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Military Pyrotechnics

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Abstract: Phenomena such as varied light emissions, sound, burning rates, heats of reaction and reaction products occur during inorganic redox reactions. The peculiarity of these redox reactions is that they take place as solid–solid, solid–liquid or solid–gas state reactions and not as redox reactions in a solvent as normally postulated in inorganic chemistry. By variation of different parameters such as the reducing agent, the oxidizer, the oxygen balance or the particle size, it is possible to create a wide range of the above-mentioned effects.

Keywords: Heat of reaction · Inorganic redox reaction · Military pyrotechnics · Reaction rate · Particle size

1. Introduction

This paper is a general review about military pyrotechnics. The expression 'pyrotechnics' comes from the Greek words '**pyros**' and '**techne**' [1]:

PYROS → **Fire, heat**
TECHNE → **Art**

Pyrotechnics is one of three closely related subjects: high explosives, propellants and pyrotechnics itself. These three subjects not only have a common physicochemical background, their functions and purposes also overlap. An excellent representative for this statement is black powder. In their typical manifestations, *explosives* perform at the highest reaction speed, leaving gaseous products. *Propellants* produce gas at a moderate rate and *pyrotechnic compositions* react mostly at visibly observable rates, producing solid and liquid reaction products as well as gases.

The first recorded military use of pyrotechnic compositions is from 1480 BC. A priestess of the Egyptian world empire sent out servants to procure large amounts of incense. This incense was used in pyrotechnic compositions to produce colored smoke as well as pleasantly smelling or toxic gases. During the Peloponnesian War military pyrotechnics were used on a large scale to destroy towns under siege. The pyrotechnic compositions used consisted of sulfur, wood spun, pitch and incense. This information is mentioned in a book on strategy written by 'Ainais the Tactician' in 360 BC. During the war between Byzantium (Eastern Roman Empire) and the Arabians and Bulgarians, the besieged East Romans attacked the Arabian fleet using a pyrotechnic composition called 'Greek Fire' [2]. This consisted of sulfur, oil products and burnt lime. When it came into contact with water, the burnt lime produced so much heat that the composition started to burn. However, it must be assumed that the Chinese also started to use pyrotechnics for military applications a long time ago. They already had a long experience in producing gorgeous civilian fireworks. Between 1250 and 1280 AC, European monks started to experiment with compositions containing sulfur, charcoal and potassium nitrate [3]. The so-called 'black powder' was invented. It seems that the monks obtained some information concerning such compositions from Dutch sailors who brought it back from China. However, the wide use of pyrotechnics for military purpose only became wide spread in the last century. Before the 1970s, military pyrotechnics was very often based on alchemy and not on science. By the end of the 20th century pyrotechnics had slowly become an applied science.

In general, chemical reactions either require heat input during the whole process (endothermic reactions) or they produce heat (exothermic reactions). The heat production may be insufficient to cause a self-sustaining reaction. If the reaction produces flame or glow throughout the composition either at high reaction speed or gradually, it is suitable for pyrotechnic purposes. A pyrotechnic process differs from ordinary combustion by not requiring the presence of ambient air [2]. The exothermic reactions used in pyrotechnics are based on simple chemical redox reactions. For a long time, experience was the fundamental base of pyrotechnics. By clever choice of reducing agents and oxidizers as well as variation of the compositions, the redox reaction can be influenced to obtain the desired, well-defined effects. In pyrotechnics the expression 'effect' includes:

- Reaction rate
- Heat of reaction
- Reaction temperature
- Gas production
- Reaction products/glowing particles
- Colored light

2. Principals of Pyrotechnics

Pyrotechnic Reaction

The basis of a pyrotechnic reaction can be displayed generally as follows:

REDUCING AGENT [1] + OXIDIZER [2]
↓
REDOX REACTION
↓
OXIDIZER [1] + REDUCING AGENT [2]

During the redox reaction, the reducing agent (fuel) is oxidized and the oxidizer is reduced. The pyrotechnic reaction is mostly a solid–solid, solid–liquid or solid–gas state reaction. To predict the reaction behavior of a pyrotechnic composition, it is not or only partly possible to apply inorganic chemistry theory which is based on chemical redox reactions in solutions. Pyrotechnic reactions are high-temperature redox reactions. They take place in a tem-

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Table 1. Physicochemical data of the most important reducing agents used in pyrotechnics

Substance	MG	Density [g/cm^3]	MP[a] [°C]	BP[b] [°C]
Zr	91.22	6.52	1530	2900
Ni	58.71	8.90	1455	3177
Mg	24.32	1.74	650	1102
Ti	47.90	4.50	1727	3000
W	183.9	19.32	3380	6000
B	10.82	1.73	2050	2550
Si	28.09	2.33	1440	2630
C	12.01	2.25	subl. 4350	–
S	32.06	2.07	112.8	444.6
P	30.97	2.2	590 (43 atm)	–

[a] Melting point
[b] Boiling point

Table 2. Physicochemical data of the most important oxidizers used in pyrotechnics

Formula	MG	Density [g/cm^3]	MP [°C]	BP [°C]
KNO_3	101.11	2.109	339	dec. 400
$BaNO_3$	261.38	3.24	592	–
$NaNO_3$	85.00	2.257	312	–
$KClO_4$	138.65	2.52	dec. 610	–
BaO_2	169.36	4.96	450	diss. 795
PbO_2	239.21	9.375	dec. 290	–
Pb_3O_4	685.63	9.1	dec. 500	–
$BaCrO_4$	253.37	4.498	–	–
$PbCrO_4$	323.22	6.12	844	–
$CaCrO_4$	192.09	–	–	–

perature range of 1500–4000°C. Due to this fact also the reaction products of a pyrotechnic redox reaction are in most cases not the same as expected according classical chemistry theory.

3. Chemicals

To produce pyrotechnic compositions, it is important to use well-defined chemical products. The following important parameters for chemicals used in pyrotechnics must be known:

- Purity
- Particle size
- Particle shape
- Particle surface
- Crystal structure
- Water content

3.1. *Reducing Agents (Fuels)*

There are several types of reducing agents with different reactivities available, *e.g.* zirconium, titanium, silicon and boron. The physicochemical data [4] of some reducing agents used in military pyrotechnics are listed in Table 1.

Today very often alloys of zirconium and nickel containing 70% zirconium and 30% nickel, 50% zirconium and 50% nickel or 30% zirconium and 70% nickel are used as fuels.

3.2. *Oxidizers*

Table 2 shows the physicochemical data of oxidizers [4] often used in pyrotechnic compositions. Oxidizers such as nitrates, perchlorates and peroxides of barium, strontium, and lithium are also used as auxiliary substances. Depending on their emission spectra, they produce colored light during the redox reaction [5][6].

3.3. *Additional Substances*

Most pyrotechnic compositions are mixtures consisting of very fine powders. To produce granules it is necessary to add binders. Different types of binders are in use:

- Natural products (*e.g.* acaroids resin, Arabian rubber)
- Semi synthetic products (*e.g.* cellulose nitrate, dextrin)
- Synthetic products (*e.g.* polyvinyl chloride (PVC), polynitropolyphenylene (PNP), poly glyn, poly nimmo and other polymers.

Additional pyrotechnic compositions contain auxiliary supplies. Due to the large variety of auxiliary supplies it is not possible to present a detailed overview in this paper. To produce different colored light emissions, it is necessary to have auxiliary substances in a pyrotechnic composition. Very often such substances have a double function, they act on one hand as an oxidizer and on the other hand they are responsible for producing colored light during the redox reaction. Some famous emitters of colored light are the oxides or nitrates of sodium, potassium, barium, copper and strontium [7] (see also Pyrotechnics in Fireworks [8]).

4. Preparation of Pyrotechnic Compositions

The mixing and granulating process is an important procedure during the manufacture of pyrotechnic compositions. The fuel and the oxidizer must be in a close contact with each other. Usually the reducing agent and oxidizer are mixed repeatedly in a Turbula mixer alternating with passing the mixture through sieves with defined meshes. After mixing, the fine powder has to be granulated by adding a dissolved binder. The formed dough is then passed through sieves with adequate mesh sizes to obtain well-defined granules.

5. Parameters Influencing the Pyrotechnic Redox Reaction

Some of the most important parameters that influence the pyrotechnic performance of a chemical redox reaction are:

- Type of chemical
- Oxygen balance
- Particle size/active surface
- Binder
- Mixing process

5.1. *Type of Chemical*

The influence of the chosen substances can be demonstrated with the heat of reaction (ΔH_R) of compositions containing various oxidizers and boron or zirconium as reducing agent [9]. Fig. 1 presents the maximum measured values of the heats of reaction of pyrotechnic redox systems. These systems contain boron as a reducing agent and potassium perchlorate, potassium nitrate, strontium peroxide, barium nitrate, and lead III,IV oxide as an oxidizer. Because of the different enthalpies of formation, a change of the oxidizer in compositions containing boron as reducing agent results in heats of reaction between 7330 J/g (B/KNO_3) and 1360 J/g (B/Pb_3O_4). Using

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zirconium instead of boron as reducing agent, the measured heats of reaction are found between 4470 J/g (Zr/KNO_3) and 1710 J/g (Zr/Pb_3O_4). A comparison of the maximum heats of reaction of different pyrotechnic redox systems containing the reducing agent zirconium is plotted in Fig. 2.

Fig. 3 and 4 show the influence of the reducing agents boron and zirconium mixed with various oxidizers on the maximum measured reaction rates. These reaction rates vary in a range of some mm/s to about 290 m/s. It has to be mentioned that reaction rate data presented in this paper are measured values. They depend on the experimental set up. Therefore it is important that the experimental set up is well defined.

5.2. *Particle Size and Specific Surface of Particles*

The particle size and the specific surface also influences significantly the reaction rate of pyrotechnic compositions. In Fig. 5 this effect is demonstrated as an example with different reaction rates of the redox system titanium/potassium perchlorate [10]. As already mentioned the reaction is influenced by the type of reducing agent as well as the particle size and its active surface. Depending on the reducing agent, a decrease of the mean particle size by a factor two leads to an increase of the reaction rate by a factor four to five. This can be seen in Fig. 5. The reason for this effect is that a decrease of the particle size results in an increase of the specific surface of the reducing agent. In the case of the investigated titanium powder, the decrease of the medium particle size by a factor two leads to an increase of the specific surface by a factor three.

The particle size and the specific surface respectively influences strongly the kinetic of a redox reaction. However, the particle size of a reducing agent does not influence the heat of reaction (Fig. 6).

5.3. *Oxygen Balance*

Very important parameters of a pyrotechnic composition are the reaction rate and the heat of reaction. By varying the oxygen balance of a pyrotechnic redox system, it is possible to vary the heat of reaction and the reaction rate in a wide range [11]. It is assumed and can be demonstrated by experiments that the composition of a pyrotechnic system with an equalized oxygen balance shows the highest heat of reaction, but not the highest reaction rate. This is because pyrotechnic reactions are usually solid–solid state reactions. Fig. 7 and 8 show, as an example for this statement, the measured heats of reaction and the reaction rates respectively of compositions of the redox system zirconium nickel alloy 50:50/potassium perchlorate. Compositions showing positive and negative oxygen balances as well as the composition with equalized oxygen balance were investigated.

5.4. *Binder and Binder Content*

The type of binder as well as the content of binder in pyrotechnic compositions influences the two main parameters of redox reactions used in pyrotechnics. However, the influence of the binder on the heat of reaction is much smaller than on the reaction rate. The influence of different binder contents on the reaction rate and on the heat of reaction is demonstrated as an

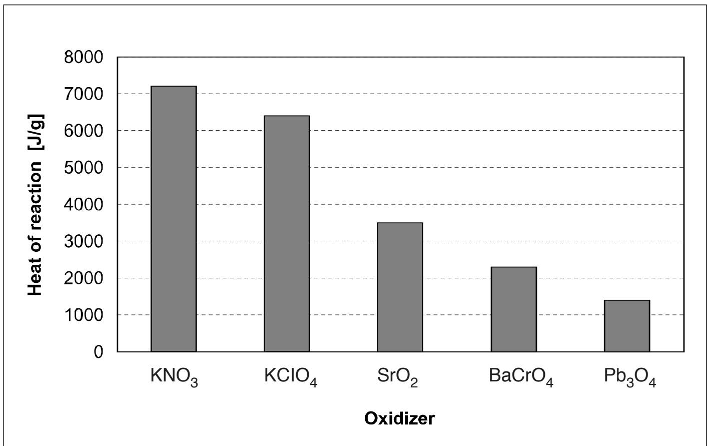


Fig. 1. Measured maximum heats of reaction of pyrotechnic compositions containing boron and different oxidizers [6]

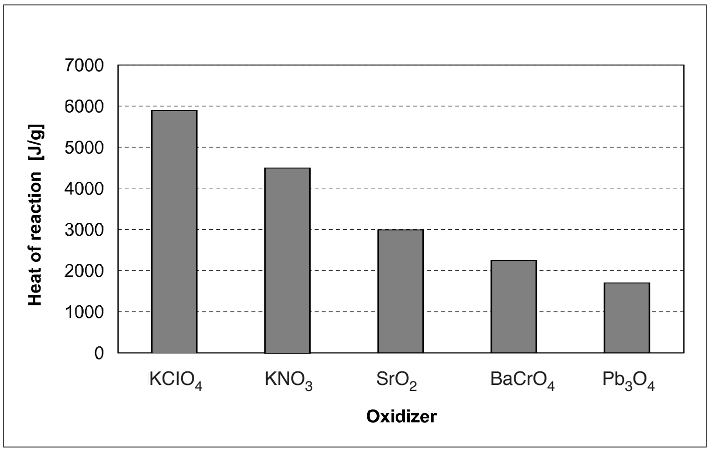


Fig. 2. Measured maximum heats of reaction of pyrotechnic compositions containing zirconium and different oxidizers [6]

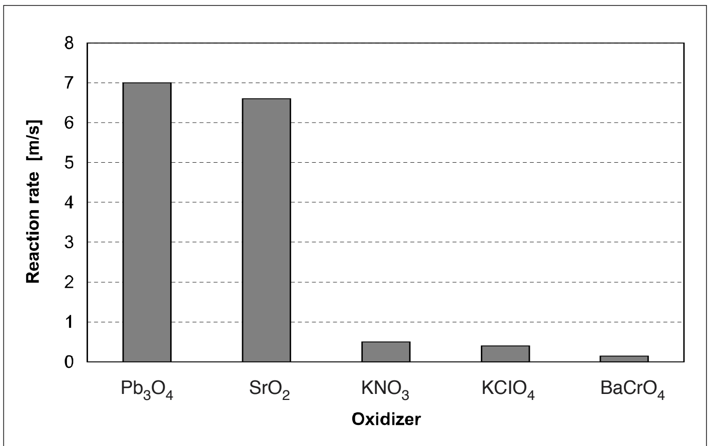


Fig. 3. Measured maximum reaction rates of pyrotechnic compositions containing boron and different oxidizers [6]

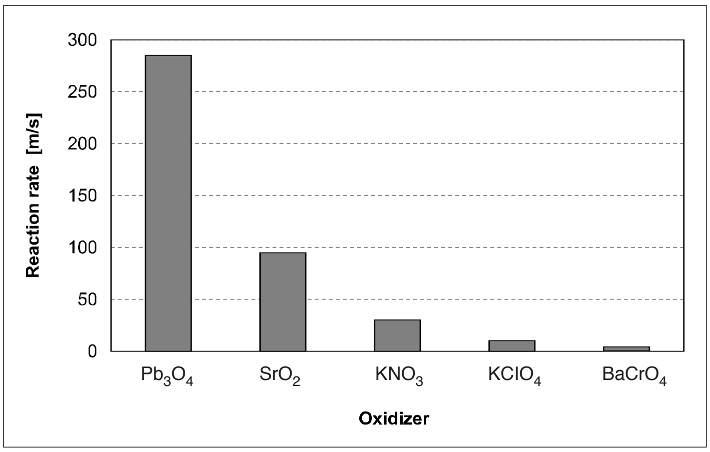


Fig. 4. Measured maximum reaction rates of pyrotechnic compositions containing zirconium and different oxidizers [6]

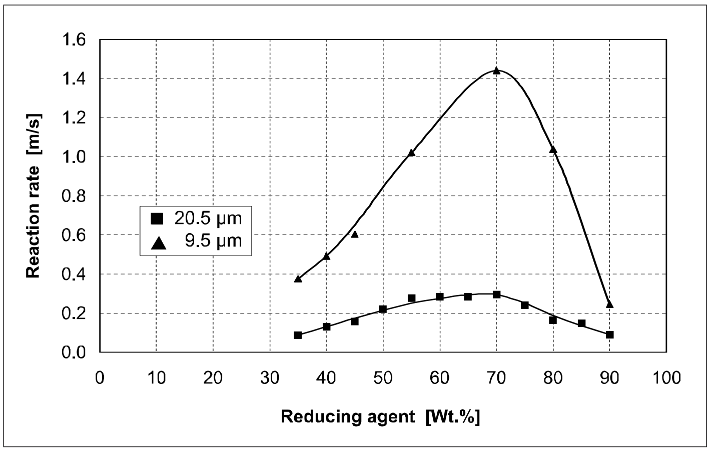


Fig. 5. Reaction rates of the redox system titanium/potassium perchlorate using different particle sizes of titanium [9]

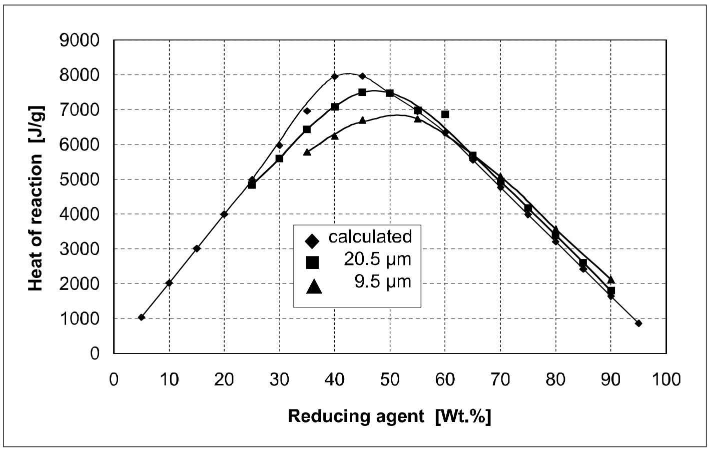


Fig. 6. Heats of reaction of the redox system titanium/potassium perchlorate using different particle sizes of titanium [9]

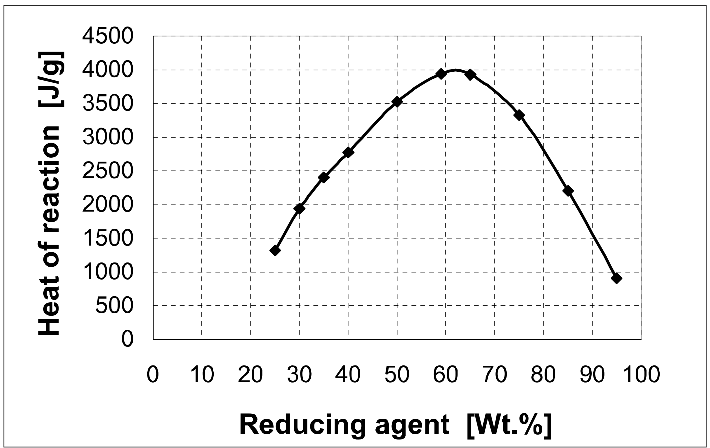


Fig. 7. Heats of reaction of compositions based on the redox system zirconium nickel alloy 50:50 with different oxygen balances

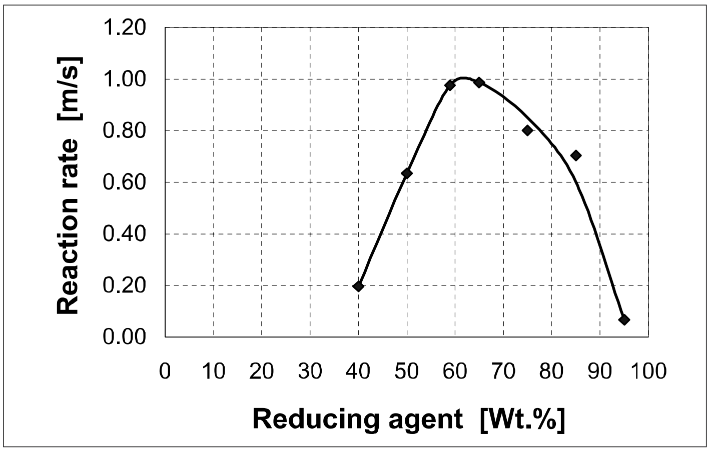


Fig. 8. Reaction rates of compositions based on the redox system zirconium nickel alloy 50:50 with different oxygen balances

example with the pyrotechnic system titanium/potassium perchlorate, using polynitropolyphenylene as an energetic binder [12]. Fig. 9 and 10 show the measured data.

5.5. *Mixing Process*

The secret of maximizing the rate of reaction for a given pyrotechnic composition can be revealed in a single word – homogeneity [13]. Because of cost savings, pyrotechnic compositions are often mixed in a dry state, passing the composition several times through a sieve with defined mesh size. Due to the fact that a lot of pyrotechnic reactions are solid–solid state reactions, any operation that increases the degree of closeness of participating particles of a high-energy mixture results in an enhancement of reactivity. Reactivity, in general, refers to the rate – in grams or moles per second – at which starting materials are converted into products.

Fig. 11 and 12 show very clearly the differences of a bad and a good mixing process with a composition containing boron and barium chromate [14]. As can be seen many compositions are not in an ideal state of mixing.

6. Thermal Behavior of Pyrotechnic Compositions

The knowledge of the thermal behavior, the stability and the compatibility of pyrotechnic compositions is very important for safety and shelf life assessment. To investigate these important parameters, differential scanning calorimetry (DSC), differential thermal analysis (DTA), thermal gravimetry analysis (TGA) coupled with mass spectrometry (MS) [15][16] and heat flow calorimetry [(HFC)] are used. Fig. 13 shows the thermal behavior of a commonly used igniter composition for rocket propellant based on boron and potassium nitrate. At a temperature of about 137 °C the first endothermal process can be observed due to a crystal state change of potassium nitrate. At the second endothermal peak at 334 °C potassium nitrate melts and finally at a peak temperature of about 564 °C the exothermal redox reaction takes place.

7. Military and Civilian Use of Pyrotechnic Compositions

The following section gives an overview of the use of pyrotechnic redox systems in ammunition and in safety devices of cars.

7.1. *Igniters and Initiators*

The function of ***igniters*** is to induce combustion, which can be more or less fast. Examples of igniter compositions:
- Boron/potassium nitrate/binder
- Sulfur/charcoal/potassium nitrate (black powder)

The task of ***initiators*** is to induce a detonation. Initiators contain small amounts of primary explosives.
Example of an initiator composition:
- Tetrazene/antimony trisulfide/quartz powder/lead azide

7.2. *Timing Devices*

The task of time delay compositions is to initiate a process after a well-defined time. The process can be a detonation, the ignition of another pyrotechnic composition or the actuation of a switch. The reaction rates of time delay compositions can be found within a wide range. Some compositions show reaction rates of about 300 m/s (zirconium/lead-II, IV-oxide), others react at a rate of 0.1 m/s (boron/barium chromate).

7.3. *Camouflage and Delusion Devices*

Pyrotechnic camouflage compositions are used to produce fog and smoke. The reaction products of pyrotechnic fog compositions are hygroscopic particles which react together with the humidity in the air to form fog.
Examples of camouflage compositions:
- Red phosphorus/potassium nitrate/binder
- Zinc oxide/ammonium chloride/ammonium perchlorate/PVC

Pyrotechnic delusion compositions are used to protect aircrafts against ground-to-air and air-to-air heat-seeking missiles.
Example of an often used delusion composition:
- Magnesium/Teflon/Viton

7.4. *Illumination and Tracer Devices*

Illumination and tracer compositions contain special metals or metal salts which produce colored light emission. Such compositions are used as tracers in ammunition for rifles, in grenades to illuminate the battle field and in signaling ammunition.
Example of an illumination composition:
- Magnesium/sodium nitrate/binder

Example of a tracer composition:
- Magnesium/strontium peroxide/strontium nitrate/binder

7.5. *Incendiary Devices*

Incendiary compositions are pyrotechnic mixtures producing a large amount of heat.
Examples of incendiary compositions:
- Napalm (fuel/organic aluminum component)
- Coruscatives (Metals which react after ignition to alloy)
- Thermites (Reaction between metal and metal oxide)

7.6. *Gas Production Devices*

Missiles often use switches based on a pyrotechnic system producing gas as a reaction product. A civilian use of this effect is the air bag in cars. In this case the production of non-toxic gases in a very short time is used to save the life of car passengers in the event of an accident. The first generation of gas generators for air bags was based on cellulose nitrate, the second generation was mostly based on sodium azide and today the third generation is based on high explosives. In all cases pyrotechnic compositions are also responsible for igniting the gas-producing component very quickly.

8. Aging of Pyrotechnics

Manufacturers of pyrotechnic components normally give a lifetime guarantee of five to seven years. The following parameters influence the aging of pyrotechnic compositions:
- Humidity
- Temperature
- Time

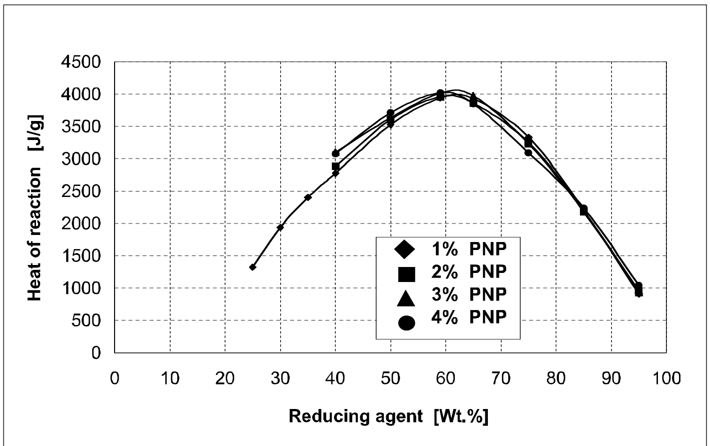


Fig. 9. Heats of reaction of compositions of the redox system titanium/potassium perchlorate with different binder content [10]

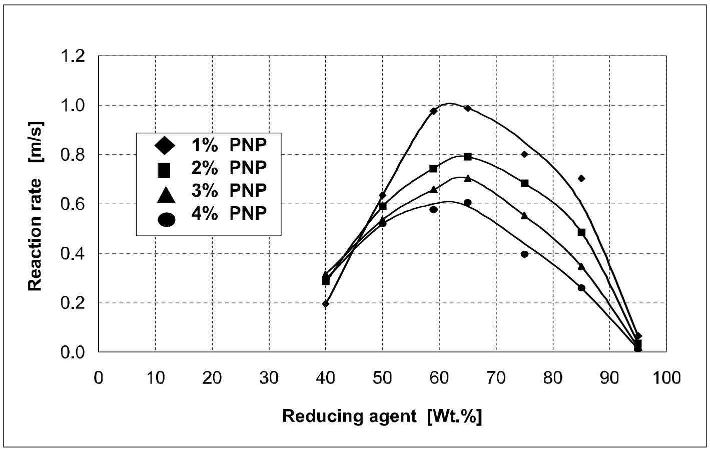


Fig. 10. Reaction rates of compositions of the redox system titanium/potassium perchlorate with different binder content [10]

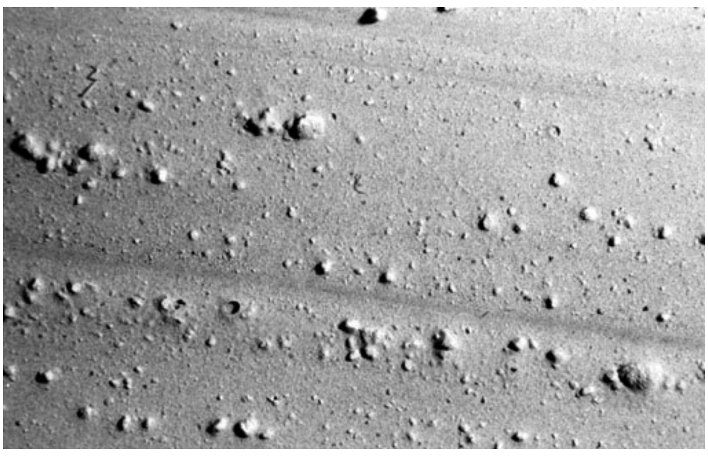


Fig. 11. Composition containing zirconium and barium chromate mixed in a Turbula mixer [11]

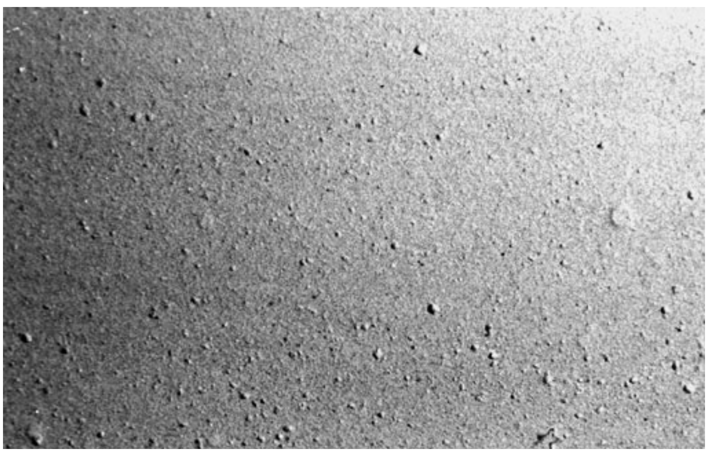


Fig. 12. Composition containing zirconium and barium chromate mixed with an ultrasonic process [11]

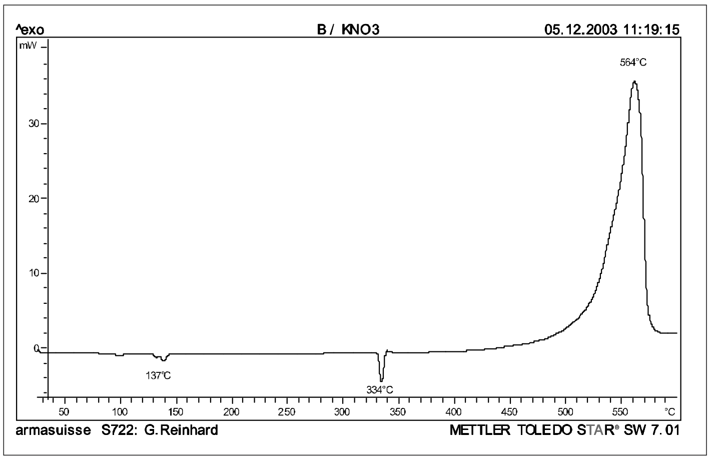
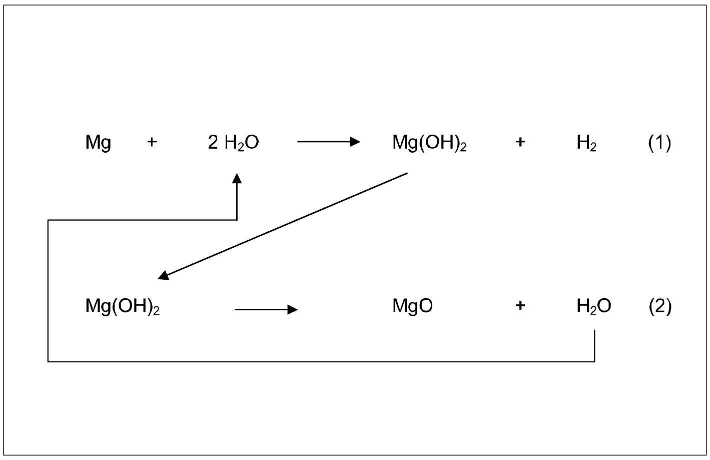


Fig. 13. Differential scanning calorimetry plot of a pyrotechnic composition containing boron and potassium nitrate



Scheme. Reaction of magnesium and water

Many pyrotechnic redox systems contain magnesium as a reducing agent. Magnesium is very sensitive to humidity. The Scheme shows the reaction mechanism of magnesium and water.

It was observed that the reaction products $Mg(OH)_2$ and MgO lead to an increase in volume due to their higher density. This increase in volume is frequently responsible for failures of pyrotechnic components.

9. Safety

Most pyrotechnic compositions show a very high sensitivity to electrostatic discharges and friction. In many cases, the electrostatic charge of a human being is strong enough to initiate a tripping of the pyrotechnic redox reaction.

Pyrotechnic redox reactions are mostly violent. Such reactions create temperatures between 1500 and 4000 °C. During these reactions, large quantities of tarried metal or metal oxide particles are produced, partly in liquid form. These particles can lead to severe injuries.

Experiments show that the reaction of larger amounts of pyrotechnic compositions may run into an unwanted deflagration or detonation.

Therefore the handling of pyrotechnic compositions or components should be performed only by well-trained specialists.

10. The Future of Military Pyrotechnics

As already mentioned, the distribution, the particle size, and the morphology affect the sensitivity and the reactivity of pyrotechnic compositions. Today, much research is done on new pyrotechnic compositions containing nanostructured metal oxides produced by sol–gel technology [17–20] and nanometer-sized reactive metal powders. The goal of this research is to introduce nanometer-sized metal powder into the pores of nanostructured metal oxide during the gelation process. It was already found that such pyrotechnic composites show a tenfold reduced sensitivity to mechanical influences and a two to three times increased performance (combustion rate) [20][21].

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