combustion reaction of composition 1 (see Table 13.9) may be expressed by the equation



with a calculated heat liberation of 6.7 kJ g<sup>-1</sup>.

Compositions 2-5 contain an excess of fuel which is partly oxidised by the atmospheric oxygen, and partly forms the nitride AlN. As is apparent from Table 3.9, the rate of combustion increases as the aluminium content of the composition increases, but only up to a certain limit (45 percent); compositions with a moderate excess of fuel (aluminium content 36-39 percent) show better illumination indices.

| Number of composition | Composition                       |         | Density               | Linear combustion rate | Light intensity | Specific integral quantity of light | Light output            |
|-----------------------|-----------------------------------|---------|-----------------------|------------------------|-----------------|-------------------------------------|-------------------------|
|                       | (%)                               |         | (Mg m <sup>-3</sup> ) | (mm s <sup>-1</sup> )  | (kcandle)       | (candle.s g <sup>-1</sup> )         | (L watt <sup>-1</sup> ) |
|                       | Ba(NO <sub>3</sub> ) <sub>2</sub> | Al dust |                       |                        |                 |                                     |                         |
| 1                     | 74                                | 26      | 2.7                   | 3.0                    | 51              | 13,800                              | 27                      |
| 2                     | 64                                | 36      | 2.7                   | 5.0                    | 86              | 14,500                              |                         |
| 3                     | 61                                | 39      | 2.6                   | 5.5                    | 87              | 13,300                              |                         |
| 4                     | 55                                | 45      | 2.6                   | 6.6                    | 82              | 10,700                              |                         |
| 5                     | 49                                | 51      | 2.6                   | 5.9                    | 60              | 8,600                               |                         |

Table 13.9 Illumination indices of mixtures of barium nitrate and aluminium

### Section 5. Multi-component illuminating compositions

As has already been said, the basic indices of an illuminating composition are the specific integral quantity of light and the linear rate of combustion.

A real recipe for an illuminating composition is developed by working from a given linear rate of combustion, striving in this case to obtain a value of the specific integral quantity of light of no less than 20,000-25,000 candle-sec g<sup>-1</sup>. Various organic substances such as resins, mineral oils, drying oils paraffin, stearin, and so forth are added to the binary mixtures of oxidiser and metal powder described above to retard the process of combustion of the composition, give it strength in a pressed (compacted) form, and increase its chemical stability.

Usually, multi-component compositions constructed in such a manner have a considerably lower linear rate of combustion than the corresponding binary mixtures, and also a considerably lower light intensity. The introduction of organic substances reduces the specific integral quantity of light of compositions containing magnesium powder to a much lower degree than is observed for compositions containing aluminium dust or aluminium powder as a fuel.

Ellern <sup>9</sup> gives two recipes for illuminating compositions for parachute flares (in percentages by weight). He indicates that a polymerisation catalyst is added to the polyester resin. Composition I burns faster than composition II, and gives a greater light intensity per cm<sup>2</sup> of burning surface.

|                    | I  | II |
|--------------------|----|----|
| magnesium          | 52 | 48 |
| sodium nitrate     | 39 | 42 |
| polyester resin    | 9  | 8  |
| polyvinyl chloride | -  | 2  |

The following recipe may also serve as an example of an illuminating composition containing sodium nitrate:

|                |    |
|----------------|----|
| magnesium      | 45 |
| sodium nitrate | 48 |
| binding agent  | 7  |

Stars weighing 36-38 g of this composition burn for 10 seconds and give a light intensity of about 120,000 candlepower. From this, the specific integral quantity of light obtained is equal to  $L_0$  approximately 30,000 candle.s g<sup>-1</sup>.

Ellern <sup>9</sup> also gives recipes of illuminating compositions using barium nitrate as an oxidiser (with a small admixture of strontium nitrate):

|                   | III | IV |
|-------------------|-----|----|
| magnesium         | 52  | 17 |
| aluminium         | -   | 15 |
| barium nitrate    | 38  | 55 |
| strontium nitrate | 7   | 5  |
| linseed oil       | 3   | 3  |
| asphaltite        | -   | 5  |

Composition IV has almost the same rate of combustion as composition II, but a lower light intensity.

As an example of a three-component composition, we may give a composition consisting of 30% magnesium, 66% barium nitrate, and 4% iditol.

Compositions containing aluminium frequently spark vigorously on combustion, particularly when coarsely pulverised aluminium is used, or when a large quantity of organic binders is added. The phenomenon of sparking is caused by the discharge from the flame of particles of unburned metal and glowing slag (ash) by the gases formed as the composition burns. On careful observation through blue goggles we may note that the glowing particles of metal have a greater brightness and sharply different colour from the dark-red particles of unburned slag.

The discharge of unburned particles of metal from the flame is called "forced" sparking, to distinguish it from the other type of sparking - slag sparking.

The reduction of the illumination characteristics of compositions when organic binders are added to compositions containing aluminium is due most probably to the fact that complete combustion of the metal does not occur in the presence of "forced" sparking; the combustion temperature of the composition therefore drops considerably.

The oxygen balance of illuminating compositions usually becomes sharply negative when a considerable quantity of organic matter is added to them.

Thus, we must assume that it is undesirable to add more than 5-6% of organic binders and organic substances with similar properties to illuminating compositions. We should remember this even more strongly because of the fact that other methods of retarding the combustion of such compositions have long been known that are entirely applicable, in particular, to illuminating compositions, namely: 1) change the particle size of the metal powders; 2) add sulphur, a low-melting and low-activity substance, to aluminium compositions.

The oxidation of aluminium in illuminating compositions containing sulphur is partially due to the sulphur, and aluminium sulphide  $\text{Al}_2\text{S}_3$  is formed. But aluminium sulphide is only an intermediate reaction product, since it oxidises with atmospheric oxygen in the outer zone of the flame. The melting point of  $\text{Al}_2\text{S}_3$  is  $1100^\circ\text{C}$ .

The reaction of aluminium and sulphur is:



and it occurs easily at high temperatures. This may explain why illuminating compositions containing sulphur spark comparatively little during combustion when coarse grained aluminium has been used in their preparation. The addition of more than 10% sulphur to aluminium compositions leads to a reduction in the illumination indices of the preparations.

Practice has shown the addition of sulphur to aluminium illuminating compositions is entirely feasible. The following World War I illuminating composition gave  $u = 1.7 \text{ mm s}^{-1}$ ;  $L_0 = 11,699 \text{ candle.s g}^{-1}$  with a flare 10.5 cm in diameter and at a density of  $2.3 \text{ Mg m}^{-3}$ :

|                  |    |
|------------------|----|
| aluminium powder | 8  |
| aluminium dust   | 10 |
| barium nitrate   | 76 |
| sulphur          | 4  |
| castor oil       | 2  |

A few percent of the so-called "flame additives" are frequently added to illuminating compositions to increase their illumination indices. Non-hygroscopic, low-solubility sodium salts, such as sodium fluoride, cryolite, etc., are most frequently used for this purpose. Such additives rarely increase the illumination indices by more than 15-20 percent. These additives (in quantities of a few percent) have no great influence on the rate of combustion of illuminating compositions.

In some cases various greasing agents are added to reduce the dust losses of compositions containing finely pulverised components (such as aluminium dust, for example). Various oils are used more often than other materials. The introduction of greasing agents also helps increase the stability of the composition during storage.

Such substances as stearic acid or the stearates of certain metals are added to illuminating compositions to protect the metallic powders against corrosion and also to retard the process of combustion. To obtain Mg and Al powders that are stable in storage with respect to water and aqueous solutions of salts, it has been proposed (American patent 2.894.864 (1959)) that the processing of powders be accomplished by a 10% solution of stearic acid in a 1:1 benzene-alcohol solution.

As an additional oxidiser in illuminating compositions, various explosives (nitro compounds), may be used together with the nitrates of metals. Thus, the following recipe for an illuminating composition is given in Norwegian patent 99.194 (1961) :

|                       |        |
|-----------------------|--------|
| alkali metal nitrates | 50-60% |
| dinitrotoluene        | 13-25% |
| magnesium             | 20-28% |
| cellulose             | 4-8%   |

During World War II the German army used gypsum illuminating compositions<sup>9</sup>. Gypsum, with its included water, was used in this case both as a binder and as an oxidiser, partly replacing the sodium nitrate.

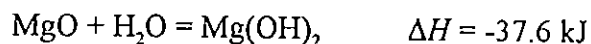
|                                         | V  | VI |
|-----------------------------------------|----|----|
| Mg - Al alloy                           | 41 | -  |
| magnesium                               | -  | 40 |
| NaNO <sub>3</sub>                       | 11 | 13 |
| CaSO <sub>4</sub> · 0.5H <sub>2</sub> O | 32 | 40 |
| water                                   | 1  | 7  |
| CaCO <sub>3</sub>                       | 15 | -  |

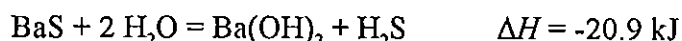
The following recipe is for an effective illuminating composition that burns under water<sup>9</sup>:

|                                   |     |
|-----------------------------------|-----|
| Magnesium                         | 16% |
| Aluminium                         | 12% |
| BaSO <sub>4</sub>                 | 40% |
| Ba(NO <sub>3</sub> ) <sub>2</sub> | 32% |

8 parts of linseed oil and 1 part of MnO<sub>2</sub> are added as a binder. This is an experimental recipe from the time of World War II.

In the combustion of such a composition in water, secondary weakly exothermic reactions may occur:





## Section 6. The bases of photometry and radiometry of the flames of pyrotechnic compositions.

The radiant energy of pyrotechnic flames is used in practice for effects on the human eye, on photographic materials, on photo-elements, and on other electronic devices.

As is apparent from Fig. 13.2, the radiation energy of illuminating compositions is distributed along the spectrum in such a manner that its main part falls in the infrared (IR) part of the spectrum, and the maximum radiation falls in the wavelength range 1.2 - 1.8  $\mu\text{m}$ .

Because of the development of infrared engineering, this part of the radiant energy, which previously was lost, turned out to be useful for night photography, seeing in darkness, etc.<sup>177, 181</sup>.

Pyrotechnic radiators have certain advantages over electric sources of radiant energy. In the form, for example, of illuminating or signal cartridges, they have small dimensions, do not require electric power, and are easily discharged at an enemy position; their shortcoming is the brief duration of their action.

On the problem of IR-radiation sources and their use in war, see Ango<sup>172</sup>, Deribere<sup>176</sup>, Ivanov and Tyapkin<sup>177</sup>, Margolin and Runyantsev<sup>181</sup>.

The quantitative characteristics of the light source and estimation of the intensity of illumination as it affects the human eye, is described in terms of quantities already known to us (see Section 1 of this chapter): candle, stilb, and lux.

To describe the effect of radiation on various photoelectronic devices, the following terms are used: radiation intensity, energy brightness, and irradiancy. The mutual connection and dimensions of these quantities are described in courses on optics<sup>178</sup>; certain handbook data are given in Table 13.10.

The basis of practical photometry and radiometry of flames is the principle of measuring the illumination or irradiancy, as a measure of the effect on the appropriate detector.

With respect to illumination or irradiancy, light force (radiation) is calculated using the equation  $I = E.R^2$ .

Radiant energy detectors for the visible part of the spectrum are basically photo elements. For IR radiation, thermoelements are used together with photoelements and photoresistors, as well as bolometers and optical-acoustic detectors.

The basic characteristics for any radiation detector are its spectral and integral sensitivity, and also its stability in time.

| Energy quantity                  | Formula                                     | Units                           |
|----------------------------------|---------------------------------------------|---------------------------------|
| radiation intensity <sup>1</sup> | $I_{\text{en}} = \frac{d\Phi}{d\omega}$     | watts per steradian             |
| irradiancy <sup>2</sup>          | $E_{\text{en}} = \frac{d\Phi}{dS}$          | watts/cm <sup>2</sup>           |
| energy brightness <sup>3</sup>   | $B_{\text{en}} = \frac{dI_{\text{en}}}{dS}$ | watts/steradian/cm <sup>2</sup> |
| <sup>1</sup> radiant intensity   | $J, \text{ W sr}^{-1}$                      |                                 |
| <sup>2</sup> radiant emittance   | $W, \text{ W cm}^{-2}$                      |                                 |
| <sup>3</sup> radiance            | $N, \text{ W cm}^{-2} \text{ sr}^{-1}$      |                                 |

Table 13.10 Dimensions of Radiation Units  
(Note: modern terms given as footnotes for reference)

Spectral sensitivity is the sensitivity of a detector to radiation of different wavelengths; it is determined by the nature of the substance from which the light-sensitive layer in the instrument is made, and may vary within wide limits, from 0.3 to 5  $\mu\text{m}$ . (Fig 13.3).

Radiant energy detectors such as thermoelements, bolometers, and optical-acoustic detectors do not have any selectivity to radiation in different parts of the spectrum. [?]

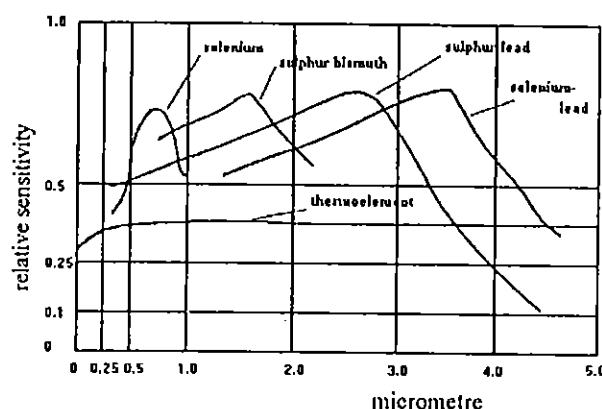


Fig 13.3 Spectral sensitivity of photoelements

In practice it is frequently required to measure radiation intensity in a narrow region corresponding to the sensitivity of the human eye, photographic material, or an optical system, rather than over the wide spectral range perceived by the detector. To accomplish this, light filters are used, which pass only the radiation of a definite spectral composition. Coloured glasses are used for the visible part of the spectrum, special glasses, mica, lithium fluoride, rock salt, sylvite; potassium bromide and others are used for IR filters.

Photoelements convert radiant energy into electrical energy directly; this phenomenon is called the photoelectric effect. The magnitude of the photoeffect is characterised by two laws:

1. Stoletov's law: the photo-electric current is directly proportional to the radiant flux falling on the photoelement;

2. Einstein's law: the maximum energy of photoelectrons increases linearly as the frequency of the incident light increases, regardless of its intensity. By measuring the photocurrent formed in a photoelement, we may determine the illumination (irradiancy) created by the radiation.

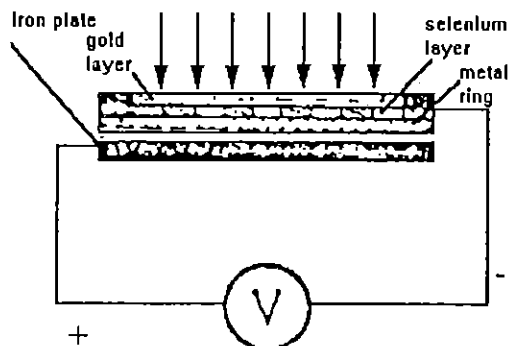


Fig 13.4 Selenium photoelement

photoelements supplied with appropriate light filters, and an electric current measuring device for measuring the photo-currents.

Selenium photoelements have come into extensive use for the photometry of pyrotechnic flames <sup>179</sup>.

A photoelement (Fig. 13.4) is a circular iron plate with a thickness of 1-2 mm, and a diameter of 30-60 mm, on which is applied a thin layer of selenium (or some other light-sensitive material). A semi-transparent layer of gold is applied by cathode spraying to the upper layer of selenium; on this layer a metal ring is placed as a conductor. Between the selenium and the semi-transparent layer a barrier layer, or barrier film, is formed, which does not permit electrons to pass from the semi-transparent layer through the selenium to the iron plate. The barrier layer does not hamper the reverse motion of the electrons (from the iron plate through the selenium to the semi transparent layer).

If light falls on the photoelement from the side of the semi-transparent layer, it, releases electrons from the selenium which may move only from the selenium to the semi-transparent layer; the latter becomes negatively charged, and the iron plate positively charged. By closing the ring with the iron plate attached to a wire we obtain an electric current in the circuit, the value of which remains proportional to the quantity of light falling on the photoelement for a comparatively long period of time.

The current obtained is determined by two basic characteristics:

1. general, or integral, sensitivity
2. spectral sensitivity of the photoelement.

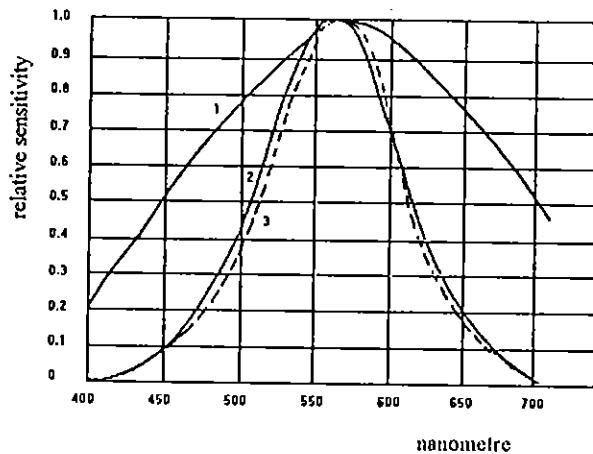


Fig 13.5 Spectral sensitivity of a selenium photoelement

The Integral sensitivity is the ratio of the current obtained in the photoelement circuit to the luminous flux causing it. For modern selenium photoelements, it is 400-500  $\mu\text{A lumen}^{-1}$  for a photoelement area of about 10  $\text{cm}^2$ .

As is apparent from Fig 13.5, the spectral sensitivity of a selenium photoelement (curve 1) is close to that of the average human eye (curve 2). To match the sensitivity of the photoelement exactly to that of the human eye, yellow-green compensating filters are used (curve 3). Compensating light filters are selected individually for each photoelement in such a way that a considerable attenuation of the

intensity of the light will fall in the wavelength regions 400-530 nm and 580-700 nm. For

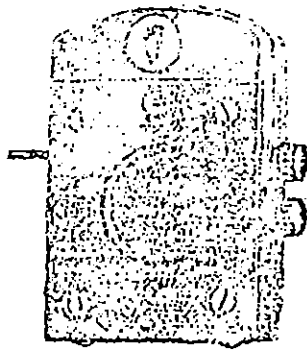
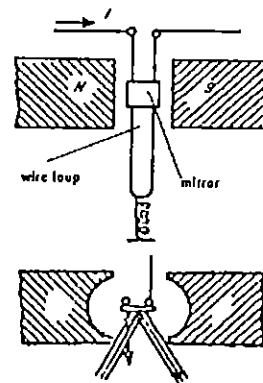


Fig 13.6 Selenium photoelement in a housing



13.7 Oscillograph loop circuit

convenience in use, a photoelement with its light filters is placed in a housing (Fig. 13.6), which has an optical sight for precision aiming, contact screws for attaching wires, and a threaded aperture for mounting it on a stand.

Electric measuring instruments used in photometry (radiometry) are in the physical shape of either a needle galvanometer or a loop oscillograph<sup>174</sup>. The main part of the oscillograph is a loop or vibrator (Fig. 13.7). As is apparent from the figure, a loop of thin wire is placed in the magnetic field of a permanent magnet. A small mirror of square or round shape, with an area of about 1  $\text{mm}^2$ , is attached to the loop. When a current flows from the photoelement through the wire, the couple originating from the reaction between the current and the magnetic field rotates the loop together with the mirror around its vertical axis. If the loop mirror is illuminated, the rotation of the reflected ray will show the angle of rotation of the mirror.

A diagram of a device for measuring light intensity is given in Fig. 13.8. The beam of light from the source passes through the diaphragm in the loop mirror. The reflected beam is focused on the

lens and falls on moving photographic paper or photographic film. During combustion of the flare the photocurrent changes as a consequence of the change in illumination of the photoelements and an oscillogram of the process of combustion is recorded on the photographic film which moves at an uniform rate.

The following requirements are imposed upon electric measuring instruments used for measuring photocurrents:

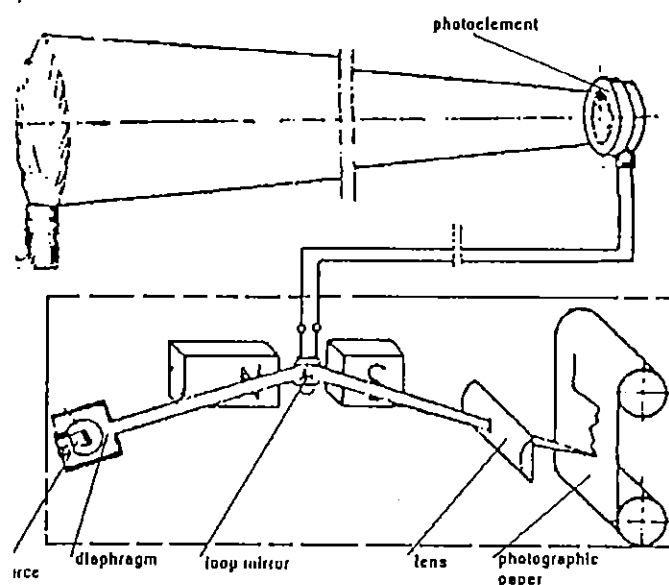


Fig 13.8 Diagram of measurement of a light source

1. the sensitivity to current must be not less than  $1 \cdot 10^{-6}$  A/division of the scale or per millimetre of width of the oscillogram;
2. the minimum internal resistance must not exceed 100 ohms;
3. the temperature coefficient, i.e., the variation in the readings caused by the change in temperature must be not more than 0.2% per °C;
4. the number of divisions of the scale of the galvanometer must not be less than 50, and the height of the ordinate of an oscillograph must not be less than 35 mm;
5. the minimum period or damping must be: for needle-type instruments 3-5 sec, for loop oscillographs not less than 25 cps;
6. there must be a method of adjusting the needle or light spot.

The instruments fabricated by industry and satisfying these requirements are the POB-14 (N-700) and the M-82 millivolt-milliammeter.

In order to convert from electric quantities to light (or energy) quantities, we must calibrate a detector with an electric measuring instrument and a standard radiation source.

Thus, the calibration lies in determining the value of the divisions of the galvanometer scale or the values of 1 mm of height of an oscillogram, in lux or watts/mm. As standard visible radiation sources, light-measuring lamps are used, and as standard infrared radiation sources various models of a black body.

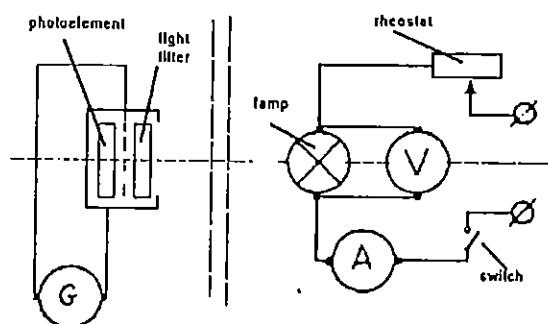


Fig 13.9 Diagram for the calibration of a luxmeter

In the first case, calibration consists of varying the distance between the lamp and the photo-sensitive layer of the light detector to produce different levels of illumination. The calibration is performed for 6 to 10 values of illumination, under the following conditions:

1. the illumination at the surface of the light detector must not exceed 2000 lux;
2. the readings of the instruments must be within limits of 10-90% of the width of the oscillograph paper or the galvanometer scale;
3. the light-measuring lamp must be warmed up, and the light detector exposed to the light for 3-5 minutes.

Calibration of luxmeters and radiometers is performed on the so-called photoelectric bench, which is a guide rail, on which is fastened the stand for the lamp and a carriage for installation of the light detector and a number of auxiliary attachments (distance measuring device, screens, illuminators, etc.), as in Fig. 13.9. The photometric system used for calibration must allow the light detector to be moved along the optical axis from 0.2 to 3 m. The accuracy of measurement of the distance between the lamp filament and the light-sensitive layer must be better than 1 mm. Also the light detector must be protected against reflected and incident light falling upon it and the lamp filament and the light-sensitive layer of the light detector must be parallel.

The following successive operations must be carried out during calibration:

1. install the lamp and the light detector on the photometric bench;
2. hook up the light detector to one of the oscillograph vibrators or to a galvanometer;
3. with no light (?), inscribe the zero line on the oscillograph or, having removed the catch, place the galvanometer needle at zero;
4. write the deviation of the light beam or the baffle or pointer of the galvanometer caused by different illumination;
5. develop the film, measure the deviations on the oscillogram, and construct a graph in millimeters (Fig. 13.10).

Sometimes a graph is not constructed, but the value of a division of the instrument in lux is determined, but this is less accurate, since in this case the average value of a division is assumed.

This problem is treated by Meshkov<sup>182</sup>, Bur'yanov<sup>174</sup>, Bel'skiy and Bessekerskiy<sup>173</sup>, Luk'yanov<sup>179</sup>, Margolin and Rumyantsev<sup>181</sup>, Shkurin<sup>184</sup>, Landsberg<sup>178</sup>, and Zhironov<sup>5</sup>.

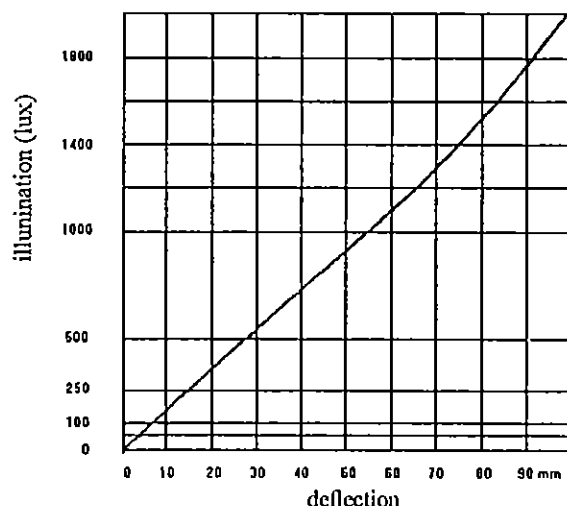


Fig 13.10 Graph of calibration of a luxmeter

**Section 7. Effect of ignition conditions on the radiation intensity of a flame and apparatus for static tests.**

The radiation intensity of a flame is determined by the temperature and spectral composition of the radiation, and also by the flame's dimensions and shape. The first two factors depend basically upon the recipe of the composition and the dimensions and shape of the flame not only upon the diameter of the flare, but also upon the combustion conditions of the composition.

Depending upon the conditions created in the combustion of the composition, the flame of pyrotechnic products may take various shapes and dimensions. Blowing on the flame with air at a high velocity (more than  $100 \text{ m s}^{-1}$ ), burning compositions in a vacuum or under pressure, and absorption of the radiation by the products of combustion of the compositions (by the smoke) have an especially great effect on radiation intensity.

The radiation of a flame is affected to a lesser degree by its reflection by surrounding objects, the transparency of the air, temperature and the humidity of the atmosphere, but these factors can, under certain conditions, affect the radiation intensity within wide limits, and introduce significant errors into the measurement of it.

It is advisable to determine the efficiency of flame pyrotechnic compositions under field conditions, but such experiments are costly and time consuming, and it is practically impossible to guarantee stability and reproducibility of the results.

Photometric chambers are comparatively simple devices for measuring the intensity of the light and the time of combustion of pyrotechnic products. These devices stabilise the effect of external conditions to some extent, allow removal of the smoke as the product burns, and allow the tests to be performed in the daytime.

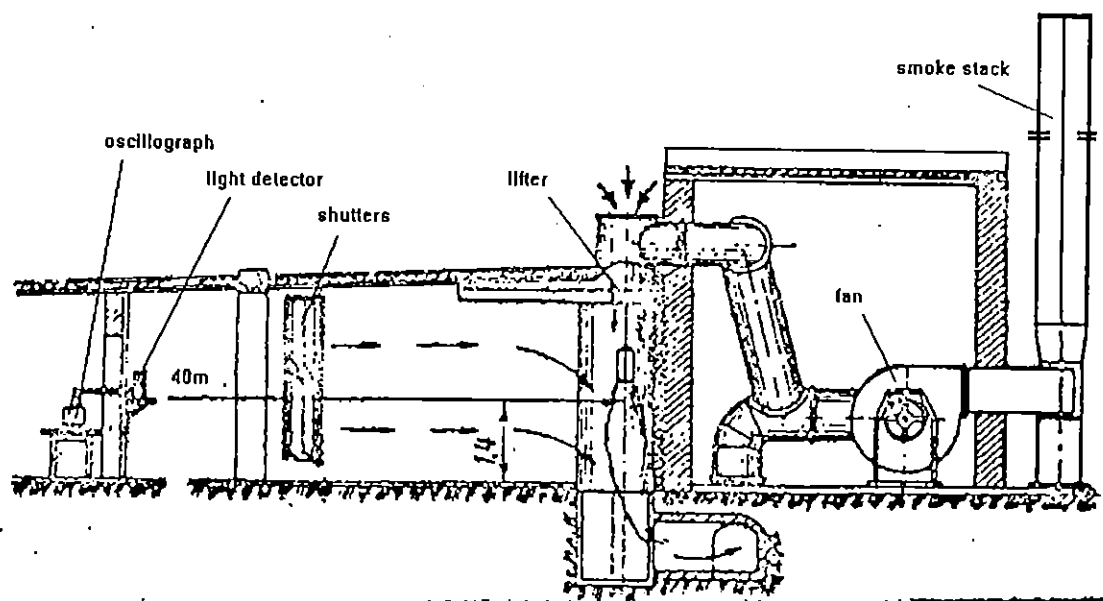


Fig 13.11 Diagram of a photometric chamber

A typical large photometric chamber includes a furnace for burning the composition, a tunnel (for photometry), and a forced ventilation system (Fig. 13.11). This photometric chamber has a tunnel of rectangular cross-section, with a width of 2-3 m, a height of 2.5-4 m, and a length of 40-50 m, ending, at one end, with compartments for the apparatus and personnel, and at the other end with a furnace for burning the compositions and a ventilation system.

The combustion furnace is a vertical shaft of round or rectangular shape, with its interior lined with refractory brick and equipped with air lines for feeding in air and removing products of combustion. The ventilation system to remove the combustion products and to provide the necessary velocity of air around the burning product usually consists of two powerful fans (VRS No 8 or No 10), air lines, and a smoke stack.

An essential shortcoming of a photometric chamber is that the walls become coated with white slag which causes multiple reflections of the light from the flame which may exceed the actual light emitted by the flame. The reflecting efficiency of the walls does not remain constant, but can vary from 40 - 150%, leading to considerable errors in the measurements.

Recently, a method of determining the reflecting capability (coefficient of multiple reflection  $\eta$ ) of the furnace during the tests has been used: the illumination created by a filament lamp with an output of not less than 5 kw is measured using a sensitive photometer. The lamp is installed in the combustion furnace in place of the product to be burned. Both the direct light from the lamp and the light multiply reflected from the walls of the furnace fall on the light detector. The coefficient of multiple reflection is calculated with the formula:

$$\eta = \frac{I_t - I_1}{I_t}$$

where  $I_t$  is the total light output (lamp + reflections)  
 $I_1$  is the light output of the lamp alone.

The coefficient of multiple reflection thus determined is used to apply a correction to the measured radiation intensity.

The pyrotechnic product is placed in the air flow in a manner dependant upon its intended use (Fig. 13.12). The arrangement of pyrotechnic products during photometry is of significance, since a pyrotechnic flame, like any other real light source, radiates a different quantity of light in different directions <sup>2, page 192</sup>.

When a pyrotechnic is burning not only the light output is fixed, but also the time of combustion and nature of combustion (uniformity, pulsation, etc.).

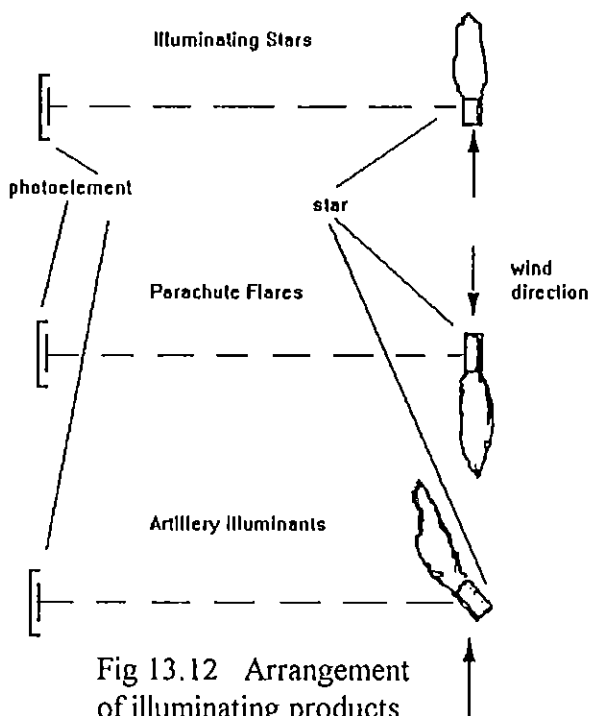


Fig 13.12 Arrangement of illuminating products during photometry

Before the photometric measurements are started, the distance between the photoelements and the product is calculated in accordance with the formula:

$$l = \sqrt{\frac{I}{a \cdot n}}$$

where  $l$  is the distance in metres  
 $I$  is the assumed light intensity, candle  
 $a$  is the value of one scale division, lux  
 $n$  is the desired galvanome

ter or oscillograph deflection.

The following sequence of operations is carried out in photometry:

1. the product is placed at the point selected for burning as indicated in Fig 13.12;
2. the photoelement (photoelectric cell) is installed at the necessary distance and aimed at the product in such a manner that the flame appears at the intersection of the cross-hairs of the optical sight;

3. the functioning of the luxmeter is checked, by illuminating the photoelement and at this time observing whether or not the galvanometer needle or the oscillograph light spot is deflected to the desired amount;
4. the fan is turned on;
5. the product is ignited;
6. the beginning of combustion is marked with a stop watch;
7. the readings of the galvanometer are recorded and the nature of the combustion observed;
8. the end of combustion is marked by stopping the stop watch.

The galvanometer readings are taken at intervals of 3 - 5 seconds; the deflections are measured at the same time intervals (see below).

From the inverse square law

$$E = I/R^2 \text{ so } I = ER^2.$$

where  $E$  is the illumination in lux

$I$  is the light intensity in candlepower

$R$  is the distance in metres.

The average illumination is determined as the average magnitude of all galvanometer deviations recorded, or of all oscillogram ordinates, multiplied by the value of a division on the scale:

$$E_{av} = \frac{n_1 + n_2 + n_3 + \dots + n_i}{i} \cdot a$$

Where  $n$  represents the numerical values of individual galvanometer readings or oscillograph ordinates;  $i$  is the total number of readings; and  $a$  is the value of a division of the scale. By substituting the value  $E_{av}$  into the formula for the illumination law, we obtain the average light intensity:

$$I_{av} = \frac{n_1 + n_2 + n_3 + \dots + n_i}{i} \cdot aR^2$$



## Chapter XIV

### Photomixtures

#### Section 1. Designation of photomixtures. Night aerial photography. Photographic materials.

Photomixtures, photo-illuminating or photoflash compositions, are intended to produce light pulses ("flashes") of very short duration, usually not exceeding a few tenths of a second.

Photoflashes are used in amateur photography as an artificial light source at night when adequately powerful electric lighting set-ups, photoflood lamps, etc., cannot be used. During World War II, photomixtures in photoflash bombs, were used very widely in night aerial photography.

The following are needed for night aerial photography:

1. A light source - a bomb charged with photomixture (photobomb, FOTAB);
2. An aerial-photography camera suitable for night operations;
3. Photomaterials for night aerial photography.

Photomixtures used in amateur ground night photography must provide minimum flash duration to obtain clear photographs of moving objects. This is even more important for photomixtures used in night aerial photography.

This requirement is necessitated by the high speed relative to the earth's surface of the aircraft carrying the camera. During the exposure, all points in the image of the object being photographed consequently shift a certain distance. As well as the translational motion of the aircraft, the image is affected by the longitudinal and transverse vibrations of the aircraft. The shift of the image during exposure is a feature of aerial photography which makes it difficult to obtain clear photographs. If the shift is considerable the image becomes blurred, and it is difficult or impossible to interpret the aerial photograph.

In ground photography, the camera is in a fixed position at the moment of exposure; the object being photographed is either fixed, or is moving at a low velocity. Therefore, when using photoflash equipment, a camera is used with an shutter held open. In that case, the duration of the exposure is determined by the duration of the flash itself. Since the duration of the illumination of flash-bulbs varies from hundredths to a few tenths of a second, even photographs of moving objects are usually sufficiently clear.

The first cameras used for night aerial photography did not have shutters, i.e., the exposure time was equal to the duration of the flash. However, aerial photographs obtained by this method had a large image shift because of the relatively long exposure time and were unsuitable for detailed interpretation. Besides, with highly sensitive films, the frame was fogged by various foreign ground light sources (fires, various lights, shell bursts, and so forth), which left longitudinal traces on the film, greatly hampering its interpretation.

After numerous investigations, these difficulties were overcome by the use of a night aerial camera with a shutter acting automatically by means of a photoelectric relay, and responding to the flash of the photobomb.

The radiation intensity of the flash of a photobomb varies in time: at the beginning of the flash it rises sharply from zero to some maximum value, and then drops comparatively slowly from the maximum to zero. Therefore, in photography with an automatically tripped shutter it is extremely important that the objective lens of the camera be opened at precisely the moment of highest flash intensity. This is achieved by means of a careful regulation of the tripping mechanism and by matching the shutter operation with the light - time curve of the photobomb flash.

Figure 14.1 shows combined graphs of the operation of shutters and variations in the intensity of the flash radiation of a photobomb as determined by Safronov<sup>188</sup>. In practice, only the area that is not shaded is used. We should also note that excessive reduction of the flash time  $t$  is

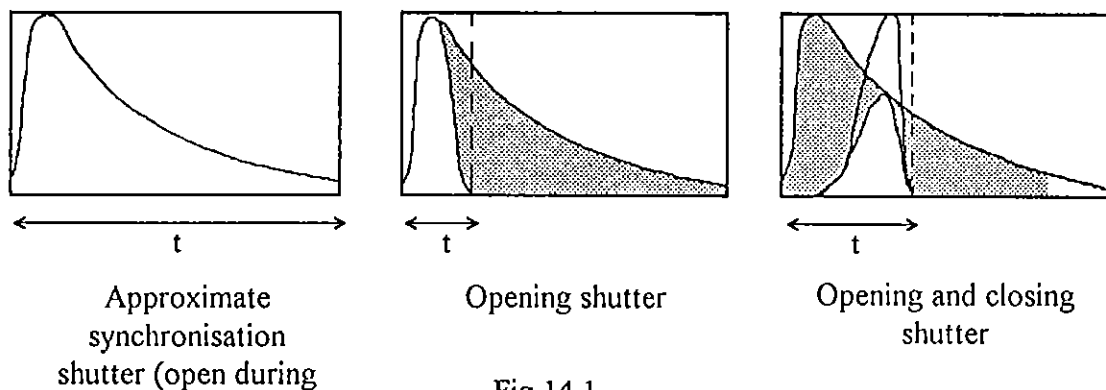


Fig 14.1

Combined curves of operation of shutters and the radiation from the flash of a photobomb

unreasonable since this may lead to incomplete use of the light energy (reduction of the effective specific integral intensity of the light of the photoflash), as a consequence of the inertia of the mechanism used to open the shutter, which amounts to about 14 ms.

The variety of photographic materials (emulsions) used at the present time for night aerial photography is very wide<sup>186, 187</sup>. These materials differ with respect to sensitivity to light, contrast, and according to their spectral sensitivity curves.

Light sensitivity is characterised by a quantity inversely proportional to the amount of illumination that creates a given photographic effect (light-sensitivity criterion), when developed in a specified photographic emulsion.

The light-sensitivity criterion selected is a photographic effect which may be expressed quantitatively (some optical density, gradient, etc.). According to GOST (All-Union State Standard) 2817-50, a blackening density equal to  $D_0 + 0.2$  is accepted for the criterion, where  $D_0$  is the density or the fogging and the unit of the quantity of illumination that produces this effect upon development under specified conditions is  $H_0 = 1 \text{ lux.s}$ .

In night aerial photography, films of high light sensitivity are used. This is necessitated by the increase in the height at which the photography is performed, because of the increase of air defence facilities.

A change in the blackening density of a photographic emulsion due to a change in the quantity of illumination acting on it under various development conditions is determined by the contrast, which is expressed numerically as the contrast factor  $\gamma$ .

Photographic emulsions are not uniformly sensitive to all parts of the spectrum. Modern photographic emulsions can be divided into the following groups on the basis of spectral sensitivity:

1. Unsensitised materials, having a sensitivity in the blue-violet part of the spectrum with a boundary of up to 500 nm, which corresponds to the natural sensitivity of silver halide.
2. Orthochromic and iso-orthochromic photographic materials, also having a sensitivity in the green and yellow regions of the spectrum, with sensitisation limits of 580 and 600 nm, respectively.
3. Isochromic photographic materials, sensitive to all visible light and sensitised to 640 nm.
4. Panchromatic photographic materials, sensitive to light of the entire visible spectrum up to 680-700 nm, but having a somewhat reduced light sensitivity in the yellow-green part of the spectrum (500-550 nm).
5. Infrachromatic photographic materials, which are sensitive to all visible light and also to the invisible infrared part of the spectrum.

Spectrograms of various photographic emulsions are given <sup>186</sup> in Fig. 14.2.

The spectral composition of the radiation from the flames of photomixtures differs from the composition of natural daylight. The colour temperature of the radiation from the flame of a photomixture corresponds to approximately 2500K. Therefore, for more efficient use of the luminous energy of a photobomb, it is necessary to use panchromatic materials with the maximum sensitivity in the orange-red part of the spectrum. Since the maximum radiation of a photoflash lies in the infrared region, the best photographic effect would be expected in with infrachromic materials. However these materials have relatively low sensitivity to light and therefore are not used in night photography.

## Section 2. Photobombs.

For use in night aerial photography, photomixtures are packed in the casings of aerial photo-illuminating bombs (abbreviated FOTAB).

A photobomb must satisfy a number of special requirements. The main one is that when the FOTAB explodes, it provides a flash with characteristics (light intensity, duration of flash, spectral composition of radiation) that must be matched with the operation of the aerial camera's shutter, as well as with the overall and spectral sensitivity of the photographic film being used.

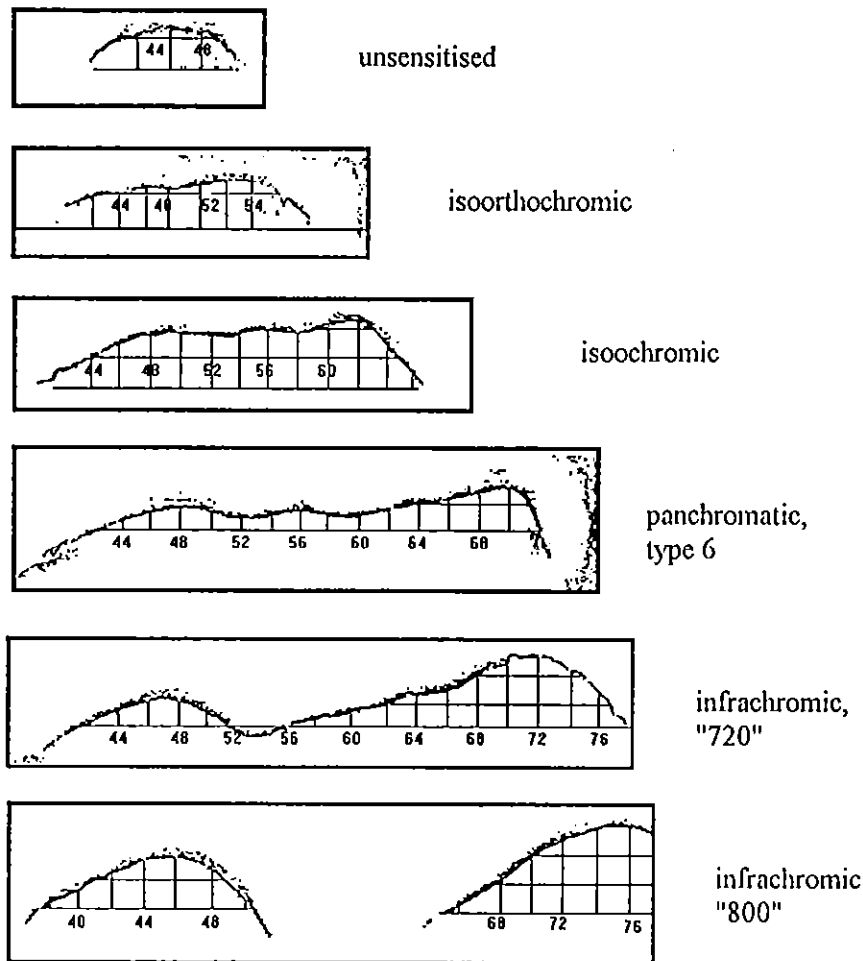


Fig 14.2 Spectrograms of emulsions, differently sensitised and exposed to a half watt lamp

The design and ballistic properties of the bomb must keep it stable as it falls and it must be set to burst at the most advantageous point of its trajectory.

The required position at burst may vary depending upon the flight altitude and speed, the quality of the photographic film being used, the speed of the camera lens, the object being photographed, etc. The design of a photobomb must allow the height of burst to be varied as required by changes in these conditions.

Uniformity in the characteristics of photobombs must be ensured, and the intensity of the flash and its duration for an individual bomb must not differ greatly from the values established for photobombs of that type.

In addition, photobombs usually must also satisfy requirements of simplicity and safety during filling and use, stability of basic characteristics during long-term storage, and a number of other special requirements.

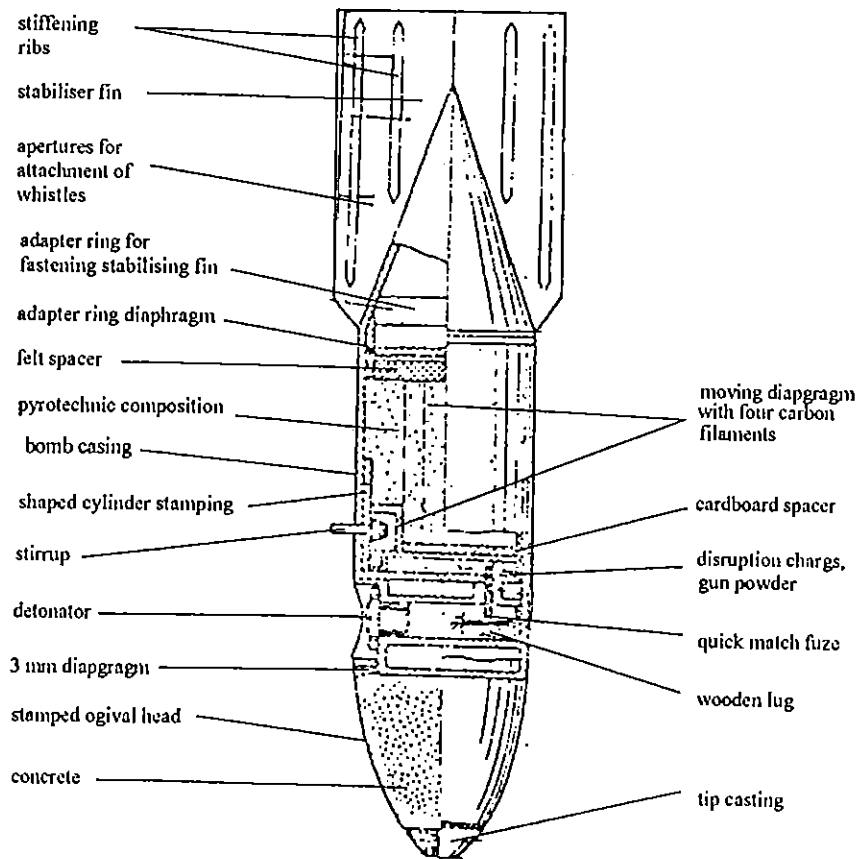


Fig 14.3 BLC-50 Photobomb

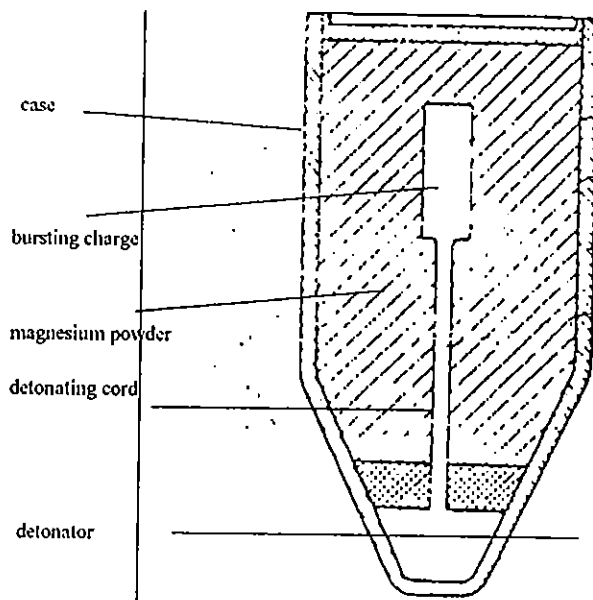


Fig 14.4 Design principles of a photobomb (US Patent 2.775.938)

The air forces of various countries have a large number of different types of photobombs in their armament. The BLC-50 photobomb, which was used by the former German Luftwaffe, is shown in Fig 14.3.

In American patent 2.775.938 of 1 January 1957<sup>190</sup>, a photobomb of different design and effect is described (Fig 14.4). In this design a detonator is connected by a detonating cord to a bursting charge in the centre of the bomb. Around this bursting charge is placed magnesium powder. The patent claims that finely divided aluminium may also be used. Complete combustion of the magnesium (or aluminium) powder dispersed by the bursting charge may be achieved, according to the claim of the patent, by coating the particles with a thin film of sodium. This is accomplished in an atmosphere of some inert gas at a temperature of 200-250°C; the sodium used is 5-25 percent of the weight of the metallic powder.

### Section 3. Methods of determining photoflash characteristics.

The quantitative characteristics of photoflash devices include:

- $I_{\max}$  - the maximum light intensity of the flash, in candle-power;
- $t_{\text{tot}}$  - the duration of the entire flash, in seconds;
- $t_{\max}$  - the time from the beginning of the flash to its maximum intensity.

In many cases when comparing photomixtures we also calculate the integral light intensity of the flash  $L$ , which is the integral  $\int_0^t I \cdot dt$  and expressed in candle.sec, and also the specific integral light intensity of the flash  $L_0$ , which is the ratio of the total light intensity of the flash  $L$  to the weight of the composition burned, and also the effective integral light intensity  $L_{\text{eff}}$  i.e., the specific light intensity perceived by the camera for the given exposure time of the shutter, such as, for example,  $\tau = 1/25$  sec.

A complete qualitative characterisation of the flash radiation is provided by:

1. the spectral distribution curve of the energy of the flash;
2. the colour temperature of the flash;
3. the changes in colour temperature and spectral distribution of the energy during the entire time of the flash.

The determination of the quantitative and qualitative characteristics of photoflash devices is very difficult because of the extremely short duration of the light phenomena accompanying the explosion or burning of photomixture charges. Precise measurement of the quantitative characteristics of photoflash radiation has become possible only since the development of the recording photoelectric luxmeters described above (Chapter XII, Section 6), which make it possible to obtain a recording of the variation in the light intensity during the flash.

The total duration of the flash and other time characteristics are calculated by dividing the length of the oscillogram by the linear rate of displacement of the photographic emulsion. In order to calculate the maximum light intensity of a flash from the height of the maximum ordinate on an oscillogram, we calibrate the light meter by means of a standard lamp of known intensity. Then, from the graph, we find the magnitude of the illumination corresponding to the maximum

oscillogram height. By multiplying this illumination by the square of the distance between the photoelements and the flash being studied, we determine  $I_{\max}$ .

For a determination of the qualitative characteristics of photoflash radiation, we use spectrographs of different designs.

Spectrograms of the radiation of certain photomixtures are shown in Fig. 14.5. In all cases, an intense continuous spectrum is visible in the photographs of the spectra of photoflash radiation, and in the background of this spectrum lines and bands can be seen.

Continuous spectra are due to the radiation of the glowing particles of solid and liquid products of combustion of the photomixture. The intensity of continuous spectra and the duration of the maximum radiation energy depend upon the temperature of the photoflash flame and upon the nature of the radiating products. The lines and bands in the spectrum of photoflashes are caused by the atomic and molecular luminosity of the products of combustion present in a gaseous or vapour form. The system of bands and lines in the spectrum changes essentially when the composition of the photomixture changes.

By appropriate processing of spectrograms we construct a graph of the distribution of the energy in the radiation spectrum of the photoflash. A typical spectral distribution of the radiation energy emitted by a photobomb flash is shown in Fig 14.6. As is apparent, the maximum radiation of the flash lies in the infrared part of the spectrum.

We must remark that the spectrograms given below, and the spectral energy distribution curves constructed on the basis of them, characterise the total effects of all the radiation of the flash from the beginning of the combustion of the photomixture to total extinction of the light.

It is sometimes important to know the spectral composition of the radiation at particular moments during the flash. In such a case the spectrogram is not taken on a fixed photographic plate, but on an emulsion that is moved at a known rate across the focal plane of the spectrograph.

An analysis of spectrograms as a function of time has shown that the spectral distribution of the radiation varies continuously over the duration of the flash. In this case, the radiation in the red region of the spectrum is of the longest duration, while that in the violet region is of the shortest duration. The highest colour temperature of the flash, characterised by radiation at all wavelengths of the visible spectrum, occurs at the moment of maximum light intensity.

Hence it follows that the radiation intensity and efficiency of photoflash devices, other things being equal, is determined primarily by the temperature of the flame.

#### Section 4. Photomixtures. Requirements for them. Factors affecting the optical characteristics of flashes and the properties of the photomixtures.

Some of the first photoflash compositions were powders or fine ribbons of magnesium and certain other metals that burn readily in the air. However, the burning of magnesium and other metallic powders in the air occurs comparatively slowly, and the radiation intensity is relatively low.

The available copy of Shidlovsky's figure is too poor to be reproduced.

Fig 14.5 Spectra of the flame of burning magnesium and various photomixtures

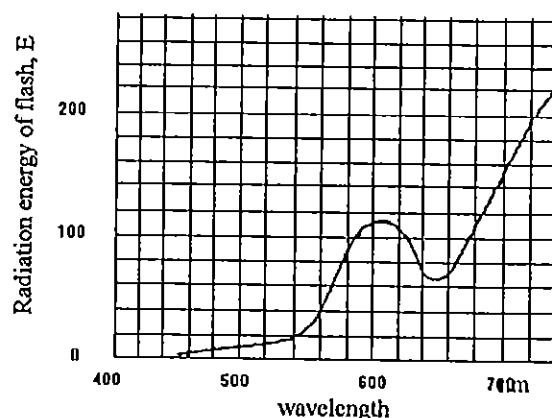


Fig 14.6 Spectral distribution of radiant energy from a photoflash

Slightly better results could be achieved by blowing the metallic powders into the flame of an open gas burner.

In oxygen, the combustion of magnesium, aluminium, alloys of them, zirconium, and certain other metals in the form of fine wire or foil occurs at a high speed and with a great output of light.

Most frequently photomixtures are prepared by mixing magnesium powder or powders of other metals with various salts containing an adequate quantity of oxygen.

The following special requirements are imposed upon photomixtures:

1. Minimum flash duration;
2. Maximum light intensity;
3. Closest possible correspondence of the spectral composition of the flash radiation and the spectral sensitivity of the aerial-photography film.

Flash duration, i.e., the time during which the emission of the flame can be observed, and the time during which the photomixture is burning are not identical, and are determined by two entirely different processes. While the combustion time is determined by the rate of the chemical reaction between the fuel and the oxidiser, the duration of the emission of the flame is determined by the physical heating and cooling processes of the products of combustion, supported by the heat liberated by the combustion reaction. However, the rate of the combustion reaction is the decisive factor determining the duration of the flash.

The rate of combustion of a photomixture, in turn, depends upon:

1. the recipe of the composition, i.e., upon the nature of the components used and their proportions in the composition;
2. the degree of subdivision of the components;
3. the density of the photomixture;
4. the nature and intensity of the initiation stimulus;
5. the quantity of photomixture burned simultaneously and its arrangement in space.

Photomixtures containing aluminium powder burn more slowly than mixtures containing magnesium powder.

The rate of combustion of photomixtures depends to a great degree upon the nature of the oxidisers used in them. Mixtures containing potassium perchlorate and other similar highly active oxidisers burn more rapidly than mixtures containing nitrates, oxides, or sulphates of the metals. Thus, for example, according to Katz <sup>7</sup>, page 170, in American standard M-46 photobombs the maximum light intensity (500,000,000 candle) is reached approximately 0.013 seconds after the beginning of the flash when a composition containing potassium chlorate is used, but after approximately 0.025 seconds when compositions containing barium nitrate are used.

Hart <sup>107</sup> indicates that a photobomb containing 10 kg of composition gives a light intensity of 800,000,000 candles with a total time of combustion of 0.04 sec.

| Mixture with 1 g<br>magnesium powder (g) |      | Flash duration<br>(s) |
|------------------------------------------|------|-----------------------|
| KMnO <sub>4</sub>                        | 0.75 | 0.03                  |
| KNO <sub>3</sub>                         | 1.00 | 0.07                  |
| Ba(NO <sub>3</sub> ) <sub>2</sub>        | 1.00 | 0.07                  |
| Sr(NO <sub>3</sub> ) <sub>2</sub>        | 1.00 | 0.10                  |
| Th(NO <sub>3</sub> ) <sub>4</sub>        | 1.00 | 0.22                  |
| Th(NO <sub>3</sub> ) <sub>4</sub>        | 0.50 | 0.24                  |

Table 14.1 Flash duration of magnesium photomixtures

From the work of Yutsevich <sup>189</sup> it follows that "the flash of a FOTAB with a flight altitude of the order of 8-10 km, occurs at a distance of 6-8 km from the aircraft." He also reports that at a flight altitude of 10 km and a flight speed of 300 km/hr, the average illumination of the terrain will be of the order of 200 lux. If we assume the height of burst of the FOTAB over the terrain is 5 km, a light intensity of  $5 \cdot 10^9$  candles would be required to produce such illumination.

Information on the flash duration of certain magnesium photomixtures is given in Table

14.1. As a rule, stoichiometric mixtures give flashes of shortest duration. Mixtures with an excess of fuel or oxidiser give flashes of considerably longer duration. The more finely divided are the ingredients of the photomixture, the more rapidly it will burn. The degree of pulverisation of the metallic fuel is of greater significance.

Photomixtures are normally used in a powdered state. In this case they burn at high rates which are measured in hundreds and sometimes even thousands of meters per second. As long as the powdered state of the photomixture is preserved the density with which the powder is packed has essentially no effect on the rate of combustion of the composition.

However, when photomixtures are pressed into pellets under high pressure, they burn as fast burning illuminating compositions at a constant rate of 10 - 15 mm s<sup>-1</sup>.

The rate of combustion of a photomixture depends noticeably upon the nature and intensity of the initiatory stimulus, as well as on its placement in the charge. To reduce the total time of combustion of a photomixture, an explosive impulse (detonating cap, a pellet of some sort of

explosive, etc.) is used rather than a heat impulse (spark plug, charge of gunpowder, Bickford fuze, etc.).

The quantity of photomixture burned simultaneously is also of great significance. As the quantity increases, its rate of combustion also increases. When photomixtures are burnt in quantities exceeding several dozen grams, the combustion shifts to an explosion. A charge of photomixture concentrated in the form of a compact mass burns more rapidly than the same charge poured out to form a long train.

| Quantity of composition<br>(g) | Total duration of flash<br>(s) | Time from start of flash to peak<br>(s) |
|--------------------------------|--------------------------------|-----------------------------------------|
| 50                             | 0.028                          | 0.011                                   |
| 100                            | 0.040                          | 0.013                                   |
| 500                            | 0.074                          | 0.017                                   |
| 1,000                          | 0.080                          | 0.026                                   |
| 1,400                          | 0.120                          | 0.030                                   |

Table 14.2 Effect of size on performance of a photoflash composition

However, although an increase in the quantity of composition being burned increases the rate of combustion, the duration of the flash is increased, not shortened. This is explained by the increased total time of combustion of the increased quantity of the mixture, and by the increased cooling time of the products of combustion of the mixture.

Data on the flash duration for charges of different weights are shown in Table 14.2.

The light intensity of a photoflash is determined by the following factors:

1. heat of combustion of the mixture, and the flame temperature, which depends upon it;
2. presence in the flame of solid and liquid particles of combustion products with high emissivity;
3. chemical composition of the photomixture, upon which factors 1 and 2 depend, and also the spectral composition of the flash radiation;
4. the size of the photomixture charge;
5. the size of the flash flame;
6. the strength of the casing in which the charge of photomixture is placed.

To obtain intense flashes, photomixtures must have the maximum heat effect (more than  $8 \text{ kJ kg}^{-1}$ ,  $2 \text{ kcal g}^{-1}$ ). Therefore, we use metal powders having a high calorific value - magnesium, zirconium, titanium, magnesium alloys, or aluminium - as fuels in photomixtures. In the selection of a metallic fuels and oxidisers for photomixtures, we use the same considerations as in the selection of metallic fuels for slow-burning illuminating compositions.

In certain cases, special substances colouring the flame or other additives are added to the basic binary mixture of oxidiser and fuel to obtain the necessary time of combustion, necessary colour of flame, etc..

At the present time, a large number of different photoflash compositions have been patented, including some using rare earth elements in a pure form or as compounds. Many of these recipes have not found widespread practical application because of the short supply of the compounds used in them.

The most efficient and easily accessible for widespread practical use are mixtures of barium nitrate or strontium nitrate with powdered magnesium or other metals.

Thus, for example a panchromatic mixture of 60% strontium nitrate and 40% magnesium powder gives an intense radiation in the red part of the spectrum from the strontium oxide, and therefore it may be used with success for night photography using panchromatic photographic materials.

Photomixtures containing sodium nitrate or sodium nitrite are not used because of the high hygroscopicity of these salts.

It is well known that flashes with the greatest light intensity are given by photomixtures with a slight excess of metal. In this case the excess of fuel reacts with the oxygen of the air. The total heat effect here is accordingly increased, and the dimensions of the flame also increase.

| Quantity of photo-mixture (g) | Maximum light intensity (candle. $10^6$ ) | Specific light intensity (kcandle $g^{-1}$ ) | Projected area of flame ( $m^2$ ) |
|-------------------------------|-------------------------------------------|----------------------------------------------|-----------------------------------|
| 50                            | 8.5                                       | 170                                          | 0.36                              |
| 100                           | 15.3                                      | 153                                          | 0.75                              |
| 200                           | 22.6                                      | 113                                          | 1.35                              |
| 500                           | 43.7                                      | 88                                           | 3.60                              |
| 1,000                         | 50.2                                      | 50                                           | 6.50                              |
| 1,400                         | 52.9                                      | 38                                           | 7.30                              |

Table 14.3 Effect of mass of photoflash composition on efficiency

A result of the simultaneous rise of the flame temperature and the radiating surface of the flame is an increase in the intensity of the photoflash during the combustion of a photo-mixture overloaded with metal.

As the quantity of the photomixture increases, the flash intensity rises. However, this increase in the light intensity of the flash is not proportional to the increase in the quantity of the mixture. From Table 14.3 it is apparent that the specific light yield per gram of the composition drops sharply as the quantity of

composition burned increases. As is further apparent the size of the flame increases, up to certain limits, almost in proportion to the quantity of photomixture taken for combustion, but when the charge of photomixture is further increased, the increase in the size of the flame, and the increase in the light intensity, gradually slow down and lag progressively farther and farther behind the increase in the quantity of photomixture.

The strength of the casing in which the composition is enclosed has some influence on the light yield of the flash, and especially on its duration. The photomixture burns more rapidly in strong metallic casings than in cardboard casings.

The sensitiveness of photomixtures to mechanical and thermal effects is of great importance. This property determines the degree of hazard for the production process for the photomixture, the hazards of filling photobombs with it, and also of using them.

Mixtures containing chlorates and permanganates as oxidisers are most sensitive to shock and friction. Cases of explosions of such mixtures have been recorded. Tomlinson and Audrieth <sup>122</sup> prefer to use the more stable potassium chlorate whenever possible. They note that mixtures containing permanganates and powdered metals are very sensitive to shock and friction.

One of the most widely used photomixtures, consisting of fine powders of barium nitrate and an alloy of aluminium and magnesium is, in their opinion, not only highly flammable but extraordinarily sensitive to friction and to shock.

Photomixtures become especially sensitive to shock if they contain even insignificant amounts of organic impurities.

Ellern <sup>9</sup> gives a recipe for the standard photomixture (Mixture F) used in the American army:

|                         |     |
|-------------------------|-----|
| aluminium, "pulverised" | 40% |
| barium nitrate          | 30% |
| potassium perchlorate   | 30% |

He also gives the light output of a FOTAB filled with this mixture (see Table 14.4). From this Table it is apparent that as the weight of the charge of photomixture increases, the light intensity increases, but the integral quantity of light (candle.s) decreases (c.f., Table 12.3). From a

| Type of filling  | Recipe of composition | Weight of composition<br>(kg) | Maximum light intensity<br>(candle.10 <sup>6</sup> ) | Integral quantity of light<br>(candle.s.10 <sup>6</sup> ) | Integral quantity of light<br>(candle.s g <sup>-1</sup> ) |
|------------------|-----------------------|-------------------------------|------------------------------------------------------|-----------------------------------------------------------|-----------------------------------------------------------|
| photocartridge   | Mixture F             | 0.20 - 0.23                   | 120                                                  | 1.5                                                       | 16,700                                                    |
| photocartridge   | Mixture F             | 0.7                           | 400                                                  | 5.0                                                       | 15,700                                                    |
| FOTAB            | Mixture F             | 32 - 36                       | 3,200                                                | 76 - 90                                                   | 5,500                                                     |
| FOTAB            | Mixture F             | 104                           | 4,500                                                | 111                                                       | 1,100                                                     |
| German dust bomb | Aluminium dust only   | 15                            | 450                                                  | 63                                                        | 4,200                                                     |
| German dust bomb | Aluminium powder only | 30                            | 800                                                  |                                                           |                                                           |

Table 14.4 Light characteristics of FOTAB of foreign armies

comparison of the light intensity of two bombs with charge weights of 32-36 kg and 104 kg it is apparent that it is not sensible to try to develop large FOTAB of great effect.

There is no oxidiser in the German "dust bombs", but only aluminium dust or aluminium powder, finely ground, surrounding a central bursting charge. However, as indicated by Ellern <sup>9</sup>, an AM alloy should be preferred over aluminium powder, and this alloy is used abroad at the present time.

Photocartridges and FOTAB may also be used as simulators for the explosion of projectile, gun flashes or atomic bursts as well as for their primary purpose of night aerial photography.

## Chapter XV

### Tracer Compositions

#### Section 1. Brief exposition of the principles of tracers. Illumination calculations.

Special devices called tracers are used to make the trajectory of projectiles, bullets, and other objects moving at a high speed visible both by day and by night <sup>191</sup>.

A tracer is a metallic shell in which tracer composition is pressed under great pressure (from 3 to 8 Mg cm<sup>-2</sup>)<sup>1</sup>. Small-calibre projectiles, as a rule, are filled by direct pressing of the tracer composition into the body of the projectile.

Tracers are used for observing the flight of:

1. aircraft rockets;
2. rocket-propelled antitank projectiles;
3. projectiles fired from artillery pieces;
4. tracer bullets.

Tracers of the first and second groups are ignited by electric devices, supplied from an outside electric-power source.

Projectile tracers may be ignited either directly from the powder gases (tracers with "flame ignition"), or from fuzes (of the "Bofors" type). Tracer bullets usually have flame ignition.

Tracer projectiles and bullets are used for destroying rapidly moving targets: aircraft, tanks, armoured cars, etc. Projectile tracers are placed in the base of the projectile. The designs of projectile tracers are very diversified.

Thus, for example, in armour-piercing projectiles a cup with the composition pressed into it is inserted into a nut which is then fastened to the fuze (Fig. 15.1). In some cases the tracer is a massive metallic shell (liner) filled with tracer composition (Fig. 15.2).

In small calibre fragmentation projectiles designed for anti-aircraft artillery, the heat developed by the tracer compound as it burns out is frequently used to explode the charge for the purpose of destroying the projectile in flight (Fig. 15.3). Firing initiates the combustion of the igniter composition and the tracer composition, both of which are pressed directly into the projectile casing at its base. The projectile has a percussion fuze and a bursting charge. If the projectile does not hit the target, the tracer composition burns out, the heat from its combustion is transferred to the pyrotechnic self-destruction charge, which is a metal shell filled with a pellet of powder, and the heat from the combustion of the latter is transferred via a metal rod to the detonator which explodes the bursting charge.

Designs of tracer and armour-piercing tracer bullets are shown in Figs. 15.4 and 15.5.

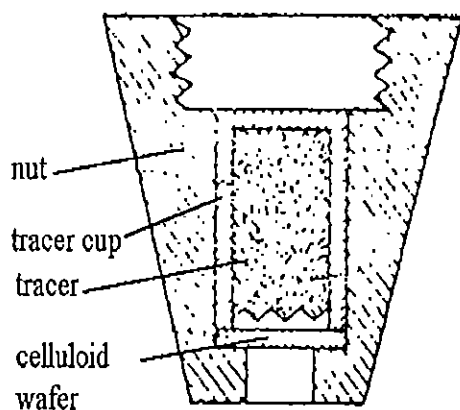


Fig 15.1 Tracer for MD-5

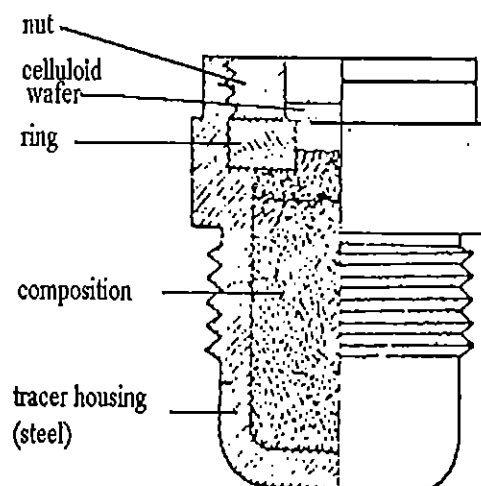


Fig 15.2 Tracer

The use of smoke compositions in tracer devices for day-time firing is feasible if the distance to be traced is not more than 1-2 km.

In literature dating from World War I we find references to the use of tracer bullets filled with yellow phosphorus as a smoke-forming agent. Attempts were also made to use compositions with recipes resembling those of signal smoke compositions for obtaining a smoke trail.

At the present time, tracers are filled primarily with flame compositions. By increasing the light intensity of the flame, we achieve visibility of the tracer also during daylight conditions.

#### Calculation of the Necessary Light Intensity of the Flame of Tracer Compositions

Visual perception of a glowing point located at a large distance away depends primarily upon the overall illumination of the terrain and the brightness of the background against which it is observed.

The brightness of the background may vary within wide limits depending upon the time of day and the weather; the brightness of the night

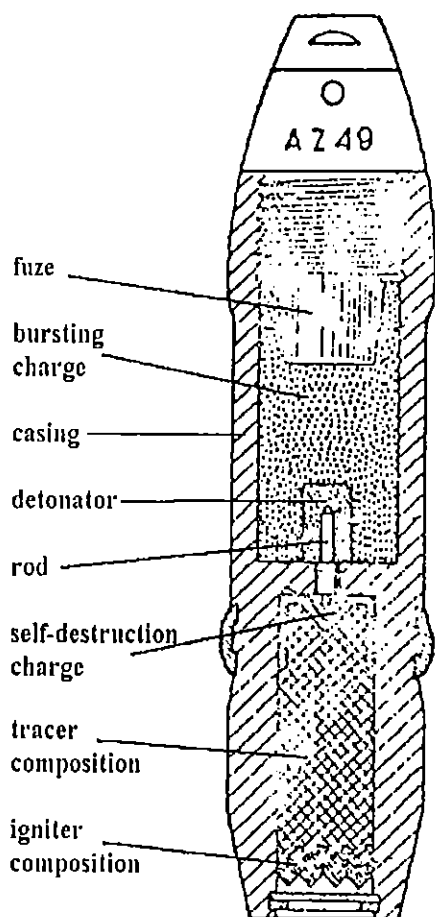


Fig 15.3 Self destroying fragmentation projectile

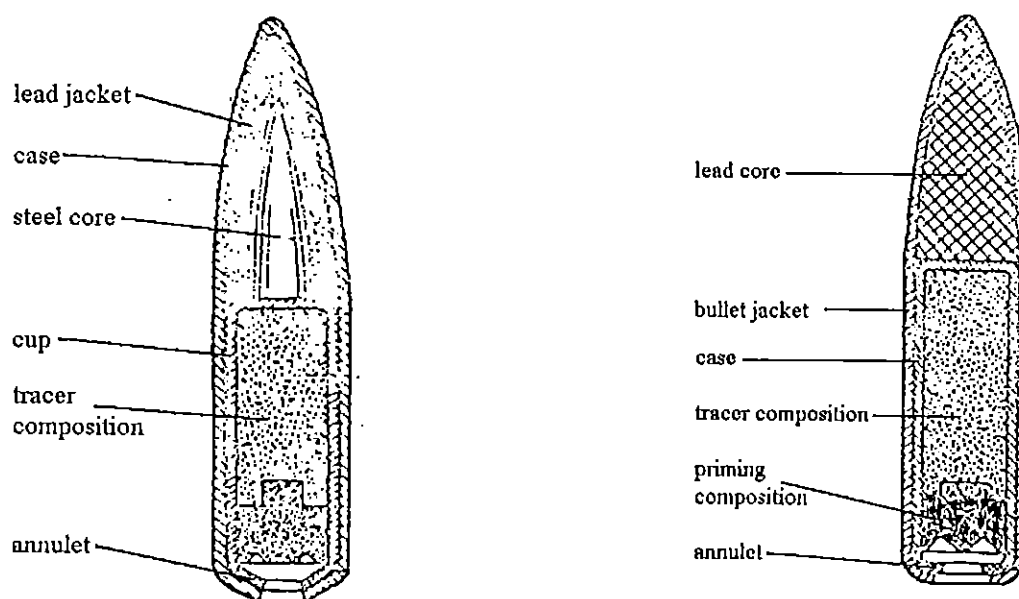


Fig 15.4 BT-32 armour  
piercing tracer bullet

sky at new moon amounts to only  $1.10^{-8}$  sb; the brightness of white clouds at noon is from 0.5 to 3 sb.

For visual perception of a glowing point it is necessary that the illumination created by it on the surface of the pupil exceed the threshold illumination, corresponding to the given brightness of the background. The threshold illumination is what we call the minimum illumination still perceptible to the human eye.

The value of threshold illumination in night and day conditions are given in Table 15.1. As is apparent from the table, the sensitivity of the eye is considerably lower by day than by night. In order, for example, to observe a white trace by day at a distance of up to 2 km, we should provide a light intensity of not less than:

| Colour of<br>flame | Threshold illumination $E_{thr}$<br>(lux) |                      |
|--------------------|-------------------------------------------|----------------------|
|                    | By night                                  | By day               |
| red                | $0.8 \times 10^{-6}$                      | $0.5 \times 10^{-3}$ |
| green              | $1.2 \times 10^{-6}$                      | $0.9 \times 10^{-3}$ |
| yellow             | $2.0 \times 10^{-6}$                      | $1.0 \times 10^{-3}$ |
| white              | $3.0 \times 10^{-6}$                      | $1.5 \times 10^{-3}$ |

Table 15.1 Values of threshold  
illumination

$$I = E_{thr} r^2 = 1.5 \times 10^{-3} (2 \times 10^3)^2 = 6000 \text{ candles}$$

during combustion of the composition.

Absorption of light by the atmosphere means that the tracer must have an even greater light intensity. Considering the absorption of light by the atmosphere, the minimum light intensity required from a tracer is expressed by the formula:

$$I = \frac{E_{thr} \cdot r^2}{a^{\frac{r}{1000}}}$$

where  $\alpha$  is the transmission factor for an atmospheric layer 1 km thick,  
 $r$  is the distance from the point source to the eye in metres.

The relation between the transmission factor and the atmospheric conditions is indicated in Table 15.2.

| Value according to code | Transmission factor $\alpha$ | Visual estimate of atmospheric conditions |
|-------------------------|------------------------------|-------------------------------------------|
| 0                       | —                            | very thick fog                            |
| 1                       | —                            | thick fog                                 |
| 2                       | 0.0004                       | average fog                               |
| 3                       | 0.02                         | light fog                                 |
| 4                       | 0.14                         | very thick haze                           |
| 5                       | 0.38                         | thick haze                                |
| 6                       | 0.67                         | light haze                                |
| 7                       | 0.82                         | satisfactory visibility                   |
| 8                       | 0.92                         | good visibility                           |
| 9-10                    | 0.97                         | exceptionally good visibility             |

Table 15.2 Relation between the Transmission Factor and Atmospheric Conditions

The range of visibility of a point source depends only upon its light intensity, and not upon its brightness.

## Section 2. Requirements imposed upon tracer compositions.

First of all, tracer compositions must satisfy those requirements analogous to those imposed upon illuminating compositions, namely:

1. liberate the maximum quantity of luminous energy on combustion;
2. burn at a fixed, moderate rate, of the order of a few millimetres per second.

Additional requirements are imposed upon tracer compositions, because of the rigid and very specific conditions in which the processes of ignition and combustion occur. These specific requirements are as follows:

1. In most cases (particularly in those designs of tracers in Figs. 15.1-15.5), tracer compositions are subject directly to the effect of the high pressures that are developed in the combustion of powder in the bore of a gun barrel.
2. At the moment of firing, the projectile as a whole and consequently also the composition in the tracer experience very high mechanical stresses.

3. The rotation of the projectile in flight (the rate of rotation of small calibre projectiles is measured in tens of thousands of revolutions per minute) produces a very great centrifugal force in the composition, and also in the products of combustion.
4. During the free flight of the projectile a vacuum is formed behind its base, and eddying air currents are created.
5. The small dimensions of the flame associated with the small overall dimensions of the tracers, facilitate a rapid cooling.

Therefore, tracer compositions, besides everything else, must satisfy the following conditions:

1. In a pressed form, they must have a strength considerably greater than all other forms of pyrotechnic compositions.
2. In this highly compacted state they must ignite without fail from the appropriate igniting composition.
3. The maximum quantity of slag products must be left in the tracer shell after combustion.

Failure to fulfil the first condition leads to partial or complete burning-out of the composition in the bore of the gun barrel as a consequence of which a "short" trace or none at all occurs in flight, and excessive wear on the gun occurs.

The second condition makes it necessary to use fuels that ignite readily (such as magnesium) in the composition.

The last requirement is important only when the weight of the tracer compositions is significant in comparison to the total weight of the ammunition. This requirement is caused by the necessity of obtaining a predictable trajectory for the tracer bullet or projectile. The greater the amount of slag left in the product after combustion of the composition, the less weight the projectile will lose, and the smaller its deviation from a normal trajectory will be. Slag formation is of particularly great significance for tracer bullets, the weight of composition of which is equal to approximately 10% of the total weight of the bullet.

Together with this, we should note that in practice this last requirement is not always adequately fulfilled. Although, as a rule, the weight of the solid products of the reaction amounts to not less than 60-80% of the weight of the composition, a part of them is discharged with the flow of gases from the reaction zone into the atmosphere.

Experimental data <sup>2</sup> page 109 show that the weight of the slag remaining in a tracer amounts to 35-45% of the initial weight of the composition.

Besides the basic requirements listed, it is desirable that a tracer composition flows freely in a powdered state, since the measurement of the quantities of composition for pressing into pellets is usually performed by volume, by means of special shaker devices.

### Section 3. Recipes for tracer compositions. Testing methods.

The principles of formulation and the recipes of tracer compositions (especially white tracer compositions) are very close to those of illuminating compositions.

The essential components for any tracer composition are: 1) oxidiser; 2) fuel; and 3) binder.

The hot high pressure gases from a powder charge, could produce a dangerously accelerated burning of the pyrotechnic composition. In connection with this, Ellern<sup>9</sup> indicates that perchlorates must not be used as oxidisers in tracer compositions, and this refers even more strongly to chlorates.

The most commonly used oxidisers for tracer compositions are barium nitrate, and strontium nitrate for red tracer compositions; sodium oxalate is added to yellow tracer compositions.

Magnesium is almost exclusively used as the basic fuel in tracer compositions. The use of aluminium as a fuel is very difficult because of the difficulty with which such compositions are ignited.

The process of combustion of tracer compositions may be retarded by adding a certain quantity of organic binder to them, such as calcium resinate, shellac, asphaltite, ethyl cellulose, etc.

Some recipes for white, red, and yellow tracer compositions and their illumination characteristics are given in Table 15.3. The binder in compositions 1 and 2 is shellac, and in composition 4 it is calcium resinate. Besides the components listed in the table, strontium peroxide, strontium carbonate, strontium fluoride, graphite, calcium silicide, and other substances are used in tracer compositions.

The recipes and manufacturing technology of German tracer compositions used during World War II are described in reference<sup>192</sup>.

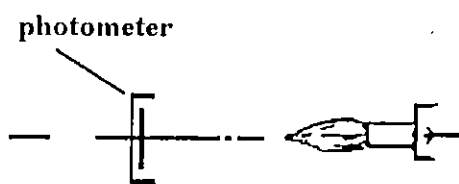


Fig 15.6 Photometry arrangement for tracer

The light intensity and combustion time of tracer compositions are sometimes determined by burning them statically (Fig 15.6)

However, such tests usually cannot give any idea of the light intensity and combustion time of the tracer in flight. Usually the rate of combustion of the composition increases slightly and the light intensity changes somewhat.

It would be most desirable to perform laboratory tests of tracer compositions under conditions as close as possible to those of their actual use, i.e., provide rotation of the tracer cup during the tests and perform the test itself in a wind tunnel or in some other apparatus in which air is blown around the tracer at a velocity close to the flight speed of the projectile.

| Components                                                                           | Composition Number, and percentage components in composition |       |       |                |       |       |                |                |
|--------------------------------------------------------------------------------------|--------------------------------------------------------------|-------|-------|----------------|-------|-------|----------------|----------------|
|                                                                                      | 1                                                            | 2     | 3     | 4 <sup>+</sup> | 5     | 6     | 7 <sup>+</sup> | 8 <sup>+</sup> |
|                                                                                      | white                                                        | white | white | white          | white | red   | red            | yellow         |
| magnesium                                                                            | 35                                                           | 25    | 36    | 35             | 44    | 30    |                | 33             |
| AM alloy                                                                             |                                                              |       |       |                |       |       | 37             |                |
| barium nitrate                                                                       | 55                                                           | 65    | 49    |                | 39    |       |                |                |
| strontium nitrate                                                                    |                                                              |       |       | 32             |       | 60    | 56             | 40             |
| barium peroxide                                                                      |                                                              |       |       | 31             | 3     |       |                |                |
| sodium oxalate                                                                       |                                                              |       |       |                | 8     |       |                | 17             |
| PVC                                                                                  |                                                              |       |       |                |       |       | 7              |                |
| resin binder                                                                         | 10                                                           | 10    | 15    | 2              | 6     | 10    |                | 10             |
| rate of combustion    mm s <sup>-1</sup>                                             | 4.7                                                          | 3.1   | 4.0   |                |       | 3.1   |                |                |
| specific integral quantity of<br>light                      candle.s g <sup>-1</sup> | 5,300                                                        | 4,400 | 6,500 |                |       | 4,400 |                |                |

<sup>+</sup> recipe from Ellern <sup>9</sup>

Table 15.3 Recipes and characteristics of white, red, and yellow tracer compositions burned in 10 mm cases.

Besides these tests, the determination of the density of tracer compositions in a pressed state is of great significance. Sometimes, the quality of pressed pellets of tracer compositions is investigated under a microscope to detect cracks. In some cases, the rate of combustion of tracer compositions is also determined at increased and reduced pressures.

It is possible to make a final estimate of the quality of tracer products only after they are tested in the field.

In estimating the efficiency of pyrotechnic tracers, it is necessary to consider that:

1. the flame of the tracer is subject to the effect of an air flow of very high velocity;
2. the useful radiant flux penetrates through the smoke screen created by the tracer;
3. tracers in some cases operate at high altitudes under conditions of a rarefied atmosphere.

To reproduce these conditions special test stands are used, consisting of devices for fastening the tracers in place and blowing air around them, with an air compressor and a control panel.



## Chapter XVI

### Signal Flare Compositions

#### Section 1. Signalling systems. Requirements imposed upon signal flare compositions.

Signal flare compositions are intended for making signals by day and by night.

The most commonly used signalling system using pyrotechnic flare compositions is a three-colour system using red, yellow, and green flares. If necessary, a yellow flare may be replaced by a white flare, obtained by the combustion of an illuminating composition.

The use of four colour or five colour signal systems, the latter including red, yellow, green, blue, and white (moon-white), colours, is not entirely sensible since the differentiation of the colours at long distances becomes unreliable.

Night signalling pyrotechnic devices used at the present time are signal cartridges, rifle signal grenades, and high-intensity night signals.

Signal flare compositions must satisfy the requirements that are common to all forms of pyrotechnic compositions (see Chapter I, Section 3), and also the following special requirements:

1. The flame produced as signal flare compositions burn must have an adequately characteristic colour that can be distinguished clearly. In quantitative terms, the colour of the flame should have a "purity" (see Section 2 of this chapter) not less than 70-75%.
2. The maximum quantity of luminous energy should be liberated on combustion of the compositions; the specific integral quantity of light generated by these compositions must be of the order of several thousand candles  $\text{g}^{-1}$ . The light intensity of signal stars must be no less than several thousand candles to ensure distinct recognition under night conditions. Thus, for example, for a green flare signal to be observed at night at a distance of 10 km, at a threshold illumination of  $1.2 \cdot 10^{-6}$  lux and an atmospheric transmission factor of  $\alpha = 0.8$  (see Tables 15.1 and 15.2 in Chapter XV), its light intensity must be no less than:

$$I = \frac{1.2 \cdot 10^{-6} \cdot (10^4)^2}{0.8^{10}} = 1120 \text{ candles}$$

3. The combustion of the compositions must occur at a rate of about a few millimetres per second. Usually signal stars burn at the rate of  $3\text{-}6 \text{ mm s}^{-1}$ .

#### Section 2. Nature of flame radiation

An ideal signal flare composition would have a flame which would radiate entirely in some single part of the spectrum. The radiation would be monochromatic, and the colour purity of the flame would be 100%. In practice, the flames of signal flare compositions radiate in other parts of the spectrum, although more weakly.

The ratio of the intensity of monochromatic flame radiation  $E_\lambda$  to the intensity of all visible radiation  $E_{\text{tot}}$  is called the colour purity of the flame  $p$  and is usually expressed as a percent.

Thus, for example, the colour purity of red signal flare compositions may be expressed by the equation:

$$p = \frac{E_\lambda \cdot 100}{E_{\text{tot}}} = \frac{E(620 \div 760 \text{ nm}) \cdot 100}{E(400 \div 760 \text{ nm})}$$

In calculations,  $E_\lambda$  and  $E_{\text{tot}}$  may be expressed in light flux units or lumens, or as a quantity proportional to a lumen i.e., candle.

In some cases, it is more convenient to use the following expression to determine the colour purity of a flame:

$$p = \frac{E_\lambda \cdot 100}{E_\lambda + E_{\text{wh}}}$$

where  $E_{\text{wh}}$  is the intensity of a white colour with which the monochromatic radiation is diluted.

A flame having a low colour purity cannot have a sharply defined colour when observed visually, since an ordinary white colour can be obtained by a mixture of  $\frac{1}{3}$  red,  $\frac{1}{3}$  green,  $\frac{1}{3}$  blue luminous fluxes.

Substances in the gaseous state that are excited by some means or other give a discontinuous radiation spectrum - either linear or banded. Consequently, the flame of signal flare compositions, unlike that of illuminating compositions, must radiate predominantly from the gaseous phase.

A line radiation spectrum is produced only by monatomic vapours and gases, and therefore it is also called an *atomic* spectrum. The lines in such a spectrum are arranged in regular characteristic groups called series.

To obtain a coloured flame from atomic radiation, we use elements having bright spectral lines in only one part of the spectrum. These elements include primarily sodium, lithium, thallium, and indium. They have characteristic bright lines: sodium - yellow 589 and 589.6 nm, lithium - red 671 nm, and orange 610 nm, thallium - green 535 nm, and indium - blue 451 nm. The salts of these metals dissociate easily at high temperatures (1000°C or above), to give a line spectrum of the vapours of the metal in the flame.

In practice, the radiation of lithium, thallium, and indium metals are not used in signal flares because of the critical supply of compounds of these metals.

The atomic radiation of sodium vapour is widely used in yellow flare compositions.

A band spectrum consists of one band or a number of bands of various widths, situated in different parts of the spectrum. However, by means of a powerful spectroscope of large dispersion we can observe that these bands consist of a great number of lines located very close to

each other. A band spectrum is obtained from the radiation of molecules of substances in a gaseous state, and therefore it is often known as a molecular spectrum.

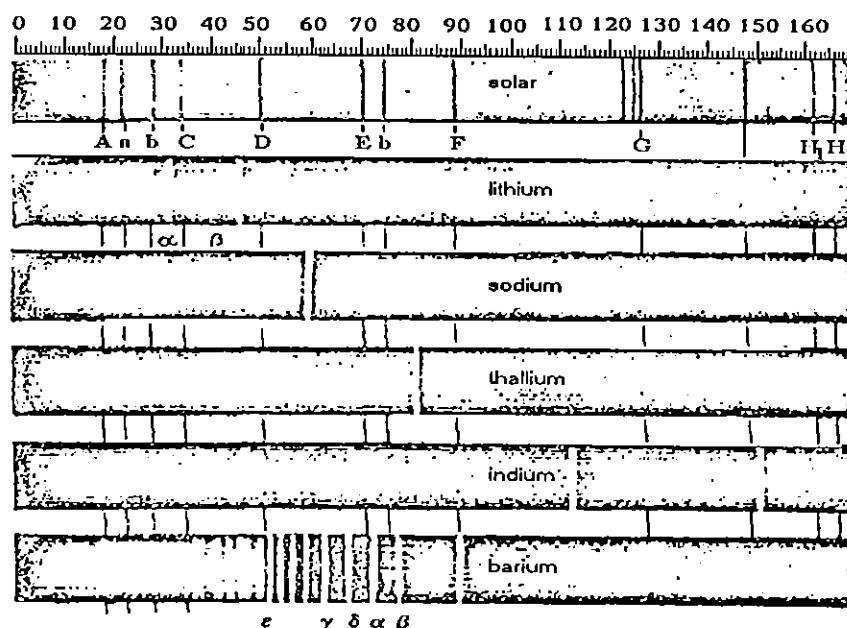


Fig 16.1 Spectra of the sun and of the vapours of the metals  
Li, Na, Tl, In, and Ba

**Section 3.** Principles for compounding signal flare compositions, and the basic requirements imposed upon their components.

1. The quantity of energy liberated in the combustion of a composition must be adequate to excite or ionise the atoms or molecules present in the vapour state in the flame. In practice, a sufficiently powerful colour radiation is obtained only from compositions whose heat of combustion is not less than 3.3 MJ kg<sup>-1</sup> (0.8 kcal/g).
2. When molecular radiation is used, the flame temperature of the compositions must not exceed the limits at which the molecules of the radiators begin to dissociate. Thus, for example, the flame temperature of green flare compositions must not exceed 2000°C.
3. The flame should contain only a small quantity of solid reaction products. The introduction into signal flare compositions of a large quantity (more than 15-20%) of metal powders (magnesium or aluminium), which produce oxides that do not volatilise easily in combustion, greatly increases the brightness of the flame, but at the same time reduces its colour purity.
4. The components of the composition must be selected in such a way that undesirable radiation of gaseous reaction products in other parts of the spectrum is minimised.
5. The elements or compounds giving a colour to the combustion flame must volatilise easily, and even at a temperature of 1000-1200°C should have vaporised entirely. Therefore, to

obtain a coloured flame, we frequently use the radiation of the chlorides of alkali earth metals, which are compounds of high volatility.

Signal flare compositions usually contain the following components:

1. oxidisers;
2. organic fuels, used as binders;
3. flame colouring salts. (these substances are quite frequently present)
4. substances improving the colour of the flame - organochlorine compounds
5. inorganic fuels - magnesium or aluminium powders.

Oxidisers used in signal flare compositions must be salts of metals which provide the required colour of the flame. Thus, for example, in yellow flare compositions sodium salts are used, in red flares strontium salts, etc.. If this is not possible for some reason (for example because of the hygroscopicity of the salt), and the oxidiser used is a salt of some other metal, the decomposition products of such an oxidiser must create minimum radiation in the flame in order to avoid significant deterioration of the flame colour. Potassium salts are frequently used as such oxidisers.

Organic binders used in signal flare compositions must not spoil the colour of their flame during combustion. Substances which produce an almost colourless flame during combustion, as happens when sulphur, hydrogen, carbon dioxide are burned in the air, would be ideal binders.

According to Tideman and Stsiborskiy <sup>7 page 197</sup>, organic substances containing at least 50% oxygen give an almost colourless flame when they are burned in the air. The yellow colour obtained when organic substances containing little oxygen are burned in the air is due to the presence of unburned solid particles of carbon in the flame.

Since the majority of signal flare compositions have a negative oxygen balance, the conditions during combustion are unfavourable for complete combustion of their binders. Consequently, organic substances used for the preparation of signal flare compositions must contain the maximum possible quantity of oxygen; this requirement is especially critical for green flare compositions. The elementary compositions of organic substances most frequently used in signal flare compositions are given in Table 4.2. Consideration of this table, indicates that one of the best binders from this standpoint, is iditol, and the worst is rosin or its derivatives.

Starch and sugar are not binders, but because of their high oxygen content, they may act, even advantageously, as a partial replacement for binders.

Metaldehyde ( $C_4H_4O$ )<sub>4</sub> was highly recommended at one time as a fuel in signal flare compositions. It is a product of the polymerisation of acetaldehyde at low temperatures.

Urotropine  $C_6H_{12}N_4$  (see Chapter III) has been reported in a patent as a fuel. It contains 51.4% carbon; 8% hydrogen; and 40.0% nitrogen; it has a negative heat of formation, burns in the air with an almost colourless, slightly bluish flame. Urotropine has no binding properties.

Polyvinyl chloride, an organochlorine substance most frequently used during World War II in red and green signal flare compositions, has the formula  $(\text{CH}_2=\text{CHCl})_n$ . It is a white powder or granule with a softening temperature of about  $80^\circ\text{C}$ , a density of 1.4 at room temperature, and a chlorine content of 56%. Polyvinyl chloride is soluble in dichloroethane and in other chlorine substituted aliphatic hydrocarbons, and is plasticised by tricresyl phosphate or dibutyl phthalate. When heated to approximately  $160^\circ\text{C}$ , polyvinyl chloride begins to decompose with the liberation of hydrogen chloride<sup>86</sup>.

#### Section 4. Yellow flare compositions.

Yellow flames are obtained in pyrotechnics only from the atomic radiation of sodium. The sodium salts included in yellow signal flare compositions must dissociate easily at high temperatures, have the maximum possible sodium content, and if possible be non-hygroscopic.

The intensity of a sodium line in a flame is proportional to the quantity of sodium introduced into the flame. Besides the yellow D-line of sodium (589-590 nm), other sodium lines (616, 568, 590, and 498 nm) may also appear at high temperatures, but their intensities are relatively low and they have no practical significance.

The greatest quantity (up to 60-70%) of sodium salt may be added to a composition when it is the oxidiser. Sodium nitrate  $\text{NaNO}_3$ , in spite of its hygroscopicity, was used as an oxidiser in yellow flare compositions during World War II (the physico-chemical properties of  $\text{NaNO}_3$  are described in Chapter II).

Of the other oxidisers, potassium salts are used almost exclusively in yellow flare compositions, since they produce a comparatively weak radiation in the flame.

The potassium compounds formed in the flame emit an atomic potassium radiation, but the potassium lines have a low intensity in comparison to the D-line of sodium, and therefore the presence of potassium vapour in the flame has almost no effect on the colour purity of the flame, equal to 80-85%. Of the potassium salts, we use primarily potassium nitrate  $\text{KNO}_3$  as an oxidiser, and also potassium chlorate and potassium perchlorate. In this case, to impart a yellow colour to the flame, sodium oxalate, sodium fluoride, cryolite, and sodium silicofluoride are the most commonly used sodium salts. Some physico-chemical properties of these salts are given in Table 16.1. As a consequence of the insignificant solubility of these salts in water, they show little or no hygroscopicity.

Old recipes for yellow flare compositions usually contain potassium chlorate as an oxidiser and a resin as a fuel. For example, we may cite a composition consisting of the following ingredients: 60%  $\text{KClO}_3$ , 25%  $\text{Na}_2\text{C}_2\text{O}_4$ , 15% iditol. Its products of combustion are  $\text{KCl}$ ,  $\text{Na}_2\text{CO}_3$ ,  $\text{H}_2\text{O}$ ,  $\text{CO}_2$ , and  $\text{CO}$ . Such compositions liberate little heat on combustion (less than  $4.5 \text{ kJ g}^{-1}$ ) and their flame has a low light intensity.

Brighter yellow flare compositions contain magnesium and potassium nitrate or sodium nitrate as oxidiser.

As an example we will consider the following recipe.

|                   |     |
|-------------------|-----|
| potassium nitrate | 37% |
| magnesium         | 30% |
| sodium oxalate    | 30% |
| resin             | 3%  |

Such a composition liberates a considerable quantity of heat ( $>4.2 \text{ kJ g}^{-1}$ ) on combustion, and its specific integral quantity of light is about  $4000 \text{ candle.s g}^{-1}$ .

The following composition was used in Germany during World War II. The light intensity of yellow flare stars of 22 mm diameter made from this composition is 11,000 candles.

|                    |     |
|--------------------|-----|
| sodium nitrate     | 56% |
| magnesium          | 17% |
| polyvinyl chloride | 27% |

The use of potassium perchlorate as an oxidiser is typical of American signal flare compositions. As an example we may mention the composition <sup>9</sup> :

|                                 |     |
|---------------------------------|-----|
| magnesium                       | 19% |
| potassium perchlorate           | 50% |
| sodium oxalate                  | 15% |
| hexachlorobenzene               | 7%  |
| gilsonite (an organic material) | 9%  |

A variation of this composition produces an amber flame:

|                       |     |
|-----------------------|-----|
| magnesium             | 25% |
| potassium perchlorate | 50% |
| sodium oxalate        | 13% |
| hexachlorobenzene     | 2%  |
| sodium resinate       | 10% |

The use of organofluorine (sic; presumably organochlorine) substances, such as polyvinyl chloride or hexachlorobenzene in yellow flare compositions does not appear to be essential, since a yellow flame has an atomic type of luminosity.

#### Section 5. Red flare compositions.

In practice, red flame is always obtained by introducing strontium compounds into the composition. The luminosity of atomic strontium cannot be used, since its radiation falls in the short wave part of the spectrum at 461 nm.

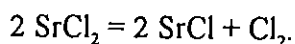
| Formula of substance  | Molecular weight                  | Sodium content (%) | Density ( $\text{Mg m}^{-3}$ ) | Solubility of salt (g/100g solution at 20°C) | Note                                                                   |
|-----------------------|-----------------------------------|--------------------|--------------------------------|----------------------------------------------|------------------------------------------------------------------------|
| sodium oxalate        | $\text{Na}_2\text{C}_2\text{O}_4$ | 134                | 34                             | 2.3                                          | 3.7 decomposes above 200°C to form $\text{Na}_2\text{CO}_3$ and CO     |
| sodium fluoride       | $\text{NaF}$                      | 42                 | 55                             | 2.7                                          | 4.1 m.p. 992°C<br>b.p. 1695°C                                          |
| cryolite              | $\text{Na}_3\text{AlF}_6$         | 210                | 33                             | 2.9                                          | dissolves with difficulty m.p. 920°C                                   |
| sodium silicofluoride | $\text{Na}_2\text{SiF}_6$         | 188                | 24                             | 2.7                                          | 0.65 dissociates almost completely to 2 NaF + $\text{SiF}_4$ at 1000°C |

Table 16.1 Physico-chemical properties of salts imparting a yellow colour to a flame

Strontium oxide produces a broad, washed-out band in the orange-red part of the spectrum with the radiation maximum at about 606 nm. The flame obtained from the radiation of strontium oxide has practically no red colour, but only a pink colour, since the high sublimation temperature of strontium oxide (above 2500°C) makes it difficult to create a significant concentration of its vapour in the flame.

Strontium nitrate produces spectrum identical to that of strontium oxide (See Fig 16.2)

Strontium chloride dissociates at high temperatures forming strontium monochloride and releasing free chlorine. Strontium monochloride  $\text{SrCl}$  may be obtained by heating a mixture of  $\text{SrCl}_2$  and Sr to 1000°C in an atmosphere of argon.:



The spectrum of  $\text{SrCl}$  shows characteristic doublet bands. The relative intensity  $E$  of these bands is:

|           |     |     |     |     |        |
|-----------|-----|-----|-----|-----|--------|
| $\lambda$ | 688 | 674 | 664 | 648 | 636 nm |
| $E$       | 3   | 10  | 10  | 10  | 10     |

Strontium chloride  $\text{SrCl}_2$  has a melting point of 870°C; above this temperature it has a considerable vapour pressure. Its boiling point, calculated by extrapolation, is 1250°C. When heated in an oxygen atmosphere, it is gradually converted to  $\text{SrO}$ .

Strontium chlorate gives a radiation spectrum in the flame identical to that of strontium chloride.

Strontium fluoride has two systems of bands in the visible part of the spectrum: in the red-orange from 678 to 628 nm and from 586 to 562 nm in the yellow-green. The latter emission prevents its use in red flare compositions.

The formulation of red flare compositions relies in practice only on the radiation of strontium oxide or strontium monochloride, and the radiation of the latter is much more intense, and besides, lies closer to the extreme red part of the spectrum.

This explains the tendency to introduce chlorine into all recipes for red flare compositions. It is inadvisable to use strontium chlorate because of its hygroscopicity and because of the high sensitiveness to mechanical stimuli of compositions made with it. Strontium chloride is also rarely used because of its hygroscopicity. The hygroscopic point of  $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$  is 65.6%.

Chlorine is most frequently introduced into the composition in the form of potassium chlorate or potassium perchlorate, or else as organochlorine compounds.

Strontium carbonate, oxalate, nitrate or, much more rarely, strontium sulphate are used to impart the colour to the flame. The physico-chemical properties of these salts are given in Table 16.2, except those of strontium nitrate, which were already described in Chapter II. All of the strontium salts given in this table are very slightly soluble in water.

| Substance                                                              | Molecular weight | strontium content (%) | Density ( $\text{Mg m}^{-3}$ ) | Note                                                                                                         |
|------------------------------------------------------------------------|------------------|-----------------------|--------------------------------|--------------------------------------------------------------------------------------------------------------|
| strontianite<br>$\text{SrCO}_3$                                        | 148              | 70                    | 3.6                            | dissociates entirely at $1300^\circ\text{C}$ to $\text{SrO}$ and $\text{CO}_2$                               |
| strontium oxalate<br>$\text{SrC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ | 196              | 53                    | -                              | loses its water entirely at $150^\circ\text{C}$ ; decomposition of the oxalate begins at $200^\circ\text{C}$ |
| Celestine<br>$\text{SrSO}_4$                                           | 184              | 56                    | 3.9                            | decomposition begins at $1130^\circ\text{C}$ ; melting point $1605^\circ\text{C}$                            |

Table 16.2 Properties of some strontium salts.

The recipes of certain red flare compositions are given in Table 16.3.

It is advantageous to compound red flare compositions with a negative oxygen balance, since the presence of a reducing atmosphere in the flame inhibits the oxidation of  $\text{SrCl}$  to  $\text{SrO}$  and increases the colour purity of the flame.

An excess of free chlorine in the flame shifts the equilibrium  $2 \text{SrCl} + \text{O}_2 = 2 \text{SrO} + \text{Cl}_2$  to the left and improves the flame colour. Organochlorine compounds such as polyvinyl chloride, hexachlorobenzene, and others, may also be added to red flare compositions. In this case, the

chlorates may be entirely replaced by other oxidisers which reduce the sensitiveness of the compositions to mechanical stimuli.

| Ingredient                                                                         | Number of Composition, and percent content of ingredients |                |                |                |                |    |
|------------------------------------------------------------------------------------|-----------------------------------------------------------|----------------|----------------|----------------|----------------|----|
|                                                                                    | 1 <sup>1</sup>                                            | 2 <sup>1</sup> | 3 <sup>2</sup> | 4 <sup>3</sup> | 5 <sup>4</sup> | 6  |
| potassium chlorate                                                                 | 60                                                        | 60             |                |                |                |    |
| strontium nitrate                                                                  |                                                           |                | 30             | 57             | 52             | 55 |
| strontium carbonate                                                                | 25                                                        |                |                |                |                |    |
| strontium oxalate                                                                  |                                                           | 25             |                |                |                |    |
| magnesium                                                                          |                                                           |                | 40             | 23             | 20             | 30 |
| resin                                                                              | 15                                                        | 15             | 5              |                |                |    |
| hexachlorobenzene                                                                  |                                                           |                | 5              |                |                |    |
| polyvinyl chloride                                                                 |                                                           |                |                | 20             | 15             | 15 |
| monostyrene                                                                        |                                                           |                |                |                | 13             |    |
| potassium perchlorate                                                              |                                                           |                | 20             |                |                |    |
| <sup>1</sup> colour purity 80-90%; resin is iditol.                                |                                                           |                |                |                |                |    |
| <sup>2</sup> recipe after Ellern <sup>9</sup> .                                    |                                                           |                |                |                |                |    |
| <sup>3</sup> 22 mm diameter stars gave a light intensity of about 10,000 candles.  |                                                           |                |                |                |                |    |
| <sup>4</sup> hardening of monostyrene accomplished with stannic chloride catalyst. |                                                           |                |                |                |                |    |

Table 16.3 Recipes for red flare compositions

The organochlorine compounds must contain as much chlorine as possible, not less than 50%; they must be non-hygroscopic and non-volatile.

Note that calcium compounds are not used in red flare compositions because they impart a non-characteristic orange-red coloration (see the spectrum of  $\text{CaCl}_2$  in Fig 16.1).

## Section 6. Green flare compositions.

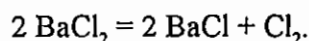
In practice a green flame is obtained in pyrotechnics only by the use of barium compounds.

The radiation of atomic barium cannot be used, since it (see Fig. 16.2) gives a whole series of lines in different parts of the spectrum (668, 611, 597, 554, 455, 429 nm and others); of these, the most intense are the yellow-green 554 nm and the blue 455 nm lines.

Barium oxide is a compound with a high melting point and low volatility; it produces broad, indistinct bands in the yellow and green parts of the spectrum. When BaO is introduced into the flame, it imparts a dull yellow-green tint.

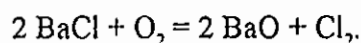
Barium nitrate produces an identical spectrum in the flame.

Barium chloride dissociates in the flame forming barium monochloride and releasing free chlorine:



The emission spectrum of BaCl consists of numerous bands in the green region (Fig 16.2).

The melting point of BaCl<sub>2</sub> is 960°C; its boiling point, calculated by extrapolation is 1835°C. A decomposition reaction of barium monochloride may occur in an oxidising flame with the formation of barium oxide which always leads to a considerable weakening of the green colour of the flame:

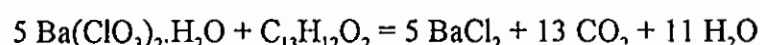


Barium chlorate gives a radiation spectrum in the flame identical to that of barium chloride.

Barium fluoride dissociates when heated releasing fluorine and forming barium monofluoride BaF which has a series of radiation bands in the green (from 494 to 505 nm) and red parts of the spectrum; barium fluoride is not used, therefore, in green-flare compositions.

In practice, a good purely green flame can be obtained only from the radiation of barium monochloride. Consequently, some sorts of compounds containing chlorine must always be added to green-flare compositions. The chlorine containing compounds used in green flare compositions are usually barium or potassium chlorate, potassium perchlorate, and organochlorine compounds. Barium perchlorate cannot be used because of its excessive hygroscopicity.

The reaction of the combustion of compositions containing 89% barium chlorate and 11% iditol may be expressed by the equation



The colour purity of the flame of this composition is 70-80%. Because of the high barium chlorate content, this composition has high sensitiveness and considerable explosive properties, and is not being used at the present time.

Compositions containing potassium chlorate usually contain barium chlorate or barium carbonate as the salt colouring the flame. A composition containing 27% potassium chlorate, 53% barium nitrate, and 20% shellac may serve as an example.

The sensitiveness of such compositions is comparatively low, but the colour of the flame is only yellow-green. The replacement of the resin by sulphur in green flare compositions containing

Figure in the available copy of Shidlovsky is too poor for reproduction.

Fig 16.2 Spectra of barium compounds

potassium chlorate causes a marked improvement in the colour of the flame, but the compositions become very sensitive, and if the sulphur is not adequately pure they are also inclined to spontaneous ignition. The introduction of organochlorine substances into green flare compositions creates a high concentration of chlorine in the flame and thus improves the colour.

As examples of compositions not containing chlorates and therefore presenting little danger in handling, we may give compositions consisting of the following components. The second composition gave about 3500 candles as a 22 mm diameter star.

|                   |     |                    |     |
|-------------------|-----|--------------------|-----|
| barium nitrate    | 40% | barium nitrate     | 59% |
| magnesium         | 28% | magnesium          | 19% |
| hexachlorobenzene | 30% | polyvinyl chloride | 22% |
| linseed oil       | 2%  |                    |     |

American green flare compositions frequently contain potassium perchlorate. For example <sup>9</sup>:

|                       |     |
|-----------------------|-----|
| barium nitrate        | 45% |
| potassium perchlorate | 16% |
| magnesium             | 26% |
| hexachlorobenzene     | 7%  |
| vegetable oil         | 2%  |
| copper oxide          | 2%  |

A description of recipes and the technology of the preparation of German signal flare compositions used during World War is given in reference <sup>195</sup>.

Copper salts impart a bright green colour to the flame of a burner, but so far no one has succeeded in obtaining a green flare composition of satisfactory quality based on copper compounds. This problem is of no special interest for military pyrotechnics because of the short supply and hygroscopicity of most copper salts.

The presence of boron compounds in these compositions gives the flame a green hue, but the colour purity of the flame is inadequate.

#### Section 7. Blue and white flare compositions.

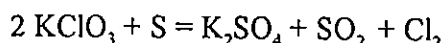
Good blue flare compositions giving a flame of adequate brightness and a sharply expressed blue colour on combustion as yet are unknown.

Blue flame is obtained almost exclusively from cuprous chloride,  $\text{CuCl}$ .

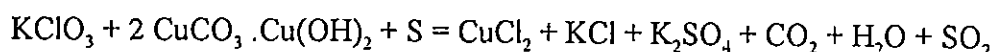
The presence of copper compounds in a flame imparts a green or blue colour to it. The colour of the flame depends in this case upon the copper compound taken, upon the temperature of the

flame and its reducing ability. Blue radiation of cuprous chloride can be obtained only in the reducing zone of a flame and at temperatures not exceeding 1000 - 1200 °C. In blue flare compositions it is essential that chlorine-containing compounds be present. A typical blue flare composition has the recipe:

In the absence of sulphur, cuprous chloride is not formed in the flame. In this case the sulphur reacts with the potassium chlorate, with the liberation of free chlorine:



The combustion reaction of the composition may be expressed approximately as follows:



This blue flare composition is sensitive to mechanical stimuli and has poor chemical stability.

|                                                     |     |
|-----------------------------------------------------|-----|
| potassium chlorate                                  | 61% |
| mineral blue $2\text{CuCO}_3 \cdot \text{Cu(OH)}_2$ | 19% |
| sulphur                                             | 20% |

Copper salts other than mineral blue may be used in blue flare compositions: *malachite*  $\text{CuCO}_3 \cdot \text{Cu(OH)}_2$ , cupric sulphide  $\text{Cu}_2\text{S}$  (sic), cuprous thiocyanate  $\text{CuCNS}$ , and also metallic copper.

Organochlorine compounds may also be used in blue flare compositions. Sulphur is not essential.

The flame colour purity of the better blue flare compositions (or, more precisely sky blue) seldom exceeds 85-90%.

A German white flare composition used during World War II had the following recipe:

|                   |     |
|-------------------|-----|
| barium nitrate    | 56% |
| potassium nitrate | 11% |
| barium fluoride   | 6%  |
| aluminium         | 19% |
| sulphur           | 8%  |

Barium nitrate imparts a greenish tint to the flame, potassium nitrate colours it pink; used together in a composition, the flame obtained is a pale pink colour.

## Section 8. Methods of testing.

Special tests of signal flare compositions include the determination of the light intensity and the colour of their flame.

The light intensity of signal flare compositions is determined by means of a photoelectric luxmeter in accordance with the same methodology used in determining the light intensity of illuminating compositions. The determination of the colour of the flame reduces to establishing the colour tone and the colour purity of the flame. The differences are expressed by the definitions "red," "green," "yellow," etc., and there are also differences in colour tone.

If we say that the colour tone of a flame  $\lambda = 520$  nm, and the colour purity of the flame  $p = 40\%$ , then we should understand that the colour perception of the human eye from seeing such a flame will be the same as the colour perception from the light flux obtained by a mixture of 40% monochromatic radiation with a wavelength  $\lambda = 520$  nm and 60% radiation of a white light source.

The first attempts at a quantitative definition of the colour co-ordinates of a flame produced by pyrotechnic compositions belong to the Russian scientist Konstantinov (1846). In essence, he proposed a method based on the use of several coloured light filters, and this is used up to the present time.

At the present time the colour and the tints of coloured flames are measured according to an international system (XYZ)<sup>193</sup>, according to which the quality of the colour is determined by its three-colour coefficient X, Y, Z, i.e., that proportion in which we should mix three basic colours: X (red), Y (green), and Z (blue) so that the quality of the mixture would coincide with the quality of the given colour. Then, using a special diagram (Fig. 16.3), we shift from the three-colour coefficient XYZ to the colour tone, which determines the wavelength of that monochromatic radiation which must be added to white radiation to reproduce the colour of interest to us.

The second quantity characterising the colour of the radiation, namely the colour purity, is determined with the same XYZ graph.

The coefficients X, Y, and Z for coloured flames were determined as early as the late 1930's by the GOI (State Optical Institute) three-colour colorimeter designed by Demkina, based on the visual selection of two fields of vision that were the same in colour tone and brightness. The brief duration of the combustion process of signal stars considerably hampered this work, making it even more difficult than it should be.

Some data obtained with this instrument are given in Table 16.4. Note that the sum of X, Y and Z is always equal to one. To convert from X, Y, Z to  $p$  and  $\lambda$  we find a point on Fig 16.3 with co-ordinates X,Y; the value of  $p$  (colour purity) is given by the arc surrounding point B (white light source). The rays diverging from point B give the colour tone  $\lambda$  in nm.

In recent years objective photoelectric three-colour recording colorimeters have been developed, providing a high accuracy of measurement. Among these are the VEI universal photoelectric colorimeter designed by Shklover and Ioffe<sup>194</sup>.

The basic and most important component part of the colorimeter is the colorimetric head, which includes three selenium photoelements covered with coloured light filters. The light filters are

matched in such a way that each of the three detectors reproduces the curve of the corresponding component with respect to spectral sensitivity: red - the curve of the component X, green - Y, and blue - Z. The front aperture in the colorimetric head is covered with a glass that absorbs ultra-violet radiation and is also shielded by a removable shade to prevent extraneous light from entering. The main units of the colorimeter i.e. the colorimetric head and the calibrated lamps are fastened to a metric optical bench.

The photocurrent originating in the photoelement is measured with a sensitive galvanometer (sensitivity  $5 \cdot 10^{-9}$  A mm<sup>-1</sup>) or a multiloop oscillograph. The process of measuring colour with this instrument reduces to reading the galvanometers and calculating the magnitudes of X, Y, Z in accordance with calibration equations established in advance. A special nomogram is available to simplify calculations, .

The colorimeter is calibrated with standard electric lamps with nameplates issued by the VNIIM (All-Union Scientific Research Institute for Metrology). The given colorimeter is more accurate than the best of the visual colorimeters.

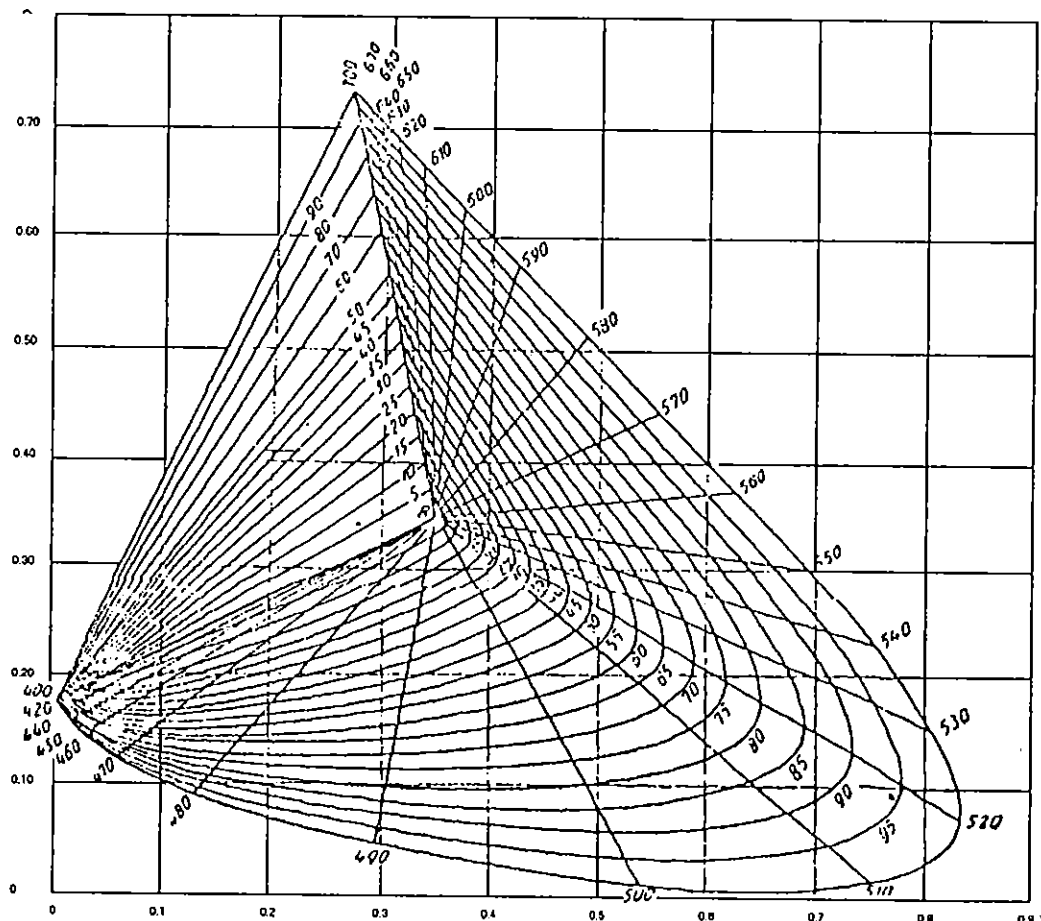


Fig 16.3 Graph for conversion from three-colour coefficients X, Y, Z to colour tone and colour purity

| Colour of flame | Components of separation                                                                                       | Coefficients |      |      | Colour tone $\lambda$<br>(nm) | Colour purity $p$<br>(%) |
|-----------------|----------------------------------------------------------------------------------------------------------------|--------------|------|------|-------------------------------|--------------------------|
|                 |                                                                                                                | X            | Y    | Z    |                               |                          |
| red             | KClO <sub>3</sub> , SrC <sub>2</sub> O <sub>4</sub> , iditol                                                   | 0.65         | 0.31 | 0.04 | 622                           | 87                       |
| yellow          | KClO <sub>3</sub> , Ba(NO <sub>3</sub> ) <sub>2</sub> , Na <sub>2</sub> C <sub>2</sub> O <sub>4</sub> , iditol | 0.35         | 0.39 | 0.08 | 593                           | 80                       |
| green           | Ba(ClO <sub>3</sub> ) <sub>2</sub> , iditol                                                                    | 0.33         | 0.53 | 0.14 | 556                           | 75                       |

Table 16.4 Determination of the colour of signal flare composition flames using a three colour colorimeter after Demkina

Aside from measurement of colour, this same instrument may also be used for measuring the light intensity of pyrotechnic light sources, since the spectral sensitivity of the Y detector (yellow-green) reproduces the curve of relative perceptibility.

## Chapter XVII

### Incendiary Compositions

The purpose of incendiary compositions is the destruction of all sorts of combustible materials, and the rendering useless of metallic structures. We should especially mention the use of incendiary compositions against living targets (flame-thrower compositions).

#### Section 1. Incendiary materials.

A number of substances and materials may be caused to burn in the air by means of incendiary compositions. However, the following materials are set on fire more frequently than others:

1. wood, in the form of building materials, fuel, wooden structures, etc.;
2. grasses and grains, in dry form (fodder, grain warehouses) or standing (crops);
3. liquid petroleum products in the form of light fuels (gasoline, ligroin, kerosene, etc.) or heavy fuels (crude oil, fuel oil, heavy oils, and others)

Some of the materials mentioned are difficult to set on fire, and others catch without any special difficulty.

Different incendiary compositions and devices must be used to deal with materials which are more, or less easy to ignite. In order to set various materials on fire with the least expenditure of pyrotechnic devices, we must know their properties. Therefore, some properties of wood and certain other combustible materials are given below.

Wood. The moisture content in wood may differ within very wide limits. Thus, green standing timber, which is one of the most difficult materials to set on fire, contains about 100% moisture (expressed relative to the weight of absolutely dry wood); air-dried wood contains from 15 to 35% moisture.

The ignition temperature of wood varies from 300 to 400°C.

The combustion process of wood consists of the liberation of its volatile components during heating, and their subsequent combustion. We may characterise the processes occurring in the heating of wood in the following manner.

|           |                                                                                         |
|-----------|-----------------------------------------------------------------------------------------|
| 110°C     | the wood dries; volatile substances begin to be liberated.                              |
| 110-150°C | the wood turns yellow and the liberation of volatile components becomes more intensive. |
| 150-230°C | the wood acquires a brown tint and begins to char.                                      |
| 230-300°C | charring (carbonisation) occurs, and above 300°C wood begins to burn.                   |

The incendiary composition sets wood on fire by heating as large a part of the wooden structure as is possible to a temperature of 300 - 400°C.

The poor thermal conductivity of wood is a great obstacle to this.

Further propagation of combustion after ignition of the wood occurs because of the heat liberated during combustion. The calorific value of 1 kg of air-dried wood is 16.7 MJ. The combustion temperature of wood is approximately 800-1000°C. The burning of wood occurs more fiercely if air has ready access to the burning surfaces.

It is very difficult to set green wood on fire, since a great quantity of the heat is expended in evaporating the moisture from it.

Grasses and cereal crops can be set on fire much more easily than wood. Dry hay ignites especially easily.

Liquid petroleum products. The flammability of liquid petroleum products is determined by their flash point. Gasoline, ligroin, and other liquids having a low flash point ignite immediately upon contact with a flame. Such liquids as petroleum, high flash point kerosene, and others, whose flash point (see Table 3.7 in Chapter III) is considerably higher than room temperature require preliminary heating for ignition. We should mention that it is not the liquid that burns, but only the vapour, and ignition, therefore, can set in only when a minimum concentration of vapours has been created over the surface of a combustible liquid, in which case the ignition of the vapour and air mixture can occur.

The minimum concentrations of vapours of various substances, in mg per litre of air, needed for ignition are:

|               |    |
|---------------|----|
| Ethyl alcohol | 73 |
| Acetone       | 65 |
| Benzene       | 49 |
| Ethyl ether   | 39 |
| Gasoline      | 33 |

We will explain what has been said by an example. At 0°C the concentration of vapours of ethyl alcohol is 34 mg l<sup>-1</sup>, and for ethyl ether, which is considerably more volatile, 780 mg l<sup>-1</sup>.

The concentration of ethyl alcohol vapour at 0°C is below the minimum concentration indicated and therefore the ethyl alcohol will not ignite at 0°C (its flash point is +12°C); the concentration of ether vapours at 0°C considerably exceeds the magnitude indicated, and therefore the ether will ignite without fail not only at 0°C, but even at a lower temperature (its flash point is - 20°C).

For information concerning the combustion of organic liquids, see the monograph by Blinov and Khudyakov <sup>197</sup> and the article by Khudyakov <sup>206</sup>.

## Section 2. Classification of incendiary compositions and requirements imposed upon them.

All existing incendiary compositions can be divided into two major groups depending upon whether they require atmospheric oxygen for combustion.

### I. Compositions with an Oxidiser

1. Thermites and thermite-incendiary compositions, in which the basic oxidiser is a metallic oxide.
2. Compositions in which the oxidiser is a salt that contains oxygen.

### II. Compositions without an Oxidiser

1. Petroleum products.
2. "Elektron" alloy.
3. Phosphorus and its compounds.
4. Other incendiary substances and mixtures.

Sometimes we separate flame-thrower mixtures and substances that ignite upon contact with water or with the oxygen of the air (metallic sodium and others) from Group II.

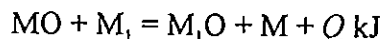
All types of incendiary compositions must satisfy the following requirements:

1. They must have as high a combustion temperature as possible; the combustion temperature of any incendiary composition must be no lower than 800-1000°C.
2. They must burn at a certain rate, matched most advantageously for the ignition of the given flammable materials. We should note that the rate of combustion of incendiary compositions varies as a function of the purpose and design of the incendiary device, within very wide limits; thus, the burning of compositions in incendiary bullets occurs almost instantaneously, the rate of combustion of pressed thermite compositions is measured in millimetres per second; liquid petroleum products burn even more slowly.
3. They must ignite readily from ordinary igniting compositions, since the use of intermediate compositions is undesirable in many cases.

### Section 3. Thermite

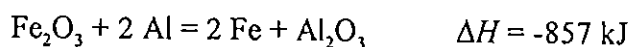
In the 1860's the prominent Russian scientist Beketov succeeded in developing a reaction between barium oxide and aluminium, and in so doing and in his further researches on the preparation of alkali metals by the reaction of metallic aluminium on their compounds, laid the foundations of a new branch of metallurgy - aluminothermy.

Reactions according to the equation:



where MO is the metal oxide and  $M_1$  is the metal used for reduction (aluminium), have been called aluminothermic reactions, and reactive mixtures of metal oxides with another metal have come to be known as thermites.

As an example, we may give the well-known combustion reaction of ferroaluminium thermite:



Aluminothermic reactions have found extensive use in civilian industry for large-scale production of pure carbon-free metals: chromium, manganese, and others<sup>201</sup>. Ferroaluminium thermite is widely used for welding various metals (aluminothermic welding of rails)<sup>283, 204</sup>.

Characteristic features distinguishing the process of combustion of thermite from the combustion of other pyrotechnic compositions are:

1. almost total absence of gaseous reaction products on combustion, which leads to a flameless type of combustion;
2. high temperature of the combustion reaction; for the majority of thermites used, it varies from 2000 to 2800°C;
3. the formation of molten slags during combustion.

We should also indicate the difficulty of igniting thermites (the spontaneous ignition temperature of all aluminium thermites is higher than 800°C, while that of ferroaluminium thermite is 1300°C). Thermites have a high density, since oxides having a high density are used in their preparation (for example,  $\text{Fe}_2\text{O}_3$  with a density of 5.1).

Thermites used as incendiary compositions must satisfy the following requirements:

1. liberate the maximum quantity of heat in combustion;
2. produce a high combustion temperature;
3. the slags formed when they burn must be highly fluid, with low melting points and low volatility;
4. must ignite readily;
5. must be difficult to extinguish with ordinary fire-extinguishing devices;
6. the linear rate of their combustion must be expressed in a few millimetres per second.

The fuel (metal) used in thermites must:

1. liberate the maximum quantity of heat as it burns;
2. form an oxide with a low melting point and low volatility;
3. have a high density.

According to the experiments of Zhemchuzhnyy, the quantity of heat liberated in the combustion of thermites must at least 2.3 MJ kg<sup>-1</sup> (0.55 kcal per gram) of the composition; otherwise the combustion reaction will proceed only with difficulty and will not run to completion. Working from this principle and considering the great quantity of heat that must be expended on the decomposition of a metallic oxide, it becomes obvious that only high-energy fuels can be used in thermites.

The properties of certain simple substances relevant to their use in thermites are given in Table 17.1.

Aluminium is the most suitable fuel for thermites because of both its heat content and its considerable density, and its comparatively low melting point (2050°C).

| Fuel | Density of fuel<br>(Mg m <sup>-3</sup> ) | Formula of oxide               | Heat of formation of oxide per kg-atom of oxygen<br>(MJ) | Recipe of thermite (%)         |      | Heat of combustion of thermite<br>(MJ kg <sup>-1</sup> ) |
|------|------------------------------------------|--------------------------------|----------------------------------------------------------|--------------------------------|------|----------------------------------------------------------|
|      |                                          |                                |                                                          | Fe <sub>2</sub> O <sub>3</sub> | fuel |                                                          |
| Al   | 2.7                                      | Al <sub>2</sub> O <sub>3</sub> | 556                                                      | 75                             | 25   | 3.89                                                     |
| Mg   | 1.7                                      | MgO                            | 602                                                      | 69                             | 32   | 4.39                                                     |
| Ca   | 1.5                                      | CaO                            | 636                                                      | 57                             | 43   | 3.89                                                     |
| Ti   | 4.5                                      | TiO <sub>2</sub>               | 456                                                      | 69                             | 31   | 2.38                                                     |
| Si   | 2.3                                      | SiO <sub>2</sub>               | 435                                                      | 79                             | 21   | 2.43                                                     |
| B    | 2.3                                      | B <sub>2</sub> O <sub>3</sub>  | 422                                                      | 88                             | 12   | 2.47                                                     |

Table 17.1 Fuels for thermites

It is assumed that aluminium is always trivalent in its compounds. However, monovalent aluminium compounds also exist (Al<sub>2</sub>O, Al<sub>2</sub>S, AlF, and others)<sup>196</sup>, that are stable in a gaseous state at high temperatures, and decompose when cooled into metal and the corresponding compounds of trivalent aluminium.

Dautzenberg<sup>208</sup> indicates that the evaporation of the products of combustion of ferroaluminium thermite is governed essentially by the formation of a sub-oxide of aluminium that is volatile at 1450°C, namely Al<sub>2</sub>O. It originates in the reaction of hot aluminium oxide Al<sub>2</sub>O<sub>3</sub> with the unreacted aluminium:



and is then oxidised in the air to Al<sub>2</sub>O<sub>3</sub>. The smoke formed on combustion of the iron thermite (especially noticeable when large quantities of thermite are burned) consists chiefly of alumina Al<sub>2</sub>O<sub>3</sub>.

The use of magnesium is hampered, aside from economic considerations and its low density, by the even higher melting point of its oxide (2800°C). It has been experimentally established that ferromagnesium thermite does not give any molten slag at all.

The use of Ca, Ti, Si, and B as specific fuels in thermites is not feasible, but their alloys may be of some interest from this standpoint

Goldschmidt<sup>7 page 206</sup> indicates that the alloy CaSi (2:1 by weight) as a thermite fuel produces slags with a very low melting point due to the formation of calcium silicate CaSiO<sub>3</sub>, which has a melting point of 1512°C.

Oxides used for the preparation of thermites must satisfy the following requirements:

1. have the minimum heat of formation;
2. contain an adequate quantity of oxygen (not less than 25-30%);
3. have the highest possible density;
4. must reduce to a metal having a low melting point and a high boiling point.

The properties of certain oxides are given in Table 17.2.

| Oxide                          | Heat of formation per kg-atom oxygen (MJ) | Oxygen content of oxide (%) | Density of oxide (Mg m <sup>-3</sup> ) | Thermite recipe (%) |                   | Heat of combustion of thermite (MJ kg <sup>-1</sup> ) |
|--------------------------------|-------------------------------------------|-----------------------------|----------------------------------------|---------------------|-------------------|-------------------------------------------------------|
|                                |                                           |                             |                                        | oxide content       | aluminium content |                                                       |
| B <sub>2</sub> O <sub>3</sub>  | 422                                       | 69                          | 1.8                                    | 56                  | 44                | 3.05                                                  |
| SiO <sub>2</sub>               | 435                                       | 53                          | 2.2                                    | 63                  | 37                | 2.34                                                  |
| Cr <sub>2</sub> O <sub>3</sub> | 376                                       | 32                          | 5.2                                    | 74                  | 26                | 2.51                                                  |
| MnO <sub>2</sub>               | 259                                       | 37                          | 5.0                                    | 71                  | 29                | 4.68                                                  |
| Fe <sub>2</sub> O <sub>3</sub> | 276                                       | 30                          | 5.1                                    | 75                  | 25                | 3.89                                                  |
| Fe <sub>3</sub> O <sub>4</sub> | 276                                       | 28                          | 5.2                                    | 76                  | 24                | 3.55                                                  |
| CuO                            | 159                                       | 20                          | 6.4                                    | 81                  | 19                | 3.93                                                  |
| Pb <sub>3</sub> O <sub>4</sub> | 180                                       | 9                           | 9.1                                    | 90                  | 10                | 1.97                                                  |

Table 17.2 Properties of certain oxides

Data on the properties of the reduction products of these oxides are found in Chapters II and III. Chromium melts at 1800°C and boils at 2300°C. Copper melts at 1083°C and boils at 2360°C.

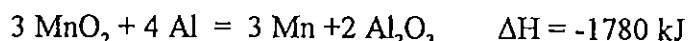
Oxides of elements of low atomic weight are little suited for use in thermites, since they have a considerable heat of formation and a low density.

The use of the oxides of metals having a high atomic weight (such as Pb<sub>3</sub>O<sub>4</sub>, for example) is limited by their low oxygen content; thermites made with them contain little fuel and liberate an inadequate quantity of heat upon combustion.

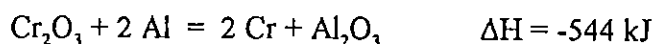
We should consider the use of oxides of metals having an average atomic weight (approximately from 40 to 80) as most feasible (see Table 17.2).

Cupric oxide releases its oxygen very readily in the presence of the appropriate reducing agent; the combustion of copper-aluminium thermite occurs at high rate and resembles an explosion (Pb<sub>3</sub>O<sub>4</sub>, and especially by PbO<sub>2</sub> behave similarly).

The metallic manganese liberated in the combustion of manganese-aluminium thermite has a lower boiling point (2000°C) than iron; it evaporates rapidly during combustion.



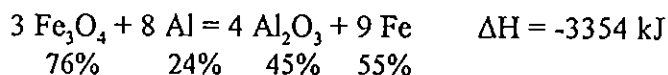
Chromium-aluminium thermite burns comparatively slowly, but liberates a considerably lower quantity of heat in combustion than other thermites:



We should consider ferroaluminium thermite as the most suitable from all standpoints for use as an incendiary composition.

The addition of  $\text{SiO}_2$  (sand) to ferroaluminium thermite somewhat reduces the solidification temperature of its slags because of the formation of the alloy FeSi, but also reduces somewhat the calorific value of the thermite. The melting point of the alloy FeSi containing 22% Si is 1250°C.

Iron scale  $\text{Fe}_3\text{O}_4$  (ferroso-ferric oxide) rather than ferric oxide  $\text{Fe}_2\text{O}_3$  is most frequently used to prepare ferroaluminium thermite. The equation of the combustion reaction of the thermite is:



One of the shortcomings of ferroaluminium thermite is its low degree of fluidity, and the rapid solidification of the slags formed during its combustion.

Powdered ferroaluminium thermite has a density of 1.8-2.0, while the pressed material (with the addition of a few percent of a binder) is 3-3.4. Thermite can be well compacted even without the addition of a binder by using high-power presses which can produce 3000-6000 kg/cm<sup>2</sup>. The pressed thermite has a high mechanical strength.

Iron scale and coarsely pulverised (No. 8-10 screen) aluminium powder are used for the preparation of thermites; finely dispersed aluminium cannot be used because of the combustion process of the thermite is accelerated.

Unpressed thermite specimens of normal granulation, weighing 1 kg, burn in 15-20 sec; the same specimens compacted under a pressure of 200 kg/cm<sup>2</sup> burn in 35-50 seconds.

Gorlov reports <sup>199</sup> that a cylindrical thermite briquette 15.5 cm high and 5.5 cm in diameter, weighing 1 kg burns in 40 seconds. According to this same report, 50 g of thermite will melt through a sheet of iron 2 mm thick within a few seconds.

Pure ferroaluminium thermite free of additives has no explosive properties, is not sensitive to bullet impact, and it comparatively insensitive to mechanical or thermal stimuli. Ferroaluminium thermite cannot be ignited by matches, quickmatch, or ordinary igniting compositions. Several

mixtures have been proposed to ignite powdered thermite. They all contain magnesium powder of fine aluminium dust as the fuel, and include:

|                  |     |                  |    |                                |    |
|------------------|-----|------------------|----|--------------------------------|----|
| MnO <sub>2</sub> | 68  | BaO <sub>2</sub> | 88 | BaO <sub>2</sub>               | 31 |
| Al powder        | 7.5 | Mg               | 12 | Fe <sub>3</sub> O <sub>4</sub> | 29 |
| Al dust          | 7.5 |                  |    | Al powder                      | 40 |
| Mg powder        | 17  |                  |    |                                |    |

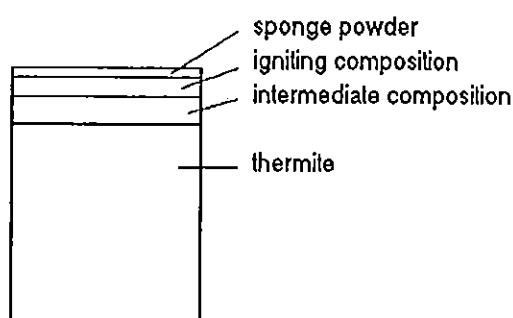


Fig 17.1 Diagram of the ignition of a pressed thermite

Ordinary illuminating compositions may be used to ignite powdered thermites.

Pressed thermites are considerably more difficult to ignite than powdered thermites, and intermediate compositions containing 40 - 60% thermite are used (Fig 17.1).

#### Section 4. Thermite incendiary compositions.

Thermite incendiary compositions are distinct from thermites, and contain additives. Usually the thermite content is 50 - 80%. The additives are intended to increase the heat of combustion, produce flame, improve the ignitability of the thermite, increase (or reduce) the burning rate, and increase the strength of the pressed composition.

The following recipe for a mixture used for filling incendiary bombs serves as an example of a thermite composition with additional oxidiser: The heat of combustion of this composition is about 4.6 kJ g<sup>-1</sup>; on combustion are formed by weight 2.5% gaseous products and 97.5% solid slags.

|                |     |
|----------------|-----|
| barium nitrate | 26% |
| iron scale     | 12% |
| aluminium      | 4%  |

Russian 76 mm projectiles are filled with the following pressed thermite incendiary composition, which liberates a greater quantity of gaseous products, and has a flash point (ignition

temperature?) between 600 to 700°C:

|                   |     |           |     |
|-------------------|-----|-----------|-----|
| barium nitrate    | 44% | aluminium | 13% |
| potassium nitrate | 6%  | magnesium | 12% |
| ferric oxide      | 21% | binders   | 4%  |

The addition of nitrate to thermite increases its heat effect, creates a flame during combustion, and reduces its flash point, but also makes the composition more sensitive to mechanical effects.

Other oxidisers, such as, barium sulphate or calcium sulphate may also be added to thermite compositions.

Sulphur, water glass, or organic materials (resins) are added to thermite compositions as binders.

Ellern<sup>9</sup> gives the following recipe for such a composition: thermite 69%, barium nitrate 29%, sulphur 2%.

The combustion of thermites containing sulphur is accompanied by the formation of a flame as a consequence of the partial combustion of the sulphur to  $\text{SO}_2$ ; the slags obtained are lower melting and flow better, since, they contain sulphur compounds (Table 17.3) as well as aluminium oxide.

| Compound                | Molecular weight | Heat of formation (MJ kg-molecule <sup>-1</sup> ) | Notes                                                                                       |
|-------------------------|------------------|---------------------------------------------------|---------------------------------------------------------------------------------------------|
| $\text{Al}_2\text{S}_3$ | 150              | 585                                               | $\text{Al}_2\text{S}_3$ melts at 1100°C, and reacts with water to form $\text{H}_2\text{S}$ |
| $\text{MgS}$            | 56               | 351                                               | decomposed by water                                                                         |
| $\text{CaS}$            | 72               | 464                                               | decomposed by water                                                                         |
| $\text{FeS}$            | 88               | 96                                                | insoluble in water; melts at 1193°C                                                         |
| $\text{MnS}$            | 87               | 184                                               | dissolves with difficulty in water                                                          |
| $\text{SiS}_2$          | 92               | 142                                               |                                                                                             |

Table 17.3 Properties of sulphur compounds.

Gorlov<sup>199</sup> has indicated that to prevent the formation of nodules when mixing thermites with molten sulphur it is necessary to heat the components to 120 - 140°C and prevent them cooling during mixing. The last fact makes the pressing of thermites very labour intensive, and requiring of great caution.

If water glass (a 15% aqueous solution of sodium silicate) is used as a binder in thermite compositions, is necessary to dry the composition. The sodium silicate has a highly basic reaction,

and very rapid corrosion of the aluminium, and sometimes a considerable heating of the mixture (up to 100°C) can occur on drying.

Asphalts, rosin, drying oil, bakelite, etc, are used as organic binders for thermites.

#### Section 5. Incendiary compositions with salt oxidisers.

Mixtures with a high content of magnesium or aluminium powders are the most effective:

|     |                       |     |           |     |          |    |
|-----|-----------------------|-----|-----------|-----|----------|----|
| I   | potassium nitrate     | 65% | aluminium | 26% | charcoal | 9% |
| II  | potassium perchlorate | 66% | aluminium | 34% |          |    |
| III | potassium perchlorate | 50% | magnesium | 50% |          |    |

Large devices (medium calibre projectiles and aerial bombs) are usually filled with thermite incendiary compositions, and compositions with oxidiser salts are more suitable for filling small calibre projectiles or incendiary bullets intended for setting liquid fuel on fire.

Compositions similar to mixture III do not produce any liquid slags at all when they burn, and their incendiary effect is based exclusively on the direct effect of the flame.

The following requirements are imposed upon them:

1. the flame formed in the combustion of these compositions must have the maximum temperature and have considerable size;
2. the effect of the flame on liquid fuel must occur during over a sufficient period of time, i.e., more than tenths of a second.

Such compositions may be initiated by a mechanical stimulus (impact against armour) or by means of explosives placed in the same device. In the latter case, the combustion of these compositions may occur at very high speeds, expressed in tens, hundreds, and even thousands of metres per second.

Mixtures of explosives with aluminium powder or dust may also be considered as special incendiary mixtures.

During World War II it was established that the incendiary effect of explosives is greatly enhanced when metal powders are added to them. As an example, we might cite the explosive mixture for German 20 mm projectiles: 76% RDX, 20% aluminium, and 4% phlegmatiser.

#### Section 6. Liquid petroleum products and solidified fuels. Flame thrower mixtures.

Liquid petroleum products. During World War II, liquid petroleum products found a widespread application in various incendiary devices. Thus, for example, incendiary bombs were filled with

petroleum, fuel oil, kerosene, gasoline, and other petroleum products. In some cases they were used to impregnate wadding, cotton, or cotton wastes, to increase the combustion time and reduce the atomisation of the liquid.

The main advantages of liquid petroleum products as incendiary substances are:

1. the great heat effect (1 g of kerosene produces 42 kJ on combustion, and thermite only 3.3 kJ);
2. the formation of a large flame during combustion, and, consequently, the development of a large seat of fire;
3. the low combustion rates;
4. the comparatively low cost and sufficiently broad raw material base.

Their disadvantages are:

1. low combustion temperature (700-900°C, while thermite develops a temperature of 2400°C during combustion);
2. low density (0.7-0.8, while the density of pressed thermite is 3-3.4);
3. absence of solid combustion products (slags);
4. excessively high mobility and tendency toward spreading;
5. excessive ease of evaporation, as a consequence of which there is a violent combustion process when a sufficiently powerful thermal impulse is communicated to the liquid.

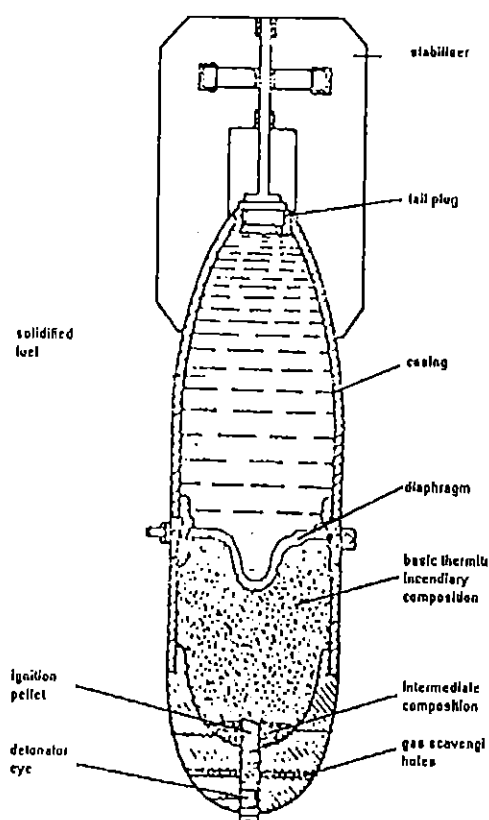


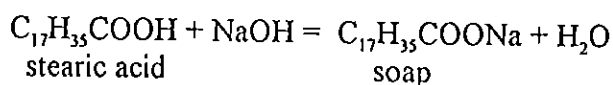
Fig 17.2 ZAB-50 Combined charge incendiary bomb.

The two latter shortcomings may be eliminated to a considerable degree if we use liquid petroleum products in the so-called solidified (or jelled) state.

Solidified fuels is the term used for combustible liquids (hydrocarbons) that have been converted to a gelatinous state by means of appropriate treatment. Such fuels, independently or in combination with thermite, may be used for filling heavy bombs, intended for setting large wooden structures on fire (Fig. 17.2).

One possible method of obtaining solidified fuels is by dissolving stearic acid in petroleum products, with subsequent treatment of the resulting solution with an alcohol solution of sodium hydroxide.

The reaction that occurs when these two solutions are mixed may be expressed by the equation



The hot liquid is poured through hoses into the casings of incendiary bombs where it cools to a gelatinous mass. "Solid petroleum", "solid kerosene", etc., are obtained by these methods.

In practice, we may use technical stearin, which is a mixture of stearic and palmitic ( $C_{16}H_{32}O_2$ ) acids, instead of stearic acid to obtain solidified fuels. The properties of these acids are given in Chapter IV.

The following special requirements are imposed upon solidified fuels:

1. low volatility;
2. ease of ignition;
3. maximum heat of combustion;
4. high combustion temperature;
5. no change in consistency during transport and storage;
6. absence of transitions (?) over the temperature range  $-30$  to  $+40^{\circ}\text{C}$ .

Petrol and kerosene solidified in this manner are easily ignited by a match.

The calorific value of the solidified fuel is close to that of the corresponding petroleum product, but is slightly lower, particularly where the solidifying additives exceed 10 -15% of the total weight of the fuels. The solidified products melt around  $60^{\circ}\text{C}$ , and their densities are close to those of the corresponding petroleum products.

Another form of solidified fuel is "jellied" fuel. In the USA, jellied fuel has become known as *napalm*<sup>209</sup>. This term covers both the jellied fuel itself and the powder which causes it to gel. The jelling powder - napalm - is a mixture of aluminium salts with oleic, naphthenic, and other organic acids. The raw materials for its preparation are:

1. oleic acid, naphthenic acid, and the fatty acid of coconut oil;
2. an aqueous solution of NaOH;
3. an aqueous solution of aluminium alum.

When these substances are mixed (Fig 17.3) aluminium salts precipitate. The suspension is centrifuged to reduce its water content below 35% and the moist napalm is fed into a rotary drier

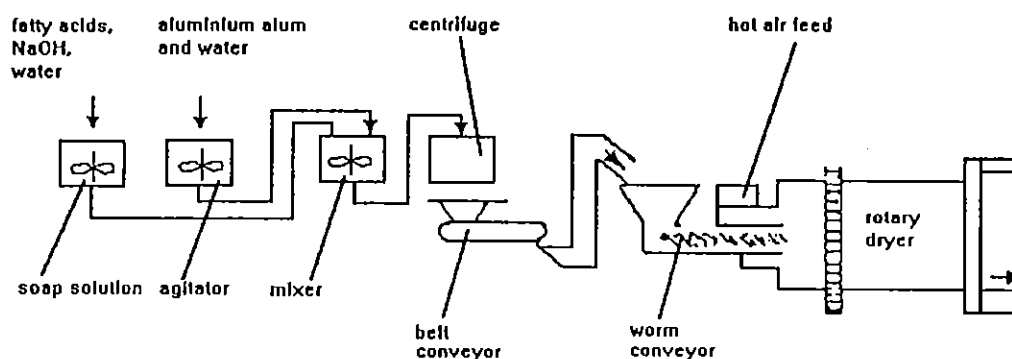


Fig. 17.3 Diagram of napalm production

where it is exposed to hot air at about 160°C. The final water content of the napalm after drying is 0.4 - 0.8%.

The dry napalm is ground into a powder in mills. The napalm powder is used to jelly petrol; the quantity added to the petrol depends upon the degree of jellying required, and amounts to 4 - 10%. The jellied petrol is used for flame-throwers and for filling the casings of incendiary bombs. The distinctive properties of napalm jellied fuel are its considerable viscosity and adhesiveness (stickiness), which makes it a suitable material for setting fire to wooden structures.

The preparation, transportation, storage, and use of "solid gasoline" in the national economy has been described in reference <sup>202</sup>. The solidifiers are casein urea-formaldehyde resins, or solutions of polyvinyl alcohol. Formaldehyde is the solidifier for polyvinyl alcohol. The volumetric content of petrol in "solid petrol" is 87 - 90%.

Flame-thrower mixtures. The flame-thrower found its first military application in World War I in 1915. A jet of flame was discharged to a maximum of 40 m. In World War II, in 1940, the Germans also used flame-throwers. The effective range of a flame-thrower jet discharged by a light tank, according to reports in the foreign press, is 50-75 m.

Flame-thrower liquids must satisfy the following requirements:

1. have the highest possible density (to provide the needed range of the jet);
2. ignite without fail from the appropriate igniting device;
3. develop the maximum temperature during its combustion;
4. burn relatively slowly in the air (if it burns rapidly, only an insignificant quantity of it reaches the target).

Mixtures of various liquid hydrocarbons or oils are the usual flame-thrower liquids.

Thus, for example, in the USA they have used a flame-thrower mixture containing 25% petrol, 25% kerosene, and 50% petroleum. Jellied combustible liquids of the napalm type have also been used.

A solution of phosphorus in CS<sub>2</sub> has not found any significant use as a flame-thrower liquid. The temperature of the flame formed in the combustion of the flame-thrower jet consisting of liquid petroleum products does not exceed 700-900°C.

According to patent information (British patent 656.089, 1951), an increase of the temperature in the flame of the flame-thrower jet may be achieved by adding a considerable quantity of magnesium powder (up to 50 - 60%) to the petroleum products and simultaneously by the addition of 10% anhydrous sodium sulphate.

The flame-thrower jet is ignited by means of a special igniter cartridge.

The possibility of adding tetranitromethane to flame-thrower mixtures has been considered <sup>199</sup>. The addition of C(NO<sub>2</sub>)<sub>4</sub> reduces the flash point of the mixture, increases its rate of combustion, and makes it non-explosive.

### Section 7. "Elektron" Alloy.

The non-ferrous alloy "elektron" contains about 90% magnesium, and also aluminium, zinc, manganese, and other metals.

An example of an elektron composition for casings of incendiary bombs is:

|                    |            |
|--------------------|------------|
| Magnesium          | 90 - 94%   |
| Aluminium          | 0.5 - 8.0% |
| Zinc and manganese | 1.5 - 5.0% |

Elektron alloy has a density of 1.80-1.83 and has high mechanical properties. Its melting point is 630-635°C. It is quite stable towards basic solutions, but corrodes easily under the effect of even weak acid solutions or ammonia salt solutions. On combustion, elektron develops a high temperature (up to 2000°C) and liberates a considerable quantity of heat (ca. 25 kJ g<sup>-1</sup>).

Elektron is used as an incendiary material for various incendiary devices, and primarily for making the casings of small aerial bombs (with a weight of about 1 kg).

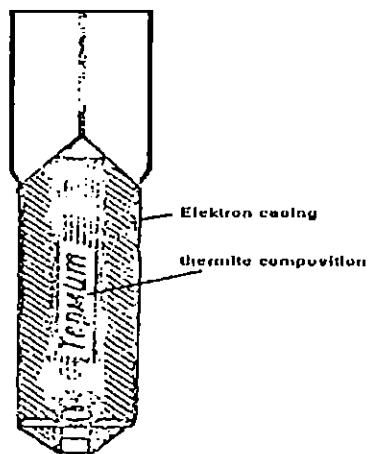


Fig 17.4 German 1 kg Incendiary Bomb

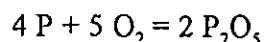
The elektron in these devices reacts with the oxygen of the air. In this case, a small, blindingly bright, white flame is formed, and white magnesium oxide smoke is liberated.

Elektron is ignited by means of pressed or powdered thermite or thermite incendiary compositions placed inside the casings of the elektron bombs (Fig. 17.4).

During combustion, the oxidation of elektron may be supported not only by means of the oxygen (and nitrogen) of the air, but also by the oxygen present in the wood in contact with it.

### Section 8. Phosphorus and its compounds.

Phosphorus, its solutions, and its compounds are ordinarily used to set on fire materials that ignite readily. The basic advantage of white phosphorus over other incendiary materials is the fact that in a finely divided state it ignites spontaneously and burns in the air:



A yellow-white flame is formed during combustion and a large quantity of a white smoke consisting of phosphorus pentoxide, which is very stable in air, is liberated.

Gorlov <sup>199</sup> has noted that phosphorus mortar bombs or hand grenades are very effective in trench warfare. The explosion of such bombs, which create a great quantity of smoke, has a demoralising effect on the enemy. The very fine splashes of the molten burning phosphorus burn through clothing and inflict the most serious wounds upon the skin.

Among the advantages of white phosphorus as an incendiary material, we should also mention its capability of repeated spontaneous ignition after it is extinguished.

White phosphorus is a pale-yellow, soft, waxy material. Its density is 1.83, melting point 44°C, and boiling point 290°C.

The basic disadvantages of white phosphorus as an incendiary material are its low combustion temperature (no higher than 1000°C), and also the difficulties of filling the appropriate devices with it; to avoid spontaneous ignition of white phosphorus, it must be poured into incendiary devices under water.

It should also be noted that white phosphorus is very toxic (a dose of 0.1 g of white phosphorus is lethal).

Red phosphorus, which is considerably less reactive, is very rarely used as an incendiary material. In some cases, however, incendiary devices have been filled with a mixture of red and white phosphorus.

Phosphorus solutions. The best solvent for white phosphorus is carbon disulphide (100 g of a saturated solution at 0°C contains 81 g phosphorus). White phosphorus is also dissolved easily in many organic solvents, such as benzene, and turpentine.

When a phosphorus solution in CS<sub>2</sub> (a highly volatile solvent) is evaporated, the extremely fine particles of phosphorus remaining ignite easily in the air and set the surrounding carbon disulphide vapours on fire.

Sometimes liquid petroleum products, tar oil, nitrocompounds, and other substances are added to a solution of phosphorus in carbon disulphide to retard the combustion process.

Red phosphorus is not soluble in carbon disulphide.

| Formula of compound            | Phosphorus content (%) | Density (Mg m <sup>-3</sup> ) | Temperature (°C) |               |
|--------------------------------|------------------------|-------------------------------|------------------|---------------|
|                                |                        |                               | Melting point    | Boiling point |
| P <sub>4</sub> S <sub>10</sub> | 27.9                   | 2.06                          | 290              | 514           |
| P <sub>2</sub> S <sub>7</sub>  | 35.6                   | 2.19                          | 310              | 523           |
| P <sub>4</sub> S <sub>3</sub>  | 56.3                   | 2.09                          | 172              | 408           |

Table 17.4 Properties of phosphorus sulphides

Phosphorus compounds. The sulphides, primarily the sesquisulphide  $P_4S_3$ , are used most frequently as incendiary materials. Some properties of phosphorus sulphides are shown in Table 17.4.

Phosphorus sesquisulphide  $P_4S_3$  dissolves readily in  $CS_2$  (100 g  $CS_2$  at  $0^\circ C$  dissolve 27 g of  $P_4S_3$ ), and less easily in petrol. Pure  $P_4S_3$  is stable to water at room temperature, but it decomposes in boiling water with the liberation of hydrogen sulphide.

The higher sulfides  $P_4S_7$  and  $P_4S_{10}$  are not stable to water (they decompose to liberate  $H_2S$ ); they are less soluble than  $P_4S_3$  in carbon disulphide and other solvents.

A liquid alloy is formed when white phosphorus and sulphur are mixed at room temperature; the phosphorus content in the eutectic, solidifying at  $-7^\circ C$ , is approximately 75%.

An alloy of  $P_4S_3$  with phosphorus gives a eutectic solidifying at  $-40^\circ C$ .

A sulphur-phosphorus phase diagram is shown in Fig. 17.5 <sup>48 Vol 8</sup>.

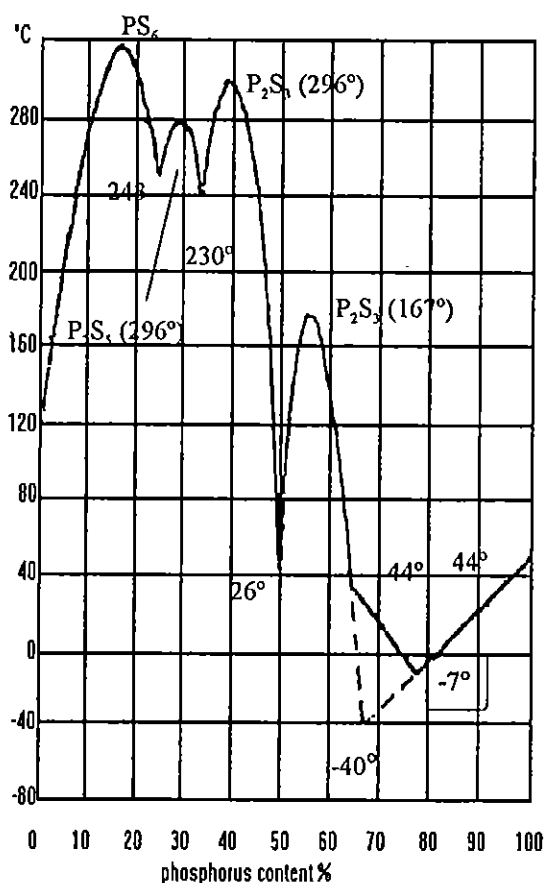
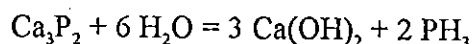


Fig 17.5 P - S phase diagram

Phosphides. Calcium phosphide is completely stable in a dry atmosphere, but in moist air or when wetted with water, it decomposes to calcium hydroxide and phosphine:



Because the product contains  $\text{P}_2\text{H}_4$  as well as phosphine  $\text{PH}_3$ , it ignites spontaneously in the air.

$\text{Ca}_3\text{P}_2$  forms reddish-brown crystals, of density 2.5. The preparation of calcium phosphide by burning a mixture of  $\text{Ca}_3(\text{PO}_4)_2 + \text{Al}$  and the use of  $\text{Ca}_3\text{P}_2$  to originate a secondary seat of fire is described in a patent issued in the Federal Republic of Germany<sup>210</sup>.

At the present time, calcium phosphide is used more frequently for filling special signal devices used by the Navy than as an incendiary material.

The properties of magnesium phosphide are similar to those of calcium phosphide, but it liberates a somewhat larger quantity of heat on reaction with water.

### Section 9. Halogen compounds of fluorine.

Free fluorine combines extremely vigorously with organic substances; as a result of this reaction, a great quantity of heat is liberated and the combustible materials are ignited.

However, the use of free fluorine as an incendiary material is practically impossible, since fluorine is a gas that is difficult to liquefy (its boiling point at 1 atmosphere is  $-187^\circ\text{C}$ ). Halogen-fluorine compounds (halogen fluorides), however, have an adequately high chemical activity in many cases, and have a higher boiling point, being either liquids or fairly readily liquifiable gases.

The evaluation of such compounds may be performed in accordance with the following indices:

1. Fluorine content (in weight percentage).
2. Boiling point at  $p = 1$  atmosphere.
3. Density in the liquid state (when  $t = 25^\circ\text{C}$ ).
4. Heat of formation from elements in kJ/g.

The physical properties of certain halogen fluorides are given in Table 17.5<sup>207, 94</sup>.

Chlorine trifluoride ( $\text{ClF}_3$ ) is of the greatest interest for pyrotechnists, since it is the most reactive of all the halogen fluorides.

Chlorine monofluoride contains the lowest percentage of fluorine and is difficult to liquefy.

Iodine compounds have a considerable heat of formation, and in accordance with this are less reactive.

Halogen fluorides are used in industry as fluorinating agents.

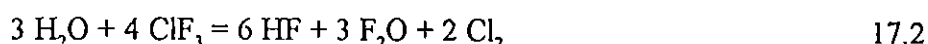
Chlorine trifluoride  $\text{ClF}_3$  is a colourless gas that liquefies easily. Its melting point is  $-76.3^\circ\text{C}$ . The dependence of the vapour pressure upon temperature is expressed by the equation:

$$\log p \text{ mm} = 7.42 - 1292/T \quad 17.1$$

The critical temperature of  $\text{ClF}_3$  lies between  $154\text{--}174^\circ\text{C}$ , and the calculated critical pressure is 57 atmospheres. The molar heat content at  $+5^\circ\text{C}$  is  $117 \text{ J g-mole}^{-1} \text{ K}^{-1}$ .

Its heat of decomposition :  $\text{ClF}_3 = \text{ClF} + \text{F}_2 \quad \Delta H = 111 \text{ kJ}$

Soft steel does not react with  $\text{ClF}_3$  up to  $250^\circ\text{C}$ ; copper up to  $400^\circ\text{C}$  and nickel up to  $750^\circ\text{C}$  are still more stable;  $\text{ClF}_3$  reacts violently with water.



Organic substances usually ignite on reaction with  $\text{ClF}_3$ .  $\text{ClF}_3$  is obtained by direct reaction of chlorine and fluorine.

The experimental industrial production of  $\text{ClF}_3$  for use as an incendiary material was undertaken in Germany during World War II.

In recent years  $\text{ClF}_3$  has been widely advertised in the USA both as a fluorinating agent and as an oxidiser in rocket engines. We should note that the high reactivity of  $\text{ClF}_3$  makes its handling very difficult and dangerous for the experimenter; we must always remember the toxicity of  $\text{ClF}_3$  and its decomposition products, and also the possibility of explosion on contact with many substances.

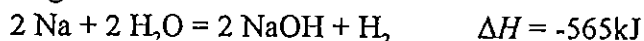
| Compound       | Fluorine content (%) | Boiling point ( $^\circ\text{C}$ ) | Density at $25^\circ\text{C}$ ( $\text{Mg m}^{-3}$ ) | Heat of Formation        |                         | Note   |
|----------------|----------------------|------------------------------------|------------------------------------------------------|--------------------------|-------------------------|--------|
|                |                      |                                    |                                                      | ( $\text{kJ mol}^{-1}$ ) | ( $\text{kJ kg}^{-1}$ ) |        |
| $\text{ClF}_3$ | 61.6                 | 11.7                               | 1,810                                                | 158                      | 1,700                   | gas    |
| $\text{ClF}$   | 34.9                 | -101                               | -                                                    | 55.6                     | 1,050                   | gas    |
| $\text{BrF}_5$ | 54.3                 | 40                                 | 2,460                                                | 519 (gas)                | 3,000                   | liquid |
| $\text{BrF}_3$ | 41.6                 | 125                                | 2,800                                                | 314                      | 2,300                   | liquid |
| $\text{BrF}$   | 19.2                 | 20                                 | -                                                    | 76.9                     | 800                     | liquid |
| $\text{IF}_7$  | 51.2                 | 4                                  | 2,750                                                | 970                      | 3,700                   | gas    |
| $\text{IF}_5$  | 42.8                 | 100                                | 3,190                                                | 856                      | 3,800                   | liquid |

Table 17.5 Properties of the halogen fluorides

## Section 10. Other incendiary substances and mixtures

Elements apart from magnesium and phosphorus which have found application as incendiary materials include the alkali metals - potassium and especially sodium.

The basic advantage of metallic sodium over other incendiary materials is that it reacts vigorously with water liberating hydrogen:



Under certain conditions, hydrogen may form a fulminating mixture with air which can explode to scatter particles of water and burning alkali metal in all directions so increasing the number of seats of fire.

The shortcomings of alkali metals as incendiary materials are:

1. low density (sodium 0.97; potassium 0.86)
2. slow reaction with dry air

Alkali metals ignite with difficulty in dry air, and a fire may readily be extinguished even if one is started.

The combustion temperature of alkali metals in air is low (not more than 1000°C).

Alkali metals are used in incendiary devices exclusively in combination with other incendiary materials or compositions: phosphorus, liquid petroleum products, solidified fuels, or thermite.

The practice of filling metallic sodium or potassium into incendiary devices is somewhat complicated by the necessity of storing the metals under kerosene to prevent their oxidation in moist air.

Metallic sodium melts at 98°C and boils at 877°C; metallic potassium melts at 63°C and boils at 762°C. An eutectic alloy of metallic sodium and potassium is a liquid with a sodium content of 23% which solidifies at -12.5°C <sup>67</sup> [n.b. not 12.5°C].

Many substances are described in the literature which ignite spontaneously in the air, and which could, if desired, be used in incendiary devices. Among these, in addition to white phosphorus and phosphines described above, we must include the silanes which are formed by the reaction of metal silicides (such as  $\text{Mg}_2\text{Si}$ ) with hydrochloric acid. Similarly, boranes are obtained by the reaction of metal borides (such as  $\text{Mg}_3\text{B}_2$ ) with diluted acids.

Among self-igniting substances we find the most diverse alkyl-metal compounds, such as, for example, dimethyl zinc, alkyl derivatives of magnesium, aluminium, and other metals. Alkyl compounds of alkali metals are even more active.

Among materials that ignite spontaneously in the air we must also include the pyrophoric metals which are produced in a very finely divided state and which because of the method of preparation

(in a reducing atmosphere) have no deactivating oxide film on their surfaces. Most metals (except the noble metals) may be produced in a pyrophoric state by some method or other.

### Section 11. Methods of testing incendiary compositions. Extinguishing incendiary compositions

An incendiary composition transfers heat to an object that is to be set on fire, by means of red-hot solid and liquid slags and by the direct effect of the flame. The total quantity of heat transferred from the burning incendiary composition to the object being set on fire will depend upon:

1. the average difference between the temperature of the slags and the flame of the incendiary composition, and the temperature of the object being set on fire,  $\Delta t_m$ ;
2. the surface of contact of the slag and flame with the object being set on fire,  $F$ ;
3. the time for which they are in contact,  $t$ ;
4. the coefficient of heat transfer from the products of combustion of the incendiary composition to the material that is being set on fire,  $k$ ;

$$Q = k \cdot \Delta t_m \cdot F \cdot t$$

In certain cases it is helpful to define separately the quantity of heat  $Q'$  transmitted to the object being set on fire by means of solid or liquid slags, and the quantity of heat  $Q''$  transmitted to the object being set on fire by the gaseous reaction products (the flame);

$$Q = Q' + Q'' \quad 17.3$$

$$Q = k' \cdot \Delta t'_m \cdot F' \cdot t' + k'' \cdot \Delta t''_m \cdot F'' \cdot t'' \quad 17.4$$

Usually for compositions producing some significant quantity of slag on combustion,  $Q'$  is considerably greater than  $Q''$ ; this signifies that the major part of the heat is transferred to the object being set on fire by the slags, not by the flame. This occurs because

$$k' > k'' \text{ and } t' > t''$$

Because the coefficient  $k$  is unknown for heat transfer from the products of combustion of incendiary composition to wood and other combustible materials, it is not possible to perform any sort of thermal calculations on the basis of the formulae given.

Besides the total quantity of heat transferred to the material being set on fire, the "thermal head", i.e., the quantity of heat transmitted from the composition to the material being set on fire per unit time,  $Q/T$ , in  $\text{kJ s}^{-1}$ , is also of very great importance. Obviously, the "thermal head" in the combustion of thermite will be significantly greater than, for example, in the combustion of a solidified fuel.

Experimental determination of the efficiency of incendiary compositions may be reduced to the determination of the quantity of heat liberated by 1 g of the composition as it burns, to a flat surface of any sort of material. To obtain results close to the true ones, it is desirable that the thermal conductivity of the material selected be close to the thermal conductivity of the material being set on fire (such as wood, for example).

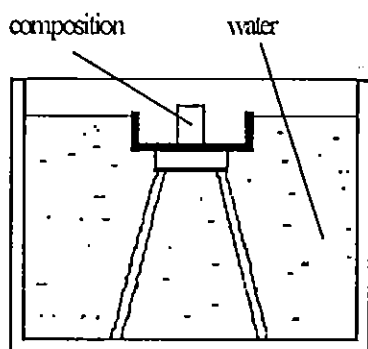


Fig 17.6 Diagram showing arrangement of calorimeter

The magnitude of the so-called "gram heat emission" of a composition, of course, will depend to a considerable degree upon the test conditions (the material of the slab, the weight of the composition used, and its arrangement on the slab), and therefore we may compare only the results obtained under the same conditions. In Fig. 17.6 we show a schematic diagram of a calorimeter for determining the "gram heat emission" of incendiary compositions.

Paushkin determined the gram heat emission of a number of compressed incendiary compositions

and fuels by burning them in an open steel vessel within a calorimeter. These data, which are of considerable interest and make possible a quantitative comparison of effectiveness of incendiary compositions, are shown in Table 17.6.

In parallel with these experiments, Paushkin performed tests of the most effective incendiary materials and compositions by burning them on a flat wooden object placed in a calorimetric vessel. In spite of the fact that, as the author himself indicates, these data should be considered as tentative because some of the wood was also burnt, they are very interesting, since they give us a conception of the quantity of heat transferred from incendiary materials under real conditions (Table 17.7).

| Composition or substance               | Heat emission in a steel cup (MJ kg <sup>-1</sup> ) | Heat of combustion of composition (MJ kg <sup>-1</sup> ) | Coefficient of heat utilisation (%) |
|----------------------------------------|-----------------------------------------------------|----------------------------------------------------------|-------------------------------------|
| KNO <sub>3</sub> + Mg                  | 0.71                                                | 7.5                                                      | 10                                  |
| Ba(NO <sub>3</sub> ) <sub>2</sub> + Mg | 2.0                                                 | 6.7                                                      | 31                                  |
| KClO <sub>4</sub> + Mg                 | 1.8                                                 | 10.0                                                     | 17                                  |
| BaO <sub>2</sub> + Mg                  | 1.4                                                 | 2.1                                                      | 63                                  |
| Fe <sub>2</sub> O <sub>3</sub> + Mg    | 2.59                                                | 4.6                                                      | 60                                  |
| Fe <sub>2</sub> O <sub>3</sub> + Al    | 2.63                                                | 3.8                                                      | 75                                  |
| Cr <sub>2</sub> O <sub>3</sub> + Al    | 2.01                                                | 2.5                                                      | 80                                  |
| MnO <sub>2</sub> + Al                  | 1.97                                                | 4.6                                                      | 42                                  |
| magnesium                              | 7.9                                                 | 25.5                                                     | 30                                  |
| kerosene                               | 6.3                                                 | 41.8                                                     | 15                                  |

Table 17.6 Heat utilisation by stoichiometric incendiary compositions or compounds

| Incendiary substance or composition | Heat emission on wood<br>(MJ kg <sup>-1</sup> ) | Coefficient of heat utilisation<br>(%) |
|-------------------------------------|-------------------------------------------------|----------------------------------------|
| ferroaluminium thermite             | 0.6                                             | 17                                     |
| kerosene                            | 1.7                                             | 4                                      |
| magnesium                           | 2.1                                             | 8                                      |

Table 17.7 Heat utilisation by incendiary compositions or compounds

From Tables 17.6 and 17.7 it is apparent that the most efficient incendiary materials, with respect to gram heat emission, are magnesium (or elektron), followed by petroleum products and then by ferroaluminium thermite.

Vernidub and Sukhikh propose the following among other special laboratory tests to determine the efficiency of incendiary compositions:

1. determination of the quantity of solid slags (as percentages of the initial weight of the composition) remaining on the surface of the material being set on fire;
2. determination of the tendency of the slags to flow - measuring the area occupied by the slags after burning a fixed weighed portion of the composition on horizontal and inclined surfaces;
3. determination of the solidification temperature of the slags; for low-melting slags (melting point less than 1500°C) this determination may be performed by means of a thermoelectric pyrometer (thermocouple);
4. determination of the dimensions of the flame obtained on combustion of the composition (photographing the flame);
5. testing incendiary compositions for direct ignition of the corresponding types of combustible materials (liquid fuels, etc.).

For certain types of incendiary compositions (such as thermite, for example), tests are sometimes made in which iron sheets of a definite thickness are melted through, and the adhesion of the slags to the appropriate metal products is determined.

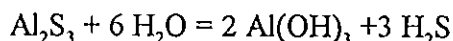
Extinguishing incendiary compositions. Ordinary fire-fighting equipment is usually sufficient to extinguish fires caused by incendiary compositions. Extinguishing the incendiary compositions themselves is very difficult, because of the short combustion time of modern incendiary devices (not more than 5-10 min), and therefore success of the operation depends to a considerable degree upon the timeliness of the start of fire fighting.

When thermite incendiary compositions are extinguished with small quantities of water, they may decompose and form explosive mixtures of hydrogen with air.

It has been experimentally established <sup>199</sup> that water, in large quantities, delivered under pressure by a strong jet, is the best means of extinguishing thermite-incendiary and elektron bombs, since it

causes a sharp local reduction in the temperature and stops the process of combustion. Thermite-incendiary and elektron-incendiary bombs weighing up to 5 kg may be extinguished by simply flooding them with water in the greatest possible quantity. Sand should be used to limit the effect of incendiary bombs.

In extinguishing thermite compositions containing sulphur, it must be remembered that the liberation of large quantities of hydrogen sulphide occurs when water is used on the burning composition:



Water cannot be used to extinguish metallic sodium or potassium. The most reliable means of extinguishing them are sand or dry soda.

Aqueous solutions of  $\text{KMnO}_4$  or  $\text{CuSO}_4$  are the best means of extinguishing phosphorus. The effect of a  $\text{KMnO}_4$  solution is based on the formation of a protective coating of manganese dioxide on the surface of the phosphorus; when a copper vitriol solution is used, a very dense protective layer of metallic copper is formed.

Solidified fuels are extinguished by the same means as are liquid hydrocarbons. The most suitable devices are thick foam fire extinguishers, water spray (fog), and also concentrated aqueous solutions of ammonia salts.

Modern methods of extinguishing combustible liquids are described in detail in reference <sup>197</sup>.



## Chapter XVIII

### Screening Smoke Compositions

#### Section 1. General information on aerosols.

In true solutions, the particles of the dissolved substance consists of individual molecules, atoms, or ions; in colloidal systems, on the other hand, the number of atoms or molecules incorporated in a particle is measured in hundreds or thousands.

Colloidal systems consist of the dispersion medium and the substance dispersed in it - the disperse phase.

In cases where the dispersion medium is the air, the colloidal system is called an aerosol.

If the dispersed phase in air is a liquid, the system is called a mist (or fog), and if the dispersed phase is in the solid state, the aerosol is called a smoke.

Consequently, a smoke is a very fine suspension of solid matter in the air. The dimensions of particles of various smokes and mists vary from 1 nm to 10  $\mu\text{m}$ . The radius of the aerosol particles used for smoke screening vary within very narrow limits - from 200 nm to 800 nm.

The term dust is usually applied to a suspension of larger particles of solid matter, ranging from 10  $\mu\text{m}$  to 110  $\mu\text{m}$  in the air.

In industry, smoke is usually a harmful phenomenon and is studied chiefly to find ways to eliminate it; smoke control is effected by means either of a strong electric field or various types of filters.

In military engineering, smokes and mists are used to produce smoke screens for screening (masking, camouflage) purposes; coloured smokes are used for daytime signalling (see Chapter XIX).

The concentration of smokes and mists may be expressed by two methods:

1. by weight, in g per cubic metre (or in  $\text{mg l}^{-1}$ ) -  $c_p$ ;
2. by the number of smoke or mist particles per unit volume (per ml) -  $c_N$ ; the latter quantity is called the partial concentration.

The weight concentration  $c_p$  of smokes used to form smoke screens is usually expressed in tenths of a milligram per litre ( $\text{mg l}^{-1}$ ), which corresponds to a content of several million smoke particles per ml of air.

Particles of a smoke or mist are continually moving in the air. This motion is caused by the strong gravity, which forces the particles to move downward. The rate of descent of particles whose radius is less than 10  $\mu\text{m}$  is constant and may be calculated from the Stokes formula. It should be

noted that in the derivation of the Stokes formula it is assumed that the aerosol particles are settling, not coagulating, and have a spherical shape; the latter assumption is valid only for mists, while smoke particles may have the most diverse shape.

$$v = \frac{2}{9} r^2 \cdot g \cdot \frac{(\rho - \rho')}{\eta} \cdot 10^3 \text{ m s}^{-1}$$

where  $v$  is the rate of descent of a particle,  $\text{m s}^{-1}$

$r$  is the radius of the particle,  $\text{m}$

$g$  is the acceleration of gravity, equal to  $9.81 \text{ m s}^{-2}$

$\rho$  is the density of the particle,  $\text{Mg m}^{-3}$

$\rho'$  is the density of the medium (in this case, air),  $\text{Mg m}^{-3}$

$\eta$  is the viscosity of the air equal to  $1.81 \times 10^{-5} \text{ N s m}^{-2}$

(n.b  $1 \text{ poise} = 0.1 \text{ N s m}^{-2}$ ).

For particles having radii of less than  $0.4 \mu\text{m}$ , the assumptions of the homogeneity of the medium and the absence of slip, which are the basis of the Stokes formula are no longer valid. The Cunningham formula<sup>sec 211</sup> should be used to calculate the rate of descent of such small particles.

The quantity  $\rho'$  for air is so small that it may be assumed equal to zero without misgiving. By replacing  $2g/9\eta$  by the constant  $k$ , we obtain the Stokes formula for an aerosol in a simpler form:

$$v = k \cdot r^2 \cdot \rho$$

where  $k = 1.2 \times 10^5 \text{ m}^2 \text{ kg}^{-1} \text{ s}^{-1}$ .

The path  $s$  (in  $\text{m}$ ), traversed by a particle under the effect of the force of gravity in a time  $t$ , is calculated by the formula:

$$s = k \cdot r^2 \cdot \rho \cdot t$$

The particles of smoke (or mist) are continuously in constant random motion which is called Brownian motion which is a consequence of the collisions between the particles of the aerosol and the molecules of the gaseous medium. The finest particles of smoke or mist show the most energetic Brownian motion.

Smoke particles move with the medium itself, i.e., together with air streams. The small smoke clouds with particles not exceeding  $1 \mu\text{m}$ , are usually dispersed by the atmospheric air currents, and are not able to settle under the influence of gravity or to scatter as a result of collisions with the molecules of the gaseous medium. Therefore, in investigating the physico-chemical properties (optical, electric, etc.) of a smoke, we frequently use a glass-walled chamber for protection against the dispersing effect of convection currents, and this chamber also makes it possible to observe the processes occurring in the system. Sometimes the chamber is made with double walls with an air space between them for purposes of thermal insulation, .

One of the basic problems of the physico-chemical investigation of a smoke system is the determination of the dimensions of smoke particles. To determine this, the aerosol particles are

trapped on glass plates and visually through a microscope or photographed. In this case, the number of particles in the field of vision is counted.

The flow ultramicrophotometer designed by Deryagin and Vlasenko <sup>57</sup> is used to determine the concentration of particles in the air. The particles are counted in reflected light within a microscopically small volume through which the aerosol is pumped. This instrument makes it possible to determine concentrations of aerosols containing more than  $10^{14}$  particles per  $m^3$  under field conditions.

In addition, methods exist for determining the dimensions and shape of smoke particles ( $MgO$ ,  $ZnO$ ,  $Al_2O_3$ , and others) by means of the electron microscope.

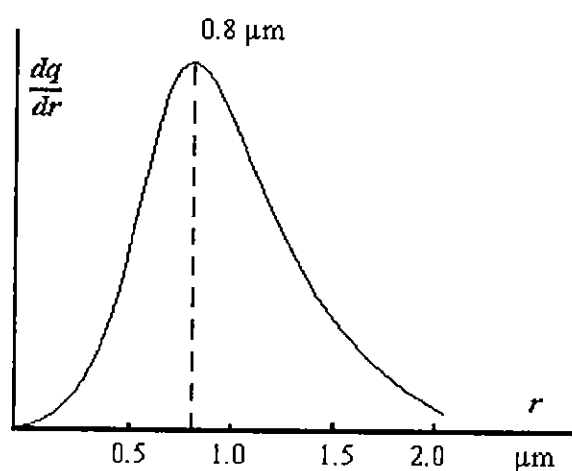


Fig 18.1 Distribution of particles in a  $NH_4Cl$  smoke

In most cases, smokes and mists are polydisperse systems i.e., they contain particles of different sizes (Fig 18.1). In this figure,  $dq/dr$  is the weight percentage of the smoke particles having the indicated values of the radius  $r$ .

We should also know the electrical properties of smokes and mists, since the persistence of a smoke or mist depends upon the sign and magnitude of the charge of the particles.

The phenomenon of coagulation is observed in aerosols from the moment of their formation. Coagulation of an aerosol is the enlargement (sticking together) of the smoke or mist particles. The formation of very large particles leads to their rapid precipitation from the

gaseous medium. The rate of coagulation of aerosols is directly proportional to the square of their partial concentration. For smokes, the process of coagulation is frequently called flocculation (from the English word flocks, meaning flakes). The ability of smokes to flocculate is reduced when an electric charge of uniform sign or a film of adsorbed gas is present on the particles; the absence of a charge, or, in particular, the presence of charges of different sign on the particles facilitate flocculation of the smoke.

Smoke particles can acquire a charge under the following circumstances:

1. by friction against the gaseous medium;
2. as a result of particle dissociation at the moment of formation of the smoke;
3. by means of capture of gas ions from the dispersion medium.

## Section 2. Optical properties of aerosols.

Smoke or mist reduces the air's transparency to light. A beam of light entering the air does not pass entirely through it; a considerable part of the light is absorbed or scattered by the particles of smoke or mist.

The phenomenon of light scattering by colloidal particles has been named the Tyndall effect. The intensity of scattered light is determined by an instrument called a Tyndallometer.

In smokes whose particle dimensions are greater than the wavelength of the light, the intensity of the scattered light  $I_s$  is expressed by the formula:

$$I_s = k \cdot \frac{C}{r}$$

where  $k$  is a proportionality factor;

$C$  is the weight concentration of the aerosol

$r$  is the radius of the aerosol particles.

When the dimensions of the aerosol particles are considerably less than the wavelength of the light passing through it, the intensity of the scattered light increases rapidly as the size of the particles increase:

$$I_s = k \cdot C \cdot r^3$$

Aerosols whose particles are of a size close to the wave-length of visible light, i.e., 0.1 - 10  $\mu\text{m}$  have the greatest ability to scatter light and consequently also have the maximum screening effectiveness. The intensity of the scattering of light increases considerably as the wavelength of the light is reduced. According to Rayleigh's formula, the intensity of scattered light for any given disperse system will be expressed by:

$$I_s = I_0 \frac{k \cdot C \cdot r^3}{\lambda^4}$$

where  $I_0$  is the intensity of the incident light

$\lambda$  is the wavelength of the incident light.

Long-wave, red, and especially infrared rays are least subject to scattering by smokes and mists.

The quantitative relationship between the absorption of light by an aerosol of constant dispersivity, the concentration of the aerosol, and the thickness of the absorbing layer may be expressed by the Lambert-Bougie-Beer formula:

$$I = I_0 \cdot e^{-k \cdot C \cdot l}$$

where  $I_0$  is the intensity of the light entering the absorbing layer

$I$  is the intensity of the light leaving the absorbing layer

$l$  is the thickness of this layer

$e$  is the base of the natural logarithms.

For smoke screens, the concept of *covering ability* of the smoke is of great significance. This, other things being equal, is an inverse function of the intensity of the light that passed through to the intensity of the light that entered the smoke (i.e if this ratio is small, the "covering ability" is greater).

In practice, the covering ability (optical density)  $D$  of a smoke is frequently determined by the formula:

$$D = \frac{1}{l}$$

where  $l$  is the thickness of the layer of smoke that totally obscures the light of a lamp used as a measurement standard. A 25 watt lamp has been used in some tests, and the tests themselves were conducted in a chamber 1.8 m wide and high, and 2.4 m long.

For a comparison of smoke-forming agents we sometimes use the so-called *total obscuration power*  $W = v.D$ , where  $v$  is the volume of the smoke or mist obtained from a unit weight of the smoke-forming agent, and  $D$  is the covering ability of the smoke. The quantity  $W$  is expressed as area of the screen (in  $\text{m}^2$ ) obtained from 1 kg of smoke-producing agent, and which provides complete obscuration.

The values of the total obscuration power for certain smoke-forming agents and combustible mixtures, after Prentiss's data, are given in Table 18.1.

| Smoke-forming agent or mixture                | Total obscuring power, $W$<br>( $\text{m}^2 \text{ kg}^{-1}$ ) |
|-----------------------------------------------|----------------------------------------------------------------|
| white phosphorus                              | 1,042                                                          |
| $\text{NH}_3 + \text{HCl}$                    | 567                                                            |
| American HC mixture based on hexachloroethane | 466                                                            |
| $\text{TiCl}_4$                               | 430                                                            |
| $\text{SiCl}_4$                               | 340                                                            |
| $\text{SO}_3.\text{HCl}$                      | 317                                                            |

Table 18.1 Total obscuring power of smoke mixtures

### Section 3. Methods of obtaining aerosols.

Smokes or mists can be obtained by the dispersion or the condensation methods.

These two methods differ in that in dispersion, the specific surface area of the initial system increases, and in condensation it is reduced.

Producing smoke or mists by the dispersion method reduces to dividing a solid (or liquid) substance by means of crushing (or spraying) it or by atomising it by means of an explosion. The expenditure of energy needed to obtain aerosols by the dispersion method may be related quantitatively to a defined amount of mechanical work.

The condensation process proceeds spontaneously and requires only the expenditure of a quantity of energy to obtain a supersaturated vapour. In the condensation of the vapour, individual

molecules adhere together to form larger aggregates called colloidal particles. The supersaturated vapour can be obtained by two methods:

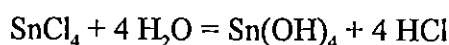
1. cooling a heated vapour;
2. obtaining, from gaseous products, a solid or liquid substance that saturates the space with its vapour.

The dispersion method usually produces aerosols with larger particles than the condensation method. This, and the often quite complex and cumbersome equipment required for the dispersion method means that in practice aerosols are usually obtained by the condensation method.

In certain cases, both the dispersion and condensation methods may be used simultaneously to obtain aerosols; we may call this the combined method of producing aerosols.

The development of smoke screens is accomplished in practice by the following methods:

1. By dispersion of highly volatile liquids (such as  $\text{SnCl}_4$ ) in the air, which then forms smoke, reacting in a finely atomised state with the moisture of the air

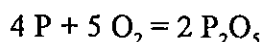


Certain physico-chemical properties of liquid smoke-forming agents of such a type are given in Table 18.2.

| Smoke-forming agent    | Density<br>( $\text{Mg m}^{-3}$ ) | Melting<br>point<br>$^{\circ}\text{C}$ | Boiling<br>point<br>$^{\circ}\text{C}$ | Products of reaction with<br>moisture of the air |
|------------------------|-----------------------------------|----------------------------------------|----------------------------------------|--------------------------------------------------|
| stannic chloride       | 2.2                               | -33                                    | 114                                    | $\text{Sn(OH)}_4$ , HCl                          |
| titanium tetrachloride | 1.8                               | -23                                    | 136                                    | $\text{Ti(OH)}_4$ , HCl                          |
| silicon tetrachloride  | 1.5                               | -69                                    | 59                                     | $\text{Si(OH)}_4$ , HCl                          |
| chlorosulphonic acid   | 1.8                               | -80                                    | 158                                    | $\text{H}_2\text{SO}_4$ , HCl                    |
| sulphur trioxide       | 1.9                               | +17                                    | 45                                     | $\text{H}_2\text{SO}_4$                          |

Table 18.2 Properties of liquid smoke-forming agents

2. By burning various substances in the air to give products which condense when cooled. White phosphorus is used most frequently for this purpose:



The vapours of phosphorus anhydride react with the moisture of the air forming metaphosphoric and orthophosphoric acids, which have very low vapour pressures at room temperature.

3. By evaporation or incomplete combustion of oils. In the first case, the vaporised oil condenses in the air in the form of small drops as a mist; in the second case, part of the carbon is liberated in a free state as carbon black, forming black clouds that at first are very effective in screening objects from observation. But carbon black flocculates very rapidly, its particles stick together upon contact and form flocks that increase steadily in size and fall rapidly to the ground. The black smoke has a poor covering ability. An intermediate method is to burn part of the oil with simultaneous evaporation of the rest. In this case, the liquid particles of oil envelop the black particles of carbon black, and this at first prevents flocculation. Such a mist of gray-black colour is more persistent until such time as one of its component parts, the oil, evaporates. The flocculation of the mist is only somewhat postponed.
4. By burning pyrotechnic smoke compositions which contain various smoke-forming agents or form them in the process of the combustion reaction.

#### Section 4      Screening smoke compositions and the requirements placed upon them.

The following special requirements are imposed upon neutral screening smoke compositions:

1. the smoke obtained from the combustion reaction must have the maximum covering ability (not less than 500 m<sup>2</sup> kg<sup>-1</sup>) and must be adequately stable in the air;
2. the compositions must not produce a flame when burned in smoke pots;
3. the slag formed on combustion of the compositions must be friable (porous) and must not prevent smoke from passing through it.

The products of combustion of these compositions intended for establishing a smoke screen to hide one's own troops must not have any harmful effect on the health of the troops.

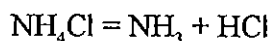
Two sharply differing types of screening-smoke compositions exist. Some of them contain smoke-forming agents in their prepared form; in others the smoke-forming agents are obtained during combustion (metal-chloride smoke mixtures)

Compositions of the first type contain the following components: oxidiser, fuel, and smoke-forming agent.

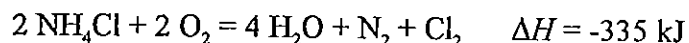
Substances that sublime readily are used as smoke-forming agents, such as ammonium chloride (sal ammoniac), and aromatic hydrocarbons: naphthalene, and anthracene. Smoke is formed by the sublimation and subsequent condensation on cooling of the smoke-forming agents.

Ammonium chloride dissolves easily in water, and its density is 1.52. A noticeable sublimation of ammonium chloride begins by 250°C, and at 339°C its vapour pressure reaches 760 mmHg. Its melting point in an enclosed volume is 520 °C, and its heat capacity is 1.63 MJ kg<sup>-1</sup>.

At increased temperatures ammonium chloride dissociates into ammonia and hydrogen chloride as well as subliming



The reaction is reversible and shifts to the left on cooling <sup>1</sup>. At higher temperatures, ammonium chloride may be oxidised by atmospheric oxygen:



The degree of dissociation of ammonium chloride in the temperature range 200 - 400°C varies from 57 to 79%.

The use of ammonium sulphate as a smoke-forming agent in smoke compositions is scarcely feasible since it is much less volatile than ammonium chloride. Ammonium fluoride is also little suited for use as a smoke-forming agent as it already decomposes partially into ammonia and hydrogen fluoride at room temperature.

Of the other inorganic compounds, the halogen compounds of many metals (zinc, iron, and aluminium) have a high volatility at relatively low temperatures (below 1000°C), but they contain water of crystallisation and are so hygroscopic that their dehydration presents great difficulties.

Among the organic compounds, hydrocarbons of both the aliphatic and aromatic series may be used as smoke agents. Thus, for example, spindle oil, machine oil, and cylinder oil may be vaporised without decomposition.

Among the aromatic hydrocarbons, naphthalene and anthracene have found the most extensive use as smoke agents in pyrotechnic compositions.

The physico-chemical properties of naphthalene are described in Chapter IV. The essential shortcoming of naphthalene is its considerable volatility even at room temperature.

Anthracene  $\text{C}_{14}\text{H}_{10}$  forms white crystals; its density is 1.25, melting point 218°C, and boiling point 342°C.

Phenanthrene  $\text{C}_{14}\text{H}_{10}$  is an isomer of anthracene, and has a melting point of 99°C and a boiling point of 240°C; it sublimes readily at a temperature of about 200°C. Technical anthracene, which is a greenish-yellow mass containing anthracene (up to 25%), phenanthrene, carbazol ( $\text{C}_{12}\text{H}_9\text{N}$ ) and other hydrocarbons, is frequently used as a smoke-forming agent in smoke compositions. The flash point of crude anthracene is 150-162°C.

Charcoal is sometimes used as a fuel in screening-smoke compositions.

As well as acting as a smoke-forming agent, naphthalene and anthracene can also act as a fuel in some compositions, partly subliming and partly burning. Potassium chlorate is usually used as the oxidiser in screening-smoke compositions.

Typical smoke compositions similar to Yershov's mixture contain:

|                    |        |
|--------------------|--------|
| potassium chlorate | 20-30% |
| ammonium chloride  | 50%    |

|                             |       |
|-----------------------------|-------|
| naphthalene (or anthracene) | 20%   |
| charcoal                    | 0-10% |

The small content of chlorate in the composition and the large content of an almost inert substance, ammonium chloride, confers comparatively low sensitiveness to mechanical stimuli on such compositions.

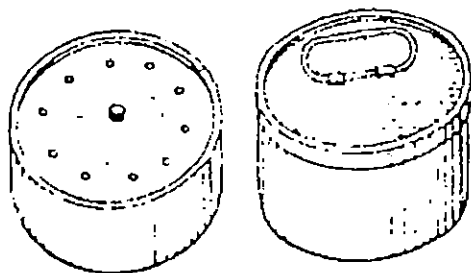


Fig 18.2 Open and closed smoke pots

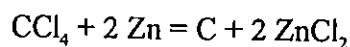
The oxygen balance of smoke mixtures similar to Yershov's mixture is highly negative, and the gaseous phase that forms on combustion contains a considerable quantity of CO and highly flammable vapours of naphthalene or anthracene. When such compositions are used as a filling for various products, they are enclosed in a shell provided with individual outlet or exhaust holes, which protect the burning surface of the composition from the oxygen of the air (Fig. 18.2).

In spite of the precautionary measures used, smoke compositions sometimes produce sparks as they burn. If that happens the uniformity of combustion is disrupted, flames appear at the apertures of the pot, and the smoke released is reduced sharply in quantity, and also acquires a grayish tint. Special substances, flame quenchers, are therefore added to smoke compositions that are too active.

The best flame-quenching agents are carbonates: soda, chalk, magnesium carbonate, which liberate carbon dioxide gas during combustion. This dilutes the flammable reaction products to some extent.

Depending upon the properties of the smoke composition, the content of flame quenchers in it may reach as high as 10 - 15% in some cases.

Compositions of the second type are metal chloride smoke mixtures. In such compositions the smoke-forming agents are obtained from a combustion reaction, for example:



The smoke formed here is grey since it contains white particles of zinc chloride as well as black particles of carbon.

Zinc chloride forms white, highly hygroscopic crystals; its density is 2.91, its melting point is 365°C, and its boiling point 732°C. It undergoes partial hydrolysis in moist air.

For the properties of  $\text{CCl}_4$ , see reference <sup>7</sup> page 235.

Apart from the two basic components - the organochlorine compounds and the metal powder - metal chloride smoke mixtures contain a number of components that perform auxiliary functions. All mixtures containing  $\text{CCl}_4$  also contain an absorbant for this liquid. As absorbants, infusorial earth ( $\text{SiO}_2$ ), zinc oxide, or magnesium carbonate are most frequently used. For more details on absorbants, see reference <sup>211</sup> page 159.

An additional oxidiser, such as  $\text{NaClO}_3$ ,  $\text{KClO}_3$ ,  $\text{KClO}_4$ , and an additional smoke-forming agent, such as ammonium chloride, are sometimes added to metal chloride smoke mixtures.

When an additional oxidiser such as a chlorate (or perchlorate) is present in the mixture, the smoke obtained is considerably whiter, since the carbon formed in the combustion of the mixture burns forming CO (or  $\text{CO}_2$ ).

Ellern <sup>9</sup> page 48 has indicated that mixtures containing  $\text{CCl}_4$  are no longer used. Pavlov <sup>212</sup> has written an article on the use of screening smoke by the US army.

Carbon tetrachloride has been replaced in modern smoke mixtures by solid organochlorine compounds - hexachloroethane, hexachlorobenzene, hexachlorocyclohexane, and others. Mixtures which do not contain the liquid  $\text{CCl}_4$  do not need absorbants.

An example of a smoke forming mixture consisting only of solid components is the following composition:

|                    |     |
|--------------------|-----|
| hexachloroethane   | 30% |
| potassium chlorate | 29% |
| zinc               | 38% |
| charcoal           | 3%  |

During World War II German smoke pots were filled with a composition consisting of the following components:

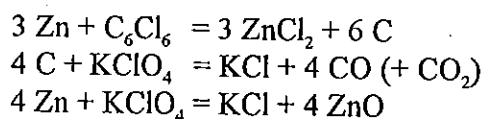
|                  |     |
|------------------|-----|
| hexachloroethane | 53% |
| zinc             | 44% |
| magnesium oxide  | 3%  |

One of the shortcomings of hexachloroethane is its considerable volatility at room temperature, which even exceeds that of naphthalene. Thus, at  $60^\circ\text{C}$  the vapour pressure of naphthalene is 2 mm, and that of hexachloroethane is 6 mm. From this standpoint, hexachlorobenzene has much better properties.

Gordon and Campbell <sup>213</sup> have investigated the ternary mixture A, consisting of zinc,  $\text{C}_6\text{Cl}_6$  and  $\text{KClO}_4$ , and also binary mixes of the same components. According to their data, the heat of combustion of mixture A is equal to  $2.17 \text{ MJ kg}^{-1}$ , and the volume of the gases  $v_g = 77 \text{ l kg}^{-1}$  (85% CO and 15%  $\text{CO}_2$ ).

The initiation temperature of mixture A is  $325^\circ\text{C}$ , and that of binary mixture B, which is Zn/ $\text{KClO}_4$  (65/35), is  $520^\circ\text{C}$ . The heat of combustion of mixture B is  $3.43 \text{ MJ kg}^{-1}$ . On the basis of

their investigations, the authors have concluded that pre-initiation, initiation, and combustion of mixture A are accomplished by means of the successive occurrence of three reactions:



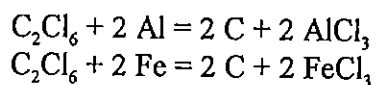
Certain properties of solid organochlorine compounds are given in Table 18.4.

| Compound and formula                                  | Chlorine content (%) | Molecular weight | Density ( $\text{Mg m}^{-3}$ ) | Temperature in °C |                            |
|-------------------------------------------------------|----------------------|------------------|--------------------------------|-------------------|----------------------------|
|                                                       |                      |                  |                                | Melting point     | Boiling point              |
| hexachloroethane<br>$\text{C}_2\text{Cl}_6$           | 90                   | 237              | 2.1                            | 185               | sublimes vigorously at 185 |
| hexachlorobenzene<br>$\text{C}_6\text{Cl}_6$          | 75                   | 285              | 1.6                            | 227               | 323                        |
| pentachlorobenzene<br>$\text{C}_6\text{Cl}_5\text{H}$ | 71                   | 250              | 1.8                            | 86                | 277                        |
| octachloronaphthalene<br>$\text{C}_{10}\text{Cl}_8$   | 70                   | 404              | -                              | 203               | -                          |

Table 18.4 Properties of organo-chlorine compounds

Ellern <sup>9</sup> reports that metal chloride mixtures are quite stable in storage when dry, but in the presence of moisture some are subject to spontaneous heating and even spontaneous ignition. Therefore the mixture  $\text{C}_2\text{Cl}_6 + \text{Zn}$  is no longer used.

Metal chloride smoke mixtures may use powdered aluminium, powdered iron, and calcium silicide as well as zinc dust. The combustion of such mixtures occurs with the formation of the chlorides of the corresponding metals:



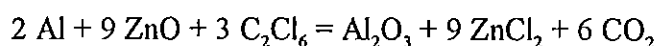
Below we give the recipes of binary mixtures of metallic powders and hexachloroethane calculated on the basis of total oxidation of the fuels:

|     |                  |       |
|-----|------------------|-------|
| and | Hexachloroethane | 81.4% |
|     | Aluminium        | 18.6% |
|     | Hexachloroethane | 67.9% |
|     | Iron             | 32.1% |

A mixture of hexachloroethane with aluminium burns fiercely. In order to retard its combustion, considerable quantities of substances that act simultaneously as additional smoke forming agents are added to it (ammonium chloride, zinc oxide, and others). Thus, for example, the HC white smoke composition has the following recipe <sup>9</sup> :

|             |          |
|-------------|----------|
| $C_2Cl_6$   | 45 - 47% |
| ZnO         | 47 - 48% |
| Al          | 5 - 8%   |
| $ZnCO_3$    | 0 - 1%   |
| Zinc borate | 0 - 1%   |

The following reaction occurs on combustion of a mixture containing some aluminium <sup>9</sup>:



However, the smoke formed on combustion of such a mixture contains a certain quantity of carbon black, and in colour appears more grey than white.

| Composition of mixture (%) |      |    |      | Expansion in a Trauzel bomb (cm <sup>3</sup> ) |
|----------------------------|------|----|------|------------------------------------------------|
| $CCl_4$                    | 76   | Mg | 24   | 215                                            |
| $CCl_4$                    | 81   | Al | 19   | 156                                            |
| $C_2Cl_6$                  | 81.5 | Al | 18.5 | 64                                             |

Table 18.5 Trauzel tests of metal chloride mixtures (20 g mixture; lead rod in bomb channel instead of sand filling)

New American recipes contain  $C_2Cl_6$ , ZnO, and  $NH_4ClO_4$ , and are wetted with a solution of polyvinyl acetate. Such mixtures can be filled without pressure, and after evaporation of the solvent become firm, and elastic.

Aluminium chloride, formed during the combustion of mixtures containing  $C_2Cl_6$  and a considerable percentage of aluminium, is a white, easily sublimable, very hygroscopic substance.

A mixture of hexachloroethane with iron powder burns slowly and with little activity, releasing a brown smoke of ferric chloride during combustion. Anhydrous ferric chloride  $FeCl_3$  sublimes at a temperature as low as 250°C and boils with partial decomposition at 316°C. It absorbs moisture thirstily from the air forming the crystalline hydrate  $FeCl_3 \cdot 6H_2O$ .

Mixtures of  $CCl_4$  or  $C_2Cl_6$  with magnesium or aluminium may explode on application of an adequate stimulus (a No. 8 detonator cap) when enclosed in a strong casing, but the force of the explosion is not great, judging from the data obtained (Table 18.5).

The highly volatile silicon tetrachloride  $\text{SiCl}_4$  is formed on reaction of hexachloroethane with calcium silicide, which produces silicic acid smoke on reaction with the moist air. As an example of a smoke mixture containing calcium silicide, we may give the following recipe:

|                  |     |
|------------------|-----|
| hexachloroethane | 45% |
| zinc oxide       | 45% |
| calcium silicide | 10% |



## Chapter XIX

### Coloured Smoke Compositions

Coloured smoke compositions are used in warfare chiefly for daylight signals; they are also used as bombing and artillery firing aids, for fire correction and for target indication. In transport they are used for making distress signals (emergency signals), on land, and especially at sea.

#### Section 1. Coloured smoke clouds for signalling and methods of obtaining them.

Smoke clouds of four colours are usually used for daytime signalling: red, yellow, green, and blue. It is sometimes proposed that black smoke can also be used for daylight signalling, and black smoke is given either as a fifth signal or as a replacement for one of the colours, particularly blue or green which are more difficult than the others to distinguish from each other, particularly at long range.

The basic shortcoming of daytime signalling by coloured smokes is the effect meteorological conditions have on the observation of the smoke and on the reliability of the determination of its colour.

The factors which primarily affect the observation of smoke signals are:

1. the shape and dimensions of the coloured smoke cloud;
2. the brightness and colour of the background against which the smoke signal is observed;
3. the height of the sun above the horizon and the position of the observer in relation to the sun and the smoke cloud;
4. the wind velocity;
5. atmospheric precipitation (snowfall, rain, fog).

The best conditions for observing and distinguishing the colour of smoke clouds are clear, calm weather, with a wind velocity of not more than  $2-3 \text{ m s}^{-1}$ . With a wind velocity of more than  $6 \text{ m s}^{-1}$ , the smoke cloud is very rapidly dispersed. The colour of a smoke cloud is most difficult to distinguish when it lies directly between the sun and the eye of the observer (Fig. 19.1); when observed under such conditions, many coloured clouds appear almost white. On the other hand, when the sun is behind the observer, a coloured cloud acquires a dark tint.

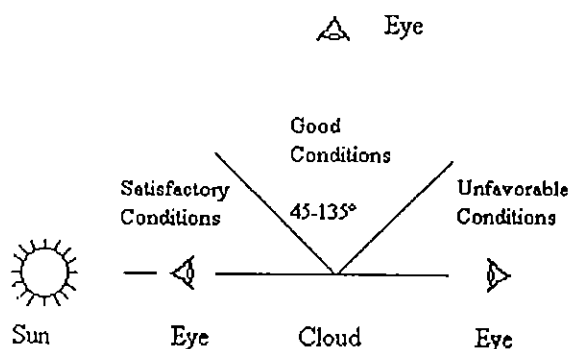


Fig 19.1 Observation of coloured signal smokes.

The best conditions for observing the colour of a cloud are when the angle formed by the sun, the smoke cloud, and the eye of the observer is between  $45$  and  $135^\circ$ .

The stability of a signal cloud in the air is greatly affected by its shape and size.

Parachute signal devices usually produce a coloured smoke trail as they descend. This trail is rapidly dispersed by the air currents, but the smoke is continuously replenished by further discharges from the smoke cartridge into the atmosphere.

In devices not equipped with a parachute, smoke formation must be achieved almost instantaneously; a compact coloured cloud is formed in the air which, depending upon the quantity of smoke composition used and on the meteorological conditions, may be clearly observed for a few dozen seconds to a few minutes.

Generation of coloured signal smoke by the dispersion method is accomplished by atomisation of finely divided mineral pigments (dyes) by means of explosives or powder. The mineral pigments most frequently used are red lead, cinnabar, and ultramarine blue. However to obtain a coloured cloud of satisfactory quality and duration, we must expend too large a quantity of coloured pigment (1-2 kg). Coloured smoke obtained by mechanical atomisation of mineral pigment is very rapidly dispersed, since its particles are too large (10 - 100  $\mu\text{m}$ ) and settle rapidly.

There has been no particular success in obtaining coloured smokes by the condensation method by means of chemical reactions between inorganic substances. Almost all the mixtures proposed have given rather unsatisfactory results on testing, both with respect to the quantity of smoke obtained, and to its colour characteristics.

Relatively acceptable results have been obtained only for black smoke compositions, in which the smoke is obtained by the combustion of metal chloride mixtures containing carbon-rich aromatic compounds as a third component.

As an example, we may give the following recipe for a black signal smoke composition:

|                             |     |
|-----------------------------|-----|
| hexachloroethane            | 60% |
| magnesium                   | 19% |
| naphthalene (or anthracene) | 21% |

According to the literature, the mixture burns at a rate of 4 mm s<sup>-1</sup> and produces a dense black smoke; this mixture is sensitive to shock. Its shortcomings are the rapid volatilisation of the hexachloroethane and the naphthalene from it, and the low melting point of a mixture of hexachloroethane and naphthalene. A mixture of 8 parts naphthalene to 20 parts hexachloroethane melts at 53°C. Therefore, it has turned out to be expedient to replace the naphthalene by anthracene.

The combustion of such mixtures must occur with free access of air, otherwise the naphthalene or anthracene will not burn but sublime, and the smoke obtained will not be black, but grey.

Recipes for black smoke compositions which do not contain organochlorine compounds include:

|    |                    |     |
|----|--------------------|-----|
|    | potassium chlorate | 45% |
|    | naphthalene        | 40% |
|    | charcoal           | 15% |
| or |                    |     |
|    | potassium chlorate | 55% |
|    | anthracene         | 45% |

Features which distinguish such black smoke mixtures from white screening smoke compositions, are the absence of ammonium chloride, and the high content of potassium chlorate. In this case the combustion temperature of the mixture rises considerably and the naphthalene does not sublime, but undergoes incomplete combustion, accompanied by the liberation of a great quantity of carbon black.

Of the coloured smokes obtained by chemical reactions, it appears that only a yellow-orange smoke composition is worth attention <sup>9</sup>: Mg 16%, C<sub>2</sub>Cl<sub>6</sub> 48%, Fe<sub>2</sub>O<sub>3</sub> 36%. Ferric chloride FeCl<sub>3</sub> formed during combustion gives the smoke its colouring.

The best quality signal smokes of all colours (red, yellow, green, and blue) have been produced by the sublimation of organic pigments (dyes). The dye is volatilised from a mixture containing an oxidiser and a fuel, and is expelled by the gaseous combustion products of the reaction into the atmosphere, where it condenses to form the coloured smoke. An example of such a mixture is the following blue smoke composition:

|                    |     |
|--------------------|-----|
| potassium chlorate | 35% |
| lactose            | 25% |
| synthetic indigo   | 40% |

## Section 2. Pigments used in signal smoke compositions.

The following special requirements are imposed upon the organic pigments used in signal smoke compositions:

1. they must sublime rapidly at temperatures as low as 400-500°C;
2. their sublimation must be accompanied by the smallest possible decomposition of the pigment;
3. the coloured smoke formed by the condensation or the vapours of the pigment in the air must have a sharply defined specific colour (red, yellow, blue) and must be adequately persistent in the air.

The sublimation rate of the pigment depends primarily upon its vapour pressure at high temperatures. The vapour pressure of certain pigments at 260°C and their latent heats of sublimation are found in reference <sup>7 page 243</sup>.

Without a doubt, the sublimation rate will depend also upon the heat capacity and the latent heat of sublimation of the pigments; a pigment will sublime more rapidly if less heat must be expended

to transform it to a vapour state. The average specific heat capacity in the temperature range 20-200°C of the majority of pigments used is 1.3 - 1.7 J K<sup>-1</sup>.

Since organic pigments decompose when subjected to prolonged high temperature, it is necessary to sublime them rapidly.

Pigments are tested quantitatively for thermal stability and ability to form coloured vapours by taking a small portion on the end of a spatula and placing it in a porcelain crucible that has been heated over an ordinary gas burner to 400-600°C. If the pigment forms coloured vapours, this indicates that it is relatively thermally stable and that we should perform further testing of it in pyrotechnic compositions. If the pigment decomposes during the tests liberating colourless vapours or vapours of a dirty-grey colour, then it is unsuitable for use in signal smoke compositions.

It has been experimentally established that pigments having the simplest chemical structure are the most thermally stable.

Besides this, it has been ascertained that certain chemical groups in an organic pigment may prevent the formation of coloured vapours on heating. Among the groups in a pigment which hamper its vaporisation are:

1. The sulpho group R - SO<sub>3</sub>H, R - SO<sub>3</sub>R, or R -SO<sub>3</sub>Na;
2. The group R - O - Me (Me is a metal).

3. The benzidine group in azo dyes: 

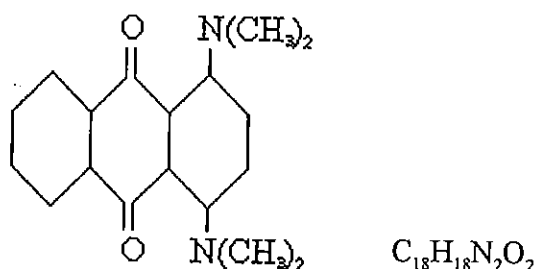
Sulphur-containing dyes that are insoluble in water also fail to produce coloured vapours, and consequently are also unsuitable for use in signal smokes.

Mononitroamino compounds (intermediate), azo dyes, diphenylmethane, triphenylmethane, thiazine, and anthraquinone dyes are most frequently used to produce coloured smokes. See <sup>214</sup> for the classification of these dyes.

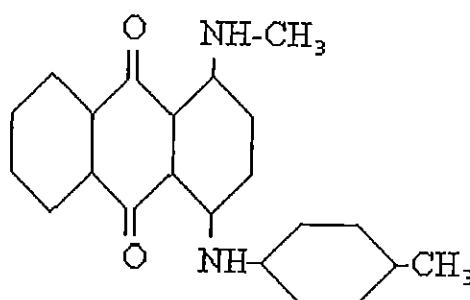
The following intermediate products and dyes are used most commonly in coloured smoke compositions:

1. Paranitroaniline - a yellow coloured smoke.
2. Auramine O - a yellow coloured smoke (used with an additive of the brown pigment chrysoidin).
3. Butter orange (benzeneazobetanaphthol) - an orange coloured smoke.
4. Rhodamine B - a raspberry-red smoke.
5. Sudan red (2-anisidine-azobetanaphthol) - red smoke.
6. Methylene blue - a blue coloured smoke.
7. Indigo - a blue coloured smoke.

Information on the chemical composition and properties of these dyes can be found in the second edition of this book <sup>7</sup>.



Anthraquinone dyes may also be used to obtain coloured smoke. 1,4 dimethylaminoanthraquinone is an example of this class of dyes which produce a good blue coloured smoke upon sublimation: "Sudan blue G" is also among the anthraquinone dyes, and chemically it is 1-methylamino-4-paratoluilanthraquinone which was used in German blue smoke compositions.



1-methylaminoanthraquinone is used to obtain a red smoke.

### Section 3. Coloured smoke compositions.

The sublimation of organic dyes for production of coloured signal smokes is accomplished by the heat liberated on combustion of the so-called "thermal mixture," consisting of the oxidiser and fuel.

The thermal mixture must liberate the heat needed to vaporise the pigment, but must not develop a high temperature during combustion to avoid causing decomposition of the dye. Besides this, the thermal mixture must liberate a considerable quantity of gaseous reaction products during combustion, to facilitate the rapid removal of the vapours of the subliming dye from the vicinity of the combustion reaction. For these reasons, metal powders cannot be used as fuels in coloured smoke compositions.

Organic substances are the most suitable fuels in this case. In practice, carbohydrates are most frequently used, since they form a great quantity of gaseous reaction products during their combustion, and do not release too great a quantity of heat (Table 19.1).

It is apparent from Table 19.1 that mixture 2, in which the combustion of the lactose proceeds only as far as carbon monoxide, is preferable. Experience shows that the use of such a thermal

mixture in coloured smoke compositions, calculated for incomplete combustion of the fuel, gives us the opportunity of obtaining a smoke of the best quality.

| Number of mixture | Combustion reaction of mixture                                                                                                                   | Fuel content of mixture (%) | Heat of combustion (MJ kg <sup>-1</sup> ) | Specific volume of gaseous reaction products (m <sup>3</sup> kg <sup>-1</sup> ) |
|-------------------|--------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------------|-------------------------------------------|---------------------------------------------------------------------------------|
| 1                 | $8 \text{ KClO}_3 + \text{C}_{12}\text{H}_{22}\text{O}_{11} \cdot \text{H}_2\text{O} = 8 \text{ KCl} + 12 \text{ CO}_2 + 12 \text{ H}_2\text{O}$ | 26.9                        | 4.43                                      | 0.401                                                                           |
| 2                 | $4 \text{ KClO}_3 + \text{C}_{12}\text{H}_{22}\text{O}_{11} \cdot \text{H}_2\text{O} = 4 \text{ KCl} + 12 \text{ CO} + 12 \text{ H}_2\text{O}$   | 42.3                        | 2.63                                      | 0.632                                                                           |

Table 19.1 Heat of the combustion reaction and specific volume of gaseous reaction products of binary mixtures

Milk or beet sugar, starch and sawdust are among the carbohydrates used. The first two substances are products of the food-processing industry, and it is possible that they may be replaced by fuels used in insecticide smoke compositions, such as dicyandiamide, for example (see Chapter III).

Berthollet's salt is used almost exclusively as an oxidiser in coloured smoke compositions; however, occasionally recipes are given in the foreign literature for compositions using potassium perchlorate as the oxidiser. Becher <sup>8</sup> indicates that a thermal mixture of potassium chlorate with carbohydrates may be replaced by nitrocellulose if desired.

The quantity of dye in coloured signal smoke compositions varies from 40% to 60% depending upon its chemical nature and the rate of combustion required of the composition. In particular cases a substance retarding ignition of the dye vapours is introduced into the compositions. Such substances are called flame quenchers. We often use  $\text{NaHCO}_3$  for this purpose. The role of a flame quencher is to reduce the temperature of the combustion and form an inert gas ( $\text{CO}_2$ ) on decomposition, which reduces the contact of the dye vapours with the air.

Ellern <sup>9</sup> gives the following recipe for a coloured smoke composition with a "plastic binder":

|                  |     |
|------------------|-----|
| Organic dye      | 51% |
| Cane sugar       | 18% |
| $\text{KClO}_3$  | 23% |
| $\text{NaHCO}_3$ | 8%  |

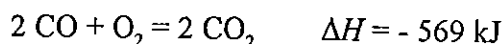
A solution of 2.2 parts of polyvinyl acetate in 50 parts dichloromethane are added to 100 parts of this mixture. The solvent is removed when the composition is dried.

A typical coloured smoke composition not containing a flame quencher is:

|                    |          |
|--------------------|----------|
| Potassium chlorate | 30 ± 10% |
| Dye                | 50 ± 5%  |
| Carbohydrate       | 20 ± 5%  |
| Resin binder       | 0 - 5%   |

The binder is used only if the composition is to be granulated. Granulation increases the combustion surface of the composition and thus reduces the total time of smoke generation. In addition it improves the colour of the smoke, since in a granulated composition the dye vapours may pass more rapidly from the reaction sphere and need not pass through high temperature slag, which in some cases has a very dense consistency. Chlorate compositions are prepared with granules from 2 to 5 mm. Granulation of the composition eliminates its exfoliation (?) during transport, filling and use.

Signal smoke compositions must burn in the absence of atmospheric oxygen. The composition is placed therefore in a porous shell - a sack or cardboard or tin-plate canister, with a number of holes for discharge of the smoke. If atmospheric oxygen is allowed access, the combustion temperature of the composition rises considerably because of the further combustion of the carbon monoxide



which is accompanied by the formation of a flame, and leads to almost total combustion of the coloured dye vapours.

But partial decomposition of the dyes still occurs even when the reaction proceeds without a flame. The quantity of smoke formed in the combustion of chlorate smoke compositions usually ranges from 30% to 70% of the initial weight of the dye and, moreover, the smoke itself contains only 60-80% of the dye (the remaining 20-40% goes into the resinous products of its decomposition).

For recipes of chlorate signal smoke compositions, see <sup>7</sup> page 252.

Of the compositions containing nitrates we may indicate the following which has the important shortcoming of high hygroscopicity:

|                |     |
|----------------|-----|
| sodium nitrate | 25% |
| sawdust        | 35% |
| rhodamine      | 40% |

For artillery fire correction under battle conditions (especially when many guns are firing simultaneously), it is frequently necessary to mark the point of fall, or of air burst of high-explosive fragmentation projectiles. In daytime this is achieved by the formation of a cloud of

intensely coloured smoke when the projectile bursts. Such projectiles may also be used in air defence.

It is well known that mixtures of organic dyes with various explosives are used to produce coloured smoke bursts in artillery firing. When the charge is exploded, organic dye sublimates and forms coloured smoke.

In 1941-1945 German target-indicating projectiles were filled with mixtures of powerful explosives (PETN, hexogen) with azo dyes. The dye content in such mixtures amounted to 55-65%.

In an American patent <sup>218</sup> the following description of the design and filling of three- and five-inch target-indicating projectiles is given. The colouring matter (organic dyes) are placed in the projectile casing so that during the explosion they are converted into a vapour state; then, coming in contact with the cold air, the sublimated dyes are condensed in the form of a fine intensely coloured smoke.

Dyes amounting to about 10% of the weight of the bursting charge need not be mixed with the explosive, but are placed between the walls of the casing and the central bursting charge. For low-melting dyes (melting point less than 150°C), it is possible to fill the casing by the centrifugal casting method; to reduce the melting point, the dye may be mixed with paraffin or thermoplastic resin.

The following are suitable explosives since they give almost no dark cloud of carbon black during the explosion: 1) nitroguanidine, 2) a mixture of ammonium picrate and ammonium nitrate ( $\text{NH}_4\text{NO}_3$ , from 40 to 75%).

Dyes that have shown good results include the following:

- |                          |                                                                          |
|--------------------------|--------------------------------------------------------------------------|
| 1. Red or orange smokes: | butter orange and diethyl- <i>m</i> -aminophenolphthalein hydrochloride; |
| 2. Yellow smoke:         | aminoazotoluene and benzeneazodimethylaniline;                           |
| 3. Blue smoke:           | quinizarine blue, anthraquinone violet.                                  |

Bursts of orange-red smoke are observed in the air better than other colours.

Ellern <sup>9</sup> indicates that EC smokeless powder may be used to obtain coloured smoke, and gives a recipe of the composition:

|             |     |
|-------------|-----|
| Organic dye | 50% |
| EC powder   | 50% |

EC powder is a mixture of partially gelatinised nitrocellulose (NC) with an admixture of nitrate, namely:

|                                   |      |
|-----------------------------------|------|
| NC                                | 80.4 |
| KNO <sub>3</sub>                  | 8.0  |
| Ba(NO <sub>3</sub> ) <sub>2</sub> | 8.0  |
| starch                            | 3.0  |
| diphenylamine                     | 0.6  |

For recipes of signal smoke compositions used during World War II, also see reference<sup>216</sup>.

#### Section 4. Methods of testing coloured smoke compositions.

Special investigations of coloured smoke compositions consist of studying the properties of the coloured smoke formed during their combustion. The following tests are performed more frequently than others:

1. determination of the total quantity of smoke obtained in the combustion of 1 g of smoke composition;
2. determination of the stability of the smoke in the air, and also the determination of the dimensions of the smoke particles;
3. determination of the colour quality of the smoke.

These tests are conducted in the same smoke chamber as for investigations of screening smokes.

The total quantity of smoke formed in the combustion of a smoke composition in the chamber is determined placing pre-weighed glass plates (9 x 12 cm) on the bottom and side walls of the chamber, and re-weighing them after the experiment.

The stability of a coloured smoke in the air may be determined by any of the methods normally used to investigate aerosol stability.

The colour of smokes may be determined quantitatively by methods used for measuring the colour of coloured cloths and, in general, of all coloured materials. It is true that here we must bear in mind only the definition of the colour of the smoke in reflected light, but it is precisely this definition that is of the greatest value.

The results in Table 19.2 were obtained for the colour characteristics of signal smokes in reflected light using a Pulfrich spectrophotometer.

Work on the determination of the colour quality of smokes has also been conducted abroad<sup>217</sup>. The determination of the colour of the smoke in transmitted light is of no special interest for pyrotechnists and does not permit us to judge the quality of the smoke obtained.

| Composition of coloured smokes<br>(%) |    |                     |    |                   |    |              |    | Colour characteristics of<br>the smoke |                                  |                                     |
|---------------------------------------|----|---------------------|----|-------------------|----|--------------|----|----------------------------------------|----------------------------------|-------------------------------------|
|                                       |    |                     |    |                   |    |              |    | Colour<br>tone                         | Colour<br>purity <i>p</i><br>(%) | Intensity<br>of smoke<br>(relative) |
| KClO <sub>3</sub>                     | 40 | auramine            | 26 | chrysoidin        | 14 | carbohydrate | 20 | 584                                    | 75                               | 12.6                                |
| KClO <sub>3</sub>                     | 40 | butter<br>orange    | 20 | rhodamine         | 20 | carbohydrate | 20 | 600                                    | 54                               | 8.9                                 |
| KClO <sub>3</sub>                     | 40 | ammonium<br>oxalate | 7  | methylene<br>blue | 40 | carbohydrate | 13 | 487                                    | 11                               | 14.1                                |

Table 19.2 Colour characteristics of signal smokes

## Chapter XX

### Solid Pyrotechnic Fuels

The term "solid pyrotechnic fuel" is not generally accepted. It was introduced by us in order to distinguish those fuels which among the numerous forms of solid fuels for jet (or rocket) engines are close in their composition and properties to certain pyrotechnic compositions.

#### Section 1. Classification and energy characteristics.

At the present time, various solid pyrotechnic fuels have been developed which may be divided into four characteristic types:

- 1) fuels for ramjet engines (PVRDT), or rocket-ramjet engines (RPDT);
- 2) fuels for water-jet engines (GRD);
- 3) fuels for combined engines (KRD);
- 4) in their nature, composite propellants for rocket engines (RDTT) are also similar to solid pyrotechnic fuels.

The designation of the fuel determines its composition and properties. In all jet engines, the source of energy is the energy liberated on combustion of the fuel. The energy of the fuel is converted into kinetic energy when the reaction products are exhausted from the nozzle of the jet engine.

To determine the power characteristics of solid fuels (and also the characteristics of the products of their combustion), a high degree of accuracy in the calculations is needed, and all the physico-chemical processes occurring in the combustion of the fuel and the exhaust of the products of combustion from the nozzle must be considered. Usually it is considered that the process of the exhaust of the combustion products from the nozzle occurs isentropically, i.e.,  $\Delta S = 0$ .

Therefore, the variation in the kinetic energy of the jet as it flow out from the nozzle occurs because of the change in the heat content of the products of combustion of the fuel:

$$\Delta I = \frac{G_{fu}}{2g}(u_{no}^2 - u_{cc}^2)$$

where  $\Delta I$  is the change in the heat content of the products,  $\text{kJ kg}^{-1}$

$G_{fu}$  is the fuel consumption,  $\text{kg s}^{-1}$

$u_{no}$  is the exhaust velocity of the gases at the nozzle,  $\text{m s}^{-1}$

$u_{cc}$  is the exhaust velocity of the gases at the end of the combustion chamber

Thus, the task reduces to the determination of the heat content of the products of combustion of the fuel (propellant) in the combustion chamber and at the cross-section or the nozzle. For this purpose, special thermodynamic calculations are made, the basis of which is the equality of the total heat content of the propellant to the total heat content of the reaction products at the given

pressure, and also the principle of total thermodynamic equilibrium in the products of combustion at the given temperature and pressure<sup>224, 221, 232, 229</sup>. In this case, the heat of formation of the fuel component, the variation in the thermodynamic characteristics of the products of combustion with temperature<sup>233</sup>, and the dissociation of the products of combustion at high temperature in the combustion chamber are taken into consideration.

Such calculations determine the temperature of the products of combustion of the fuel at various pressures, the composition and characteristics of the products of combustion, and the specific thrust (specific impulse) at the given pressure in the chamber.

The results of these calculations are the initial data for subsequent calculations of the motor and for various processes occurring in the motor on combustion of the fuel, namely calculations of the nozzle, the geometry of the charge or solid propellant, condition of the flow of the products of combustion throughout the engine chamber or along the central channel of the charge, calculations of the heat insulation of the engine and of heat losses.

Energy conversion occurs differently in different types of jet engines.

1. Air-breathing solid-propellant ramjet engines develop thrust in flight by varying the momentum of the jet of air flowing through the engine. A diagram of this engine is shown in Fig. 20.1.

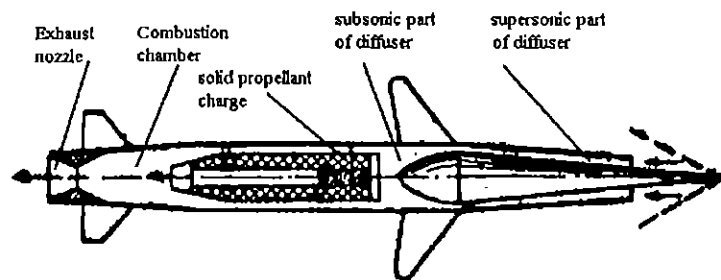


Fig 20.1 Diagram of an air-breathing solid-fuel ramjet engine

The variation in the momentum of the air flow in the engine results from the heat liberated in the combustion chamber during the combustion of the fuel. Thus, the air flowing into the engine through a special air intake (diffuser) is both the oxidiser and the working fluid. As the basic characteristics of a ramjet engine, we normally use the specific thrust of the engine and the thrust coefficient. The specific thrust  $I$  characterises the economy of operation of the engine. The value of the thrust coefficient  $C_R$  determines the maximum quantity of thrust that may be obtained using the given fuel in a defined engine. From the theory of PVRD it is known that the magnitude of the specific thrust and the thrust coefficient depend upon the velocity and flight altitude<sup>222, 219, 230</sup>:

$$I = \frac{R}{G_{fu}} = \frac{\alpha \cdot L_0 \cdot V_H}{g} \cdot (\beta \sqrt{\theta} - 1)$$

$$C_R = \frac{R}{S_p \cdot \frac{\gamma_H \cdot V_H^2}{2g}} = 2(1 - \frac{1}{\beta \cdot \sqrt{\theta}})$$

where  $R$  is the engine thrust, kg

$G_{fu}$  is the fuel consumption, kg s<sup>-1</sup>

$d$  is the excess air ratio

$L_0$  is the stoichiometric constant

$V_H$  is the flight speed, m s<sup>-1</sup>

$\beta$  is the mass increase ratio, equal to the ratio of the flow rate of the products of combustion to the air flow rate

$\theta$  is the relative heating of the air

$S_p$  is the area of the cross-section of the rocket, m<sup>2</sup>

$\gamma_H$  is the air density at the flight altitude, kg m<sup>-3</sup>

The stoichiometric constant of the fuel  $L_0$  is the quantity of air, in kg, theoretically needed for the combustion of 1 kg of fuel. The relative heating  $\theta$  in the operation of a solid propellant engine depends upon the calorific value of the fuel  $H_u$  and the ratio between the flow rate of the air and the flow rate (consumption) of the fuel  $\alpha \cdot L_0$ :

$$\theta = \frac{T_{\infty}}{T_a} = 1 + \frac{H_u}{(1 + \alpha \cdot L_0) \cdot C_p \cdot T_a}$$

where  $T_{\infty}$  is the stagnation temperature of the products of combustion in K;

$T_a$  is the stagnation temperature of the incoming flow of air, K

$C_p$  is the heat content of the products of combustion, kJ kg<sup>-1</sup>.

Therefore, the most economical PVRDT of the greatest specific thrust may be obtained by using propellants that have the greatest calorific value (in kJ kg<sup>-1</sup>) when they are burned in air.

**Example 1.** Calculate the specific thrust  $I$  of a PVRDT at a  $V_H = 500$  m s<sup>-1</sup> at an altitude of 10 km; the flow rate of the air through the engine is 20 kg(force) s<sup>-1</sup>;  $G_{fu} = 2$  kg(force) s<sup>-1</sup>. The propellant is magnesium.

At the given values of  $V_H$  and a flight altitude of 10 km;  $T_a = 355$  K. The heat content of the products of combustion may be assumed as equal to  $c_p = 1.25$  kJ kg<sup>-1</sup> K<sup>-1</sup>. The calorific value of magnesium is 24.59 MJ kg<sup>-1</sup>.

$$\alpha \cdot L_0 = \frac{G_a}{G_T} = 20/2 = 10$$

where  $G_a$  is the flow rate of the air.

The relative heating is

$$\theta = 1 + \frac{24.59 \cdot 10^3}{(1 + 10)1.25 \cdot 355} = 6.04$$

$$\beta = \frac{20 + 2}{20} = 1.1$$

The specific thrust is

$$I = \frac{10 \cdot 500}{9.81} \cdot (1.1 \sqrt{6} - 1) = 865 \text{ kg.s kg}^{-1}$$

**Example 2.** Calculate the specific thrust  $I$  under the same conditions as in example 1; the propellant is aluminium.

Calorific value of aluminium is  $30.7 \text{ MJ kg}^{-1}$ .

$$\theta = 1 + \frac{30.7 \cdot 10^3}{(10 + 1) \cdot 1.25 \cdot 355} = 7.29$$

The specific thrust is

$$I = \frac{10 \cdot 500}{9.81} \cdot (1.1 \sqrt{7.29} - 1) = 1004 \text{ kg.s.kg}^{-1}$$

To obtain a large thrust coefficient  $C_R$ , which is required for flight at a supersonic speed, a propellant with a high heating power is needed:

$$V_H = \frac{H_u}{1 + L_0}$$

The heating power is the quantity of heat per kilogramme of the products of combustion in a stoichiometric composition of a mixture of fuel with air. Therefore, solid propellants for PVRDT must have a high calorific value and as low a value as possible of the stoichiometric constant  $L_0$ . In particular, liquid hydrocarbon fuels, having a high calorific value of  $37 - 42 \text{ MJ kg}^{-1}$  do not satisfy the latter requirement, since they have a high stoichiometric constant  $L_0 = 13-15$ <sup>222</sup>. However, solid propellants for PVRDT consist of a metallic fuel, an organic fuel which doubles as a binder, and special additives<sup>258</sup>. Certain fuels for PVRD also contain an oxidiser. Non-ferrous metals such as Mg, Al, and their alloys are used as a metallic fuel<sup>258, 268</sup>. These metals have a relatively high calorific value and heating capacity. The best theoretical characteristics are provided by Be, but we must consider the high cost and incompleteness of combustion of this metal<sup>268</sup>.

The use of metals in propellants for PVRDT is especially necessary for high flight speeds (when a very high temperature is developed in the combustion chamber), since the products of combustion of the metals have a high thermal stability.

From data in the literature it is known that a fast burning fuel for PVRDT can be made from a magnesium-aluminium alloy, a small quantity of binder, and a small quantity of oxidiser<sup>258</sup>. Charges are prepared from such a fuel by compaction at a high specific pressure.

Slow burning fuels for PVRDT contain up to 50% of an epoxy resin together with a metal and an oxidiser. Charges are prepared from such a fuel by casting into the casing or chamber, where they harden. Either end burning or radial burning charges are used for PVRDT<sup>253, 265</sup>.

In certain cases, the application of a rocket ramjet engine is feasible. This engine is an organic combination of a rocket (RDTT) and a ramjet engine in a single design<sup>258</sup>. Solid propellants for

such engines must have an adequately high specific thrust together with a high calorific value. It is also desirable to introduce into solid propellants for a RPDT (rocket-ramjet engine) dispersed particles of metal that ignite easily <sup>230</sup>. At the same time, fuels for RPDT must have a high combustion temperature and produce an adequate quantity of gaseous reaction products on combustion. The characteristics of ramjet engines depend essentially upon the completeness of combustion of the fuel in the engine <sup>222, 219</sup>. This is characterised by the combustion efficiency  $\phi_{\infty}$  which is the ratio of increase in heat content of the products of combustion to the chemical energy of the fuel introduced into the chamber. Obtaining a high degree of completeness of combustion requires the solution of such important problems as the mixing of the products of combustion of the fuel and the air, and complete combustion of the gaseous and solid particles in combustion chamber conditions. Fuels based on an alloy of aluminium and magnesium together with an epoxy resin give a completeness of combustion varying from 0.4 to 0.8 depending upon the test conditions <sup>258</sup>.

2. Water jet engines (GRD) use sea water as an oxidiser. A diagram of such an engine is shown in Fig. 20.2. Water jet engines are used in torpedoes <sup>256</sup>. During the motion of the torpedo the sea water enters through special water intakes to the engine and is used both as an oxidiser and as the working fluid. The thermal energy of the fuel is expended in the combustion chamber in the evaporation of water. A mixture of water vapour and gaseous products of combustion of the fuel flow out of the nozzle and provide the thrust needed. For submarine engines, the specific volumetric thrust is the determining factor, i.e., the thrust developed by the engine by the combustion of one litre of fuel per second. Therefore, the most important characteristic of the water jet fuel is the heat liberated in the combustion of one litre of fuel in its reaction with water, and the quantity of water  $L_0$  (in kg) needed for the combustion of 1 kg of fuel.

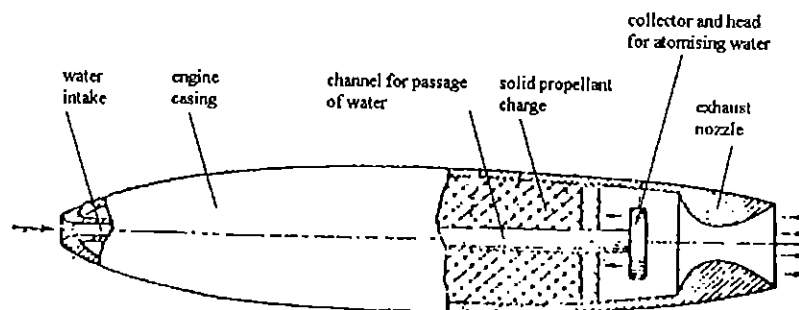


Fig 20.2 Diagram of a solid fuel water jet (hydroreactive) engine

A high specific heat of the reaction (in  $\text{kJ m}^{-3}$ ) with water is one of the basic requirements for the hydroreactive fuel. Besides this, substances used as fuel must react vigorously with water <sup>264</sup>.

Certain metals such as Al, Zr, Mg, and also Li and its alloys have very high energy characteristics, both with sea water as an oxidiser and also with an oxidiser that is included in the composition of the propellant <sup>256, 261</sup>.

Special methods are required to ensure that the combustion of the propellant proceeds largely to completion. One method of preparing a charge of solid hydroreactive fuel is by pressing a mixture of metal powders and oxidiser <sup>256</sup>. Such a fuel must have a negative oxygen balance; perchlorates may be used as oxidisers. Sometimes finely divided metal powders are added to these fuels to increase the rate of combustion: these metals include cobalt, copper, ferrovanadium, lead, and tin. For the preparation of these charges, a thoroughly mixed mixture of fuel components is compacted at a high specific pressure <sup>248</sup>. However, the greatest specific thrust in a ramjet GRD may be obtained by using pure metals as the fuel. The magnitude of the specific thrust of a GRD depends upon the ratio of the flow rate per second of the salt water oxidiser,  $G_w$  to the fuel consumption per second  $G_{fu}$ :

$$\frac{G_w}{G_{fu}} = \alpha \cdot L_0$$

where  $\alpha$  is the excess water ratio.

The energy capabilities of hydroreactive fuels are shown in Fig. 20.3 <sup>256</sup>.

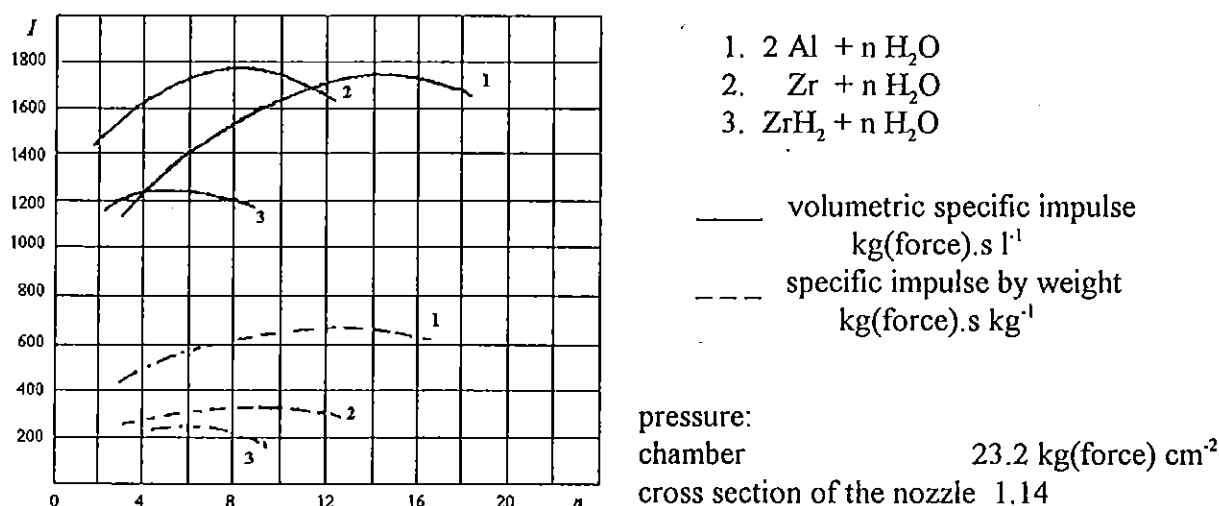


Fig 20.3 Dependence of the specific impulse  $I$  of a GRD on the excess of water in moles,  $n$

3. Fuels for combined engines (KRD) are a comparatively new type of solid fuels. A KRD operates using solid fuels and a liquid oxidiser, and is classed among rocket engines.

At a given pressure in the chamber of a rocket engine, the specific thrust does not depend upon the flight conditions of the surrounding medium, but is determined only by the properties of the fuel and the liquid oxidiser used. Rocket engines using mixed fuel (solid-liquid), i.e., have considerable advantages over RDTT, since they have a higher specific thrust, permit higher engine thrust and allow it to start many times by means of varying the flow rate

and cutting off the liquid components <sup>252</sup>. One of the possible designs of a combined engine is shown in Fig. 20.4.

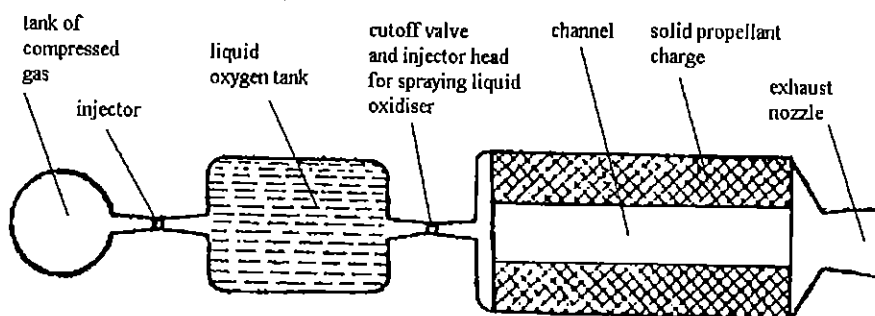


Fig 20.4 Diagram of a combined rocket engine

Nitric acid  $\text{HNO}_3$ , or the oxides of nitrogen such as  $\text{N}_2\text{O}_4$ , perchloryl fluoride  $\text{FCIO}_4$ , hydrogen peroxide  $\text{H}_2\text{O}_2$ , or chlorine trifluoride  $\text{ClF}_3$ , are used as liquid oxidisers

From the standpoint of operation of the engine, the best characteristics are provided by fuels capable of spontaneous ignition upon contact with the liquid oxidiser i.e., hypergolic propellants. At the present time, multi-component solid propellants are known which provide an adequately high value of the specific impulse <sup>252</sup> in the presence of a liquid oxidiser. This fuel consists of a metal powder, thermoplastics, a hypergolic component, and its plasticiser. Of the metals, Al, Be, Mg, or Li are used, and the metal particles must have dimensions of not more than  $10\text{ }\mu\text{m}$ .

As plasticisers we use polyvinyl chloride, plasticised butyl phthalate, rubber, or polyurethane <sup>252</sup>. As hypergolic components we use solid amines, such as paratoluidine, paraphenyldiamines or 1,5-diaminonaphthalene <sup>252</sup>.

The addition of up to 20% ammonium perchlorate to the solid phase leads to a reduction in the delay time of ignition and the formation of a smoother free combustion surface, which improves the combustion characteristics <sup>252</sup>.

4. Solid propellant rocket engines (RDTT) <sup>244, 251, 266</sup> have attained a considerable state of development in recent times because of the development of high energy composite propellants.

A typical diagram of a RDTT is shown in Fig. 20.5. The basic advantages of the RDTT are: comparative simplicity of design, constant readiness for action, convenience and relative safety in operation, and high degree of operating reliability. In the combustion of the fuel in a RDTT, a great quantity of gases having a high temperature is liberated. A pressure of the order of several dozen atmospheres is developed in the combustion chamber. The gaseous reaction products expand up to the external pressure as they are discharged from the nozzle,. The process of expansion is accompanied by an acceleration of the gas in the nozzle, i.e., the thermal energy is converted to the kinetic energy of the gases. The thrust of the engine is determined from the equation of conservation of momentum

$$R = \frac{G_{fu}}{g} \cdot u_{no} + (p_{no} - p_h) \cdot S_{no}$$

where  $R$  is the engine thrust, kg;

$G_{fu}$  is the fuel consumption, kg s<sup>-1</sup>;

$u_{no}$  is the exhaust velocity of the gases at the outlet from the nozzle, m s<sup>-1</sup>;

$p_{no}$  is the pressure in the cross-section of the nozzle, kg(force) cm<sup>-2</sup>;

$p_H$  is the atmospheric pressure, kg(force) cm<sup>-2</sup>;

$S_{no}$  is the area of the exhaust section of the nozzle, cm<sup>2</sup>.

The basic characteristics of the propellant is the specific thrust i.e., the thrust developed by the engine with a fuel consumption of 1 kg s<sup>-1</sup>:

$$I = \frac{R}{G_{fu}} = \sqrt{\frac{2k}{k-1} \cdot \frac{R_{gas}}{M \cdot g} \cdot T \cdot \left[ 1 - \left( \frac{p_{no}}{p} \right)^{\frac{k-1}{k}} \right]}$$

where  $k$  is the adiabatic exponent of the gaseous products of combustion;

$M$  is the average molecular weight of the gaseous products of combustion

$R_{gas}$  is the universal gas constant, in kg.m K<sup>-1</sup>.mole<sup>-1</sup>

$T$  is the temperature in the chamber

$p$  is the pressure in the chamber.

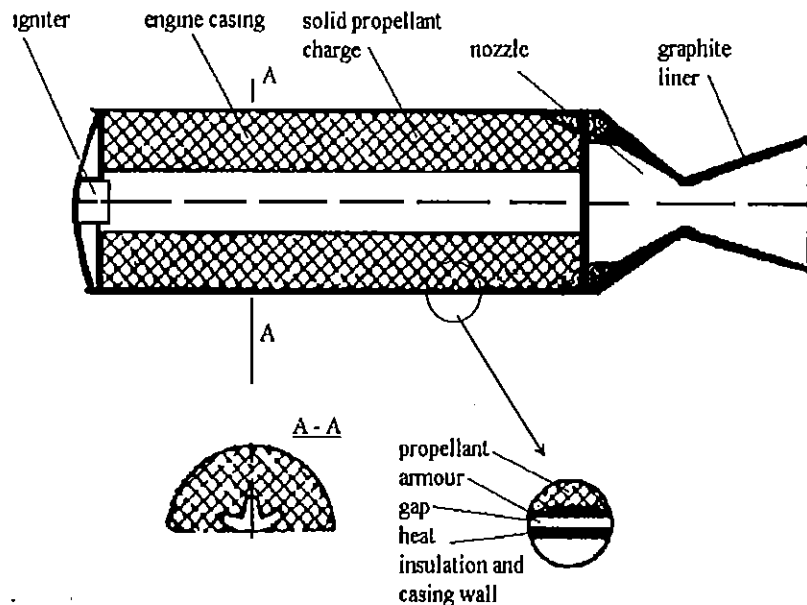


Fig 20.5 Diagram of a solid propellant rocket engine

Example. Calculate the specific thrust of a composite propellant when  $p = 40 \text{ kg cm}^{-2}$ ; combustion temperature of the propellant  $T = 2790 \text{ K}$ ,  $M = 25.5$ ,  $k = 1.22$ ,  $R_{\text{gas}} = 848$ .

$$I = \sqrt{\frac{2 \cdot 1.22}{1.22 - 1} \cdot \frac{848}{25.5 \cdot 9.81} \cdot 2790 \cdot \left[ 1 - \left( \frac{1}{40} \right)^{\frac{1.22 - 1}{1.22}} \right]} = 226 \text{ s}$$

Methods of calculating and measuring specific thrust are expounded adequately and completely in references <sup>224, 221, 232, 229</sup>. Propellants have the greatest specific thrust if they have a high combustion temperature and their combustion products have the lowest molecular weight. Of all types of solid propellants for rocket engines, composite rocket propellants satisfy these requirements most completely. These fuels usually consist of thoroughly mixed organic fuels that also serve as binders, and solid crystalline oxidisers <sup>230</sup>. To increase the specific impulse of such fuels they usually contain 10-20% non-ferrous metals or their alloys - Al, Mg, Bi, Be <sup>221, 247, 265</sup>. Since they have a high reaction heat and form thermally stable products on combustion, these metals make it possible to raise the temperature of the products of combustion of the fuel, and consequently also the specific thrust of the fuel. However, the products of these metals, after reaction with oxygen or chlorine, are high melting and high boiling substances (see Chapter III), and even at combustion temperatures are largely in a condensed form. Therefore, the addition of a considerable quantity of metal to compositions for rocket fuels is inadvisable.

The greatest increase in specific thrust is obtained when binary alloys of mixtures of non-ferrous metals are added to rocket fuels. In this case the quantity of the metal (such as Al) combining with the oxygen, and the quantity of the metal (such as Li) combining with the halogen must correspond to the content of oxygen and halogen in the oxidiser being used <sup>241</sup>. The optimum magnitude of specific thrust is obtained for fuels having a negative oxygen balance as a consequence of the reduced value of the average molecular weight of the combustion products and less loss of energy to dissociation than in stoichiometric fuels.

Fuels used in practice usually contain 80-85% oxidiser, and satisfactory technological properties can be obtained: in certain cases the tendency of perchlorate propellant to detonation can be limited <sup>221</sup>. Composite propellants have the most diverse compositions and mechanical properties. Brief information on the composition and properties of composite propellants is given in the book by Kurov and Dolzhanskiy <sup>226</sup>. A more detailed collection of them, with an indication of both the mixtures and the properties of individual components, is given in the book by Paushkin <sup>228</sup>, in Zaehring's handbook <sup>262</sup>, in reference books <sup>220, 225</sup>, and in the articles by Maxwell and Young <sup>227</sup>, Tavernier <sup>259</sup>, a number of other articles published in the foreign press <sup>236, 245, 241, 243, 247, and 254</sup>, and also in abstracts <sup>239</sup>.

Certain typical composite propellants for PDTT are given in Table 20.1. The properties of propellants which do not contain metallic fuels are given in Table 20.2, adapted from reference <sup>221</sup>. Thus, the four types of solid fuels considered for various jet engines are, in principle, heterogeneous systems, being mixtures of an inorganic oxidiser, an organic fuel, and a metallic fuel. The inorganic oxidiser and the metallic fuel are added to the fuel composition in the form of finely divided powders. The composition of the fuel, the technology of preparation, and the

characteristics are determined chiefly by the type of jet engine. In Table 20.3 we give the compositions of various types of solid pyrotechnic fuels and their characteristics.

| Propellant ingredients                                                                                                        | Specific thrust<br>(s)                    | Physico-mechanical<br>properties        | Proposed use                                     | Literature<br>source |
|-------------------------------------------------------------------------------------------------------------------------------|-------------------------------------------|-----------------------------------------|--------------------------------------------------|----------------------|
| NH <sub>4</sub> ClO <sub>4</sub><br>co-polymer of butadiene<br>and acrylic acid                                               | 230 - 250<br>( $p = 70 \text{ kg/cm}^2$ ) | good                                    | Minuteman first<br>stage.<br>Nike-Zeus, Sabre.   | 266<br>265           |
| (NH <sub>4</sub> ClO <sub>4</sub> /Al 80/20)<br>80%;<br>co-polymer of butadiene<br>and acrylic acid;<br>plasticiser, hardner. | ~245                                      | good                                    | Rocketdyne design                                | 267                  |
| NH <sub>4</sub> ClO <sub>4</sub><br>PVC<br>plasticiser oil<br>Al up to 20%                                                    | 250<br>( $p = 70 \text{ kg/cm}^2$ )       | good; preserved at<br>low temperatures. | Sergeant, Lacrosse,<br>Meteor, Bomarc,<br>Falcon | 265<br>263           |

Table 20.1 Properties of propellant compositions

| Composition of fuel                                                   | 75% NH <sub>4</sub> ClO <sub>4</sub><br>+<br>25% fuels and<br>additives | 80% NH <sub>4</sub> ClO <sub>4</sub><br>+<br>20% fuels and<br>additives | 80% NH <sub>4</sub> NO <sub>3</sub><br>+<br>20% fuels and<br>additives |
|-----------------------------------------------------------------------|-------------------------------------------------------------------------|-------------------------------------------------------------------------|------------------------------------------------------------------------|
| Molecular weight of combustion products                               | 24                                                                      | 25.5                                                                    | 22                                                                     |
| Adiabatic exponent                                                    | 1.24                                                                    | 1.22                                                                    | 1.26                                                                   |
| Isobaric combustion temperature K                                     | 2420                                                                    | 2790                                                                    | 1755                                                                   |
| Specific thrust, $I$ , ( $p = 70 \text{ kg cm}^{-2}$ ) s              | 224                                                                     | 236                                                                     | 195                                                                    |
| Index $\nu$ at $p = 70 \text{ kg cm}^{-2}$                            | 0.4                                                                     | 0.4                                                                     | 0.4                                                                    |
| Rate of combustion ( $p = 70 \text{ kg cm}^{-2}$ ) $\text{cm s}^{-1}$ | 0.5 - 1.5                                                               | 0.8 - 2.0                                                               | 0.2 - 0.3                                                              |
| Density $\text{Mg m}^{-3}$                                            | 1.66                                                                    | 1.72                                                                    | 1.55                                                                   |
| Temperature coefficient                                               | $1.2 - 2.4 \times 10^{-3}$                                              | $1.2 - 2.4 \times 10^{-3}$                                              | $2.5 \times 10^{-3}$                                                   |

Table 20.2 Characteristics of composite propellants for RDTT which do not contain metal additives

| Designation of fuel                 | Special requirements                                                                                                   | Composition of fuel                                               |                                                               |                                                      | Technology of fabrication of charge         | Specific thrust                            | Notes                                                                                |
|-------------------------------------|------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------|---------------------------------------------------------------|------------------------------------------------------|---------------------------------------------|--------------------------------------------|--------------------------------------------------------------------------------------|
|                                     |                                                                                                                        | Organic fuel                                                      | Oxidiser                                                      | Metallic fuel                                        |                                             |                                            |                                                                                      |
| for PVRDT                           | High calorific value, atmospheric combustion must be largely complete                                                  | epoxy-type resins up to 50%                                       | crystalline content of fuel small                             | Mg, Al, Li, or their alloys; content in fuel differs | casting or pressing                         | 500-800 s                                  | $I$ for range $a.L_0 = 8.5$ and Mach number 1.5 - 3.2 <sup>234</sup> .               |
| for RPDT                            | High calorific value, atmospheric combustion must be largely complete. Significant specific impulse.                   | epoxy-type resins up to 50%                                       | crystalline content of fuel small. Content in fuel increased. | Mg, Al, Li, or their alloys; content in fuel differs | No information                              | No information                             | -                                                                                    |
| for ramjet GRD                      | high specific heat of reaction with water; considerable rate of reaction with water.                                   | -                                                                 | inorganic salts (perchlorates)                                | Mg, Al or their alloys, >30%                         | Compacting at high specific pressure        | 1200 - 1600 g.s cm <sup>3</sup>            | $I$ given for an excess water ratio $a = 1.33$ - 1.57 <sup>234</sup>                 |
| for KRD                             | high specific thrust with liquid oxidiser, self-igniting on contact with liquid oxidiser, i.e., hypergolic propellant. | PVC, rubbers, polyurethanes, amines,.                             | NH <sub>4</sub> ClO <sub>4</sub> up to 20%                    | Mg, Al, Li, or their alloys                          | casting                                     | 250 - 290 s at $p = 70 \text{ kg cm}^{-2}$ | % of metal indicated with respect to weight of solid propellant and liquid oxidiser. |
| composite solid propellant for RDTT | high specific thrust, low molecular weight of combustion products.                                                     | rubbers, resins, vinyl polymers, polyurethanes and others, 15-25% | nitrates and perchlorates up to 80%.                          | Mg, Al, Li, or their alloys, 10-20%                  | free casting under pressure or in a vacuum. | 230 - 250 s at $p = 70 \text{ kg cm}^{-2}$ | -                                                                                    |

Table 20.3 Compositions and characteristics of types of solid pyrotechnic fuels.

## Section 2. Operational requirements.

In addition to the special requirements considered earlier, all types of rocket fuels must satisfy a great number of other general requirements.

1. High density of solid propellant. An increase in the density of the propellant always leads to a reduction in the volume of the combustion chamber and a reduction of the weight of the engine design. The density of modern fuels does not exceed  $1.8 \text{ Mg m}^{-3}$ .
2. Adequate mechanical strength and high modulus of elasticity of the charge. Breakdown of a charge of solid rocket propellant in storage or during combustion must not occur since it leads to an increase in the surface of combustion, an increase in the pressure in the chamber, and explosion.
3. The composition of the charge must be homogeneous or uniform combustion of the charge cannot occur, and the ballistic qualities of the rocket are reduced
4. The fuel must be stable in storage when subjected to temperature variations.
5. Combustion in the engine chamber at a reduced [sic] pressure of the order of 15-35 atm must be stable <sup>236, 226</sup>. A high pressure in the chamber requires an increase in the thickness of the chamber walls, which leads to an increase in the weight of the design.
6. Minimum dependence of the rate of combustion upon the initial temperature of the charge. This dependence is characterised by the temperature coefficient of the rate of combustion.

Solid pyrotechnic propellants have a low temperature coefficient (for real values of the temperature coefficient of pyrotechnic compositions, see Chapter X).

7. The dependence of the rate of combustion of the fuel upon pressure should be as low as possible. Fuels having a weak dependence of the rate of combustion upon pressure have a lower value of the index  $\nu$ . Such fuels give the most stable ballistic characteristics, since random oscillations of pressure do not cause any noticeable change in the rate of combustion of the fuel.
8. It must be possible to prepare large sized charges from the solid pyrotechnic fuel with the required physical properties (see paragraph 2 above). The technological process of preparation of the charge must be as simple as possible.

In the majority of cases, a flow of the products of combustion along the burning surface exists during the combustion of charges of solid fuel in an engine. If the velocity of such a flow is higher than some certain threshold value, so-called erosion combustion is observed, accompanied by an increase in the linear rate of combustion of the fuel. The increase in rate of combustion of the fuel  $u$  in erosion combustion is determined approximately by the expression:

$$\frac{u_{er}}{u_0} = 1 + K_{er} \cdot (\nu - \nu_{thr})$$

where  $u_0$  is the normal rate of combustion of the fuel;

$K_{er}$  is a constant for a particular fuel

$\nu$  is the velocity of the flow of the products of combustion along the burning surface

$\nu_{thr}$  is the threshold value of the velocity of the gas flow.

For example, if  $\nu_{thr} = 200 \text{ m s}^{-1}$ ,  $K_{er} = 0.002 \text{ s m}^{-1}$ , and  $\nu = 450 \text{ m s}^{-1}$ , the increase in the rate of combustion of the fuel in erosion combustion will be

$$\frac{u_{sp}}{u_0} = 1 + 0.002(450 - 200) = 1.50$$

The erosion effect is usually manifested at a high filling density and must be considered in the development of full-scale charges of solid fuel.

### Section 3.    Oxidisers

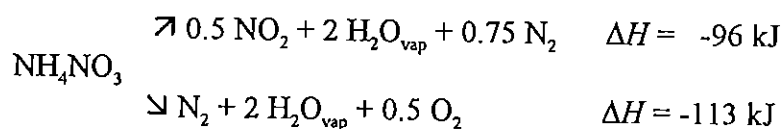
The selection of an oxidiser determines the properties of the fuel to a great degree. The nitrites and perchlorates of potassium, sodium, lithium, and ammonium have found practical application as oxidisers for solid pyrotechnic fuels. Some properties of these oxidisers are given in Table 20.4.

A high content of free oxygen and a high density of the oxidiser are especially important for cast propellants, since they make it possible to add to the fuel a great quantity of organic binder and ensure good mechanical properties for the composition. Ammonium nitrate is cheapest and most suitable for the large scale. The decomposition of ammonium nitrate leads to varying products depending upon the conditions under which the reaction occurs.

| Formula                   | Molecular weight | Density<br>( $\text{Mg m}^{-3}$ ) | Melting point<br>( $^{\circ}\text{C}$ ) | Heat of formation<br>( $\text{kJ mole}^{-1}$ ) | Oxygen content (%) |        | Hygroscopic point at $20^{\circ}\text{C}$ | Solubility in 100 g $\text{H}_2\text{O}$ at $25^{\circ}\text{C}$ |
|---------------------------|------------------|-----------------------------------|-----------------------------------------|------------------------------------------------|--------------------|--------|-------------------------------------------|------------------------------------------------------------------|
|                           |                  |                                   |                                         |                                                | total              | active |                                           |                                                                  |
| $\text{NH}_4\text{ClO}_4$ | 117              | 1.95                              | -                                       | 289                                            | 55                 | 27     | 96                                        | 24.9                                                             |
| $\text{LiClO}_4$          | 106              | 2.4                               | 247                                     | 385                                            | 61                 | 61     | -                                         | 59.7                                                             |
| $\text{KClO}_4$           | 139              | 2.5                               | ca 610                                  | 433.3                                          | 46                 | 46     | 99                                        | 2.5                                                              |
| $\text{KNO}_3$            | 101              | 2.1                               | 336                                     | 498                                            | 48                 | 48     | 92.5                                      | 38.1                                                             |
| $\text{NaNO}_3$           | 85               | 2.2                               | 308                                     | 464                                            | 56                 | 56     | 77                                        | 91                                                               |
| $\text{NH}_4\text{NO}_3$  | 80               | 1.7                               | 169                                     | 368                                            | 60                 | 60     | 67                                        | 180                                                              |

Table 20.4 Physico-chemical properties of oxidisers for solid pyrotechnic fuels

Two of many possible equations of decomposition of ammonium nitrate are:



The heat of the reaction corresponds to the liberation of  $1.0$ – $1.4 \text{ MJ kg}^{-1}$ . The ability of  $\text{NH}_4\text{NO}_3$  to undergo combustion at an increased pressure has been experimentally established<sup>246, 237</sup>, and in the presence of a catalyst also at atmospheric pressure<sup>237</sup>.

The thermal decomposition of ammonium nitrate with different catalytic additives has been studied in recent years by Hainer, Guichon and Jacques<sup>237, 119</sup> and by Rozman<sup>166</sup>, as well as by the author of this book<sup>237, 119</sup> page 401.

It has been established that chromium compounds such as potassium chromate, ammonium dichromate<sup>223</sup> page 344, and also chromium trioxide have a strong catalytic effect on the thermal decomposition of ammonium nitrate, copper (II) chlorides affect it to a lesser degree. The combustion of ammonium nitrate with catalytic additives was studied by Taylor<sup>260</sup>, and also by the author of this book<sup>237</sup>. Chromium compounds, which greatly increase the rate of thermal decomposition of  $\text{NH}_4\text{NO}_3$  at  $200^{\circ}\text{C}$  when they are added in quantities of 5–10% make it capable of combustion under ordinary conditions of temperature and pressure.

Ammonium nitrate is not sensitive to friction in a porcelain mortar at room temperature, and has little sensitiveness to shock. It is difficult to induce an explosion in it, the explosion temperature is about  $1000^{\circ}\text{C}$ ; the rate of detonation is from  $1000$  to  $1500 \text{ m s}^{-1}$ .

Not all solid propellants containing ammonium nitrates that have been tested provide an adequately high value of specific thrust. Therefore, ammonium perchlorate, which is more costly and more dangerous to handle, is usually preferred. The properties of ammonium perchlorate are described in the books by Kast and Escales, and also in Blinov's monograph<sup>19</sup>.

Ammonium perchlorate possesses specific explosive properties: its explosion temperature is about 1200°C, and its rate of detonation varies from 2500 to 3500 m s<sup>-1</sup>. The manufacture of perchlorates, their properties, and their applications are described in Schuhmacher's monograph <sup>49</sup>.

The thermal decomposition of NH<sub>4</sub>ClO<sub>4</sub> with various catalytic additives has been studied in recent years by Jacobs <sup>249</sup>, Arden, Pawling, and Smith <sup>240</sup>, Shol'moshi and Reves <sup>238</sup>, and also by the author of this book, in collaboration with Shmagin <sup>237</sup>.

The thermal decomposition of ammonium perchlorate may be expressed approximately by the equation:

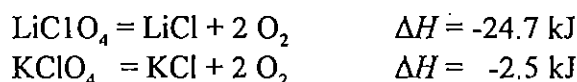


and the heat liberated is 1070 kJ kg<sup>-1</sup>. Copper compounds (oxides and chlorides) greatly accelerate the thermal decomposition of NH<sub>4</sub>ClO<sub>4</sub>, and according to the work of Birkumshaw <sup>235</sup> page 329, so does manganese dioxide.

The rate of combustion of NH<sub>4</sub>ClO<sub>4</sub> with catalytic additives has been investigated by Friedman, Nugent, and others <sup>246</sup>.

The rate of combustion of fuels based on ammonium perchlorate is about 4 - 20 mm s<sup>-1</sup> (at p = 70 kg cm<sup>-2</sup>). These fuels have a low index  $\nu$  in the equation  $u = A + Bp^\nu$  and differ in the temperature coefficient of the rate of combustion.

The decomposition of such oxidisers as lithium perchlorate and potassium perchlorate is a very weakly exothermic process. The summary reactions of their decomposition may be expressed as:



The rate of the latter reaction increases in the presence of the halides of potassium in the sequence KCl < KBr < KI <sup>223</sup>. In the decomposition of the oxidisers LiClO<sub>4</sub> and KClO<sub>4</sub>, chlorides are formed, which are comparatively high boiling compounds.

Fuels based on KClO<sub>4</sub> have quite a low specific impulse (180-220 sec). Although these fuels have a high density (1.7-2 Mg m<sup>-3</sup>) and high rate of combustion from 3 to 6 mm/sec (at p = 70 kg cm<sup>-2</sup>), their combustion at pressures below 70 kg cm<sup>-2</sup> is unstable.

Nitronium perchlorate NO<sub>2</sub>ClO<sub>4</sub> and nitrosyl perchlorate NOClO<sub>4</sub> have also been proposed as oxidisers for TRT (solid rocket propellants), but these compounds are too hygroscopic and hydrolyse in the presence of atmospheric moisture with the formation of free acids <sup>228</sup>.

#### Section 4. Organic and metal fuels

From the standpoint of fuel energetics, fuel binders must contain the maximum quantity of hydrogen have a low heat of formation and a high density. For composite propellants for RDTT,

fuels containing oxygen (such as, for example, in groups C - O - NO<sub>2</sub>) are of definite interest, since they make it possible to introduce a near optimum quantity of oxidiser into the composition of the fuel.

The selection of a combustible binder is most frequently determined by technological considerations and requirements for the physico-chemical characteristics of the fuel.

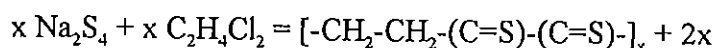
For large motors, casting the fuel directly in the casing is the most preferable method of fabrication. The binder must therefore be a liquid before filling. This liquid must be adequately viscous so that the oxidiser powder added to it does not settle to the bottom of the mixer. Together with this, the mass formed must preserve its ability to flow in the presence of 75-85% solid components.

To provide the necessary properties of the fuel, the solidification temperature of the binder must be low. A high modulus of elasticity of the charge is achieved when the binder is a high-molecular compound (polymer).

Polymerisation of the binder (with the addition of a catalyst) occurs after the preparation of the fuel (mixing of the binder and the oxidiser) and pouring into the engine casing; the process of polymerisation may be performed both at room temperature and under heating.

Synthetic rubbers, various resins (phenol, polyester, epoxy) and various polymers: polysulphides, polyurethanes, polyacrylates, polyamides, polyethylene, polybutadiene, polyisobutylene, and others are used as binders <sup>221</sup>.

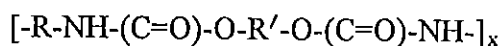
Polysulphide rubber is obtained by the polycondensation reaction of dihalo alkyls with the polysulphides of alkali metals, such as, for example, dichloroethane with sodium tetrasulphide:



Polysulphide rubbers ("thiokols") obtained from dichloroethyl ester have an empirical formula of C<sub>4</sub>H<sub>8</sub>OS<sub>4</sub> and a calorific value of 23.4 MJ kg<sup>-1</sup>.

The starting materials for the preparation of polyurethanes are diisocyanates (such as hexamethylenediisocyanate C=N=C-(CH<sub>2</sub>)<sub>6</sub>-C=N=O); bifunctional alcohols (such as butandiol HO-(CH<sub>2</sub>)<sub>4</sub>-OH). The polymerisation reaction between these compounds begins at room temperature and ends at an elevated temperature (up to 200°C). The molecular weight of the material obtained increases as the temperature rises and reaches 10,000-15,000. The elastic properties of polyurethanes are retained at low temperatures.

Polyurethanes contain the radicals -(CH<sub>2</sub>)<sub>n</sub>- and groups NH and O=C<. According to Zaehring <sup>262</sup>, the structure of the polymer chain of polyurethanes may be expressed as:



Assuming conventionally that the composition of the radicals R and R' are  $(\text{CH}_2)_6$  and  $(\text{CH}_2)_4$ , respectively, we obtain the empirical formula  $\text{C}_{12}\text{H}_{22}\text{O}_4\text{N}_2$  for polyurethane. The calorific value of polyurethanes is  $30.3 \text{ MJ kg}^{-1}$ .

The addition of up to 20% metallic fuel as powders of non-ferrous metals or their alloys, to rocket fuel compositions increases the specific thrust of the solid rocket fuel. In such fuels as PVRDT or GRD propellants, the metallic fuel is the basic component. In applications of such fuels, completeness of combustion of the metallic fuel is particularly important. Successes in this field have been directly associated with the results of the investigation of the combustion mechanism of solid pyrotechnic fuels. Problems in the combustion of fuels and metals have been exhaustively discussed in references <sup>223, 225, 221, 229, and 134</sup>. The basic quantitative relationships of the combustion of fuels are very close to the quantitative relationships of the combustion of various pyrotechnic compositions.

## Chapter XXI

### Igniting Compositions. Other Forms of Pyrotechnic Compositions.

#### Section 1. Igniting compositions and the requirements imposed upon them.

Igniting compositions are intended for igniting basic pyrotechnic compositions (illuminating, smoke, solid rocket fuels, and others). Compositions with initiating explosives intended for filling detonating caps are not considered here, but are discussed in reference <sup>270</sup>. The effect of an igniting composition is to heat a certain section of the basic composition being ignited up to its ignition temperature.

It follows that the higher the self-ignition temperature of the basic composition, the "stronger" an igniting composition is required to be to start a combustion reaction in it.

The ignition of compositions whose ignition temperature is no higher than 500 - 600°C present no special difficulties. Compositions whose ignition temperature exceeds 1000°C are ignited with greater difficulty. To ignite such compositions (such as thermites, for example), especially if they are in a compacted state, we must select special igniting and intermediate compositions.

The following special requirements are imposed upon igniting compositions:

1. they must ignite easily from a comparatively low heat impulse; the ignition temperature of any igniting composition must be no higher than 500°C;
2. the combustion temperature of igniting compositions must be several hundred degrees higher than the ignition temperature of the basic compositions being ignited by them.

Besides this, it is sometimes required that the igniting composition liberate little light on combustion, in order to avoid disclosing the location of troops.

Sometimes the requirement of liberating the minimum quantity of gases during combustion is also imposed upon igniting compositions; such igniting compositions are called "gasless" igniting compositions, although this is not strictly accurately.

The incendiary effect of igniting compositions is determined chiefly by the quantity of heat that is transmitted to the basic composition from the slags formed during combustion. Thus, the incendiary effect of an igniting composition will be stronger if its combustion temperature is higher, and if a greater quantity of slag remains after its combustion on the surface of the basic composition being ignited.

In liquid slags the surface of contact with the composition being ignited will be greater than in unfused solid slags, and consequently the quantity of heat transferred by them to the basic composition per unit time will also be greater.

It has been experimentally established that the best igniting effect is shown by slowly burning igniting compositions which allow an adequate time for heat transfer to the basic composition

being ignited. Therefore, in pyrotechnic devices, igniting compounds are almost always used in a compacted form.

In the formulation of igniting compositions, the oxidisers must release their oxygen easily, and at a comparatively low temperature if possible, and the fuels must be easily oxidised.

There are many oxidisers that easily release their oxygen. They include permanganates, chlorates, the nitrates of alkali metals. Because of the requirements of a low sensitiveness of the composition to mechanical effects, potassium nitrate is the most frequently used oxidiser in igniting compositions.

Charcoal and iditol are frequently used as easily oxidised fuels, followed by antimony and other materials.

For easily ignited basic compositions (chlorate signal smoke compositions or chlorate signal flare compositions), igniting compositions may be used which are similar to gunpowder in their recipes.

For example:

|                   |     |
|-------------------|-----|
| potassium nitrate | 75% |
| charcoal          | 15% |
| iditol            | 10% |

Magnesium powder is added as an additional fuel to igniting compositions to intensify their incendiary effect; it leaves a solid slag of magnesium oxide after combustion.

Bystrov <sup>2</sup> gives that the following composition which may be used for the ignition of many illuminating compositions:

|                   |     |
|-------------------|-----|
| potassium nitrate | 75% |
| magnesium         | 15% |
| iditol            | 10% |

To ignite compositions which contain aluminium as the basic fuel and have a high ignition temperature, we should use igniting compositions containing not less than 15-20% magnesium powder.

For igniting compositions for tracer products, barium peroxide  $\text{BaO}_2$  is the most frequently used oxidiser. It releases its oxygen at a higher temperature than potassium nitrate, but the process of its decomposition requires the expenditure of a very small quantity of heat:



The solid decomposition product of  $\text{BaO}_2$  amount to 91% of the weight of the oxidiser.

As examples of igniting compositions for tracers, we may give the following recipes:

|                 |     |                 |     |
|-----------------|-----|-----------------|-----|
| barium peroxide | 80% | barium nitrate  | 48% |
| magnesium       | 18% | barium peroxide | 30% |
| binder          | 2%  | magnesium       | 13% |
|                 |     | iditol          | 9%  |

Numerous igniting compositions for tracers used during World War II contain the following substances in addition to barium peroxide, magnesium, and binders: barium nitrate, red lead, strontium picrate, tetranitrocarbazole, calcium silicide, sodium oxalate, graphite, and the stearates of calcium, zinc, and other metals.

Compositions of the thermite type, such as the following, have a strong igniting effect:

|              |     |                 |     |
|--------------|-----|-----------------|-----|
| ferric oxide | 69% | silicon dioxide | 55% |
| magnesium    | 31% | magnesium       | 45% |

However these compositions (especially the second) is not easily ignited since they have high ignition temperatures.

Compositions containing zirconium powder ignite easily and have a good igniting effect. Examples of such compositions used for igniting tracers are <sup>12</sup>:

|                   |     |                   |     |
|-------------------|-----|-------------------|-----|
| gunpowder         | 75% | potassium nitrate | 48% |
| potassium nitrate | 12% | zirconium         | 52% |
| zirconium         | 13% |                   |     |

Igniting compositions for tracers should not contain a great quantity of low-melting substances; otherwise liquids will be squeezed out from the burning layer while the projectile passes through the bore of the barrel.

When even the most intense igniting compositions do not succeed in igniting the basic pyrotechnic composition, we use the so-called transitional or intermediate compositions.

Intermediate compositions are obtained by mixing the igniting compositions and the basic composition in certain proportions. One case of the use of an intermediate composition has already been given, using the ignition of pressed ferroaluminium thermite as an example (see Fig 17.1).

For igniting certain basic compositions that are especially difficult to light we must sometimes use several intermediate compositions simultaneously, out of which the intermediate composition in direct contact with the basic composition contains the least quantity of igniting composition.

Striking compositions form a special type of igniting compositions. They are ignited by friction against some object (striker) to which is applied a special pyrotechnic composition.

Striker compositions have recipes close to those of compositions used in match production. For example, one striker composition contains 60% potassium chlorate, 30% antimony, and 10% resin.

The striker for this composition is coated by a phosphorus paste consisting of 56% red phosphorus, 24% powdered glass, and 20% iditol.

Striker compositions are very sensitive to friction and very dangerous to handle.

## Section 2. Igniting compositions for rocket engines.

It is well known that the reliability of operation of a rocket engine depends to a considerable degree upon the presence of an effective ignition system. Igniters that previously existed, based on gunpowder, have not satisfied the requirements imposed upon the ignition of composite solid propellants and ballistic powders. American firms have developed a number of designs of pyrotechnic igniters which at the present time are used for RDTT and ZhRD (liquid-propellant rocket engines).

The pyrotechnic ignition system is most widely distributed and is used in rocket engines of the most diverse types, in particular in the engines of the Titan, Polaris, and Minuteman rockets<sup>266</sup>. Such a system is reliable and safe, provides for fast starting of the engine at a great altitude, and requires a power source of low capacity for switching on the system.

The flare of flame formed as a result of the operation of a pyrotechnic igniter has a high temperature and quite large dimensions (a large ignition area).

In the literature a large number of designs of pyrotechnic igniters have been described: roller, basket, "rocket in rocket", and others<sup>274</sup>.

At the first stage of development, binary mixtures were used in pyrotechnic igniters, such as, for example, a mixture of aluminium powder with  $\text{KClO}_4$ <sup>266</sup>. This mixture, which is known as "Alclo" mixture, has a high heat of reaction (see Chapter VI), burns fiercely, and its ignition temperature is about 360°C. An ethyl cellulose binder was later introduced into Alclo mixture.

For ignition of composite propellants with a high content of  $\text{NH}_4\text{ClO}_4$ , the following pyrotechnic mixture is used<sup>273</sup>:

|                            |           |
|----------------------------|-----------|
| $\text{KClO}_4$            | 26 to 50% |
| $\text{Ba}(\text{NO}_3)_2$ | 15 to 17% |
| an alloy of Zr/Ni (50/50)  | 32 to 54% |
| ethyl cellulose            | 3%        |

Igniting compositions containing boron are also finding use, such as, for example:

|                  |     |
|------------------|-----|
| KNO <sub>3</sub> | 71% |
| B (amorphous)    | 24% |
| rubber           | 5%. |

The development of pyrotechnic igniters requires the performance of numerous tests to determine their working characteristics under different conditions.

The critical features in the development of pyrotechnic igniters are <sup>266</sup>:

1. the required dimensions;
2. method of attachment in the rocket engine;
3. minimum temperature needed for the flare of flame;
4. characteristics of the products of combustion, maximum permissible quantity of condensed oxides, degree of dispersivity of solid particles, and others);
5. operating conditions (vibration, g-loads, pressure of surrounding medium, maximum and minimum working temperatures, etc..

### Section 3. Other types of pyrotechnic compositions: gasless, simulating, whistler compositions.

Besides the types of pyrotechnic compositions considered above, other pyrotechnic compositions exist that are used for various special purposes. Some have recipes that are quite close to incendiary, illuminating, or other compositions already described; in other cases, their special purpose requires a new and unique recipe.

The following types of compositions are used more frequently than others for special purposes:

1. "Gasless" or low-gas compositions, which are used in time fuses and exploders, in delayed action electric fuses, and in certain special heating devices.
2. Simulating and whistler compositions, the purpose of which is understandable from the name itself.

In addition, special recipes of pyrotechnic compositions exist that are used in the preparation of fireworks and in motion picture photography <sup>284</sup>.

Fireworks pyrotechnic compositions are not considered in this book; a description of their preparation and properties is given in special literature <sup>6, 15</sup>.

"Gasless" and low-gas compositions. The distinguishing feature of most compositions of this type is the low dependence of the rate of combustion upon external pressure <sup>113</sup>. This property is very valuable when these compositions are used in time fuses and exploders. For this purpose the temperature coefficient of the rate of combustion (see Chapter X, section 2) must also be low; however, far from all "gasless" compositions satisfy this requirement.

Besides this, compositions for time fuzes must satisfy all requirements imposed upon ordinary tubular powders; we should especially emphasise the ease of ignition of the compositions, and

their reliable ignition of the following link of the ignition chain (such as a detonating cap, for example).

We place the term "gasless" compositions is placed in quotation marks because during the high temperature reaction these compositions form a certain quantity of gaseous products which solidify when cooled. But the quantity of gaseous products is so small that they may be called low gas compositions without use of quotation marks.

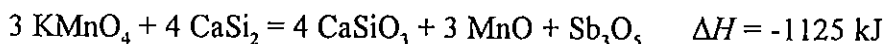
Lead, chromium, and manganese compounds are most frequently used as oxidisers in low gas compositions, for example,  $\text{Pb}_3\text{O}_4$ ,  $\text{PbO}$ ,  $\text{PbCrO}_4$ ,  $\text{BaCrO}_4$ ,  $\text{K}_2\text{Cr}_2\text{O}_7$ ,  $\text{KMnO}_4$ , and also  $\text{BaO}_2$ , which produce metallic lead (with a boiling point of  $1744^\circ\text{C}$ ) and slightly volatile oxides:  $\text{Cr}_2\text{O}_3$ ,  $\text{BaO}$ ,  $\text{MnO}$ , and others, upon decomposition.

Fuels used in low-gas compositions include Zr, Sb, Si, Mn, and  $\text{FeSi}$ .

The patent literature gives many recipes of low-gas compositions, for example (see reference <sup>7</sup> page 260 for patent numbers).

|        |                               |                     |                               |                            |                            |
|--------|-------------------------------|---------------------|-------------------------------|----------------------------|----------------------------|
| CuO 60 | $\text{Pb}_3\text{O}_4$ 35-80 | $\text{PbCrO}_4$ 40 | $\text{Pb}_3\text{O}_4$ 76-84 | $\text{PbCrO}_4$ 63        | $\text{Pb}_3\text{O}_4$ 70 |
| Zr 40  | Zr 65-20                      | PbO 44              | Si 18-22                      | $\text{Pb}_3\text{O}_4$ 25 | Si 30                      |
|        |                               | $\text{FeSi}_2$ 16  | NC 3-5                        | Si 12                      |                            |
|        |                               |                     |                               | NC 0.3                     |                            |

The literature <sup>260</sup> reports the use of a gasless composition 56%  $\text{KMnO}_4$  44% Sb for the delay in delayed action electric fuses. The combustion reaction may be expressed by the equation:

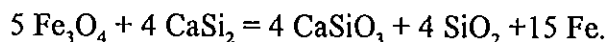


A composition containing 5% potassium chlorate, 47% selenium, and 48% metallic bismuth may be used for the same purpose (American patent 2.607.672, 1952).

"Gasless" compositions are finding use also for heating food (canned goods, soup, etc.) under front line conditions. The British used the following composition for this purpose in World War II:

|                     |     |
|---------------------|-----|
| magnetic iron oxide | 81% |
| calcium silicide    | 19% |

the combustion process of which may be expressed by the equation:



In conclusion we should note that many "gasless" or low gas compositions are close to thermite or thermite incendiary compositions in their properties, but differ from them in the greater ease with which they ignite, and in also certain cases by a higher rate of combustion.

Simulating compositions are intended for filling various pyrotechnic training devices, which create an external effect similar to the effect of real articles used in battle. Simulating devices have no injurious effects: this is achieved by making their casings of cardboard, plastics, or similar materials. The purpose of certain simulating devices is to imitate the effect obtained in the explosion of high-explosive projectiles, rifle grenades, etc. Such simulating devices must create a loud sound resembling that of the explosion of the high explosive device; besides this, it is desirable that the effect of simulating devices be accompanied by the formation of a certain quantity of smoke, similar in colour to the smoke formed in an explosive burst.

To obtain a loud noise, simulating devices are filled with powder mixture of potassium perchlorate and aluminium dust. In particular, a composition consisting of 70% potassium perchlorate and 30% aluminium may be used for this purpose, which is close to photomixture compositions in its properties. Such a composition, used in a powdered state, when an ordinary heat impulse is used on it, burns almost instantaneously with a loud sound effect and a light flash, liberating in this case a certain quantity of white smoke.

Simulating compositions liberating grey or black smoke as they burn must contain a certain amount of organic compounds rich in carbon (naphthalene, anthracene, etc.). Simulating devices also exist that liberate a coloured smoke when fired; such devices are used during manoeuvres for conventional designations of points where chemical or incendiary projectiles or bombs hit, the bursts of mine fields, etc. Coloured smoke compositions are usually used for filling these products, and sometimes a certain quantity of sawdust is added to the composition to retard its combustion.

Pyrotechnic whistler compositions. A sound effect resembling a whistle may be obtained by the combustion of a composition containing 75% potassium chlorate and 25% gallic acid  $C_6H_2(OH)_3COOH$ . The sound effect is explained by the high rate of combustion of this composition.

Becher <sup>8</sup> reports that mixtures of chlorates (K or Ba) with phenol derivatives produce a whistle during combustion and that, besides gallic acid, resorcinol, phloroglucine, and also picric acid may be used. However, mixtures containing picric acid and especially potassium picrate (such as, for example, a mixture of 60% potassium picrate  $C_6H_3N_3O_7K$  and 40%  $KNO_3$  are too dangerous to handle and are no longer used.

Experiments conducted by Maxwell <sup>271</sup> showed that the frequency of sound oscillations obtained in the combustion of these compositions is lower if the length of the tube (cardboard) into which the composition is pressed is longer. Together with this, the frequency of the oscillations is higher if the rate of combustion of the composition is greater.



## Chapter XXII

### Use of Pyrotechnics in the National Economy. Match Compositions.

The use of pyrotechnic devices and compositions in the national economy, in art, and in research work is becoming ever more diversified every year, and ever more significant.

Thermite compositions are coming into a particularly wide variety of large-scale applications, and have been used for many years for obtaining rare and valuable metals<sup>291, 208</sup>. The following metals and alloys may be obtained by means of aluminium thermal processes: Cr, Mn, Ti, W, Mo, Ni, Co, Zr, V, and others.

Ellern<sup>9</sup> indicates that when it is difficult to reduce a metal by means of an ordinary aluminium thermal reaction, several variations are available for accomplishing these processes:

1. Adding a more active oxidiser to a lower oxide, such as for example, chromates to chromium oxide.
2. Adding strong oxidisers to increase the thermal effect of the reaction, and facilitate the process, such as, for example,  $\text{BaO}_2$ ,  $\text{PbO}_2$ ,  $\text{Na}_2\text{S}_2\text{O}_8$ ,  $\text{KClO}_3$ , and others.
3. Adding other strong reducing agents to the aluminium, such as, for example, Ca, Mg, Si or  $\text{CaC}_2$ .
4. Carrying out the process with preliminary heating (in a furnace). This variation is recommended to obtain titanium and zirconium by reduction of the oxides by means of magnesium.

Venturini<sup>109</sup> considered the variation with heating for various mixtures. Obtaining metals by means of metal-thermal reactions under laboratory conditions is described in reference<sup>20</sup>.

Niobium and tantalum may be obtained by reduction of the sulphides by aluminium powder. The separation of the reaction products is achieved in this case by the vaporisation of  $\text{Al}_2\text{S}_3$  at a temperature greater than  $1550^\circ\text{C}$ .

The use of thermite compositions for welding rails is generally known<sup>283</sup>. New thermite compositions have been developed comparatively recently for welding telephone and telegraph wires.

Kazhdan<sup>7 page 277</sup> prescribes methods of welding steel wires by means of pyrocartridges and describes a pyro-cartridge (see Fig. 22.1, a) that is a cylindrical pellet compacted from magnesium thermite with a longitudinal opening and an igniting composition, and provided with a striker head. The dimensions of pyrocartridges are small, and their weight, depending upon the diameter of the wires being welded, is only 7 to 16 g. In the combustion of magnesium thermite, a high temperature is developed, sufficient to accomplish the welding of the wires, and the slag remaining after its combustion retains the form of the pyrocartridge (Fig. 22.1, b and c). As is shown in Fig. 22.2, the ends of the wires are brought close together by means of special pliers. The thermite cartridge that has been pulled over the weld point is ignited; when it burns, the ends

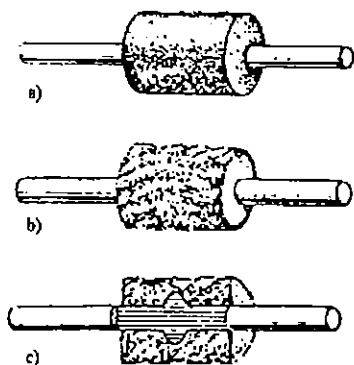


Fig 22.1 Welding pyrocartridge before and after welding

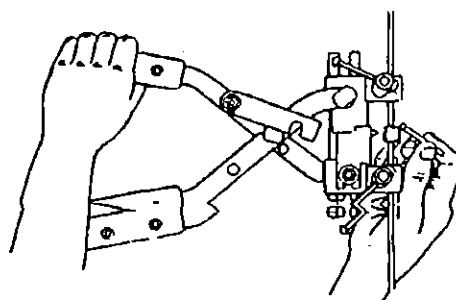


Fig 22.2 Device for welding wires by means of pyrocartridge

of the wires are pressed together with the pliers. After the wires cool, a strong welded joint is formed.

A copper thermite recipe developed in the TsNII MPS (Central Scientific Research Institute, Ministry of Railways), consisting of 64% CuO, 16% ferromanganese (80% Mn), 20% CuAl alloy (46% Al), has come into wide use for welding splice connections to rails. "The reduced metal" obtained during combustion "is a non porous manganese bronze, which reliably welds the ends of the splice piece to the head of the rail." (A.N. Kukin, *Novyye vidy termitnoy svarki* (New Types of Thermite Welding), Transzheldorizdat (Railroad Transport Publishing House), 1955).

A thermite consisting of 72.5%  $\text{Fe}_3\text{O}_4$ , 18% Al, 4.5% Mg, and 5% alloy FeMn ( $\sim 1 : 1$ ) is used for welding grounding wires to metal structures, .

It has also been proposed that thermite be used in earth-moving operations for thawing frozen ground in winter <sup>286</sup>. However, calculations show <sup>288</sup> that with a volumetric moisture content of the ground equal to 25%, not less than 40 kg of thermite would be required to thaw 1 m<sup>3</sup> of frozen ground. In the opinion of Kiselev <sup>282</sup>, a practical thermite consumption for partial thawing of the ground would amount to about 8 kg per cubic metre of ground.

The scientific workers of the Moscow Mining Institute have conducted experiments on the secondary pulverisation of ore by briquette thermite <sup>280</sup>. During the 1941 - 45 war, thermite compositions were used for heating canned goods, these compositions being placed in a metallic cartridge within the tin can. According to reference <sup>208</sup>, thermite can be used for heating water and food, and also for heating soldering irons and rivets. In certain cases, the use of thermite is also suitable for breaking up ice jams.

In 1958 thermite was used to develop a sodium cloud in the upper layers of the atmosphere. The astronomer I.S. Shklovskiy proposed that photometric observations of the rate of diffusion of the sodium cloud be used as a method of determining the density of the atmosphere. The experiment was conducted in the USSR on 19 September 1958. Ferroaluminium thermite was used to

vaporise the metallic sodium. The sodium was pulverised into small pieces, mixed with the thermite, and the entire mixture was placed in a steel cylinder. In the combustion of the thermite the sodium evaporated and its vapours were discharged through an ejection port in the cylinder <sup>290</sup>.

Smoke compositions containing insecticides (or forming them in the process of combustion) are widely used for controlling harmful insects <sup>276 pages 118-145; 293</sup>. These smoke compositions are used to charge smoke pots. The composition contain a toxic substance and a thermal mixture (see Chapter XIX). The toxic substance sublimes on combustion of the thermal mixture.

KClO<sub>3</sub> is the most common oxidiser, and anthracene, dicyandiamide (GCDA), urotropine, and other substances are used as fuels. As toxic agents we use hexachlorane (hexachlorocyclohexane, HCCH), hexachloroethane C<sub>2</sub>Cl<sub>6</sub>, DDT, and others <sup>287</sup>.

As an example we may mention a composition consisting of HCCH 50-52%, KClO<sub>3</sub> 23-26%, NH<sub>4</sub>Cl 9-12%, anthracene 9-12%, and DCDA 4-6%.

Fungicide compositions (from the Latin *fungus*, mushroom) are also known. These are mixtures containing substances used for control of fungoid, bacterial, and virus diseases of plants. As an example of such a smoke mixture, we may give a composition consisting of the following substances (by percentages): dichloronaphthoquinone 58, KClO<sub>3</sub> 22, NH<sub>4</sub>Cl 10, DCDA 5, and anthracene 5.

Special acaricide smoke compositions have also been developed (acaricides are chemical substances used for mite control). For example we might mention a composition which includes the following components (in percentages): tedion <sup>25 volume I page 82</sup> industrial 50, KClO<sub>3</sub> 20, DCDA 30. This composition forms smoke without flame, and develops a combustion temperature of about 250°C. Sulphur dioxide SO<sub>2</sub> gas used to disinfect hot houses and fruit and vegetable warehouses is obtained from the combustion of pyrotechnic smoke pots without cases (weighing 500 or 100 g), the composition of which includes sulphur 75%, potassium nitrate KNO<sub>3</sub> 17%, and diatomite 8% (an aerator and combustion catalyst), developed by Sidorov <sup>279</sup>. This composition has a strongly negative oxygen balance and therefore needs free access of air during combustion.

Smoke compositions are also used to protect crops (especially citrus fruits) against frosts <sup>276 page 104-126</sup>, to study air currents in the atmosphere, and in various other devices.

Coloured flare compositions and white, black, and coloured smoke compositions are widely used in motion-picture photography, and filming in colour today would be unthinkable without the use of pyrotechnic devices <sup>284</sup>. Various pyrotechnic signalling devices have found use in the maritime and river fleets, in air transport and in railroads.

To reduce shrinkage and to prevent the formation of scale when pouring steel into moulds, a pyrotechnic composition is poured into the upper part of the mould, above the liquid metal, and this composition consists of 70% FeSi (1:3), 10% aluminium powder, and 20% NaNO<sub>3</sub>.

Pyrotechnic hail-control rockets and cartridges have also been developed recently.

Investigations performed in recent years both in the Soviet Union and abroad have shown that by causing an artificial crystallisation of the super-cooled drops of water in the clouds we may affect the microphysical processes. This suggests the possibility, in principle, of regulating the natural processes to prevent the falling of hail, increase precipitation, and disperse super-cooled clouds and fogs. The most active substances causing crystallisation of super-cooled drops of water are the iodides of silver (AgI) and lead (PbI<sub>2</sub>). Theoretical considerations concerning artificial effects on super-cooled clouds and fogs are given in references <sup>285, 278</sup>. The method of using the iodides of lead and silver, usually not pyrotechnic, consists of introducing colloidal solutions of these substances into a cloud or a fog by spraying them from an aircraft.

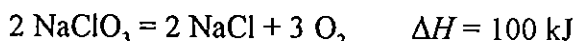
Two variations are possible: 1) the AgI or PbI<sub>2</sub> is in the composition in a prepared form; 2) these same substances are formed as the result of a chemical reaction occurring during the combustion of this composition.

A recipe for a composition of the first variation is AgI or PbI<sub>2</sub> 40 to 60%, NH<sub>4</sub>ClO<sub>4</sub> 24 to 45%, iditol 10 to 25%, and graphite (or industrial oil) 1.5 to 2%.

The following substances are introduced into compositions classed among the second type of compositions: powdered lead and substances containing iodine - NH<sub>4</sub>I, CHI<sub>3</sub> (iodoform), or C<sub>6</sub>I<sub>4</sub>O<sub>2</sub> (iodanil). To these substances is added a thermal mixture consisting of fuel and oxidiser: iditol + NH<sub>4</sub>ClO<sub>4</sub>. A composition with the following recipe may serve as an example: lead powder 20-25%, NH<sub>4</sub>I 25 to 34%, NH<sub>4</sub>ClO<sub>4</sub> 20 to 30%, resin (iditol) 10 to 20%.

Gaseous oxygen of an adequate purity for breathing, for example in submarines or in aircraft, may be obtained by the combustion of pyrotechnic compositions <sup>294</sup>. The devices used for this purpose are called chlorate candles or chlorate briquettes; the basic component in the compositions is sodium chlorate (or potassium chlorate).

Since little heat is liberated in the combustion of sodium chlorate a small quantity of fuel is added to increase the thermal effect which is needed to provide stable combustion.



In the selection of the fuel we must ensure that no toxic gaseous products are formed on its combustion (the addition of only a small quantity of CO<sub>2</sub>, obviously, is permissible). Frequently iron powder is used as a fuel; no gases are formed during its combustion, and the ferric oxide Fe<sub>2</sub>O<sub>3</sub> formed in combustion is a good catalyst for the decomposition of the chlorates.

Recipes such as the following are given in the literature <sup>294</sup>: NaClO<sub>4</sub> 74 to 80%, Fe 10%, BaO<sub>2</sub> 4%, glass fibre 12-6%. BaO<sub>2</sub> is added to prevent the liberation of free chlorine during combustion.

A composition containing 80% NaClO<sub>3</sub> in a compacted form has a density of  $2.45 \pm 0.05 \text{ Mg m}^{-3}$ ; the weight of the gaseous oxygen obtained is 34% of the weight of the candle. The heat of combustion of such mixtures is about  $840 \text{ kJ kg}^{-1}$  of composition, and the combustion temperature (measured by a thermocouple) is 500-700°C. Such mixtures may be filled by casting (melting

point of  $\text{NaClO}_3$ ,  $255^\circ\text{C}$ ). The igniting composition contains the same components, but in different ratios, providing a combustion temperature of  $900 - 1000^\circ\text{C}$ :  $\text{NaClO}_3$  60%; Fe 20%;  $\text{BaO}_2$  10%, and glass fibre 10%.

There are indications in the literature that a pyrotechnic mixture of  $\text{CsClO}_4$  and Al may be used to obtain a caesium plasma <sup>292</sup>.

In conclusion, evaluating further possibilities of using pyrotechnic compositions in the national economy, we should note that the development may proceed in two directions, which are different in principle.

1. Firstly the use of the energy (thermal, radiant, or other form) liberated in the combustion of pyrotechnic compositions.
2. Secondly the use of the substances (simple or complex) which are products of the combustion of pyrotechnic compositions.

As yet, this second variation is used on comparatively limited scales: aluminothermy (obtaining metals, and also obtaining artificial corundum  $\text{Al}_2\text{O}_3$ , obtaining oxygen (oxygen briquettes), obtaining  $\text{SO}_2$  in insecticide compositions, and obtaining AgI and  $\text{PbI}_2$  in hail-control compositions.

However, a number of gases can be obtained by means of pyrotechnics:  $\text{H}_2$ ,  $\text{Cl}_2$  (and possibly also  $\text{F}_2$ ),  $\text{N}_2\text{O}$ , and others, as well as many inorganic salts and oxides of metals. This is a little-studied part of pyrotechnics, and still awaits its own investigators and experimenters.

Match compositions. At the present time (1964) matches made throughout the world are chiefly the so-called safety matches, i.e., matches that ignite only when struck against a paste applied to the match box. Safety matches were first made in Sweden in 1855, and therefore they have obtained the title of Swedish matches.

The world production of matches is of the order of ten billion boxes per year (since the population of the earth is about three billion, the consumption of matches per person per year amounts to about 10 boxes, on the average). About 1 g of match paste is used for one box of matches. Consequently, the consumption of match paste on a world scale amounts to tens of thousands of tons per year.

It is obvious that at such a scale (ten billion boxes) the production of matches must be automated. Actually, very highly perfected automatic devices are now operating at match factories.

The chemistry of the ignition of modern matches is as follows: in the friction of the match head against the striker on the box an exothermic reaction occurs between the red phosphorus (in the striker) and the Berthollet's salt (in the match head). The ignition of the match head occurs from the heat of this reaction.

The basic composition of the match head, like all other pyrotechnic compositions, is an oxidiser-fuel system. As yet the oxidiser is exclusively  $\text{KClO}_3$ , as it is a substance that easily

releases its oxygen. There are usually two fuels in match compositions: sulphur and animal (bone) glue. The selection of fuels is based upon both chemical and technological considerations: a mixture of  $\text{KClO}_3 + \text{S}$  has a comparatively low flash point ( $220^\circ\text{C}$ ) and provides for easy ignition of the composition; the animal glue is introduced into the solution in the form of an aqueous solution (the water is removed by drying), creates the necessary consistency of the paste, and protects the match heads against becoming water soaked in storage. However, usually match igniting compositions contain 6 - 8 components, since additional oxidisers ( $\text{K}_2\text{Cr}_2\text{O}_7$ ) are added to them, as well as catalysts accelerating the decomposition of Berthollet's salt ( $\text{MnO}_2$ ), fillers (iron oxides  $\text{Fe}_3\text{O}_4$ , white zinc pigments  $\text{ZnO}$ , and others), substances increasing sensitivity or, in the terminology of matchmakers, "response") of the match head to friction (ground glass), and also a small quantity (a fraction of a percent) of organic dyes (rhodamine, Acid Green and others).

As examples, we may give the following compositions, in percentages. The match composition is on the left, and the phosphorus paste (striker on the box) is on the right.

| Match composition                 |     | Striker composition     |       |
|-----------------------------------|-----|-------------------------|-------|
| $\text{KClO}_3$                   | 51% | red phosphorus          | 37.2% |
| ground glass                      | 15% | $\text{Sb}_2\text{S}_3$ | 33.5% |
| animal glue                       | 11% | animal glue             | 9.3%  |
| $\text{ZnO}$                      | 7%  | iron oxide              | 7.0%  |
| $\text{Fe}_3\text{O}_4$           | 6%  | dextrine                | 7.0%  |
| $\text{S}$                        | 5%  | $\text{MnO}_2$          | 3.4%  |
| $\text{MnO}_2$                    | 4%  | $\text{CaCO}_3$ (chalk) | 2.0%  |
| $\text{K}_2\text{Cr}_2\text{O}_7$ | 1%  | ground glass            | 0.6%  |

Contemporary American recipes for a match igniting paste and a phosphorus paste are as follows<sup>9</sup>:

| Match paste                     |           | Striker paste                   |     |
|---------------------------------|-----------|---------------------------------|-----|
| $\text{KClO}_3$                 | 45 - 55 % | red phosphorus                  | 50% |
| silicate fillers                | 15 - 32%  | ground glass                    | 25% |
| animal glue                     | 9 - 11%   | animal glue (or casein)         | 16% |
| infusorial earth                | 5 - 6%    |                                 |     |
| $\text{S}$                      | 3 - 5%    | $\text{ZnO}$ or $\text{CaCO}_3$ | 5%  |
| $\text{ZnO}$ or $\text{CaCO}_3$ | 3%        | carbon black                    | 4%  |
| starch or dextrine              | 2 - 3%    |                                 |     |

The quality of matches is usually estimated as follows:

1. by the results of their control ignition (here the quality of both the match and the striker are checked simultaneously);
2. determination of sensitivity (with a special instrument)
3. determination of the matches' resistance to moisture, by keeping them for 24 hours at room temperature and at a 99.4% relative humidity; then control ignition is performed;
4. determination of the flash point of the match heads;
5. determination of the adhesion between the match head and the match stick.

To avoid smouldering, match sticks are permeated with a 1.5% solution of  $\text{H}_3\text{PO}_4$  before the matches are fabricated, and then coated with paraffin (dipped in melted paraffin).

Aside from ordinary (kitchen) matches, special matches are also fabricated:

1. Storm matches, burning in wind, in dampness, and under a rain.
2. Thermal matches, developing a higher temperature on combustion, and producing a greater quantity of the heat when the head burns.
3. Signal matches, the heads of which produce a coloured flame in combustion.
4. Photographic matches, producing a momentary bright flash, used in photography, etc.

A detailed acquaintance with the chemistry and technology of match production can be obtained from the literature <sup>277, 289</sup>.

In the USA matches are also fabricated that ignite upon friction against any rough surface (the so-called SAW (strike anywhere) matches). The peculiarity of such match compositions is the presence of sesquisulphide  $\text{P}_4\text{S}_3$  in them. For example, there is this recipe from reference <sup>9</sup>.

|                              |     |
|------------------------------|-----|
| $\text{KClO}_3$              | 32% |
| ground glass or other filler | 33% |
| $\text{P}_4\text{S}_3$       | 10% |
| extender                     | 4%  |
| animal glue                  | 11% |
| $\text{ZnO}$                 | 6%  |
| rosin                        | 4%  |



## Chapter XXIII

### Bases of the Technology of Pyrotechnics Production

The manufacture of pyrotechnic products is a quite complex technological process because of the high requirements upon the quality of the product, and also the danger of fire and explosion of the compositions. The following conditions must be observed:

1. High quality of components (usually of the first grade).
2. Cleanliness of production spaces and equipment.
3. Low relative humidity (not more than 65%) in the production areas.
4. Careful division and sifting of components.
5. Accurate measurement of proportions of components.
6. High quality of mixing of components.
7. Observation of precautionary measures and industrial safety rules.

The technological process has the following phases:

- I. Preparation of components: drying, pulverisation, and sifting.
- II. Preparation of compositions: measuring of proportions, mixing of components, granulation and drying of compositions.
- III. Compaction and formation of compositions: measurement and compaction by pressing, screw feeding, tamping (or casting).
- IV. Charging of products: preparation of casings and parts, assembly of products, packing.

As an example of a technological process, we show below a diagram of the production of illuminating bombs intended to be dropped from aircraft.

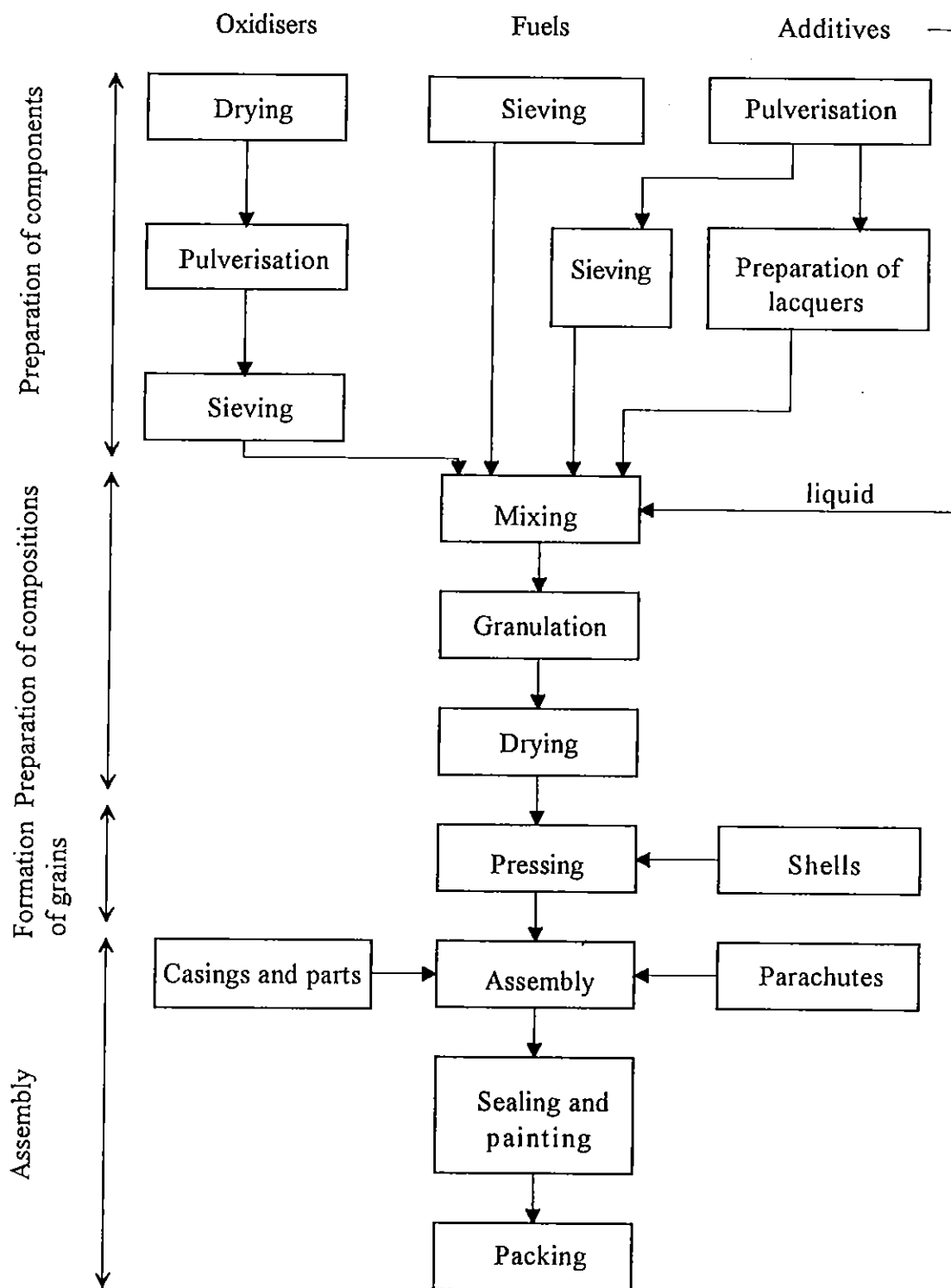
#### Section 1      Preparation of components.

The components of these compositions and other materials are allowed in production if they satisfy the requirements of the GOST (All-Union State Standard) or TU (Technical Regulations) with respect to data from chemical analysis. Components not satisfying the moisture content requirement are dried. Usually the moisture content in the components is standardised within limits of 0.1-0.5%.

#### Drying of Components

Oxidisers are most frequently dried. Fuels and binders (binding agents) usually contain little moisture and do not require drying. The drying of oxidisers is usually performed at 70 - 80°C with the water from the heating system or low-pressure steam as the heat source. The drying temperature of both oxidisers and of all other materials is dictated by the physico-chemical properties of the materials.

Small quantities of components (not more than a few dozen kg) are dried in drying cabinets, which are metal structures with shelves for trays holding the components where sections of tubing are placed for heating under the trays or along the side walls. For drying large quantities of



oxidisers tubular or vacuum dryers are used.

Tubular dryers (Fig. 23.1) are adequately economical and efficient, work without fail, and are easily cleaned by washing. The material loaded into the hopper of the dryer is fed into the upper part of the drum through the feeder. The rotating disks with scrapers, continuously move the material, forcing it onto tubes heated by steam. A slight inclination of the drum provides for movement of the material to the discharge hatch.

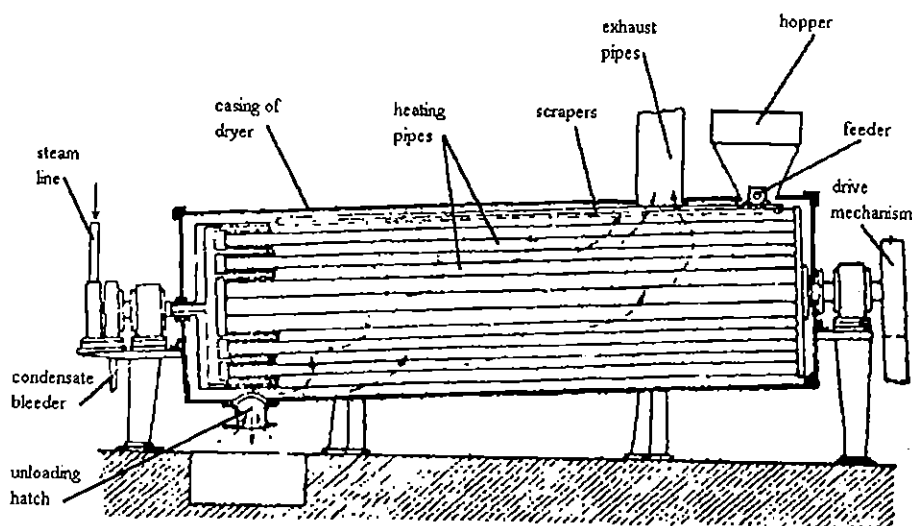


Fig 23.1 Tubular dryer

The capacity of tubular dryers is 200-500 kg/hr. The steam consumption, at maximum load, is about 500 kg/hr. At 7-8 rpm of the drum, and with it inclined at an angle of  $3^\circ$ , the capacity required does not exceed 2.5 kW.

The moisture evaporated is separated by the natural suction of the air passing through the unloading hatch and discharged through the upper pipes. The shortcomings of a tubular dryer are the difficulty of sealing the rotating pipes and the removal of dust from the unloading hatch.

Vacuum dryers (Fig. 23.2) are horizontally arranged rectangular or cylindrical chambers, equipped with a number of horizontal hollow plates, through the cavities of which steam or hot water is passed.

Pans containing the material to be dried are placed on the plates. The chambers are closed by bottom doors with rubber gaskets forming a tight seal, and special clamping devices. Rarefaction is achieved by means of RMK No. 2 or No. 3 vacuum pumps. The load of a dryer with a volume of  $3 \text{ m}^3$  does not exceed 120-150 kg. The duration of drying at  $40\text{-}50^\circ\text{C}$  and a rarefaction of 200-250 mm Hg is about 1 hour for materials with an average moisture content.

A vacuum dryer has essential advantages over other types of dryers: a reduced probability of ignition of the material being dried (or the vapours of combustible liquids separated from it),

absence of any formation of dust, and acceleration of the drying process. Its shortcomings include periodicity of operation, low capacity, considerable expenditure of manual labour (loading and unloading the pans, and pouring the material in and out of them).

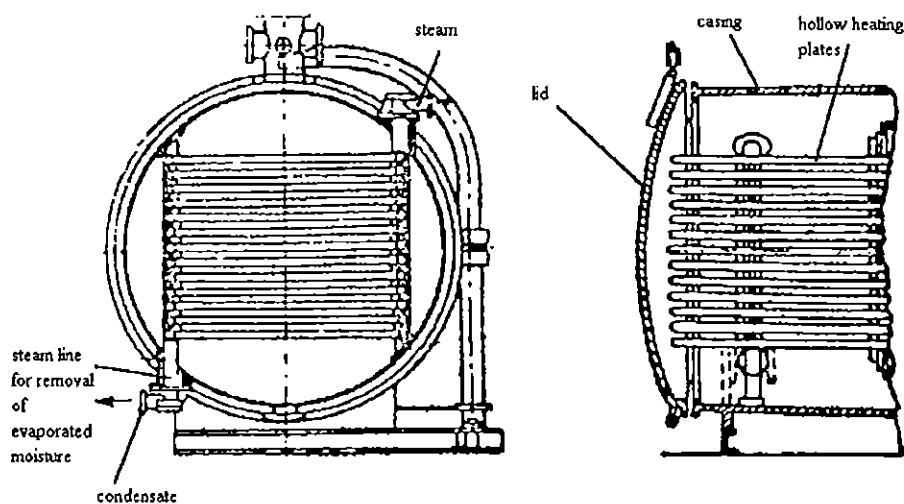


Fig 23.2 Vacuum dryer

### Pulverisation of Components

The dimensions of particles of pyrotechnic composition components must not exceed tenths of a millimetre, and sometimes they must even be as small as hundredths of a millimetre (i.e., a multiple of 10 microns). The basic components (oxidisers and fuels) usually already arrive in a pulverised form, and therefore machines intended for coarse and average milling are seldom used in the manufacture of pyrotechnics. As a rule, oxidisers stick together in lumps in the process of drying, and besides, the dimensions of the crystals in themselves considerably exceed the dimensions of the particles indicated in the technical specifications.

Metallic fuels are pulverised and sifted by the plants supplying them. With regard to fineness of milling, metallic fuels can be subdivided into several grades. In the preparation of components, metallic fuels are subjected only to control sifting, and only to obtain a very fine dispersivity (in microns) are they additionally pulverised.

Disintegrators and crushers are used for the pulverisation of components, as well as rotary ball mills and vibrating mills, and more rarely crusher rolls and roller mills.

A disintegrator (Fig. 23.3) consists of two rotating steel disks, enclosed in a cylindrical casing. Steel pegs are arranged around the circumference of each disk. Their arrangement is such that each row of pegs of one disk move into the space between the rows of pegs on the other disks. The disks are fastened at the ends of shafts, rotating in opposite directions. The material to be pulverised enters the centre of the mill from a bunker through a feeder, and then enters the clearances between the pegs and here is intensively pulverised.

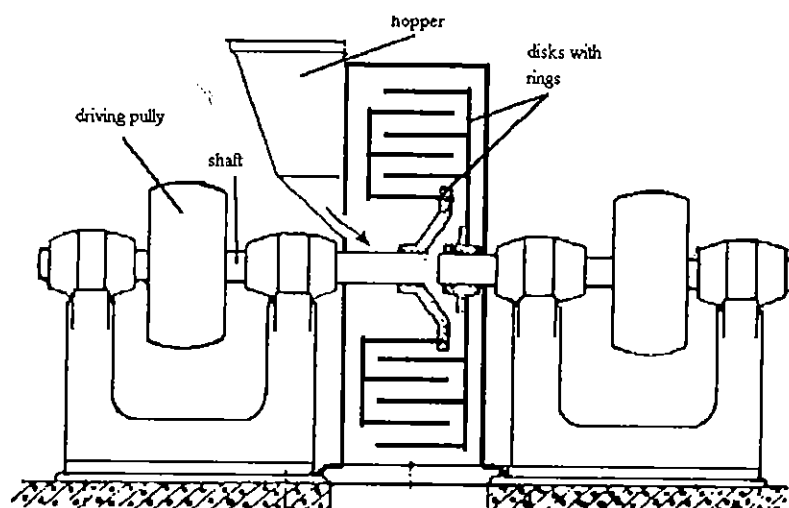


Fig 23.3 Disintegrator

Disintegrators used for preparing components have a disk diameter of 600 - 800 mm and pegs with a length of 100-160 mm. The capacity of these machines is very high, and at a rotation of disks at a rate of 1000-1200 rpm it reaches 1000 kg hr<sup>-1</sup> or more.

A crusher (Fig. 23.4), differs from a disintegrator in that it has only one rotating disk, on which there are scrapers, which prevent the material being pulverised from sticking to the casing.

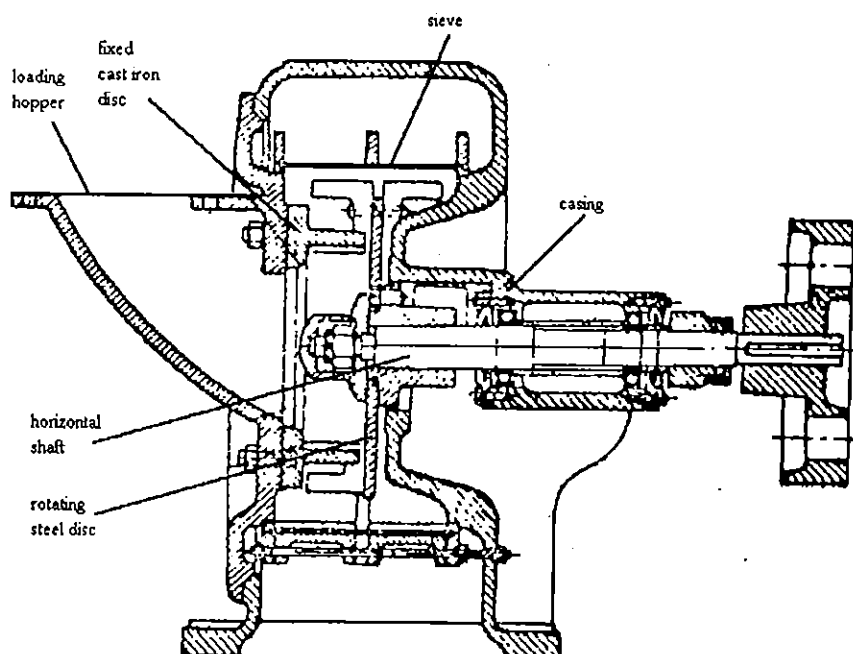


Fig 23.4 Crusher

In a crusher, besides, a drum is installed with a sieve for preliminary sifting and holding the unpulverised material. The presence of grinding elements in crushers makes it possible to pulverise viscous and fibrous materials in them (iditol, rosin, asbestos, and others).

The capacity of a crusher with a rate of rotation of the disk of 2500-3000 rpm, depending upon the properties of the material being pulverised, amounts to 500-1000 kg/hr.

Disadvantages common to both a disintegrator and a crusher are:

1. The necessity of an especially careful fitting and balancing of the moving parts, since at high speeds even a light contact between them leads to serious accidents.
2. The pumping of a large quantity of air through them, as a consequence of which intensive dust formation occurs, which requires special ventilation.
3. The complexity of disassembly and cleaning, especially for a disintegrator.

Ball mills are rotating drums. Pulverisation is performed by means ball bearings, which, as a consequence of friction against the walls of the drum and against each other, periodically rise to some height, and then fall back again. For the pulverisation of components that will not explode (inert components) the lining inside the drum is made of metal, and the balls of steel or bronze. For pulverising explosive or combustible materials the lining is made of leather, and the balls of hard wood (or ceramics). Milling time depends upon the properties and quantity of the material, the rate of rotation of the drum, and the required fineness of milling; the time is usually established by experimental methods.

Vibrating mills (Fig. 23.5) are little used as yet in pyrotechnics production, but they have the following advantages: high capacity with the very highest fineness of milling, possibility of pulverising metallic fuels in an inert medium, and small overall dimensions.

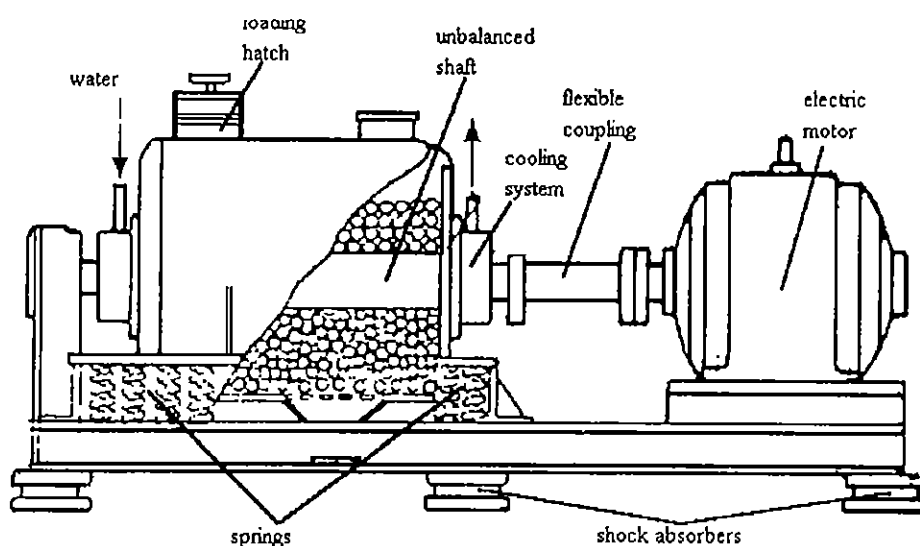


Fig 23.5 Vibrating mill

A vibrating mill has a rounded or trough-shaped cross section. Balls (milling bodies) and the materials to be pulverised are loaded into the mill. During the rotation of the unbalanced shaft, the vibrating mill makes frequent oscillations (up to 3000 per minute), perpendicular to the axis of rotation of the shaft. Because of this, all the material loaded into it is placed in circular motion in a direction opposite to the direction of rotation of the shaft, and the balls rotate around their axis. Intensive pulverisation of the material occurs. The main shortcomings of both vibrating and rotary ball mills are the considerable expenditure of energy and the great amount of noise developed in the working spaces. Besides this, because of the erosion of the balls, some contamination of the material being pulverised occurs, which also is undesirable.

### Sieving of components

The pulverised material is sieved to obtain powder with particles relatively close to each other in their dimensions, and also to separate mechanical impurities that have entered the mixture accidentally.

Silk or metallic screens are used as sieves. For silk sieves the screen number is indicated by the number of holes per linear centimetre (average in two directions, along the base and along the weft), and for metallic sieves the number of the sieve is determined by the size of the holes in the screen (in mm).

In the manufacture of pyrotechnics, ordinary shaker sieves and vibrating sieves are used.

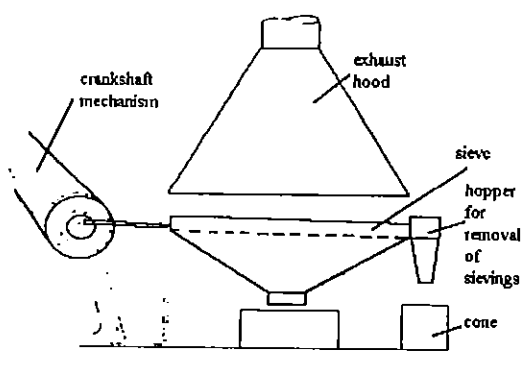


Fig 23.6 Shaker sieve

A shaker sieve (Fig. 23.6) is a wooden box, having externally the shape of a truncated pyramid. In the box, at an angle of 3-5°, is installed a sieve which extends as far as the frame. The box, together with the sieve, is fastened on flat metal springs. The shaker sieve is driven by a motor or a transmission via an eccentric gear, which gives the sieve a reciprocating motion at a rate of 200-300 oscillations per minute.

A vibrating sieve (Fig. 23.7) is a metallic table, on the cover of which an electric motor is installed, an inertia vibrator, and a round hopper with a screen, fastened on rubber mountings, installed in special seats. The material is poured into the hopper onto the sieve in a quantity of 2-3 kg. and after its cover has been closed, the motor is switched on.

The electric motor drives an inertial vibrator by a belt transmission which, being rigidly fastened to the hopper sieve transfers to it oscillations with a frequency of from 1500 to 2000 per minute. The material that has passed through the sieve is drawn off through a funnel to a collecting box.

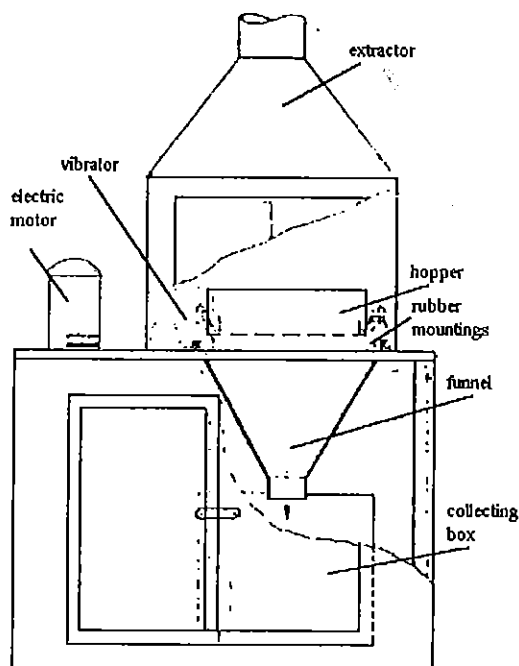


Fig 23.7 Vibrating sieve

The basic shortcomings of a shaker sieve and a vibrating sieve are the great amount of dust produced, and the large expenditure of manual labour. In performing any operation in the preparation of components, we must also bear in mind the fact that the dust of oxidisers, mixed with the vapours of dust of organic substances or the dust of metallic fuels, may form explosive mixtures. Therefore, all operations should be performed in different spaces, and everywhere ventilation plants must be installed.

For the preparation of components, separate machines are frequently used for drying, pulverisation, and sieving, most frequently installed in different spaces. In this case, the machines are loaded and unloaded manually, and the material is also transported either on hand-pushed carts or carried by hand. All of this creates difficult working conditions and low productivity. It would be much more advisable

to perform all the operations on one machine - a drying and milling unit; this would much increase productivity and would considerably improve working conditions in production.

## Section 2. Preparation of compositions.

A pyrotechnic composition must be homogeneous. A sample taken from any part of the composition must correspond to the recipe of the composition with respect to the content of the components in it. It is difficult to obtain an entirely homogeneous mixture, even with a prolonged mixing time of dry friable materials, and therefore organic additives are frequently added in the form of solvents (lacquers); this improves mixing and simultaneously increases the adhesion of the particles to each other; in order to avoid adhesive clusters subsequently and to obtain a homogeneous composition, the latter, after mixing, is subjected to a granulation operation. The compositions are dried after granulation to remove the organic solvents.

The preparation of compositions is dangerous because of the possibility of fires or explosions. If the industrial safety rules are violated, even human fatalities are possible.

The basic measures providing safety in the preparation of compositions are as follows:

- 1) the operation of mixing the components is performed in a separate building surrounded by embankments, at a safe distance from the other buildings;
- 2) the mixers are installed in strong reinforced concrete bays, one mixer in each;
- 3) control of the mixer (starting, stopping, and unloading) is accomplished in a safe place and at the required distance from the mixing bay;

- 4) the cleanliness of the compartments and equipment must be maintained; accumulations of dust, adhesion of the composition to parts of the mixer, or spilling of the composition in the space are not tolerated;
- 5) instructions on safety precautions for each working place must be strictly observed;
- 6) the measuring out of portions of the oxidisers and fuels must be performed in different spaces.

Of a great number of various types of mixers used in various branches of industry, only the rotary-blade mixer more or less satisfies the conditions of pyrotechnic production.

A rotary-blade mixer (Fig. 23.8) has a casing resembling a trough, through which passes a rotating shaft with blades of a special design. The casing of the mixer is fastened on a mounting in such a manner that it can be tipped over to allow the composition to be poured out. The mixer blades are rotated by a belt transmission via a reduction gear, driven by an electric motor. It is mandatory that the motor be explosion proof. To clean the casing of the mixer of compositions that adheres to it, rubber heads made of hard rubber with a thickness of 5-10 mm, are fastened to the ends of the blades.

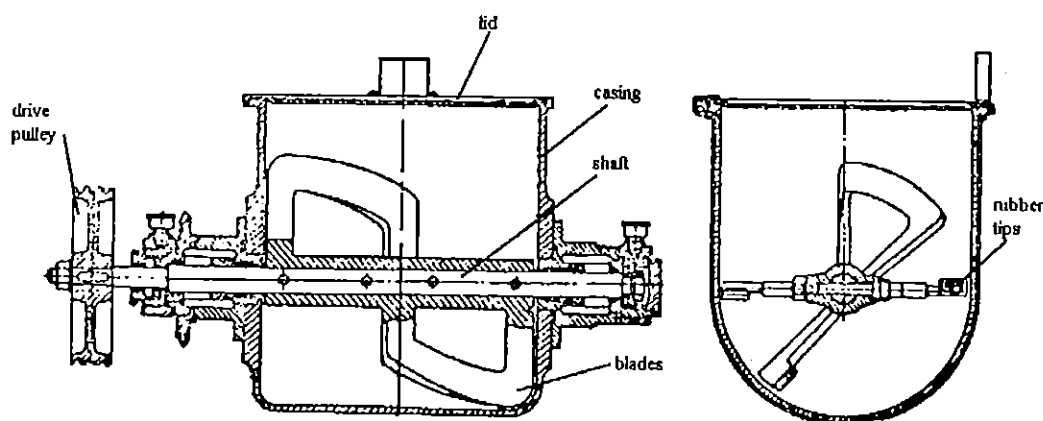


Fig 23.8 Rotary blade mixer

By no means all compositions may be mixed in a rotary-blade mixer. Some compositions are mixed by hand, although in recent years many efforts have been expended in the development of more highly perfected mixers, which would replace unproductive and dangerous manual labour.

Granulation. This operation consists of forcing the composition through a sieve with comparatively large mesh dimensions (10-12 per linear cm) after holding it at a normal temperature (drying it) for 0.5-1 hour.

For a long time this operation was performed manually by forcing the composition through the sieve from behind a armoured shield with a rubber plug fastened on the end of a long stick. Such an operation, which appears simple at the first glance, is very difficult to mechanise, and the main

reason for this is the great viscosity of the composition and the fact that it dries out in the process of granulation; this leads to clogging up of the screening and clogging up of the rubbing element, which leads to an increase of the friction, which may lead to ignition of the composition. Some favourable results in mechanisation of the granulation process have been obtained by the use of vibration of the screening or the rubbing elements.

Drying of compositions. This definition is very relative, since the dried components in the process of mixing and granulation are scarcely moistened at all; when the composition is kept in the so-called dryers, it is chiefly the organic solvents that is evaporated, until its remaining content is 0.5 - 0.6%.

Besides this, dryers are used as a storage point for an intermediate reserve of these compositions. The dryers are individual buildings, at a safe distance from other buildings, and it is mandatory that they be surrounded by embankments. Considerable quantities of the compositions are usually subjected to drying. They are placed on shelves in the dryers; a temperature of about 30-40°C is maintained in the compositions; under such conditions, the compositions are kept from several hours to a day.

### Section 3.    Compaction of compositions

Depending upon the design of the product and the effect required, compositions are given the shape of "stars," "flares," etc.; in most cases, charges of compacted compositions have a cylindrical shape. In some cases, the compositions are used directly to fill the casing of the products. In the operation of shaping the composition acquires the density and mechanical strength needed, which play a very important part in obtaining the appropriate pyrotechnic effect.

The shaping is performed by pressing, screw feeding, tamping (for rocket compositions frequently the composition is cast) in separate buildings, with the use of special equipment.

Pressing. In the formation of a composition by pressing, a press tool is used which usually consists of three basic parts: the mould, bottom plate, and die (Fig. 23.9).

The pressing tool is fabricated to high precision, from high-quality tool steel. Compositions for small products are measured out by the volumetric method directly into the mould, in which the bottom plate is inserted; for large products the composition is weighed, and the portions of the compositions are placed in cardboard boxes, from which they are poured into the moulds as needed.

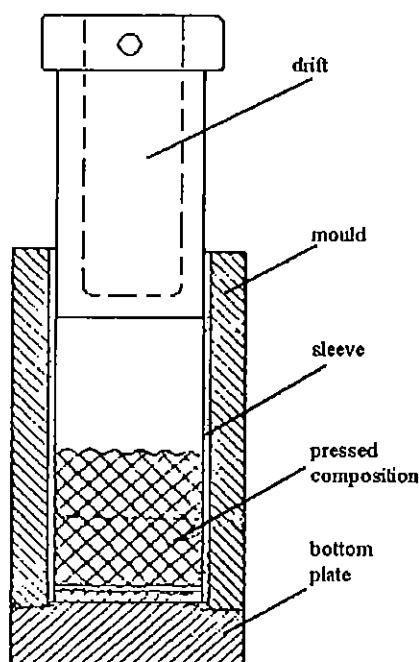


Fig 23.9 Pressing tool

The compacting pressure varies, depending upon the physical properties of the composition, the required rates of combustion, and mechanical strength.

Tracers for artillery projectiles and bullets are compacted under a pressure of up to  $70,000 \text{ Mg m}^{-2}$ , illuminating and signal stars at  $20,000 - 30,000 \text{ Mg m}^{-2}$ , and large products at pressures not exceeding  $10,000 \text{ Mg m}^{-2}$ .

To obtain a more uniform density and to avoid warping the casing, in many cases the compositions are pressed by several methods. For better adhesion between individual portions of the composition, as it is compacted, riffles of the depth needed are made on the drifts. In a case of small products, where the mould is not dismountable, the bottom plate is removed after pressing and the finished products ("stars") drawn out through the lower aperture in the mould.

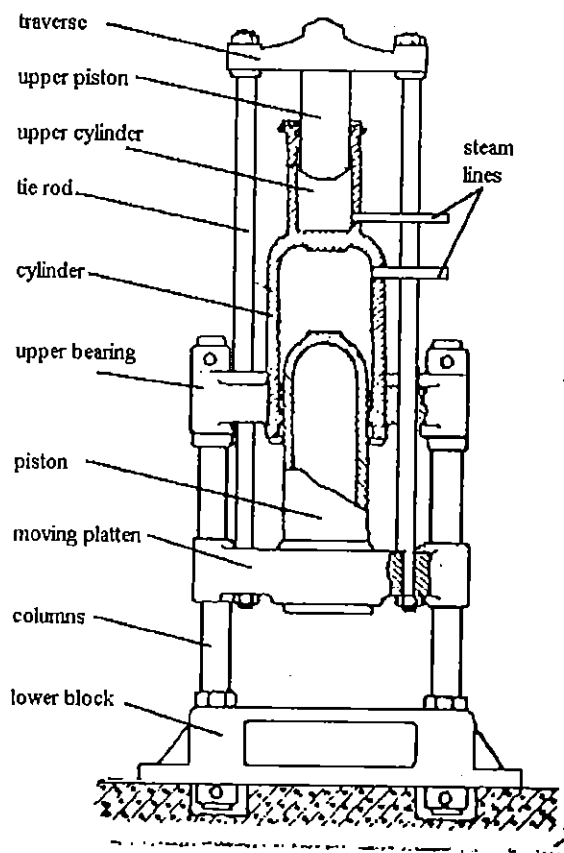


Fig 23.10 Hydraulic press

A hydraulic press (Fig. 23.10) consists of a cylinder fastened to a fixed upper bearing in which a piston with a moving crosspiece moves. Downward working presses have a return mechanism, which return the moving system to the initial position by means of a cylinder and a plunger.

Liquid (water or oil) is injected into the cylinder under high pressure ( $150-200 \text{ atm}$ ), and the piston with the moving bearing descends, forcing the pressing tool with the composition against the base of the press. By releasing the liquid from the cylinder and feeding pressure into the upper cylinder, the moving system is raised upward and the pressed form is released.

In industry, presses with lower pressure are also finding application. Although they have a simpler design, however, they are slow in speed, and inconvenient to service. In these presses the working fluid raises the piston upward, forcing the press tool with the composition against an upper fixed frame. When the fluid is released from the cylinder, the piston, with its plate, is lowered because of its own weight.

A unit capable of pressurising the fluid to high pressure is needed for the operation of hydraulic presses. This unit consists of a hydraulic pump and a hydraulic accumulator. The latter serves to equalise the pressure and flow rate of the fluid.

The capacity of presses is expressed in tons, as the product of the working pressure in the press cylinder multiplied by the area of the cross section of the piston. The capacity of presses used in making pyrotechnics is very diverse - from a few dozen tons to several thousand.

Pressing of pyrotechnic products has the following peculiarities:

1. the pressure is strictly controlled, with a manometer which measures the pressure of the fluid in the working cylinder;
2. a dwell time is used: i.e., a time during which the composition is under pressure;
3. control of the operation of the press is conducted by means of a system of mirrors or television receivers.

Mechanical presses (Fig. 23.11) are used in pyrotechnics production for pressing small products of a fixed height; in this case, it is usual to press into so-called "assemblies". A mechanical press consists of a mounting with an upper fixed bearing, a lower moving bearing, moving up and down, and creating a pressure, a drive, and shock absorbing springs. The motion is transmitted to the bearing by a clamp arm, connected with the flywheel by a connecting rod with a crankshaft. The stroke of the bearing is regulated by changing the distance between the centres of rotation of the arm by means of a control wheel.

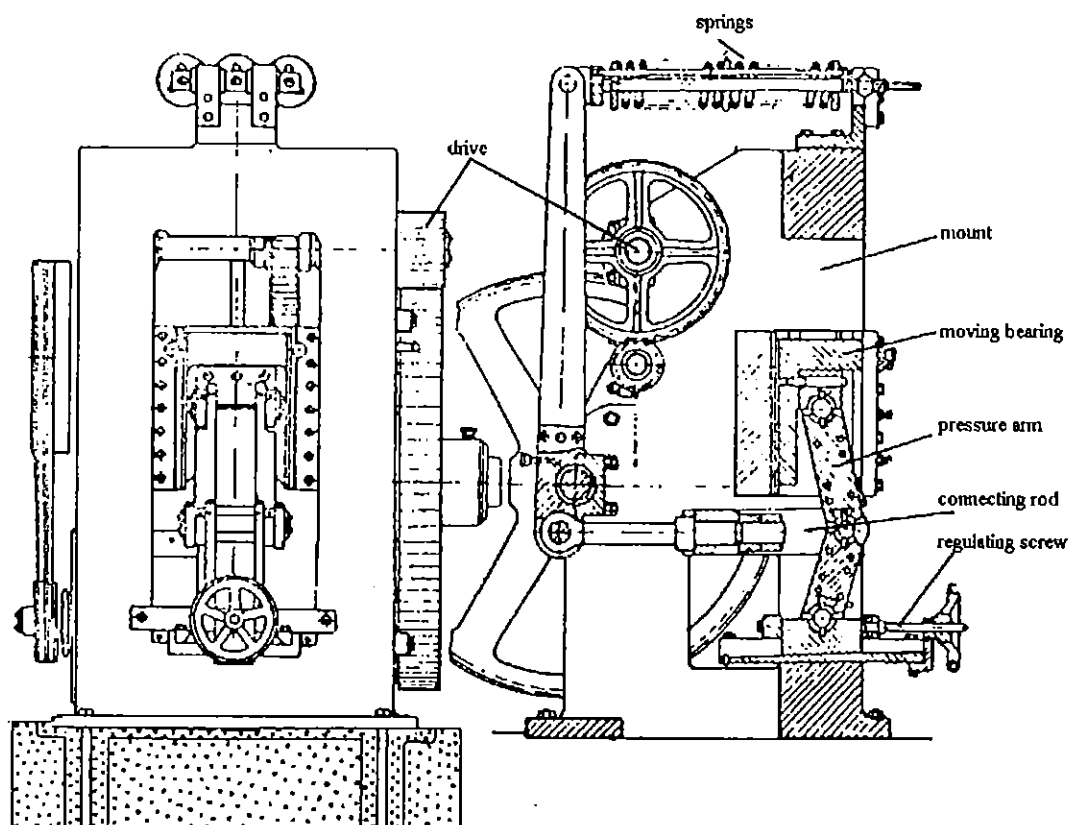


Fig 23.11 Mechanical press

"Assemblies" are several dies (from 4 to 80 pieces), mounted on one plate, and the same number of drifts, also built into a common plate, and having a common bottom plate. An "assembly" with the composition poured in is placed on the moving bearing; when the mechanism is switched on, the compaction is performed in one revolution of the flywheel.

Mechanical presses have considerable advantages over hydraulic presses with respect to the rate of compaction and simplicity of design; however, the limitation in their capacity and stroke, and also the impossibility of keeping the composition under pressure when compacting them on these presses limits their application.

#### **Section 4.     Filling pyrotechnic products**

In the filling phase, all component parts of the products are prepared, they are connected into design units, and the product itself is assembled. The filling of each form of product has its own peculiarity depending upon its overall dimensions and their design.

The filling of pyrotechnic products is usually performed in a common space, on a conveyor or on tables, but a number of bays always adjoin the assembly hall in which the preparatory operations are performed which frequently are dangerous because of the possibility of a fire or explosion.

General preparatory operations for the majority of these products are:

1. preparation of the casings of the products - opening, removal of packing, disassembly of component parts;
2. preparation of ejection charge - weighing out powder, pouring it into bags or celluloid boxes, and gluing them up;
3. packing parachutes - disassembly of canopy and shrouds, necking fastening cable, and packing;
4. preparation of pyrotechnic grains (flares) - cutting -cardboard cases, fastening in the obturators, attaching the parachute, etc.;
5. insertion of cardboard gaskets and fastening parts.

Assembly itself lies in packing all component parts and units into the prepared casing, in the sequence required by the production process and the drawing of the products.

The most important assembling operation in many types of products is insertion of the prepared grain (flare) with its parachute into the casing of the product. The presence of obturators in the pyrotechnic grain, the limitation of volume in the product for the parachute, both require the use of considerable efforts when placing them in the casing.

For this purpose, friction or screw presses are used.

A friction press (Fig. 23.12) consists of two columns connected by a traverse on which the drive mechanism is fastened. A holding screw passes across the traverse, and on its upper end a horizontal friction disc is fastened. By means of a lever, by changing the pressure of the vertical

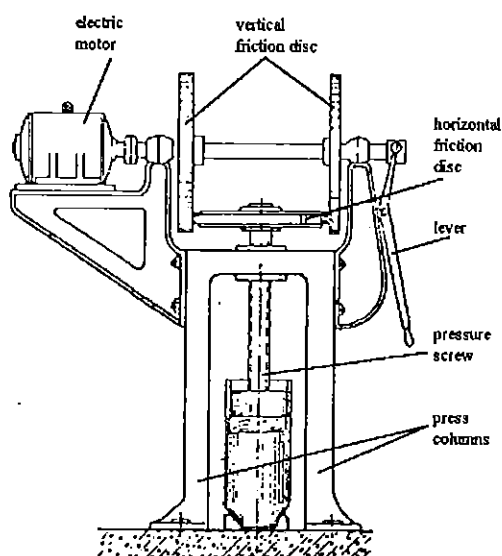


Fig 23.12 Friction press

friction disk, the pressure screw is moved up or down. Automatic switches are used to limit the stroke of the screw, .

The operation of filling the casing is performed in the following manner:

1. the prepared casing, with the knockout charge placed in it, is placed in the socket under the press, and fastened to the upright by a collar;
2. the grain (flare), with the obturators placed on it, is lowered into the casing manually, without force;
3. the connecting cable is fastened to the parachute;
4. the parachute is placed in from above with the auxiliary shrouds first having been stretched;
5. the connecting cable is fastened to the parachute;
6. the parachute is packed into the casing, it is freed from the auxiliary shrouds, and by means of the press the parachute is pressed, together with the flare, until it occupies the volume needed.

After this operation, the tail, or bottom part, is fastened on, and the assembly of the products is finished.

For protection against moisture and to provide for reliability of the products on prolonged storage, the places where the composition is connected with component parts are lacquered, and seams in the casing are coated with a sealing cement, and covered with oil paint or paraffin.

A description of the machines and apparatus considered in this chapter may be found in the literature <sup>295-300</sup>.

### **A Brief Sketch of the History of the Development of Pyrotechnics in Russia**

The art of the creation of fire and controlling it originated in deep antiquity.

Even about a hundred years ago the entire totality of the knowledge and methods needed to prepare powder, explosive mixtures, and various pyrotechnic compositions was understood by the word "pyrotechnics." However, these branches of military engineering have expanded so much that now each of them is an independent branch of knowledge.

It is well known that the first pyrotechnic composition - gunpowder - that came into use was already being produced in Russia in the 15th century in large quantities, and of good quality. In the

reign of Ivan Groznyy (Ivan the Terrible) the gunners and powder makers were already primarily native Russians. In 1563 the artillery or the troops of Ivan Groznyy consisted of 200 guns. At the same time, up to 20,000 poods of powder were produced every year .

In 1607-1621 master gunner Onisim Makhaylov wrote the *Ustav ratnykh pushechnykh i drugikh del kasayushchikhsya do voyennoy nauki* (Regulation of Arms, Guns, and Other Matters Concerning the Art Or War). In these regulations, which were a practical guide for artillerymen, information concerning rockets is also included.

In 1674 in the city of Ustyug a fireworks display was arranged and several rockets and firecrackers were set off.

In the reign of Peter I (Peter the Great) fireworks became an indispensable part of celebrations arranged for any holiday event. Peter I with his own hands made rockets, pin-wheels, and fireworks pictures; he also founded the special "Rocket Institution". By his order, illuminating rockets were used in the army as a means of signalling.

At this same period the Okhtenskiy powder plant was founded in St. Petersburg, and the production of powder was considerably increased.

M.V. Lomonosov (1711-1765), a scientist of genius supplied quite a few outstanding fireworks during the years that he was a member of the Academy of Sciences. An engraving has been preserved illustrating fireworks prepared "according to the invention of state councillor and professor Lomonosov by master fireworks technician Matvey Martynov and shown at Moscow at the New Year celebration in 1754."

Russian fireworks reached their most brilliant and elegant stage in the second half of the 18th century. Facades of fireworks set pieces at that time were made with enormous dimensions: up to 50 sazhen (fathoms), approximately in length and up to 25 sazhen in height.

Literature also helps the development of pyrotechnics. In 1779 M.V. Danilov (1722-1790) published in Moscow a manual "according to which any one may prepare and make fireworks and various illuminations."

In 1824 a book in five parts was published by the pyrotechnist F.S. Cheleyev "with the addition of the preparation of military propellant and incendiary devices".

Beginning in the 1830's, in Russia they began to make coloured flame compositions using Berthollet's salts.

In 1832 a Pyrotechnic Artillery School was established at the Okhtenskiy powder plant, which gave a five-year course. This school taught powder making, military laboratory techniques, and the preparation of fireworks. Rockets with parachutes came to be used, and war rockets were used in launching fireworks.

The outstanding Russian pyrotechnist K.I. Konstantinov (1819-1871) began his work in the 1840's. Starting in 1847 he conducted systematic work on the design and production of war rockets. From 1850 to 1859 he headed the St. Petersburg "rocket institution"; in this period he made a number of serious scientific experiments, and developed several new systems of rockets, which were successfully used in the Crimean War.

K.I. Konstantinov wrote more than 50 scientific works, including the books *O boyevykh raketakh* (On War Rockets), *Boyevyye rakety v Rossii v 1867 g.* (War Rockets in Russia in 1867), and the long article "Improvement of Fireworks."



P.S. Tsytovich  
(1833 - 1894)



S.P. Vukulov  
(1861 - 1940)

The Mikhaylovskaya Artillery Academy, which was founded in 1855 from the officer classes of the artillery academy, in which K.I. Konstantinov also lectured, became the scientific centre of military technical thought. Special pyrotechnical research was also performed there.

In the second half of the 19th century, they began to introduce many new materials into pyrotechnic compositions.

In 1869 an article by A.I. Plestsov entitled "On the Use of Magnesium in Pyrotechnics" appeared in the *Artilleriyskiy zhurnal*, (Artillery Journal).

The same journal contained articles by Captain A. Ordynskiy, F.F. Matyukevich, and P.S. Tsytovich in 1887-1889.

In the 1890's a number of manuals on the preparation of fireworks were published, among the best of which should be considered the exhaustive works of P.S. Tsytovich and F.V. Stepanov.

At the beginning of the 20th century, thermite compositions, which had been discovered and studied as early as 1865 by Academician N.N. Beketov, began to be used in pyrotechnics. S.P.

Vukolov, the closest assistant of D.I. Mendeleyev, worked (after 1907) on the improvement of signalling devices and on the development of the first specimens of tracer projectiles.

As a result of the considerable development of military engineering during World War I, 1914-1918, the Russian army took into its arsenal a number of signalling, illuminating, incendiary, and smoke-forming devices.

The Russian pyrotechnists Yershov, Sannikov, Pogrebnyakov, Artem'yev, and others developed smoke pots, illuminating and thermite incendiary projectiles, and other pyrotechnic ammunition.

A bibliography of the works of Russian pyrotechnists of the 19th century and the beginning of the 20th century is given in the second edition of our book <sup>7 page 275</sup>.

The work of our pyrotechnists in recent years cannot be entirely expounded in such a brief sketch.

We will note only that the efforts of Soviet scientists and engineers created a large quantity of new pyrotechnic compositions and pyrotechnic devices, which were applied during the Great Patriotic War of 1941-1945, and showed their high qualities, that the technology for their manufacture was developed, and new methods created for testing pyrotechnic compositions.



## Appendix 1

Heat of formation of Oxides, Fluorides, Chlorides, and Sulphides of certain elements<sup>98, 94</sup>

| Element | Compound                       | Molecular weight of compound | Heat of formation           |                                                    |                                                     |                                                          |
|---------|--------------------------------|------------------------------|-----------------------------|----------------------------------------------------|-----------------------------------------------------|----------------------------------------------------------|
|         |                                |                              | $\text{kJ mol}^{-1}$<br>(Q) | $\text{kJ g}^{-1}$<br>element<br>(Q <sub>1</sub> ) | $\text{kJ g}^{-1}$<br>compound<br>(Q <sub>2</sub> ) | $\text{kJ g-atom}^{-1}$<br>compound<br>(Q <sub>3</sub> ) |
| Li      | Li <sub>2</sub> O              | 30.0                         | 598.0                       | 43.1                                               | 19.9                                                | 199.3                                                    |
|         | LiF                            | 26.0                         | 610.6                       | 88.0                                               | 23.5                                                | 305.3                                                    |
|         | LiCl                           | 42.0                         | 401.5                       | 57.8                                               | 9.6                                                 | 200.7                                                    |
|         | Li <sub>2</sub> S              | 46.0                         | 468.4                       | 33.7                                               | 10.2                                                | 156.1                                                    |
| Be      | BeO                            | 25.0                         | 593.8                       | 65.9                                               | 23.8                                                | 296.9                                                    |
|         | BeF <sub>2</sub>               | 47.0                         | 1,003.7                     | 111.4                                              | 21.4                                                | 334.6                                                    |
|         | BeCl <sub>2</sub>              | 80.0                         | 510.2                       | 56.6                                               | 6.4                                                 | 170.1                                                    |
|         | BeS                            | 41.0                         | 234.2                       | 26.0                                               | 5.7                                                 | 117.1                                                    |
| Mg      | MgO                            | 40.0                         | 602.2                       | 24.8                                               | 15.1                                                | 301.1                                                    |
|         | MgF <sub>2</sub>               | 62.0                         | 1,104.0                     | 45.4                                               | 17.8                                                | 368.0                                                    |
|         | MgCl <sub>2</sub>              | 95.0                         | 639.8                       | 26.3                                               | 6.7                                                 | 213.3                                                    |
|         | MgS                            | 56.0                         | 351.3                       | 14.5                                               | 6.3                                                 | 175.6                                                    |
| Al      | Al <sub>2</sub> O <sub>3</sub> | 102.0                        | 1,672.8                     | 31.0                                               | 16.4                                                | 334.6                                                    |
|         | AlF <sub>3</sub>               | 84.0                         | 1,375.9                     | 51.0                                               | 16.4                                                | 344.0                                                    |
|         | AlCl <sub>3</sub>              | 136.0                        | 698.4                       | 25.9                                               | 5.1                                                 | 174.6                                                    |
|         | Al <sub>2</sub> S <sub>3</sub> | 150.0                        | 585.5                       | 10.8                                               | 3.9                                                 | 117.1                                                    |
| Ca      | CaO                            | 56.0                         | 635.7                       | 15.9                                               | 11.4                                                | 317.8                                                    |
|         | CaF <sub>2</sub>               | 78.0                         | 1,212.8                     | 30.2                                               | 15.5                                                | 404.3                                                    |
|         | CaCl <sub>2</sub>              | 111.0                        | 786.2                       | 19.6                                               | 7.1                                                 | 262.1                                                    |
|         | CaS                            | 72.0                         | 480.9                       | 12.0                                               | 6.7                                                 | 240.5                                                    |
| Ti      | TiO <sub>2</sub>               | 80.0                         | 936.8                       | 19.6                                               | 11.7                                                | 312.3                                                    |
|         | TiF <sub>4</sub>               | 124.0                        | 1,639.3                     | 34.2                                               | 13.2                                                | 327.9                                                    |
|         | TiCl <sub>4</sub>              | 190.0                        | 819.7                       | 17.1                                               | 4.3                                                 | 163.9                                                    |
|         | TiS <sub>2</sub>               | 112.0                        | 334.6                       | 7.0                                                | 3.0                                                 | 111.5                                                    |
| Zr      | ZrO <sub>2</sub>               | 123.0                        | 1,087.3                     | 11.9                                               | 8.8                                                 | 362.4                                                    |
|         | ZrF <sub>4</sub>               | 167.0                        | 1,861.0                     | 20.4                                               | 11.1                                                | 372.2                                                    |
|         | ZrCl <sub>4</sub>              | 233.0                        | 970.2                       | 10.6                                               | 4.2                                                 | 194.0                                                    |
|         | ZrS <sub>2</sub>               | 155.0                        | 618.9                       | 6.8                                                | 4.0                                                 | 206.3                                                    |

| Element | Compound                      | Molecular weight of compound | Heat of formation               |                                            |                                             |                                                  |
|---------|-------------------------------|------------------------------|---------------------------------|--------------------------------------------|---------------------------------------------|--------------------------------------------------|
|         |                               |                              | $\text{kJ mol}^{-1}$<br>( $Q$ ) | $\text{kJ g}^{-1}$<br>element<br>( $Q_1$ ) | $\text{kJ g}^{-1}$<br>compound<br>( $Q_2$ ) | $\text{kJ g-atom}^{-1}$<br>compound<br>( $Q_3$ ) |
| H       | H <sub>2</sub> O (liq)        | 18.0                         | 284.4                           | 141.1                                      | 15.8                                        | 94.8                                             |
|         | HF                            | 20.0                         | 267.6                           | 265.5                                      | 13.4                                        | 133.8                                            |
|         | HCl                           | 36.0                         | 92.0                            | 91.3                                       | 2.6                                         | 46.0                                             |
|         | H <sub>2</sub> S              | 34.0                         | 20.9                            | 10.4                                       | 0.6                                         | 7.0                                              |
| C       | CO <sub>2</sub>               | 44.0                         | 393.1                           | 32.7                                       | 8.9                                         | 131.0                                            |
|         | CF <sub>4</sub>               | 88.0                         | 690.0                           | 57.5                                       | 7.8                                         | 138.0                                            |
|         | CCl <sub>4</sub>              | 154.0                        | 104.6                           | 8.7                                        | 0.7                                         | 20.9                                             |
|         | CS <sub>2</sub>               | 70.0                         | -87.8                           | -7.3                                       | -1.3                                        | -29.3                                            |
| B       | B <sub>2</sub> O <sub>3</sub> | 70.0                         | 1,263.0                         | 58.5                                       | 18.0                                        | 252.6                                            |
|         | BF <sub>3</sub>               | 68.0                         | 1,129.1                         | 104.6                                      | 16.6                                        | 282.3                                            |
|         | BCl <sub>3</sub>              | 117.0                        | 430.7                           | 39.9                                       | 3.7                                         | 107.7                                            |
|         | B <sub>2</sub> S <sub>3</sub> | 118.0                        | 238.4                           | 11.0                                       | 2.0                                         | 47.7                                             |
| Si      | SiO <sub>2</sub>              | 60.0                         | 869.9                           | 31.0                                       | 14.5                                        | 290.0                                            |
|         | SiF <sub>4</sub>              | 104.0                        | 1,505.5                         | 53.6                                       | 14.5                                        | 301.1                                            |
|         | SiCl <sub>4</sub>             | 170.0                        | 627.3                           | 22.3                                       | 3.7                                         | 125.5                                            |
|         | SiS <sub>2</sub>              | 92.0                         | 142.2                           | 5.1                                        | 1.5                                         | 47.4                                             |
| P       | P <sub>2</sub> O <sub>5</sub> | 142.0                        | 1,534.8                         | 24.8                                       | 10.8                                        |                                                  |
|         | PF <sub>3</sub>               | 88.0                         | -                               | -                                          | -                                           | -                                                |
|         | PCl <sub>3</sub>              | 137.0                        | 330.4                           | 10.7                                       | 2.4                                         | 82.6                                             |
|         | P <sub>2</sub> S <sub>5</sub> | 222.0                        | 250.9                           | 4.1                                        | 1.1                                         | 35.8                                             |
| Na      | Na <sub>2</sub> O             | 62.0                         | 414.0                           | 9.0                                        | 6.7                                         | 138.0                                            |
|         | NaF                           | 42.0                         | 568.8                           | 24.7                                       | 13.5                                        | 284.4                                            |
|         | NaCl                          | 58.0                         | 409.8                           | 17.8                                       | 7.1                                         | 204.9                                            |
|         | Na <sub>2</sub> S             | 78.0                         | 363.8                           | 7.9                                        | 4.7                                         | 121.3                                            |
| Zn      | ZnO                           | 81.0                         | 347.1                           | 5.3                                        | 4.3                                         | 173.6                                            |
|         | ZnF <sub>2</sub>              | 103.0                        | 748.6                           | 11.4                                       | 7.3                                         | 249.5                                            |
|         | ZnCl <sub>2</sub>             | 136.0                        | 418.2                           | 6.4                                        | 3.1                                         | 139.4                                            |
|         | ZnS                           | 97.0                         | 200.7                           | 3.1                                        | 2.1                                         | 100.4                                            |

| Element | Compound          | Molecular weight of compound | Heat of formation           |                                                    |                                                     |                                                          |
|---------|-------------------|------------------------------|-----------------------------|----------------------------------------------------|-----------------------------------------------------|----------------------------------------------------------|
|         |                   |                              | $\text{kJ mol}^{-1}$<br>(Q) | $\text{kJ g}^{-1}$<br>element<br>(Q <sub>1</sub> ) | $\text{kJ g}^{-1}$<br>compound<br>(Q <sub>2</sub> ) | $\text{kJ g-atom}^{-1}$<br>compound<br>(Q <sub>3</sub> ) |
| Cu      | CuO               | 80.0                         | 158.9                       | 2.5                                                | 2.0                                                 | 79.5                                                     |
|         | CuF <sub>2</sub>  | 102.0                        | 543.7                       | 8.6                                                | 5.3                                                 | 181.2                                                    |
|         | CuCl <sub>2</sub> | 134.0                        | 217.5                       | 3.4                                                | 1.6                                                 | 72.5                                                     |
|         | CuS               | 96.0                         | 50.2                        | 0.8                                                | 0.5                                                 | 25.1                                                     |
| Pb      | PbO               | 223.0                        | 217.5                       | 1.0                                                | 1.0                                                 | 108.7                                                    |
|         | PbF <sub>2</sub>  | 245.0                        | 669.1                       | 3.2                                                | 2.7                                                 | 223.0                                                    |
|         | PbCl <sub>2</sub> | 278.0                        | 359.7                       | 1.7                                                | 1.3                                                 | 119.9                                                    |
|         | PbS               | 239.0                        | 92.0                        | 0.4                                                | 0.4                                                 | 46.0                                                     |
| Hg      | HgO               | 217.0                        | 87.8                        | 0.4                                                | 0.4                                                 | 43.9                                                     |
|         | HgF <sub>2</sub>  | 239.0                        | 418.2                       | 2.1                                                | 1.7                                                 | 139.4                                                    |
|         | HgCl <sub>2</sub> | 271.0                        | 225.8                       | 1.1                                                | 0.8                                                 | 75.3                                                     |
|         | HgS               | 233.0                        | 66.9                        | 0.3                                                | 0.3                                                 | 33.5                                                     |

## **Appendix 2**

### **Recipes of delay compositions according to Ellern<sup>9</sup>**

#### **Recipes with Zr/Ni alloy.**

|                    |     |
|--------------------|-----|
| Zr/Ni alloy        | 54% |
| BaCrO <sub>4</sub> | 31% |
| KClO <sub>4</sub>  | 15% |

The combustion times of these compositions are in the ratio 1:2:3 when the alloys contain 70%, 50%, or 30% Zr respectively. The ratio of the oxidisers may also vary.

#### **Recipes with amorphous boron.**

|                      |       |
|----------------------|-------|
| B/BaCrO <sub>4</sub> | 5/95  |
| B/BaCrO <sub>4</sub> | 10/90 |

The combustion times are given as 1 sec/cm and 0.2 sec/cm respectively.

#### **Recipes with metallic manganese.**

|                    |      |      |      |
|--------------------|------|------|------|
| Mn                 | 44.0 | 37.0 | 33.0 |
| BaCrO <sub>4</sub> | 3.0  | 20.0 | 31.0 |
| PbCrO <sub>4</sub> | 53.0 | 43.0 | 36.0 |

The combustion times of these compositions are 1.5, 3, and 5 sec/cm respectively.

#### **"Exotic" delay compositions.**

|                    |      |      |      |      |      |
|--------------------|------|------|------|------|------|
| niobium            | 15.0 | 18.0 | 50.0 |      |      |
| tantalum           |      |      |      | 29.0 | 50.0 |
| BaCrO <sub>4</sub> | 85.0 | 82.0 | 50.0 | 71.0 | 50.0 |

Experimental compositions are being developed in the USA, particularly of "gasless" mixtures.

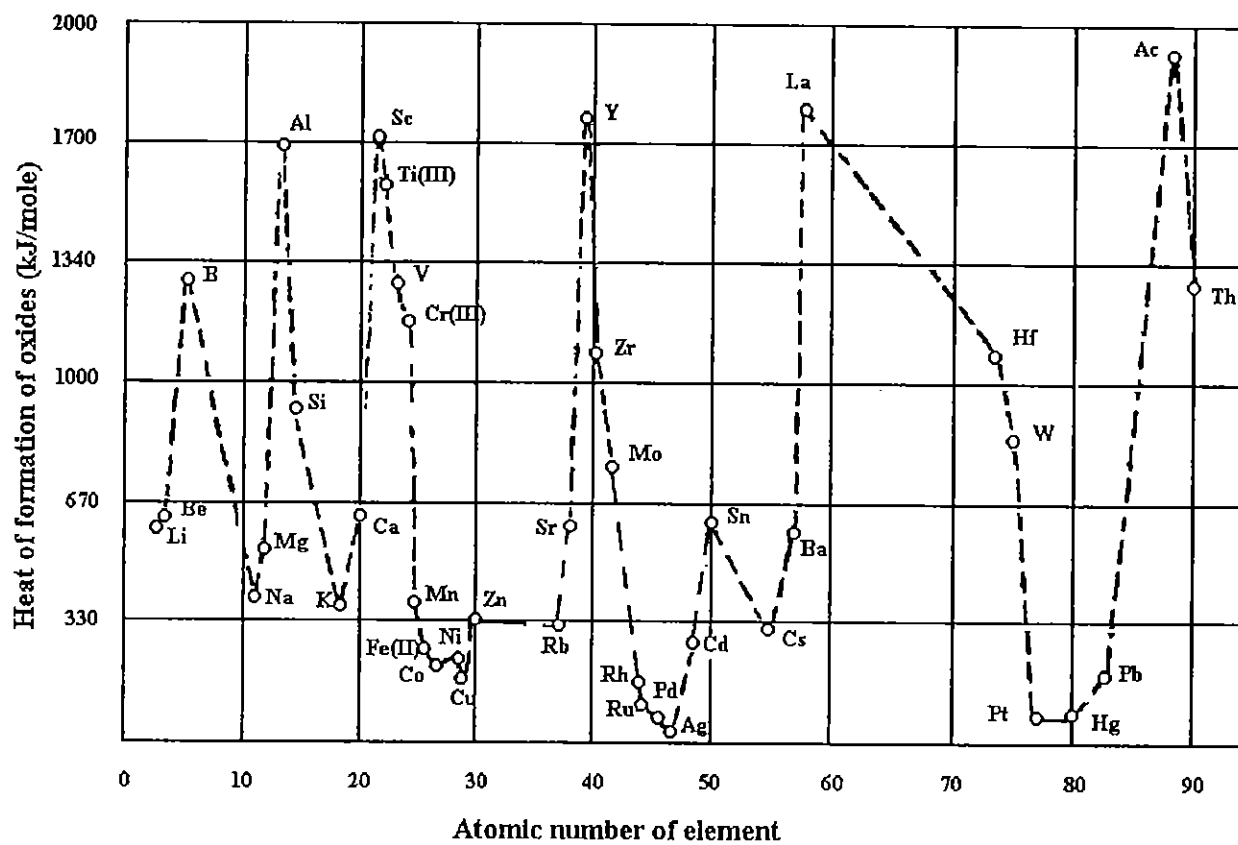
### Appendix 3

Average values of the air pressure and temperature at different elevations at mid latitudes.

| Elevation<br>above sea<br>level<br>(km) | Pressure<br>(mmHg) | Temperature<br>(°C) | Elevation<br>above sea<br>level<br>(km) | Pressure<br>(mmHg)   | Temperature<br>(°C) |
|-----------------------------------------|--------------------|---------------------|-----------------------------------------|----------------------|---------------------|
| 0                                       | 760.0              |                     | 30                                      | 10                   | -41                 |
| 2                                       | 608.0              | +5                  | 40                                      | 2                    | -11                 |
| 4                                       | 486.0              | -6                  | 50                                      | $7.6 \times 10^{-1}$ | -2                  |
| 6                                       | 372.0              | -20                 | 60                                      | $2.2 \times 10^{-1}$ | -20                 |
| 8                                       | 281.0              | -35                 | 70                                      | $5.5 \times 10^{-2}$ | -55                 |
| 10                                      | 205.0              | -48                 | 80                                      | $1.1 \times 10^{-2}$ | -68                 |
| 12                                      | 152.0              | -50                 | 90                                      | $2.0 \times 10^{-3}$ | -54                 |
| 14                                      | 114.0              | -50                 | 100                                     | $6.0 \times 10^{-3}$ | -33                 |
| 20                                      | 42.0               | -60                 |                                         |                      |                     |

## Appendix 4

Heat of formation of oxides as a function of the atomic number of the elements





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