
New insights into strobe
reactions: An intriguing oscillatory
combustion phenomenon

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New insights into strobe reactions: An intriguing oscillatory combustion phenomenon

Nieuwe inzichten in strobe reacties: Een intrigerend
oscillerend verbrandingsfenomeen

(met een samenvatting in het Nederlands)

Une nouvelle approche des réactions stroboscopique: un
curieux phénomène de combustion oscillatoire

(avec un résumé en français)

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1

Introduction



ABSTRACT

Strobes are pyrotechnic compositions which show an oscillatory combustion; a dark phase and a flash phase alternate periodically. The strobe effect has applications in various fields, most notably in the fireworks industry and in the military area (signaling, missile decoys and crowd control). All strobe compositions mentioned in the literature were discovered with trial and error methods and the mechanisms involved remain unclear. In this introduction chapter a review is given on the literature concerning strobe reactions and oscillating chemical reactions in general to provide a basis for a better understanding of the following chapters in this thesis. Many oscillatory systems have been observed in the past and theories were developed to elucidate their oscillating or unstable behavior based on chemical interactions such as autocatalysis and competing pathways or based on physical processes. Those systems are compared to experimental observations made on strobe mixtures. The features of autocatalysis and competing reactions observed in the Belousov-Zhabotinskii systems and cool flames were emphasized because of the detection of gaseous species near the surface combustion. Meanwhile, meaningful similarities were observed between Self-propagating High-Temperature Synthesis and strobe combustion: the combustion in a layer by layer fashion and the presence of hot spots on the molten areas of the surface combustion. Both chemical and physical processes are considered to explain the strobe mechanisms.

1.1 INTRODUCTION

In physics, oscillating behavior is obtained by moving a system away from its equilibrium position. For instance, the pendulum moved from one side of its equilibrium position to the other until it stabilizes. In chemistry, however a system cannot deviate from its equilibrium spontaneously, as this would contradict the second law of thermodynamics. Hence, chemical oscillators must evolve far from their equilibria and never pass through them. Therefore, they are governed by the law of non-equilibrium thermodynamics [1].

Various chemical oscillators were discovered in the past [2]. They are either homogeneous or heterogeneous, isothermal or non-isothermal, closed or open systems and induce oscillations in various variables: concentrations of species (gaseous, liquid or solid), reaction rate, temperature and/or pressure. Some oscillators have been widely studied such as the Belousov-Zhabotinskii reaction which is a liquid-phase system [3]. It exhibits regular variations in the concentration of intermediate species of the reaction. This induces a periodic change of the color of the solution. The mechanisms of this type of reaction have been widely studied in contrast with most other chemical oscillators. In particular, oscillations in non-isothermal systems remain unexplained in terms of detailed chemical mechanisms

because of their complexity. Oscillating non-isothermal combustion phenomena are observed in, for instance, cool flames [4], solid propellant burning [5–9] and pyrotechnics [10–12]. Contrary to the Belousov-Zhabotinskii reaction, most of these systems are heterogeneous and several variables oscillate at the same time. It adds complexity to the system and makes it harder to model because of the increased number of variables and parameters.

Strobe reactions belong to the group of heterogeneous systems. They are pyrotechnic mixtures that produce flashes of white or colored light by intermittence. They have mainly applications in the fireworks industry (twinklers pots). They were also developed in the military field as flares [13–17]. A few theories have been proposed to explain this phenomenon [18–21] but the current knowledge of these mechanisms is only based on empirical methods and the physical and chemical processes that trigger the occurrence of flashes is still unclear.

In this review, various chemical oscillators are summarized and their mechanisms and theories are compared to what is currently known about strobe reactions yielding hypotheses to explain their oscillatory behavior.

1.2 ISOTHERMAL OSCILLATORS

1.2.1 Isothermal oscillators

The first chemical oscillator was discovered in 1828 by Fechner. He observed repetitive bursts of effervescence (escape of gas bubbles) from iron immersed in nitric acid [22]. This is an electrochemical oscillator; the chemical reaction is accompanied by chemical charge-transfer steps at the electrode. It is the interplay of chemical and electrical variables that drive the system away from the stable stationary state. Many other electrochemical oscillators are mentioned in the literature [23, 24]. A famous one is the so-called "beating mercury heart" [25]. A drop of mercury is placed in a watch glass and covered with a dilute aqueous solution of a strong acid (e.g. HNO_3 , H_2SO_4 , HCl) containing a few crystals of $\text{K}_2\text{Cr}_2\text{O}_7$, $\text{Na}_2\text{S}_2\text{O}_8$ or KMnO_4 . If an iron wire is brought up to touch the mercury drop from the side, the drop rhythmically changes its shape with frequencies of two or three seconds. The description of electrochemical oscillators is often complex but the mechanisms involved in those systems frequently include at least one autocatalytic variable, that is either a chemical species or an electrical quantity [26].

Electrical oscillators are heterogeneous isothermal oscillating systems and it was initially believed that a homogeneous system cannot oscillate until Bray and later his student Liebhafsky discovered in 1921 the first liquid phase (homogeneous) isothermal chemical oscillator, known as the Bray-Liebhafsky reaction (BL reaction) [27, 28]. It is an iodate-catalyzed decomposition of hydrogen peroxide into water and

oxygen [29, 30]. The concentration of iodine molecule oscillates and oxygen builds up pulsating. This phenomenon is due to an alternation between a free-radical process and a non-radical process that consumes and creates iodine, respectively.

The Belousov - Zhabotinsky reaction (BZ reaction) [3, 31, 32] developed by Belousov in the 1950's and rediscovered by Zhabotinsky in 1961 is another isothermal, homogeneous, oscillating reaction. It is a solution of malonic acid, a catalyst, bromate ions, and water. The color of the solution oscillates from a light yellow to a dark blue in presence of ferroin due to variations in the concentration of intermediate species. Cerium was originally used as a catalyst and ferroin has been added later to the composition to intensify the color change (ferroin is blue in oxidized form). Zhabotinsky discovered that the oscillations also occurred without cerium and concluded that the ferroin could act as a catalyst instead of cerium. The mechanisms involved in that reaction are complicated and have been studied thoroughly. Field, Koros and Noyes [33–35] formulated a model for the most important parts of the kinetic mechanism. It is known as the FKN mechanism. It consists of two processes which compete to reduce the bromate ions; the alternation of the two processes depends on the concentration of bromate ions.

The last famous isothermal homogeneous chemical oscillator is the Briggs-Rauscher reaction (BR reaction) discovered in 1972 [36, 37]. It is a hybrid of the BL and the BZ reaction. It combines the iodate and the hydrogen peroxide from the BL reaction and the malonic acid from the BZ reaction with manganese salt as a catalyst and a starch indicator. The system undergoes 15 or more cycles of colorless \longleftrightarrow yellow \longleftrightarrow blue before ending as a purplish solution with a strong odor of iodine. Oscillations are observed in the concentration of oxygen, carbon dioxide gas and iodine ions.

Many other similar chemical oscillators have been studied [33, 38, 39]. They all undergo two competing pathways. One of these pathways produces a specific intermediate, while the other pathway consumes it. The concentration of this intermediate triggers the switching of pathways. However, the detailed chemical mechanisms remain unknown.

1.2.2 Chemical models

Chemical models were developed to describe these phenomena and most of them were inspired by the Lotka-Volterra model. It was developed for the analysis of a predator-prey problem and is described by a non-linear system [40, 41]. It is a simple scheme of an autocatalytic chemical reaction that undergoes sustained oscillations in the concentration of the autocatalytic species. However, the mechanisms present do not apply to any real chemical system. On the contrary, the Brusselator model, created 1968 by Prigogine and Lefever [42], presented in Table 1.1, proposes simple

Table 1.1 – Brusselator model.

Reactions	Rate constants
$A \longrightarrow X$	k_1
$B + X \longrightarrow Y + D$	k_2
$2X + Y \longrightarrow 3X$	k_3
$X \longrightarrow E$	k_4

mechanisms for the BZ reaction [43]. The reactants A and B are converted into products D and E by a four-step mechanism, including an autocatalytic reaction. If the concentrations of A and B are maintained constant, the concentrations of the intermediates X and Y oscillate with time. The Brusselator is the simplest model that describes the BZ reaction. Other models describe the BZ reaction with more complexities in the sub-reactions [44]. For instance, Field, Koros and Noyes presented a five-step model based on the mechanisms observed in the BZ reaction: the Oregonator model [45, 46]. This model also uses an autocatalytic step as in the Brusselator and the Lotka-Volterra models, but the BZ reaction is achieved through more than four sub-reactions. The chemical models presented above were developed for isothermal homogeneous oscillators (BL, BZ and BR reactions). However, they are often used as basis for models that describe non-isothermal or heterogeneous chemical oscillators.

1.3 INTERMITTENT COMBUSTIONS

Non-isothermal oscillators are intermittent combustion processes. They occur either in an homogeneous medium such as cool flames or in a heterogeneous medium such as solid flame combustion. The chemical oscillators mentioned in this section present variations in the concentration of an intermediate species as with the BZ oscillator but also in temperature and sometimes in pressure.

1.3.1 Combustions in homogeneous media: Cool flames

1.3.1.1 Description of the phenomena

Cool flames are homogeneous chemical oscillators but unlike the BZ reaction, the temperature of the system varies and when the system is closed the pressure can also vary. It is a phenomenon that occurs during the combustion of hydrocarbons such as carbon monoxide [47, 48] acetaldehyde [49–52], ethane [53], propane [54], n-Butane [55], di-t-butyl peroxide [56], diethyl ether [57], polypropylene [58], hexadecane [59] and many others [60]. They emit a faint bluish luminescence by intermittence, caused by the excitation of formaldehyde, and occur at relatively low

temperatures, between 500 and 800 K. Their oxidation leads to the formation of H_2O and CO_2 through several intermediate reactions known as free radical branching chain mechanisms which involves autocatalysis. Temperature and pressure pulses in the reacting gases are the result of a fast acceleration of the reaction rate. However, the pulses are not intense and only a small quantity of reactants is consumed. As a consequence, the acceleration stops and the reaction rate decreases spontaneously, while the concentration of the reactant is still high. Therefore, the cool flame process is able to self-accelerate and self-decelerate. This ability is considered as the main distinguishing property of cool flames as well as the occurrence of a negative temperature coefficient of the reaction rate i.e. a region where the rate of reaction decreases while the temperature still increases. The acceleration of the reaction rate of a self-ignition process (a hot flame) is limited exclusively by depletion of reactants, whereas the acceleration of the reaction rate of cool flames is limited by kinetic mechanisms with increasing temperature. Consequently, cool flames are thermokinetic phenomena. A careful balance between heat release and heat loss is necessary for their occurrence.

Cool flames are studied in both open and closed systems. In the former case (open system), the hypothesis of the Continuous Stirred Tank Reactor (CSTR) is often used. It can be defined as an ideal reactor where reactants are continuously admitted and products withdrawn. It assumes a perfect mixing, constant density and isothermal conditions. Because of the continuous flow, steady states are attained contrary to closed vessel systems [4].

1.3.1.2 Chemical models

The chemistry of cool flames is complex and involves many intermediate reactions. Attempts have been made to model this homogeneous oscillatory reaction [41]. Frank-Kamenetskii proposed a kinetic scheme based on the Lotka-Volterra scheme [4, 61, 62]. This three-step model involves one reactant, one product and two intermediates species that react through autocatalytic steps. The system is capable of sustaining oscillations between the concentrations of intermediates (peroxides and aldehydes). However, this scheme applies only to an isothermal system which is unacceptable for cool flame. Besides, autocatalytic steps are often involved and they have the form $A + B \longrightarrow 2B$ or $A + 2B \longrightarrow 3B$ which are cubic and quadratic autocatalytic reactions, respectively [63–66]. The terms "quadratic" and "cubic" are used because the reaction rate has the form $a[A][B]^n$ (where a is the reaction rate constant); for $n = 1$, the reaction is quadratic and for $n = 2$ the reaction rate is cubic. For instance, the autocatalator model, developed in the 1980's, combines a cubic autocatalytic step, $A + B \longrightarrow 2B$ where A is the reactant and B the autocatalyst, with a simple linear decay of B to the product C , $B \longrightarrow C$ [67–69]. Those theories were first analyzed in the Continuous Stirred-Tank

Reactor (CSTR). However this model can also be adapted to closed systems by adding a step (precursor decay) to the scheme [67, 70]. Those theories are all independent of temperature and cannot be applied to cool flames since they are thermokinetic phenomena.

Later on, Sal'nikov described a thermokinetic model [4, 71–78] in which oscillations in temperature of the reacting medium and in concentration of a critical intermediate (aldehydes) occur. The mechanisms are described in Table 1.2. A precursor P is converted to a product A via an active intermediate X. The model is capable of sustained oscillations in the concentration of X and temperature, with the usual following assumptions: $E_1 = 0$ (so the reaction rate is constant), $E_2 > 0$, $\Delta H_2 > \Delta H_1$. Under those conditions, the intermediate species X produced by the first step is immediately consumed by the second step and because of the exothermicity of the two reactions, the temperature increases. This accelerates the consumption of intermediate X while its production remains constant. Consequently, the second reaction decelerates, the temperature decreases and the concentration of intermediate X increases again. The analysis of this model shows that the system undertakes a bifurcation and exhibits self-sustained oscillations [65]. Oscillating solutions are obtained by the variation of some parameters (the bifurcation parameters). This model is consistent with the thermokinetic nature of cool flames but does not fit the other essential features of cool flame processes such as autocatalysis or the negative temperature coefficient of reaction rate.

Table 1.2 – Sal'nikov model.

Reactions	Heats of reaction	Activation energies
$P \longrightarrow X$	ΔH_1	E_1
$X \longrightarrow A$	ΔH_2	E_2

Later in 1969, Gray and Yang combined a chain-branching system with the thermokinetic approach of Sal'nikov and proposed a dynamic system with two variables: the autocatalytic chain carrier and the temperature [4, 47, 79]. The model considers the energy and the kinetic equations of a chain reaction. The scheme for initiation, branching, and termination of the chain is postulated in Table 1.3. The termination reaction is assumed to go through two parallel paths concurrently. Even if the complexity of cool flame is not fully included in this theory, the Gray-Yang model remains the best approximation of the cool flames mechanisms since it is based on a chain-thermal autocatalytic process [80].

In cool flames, the oscillating behavior is based on the production and depletion of an intermediate species as in isothermal oscillators (BL, BZ and BR oscillators). Consequently, the models used to describe those phenomena are often alike. For

Table 1.3 – The Yang and Gray model

Reactions	Rate constants	
$A \longrightarrow Y$	k_i	Initiation
$Y \longrightarrow 2Y$	k_b	Branching
$Y \longrightarrow \text{stable products}$	k_{t_1}	Termination
$Y \longrightarrow \text{stable products}$	k_{t_2}	Termination

instance, cubic autocatalysis used to model a cool flame is also found in the Brusselator mode created for the BZ reaction (see Table 1.1). The difference is that the reactions involved in cool flames are exothermic leading to thermal oscillations. Autocatalysis is the main feature to explain the periodic variations in concentration of species or temperature in homogeneous oscillators. In heterogeneous combustion, when the heterogeneities in the compositions are small compared to the thickness of the combustion wave, a homogeneous approach can be applied to describe combustion processes. However, spatial fluctuations of the temperature and the concentration cannot be neglected for most of the systems. Physical parameters are involved in the combustion process and oscillations are either the result of chemical processes as for homogeneous oscillator or/and physical processes.

1.3.2 Combustions in heterogeneous media

1.3.2.1 Various heterogeneous unstable combustions

The burning of solid propellant often results in pressure oscillations in the combustion chamber such as in a rocket motor [6] or whistles [81–83]. They are closed systems and the oscillating behavior is often the result of the confinement of the compositions [84], the geometry of the propellant and/ or the design of the combustion chamber [85–88]. In whistle devices, the confinement of the composition is responsible for the acoustic waves that induces pressure and temperature variations. These oscillations control the reaction rates the reaction resulting in a two-stage burning. Since strobe compositions are open intermittent systems, the case of oscillatory closed systems is not detailed in this review.

Thermite and Self-propagating High-temperature Synthesis (SHS) are other kinds of solid combustion in open systems that show more similarities with strobe compositions. The SHS mixtures were discovered in 1967 by Merzhanov and al [89]. They are mostly binary compositions in which, when ignited, the combustion front propagates through the powdered ingredients leaving behind a metallic alloy or a high quality ceramic material. Sometimes, spatial oscillations or "banded structures" are observed in the product material due to periodic variations of

the front flame velocity [8, 90, 91]. This is not a desired effect. It may affect the homogeneity and the mechanical properties of the product material. Many oscillating systems are mentioned in the literature: Ti + C (producing TiC), Ti + 2B (TiB₂), Ti + Al (TiAl), Ni + Al (NiAl), Ta + C (TaC), etc [7, 92–99]. Thermal kinetic (in the combustion propagation front) and spatial oscillations were observed.

Depending on variables such as the porosity of the sample (or density), the reactant particle size, the diameter and shape of the sample, the dilution of the reactants, the initial temperature (pre-heating of the sample), the initial composition (stoichiometry) [100, 101], etc. the combustion mode may evolve from stable to unstable [102–105]. For all those binary systems, three modes of combustion are observed:

- Stable, no variation of the combustion front velocity.
- Oscillatory (1D instabilities), oscillations in combustion velocity that result in a periodic structure perpendicular to the combustion front.
- Spinning or spiral wave propagation (2D instabilities) is observed under special conditions of burning of cylindrical samples and results in the formation of one or more luminous points that move in an helical fashion through the unburned part of the sample.

Most parameters that influence the occurrence of combustion instabilities have in common that they are correlated to the thermal conductivity. The first theories on SHS combustion used only physical processes to explain the self-oscillating behavior and the spinning combustion [7, 106, 107]. A second less common approach was also envisaged; it uses both physical and chemical processes to explain the instabilities [108, 109]. The chemical processes mentioned present many similarities with the homogeneous oscillators (BZ type reaction and cool flames) by involving two chemical competing pathways or autocatalysis to explain the occurrence of oscillations.

1.3.2.2 Physical approach

The instabilities of the SHS combustion were first explained using a physical approach. For the oscillatory mode where the "banded" or laminated structures were observed, the hypothesis was that the combustion front moved from one layer to the other. Not only the occurrence of this spatial structure but also their thickness depended on parameters correlated to the heat transfer coefficient [90]. The assumption was made that the top layer when ignited with an external source (burner) undertook an exothermic chemical reaction. Part of the heat released is transferred to the next cold layer. Thermal, kinetic and eventually spatial oscillations occur when the reaction time is much smaller than that of the

characteristic time of heat transfer to the next layer [7, 106]. The heat released by the reaction in the first layer increases the temperature in the next layer. The reaction rate, which obeys an Arrhenius law, also increases. The thermal conductivity is low so most of the heat is dissipated and the second layer is slowly ignited while the reaction proceeds fast in the first one. When the reactants in the first layer are entirely consumed, the front propagation velocity decreases and the cycle starts again in the next layer.

Similar mechanisms are thought to be responsible for the spinning combustion but at a different scale. The appearance of small (10 to 100 μm) bright hot spots, called "scintillations", was observed. They correspond to the high temperature region on the combustion surface [9, 101, 110, 111]. Some of these hot spots appear and dissipate; others initiate the reaction in the neighboring areas. It was also noticed that the propagation front moves forward as a consequence of their appearance. Their size is strongly dependent on the particle size and shape of the reactants. In these local scintillation zones, the reaction rate is high. The characteristic reaction time is much smaller than the time required to transfer the heat to the neighboring areas. In case of an oscillating mode, kinetic and thermal parameters allow the complete layer to be ignited at the same time while in case of spinning combustion, only a part of the layer is ignited and the reaction must propagate in the direction of the front combustion and also perpendicularly to it. It was suggested that the hot spots are located on the microstructural heterogeneities of the surface and linked to parameters such as the melting point of one of the reactants [104, 112]. The assumption was made that hot spots form in the location of the most refractory reactant at the melting point of the other reactant. For instance, in the Ti-Si system, hot spots occur in titanium particles when the melting point of silicon has been reached. As the reactant Si melts it spreads around the solid particles of titanium enhancing the inner contact between the particles and as such affecting the heat transfer between the particles. Hence, the reactant's melting points are an indicative factor of the ignition temperature of the scintillations.

Numerical studies were developed to determine the boundary between stable and unstable combustion (bifurcation point). In all cases, nonlinear systems are used to describe the combustion modes. Most of the models developed use a quasi-homogeneous approach [106, 113–115]. This approach is based on the assumption that both heat transfer and heat evolution can be described in terms of a continuous function of space coordinates and only a particular form of reaction kinetics denotes the specifics of the heterogeneous reaction. Oscillating and spinning systems were obtained by varying the heat transfer parameter. 1D, 2D and 3D models were studied [104, 116–119]. The bifurcation parameters obtained from those models depend only on the physical properties of the system such as heat capacity, heat of formation, activation energy and combustion temperature [113, 114, 120]. A

melting parameter was also added to incorporate the melting effect [115]. These bifurcation parameters provide a good estimation of the propagation mode when the activation energy is relatively low.

Recent studies highlight the discrete mode of the propagation of the combustion front in SHS compositions [107, 116] that gave rise to different numerical models where two assumptions were made. First, the reaction media consist of clearly distinguishable elementary cells or reaction cells and, second, the reaction time in the cell is smaller than the time of heat transfer to the neighboring reaction cells. Contrary to the quasi-homogeneous approach, the nature of the heat transfer is not a continuous function of space coordinates. Then, the process called the "relay-race" mechanism was used: the combustion front first undertakes a rapid burning of the specific local area (resulting in scintillations) and then a relatively long ignition delay occurs during which the neighboring areas were preheated [9]. Consequently, the propagation of the combustion front is limited by heat transfer between the reaction cells while heat releases relatively quickly inside the cell. The parameter p is introduced. It depends on the ratio between the characteristic time for heat transfer and the time of reaction. When $p \sim 1$ a quasi-homogeneous approach is sufficient to describe the mechanisms. However, when $p \gg 1$, a discrete approach is necessary. A bifurcation parameter was obtained from the following Equation (1.1) [107]:

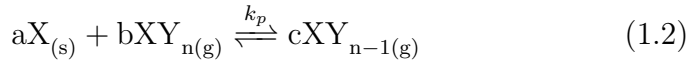
$$Ar_c = \frac{R(T_c - T_0)}{E} = \frac{R \times T_c}{E} - Ar_0 \quad (1.1)$$

Where E is the activation energy, T_0 is the initial temperature. Ar_0 is the Arrhenius number and can be controlled by preheating the composition. Ar_c depends on the Arrhenius number and can be changed by diluting the mixture with an inert material, it should change the combustion temperature T_c . For a quasi-homogeneous combustion wave a boundary factor of $Ar_c = 0.15$ was found while for discrete a combustion wave, a value of $Ar_c = 0.03$ was obtained. Contrary to the bifurcation parameters mentioned previously, this parameter applies to systems with higher activation energy.

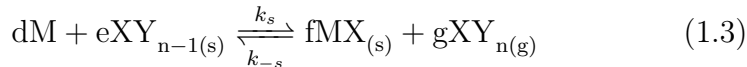
1.3.2.3 Importance of the chemical parameters

Other studies emphasize the importance of the chemical factors in the occurrence of oscillating combustion [108, 109]. They considered not only thermal oscillations but also variations in concentrations of intermediate species (e. g. suboxides)

formed during the combustion such as in isothermal oscillators and cool flames. As a result, the bifurcation condition depends on their concentration. For instance, Mo + B and Ta + C systems have been studied [108]. After ignition by any external source, a pore structure, called the "heat-affected" zone forms. At relatively low temperature, there is the formation and evaporation of B_2O_3 (for the Mo + B system) and CO_2 (oxide formed during the combustion of the Ta + C composition). As the system is heated, the next endothermic reaction (Equation (1.2)) occurs producing suboxides:



Where X is identified as B in the Mo + B system and C in the Ta + C system, XY_n corresponds to the oxide (B_2O_3 or CO_2), XY_{n-1} is the suboxide (B_2O_2 or CO) and k_p is reaction rate coefficient. a , b and c are the stoichiometric coefficients that must be adapted to the system studied. For the Mo + B system, $a = 2$, $b = 2$ and $c = 3$. For the Ta + C system, $a = 1$, $b = 2$ and $c = 2$. Simultaneously, the exothermic reaction described below takes place:



Where M is the metal (Mo or Ta), MX is the product (MoB or TaC) and k_s and k_{-s} are the reaction rate coefficients. d , e , f and g are the stoichiometric coefficients. For the Mo + B system, $d = 2$, $e = 3$, $f = 2$ and $g = 2$. For the Ta + C system, $d = 1$, $e = 2$, $f = 1$ and $g = 1$. As the temperature is increased by this reaction, the combustion wave forms and the second reaction (Equation (1.3)) becomes dominant. The decay of suboxides is 5 to 7 orders in magnitude higher than their formation. As a consequence, the reaction rate of the second reaction decreases. As the temperature goes down, the combustion wave stops and a new "heat-affected" zone is created. Then, the first reaction is dominant again followed by the subsequent acceleration of the second reaction. The diffusion of the gaseous oxides extends the reaction to the unburned part of the sample. In this theory, the variation of concentrations of suboxide is responsible for the oscillation. A simple linear system is derived from the mass balance equation. Solving these equations leads to a condition of bifurcation for the occurrence of oscillations:

$$4D \times \frac{k_{-s} - k_p}{u^2} > 0 \quad (1.4)$$

Where D is the diffusion coefficient for gas and u is the average burning velocity. However, the auto-oscillating combustion is rather described by a non-linear coupling of kinetics and thermal factors.

The hypothesis was also made that some of the SHS system showing a "banded" structure may undergo a BZ type reaction [109]. The Brusselator scheme (see Table 1.1) was used to model the Ti + B and the Ni + Al combustion processes with a bifurcation condition stated as follows:

$$[B] > \frac{k_4}{k_2} + \frac{k_3 \times k_1^2}{k_2 \times k_4^2} [A] \quad (1.5)$$

Where $[A]$ and $[B]$ are $\text{Ti}_{(s)} / \text{Al}_{(s)}$ and $\text{B}_{(s)} / \text{Ni}_{(s)}$, respectively. The coupling of this model with a quasi-homogeneous model of combustion [121] allows for more accurate modeling of the thermal and spatial oscillations observed experimentally. This model also involves oscillations in the concentration of intermediate species by the use of the Brusselator model. This confirms that not only physical processes, but also kinetic mechanisms must be taken into account in heterogeneous oscillating reactions. Chemical models used for homogeneous oscillators provide a good start to model the chemical steps involved in heterogeneous combustion.

Based on the previous sections, several oscillating systems were identified. They were either isothermal or non-isothermal, homogeneous or heterogeneous and they showed oscillations in intermediate species, temperature and/or reaction rate. Several hypotheses have been emphasized. For homogeneous oscillators (BL, BZ, BR reactions and cool flames), the oscillations in intermediate species and temperature (only for cool flames) were explained by a chemical approach: two pathways compete to create and consume intermediate species. Autocatalysis was often involved to model these types of reaction. On the other hand, the oscillating behavior observed in SHS compositions (mostly on the front propagation rate and temperature) was explained using a physical approach. Indeed, the assumption that the reaction time is much larger than the characteristic time of heat transfer was sufficient to model the observed oscillating behavior. However, the possibility of creation and depletion of intermediate species that compete was also envisaged for this kind of reaction. With this knowledge in hand, stroboscopes will be analyzed. They are pyrotechnic compositions that produce flashes of light by intermittence. They belong to the class of solid, heterogeneous combustion processes such as SHS mixtures. However, the chemical and physical processes responsible for the oscillations are not well understood. After a review of the current knowledge of strobe reactions, they are compared to the oscillating systems described previously (BZ reaction, cool flames and SHS combustion).

1.4 STROBE REACTIONS

1.4.1 Historical review

The discovery of flickering compositions was probably a coincidence related to the increased use of magnalium (magnesium-aluminum alloy) instead of aluminum in pyrotechnic mixes and propellants. The first reference to strobe compositions appears in 1898 in an old mixing book of the firm Brock's Fireworks Ltd [122] under the heading "Orion Flashing guns" (see Table 1.4). The composition burned periodically producing white flashes of light. In 1969, Russian patents [123–125] were published describing pyrotechnic compositions which produced a colored light emission at regular intervals (at a frequency around 2-3 Hz). The compositions mainly consisted of magnalium, used as the fuel, and barium nitrate or strontium nitrate, used as the oxidizer as in the Orion formulae. Other examples of strobe compositions are mentioned in the literature [10, 11, 126–128] or in patents [13–17]. Their compositions are mostly the result of trial and error and not based on understanding of strobing mechanisms.

Table 1.4 – Orion formula.

"Orion Flashing Guns" (1898)	1 (% by weight)	2
Sulfur	51	55
Fine Magnesium powder	17	18
Fine Aluminum pyroflake	6	
Barium nitrate	26	27

The first studies aimed at understanding strobe reactions were carried out by Krone [13, 18] and Wasmann [19, 129] during the 1970's. The former experimented with compositions that consisted of:

- A fuel: magnalium (50:50 ratio Mg:Al) was used in all compositions in an amount of 20 % (by weight) and with several mesh sizes.
- An oxidizer: nitrates of the earth alkali metals and some perchlorates are used in an amount of 65-75 % (by weight).
- Other compounds were added to the composition to improve or control the strobing behavior. Krone noted that the variation of 0.5 % of the composition resulted in a change of the burning behavior: the strobing effect may even disappear.

The main observation of Krone was the occurrence of a zone he called "semi-

slag" before a flash. This foam, partly solid and partly molten, contained only a trace of magnesium. Moreover, he noticed that the addition of a compound that releases a large amount of gas such as oxamide, guanidine nitrate or ammonium sulfate provided a better flash separation and an improved sharpness. Thus, Krone hypothesized that most of the magnesium was oxidized during the dark phase while the oxidation of aluminum was slow. After the magnesium was entirely consumed, the oxidation of the aluminum located in the "semi-slag" zone suddenly increased due to the higher surface area available and the action of gases such as NO_2 and NO . This reaction was fast and accompanied by a light emission. He also noticed the poor strobe effect of compositions containing potassium nitrate and sodium nitrate, whereas barium nitrate and strontium nitrate provided a better strobing behavior. According to Krone, the lower melting point of potassium and sodium nitrates causes the composition to melt down more easily. This generates extra flashes on the molten slag covering the surface of the composition causing uncontrolled burning and explosions with many flying sparks. Finally, Krone studied factors that help stabilizing the frequency of a strobe and he had the idea to use a catalyst to control the frequency of the flashes. He added a small amount of copper-chrome oxide (0.03% to 0.1%) to the composition. Later, Cardwell [127] listed products that are used as catalysts in strobe reactions (oxides of iron, cupric oxide, antimony trisulfide, some transition metal salts). Shimizu [20] also noticed the advantages of using potassium dichromate to enhance the regularity and sharpness of flashes. The conclusion of the study of Krone is that strobe mechanisms are based on competing chemical reactions with opposite reaction pathways (slow oxidation of aluminum and fast oxidation of magnesium) as observed in the BZ oscillator and cool flames.

Wasmann studied a system of copolymers of unsaturated monomers containing nitrate groups with conventional unsaturated monomers (such as pentaerythritoldinitratediacrylate with methacrylic acid methyl ester) to which metal perchlorates soluble in the monomers used are added as oxidizer (such as strontium perchlorate tetrahydrate) [19, 129]. He observed the formation of a microporous residual mixture that Krone identified as the "semi-slag". The heat accumulates in this mixture until the ignition point is reached followed by a fast burning responsible for the flash. Because of the low conductivity of the composition only a small part of the heat is transferred to the rest of the composition so the reaction decelerates and a new microporous residual mixture is formed on the surface. Contrary to Krone, Wasman explained the pulsating burning based on physical parameters that are alike mechanisms occurring in SHS combustion. His hypothesis was that the oscillations are controlled by the heat flow from the burning surface into the interior of the system. However, he also mentioned the possibility of competing reactions responsible for the oscillating behavior: "a smolder reaction of the nitrate group containing monomers and a fast reaction which is initiated by the physical process of heat accumulation in the microporous zone".

Both Krone and Wasmann [13, 18, 19, 129] studied binary strobe compositions with an oxidizer, a fuel and compounds added in small amounts to improve the strobe behavior (sharpness and regularity of flashes). Contrary to Krone theories, Wasmann described mechanisms that are based on both competing reactions and physical processes. The innovation brought by Shimizu was to consider strobe compositions as two couples of oxidizers and fuels: one for a dark reaction and another for a flash reaction. This is the current hypothesis to explain strobos mechanisms. After testing many strobe compositions [20], Shimizu argued that two reactions occur: a Dark (or Smolder) reaction and a Flash (or Light) reaction that alternate periodically. The trigger factor for the occurrence of a flash is the temperature.

The mechanisms are schematically depicted in Figure 1.1. First the composition is ignited on the surface and the dark reaction starts. The temperature in the dark zone is not uniform and hot spots appear on the surface and they magnify as the temperature increases (as the heat accumulates) [130]. Those hot spots are located in the molten part of the surface [131]. After a while, the maximum temperature of the dark zone reaches the ignition temperature of the flash composition and the flash reaction starts. A small layer of dark zone remains on the burning surface because its temperature was too low to be raised to the ignition temperature. This zone starts the next dark reaction leading up to the next flash reaction. In this manner the dark and the flash reactions alternate. Through those observations, Shimizu claimed a few necessary conditions for the production of the strobe light effect [20]:

- The dark composition must produce a smoldering temperature which is lower than the ignition temperature of the flash composition.
- The dark reaction produces a minimal amount of visible light.
- The dark composition must give rise to heat accumulation during the reaction to ignite the flash composition. The faster the heat accumulates, the higher the frequency of the light flashes.
- A catalyst may help the accumulation of heat.
- The dark zone must be uniform, because heterogeneities disturb the heat accumulation and prevent ignition of the flash composition.

This theory implies that strobe compositions contain two mixtures: one that gives rise to the dark reaction (the dark composition) and the other that gives rise to the flash reaction (the flash composition). However, nowadays various strobe compositions mentioned in the literature do not satisfy this criterion and the discovery of new strobe mixtures is still the result of a trial and error method

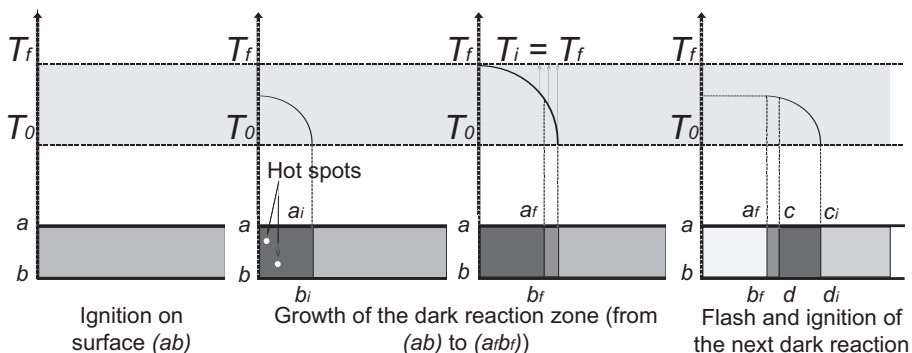


Figure 1.1 – Scheme illustrating the Shimizu hypothesis about strobe mechanisms, adapted from [20]. The evolution of the temperature is shown as a function of time, T_0 is the temperature at the beginning of the dark reaction. The composition is ignited on the surface (ab). When T_i the temperature in the layer ($aba_i b_i$) reaches the ignition temperature of the flash reaction T_f , the layer ($abaf b_f$) is consumed by the flash. Then the temperature drops and a thin layer ($a_f b_f cd$) remains the surface (cd) initiating the next dark reaction.

[132–134]. For instance, a few binary compositions containing a perchlorate and hexamine are known to burn in an oscillatory manner [132, 134] Hexamine is an organic material and remind the experiments performed by Wasmann [19, 129]. In these mixtures, hexamine is supposed to act as a fuel.

Early studies on strobe compositions (Wasmann and Krone) already revealed similarities with SHS combustion such as the layer-by-layer burning that are further confirmed by experiments (see Section 1.4.2). A critical balance between heat generated and heat transferred has even been envisaged to explain the strobe behavior. On the other hand, Shimizu highlighted the possibility of competing chemical pathways such as in BZ reactions or cool flames responsible for the oscillations. Thermokinetic models of the strobe behavior that are described in Section 1.4.3 use the cubic and quadratic autocatalysis model as the Brusselator scheme and the Sal’nikov scheme, originally created for cool flames, to model the periodic variations in temperature and also in concentration of species.

1.4.2 Physical mechanisms

Based on the strobe compositions mentioned in the literature, eleven mixtures were tested (see Table 1.5) and their combustions were recorded with a high-speed camera (Redlake digital imaging system; 5000 frames per second; 160 pixels by 160 pixels). Details on the experimental conditions for assembling the strobos and recording the strobe behavior can be found in Chapter 2 and [135].

Table 1.5 – Selection of classical strobe mixtures mentioned in the literature and tested [18, 20, 127, 134, 136]. The signs ++, +- and - mean that the strobe effect is good, intermediate and bad, respectively. The strobe effect was evaluated regarding the regularity, sharpness of flashes.

	1	2	3	4	5	6	7	8	9	10	11
Ammonium perchlorate	x	x	x	x	x	x	x	x		x	x
Sulfur									x		
Magnalium		x	x	x					x	x	x
Magnesium	x				x	x	x	x			
Barium sulfate			x								
Potassium perchlorate		x							x		x
Strontium sulfate					x				x		
Calcium sulfate						x					
Sodium sulfate								x			
Sodium nitrate							x				
Guanidine nitrate				x							
Strontium carbonate										x	
Sodium oxalate											x
Potassium dichromate		x	x		x	x		x	x	x	
Parlon										x	
Boric acid									x		
Dextrin									x		
Strobe effect	+-	++	++	++	++	+-	-	-	-	++	-

A general observation from the experiments is that some compositions give rise to a good strobe effect (regular and intense flashes, separated by clear time intervals) while others do not give a typical strobe behavior (irregular flashes). The analysis of the high-speed camera movies helps to observe and analyze the differences and it reveals important parameters for the strobe effect. Figure 1.2 shows a selection of images of the combustion of Composition 3 recorded with the high speed camera. The pictures reveal the formation of a porous layer on top of the pellet. This confirms the observations made by Wasmann, Krone and Shimizu who called this the "microporous residual mixture", the "semi-slag" and the "semi-reacted zone", respectively [18–20]. The layers of the compositions that produce a good strobe effect (compositions 3, 9 and 10) propagate on the surface of the pellet, become thicker and red while the other compositions (1, 7, 8 and 11) produced foams on their surface from where gaseous species may escape (see Figure 1.3 A). The layers formed are not uniform in color and in shape. As Krone already observed earlier, those compositions contain an oxidizer that has a lower melting point than the other compounds (nitrates or sodium sulfate, calcium sulfate, potassium perchlorate) [18]. The top layer is heated up by an exothermic reaction that Shimizu called the dark reaction [20]. This layer is consumed during the flash by what Shimizu identified as the flash reaction and the next layer is ignited on the top of the pellet. The pellet is consumed linearly, layer-by-layer which is the first similarity established

with SHS combustion.

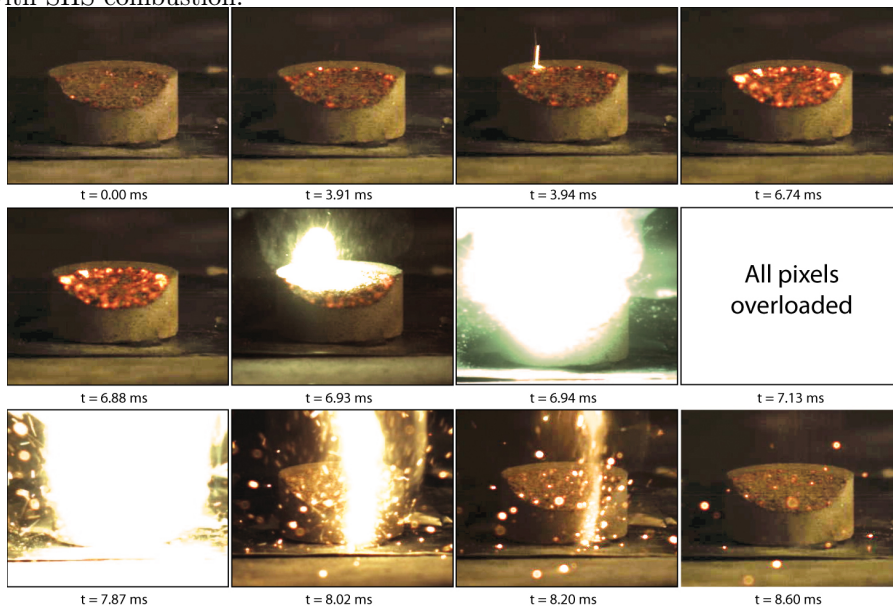


Figure 1.2 – Time resolved images of the burning of a strobe pellet (composition C) before, during and after a flash.

The second similarity is the presence of hot spots on the surface combustion, also called scintillations for SHS compositions [9]. With most strobe compositions tested, points of light were observed on the surface layer (see Figure 1.2 at $t = 3.94$ ms). They occur and grow during the dark phase. According to Shimizu [130], the hot spots are a result of the accumulation of the heat released by a reaction. Some of them are called "flash sites" because they evolve into flashes (see Figure 1.2 at $t = 6.88$ and 6.93 ms). Grose [131] suggested that hot spots occur in the molten part of the dark layer blowing off those zones by a small flash. Consequently, the flashes are ignited from the melting part of the layer. Haarmann also reported on strobe mixtures containing metal sulfates such as compositions 3, 5, 6, 8 and 10 and claimed that flashes occur each time the sulfate reaches its melting point or decomposition temperature [137]. It increases the number of similarities with SHS combustion where hot spots are supposed to occur in the melting area of the surface combustion at the melting point of the most refractory material [104, 112]. This confirms the hypothesis that mechanisms in strobe compositions and SHS are similar and theories such as the "relay-race" mechanism may be applied to stobes. The reaction cell is then identified as an entire layer.

Another phenomenon was observed for strobe compositions: the occurrence of flying particles on partly solid layers as show in Figure 1.3 B and C (compositions

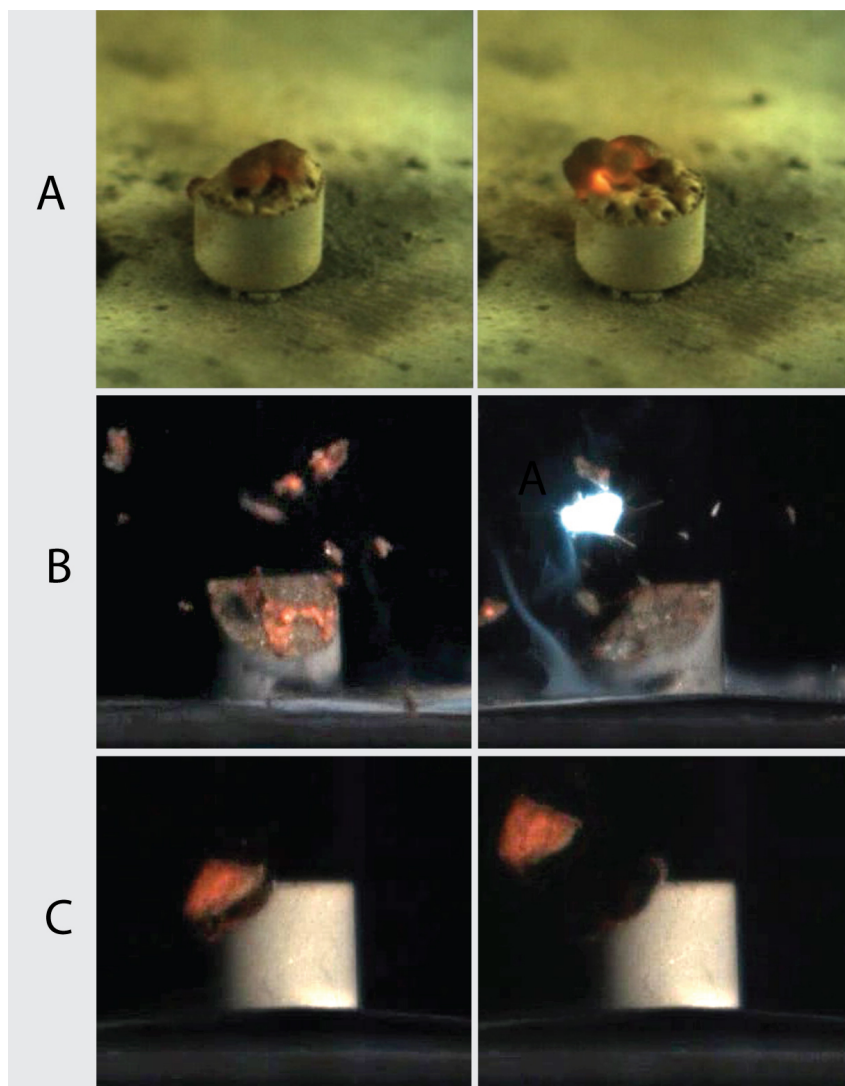


Figure 1.3 – A.: Images of the combustion of composition 8 recorded with the high-speed camera. Formation of a foam on the surface combustion. B and C: Examples of flying particles and flash sites observed during the strobe reaction of Composition 3 (B) and Composition 5 (C).

3, 5, 6, 9 and 10) and the formation of bubbles on molten layers (compositions 1, 7, 8 and 11) as observed in Figure 1.3 A. This observation reveals the presence of gaseous species that form under the surface during the dark phase. When the layer melts the gas escapes through the foam forming bubbles and when the surface remains partly solid pressure builds under the layer. Sometimes the gas escapes breaking the layer and ejecting parts of it or the entire layer. When too much gas escapes though, flashes are irregular and less sharp. It suggests that those gaseous species are necessary for the occurrence of oscillations. They may be identified as the intermediate species present in the BZ reactions [3] or in cool flames [4]. In both cases, two pathways compete to create and consume the intermediate species resulting in oscillations in their concentrations.

1.4.3 Theoretical approaches

Based on their experimental observations, two thermokinetic models were developed by Davies [21] and Feng [138]. Both models adapt a scheme that has been created to model homogeneous oscillators (BZ type reactions and cool flames). They are based on a binary composition of magnesium and ammonium perchlorate. They both hypothesize that competing oxidation reactions occur between the three phases of magnesium (solid, liquid and gaseous) with gas formed from the decomposition of ammonium perchlorate. The first one is a three-step model based on standard autocatalytic models. The model, described in Table 1.6, is studied with $n = 2$ and $m = 3$ which corresponds to cubic autocatalysis initially used to model cool flames [64]. The two first steps of the model reflect the evaporation of magnesium and its partial oxidation; this corresponds to the dark phase. The last step of the model is the rapid oxidation of gaseous magnesium which is the flash phase. The mass conservation equation applied to this system gives rise to a non-linear system of two equations. Steady-state solutions and oscillatory behavior were achieved using non-linear analysis methods. The control parameter used was related to diffusion between $Mg_{(g)}$ and O_2 . No temperature dependence is included in the model via the Arrhenius law and a pool chemical approximation has been used for $Mg_{(s,l)}$ (The concentration of this compound is supposed constant). Both observations are not consistent with the strobe reaction, but this model emphasizes the possible autocatalytic nature of the strobe reaction.

The second model proposed by Davies [21] takes into account the temperature dependence of the strobe reaction by using the Sal'nikov model originally created for cool flames [72]. This thermokinetic model is described as follows:



Where P corresponds to $Mg_{(s,l)}$, X is $Mg_{(g)}$ and B is MgO and Q_2 is the heat

released by the second reaction.

Table 1.6 – Chemical model developed by Feng and al. [138]; $A = O_2$, $B = Mg_{(g)}$, $C = Mg_{(s,l)}$, $D = MgO$

Chemical model	Simplified model
$3Mg_{(s,l)} + O_2 \longrightarrow 2MgO + Mg_{(g)}$	$A + C \longrightarrow B + D$
$mMg_{(g)} + Mg_{(s,l)} + O_2 \longrightarrow nMg_{(g)} + 2MgO$	$A + mB \longrightarrow nB$
$Mg_{(g)}(+\frac{1}{2}O_2) \longrightarrow MgO$	$B \longrightarrow D$

A set of compounds (solid and liquid magnesium) react first in a slow reaction, identified as the dark reaction. It produces intermediate species (gaseous magnesium) and then those species react in a fast and exothermic reaction, identified as the flash reaction. The mass conservation equation is applied to this model and a non-linear system of two equations is obtained with the two variables mentioned: the temperature of the mixture and the concentration of the intermediate species. Four parameters are used: the ambient temperature, the initial concentration of reactants, the ratio of activation energies and the heat transfer coefficient.

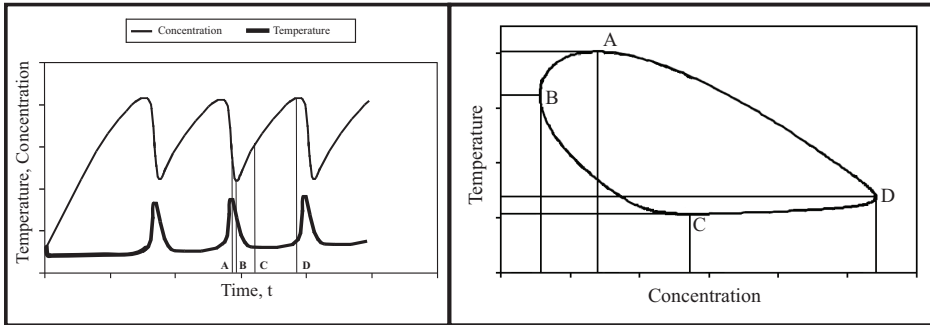


Figure 1.4 – (left) Evolution of the temperature and the concentration of intermediate species with time during a strobe reaction. (right) Correlation between the temperature and the concentration of intermediate species (reproduced from [21]).

The last parameter (the heat transfer coefficient) is a control parameter; steady-state or oscillatory behavior are obtained by varying this parameter. The left hand graph of Figure 1.4 shows the evolution of the temperature and the concentration of intermediate species with time while the right hand graph shows the correlation between the two variables. Points A, B, C and D are characteristic states of the system during one cycle. The flash occurs only if the heat generated is sufficient and if the concentration of flash species has reached a critical level to start the flash reaction. This implies that the dark and the flash reactions cannot be studied separately since the first one gives rise to the second one. The last model, developed

by Davies, uses a combination of both physical and chemical parameters which is more likely to explain the strobe mechanisms. Consequently, not only thermal oscillations are involved in strobe reactions but also periodic variations in the concentration of gaseous intermediate species. The coupling of both physical and chemical processes enabled the prediction of thermal, spatial and kinetic oscillations observed in SHS combustion [108, 109] that reinforces this theory to describe the strobe behavior.

1.5 SUMMARY AND SCOPE OF THE THESIS

Various oscillating systems are reviewed and some of their features and similarities are emphasized and used to build an hypothesis for strobe mechanisms. The first important mechanism is the autocatalysis associated with competing pathways that have been observed in the Belousov-Zhabotinskii type reactions and cool flames. This phenomenon has been applied to model strobe reactions but no experiments have been undertaken to confirm this hypothesis. In our experiments, the formation of gaseous species under the surface layer has been noticed. When they escaped too quickly because of an irregular and molten layer, the strobe effect is less efficient. Chemical reactions occur underneath the surface layer and may be necessary for the production of sharp flashes. It may be that intermediate species are produced using a first pathway (dark phase) and consumed with a second pathway (flash phase). The identification and the measurement of the concentration of those species is required to validate this hypothesis and to know if autocatalysis is involved in this process.

The second important feature is the phenomenon of heat transfer from the reacting zone to the unburned composition. Many similarities have been noticed between the SHS combustion and strobe mechanisms and confirmed by the experiments: the layer by layer burning, the occurrence of hot spots on the molten areas of the surface layer. In SHS combustion, a change of behavior was observed when a parameter related to the thermal conductivity was modified. The mechanism imagined to explain this phenomenon is called the "relay-race" mechanism and is based on the hypothesis that the characteristic reaction time is much smaller than the characteristic reaction of heat transfer to neighboring areas. This results in successive accelerations and decelerations of the velocity propagation front.

The experiments and analysis presented above give more insight into strobe reaction. The thermal conductivity of the composition and the nature of the exothermic reaction (fast / slow) is clearly involved in the oscillatory behavior, but may not be the only parameter responsible for the alternation between dark and flash phase. The gaseous species detected underneath the surface layer imply possible chemical mechanisms such as autocatalysis that are also necessary to produce the oscillatory

behavior.

For the purpose of this thesis, one classical strobe composition was chosen for its good strobe behavior (regular and sharp flashes) and the analysis of its behavior aims at determining if the theories mentioned in this chapter are valid. Chapter 2 introduces the ternary composition made of ammonium perchlorate, magnalium and barium sulfate which is a well-known strobe mixture that shows regular and sharp flashes [126, 134]. A preliminary analysis of this composition allows making first assumptions about the chemistry involved in the oscillatory behavior and also highlights the important parameters that must be studied to understand the strobe mechanisms.

Chapter 3 studies on the influence of physical parameters of the reactants. Several metal sulfates and metal nitrates that have different melting points (from 1157 °K to 1879 °K) were used instead of barium sulfate. Their behavior were analyzed and compared. It appears that compositions containing metal salts (strontium and barium sulfates) with high melting points produced a better strobe effect indicating a noticeable influence of the physical parameters on the strobing effect.

Chapter 4 proposes an experimental method to follow the thermal evolution of a few strobe compositions using light intensity measurements in the near-infrared region. The analysis of the emission spectra using the black-body theory permits the calculation of the temperature. The thermal behavior of a few classical strobe compositions based on the ternary mixture ammonium perchlorate / magnalium / barium sulfate were tested. First, the effect of the change in the heat transfer of the composition was studied. Then barium sulfate was replaced by other metal sulfate that have different melting points. Moreover the experiments was performed in different atmosphere in order to observe if a strobe composition need the oxygen or nitrogen present in the air to proceed.

Chapter 5 reports an experimental verification of a strobe model based on a delicate balance between heat generation and heat transfer to the surroundings. A flash frequency control between 1 and 30 Hz is achieved by varying the size and the weight fraction of magnalium particles. Solving a set of non-linear coupled differential equations quantitatively explains the dependence of flash frequency on the magnalium particle size and weight fraction and enables precise tuning of the flash frequency.

The new insights in strobe reactions that have been obtained in this research mark an important breakthrough in the understanding of strobos. In the final chapter the main conclusions are outlined and an outlook is presented for future research. Better insight in the nature of the various chemical reactions that contribute to the strobe effect and research into alternative (environmentally friendly) strobe compositions are challenges for further research.

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2

Study of a Classical Strobe Composition



ABSTRACT

Many strobe compositions were discovered in the past but only a few have been studied and none of them were fully understood. This chapter describes experiments on the ternary composition of ammonium perchlorate as oxidizer, magnalium as fuel and barium sulfate as metal salt. Parameters that influence the strobe performance are analyzed. First, the binary compositions ammonium perchlorate / magnesium and ammonium perchlorate / magnalium were studied to observe the differences in behavior by using magnalium instead of magnesium. Then, variations were applied to the ternary composition changing the fuel : oxidizer : metal salt ratio. Finally the effect of potassium dichromate was analyzed. It is often added to the composition because it is known to improve the regularity and sharpness of flashes. The burning behavior was recorded using a high speed camera together with emission spectra using a Charged-Coupled Device (CCD) camera coupled with a spectrometer and the temporal evolution of the intensity with a photodiode coupled with an oscilloscope. The results of the experiments give first insights into the physical and chemical mechanisms and give directions to the further studies on strobe reactions.

2.1 INTRODUCTION

Various strobe compositions have been reported in the literature but the physical and chemical mechanisms behind the strobe behavior are not always well understood [1–5]. This chapter is focused on the ternary strobe composition containing ammonium perchlorate as oxidizer, magnalium (50:50 by weight) as fuel and barium sulfate as metal salt. This is common strobe mixture that has shown good strobe behavior [4, 6, 7], see Chapter 1. Magnesium is sometimes used instead of magnalium. The binary composition ammonium perchlorate / magnesium is a well-known propellant [8–10]. The strobe mechanism of the mixture has been studied and the hypothesis was made that the exothermic thermal decomposition of ammonium perchlorate provides heat and oxygen for the oxidation of magnesium. Studies demonstrated a high level of conversion of the metal into oxides [8]. The mixture undergoes a two-stage burning. First the magnesium particles are vaporized and ejected above the combustion surface and then they are oxidized resulting in a luminous zone above the combustion surface [10]. Oscillating combustion was observed only for fuel-lean mixtures. The addition of barium sulfate emphasizes the effect by decreasing the strobe frequency and increasing the light intensity of the flashes. Barium sulfate is often replaced by other metal sulfates (strontium, sodium, calcium, potassium sulfates) and metal nitrates (barium and strontium nitrates). Other compounds are sometimes added such as color enhancers (strontium or barium carbonates) or frequency modulators (copper-chrome oxide, potassium

dichromate) [2, 4].

In the first part of the study the role of magnalium is analyzed by studying the binary compositions ammonium perchlorate / magnalium and ammonium perchlorate / magnesium. In the second part, variations are applied to the ternary composition. The change of the fuel : oxidizer : metal salt ratio influences the frequency, regularity and sharpness of flashes. The results were analyzed as a function of the weight fraction of the different compounds. Finally, the role of potassium dichromate is studied. It is often added to the strobe compositions containing magnesium and ammonium perchlorate in very small quantities in order to coat magnesium particles and prevent any oxidation reaction [4, 5]. Potassium dichromate also seems to have a regulating power on the frequency of flashes and to improve their sharpness. It was hypothesized that this compound decomposes while heating, absorbing a part of the heat released by the strobe reaction thus restraining the increasing rate of the reaction by reducing the production of heat [11]. The combustion of the compositions was investigated using several tools. First, emission spectra were recorded with a CCD (Charged-Coupled Device) camera coupled with a spectrometer. The burning behavior of the different compositions was captured with a high-speed camera. To follow the temporal evolution of the light emission, a photodiode was used in combination with an oscilloscope.

The results of the experiments provide first insights into the strobe mechanisms involved in the ternary strobe composition (ammonium perchlorate, magnalium and barium sulfate). It also highlights some parameters that influence the strobe behavior and require analysis in further studies.

2.2 METHODS AND MATERIALS

2.2.1 Compositions tested

Four types of compositions were tested in three series of experiments. In the series 1, the binary compositions of ammonium perchlorate / magnesium and ammonium perchlorate / magnalium were tested (see Table 2.1). In the series 2, the behavior of the ternary composition ammonium perchlorate/ magnalium / barium sulfate was studied by varying the initial weight percentage of three compounds (see Table 2.2). The fractions of the compounds are varying according to Composition 2.1 (see the gray point on the ternary diagram on Figure 2.1). 5% (by weight) of potassium dichromate was added to all the compositions of the series 2. The series 3 aims at observing the effect of potassium dichromate on the strobe behavior. The ternary composition ammonium perchlorate / magnalium / barium sulfate was tested with and without potassium dichromate (see Table 2.3).

The magnalium used was a 50:50 magnesium - aluminum alloy from ECKA Granules

Table 2.1 – Compositions tested in the series 1 of the experiments.

Compositions	1.1 % by weight	1.2
Ammonium perchlorate	70	70
Magnesium	30	
Magnalium		30

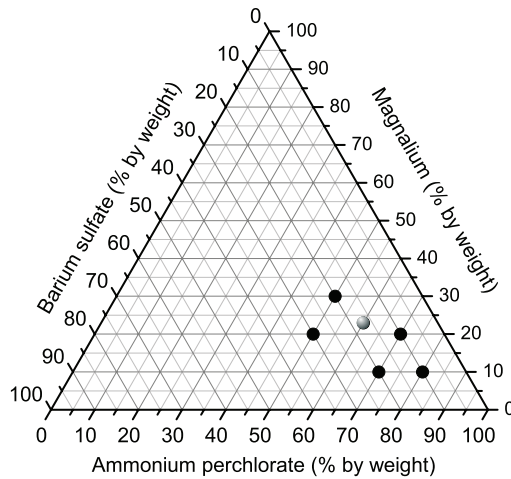


Figure 2.1 – Ternary diagram of Compositions 2.1 to 2.6. The grey point corresponds to the base Composition 2.1. The fraction of ammonium perchlorate is decreased by 10% (Composition 2.2 and 2.3) and then increased by 10% (Compositions 2.4 and 2.5) and by 20% (Composition 2.6). Compositions 2.2 and 2.4 contains more barium sulfate than magnalium while Compositions 2.3 and 2.5 contains more magnalium than barium sulfate. Composition 2.9 contains the same amount of magnalium and barium sulfate.

Table 2.2 – Compositions tested in the series 2 of the experiments.

Compositions	22.1	2.2	2.3	2.4	2.5	2.6
Ammonium perchlorate	57	47.5	47.5	66.5	66.5	76
Magnalium	21.9	19	28.5	9.5	19	9.5
Barium sulfate	16.1	28.5	19	19	9.5	9.5
Potassium dichromate	5	5	5	5	5	5

Table 2.3 – Compositions studied in the series 3 of the experiments.

Compositions	3.1	3.2
	% by weight	
Ammonium perchlorate	57	60
Magnalium	21.9	23
Barium sulfate	16.1	17
Potassium dichromate	5	0

Metal powder Technologies (Austria). Both magnesium and magnalium particle sizes were $\leq 63 \mu\text{m}$. The ammonium perchlorate particle size was $\leq 125 \mu\text{m}$ and the barium sulfate particle size was $\leq 106 \mu\text{m}$. Potassium dichromate was crushed into fine particles.

2.2.2 Equipment

To follow the light emission of strobes and to visualize the processes during the dark and the light phases, movies were recorded with a high-speed camera (IDT vision, series Y4 S3 with a Canon ET 86 lenses for the compositions of the series 1 and Redlake digital imaging system, 5000 frames per second, resolution: 160 x 160 pixels the compositions of the series 2 and 3). The emission spectra of the compositions of series 1 were recorded with a CCD (Charged-Coupled Device) camera (PIXIS System from Princeton Instrument, 1340 x 100 pixels) coupled with a spectrometer (Princeton Instrument - Acton advanced SP2750A, 0.750 m focal length, imaging triple grating monochromator). The emission spectra of the compositions of the series 2 were recorded in the Fraunhofer Institute for Chemical Technologies ICT (Germany) with a UV/VIS grating imaging spectrometer (Andor Shamrock A-SR500i B2) coupled with a Si-CCD-camera (Andor CCD DU920P-UV-BR-DD, 256 x 1024 pixels) [12].

The temporal evolution of the light intensity was recorded using a photodiode (Roithner Lasertechnik GmbH). Since the compositions tested have strong emission lines between 480 and 530 nm (due to barium chloride, magnesium oxide and magnesium atoms), a photodiode sensitive in the green spectral region (centered at 525 nm) was chosen. It was used in combination with an oscilloscope (Sigma 30 from Nicolet Technologies). The resolution was varied from 1×10^{-6} to 5×10^{-4} s depending on the frequency of flashes.

2.2.3 Methods

10 g of each composition was prepared, including a binder solution composed of 10% nitrocellulose and 90% acetone. After mixing, the compositions were pressed

(100 bars) into pellet of 1.5g (including acetone) and then dried into a vacuum oven during two hours so the final weight of the pellet is about 1.26 g. The diameter is 0.99 cm and the average height of the pellet is 0.917 cm which gives a density of 1.79 g/cm^3 . The pellet was placed on a metal plate and then ignited with a burner. All tests were conducted in triplo.

2.3 RESULTS AND DISCUSSION

2.3.1 Series 1: Comparison of the binary composition with magnesium or magalium

The high speed camera movies reveal details on the process involved in the strobe Compositions 1.1 and 1.2. Figure 2.2 shows the evolution of the pellet while a few flashes occur in Composition 1.2. The same images are observed for Composition 1.1 except that the intervals between flashes are shorter meaning that the frequency of flashes may be high so the pixels of the camera are most of the time overloaded making it difficult to observe the surface combustion during the flash phases. For both compositions, the surface is heated up by a reaction and partly melts. A foam forms on the top of the composition. It is possible to observe gaseous species escaping from this foam. While the strobe reaction proceeds producing more gasses, the layer on top of the composition melts indicating that more heat is produced giving rise to a higher combustion temperature and increasing the reaction rate. At a certain temperature, the reaction accelerates so much that the entire layer is converted into gaseous species and a flash of light is observed also from electronically excited molecular species which are formed in the flash reaction (*vide infra*). They are responsible for the bright flash light.

Table 2.4 – Mean time intervals and mean frequencies of the Compositions 1.1 and 1.2. The mean time interval is calculated by averaging the mean time intervals over three measurements. The frequencies are obtained in the same way.

Compositions	Mean time intervals (s)	Standard deviations (s)	Mean frequencies (Hz)	Standard deviations (s)
1.1	0.014	0,001	72.5	6.0
1.2	0.021	0,002	47.1	3,8

The analysis of the data recorded with photodiode is summarized in Table 2.4. Temporal evolution of the light intensity recorded with the photodiode for Compositions 1.1 and 1.2 are shown in Figure 2.3. The results confirm that the flash frequency of Composition 1.1 is higher than Composition 1.2. The increase and decrease of the intensity of the flashes of Composition 1.1 can hardly be observed on the left graph of Figure 2.3. Either the time resolution of the oscilloscope is not high enough or the flashes produced by the composition are not sharp.

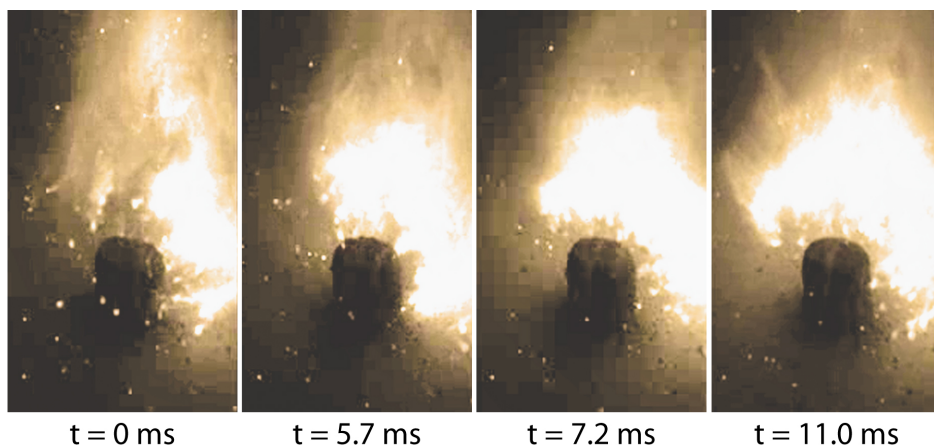


Figure 2.2 – Collection of images recorded with a high speed camera. It shows the development of a few phase during the combustion of Composition 1.2.

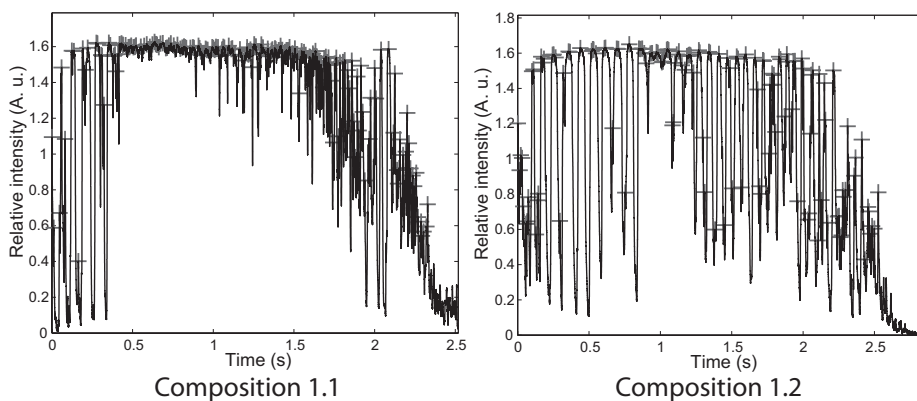


Figure 2.3 – Temporal evolution of the light intensity of the Compositions 1.1 and 1.2 recorded with a photodiode sensitive to the green spectral region.

The temporal evolution of the time intervals of the two compositions is shown in Figure 2.4. It is an indicator of the regularity of flashes: if the flashes are regular, the time intervals between two successive flashes must be constant. The graphs show that for both compositions the flashes are not regular or sharp.

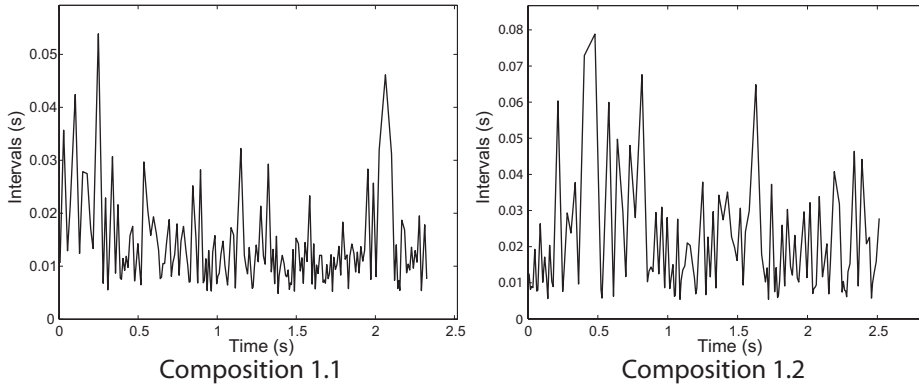


Figure 2.4 – Evolution of the time intervals between two successive flashes for Compositions 1.1 and 1.2.

The emission spectra of Compositions 1.1 and 1.2 are shown in Figure 2.5. On both overview spectra (1 and 4) the sodium emission lines are observed at 589.14 and 589.75 nm. Even though no sodium was added intentionally the lines show up, probably due to trace amounts of sodium in the starting materials. The 589 nm orange sodium emission is very efficient and is easily observed in the presence of small amounts of sodium [13]. A structured emission band between 490 and 500 nm is observed for both compositions (maxima at 492.54, 493.66, 494.97, 496.26, 497.50, 498.64, 499.68 and 500.76 nm).

The lines are assigned to emission from molecular magnesium oxide showing vibronic structure in emission [14]. It implies that the magnesium is oxidized in both compositions and during the flash magnesium oxide is formed in the excited state. Three sharp lines are also observed in both spectra at 588.16, 517.43 and 518.52 nm and are assigned to emission from the excitation of magnesium atoms [13]. In the spectrum 5 of Composition 1.2, weak molecular bands are observed at 484.32 and 486.79 nm and are assigned to the emission from aluminum oxide molecules. This indicates that, in Composition 1.2, the magnesium first decomposes and then magnesium and aluminum are oxidized. Moreover, the compositions have been tested in an argon atmosphere and the effect is still observed so the oxygen molecules needed for the oxidation of magnesium and aluminum can be supplied by the decomposition of ammonium perchlorate.

The experiments undertaken give confirmation for the hypothesis described in the introduction [8, 10]. The decomposition of ammonium perchlorate provides the oxygen and heat to evaporate and then oxidize the magnesium. The heat generated by both the decomposition of ammonium perchlorate and oxidation of magnesium increases the reaction rate causing an avalanche of reactions that result in a bright flash due to the highly exothermic reaction between gaseous species resulting in

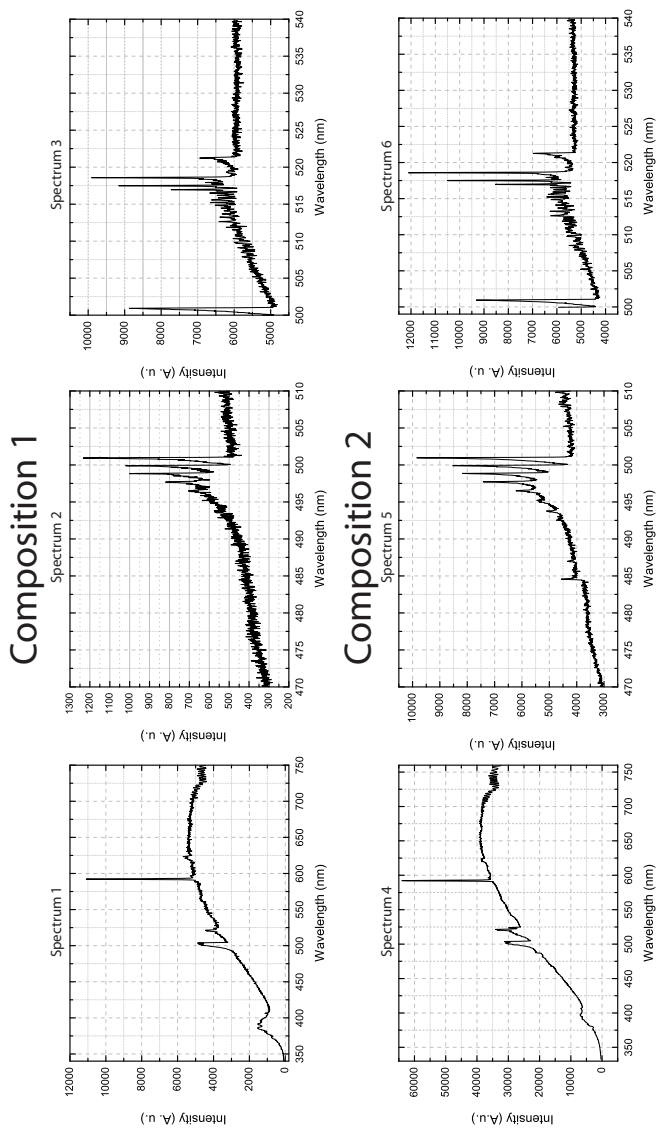


Figure 2.5 – Emission spectra of Compositions 1.1 and 1.2 recorded with a CCD camera coupled with a spectrometer. Spectra 1 and 4 show an overview of the visible area from 350 to 750 nm. The spectra 2 / 3 and 5 / 6 show the spectra range between 470 to 510 nm and 500 to 540 nm in more detail.

the formation of reaction products in the excited state, such as magnesium oxide, and black body radiation. The oscillatory combustion implies that the oxidation of magnesium in the gas phase is a faster process than evaporation. When all the gaseous magnesium has reacted, the reaction rate decreases until more reactants are supplied. The strobing effect appears with compositions containing either magnesium or magnalium implying that only the reactions between magnesium and decomposition products of ammonium perchlorate are responsible for the intermittent burning. Indeed, a composition containing only ammonium perchlorate and aluminum does not produce a strobing effect. The use of magnalium instead of magnesium increases the time intervals between two successive flashes thus decreasing the frequency. This indicates that aluminum slows down the reaction possibly due to the fact that the magnalium particles must first decompose into magnesium and aluminum atoms before the oxidation reactions can occur. This may absorb part of the heat produced by the strobe reaction. Consequently, the reactive layer (foam) that forms on the top of the composition needs more time to reach the temperature and concentration of species required to proceed to the flash phase.

2.3.2 Series 2: Strobe behavior of the ternary composition ammonium perchlorate / magnalium / barium sulfate

To study the influence of the composition on the strobe behavior, the oscillatory combustion of the well-known ternary composition ammonium perchlorate / magnalium / barium sulfate was followed using a high speed camera for a variety of compositions. The images recorded are shown in Figure 2.6. The formation of a layer, that is partly melted, on the top of the pellet is observed, just as for Compositions 1.1 and 1.2. This foam is heated up by a reaction. Then, it is entirely consumed by a flash that develops above the surface combustion and ignites the next layer. The cycle repeats itself until the whole pellet has been consumed. Contrary to Compositions 1.1 and 1.2, the layers formed become red during the heating period. This is probably because the time intervals between the flashes are longer i.e. more heat is accumulated in the top layer. White hot spots develop on the surface and sometimes parts of the layers are ejected indicating the formation and rapid expansion of gas below the surface, just as for Compositions 1.1 and 1.2. The thickness, shape and consistency of the layers formed depend on the fuel : oxidizer : metal salt ratio. A qualitative analysis of the movies also shows differences in frequency, regularity and sharpness of the flashes produced for the different compositions and is confirmed by the measurements on the time dependence of the emission intensity using the photodiodes (see Table 2.5 and Figures 2.7 and 2.8).

The first observation is that all the compositions have lower strobe frequencies than

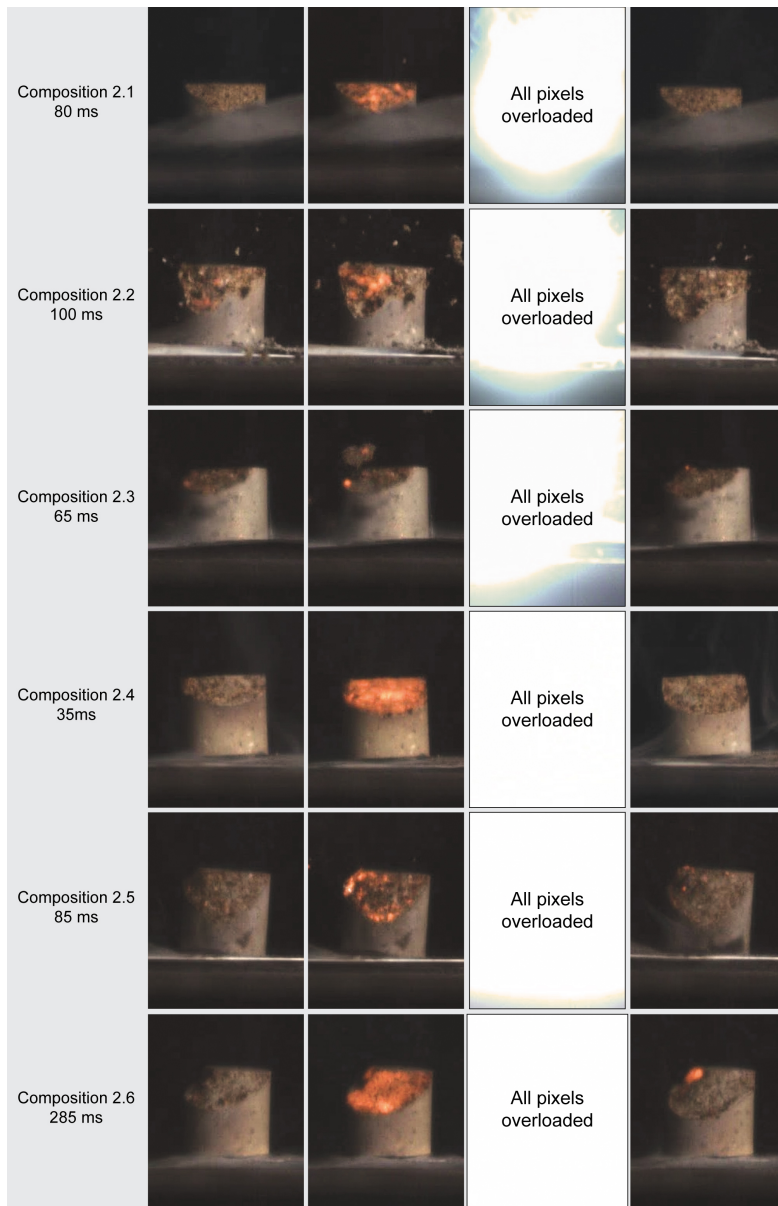


Figure 2.6 – Collection of images recorded with a high speed camera. It shows one flash phase for each compositions of the series 2. The time indicating for each series corresponds to the average time needed for the development of one flash.

Table 2.5 – Mean time intervals and mean frequencies of Compositions 2.1 to 2.6. The mean time interval is calculated by averaging the mean time interval over three measurements. The frequencies are obtained by the same way.

Compositions	Mean time intervals (s)	Standard deviations (s)	Mean frequencies (Hz)	Standard deviations (Hz)
2.1	0.080	0,011	12.6	1,7
2.2	0.108	0,029	9.8	2,6
2.3	0.065	0,304	15.5	0,5
2.4	0.344	0,179	3.4	1,2
2.5	0.086	0,012	11.9	1,7
2.6	0.284	0,065	3.7	0,8

the binary compositions ammonium perchlorate / magnesium or magnalium. The addition of barium sulfate to the composition decreases the time intervals between the flashes and also leads to the formation of more solid layers on the surface combustion. Two reasons may explain this phenomenon. First barium sulfate has a high melting point in comparison to the other compounds so its melting may absorb a large amount of heat restraining the steep rise of the reaction rate. The second reason is that barium sulfate may decompose at high temperature and this may also absorb part of the heat produced. Then, for most of the compositions (2.1, 2.4, 2.5 and 2.6), the layers formed remains attached to the pellet and the red color becomes brighter until the flash. occurs. Their shapes are regular and the pellet is consumed linearly. On the contrary, Compositions 2.2 and 2.3 produce a lot of flying particles of small (less than 1 mm as observed for Composition 2.2 in Figure 2.6) and medium (between 1 and 5 mm as observed for Composition 2.3 Figure 2.6) sizes. As a result, the difference of intensities between flashes is higher. Compositions 2.2 and 2.3 have a lower fraction of ammonium perchlorate. This compound appears to assist in producing regular layers improving the strobe effect.

The layers formed on Compositions 2.4 and 2.6 are very thick and remain attached to the pellet until the flash. Almost no flying particles are observed (see Figure 2.6). The two compositions also have the lowest frequency of flashes and are the less regular (see Figures 2.7 and 2.8). The fractions of magnalium are lower in Compositions 2.4 and 2.6. On the contrary, the composition that contains a higher magnalium fraction (Composition 2.3) appears to be faster and the flashes are produced more regularly. Moreover, for the same amount of ammonium perchlorate (Compositions 2.2 and 2.3 and Compositions 2.4 and 2.5), the compositions that have a higher fraction of magnalium (Compositions 2.3 and 2.5) have the higher frequency. Consequently, an increase of the fuel fraction leads to a rise of the flash frequency.

A careful balance of the compounds is necessary to achieve the best strobe effect.

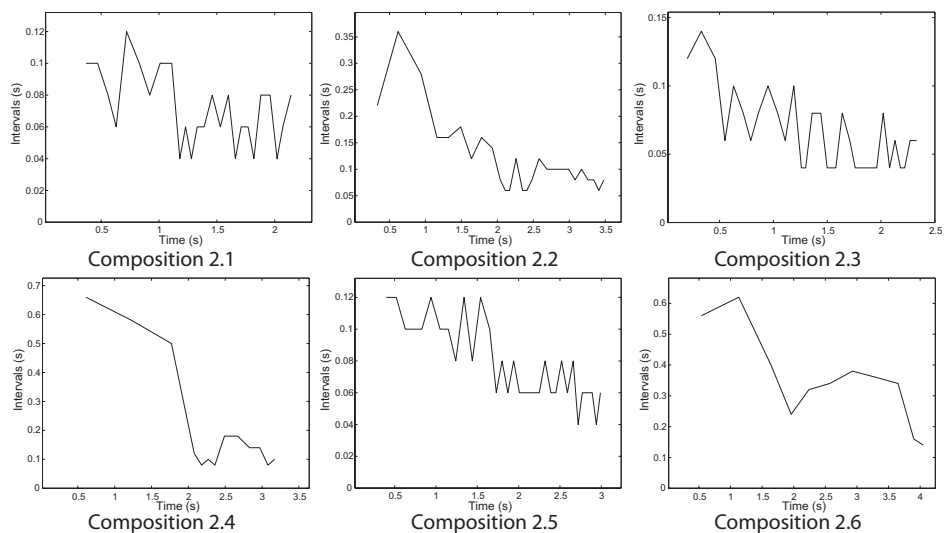


Figure 2.7 – Temporal evolution of the light intensity of Compositions 2.1 to 2.6 recorded with a photodiode sensitive to the green spectral region.

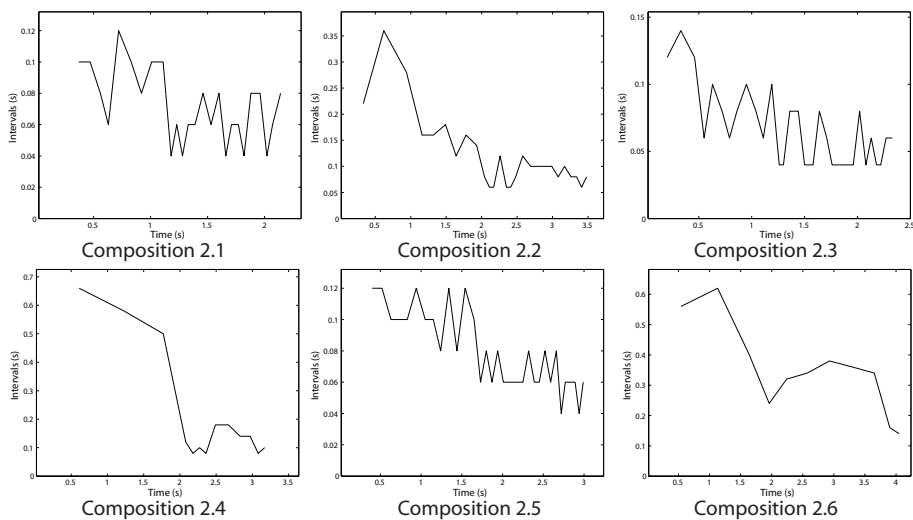


Figure 2.8 – Evolution of the time intervals between two successive flashes for compositions of Series 2.

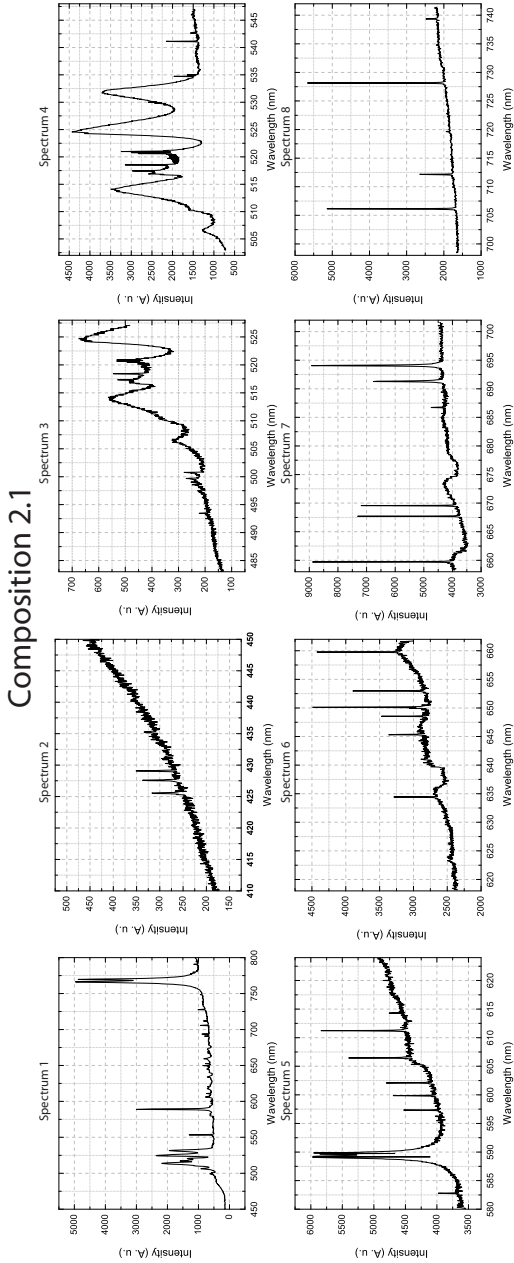


Figure 2.9 – Emission spectra of Composition 2.1 recorded with a CCD camera coupled with a spectrometer. Spectra 1 and 2 show an overview in the visible area from 300 to 650 nm and from 400 to 750 nm, respectively. Spectra 3, 4, 5, 6, 7 and 8 show specific areas in the visible in more detail.

The images and graphs obtained with the high speed camera and the photodiode provide insight into the strobe mechanisms. The analysis of the spectra gives complementary information on the chemical reactions involved. The emission spectra recorded for the Compositions 2.1 to 2.6 were identical except in intensity: the same emission lines were observed. Consequently, only the spectra of Composition 2.1 are presented in this chapter (see Figure 2.9). As noticed in Composition 1.2, the magnesium and aluminum oxide emission bands are observed between 495 and 500 nm and 465 and 470 nm, respectively, in spectrum 3 of the Figure 2.9. The sodium doublet emission also appears in spectrum 1 and spectrum 5 (detailed view), as a result of trace amount in the composition. Two other doublets were identified at 691.29 and 694.06 nm and 766.49 and 769.90 nm. They are assigned to emission lines of potassium atoms [13], probably due to the decomposition of potassium dichromate initially present in the composition. Many other sharp atomic emission lines are observed and arise from the formation of excited chromium and barium atoms during the flash phase. Chromium lines appears in the spectra 2, 3 and 4 at 425.53 nm, 427.48 nm, 429.08 nm, 520.60 nm, 520.77 nm, 520.844 nm, 534.73, 534.97 nm, 541.09 nm [13]. Barium lines are observed in spectra 4, 5, 6, 7 and 8 at 553.71 nm, 597.33 nm, 599.86 nm, 602.08 nm, 606.44 nm, 614.30 nm, 634.41 nm, 645.31 nm, 648.54 nm, 650.11 nm, 652.95 nm, 659.77 nm, 667.70 nm, 669.57 nm, 686.73 nm, 706.14 nm, 712.13 nm, 719.66 nm, 728.13 nm and 739.35 nm [13]. Additionally molecular emission bands are observed between 500 and 530 nm (in spectra 3 and 4) with maxima at 506.6 nm, 513.6 nm, 524.56 nm, 531.80 nm. They are assigned to the emission of the barium chloride molecule and give the green color to the flashes [14].

The series 2 provides more information on the mechanisms involved in the ternary composition. The melting / decomposition of magnalium followed by the oxidation of magnesium and aluminum proposed to be the main process driving the strobe effect. The oxygen is supplied by the decomposition of ammonium perchlorate. The addition a barium sulfate improves the strobe effect by producing more regular and sharp flashes and it also decreases the frequency. This can be explained first by the absorption of part the heat by the decomposition of the barium sulfate restraining the increasing reaction rate. The second explanation is that barium has a high melting point (1650 K) and so more heat is required to melt it and thus preventing the layer from melting too quickly so the gas responsible for the flashes remains captured under the surface. It escapes only when the pressure is high enough to break the layer. The last observation is that the frequency depends on the weight fraction of the fuel (magnalium). Changing the fuel fraction influences the concentration of all reactants changes the kinetics. The fuel fraction also influences the heat transfer in the composition so more magnalium can speed up the ignition of the subsequent layers in the composition.

The decomposition of barium sulfate affects the strobe behavior by influencing the frequency, regularity and sharpness of flashes. Potassium dichromate probably has the same effect but a smaller amount of this compound is needed to influence the strobe effect.

2.3.3 Series 3: Investigation of the role of the potassium dichromate

Potassium dichromate is commonly added to the strobe compositions to control the frequency of flashes. The images recorded with the high speed camera in Figure 2.10 show that without potassium dichromate the layer formed on the surface combustion is less homogeneous and looks different from the surface for Composition 3.1: it does not become incandescent and seems to contain more melted materials in certain part leading to more heterogeneity and hot spots in the layer. For instance, two flashes can be produced in the same layer but in different areas of the surface (from two flash sites). It results in two flashes with a small time interval between them which explains the irregularity of flashes and also that they are not as sharp as the flashes observed for the composition with potassium dichromate. The time dependence of the intensity recorded with the photodiode (see Figures 2.11 and 2.12) confirms that the sharpness and regularity of flashes is better in the composition containing potassium dichromate (Composition 3.1). As a result the addition of potassium dichromate decreases the frequency of flashes (see Table 2.6). This phenomenon has been explained by the fact that potassium dichromate decomposes absorbing a large amount of heat and thus restraining the increasing rate of reaction [11].

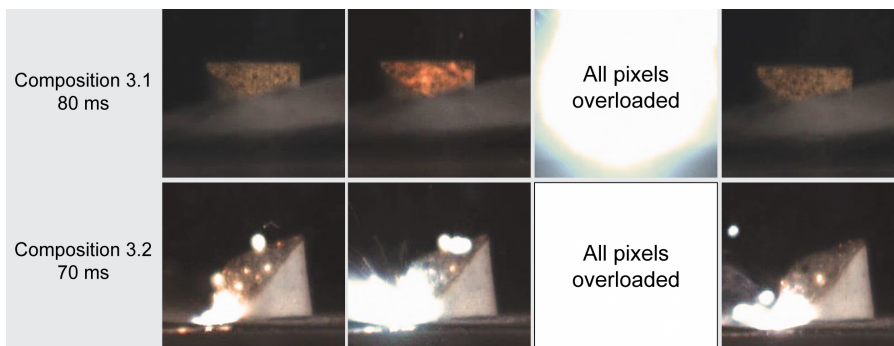


Figure 2.10 – Collection of images recorded with a high speed camera. It shows one flash of Compositions 3.1 and 3.2 with (3.1) and without (3.2) potassium dichromate. The time indicating for each composition corresponds to the mean time needed for the development of one flash.

Table 2.6 – Mean time intervals and mean frequencies of Compositions 3.1 and 3.2. The mean time interval is calculated by averaging the mean time interval over three measurements. The frequencies are obtained by the same way.

Compositions	Mean time intervals (s)	Standard deviations (s)	Mean frequencies (Hz)	Standard deviations (Hz)
3.1	0.080	0.011	12.6	1,7
3.2	0.068	0.007	14.8	1,3

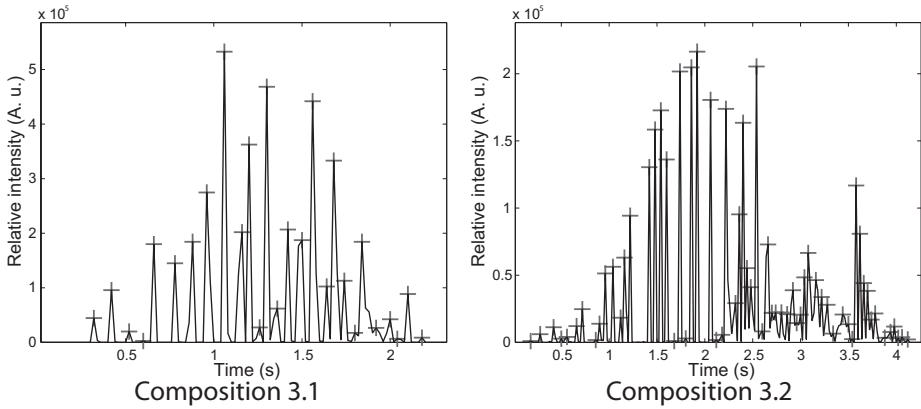


Figure 2.11 – Temporal evolution of the light intensity of Compositions 3.1 and 3.2 recorded with a photodiode sensitive to the green spectral region.

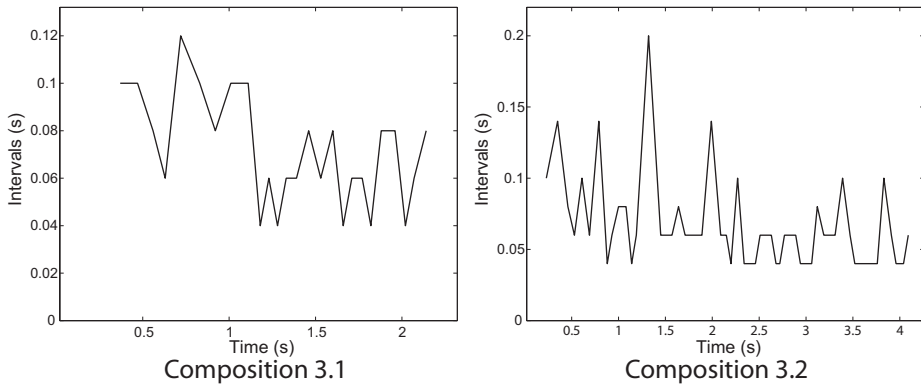


Figure 2.12 – Evolution of the time intervals between two successive flashes for compositions of Series 3.

2.4 CONCLUSION

The study of the ternary composition ammonium perchlorate, magnalium and barium sulfate shows that a careful adjustment of the mixture is necessary to produce a good strobe effect and insight is obtained in factors that influence the frequency and regularity of the strobe behavior. In all compositions, the images recorded with the high speed camera show that there is the formation of foam on the surface of the pellet. Gaseous species are produced underneath the top layer and pressure builds up. As the layer breaks, sometimes resulting in flying particles as gaseous species are released and the combustion is responsible for the flash phase.

The experiments performed indicate that the oscillating behavior is driven by the decomposition of ammonium perchlorate and evaporation / oxidation of magnesium. The use of magnalium instead of magnesium and the addition of barium sulfate and potassium dichromate to the binary composition enhance the strobe effect by improving the regularity and sharpness of flashes. It also decreases the frequency while increasing the intensity of flashes.

Several parameters influencing the strobe behavior are highlighted such as the melting point of the compounds. The addition of a high melting point barium sulfate makes the top layer formed more solid and thus improves the strobe effect. This parameter is studied in Chapter 3. The magnalium fraction influences the flash frequency: a higher magnalium content leads to faster strobes. The parameter is linked to the stoichiometry of the system but also to the heat transfer of the system and needs to be investigated further. This parameter is investigated in Chapter 4. Finally, the addition of a small amount of potassium dichromate is observed to have a strong influence on the strobe behavior.

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3

The Use of Metal Sulfates and Nitrates in Strobe Compositions



ABSTRACT

The ternary composition of ammonium perchlorate / magnalium / barium sulfate was analyzed in Chapter 2 and the influence of barium sulfate on the strobe effect was highlighted. It was shown that compositions containing barium sulfate produce sharper, more regular and intense flashes. It also decreases the flash frequency. The hypothesis proposed is that the high melting point barium sulfate helps forming more solid foams. The gaseous species produced during the process responsible for the flashes remain captured under the surface combustion for a longer time. As their concentration increases, pressure builds. Then, when the pressure is sufficient to break the layer the gasses are released at once which could explain the more regular and sharper flashes. The role of barium sulfate is studied in this chapter in more detail by replacing it by other metal salts (sulfates or nitrates) that have different melting points. Experimental results show noticeable differences in the physical and chemical processes involved in the strobe reactions.

3.1 INTRODUCTION

Metal nitrates are found in many pyrotechnics formula such as color compositions. They act as both color and oxidizing agents. Whereas the use of sulfate in pyrotechnics is mostly limited to strobe compositions, in particular, barium and strontium sulfates. The ternary mixture of ammonium perchlorate / magnalium / barium sulfate is a well-known strobe that usually shows sharp and regular flashes [1–3]. This classical composition was studied in Chapter 2. It was emphasized that the strobe effect seemed to be driven by the decomposition of ammonium perchlorate and the evaporation / oxidation of magnesium. However, the use of magnalium instead of magnesium or the variation of the fuel fraction or the addition of barium sulfate or potassium dichromate all have a noticeable influence on the frequency, regularity and sharpness of flashes. The most obvious effect of barium sulfate is that the foams formed on the surface on the strobe are more solid. They remain unbroken and attached to the pellet (few flying particles) for longer time than compositions containing less or no barium sulfate. The hypothesis stated to explain this phenomenon was that barium sulfate has a high melting point restraining the foam that forms on the surface combustion to melt too quickly. Gaseous species are produced below this foam and their excitations are responsible for the flash. Therefore, if the foam is solid enough, their concentrations increase causing a rise of the pressure under the surface. Eventually, the foam breaks and the gaseous species are all released at once and not they do not escape erratically producing more than one flashes from one layer. Consequently the flashes produced are sharper more regular. Haarmann [4] even suggested that the flashes were triggered by the temperature of the composition reaching the melting point of the

sulfate used. The foam formed on the surface combustion is then entirely melted. Besides, it was shown in the previous chapter that barium sulfate decomposes during the strobe reactions. This could also affect the frequency.

In this chapter, the role of barium sulfate is investigated. To observe the influence of the melting point on the strobe behavior, barium sulfate was replaced by other metal sulfates (strontium, calcium, potassium and sodium) and metal nitrates (barium and strontium) that have a different melting point. The results were recorded with a CCD camera coupled with a spectrometer and a high-speed camera. The comparison of the results of the metal sulfate and nitrate compositions aimed at studying the influence of the melting point of the compound on the strobe effect.

3.2 METHODS AND MATERIALS

3.2.1 Equipment

To capture the light emission of the strobes and to visualize the processes during the dark and the light phases, high-speed camera images were recorded with a High-Speed camera (Redlake digital imaging system, 5000 frames per second, resolution: 160 x 160 pixels). The emission spectra were recorded with a CCD camera (PIXIS System from Princeton Instruments, 1340 x 100 pixels) coupled with a spectrometer (Princeton Instruments - Acton advanced SP2750A, 0.750 m focal length, imaging triple grating monochromator).

3.2.2 Compositions

The composition studied is a mixture of ammonium perchlorate, magnalium and a metal salt (sulfates or nitrates - see Table 3.1). Potassium dichromate is added as a frequency modulator; it improves the sharpness and the regularity of the flashes [2]. Finally, a solution of 10% nitrocellulose in acetone is added as binder.

Table 3.1 – Base composition of strobes used for this study.

Composition (% by weight)					
Ammonium perchlorate	60.0	57.1	47.6		
Magnalium	23.0	21.9	18.2		
Barium sulfate	17.0	16.2	13.5		
Potassium dichromate	5.0 (additional)	4.8	4.0		
Binder	Nitrocellulose	20.0 (additional)	20.0 (additional)	16.7	1.7
	Acetone				15.0

Metal sulfates and nitrates were chosen because the metals themselves are in various forms commonly used in pyrotechnics. The metal sulfates and nitrates used differ in melting point. The metal salts with their melting temperatures used are described in Table 3.2.

Table 3.2 – Metal sulfates used.

Metal salts	Compositions	Molecular Formula	Melting points
Strontium sulfate	1	SrSO_4	1879 K (1606°C)
Barium sulfate	2	BaSO_4	1853 K (1580°C)
Calcium sulfate	3	CaSO_4	1733 K (1460°C)
Potassium sulfate	4	K_2SO_4	1342 K (1069°C)
Sodium sulfate	5	Na_2SO_4	1157 K (884°C)
Barium nitrate	6	$\text{Ba}(\text{NO}_3)_2$	865 K (592°C)
Strontium nitrate	7	$\text{Sr}(\text{NO}_3)_2$	843 K (570°C)

3.2.3 Methods

10 g of each composition was prepared, including a binder solution composed of 10% (by weight) nitrocellulose and 90% acetone. After mixing, the compositions were pressed (100 bars) into pellets of 1.5 g (including acetone) and then dried in a vacuum oven during two hours giving a final weight of the pellet of about 1.26 g. The diameter is 0.99 cm and the average height of the pellets is 0.917 cm i.e. the average density is 1.79 g/cm³. The pellet was placed on a metal plate and then ignited with a burner. All tests were performed in duplo.

3.3 RESULTS AND DISCUSSION

It has been claimed that a flash occurs when the metal sulfate reaches its melting point [4]. The present experiments are aimed at investigating this effect systematically. The influence of the melting point of the sulfates used on the performance of the strobe (appearance of surface combustion, sharpness and regularity of the flashes) was studied using high-speed camera images. Also, comparisons between the combustion products present during the flash were made based on the emission spectra recorded.

3.3.1 Analysis of the high-speed camera images

Figure 3.1 shows typical images recorded during a flash for the strontium and barium sulfate compositions (Composition 1 and 2). Similar phenomena are observed. The cycle starts when the pellet is ignited and a hot layer appears on

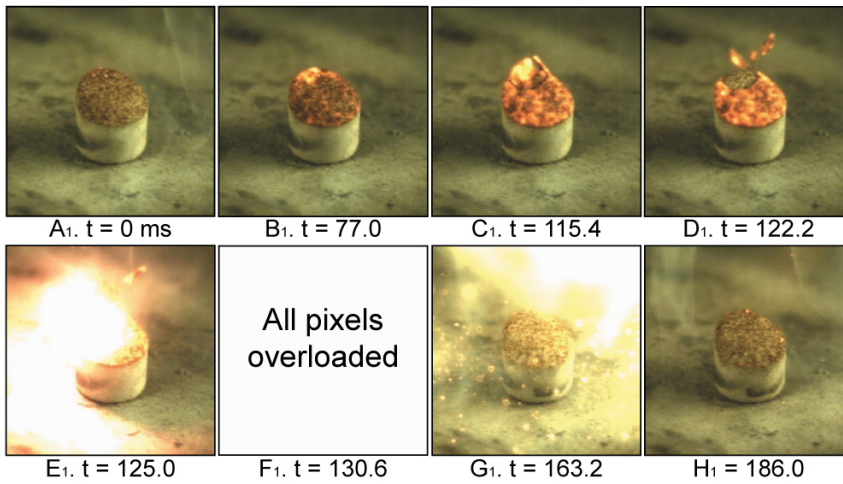
top of the pellet. This phenomenon was also observed by Krone and Shimizu who called this layer the "semi-slag" and the "semi-reacted zone" [2, 5, 6] respectively. Then, the layer propagates perpendicularly to surface of the pellet and becomes thicker. The surface is heated up by a reaction as it clearly becomes red. Sometimes small parts of this layer are ejected from the pellet (see picture $t = 122.2$ ms of Composition 1 in Figure 3.1). Then, a short flash completely consumes the layer and initiates the next cycle. The pellet is consumed linearly, layer-by-layer. Same phenomena are observed for the barium and strontium nitrates based compositions (Compositions 6 and 7 in Figure 3.3, respectively). However the layers formed on the top of the pellet are thinner and more melted (bubbling surface) Still their shape is regular and the complete layer is made of the same foam. Also, the dark phase seems shorter and the intensity of flashes lower which can be explained by the fact that very often one layer formed resulted in two successive flashes ignited from different side of the layer. In contrast, the layers produced on top of the potassium and sodium sulfate based compositions (Compositions 4 and 5 in Figure 3.2, respectively) are composed of different zones, seemingly containing molten material and sometimes foam appears at the surface (see Composition 5 at $t = 448.8$ ms in Figure 3.2). The color of the layers is not uniform and their shapes are irregular; the top of the pellet is not consumed linearly but small holes are created on the surface each time a flash occurs. For the sodium sulfate composition (Composition 5), the dark periods are longer, more material is consumed to create one layer, fewer flashes are produced from one pellet, but they are more intense. The layer produced in the calcium sulfate composition (Composition 3) is different than the other two groups of compositions (see Composition 3 in Figure 3.2). It has an irregular shape and the pellet is not consumed linearly as in the case of the strontium and barium sulfate compositions and many small flying particles are observed. However, the layer produced is more solid than for the sodium and potassium sulfate compositions.

During the dark phase, hot spots can be observed on the surface of the layer (see the picture C_2 at $t = 95.0$ ms of Composition 2 in Figure 3.1). They occur and grow while the reaction proceeds. Shimizu [7] also observed this phenomenon. Those hot spots are the result of local heat accumulation in the layer and they can evolve into small local flashes. Grose [8] hypothesizes that hot spots occur on the molten part of the dark layer consuming those zones by a small flash. It indicates that the layer is partly molten in all compositions and the flashes are probably initiated from those molten areas.

In addition, two other phenomena were observed: the occurrence of foam on the layer (see Compositions 4 and 5 in Figure 3.1 and Compositions 6 and 7 in Figure 3.3) and particles that fly away from the surface of the pellet (see the picture D_1 at $t = 122.2$ ms of Composition 1 in Figure 3.1 and D_3 at $t = 187.1$ ms of

Composition 3 in Figure 3.2). Gaseous species may form under the surface during the dark phase. When the layer melts, the gas escapes through the layer. On the other hand, when the surface remains solid, pressure builds up under the surface and the gas escapes by ejecting parts of the layer or the entire layer.

Composition 1



Composition 2

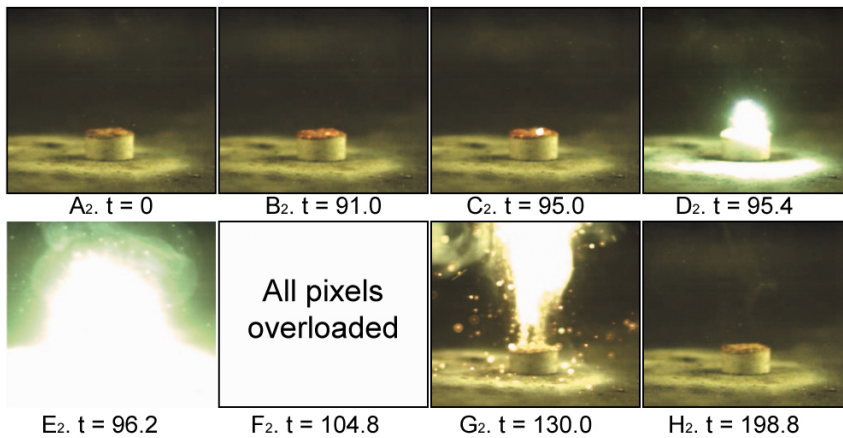
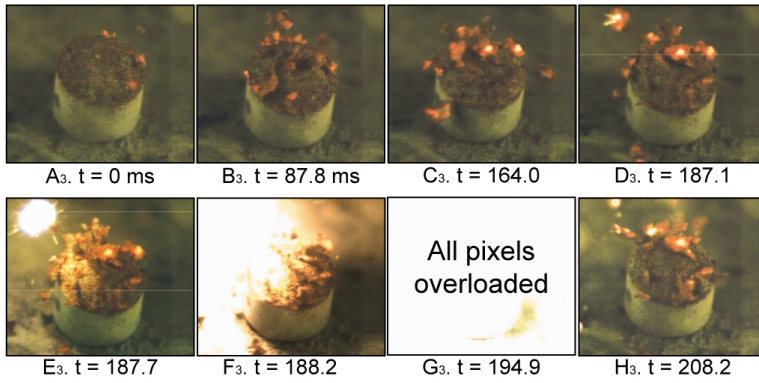
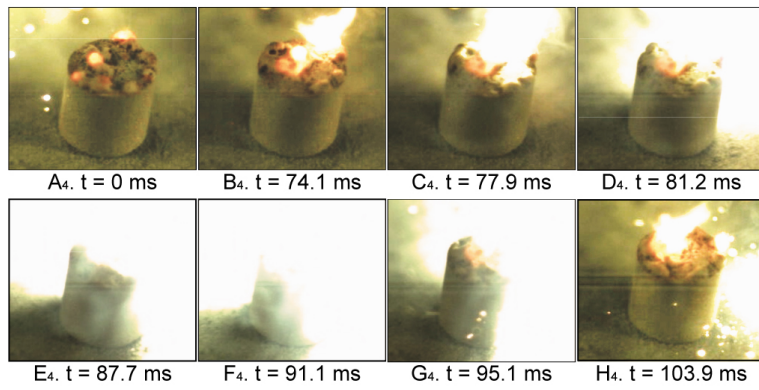


Figure 3.1 – Collection of picture showing one flash cycle of Compositions 1 and 2 containing strontium and barium sulfates, respectively.

Composition 3



Composition 4



Composition 5

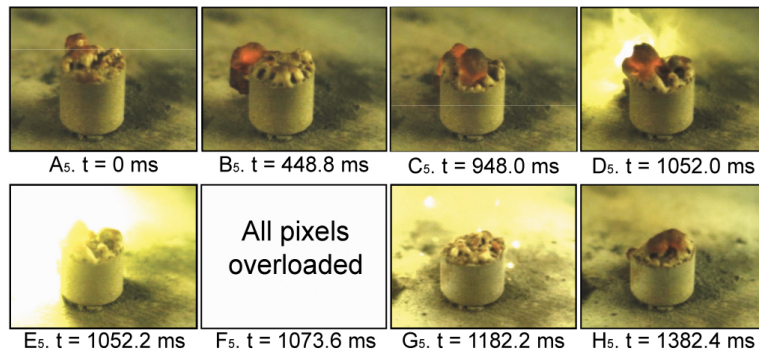


Figure 3.2 – Collection of picture showing one flash cycle of Compositions 3 to 5 containing calcium, potassium and sodium sulfates, respectively.

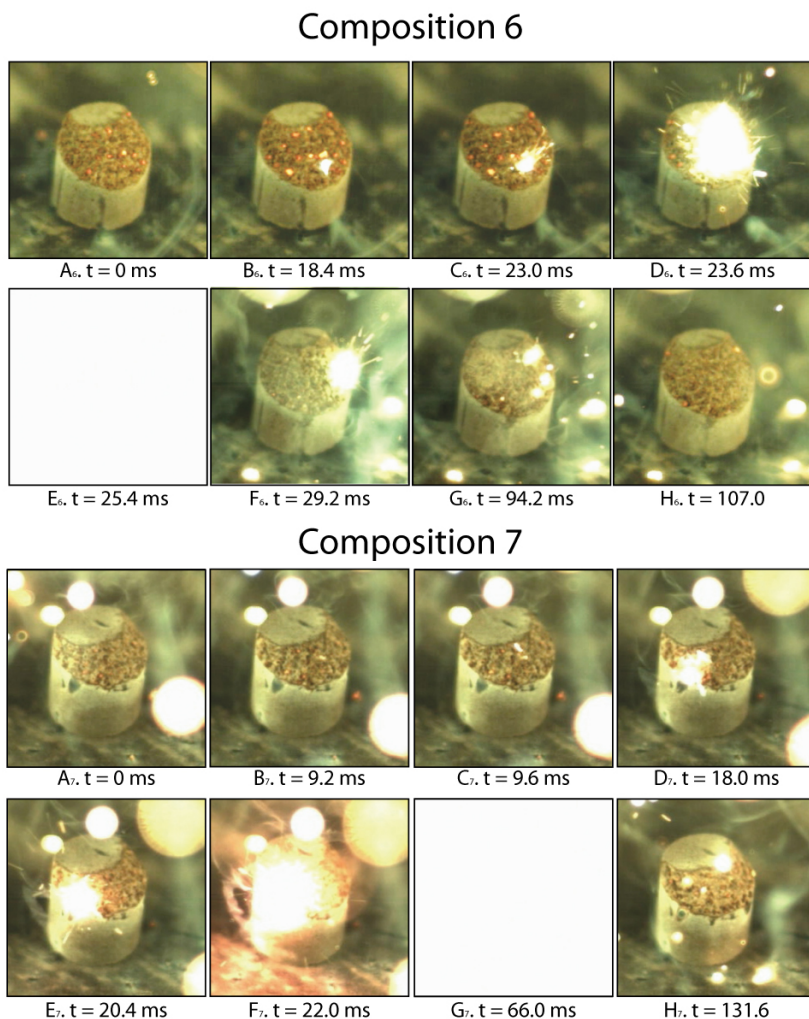


Figure 3.3 – Collection of picture showing one flash cycle of Compositions 6 and 7 containing strontium and barium nitrates, respectively.

A general observation of the high-speed camera images is that the barium and the strontium sulfate based compositions (Compositions 1 and 2) give rise to a good strobe behavior while the other compositions produce very irregular and/or longer lasting flashes. This suggests that processes during the formation of the dark layer are important for strobe reactions. It must be homogeneous and cover

the entire surface. Then, the layer is heated up homogeneously until it reaches a triggering point for the flash phase. Subsequently, the flash occurs and the next cycle starts. The presence of molten materials is important since the flashes and hot spots seem to be initiated from molten areas. However, if the compounds melt at too low temperatures, several flashes are initiated from the same layer, degrading the strobe effect while too many hot spots occur inhibiting a full flash. The layer formed is irregular and "moving" (formation of foam) when the gaseous species formed under the layer escape before the occurrence of a flash. The heat produced by the dark reaction is dissipated too quickly to ignite the flash reaction and either more material is necessary to accumulate enough heat for a full flash, resulting in a low flash frequency for, for instance, the sodium sulfate composition (Composition 5). On the other hand, the heat produced can also be distributed irregularly producing many hot spots and weak successive flashes as observed for the potassium sulfate composition (Composition 4 in Figure 3.2) and the barium and strontium nitrate based compositions (see Compositions 6 and 7 Figure 3.3).

To conclude, the barium and the strontium sulfate based compositions produce a better strobe effect which is attributed to the higher melting points of strontium and barium sulfates. It is important to maintain a solid dark layer favoring a homogeneous accumulation of heat and also of gaseous species that form under the surface. These two phenomena may be necessary for the occurrence of a flash. The temperature must be high enough to ignite the flash but a specific concentration of gaseous species may also be essential to the manifestation of sharp flashes. The different behaviors observed (sharpness and regularity of flashes, gaseous species) are investigated further using the CCD camera and the spectrometer.

3.3.2 Analysis of the spectra

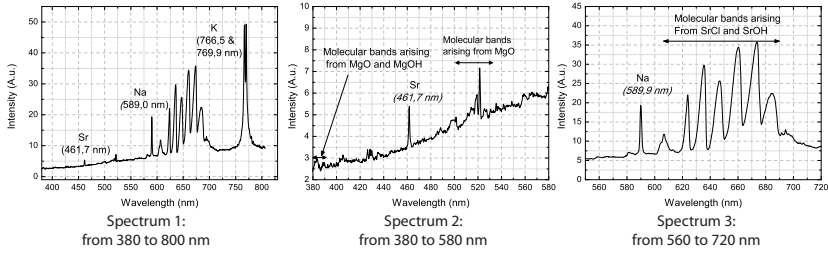
Emission spectra were recorded for all the compositions in the visible range 370 - 810 nm (see the first spectrum of all compositions in Figures 3.4 to 3.5). After which high resolution spectra were recorded of the relevant zone of all the spectra (see spectra 2 and 3 of each composition). They were analyzed with the help of databases of emission spectra of a variety of atomic and molecular gaseous species [9, 10].

The sodium line emission at 589 nm is present in all the spectra as an unresolved doublet, which is unsurprisingly particularly visible in the spectrum of the sodium sulfate composition (Composition 5 in Figure 3.6). Except for this composition, this spectral line is the result from a sodium contamination present in the ingredients used. The potassium doublet centered at 767 nm also appears in most of the spectra and a weak spectral line appears in some spectra at 405 nm which also may be the result of an emission from potassium. Note that the line is most clearly

visible for the sample with potassium sulfate. They are due to pollution in the ingredient and also because of the presence of potassium dichromate in all the compositions. Its decomposition may provide the potassium atoms responsible for those emission lines. Further analysis of spectrum 2 of all the compositions shows molecular bands that can be assigned to vibronic emission lines of magnesium hydroxide and magnesium oxide from 370 to 390 nm and from 495 to 500 nm, respectively (maxima at 497.3 nm, 498.3 nm, 499.5 nm and 500.6 nm). Those bands appear in all the spectra with different intensities. They may be quenched by other spectral lines such as in Figure 7 where the sodium lines are very intense, making the other lines and bands barely noticeable.

The spectrum of the strontium sulfate and strontium nitrate based compositions (see Composition 1 in Figure 3.4 and Composition 7 in Figure 3.5) shows spectral lines that arise from the excitation of the atoms of strontium at 461.7 nm and molecular bands due to vibronic transitions of strontium monochloride and strontium hydroxide (peaking at 623.9, 635.9 and 673.9 nm). Other bands appear at 606.3, 616.1 and 684.6 nm. They have not been fully identified but they are not present in the other spectra. Consequently, they may be assigned to vibronic transitions of a molecule containing strontium. The barium sulfate and barium nitrate based compositions spectra also contain two molecular bands that are assigned to vibronic transitions of barium monochloride at 513.7 and 524.5 nm (see Composition 2 in Figure 3.4 and Composition 6 in Figure 3.5). The spectral line present at 553.5 nm is consistent with the emission from the barium atom. Other molecular vibronic bands are present (peaking at 506.3, 516.8, 520.4, 531.6 nm). They may be the result of the vibronic transitions for barium monochloride, barium oxide or barium hydroxide. The emission spectra of the calcium sulfate composition (see Composition 3 in Figure 3.6) reveal also the presence of calcium monochloride and calcium oxide in the flame (molecular bands at 593.7, 618.7 and 621.2 nm for calcium monochloride and maxima at 605.7 and 607.3 nm for calcium oxide). In contrast, the spectra of the compositions containing potassium and sodium sulfates (Composition 4 and 5) are dominated by atomic emission lines from sodium and potassium (see Compositions 4 and 5 in Figure 3.6). Evidently, the emission from sodium and potassium is more efficient than that of the molecular species, which also leads to the observation of strong sodium emissions for compositions in which sodium is present as an unintentional contamination.

Composition 1



Composition 2

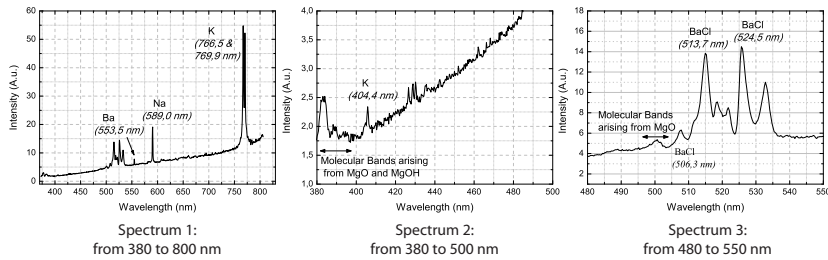
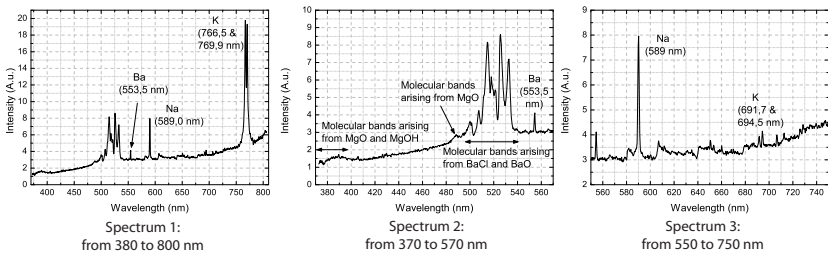


Figure 3.4 – Emission spectra recorded for the strontium and barium sulfate compositions (Compositions 1 and 2, respectively).

Composition 6



Composition 7

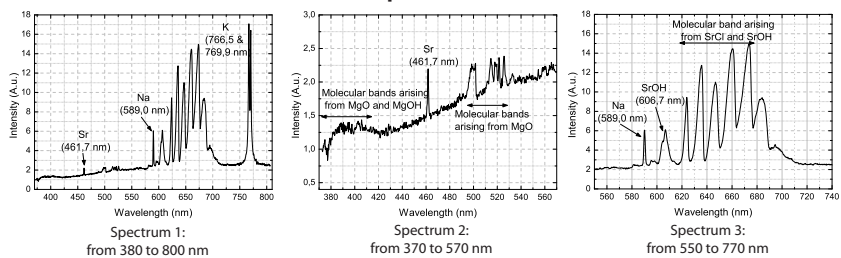


Figure 3.5 – Emission spectra recorded for the barium and strontium nitrate compositions (Compositions 6 and 7, respectively).

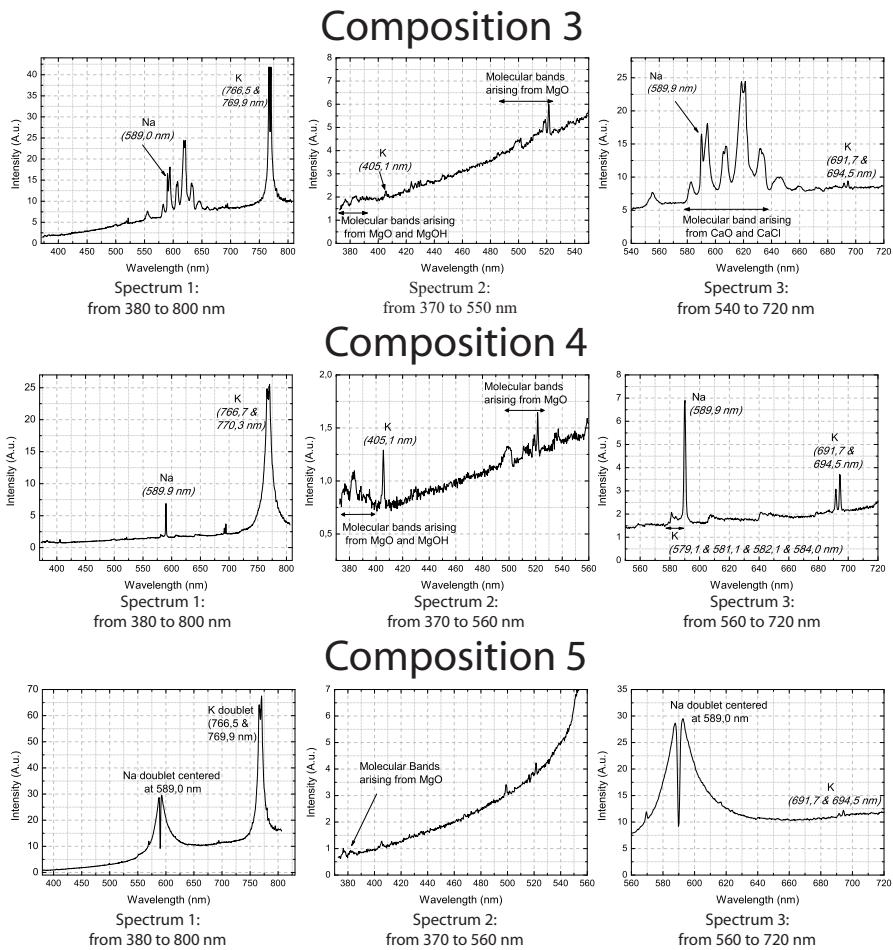


Figure 3.6 – Emission spectra recorded for the calcium, potassium and sodium sulfate compositions (Compositions 3, 4 and 5, respectively).

All the spectra show the presence of magnesium oxide and magnesium hydroxide in the combustion products. The presence of those bands imply the melting and/or evaporation of magnesium (Melting Point: 460°C [11]) and the oxidation of magnesium. Then, the burning of the barium and strontium sulfates and nitrates compositions and the calcium sulfate composition (Compositions 1, 2, 6, 7 and 3, respectively) gives rise to the formation of metal monochloride and

oxide. It suggests that those metal salts decompose during the process. On the other hand, only atomic lines appear in the spectra for the sodium and the potassium compositions. This could mean that sodium monochlorides and oxides are not produced by the reaction, or they are produced but not efficiently excited during the flash process. However, the mechanisms involved in those two groups of compositions seem different from the other compositions. This feature can also be observed with analysis of the high-speed camera high-speed camera images.

In addition, the CCD camera records the temporal evolutions of the emission spectra. Thus, the variation of the intensity of any relevant spectral line can be used to record the frequency of flashes and also evaluate the sharpness of the flashes. The temporal evolutions of the light intensities are given in Figure 3.7. The evolutions of the time intervals is depicted in Figure 3.8. It is an indicator of the regularity of flashes: if the flashes are regular, the time intervals must be constant with time. The barium and strontium sulfate based compositions (Composition 1 and 2) have regular and sharp flashes in comparison to the other compositions. The sodium and calcium sulfate compositions also have sharp flashes, but less regular and with a lower frequency for the sodium composition. The potassium sulfate based composition produces very irregular and indistinguishable flashes. The barium and strontium nitrate based compositions have quite regular and sharp flashes according to the graphs in Figures 3.7 and 3.8. They also have a higher frequency than the other compositions.

To conclude, the results obtained from the spectrometer corroborate the high-speed camera images: barium and strontium sulfate based compositions show the best strobe behavior and their sulfate ingredients also have the higher melting points. So the conclusion might be drawn that a high melting point is crucial for a regular strobe effect.

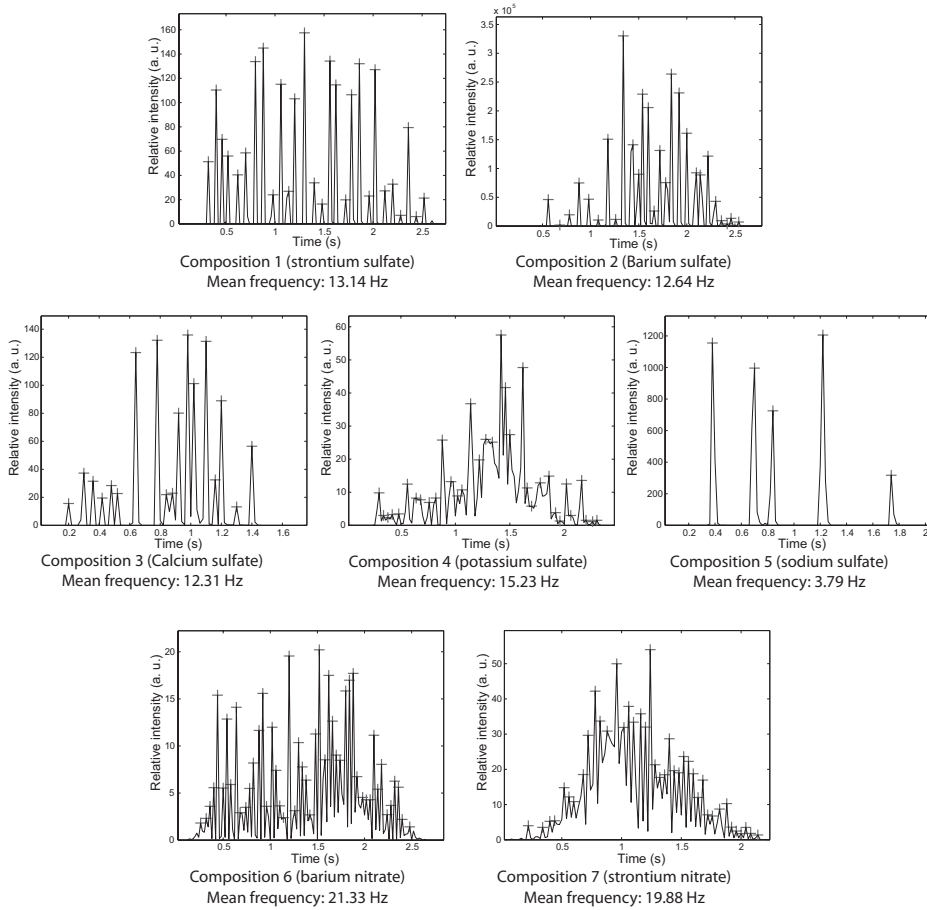


Figure 3.7 – Intensity evolution versus time for all compositions tested.

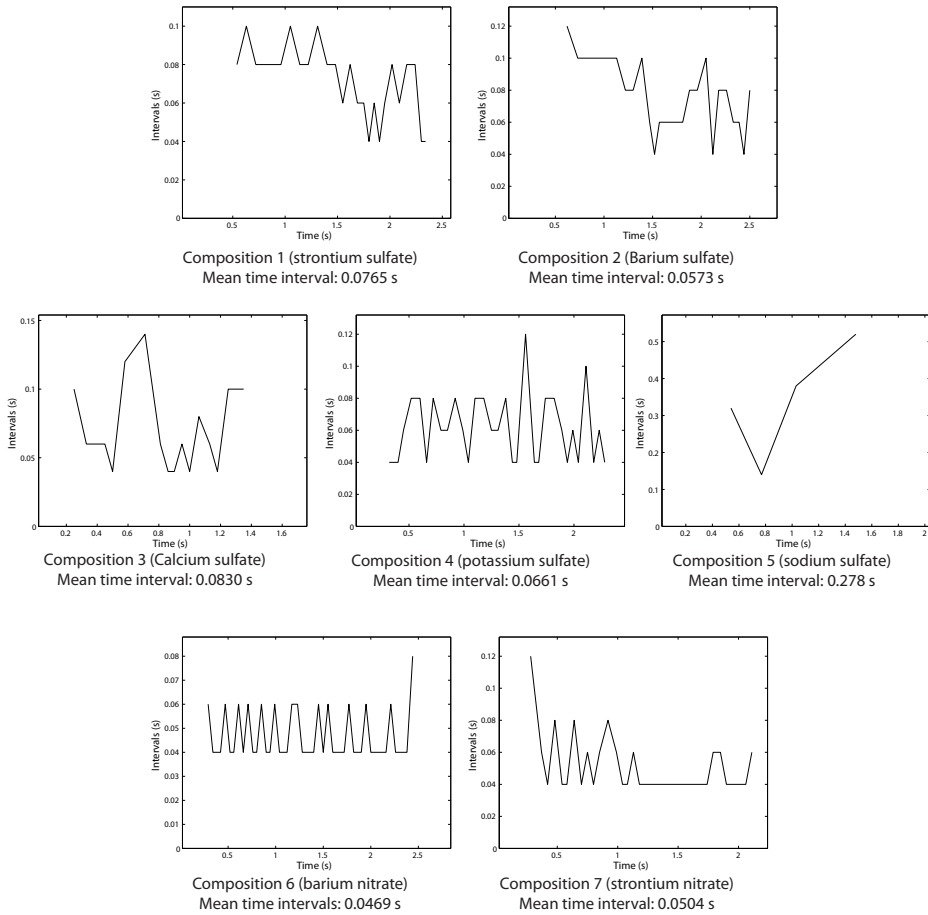


Figure 3.8 – Evolution of the time intervals between two successive flashes.

3.4 CONCLUSION

Previous studies [2, 4, 12, 13] on strobe reaction emphasize the importance of thermal and chemical parameters in the occurrence of flashes. In this paper, the influence of sulfates on a classical strobe composition was studied; seven metal salts (barium, strontium, calcium, potassium and sodium sulfates and barium and strontium nitrates) were tested in combination with ammonium perchlorate and magnalium. The sulfates and nitrates all have different melting points. The results of time resolved emission spectra (CCD /spectrometer) and high-speed camera images (high speed camera) of the ignited strobe compositions revealed that the compositions containing sulfates with higher melting points (strontium / barium sulfate compositions) give the best strobe effect.

Four groups of compositions were identified from the results: the high melting point metal sulfate compositions that includes the strontium and the barium sulfate based compositions, the low melting point metal sulfate compositions with sodium and potassium sulfates, the intermediate melting point metal sulfate compositions, for instance calcium sulfate and the nitrate compositions with lower melting points. The spectra of the first group (high melting point metal sulfates) reveal in both cases the presence of metal monochloride, oxide and hydroxide in the gas excited during the flash phase. It implies that the sulfates decompose during the process and then the metal is oxidized or forms a monochloride. In addition, the high-speed camera images show the formation of a uniform and partly solid layer on top of the pellet. This layer is heated up almost uniformly and flashes seem to be initiated from the molten areas present on the surface. The resulting strobe effect is characterized by sharp flashes at regular time intervals.

To the contrary, the strobe effect observed for the compositions of the second group (low melting point metal sulfates) is not as good; the high-speed camera images show the formation of an irregular layer that is almost liquid and that leads to irregular and longer lasting flashes. In the emission spectra recorded, only atomic peaks are observed during the flash phase. This may imply that the sulfate decomposes but the metal does not react with oxygen and monochloride. However, the most probable hypothesis is that either the temperature is not high enough to excite those molecular species efficiently and the emission intensity is too low to observe the vibronic emission lines next to the very efficient sodium and potassium emission lines or the molecular species form during the process do not emit in the visible but in another range such as microwave range line for instance sodium monochloride [14].

The strobe effect produced by the third group of compositions is an intermediate state between the good strobe produced by the first group of compositions and the erratic strobe effect of the second group. The spectra show the presence of metal

monochloride, oxide and hydroxide during the flash phase as observed for the first group. Consequently, the sulfate also decomposes during the process. However, the layer formed during the dark phase shows hot spots and irregular flashes, just like the second group, except that the top layer seems more solid.

The last group is composed out of the nitrate based compositions. Flashes produced are quite sharp and regular but their frequency is high and their intensity relatively low. High-speed images reveal the formation of thin and melted layers on the surface combustion. The spectra recorded were identical to the barium and sulfate based compositions. Consequently, the metal nitrate decomposes during the process and then the same chemical reactions are observed than in the first group of composition. Either the chemistry involved in the decomposition of nitrate influences the appearance of the layer (thinner and more melted than sulfate compositions) and the frequency of flashes or it is the melting point of the nitrate.

The results imply that metal sulfates and nitrates participate in the chemical reaction and that their melting points are important in the formation of a homogeneous layer / foam. Compositions that contain metal sulfates with a high melting point produce a better strobe effect. Metal sulfates and nitrates with low melting points seem to prevent strobe reactions with regular intervals and sharp flashes. Because of the melting of the sulfate or nitrate in the layer, the full surface cannot be ignited. This study highlights the importance of the melting point of the compounds in the strobing behavior and provide a better understanding of strobe compositions.

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4

Temperature evolution in strobe
compositions



ABSTRACT

During the burning of a strobe composition, dark phases alternate with flash phases. The physical and chemical mechanisms behind this alternation are not well understood. A few parameters are known to influence the strobe behavior (variation in frequency, regularity and sharpness of flashes, appearance of the layer on the combustion surface) such as the fraction of fuel, heat transfer in the composition and the melting point of the compounds. The thermal behavior of several compositions was studied in order to observe if these parameters influence the temperature. The compositions tested were based on the ternary strobe mixture ammonium perchlorate / barium sulfate / magnalium. The magnalium particles size was varied to change the heat transfer of the composition and barium sulfate was replaced with other metal sulfates (strontium and potassium sulfate) that have different melting points. The temperature evolution of the strobe was calculated via the measurement of the near-infrared spectra at regular time intervals. Using the gray body theory, a model was used to fit the experimental data to the theoretical equations for the wavelength dependence of the intensity using the temperature as a fitting parameter. The compositions were tested in four different atmospheres (argon, nitrogen, synthetic air, oxygen) to investigate if the oxygen or the nitrogen present in the air participate in the strobe reactions.

4.1 INTRODUCTION

Strobes are self-sustained oscillating combustion where dark phases alternate with flash phases. A few studies [1–5] were conducted to understand the causes of this alternation but the main processes driving the oscillations remain unclear. The ternary composition ammonium perchlorate / magnalium / barium sulfate is known to produce a good strobing effect [4, 5]. This composition was studied in Chapter 2 and Chapter 3 of this thesis. The formation of foam on the surface of the pellet was observed. Under this layer, gaseous species are produced and pressure builds up until the layer breaks releasing the gaseous species that are responsible for the flash phase. The results indicate that the melting and oxidation of magnalium particles are involved the oscillating behavior, the molecules of oxygen necessary for the oxidation reaction being supplied by the decomposition of ammonium perchlorate. Several parameters were found to influence the strobing effect. The frequency of flashes can be regulated by varying the heat production and transfer in the composition (fuel weight fraction and/or fuel particle size). The replacement of barium sulfate by other metal sulfates with different melting points also affect the frequency and sharpness of flashes. The effect of these parameters on the thermal behavior of the strobe is studied in this chapter.

Five different compositions were tested. The particle size of magnalium was varied

in order to change the heat transfer of the composition. Barium sulfate was replaced with strontium sulfate and potassium sulfate that have a higher and a lower melting point, respectively. The experiments were performed at the Fraunhofer Institute Chemische Technologie (ICT). The temperature was measured by analyzing the emission spectra of the strobes in the near infrared (NIR) range (1000 - 2200 nm). The model [6] developed applied a fitting of the calibrated experimental data to theoretical gray body equations. The fitting procedure also takes in account self-absorption and the molecular bands emitted by several molecules in the combustion products. This method gives a first approximation of the thermal evolution during the dark and flash phases of the strobe compositions tested. It enables the observation of the influence of the parameters mentioned above (heat transfer, melting point of the compounds) on the thermal behavior. Moreover, some propellants are known to react with the oxygen or the nitrogen present in the air such metal-fluorocarbon based energetic materials [7]. The temperature was measured for strobe compositions in different atmospheres (argon, nitrogen, synthetic air, oxygen) to check if the strobe reaction is influenced by oxygen or nitrogen in the surrounding atmosphere.

4.2 METHODS AND MATERIALS

4.2.1 Compositions

The compositions studied are shown in Table 4.1. Potassium dichromate was added as a frequency modulator; it improves the sharpness and the regularity of the flashes [4]. Finally, a solution of 10% nitrocellulose in acetone is added as binder. The magnalium used is a 50:50 magnesium / aluminum alloy.

Table 4.1 – Compositions of strobes studied

Compositions	1	2	3	4	5
Ammonium perchlorate	70	57	57	57	57
Magnalium(> 53 μm)	30	21.9		21.9	21.9
Magnalium(> 75 μm)			21.9		
Barium sulfate		16.1	16.1		
Strontium sulfate				16.1	
Potassium sulfate					16.1
Potassium dichromate		5	5	5	5

4.2.2 Methods

10 g including the binder solution of each composition was prepared. After mixing, the compositions were pressed (100 bars) into pellets of 1.5 g (including acetone) and dried in a vacuum oven during two hours giving a final weight of the pellet of about 1.26 g. The diameter was 0.99 cm and the average height of the pellets 0.917 cm giving an average density of 1.79 g/cm^3 . The pellets were placed in a pressure vessel. The ignition of the composition was achieved by a prime charge. It was placed on the top of the pellet and ignited electrically. All tests were performed in duplo.

An overview of the setup is shown in Figure 4.1. It is a metallic cylinder with a volume of 1.2 L with two opposite optical quartz windows, in which a flow is generated. Pressures up to 15 MPa can be achieved under different atmospheres. The experiments were conducted at atmospheric pressure in four different atmospheres: synthetic air, pure oxygen (O_2), pure nitrogen (N_2) and pure Argon (Ar). Compositions 1 and 2 were tested in the four atmospheres to observe the influence of the atmosphere on the strobe behavior while the other compositions were tested only in argon because argon is supposed to be an inert gas for the combustion reaction that takes place.

The emission spectra during combustion of the compositions were recorded with a InSb detector coupled with an AOTF-spectrometer system enabling the acquisition of spectra in the NIR range 1000 - 2500 nm at rates up to 1000 scans/s with a wavelength resolution of 2 - 3 nm. The intensity calibration was carried out by recording reference spectra of a black body radiator [6].

The emission spectra in the visible range were recorded using a UV/VIS grating imaging spectrometer in Czerny-Turner arrangement (Andor Shamrock A-SR500i B2) coupled with Si-CCD camera (256 x 1024 pixels) with a maximum speed of 1000 spectra/s in full vertical binning mode (Andor CCD DU920P-UV-BR-DD). The optics placed between the pressure vessel and the spectrometer (see Figure 4.1) is described in [8].

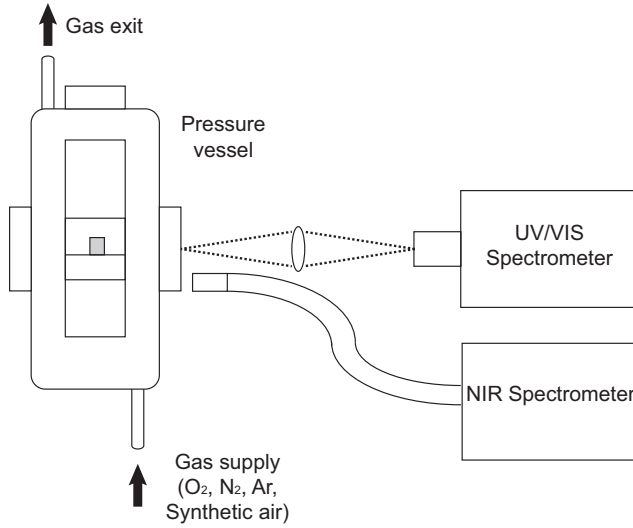


Figure 4.1 – Experimental set-up for simultaneous spectroscopic and pyrometric investigation of strobe composition.

4.3 EVALUATION OF THE TEMPERATURE: THEORY

The model to calculate the temperature from the NIR spectra is based on the black body theory and has been developed at ICT [6]. A blackbody is an ideal absorber of incident radiation. Under equilibrium conditions, a blackbody emits exactly the same amount of energy it absorbs. The emitted radiations are called black-body radiations and are related to the temperature of the body. The Planck radiation law describes the spectral volume density of radiation (also called spectral radiance of electromagnetic radiation) at all wavelengths emitted by an ideal blackbody in a cavity in thermodynamic equilibrium.

As a function of the frequency and the absolute temperature, the Planck distribution law is written as follow:

$$u_{\nu}(T) = \frac{8\pi h\nu^3}{c_0^3} \times \frac{1}{\exp(h\nu/kT) - 1} \times d\nu \quad (4.1)$$

Where $u_{\nu}(T)$ is the spectral volume density of radiation, T is the absolute temperature (K), ν is the frequency (Hz), h is the Planck's constant ($6,63 \cdot 10^{-34}$ J.s), k is the Boltzmann's constant ($1,38 \cdot 10^{-23}$ J.K⁻¹) and c_0 is the speed of light in vacuum ($3,0 \cdot 10^8$ m.s⁻¹).

The dimension of $u_\nu(T).d\nu$ is $\text{J.m}^{-3}.\text{sr}^{-1}$. The spectral intensity of a blackbody radiation $I_\nu(T, \nu)$ is obtained by integration of Equation (4.1):

$$I_\nu(T, \nu) = \frac{2h\nu^3}{c_0^2} \times \frac{1}{\exp(h\nu/kT) - 1} \quad (4.2)$$

The dimension of this quantity is $\text{J.m}^{-2}.\text{sr}^{-1}$.

In many applications, the wavelength is used instead of the frequency. Equation (4.2) can be rewritten using the relation $\lambda \times \nu = c_0$. Consequently, the spectral intensity of radiation expressed using the wavelength is equal to:

$$I_\lambda(T, \lambda) = \frac{2hc_0^2}{\lambda^5} \times \frac{1}{\exp(hc_0/\lambda kT) - 1} \quad (4.3)$$

The dimension of radiation intensity used is $\text{W.m}^{-2}.\text{sr}^{-1}.\mu\text{m}^{-1}$.

In practical applications, the surface density of a spectral flux, $q(\lambda, T)$ is often used instead of the spectral intensity of radiation:

$$q(\lambda, T) = \frac{C_1}{\lambda^5 \times (\exp(C_2/\lambda T) - 1)} \quad (4.4)$$

Where $C_1 = 2\pi hc_0$ and $C_2 = \frac{hc_0}{k}$. They are the first and the second radiation constant. C_1 is equal to $3,742.10^{-16} \text{ W.m}^2$ and C_2 is equal to $1,439.10^{-2} \text{ m.K}$. $q(\lambda, T)$ is the radiation energy emitted by a unit area of the blackbody surface at temperature T per unit time, in the wavelength band unit, in all directions within the limits of the hemispherical solid angle. The dimension of this quantity is in W.m^{-3} .

The evolution of the surface density of a spectral flux (Planck curve) is shown in Figure 4.2 as a function of wavelength and for different temperatures. The position of the maxima of the Planck curve (λ_{max}) is related to the temperature of the black body via the Wien's displacement law:

$$T \times \lambda_{max} = \frac{1}{5} \times C_2 \quad (4.5)$$

In real applications, the surface density of a spectral flux is modified by a factor called the emissivity ϵ that depends on the wavelength λ and the temperature

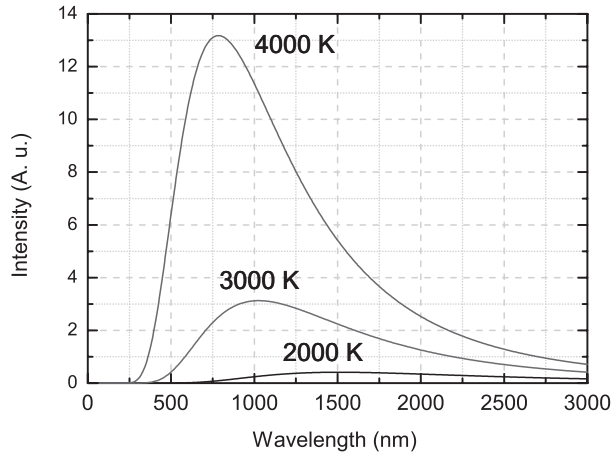


Figure 4.2 – Graph of the Planck curves showing the spectral distribution for Black body radiation at 2000 K, 3000 K and 4000 K.

T and its value is between 0 and 1. For gray body radiations, the emissivity is assumed independent of the wavelength and temperature. Such an ideal body does not exist in practice but the assumption is a good approximation for many objects. The Equation (4.4) can be rewritten as follows:

$$q_{\epsilon}(\lambda, T) = \epsilon \times q(\lambda, T) \quad (4.6)$$

The integration of the surface density of a spectral flux q results in the Stefan-Boltzmann law of radiation:

$$E = \epsilon \sigma T^4 \quad (4.7)$$

ϵ is the emissivity of a gray body,
 σ is the Stefan-Boltzmann constant ($5.67 \cdot 10^{-8} \text{ J} \cdot \text{s}^{-1} \cdot \text{m}^{-2} \cdot \text{K}^{-4}$).

The model developed by ICT fits experimental data with gray body theoretical equations (Equations (4.4) and (4.7)), the temperature being the fitting parameter. The program takes into account self-absorption and the emissions bands of several molecules: H_2O with bands around 1300 and 1800 nm (as observed on the spectra recorded in Figure 4.3), CO_2 , CO , NO). The fitting is achieved by using the least square method. It allows fitting by minimizing the sum of the square of the gap between experimental data and theoretical curve. More details on the fitting program are provided in [6]. The standard deviation in the temperature determined using the fitting procedure was evaluated to around 10% in the temperature range 500 to 4000 K.

4.4 RESULTS AND DISCUSSION

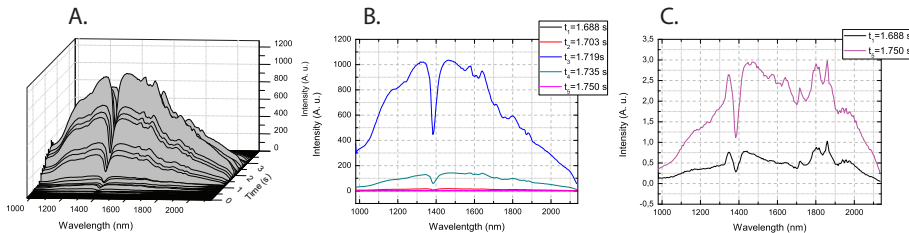


Figure 4.3 – Experimental data obtained for the strobe composition 1 in argon atmosphere. Graph A shows all the emission spectra recorded from 970 to 2150 nm over time. The graph B shows the spectra recorded during one cycle of the strobe (from $t = 1.688$ to 1.750 s). Curves t_2 to t_4 correspond to the flash phase. The last graph (D) shows the curves t_1 and t_5 from the graph C in which the difference of intensities between the curves was too large to observe these curves corresponding to the dark phase.

To follow the temperature evolution of the various strobe compositions, emission spectra were recorded in the infrared and visible spectral region during several strobe cycles. Emission spectra in the visible wavelength range are shown in Chapter 2 (Figures 2.5 and 2.9) for composition 1 to 3 and in Chapter 3 (Figures 3.4 and 3.6) for composition 4 and 5. An example of the spectra obtained with the infrared camera is shown in Figure 4.3. The fitting program was applied to derive the temperature from the spectra. The results obtained are summarized in Table 4.2 and some of the resulting graphs of the variation of the temperature in time are shown in Figures 4.4 and 4.5. The strobe behavior can be clearly recognized as a periodic change in temperature. The flash temperatures recorded for the different compositions vary between 2200 K and 3215 K while the dark temperatures are between 1510 and 2290 K. Composition 1 shows the smallest temperature differences between dark and flash phases, around 400 K while it is around 1000 K for the other compositions. This could be the result of the addition of a metal sulfate or the action of potassium dichromate. The decomposition and/or melting of these compounds may absorb part of the energy so more heat is required to produce the necessary concentration of gaseous species responsible for the flash phase. It is well known that addition of the sulfates and potassium dichromate can improve the regularity of the strobe reaction. The larger differences between the temperature in the flash and dark phase is consistent with a more regular strobe behavior with a clear separation between dark and flash phase.

It has been reported that the oxygen and nitrogen present in the air participate in the combustion while argon is supposed to be inert [7]. Therefore, the strobe compositions 1 and 2 were tested in different atmospheres (see Figure 4.4 and

Table 4.2 – Overview of the mean flash temperature (temperature measured during the flash phase), mean dark temperature (temperature measured during the dark phase), mean temperature difference between a dark and a flash phase and mean flash frequencies. The numbers were calculated for each measurement and then an average of the results was calculated over the two measurements performed for every composition. The data that are not emphasized are the results in argon atmosphere.

Compositions	Atmosphere	Flash temperatures (K)	Dark temperatures (K)	Temperature differences (K)	Frequencies (Hz)
1	Argon	2220	1790	430	13.5
1	<i>Nitrogen</i>	<i>2365</i>	<i>1690</i>	<i>560</i>	<i>11.8</i>
1	<i>Synthetic air</i>	<i>2490</i>	<i>2290</i>	<i>200</i>	<i>17.2</i>
1	<i>Oxygen</i>	<i>2540</i>	<i>2190</i>	<i>360</i>	<i>15.3</i>
2	Argon	2800	1800	1005	20.0
2	<i>Nitrogen</i>	<i>2740</i>	<i>1425</i>	<i>1310</i>	<i>19.7</i>
2	<i>Synthetic air</i>	<i>2780</i>	<i>1510</i>	<i>1215</i>	<i>16.7</i>
2	<i>Oxygen</i>	<i>2845</i>	<i>1510</i>	<i>1260</i>	<i>18.4</i>
3	Argon	3215	1835	1365	8.9
4	Argon	2545	1940	610	25.2
5	Argon	3050	1980	1195	11.8

Table 4.2). These two compositions were more thoroughly studied in Chapter 2. The results show that in all atmospheres tested, Composition 2 seems to produce higher flash temperatures than Composition 1 while the dark temperatures are slightly lower. It results in a larger temperature difference between the flash and the dark phases for Composition 2. Then, results in Figure 4.4 and Table 4.2 also show that the flash and dark temperatures and the frequency of Composition 1 tested in synthetic air and in oxygen were slightly higher. All the four measurements done for Composition 1 in synthetic air (two measurements) and oxygen (two measurements) have an average value of flash temperature between 2480 K and 2580 K and a dark temperature between 2110 K and 2300 K while the flash temperatures measured in argon were below 2400 K and the dark temperatures were below 1850 K. However, no noticeable differences are observed for Composition 2 Figure 4.4. All the flash temperatures calculated in the different atmosphere are between 2700 K and 3000 K and the dark temperatures are between 1350 K and 1950 K. The differences observed of the results of composition 1 may be due to experimental uncertainties. It is clear that the strobe reaction does not (strongly) depend on the presence of oxygen in the atmosphere and that there is no strong influence of the atmosphere on the temperature or flash frequency of the strobe composition. Consequently, the strobe reaction rely on oxygen provided by the strobe composition and not on the oxygen in the ambient atmosphere.

The difference between Compositions 2 and 3 is the particle size of magnalium $> 53 \mu\text{m}$ and $> 75 \mu\text{m}$, respectively. This effect of the fuel particle size on the strobe effect is studied in more detail in the next chapter (Chapter 5). A first analysis of the results in argon atmosphere (Figure 4.5 and Table 4.2) shows that the compositions with a larger magnalium particle size (Composition 3) produce a slower frequency, consistent with results presented in Chapter 5. The temperatures observed for Composition 3 seem slightly higher than for Composition 2 (around 400 K of differences of the flash temperature) as is the difference of temperature between the dark and the flash phase (360 K of differences). However, the differences observed are within the uncertainty of the calculation. The temperatures calculated for the two compositions are in the same range. Consequently, the processes that reduces the strobe frequency does not strongly influence the temperature.

Compositions 2, 4 and 5 contained three different metal sulfates: barium sulfate, strontium sulfate and potassium sulfate with melting points of 1853 K, 1879 K and 1342 K, respectively. The influence of the metal sulfate used has been emphasized in the previous chapter (Chapter 3). It was observed that the melting point is important in the formation of a homogeneous layer / foam. The hypothesis was made that more heat is required to melt high melting points sulfates so it avoids the layer to melt too quickly and the gas responsible for the flashes remains captured under the surface combustion. Consequently, compositions containing metal sulfate with a high melting point (barium and strontium sulfates) produced sharper and more regular flashes. No large differences of temperature are observed (see Figure 4.5 and Table 4.2). The flash temperatures calculated for Composition 5 (containing strontium sulfate) is slightly higher than those observed for the two other compositions while its dark temperature remains in the same range. It results in a large difference of temperature between the dark and the flash phases. However, the differences observed are again within the uncertainty of the calculation. The results presented are based on initial measurements of the temperature evolution during combustion of a number of strobes and provide first insights in the actual temperatures during different phases of the strobe action. The reproducibility has not been tested sufficiently to draw firm conclusions on differences between the temperature during the flash phase and the dark phase. The flash phase temperatures vary around 2700 K and in the dark phase the temperature drops below 2000 K. Especially the dark phase temperatures are difficult to determine accurately due to the low emission intensity and distortions due to molecular absorption bands.

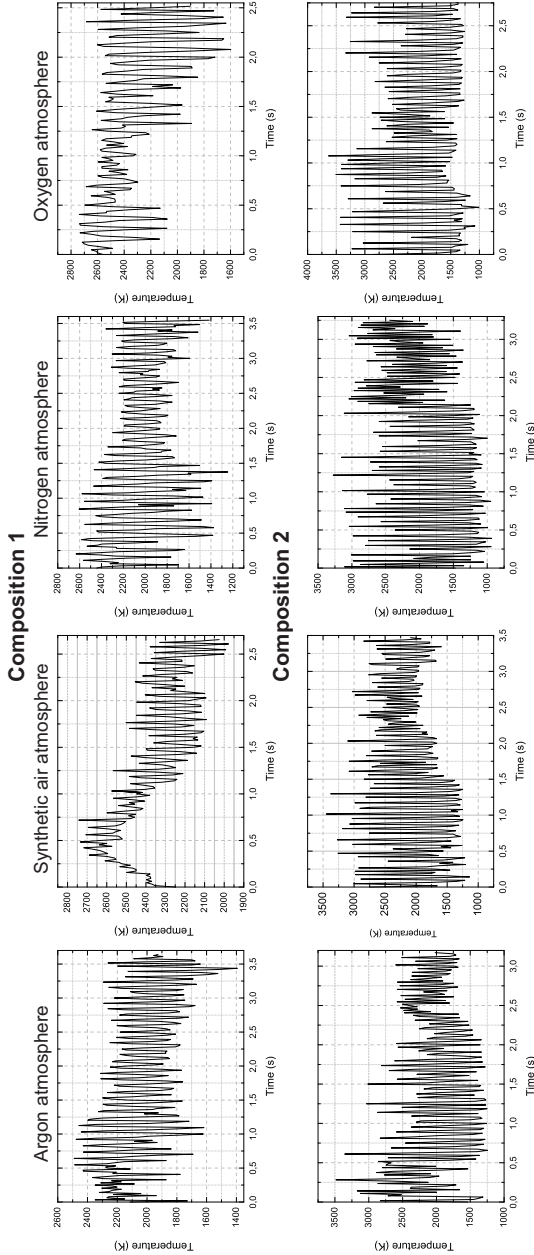


Figure 4.4 – Graphs showing the evolution of the temperature of Compositions 1 and 2 in the four different atmospheres (Argon, synthetic air, nitrogen, oxygen).

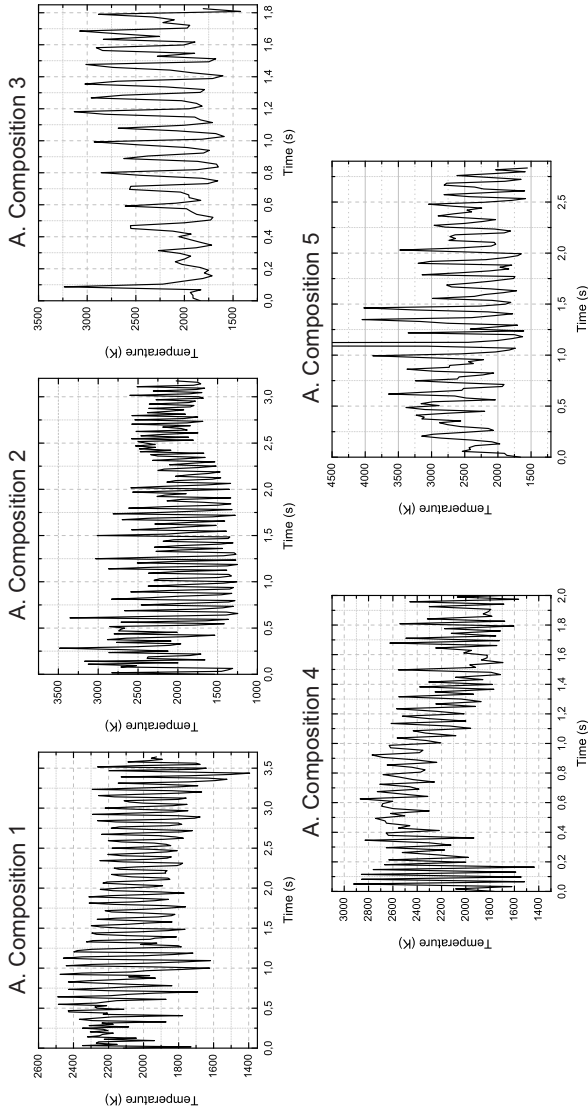


Figure 4.5 – Graphs showing the evolution of the temperature of the five strobe compositions tested in argon atmosphere.

4.5 CONCLUSION

The temperature evolution of different strobe compositions was measured using spectroscopic methods and provide the first actual temperature in strobes during the dark and flash phase. The results show a clear variation in temperature between the flash phase and dark phase, with flash phase temperature peaking around 2700 K. The influence of composition and atmosphere on the temperatures was also investigated but clear conclusions are hampered by uncertainties in the results. The influence of the atmosphere (inert or containing oxygen) is limited indicating that the strobe does not react with the ambient atmosphere. The oxygen molecules required for the oxidation reaction are provided by the decomposition of ammonium perchlorate. The addition of metal sulfates and potassium dichromate increases the flash temperature and also the temperature difference between the dark and flash phases. A change in the heat transfer or the replacement of a high melting point metal sulfate by a low melting point metal sulfate has an effect on the frequency, sharpness and regularity of flashes. However, it did not have a strong influence on the thermal behavior of the strobe compositions. The uncertainty in the temperature calculation prevents the observation of small differences between the compositions. The absence of difference may indicate that the parameters that have been varied (particle size, metal sulfate) do not have an important influence on the evolution of the temperature. A more accurate method to calculate the temperature is necessary to determine the influence of the composition on the temperature during the dark and the flash phases.

ACKNOWLEDGMENTS

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5

Theoretical strobe model

ABSTRACT

Chapter 2 emphasized parameters such as the fuel fraction on the composition that influence the strobe behavior (frequency, sharpness and regularity of flashes). However, the chemical and physical mechanisms involved in this curious combustion phenomenon remain unknown. This chapter investigates further some of those parameters. Variations were applied to the fuel particle size and weight fraction of the ternary composition ammonium perchlorate, magnalium (fuel) and barium sulfate. Both parameters are related to the heat generation and transfer within the composition. The light emission was recorded with photodiodes and a high speed camera (5000 fps). The experimental results served as input for a model to explain the strobe behavior based on layer-by-layer combustion. Moreover, it was established that the flash frequency is dependent on a delicate balance between heat generation in one layer and heat transfer to a next layer. The model gives new insights into the behavior of pyrotechnic strobes and enables a better control of the flash frequency by variation of the size and content of the metal fuel particles.

5.1 INTRODUCTION

The strobe effect has applications in various fields, most notably in the fireworks industry and in the military area. The application in fireworks is well known to the public as strobe pots or twinklers. In the military, applications involve signaling or missile decoy [1–4]. Strobes can also be used for crowd control where an accurate control of the frequency, regularity and sharpness of flashes is important: a frequency of 12 Hz is known to disturb the human visual sensory system most and even may cause an epileptic crisis [5]. A better understanding of the chemical and physical mechanisms involved in the curious combustion reaction can help to improve frequency control. The first known study of strobe compositions dates to an 1898 fireworks historical handbook from Brocks Fireworks Ltd [6]. Subsequent compositions showing oscillatory flashing behavior were discovered by trial and error. Systematic strobe mechanism studies started in the 1970s when Krone and Wasmann hypothesized two reactions (a dark and a flash reaction) that alternate at regular intervals [7, 8]. Shimizu expanded this hypothesis by identifying fuels and oxidizers for both reactions [9]. Later studies showed there cannot be both dark and flash reagents for some simple strobes, suggesting that another mechanism must be operative [10]. A thermokinetic model was suggested based on models developed for SHS (Self-propagating High-temperature Synthesis) combustion [11–14]. This type of solid-phase combustion is similar to strobe reactions in both the ingredients used as well as intermittent burning behavior [13–16]. Here a more detailed model explaining oscillatory combustion of strobes is described with experimental data supporting the theory. The model quantitatively explains the variation in flash

frequency as a function of the size and weight fraction of the magnalium fuel particles in the strobe composition.

5.2 EXPERIMENTAL

5.2.1 Compositions

The effect of particle size and fuel : oxidizer : metal salt ratio is studied. The mixtures are based on a classical strobe composition described in Table 5.1. Ammonium perchlorate serves as oxidizer while magnalium is the fuel.

Table 5.1 – Base composition for stobes used.

Composition (% by weight)			
Ammonium perchlorate	60.0	57.1	47.6
Barium sulfate	17.0	16.2	13.5
Magnalium	23.0	21.9	18.2
Potassium dichromate	5.0 (additional)	4.8	4.0

The magnalium used is 50:50 magnesium-aluminum alloy from ECKA Granules, Metal powder technologies (Austria). The powder is manufactured from aluminum and magnesium primary metals and they are granulated by mechanical grinding. The grade of the powder is $\leq 100 \mu\text{m}$. The magnalium powder was sieved in five different fractions (38 μm , 53 μm , 63 μm , 75 μm , 90 μm) so that narrow particle size distributions were achieved. Six samples of magnalium were obtained and were named magnalium samples 1 to 6. The average determined particle sizes are 24.9 μm , 41.3 μm , 58.8 μm , 60.3 μm and 96.5 μm and 114.5 μm (the determination of the particle size distribution is described in the Section 5.2.3). Six compositions were made according to Table 5.1 with the different magnalium samples.

Nine other compositions were made based on the composition described in Table 5.1 with a variation of the amount of magnalium. They are listed in Table 5.2 and in the ternary diagram in Figure 5.1. The base composition was called composition 2.0. The magnalium sample used is sample 2 (average particle size: 41.3 μm).

Ten grams of each composition were prepared, including a binder solution composed of 10% nitrocellulose and 90% acetone. After mixing, the compositions were pressed (100 bars) into pellets of 1.5 g and then dried into a vacuum oven during two hours. The final average pellet weight of the pellet was 1.26 g; the diameter was 0.99 cm; the average height of the pellets was 0.92 cm; the average density was 1.79 g/cm³. The pellets were placed on a metal plate and ignited with a butane burner. A set of three pellets was ignited for each experiment.

Table 5.2 – Compositions of the strobes used to investigate the influence of the fuel content on the strobe frequency. The ratio between the oxidizer (ammonium perchlorate) and fuel (magnalium) was varied between 60:10 and 60:45.

Compositions	Ammonium perchlorate	Barium sulfate % by weight	Magnalium	Total
2.0	60.0	17.0	23.0	100.0
2.1	60.0	17.0	10.0	87.0
	69.0	19.5	11.5	100.0
2.2	60.0	17.0	15.0	92.0
	65.2	18.5	16.3	100.0
2.3	60.0	17.0	20.0	97.0
	61.9	17.5	20.6	100.0
2.4	60.0	17.0	25.0	102.0
	58.8	16.7	24.5	100.0
2.5	60.0	17.0	30.0	107.0
	56.1	15.9	28.0	100.0
2.6	60.0	17.0	35.0	112.0
	53.6	15.2	31.3	100.0
2.7	60.0	17.0	40.0	117.0
	51.3	14.5	34.2	100.0
2.8	60.0	17.0	45.0	122.0
	49.2	13.9	36.9	100.0

5.2.2 Optical equipment

Movies were recorded with a High-Speed camera (Redlake digital imaging system, 5000 and 3000 frames per second, resolution: 160 x 160) to follow the light emission of the strobes and to visualize the processes during the dark and the light phases. The light emission and the flash frequencies were recorded using photodiodes coupled with an oscilloscope (Sigma 30 from Nicolet technologies). The time resolution was varied between 0.1 and 0.5 ms depending on the frequency of the flashes. Four different types of photodiodes from Roithner Lasertechnik GmbH were used, sensitive in different spectral regions (blue - 470 nm; green - 525 nm; red - 660 nm; infrared - 740 nm). No significant differences were observed in the time response recorded by the photodiodes in the different spectral regions.

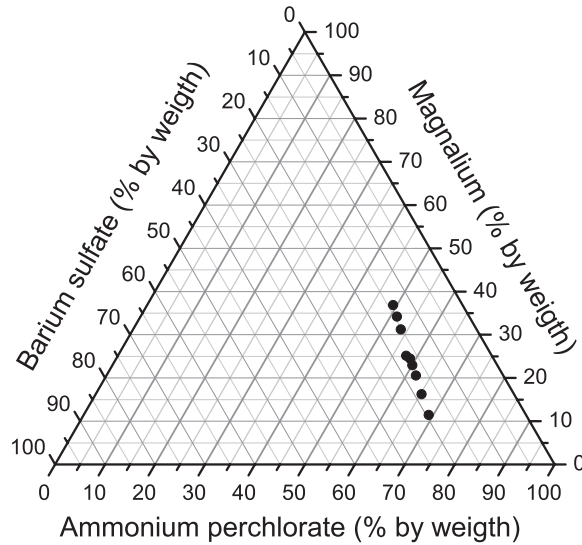


Figure 5.1 – Ternary diagram showing the compositions of Table 5.2 for studies on the influence of the magnalium content.

5.2.3 Evaluation of the particle size distribution

The particle size distribution of each sample was recorded with a particle sizer of the Malvern 2600 series that relies on the laser light scattering technique. Three different range lenses were used to obtain the most accurate results; a 100 mm lens for magnalium samples 1 and 2; a 300 mm lens for magnalium samples 3, 4 and 5 and a 600 mm lens for magnalium sample 6. The mathematical model used to analyze the results is based on a Log Normal model. The particle size distribution was measured of two different samples from each magnalium sample. The results are presented in Table 5.3. $D(\nu, 0.1)$, $D(\nu, 0.5)$ and $D(\nu, 0.9)$ are the diameters (particle size) at 10%, 50% and 90% point of the distribution, respectively. The span gives a measure of the width of the volume distribution relative to the median diameter, $D(\nu, 0.5)$ and is calculated from the percentiles using:

$$\text{Span} = \frac{D(\nu, 0.9) - D(\nu, 0.1)}{D(\nu, 0.5)} \quad (5.1)$$

The values displayed in Table 5.3 are the averages of the values obtained from the two measurement series. The parameters used further in this study to correlate the strobe frequency to the particle size are the median value $D(\nu, 0.5)$. Figure 5.2

shows the size distribution for one of each of the magnalium samples. Note that particle sizes 3 and 4 are very close and which one has the largest particle size depends on the parameter chosen to characterize particle size. The size distribution for sample 4 is larger than for sample 3.

Table 5.3 – Particle sizes and size distributions for the five samples of magnalium determined with the Malvern 2600.

Magnalium samples	$D(\nu, 0.1)$ (μm)	$D(\nu, 0.5)$ (μm)	$D(\nu, 0.9)$ (μm)	Span	Average particle size (μm)
1	10.45	23.89	40.20	1.24	24.85
2	15.66	42.50	63.46	1.12	41.29
3	26.60	60.69	70.92	0.73	58.82
4	25.15	62.67	89.80	1.03	60.31
5	68.75	93.75	128.73	0.64	96.50
6	88.18	111.88	147.83	0.533	114.52

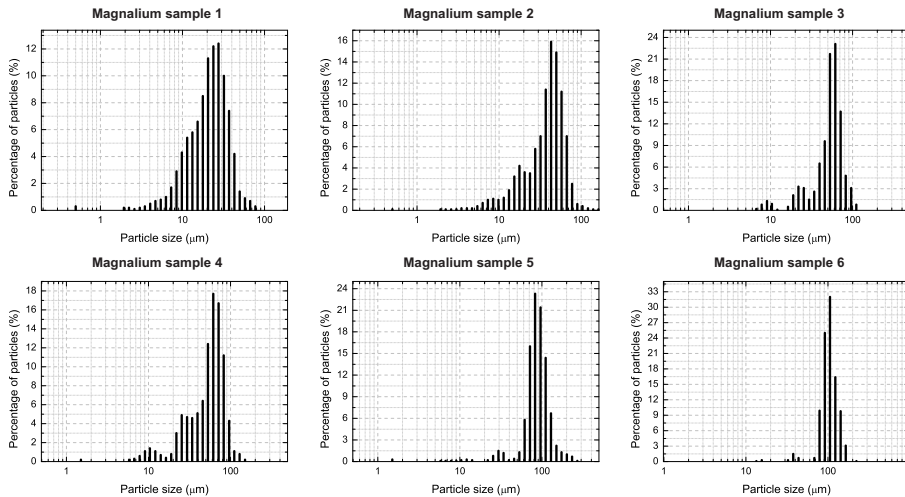


Figure 5.2 – Typical particle size distributions for a series of magnalium samples of different particle sizes used to study the influence of particle size on the strobe frequency.

5.3 RESULTS

The high-speed camera images reveal details on the process involved (see Figure 5.3). A qualitative analysis shows that the frequency of flashes increases with decreasing particle size of magnalium and with increasing magnalium weight fraction. Initially, when the pellet is ignited, a layer appears on the top of the pellet. The surface is heated up by a reaction, becomes red and white hot spots develop on the surface (see Figure 5.3(G)). For compositions with a lower frequency, the reaction proceeds for a longer time. As a result, the thickness of the layer is higher and the red color brighter. When the flash is imminent, parts of the surface layer are ejected (Figure 5.3(H)) indicating the formation and rapid expansion of gas below the surface. A bright flash of several milliseconds follows after which the process is repeated. The pellet is consumed almost linearly, layer by layer.

The data recorded with the photodiodes were analyzed and the frequencies were determined using a Matlab program that calculates the mean time interval between two successive flashes. Typical graphs are presented in Figures 5.4 and 5.5 respectively for strobes with different magnalium particle sizes and different magnalium fraction. The results are summarized in Tables 5.4 and 5.5. The strobe frequency decreases with the particle size of magnalium, in agreement with the observations made from the high-speed camera images.

The time intervals between flashes were calculated for each composition from the data obtained with the photodiodes. The temporal evolution of those intervals is shown in Figures 5.6 and 5.7. It is an indicator of the regularity of the flashes and also their sharpness. If they are regular, the time intervals between two successive flashes must be constant. The tendency observed for all compositions is a decrease of the time intervals with time indicating an acceleration of the reaction. Moreover, when the strobe is fast (small average particle size and high magnalium fraction), the flashes are less sharp. On the contrary, when the strobe is slow (for high average particle size and low magnalium percentage), the flashes are less regular.

The mean time intervals were analyzed as a function of magnalium particle size (Figure 5.8(A)) and magnalium fraction (Figure 5.8(B)). As observed in Figures 5.4 and 5.6, Compositions 1.5 and 1.6 show an erratic behavior in comparison to the other compositions. After a certain particle size of magnalium (above 60 μm), not only the frequency is changed but also the regularity of flashes. The larger particles prevent the composition to form regular layers. Consequently, they were not taken into account in the Figure 5.8(B). The time intervals between flashes increase with particle size and decrease with higher magnalium content. Using the data, it is possible to create a strobe with any desired frequency between 1 and 30 Hz. For example, a composition containing 24% magnalium with a particle size of 41 μm gives a strobe flashing at 12 Hz.

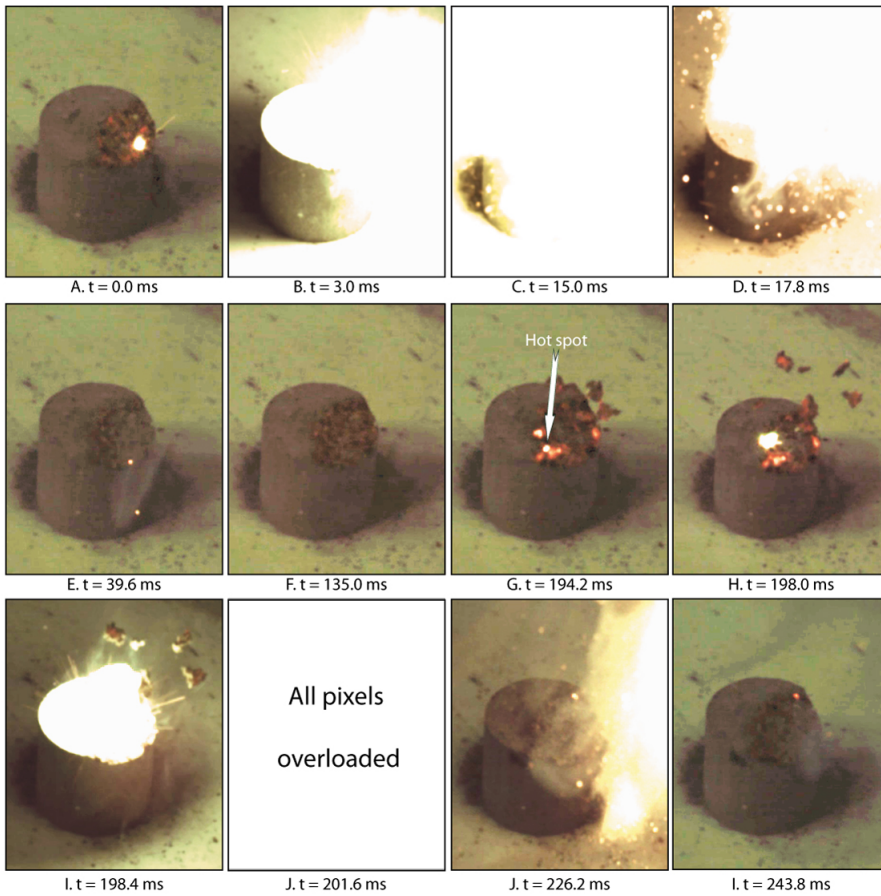


Figure 5.3 – Series of images recorded around two flashes for a strobe composition containing 23% of magnalium (average particle size $41 \mu\text{m}$) recorded with a high-speed camera. Times relative to the first image are indicated under the images.

Table 5.4 – Relation between particle size and strobe frequency for six strobe compositions with different particle sizes. Results are obtained from the time dependence of the emission intensity recorded with photodiodes for different spectral regions. No differences were observed for the various spectral regions. The average of the mean time interval is obtained by averaging the mean time intervals calculated for the three measurements of one composition. The average frequency is obtained by the same way.

Compositions	Average particle sizes (μm)	Averages of the mean time intervals (s)	Average frequencies (Hz)
1.1	24.85	0.036	27.1
1.2	41.29	0.095	10.5
1.3	58.82	0.282	3.5
1.4	60.31	0.243	4.1
1.5	96.50	1.156	1.6
1.6	114.52	1.260	0.8

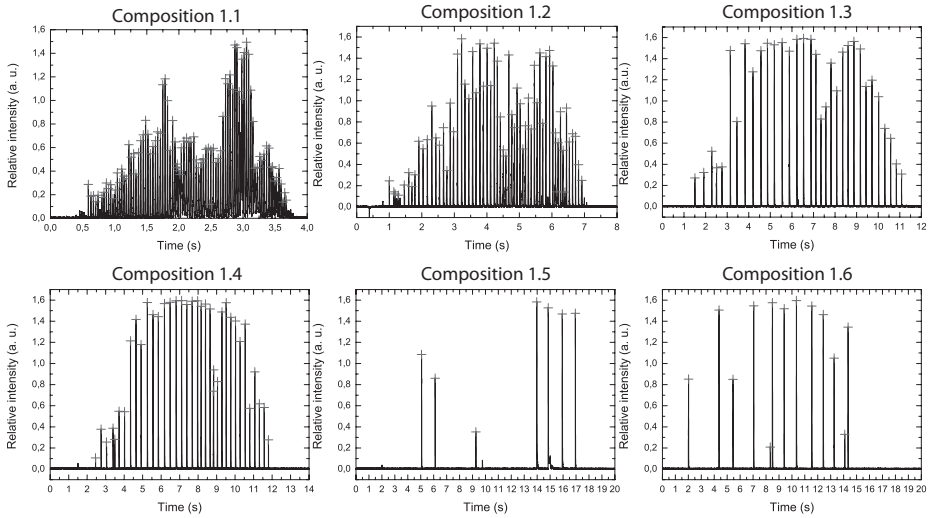


Figure 5.4 – Temporal evolution of the intensity of the light emission for compositions with different magnalium particle sizes recorded with the photodiode sensitive in the blue spectral region. The same results are obtained for the other spectral regions.

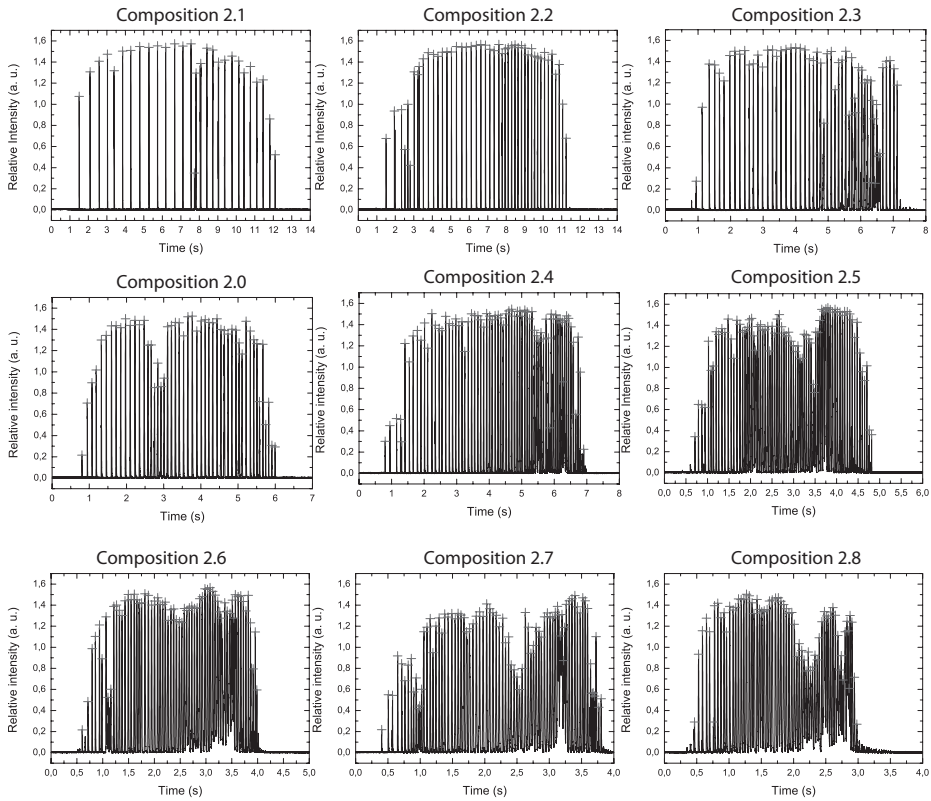


Figure 5.5 – Temporal evolution of the intensity of the light emission for compositions with different magnalium content recorded with the photodiode sensitive in the blue spectral region. The same results are obtained for the other spectral regions.

Table 5.5 – Relation between particle size and strobe frequency for eight strobe compositions with different magnalium content. Results are obtained from the time dependence of the emission intensity recorded with photodiodes for different spectral regions. No differences were observed for the various spectral regions. The average of the mean time interval is obtained by averaging the mean time intervals calculated for the three measurements for one composition. The average frequency is obtained by the same way.

Compositions	Magnalium fractions (% by weight)	Averages of the mean time intervals (s)	Average frequencies (Hz)
2.1	10	0.400	2.5
2.2	15	0.195	5.2
2.3	20	0.114	8.9
2.0	23	0.105	9.6
2.4	25	0.083	12.1
2.5	30	0.062	16.2
2.6	35	0.051	19.6
2.7	40	0.045	22.7
2.8	45	0.038	26.4

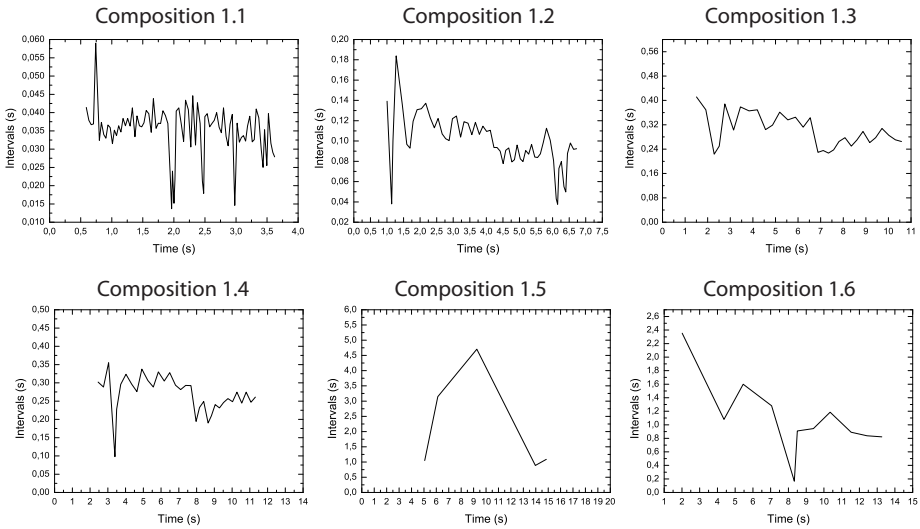


Figure 5.6 – Evolution of the time intervals between two successive flashes for strobe compositions with different magnalium particle sizes (see Table 5.3 for particle sizes).

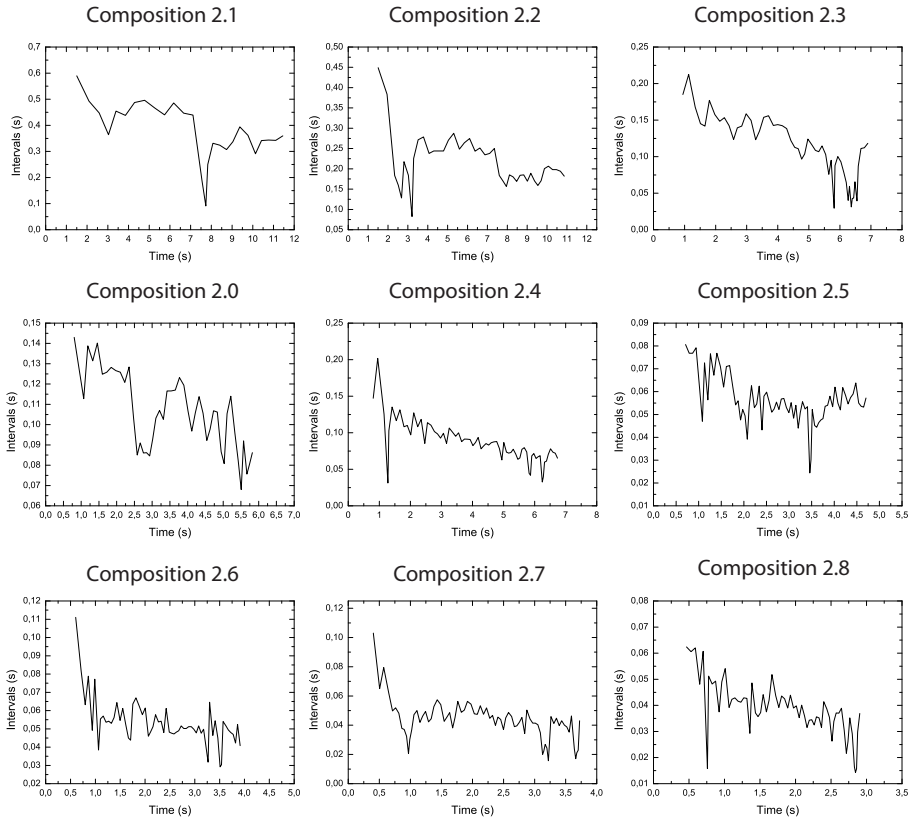


Figure 5.7 – Evolution of the time intervals between two successive flashes for strobe compositions with different magnalium fractions (see Table 5.2 for compositions).

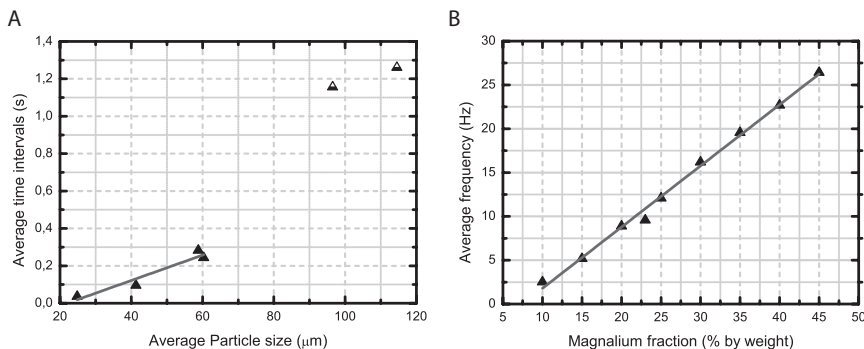


Figure 5.8 – (A) Variation of the average time interval between flashes with magnalium particle size for the composition with 23 % magnalium. (B) Increase of the flash frequency with the magnalium fraction in a strobe composition with 41 μm magnalium particles.

5.4 DISCUSSION

Strobe reactions present similarities with another kind of heterogeneous solid phase combustion, also considered as a pyrotechnic phenomenon: the Self-propagating High-temperature Synthesis (SHS described in the Section 1.3.2 in Chapter 1). They are mostly binary compositions in which when ignited, the combustion front propagates through the powdered ingredients leaving a metallic alloy or a high quality ceramic material. Spatial oscillations or laminated structures (periodic structure perpendicular to the combustion front) may be observed on the produced material due to periodic variations of the flame front velocity. Unlike strobos, this is not a desired effect and extensive studies have been conducted to understand this phenomenon [13–18]. The occurrence of oscillation appears to be dependent on the porosity / density of the sample, its diameter, the particle size and shape of the reactants, dilution with a reactant or an inert material, etc. All those parameters are related to the thermal conductivity of the compositions. The assumption was made that the sample burns in layers. This implies that the characteristic time of reaction is much smaller than the time for heat transfer from one layer to the other. The heat of reaction released by an exothermic reaction in the first layer increases the temperature and the reaction rate. Assuming a low thermal conductivity most of the energy is dissipated and the second layer is slowly ignited. When all the reactants are consumed in the first layer, the reaction only begins in the next layer decreasing the front propagation velocity. A similar layer-by-layer burning is observed in the strobe combustion. Moreover, hot spots, also called scintillations in SHS studies, occur on the surface combustion of both types of compositions (SHS and strobos) [14, 19–22]. They randomly arise on the surface, some tarnish and dissipate, other initiate the reaction in the neighboring areas,

leading to the propagation of the reaction in the layer. The hypothesis is that thermal heterogeneities coincide with the reaction media microstructure such as molten areas. This induces a rapid acceleration of the reaction.

Based on those observations, a model is created to explain the oscillating behavior of strobe reactions. It is schematically depicted in Figure 5.9. The first layer containing magnalium particles is ignited, initiating burning of magnalium to magnesium oxide and aluminum oxide, a thermally activated exothermic reaction. As the temperature rises due to the reaction heat, the reaction rate increases causing an avalanche reaction culminating in a flash of light. Emission spectra taken during the flash show black body radiation and emission from electronically excited reaction products, including MgO and AlO species (See spectra in Figure 2.9 on page 50). Heat transfer to the next lower layer initiates an avalanche reaction in this layer and depending on the balance between heat production and heat diffusion it results in an oscillatory flash behavior.

A detailed mathematical description of the model is based on a reaction of spheres where the change in volume is proportional to the surface area and the reaction rate increases exponentially with temperature (thermally activated reaction). The heat produced in the reaction is partly used to heat the magnalium particles and partly transferred to the surroundings. The strobe behavior model described in this paper is based on a set of non-linear coupled differential equations describing each layer. The strobe burns layer by layer as shown in Figure 5.9. A layer n gains heat from layer $n - 1$, produces heat from a chemical reaction, heats the particles in it and transfers heat to $n + 1$ (See the Appendix: Mathematical description of the strobe behavior model at the end of the chapter on page 110). The particle radius in layer n is then described by (Equation (5.2)):

$$\frac{(r_n/r_0)}{d\tau} = \exp\left(-\frac{k_1}{T_n}\right) \quad (5.2)$$

Where the subscript n refers to the layer n with particle radius r_n and T_n is the dimensionless particle temperature (T of the layer n divided by 300 K). The change in temperature is given by (Equation (5.3)):

$$\frac{dT_n}{d\tau} = \frac{k_2}{r_n/r_0} \exp\left(-\frac{k_1}{T_n}\right) - \frac{k_3}{r_n/r_0} (T_n - T_{n+1}) + \frac{k_3}{r_n/r_0} (T_{n-1} - T_n) \quad (5.3)$$

The first term describes the heat produced by the chemical reaction, the second term the heat loss from layer $n + 1$ and the last term the gain of heat from layer $n - 1$. The model uses five parameters $k_1, k_2, k_3, T_{ambient}$ and T_1 . The definitions for k_1 ,

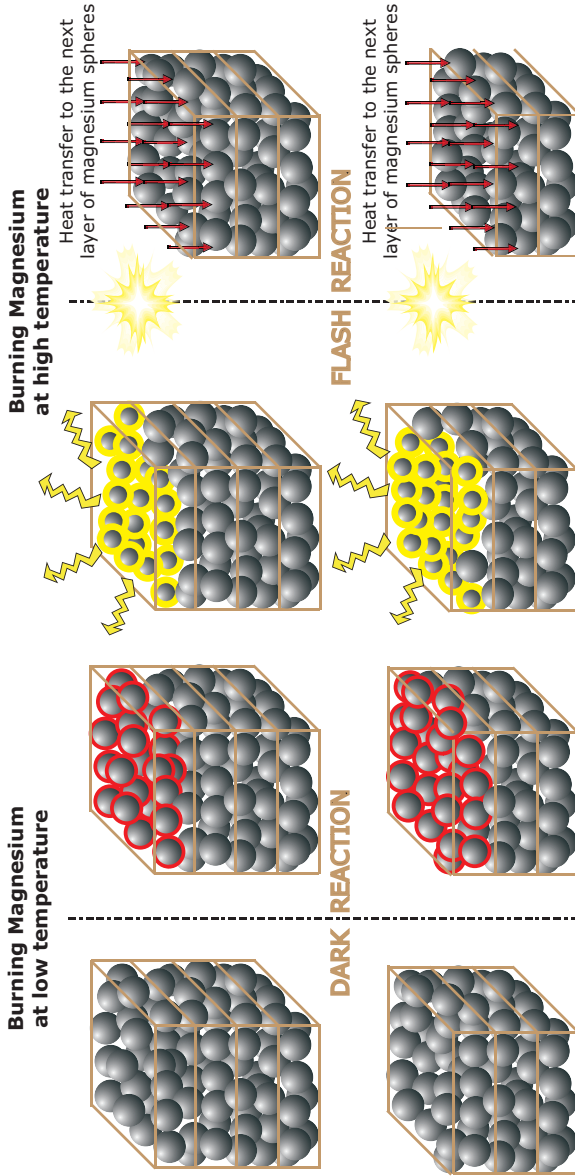


Figure 5.9 – Schematic representation of the strobe burning. The top left shows a strobe composed of (four) layers. The spheres are magnesium particles that start burning after ignition of the top layer. During the reaction heat is produced and the reaction rate increases. This induces an avalanche reaction in which the temperature rises until all material has reacted. A short flash of light is produced due to the high temperature (black body radiation) and excited species are produced during the reaction. Part of the reaction heat diffuses to the second layer and initiates an avalanche reaction in this layer as shown in the bottom part. The process continues until all layers have been consumed.

Table 5.6 – Description of the parameters used in the model to describe the evolution in temperature for different layers in a homogeneous composition of a strobe medium consisting of oxidizer and fuel particles.

Parameter name	formula	description
k_1	$\frac{E_{act}}{RT_{ambient}}$	Activation energy of the reaction divided by the gas constant and ambient temperature.
k_2	$\frac{Q}{c_p T_{ambient}}$	Heat generated in the chemical reaction divided by the specific heat and room temperature.
k_3		Proportional to heat transfer between adjacent layers.

k_2 and k_3 are provided in Table 5.6. $T_{ambient}$ is 300 K and ignition temperature for the first layer T_1 is taken as 5, corresponding to 1500 K. This temperature is slightly lower than the maximum temperature of the flame from a butane burner that is used for igniting the strobe. The two coupled differential equations are used to model the temperature evolution in each layer n under the following boundary conditions:

- The first layer is assumed to transfer heat to only the second layer, so its temperature change is given by:

$$\frac{dT_1}{d\tau} = \frac{k_2}{r_1/r_0} \times \exp\left(-\frac{k_1}{T_1}\right) - \frac{k_3}{r_1/r_0} \times (T_1 - T_2) \quad (5.4)$$

- The last layer N is taken to be an inert medium, which only accepts heat from the layer above it. So its temperature is determined by:

$$\frac{dT_N}{d\tau} = k_3 \times (T_{N-1} - T_N) \quad (5.5)$$

- At $t = 0$ all relative radii r_n/r_0 are equal to 1. The temperatures of all layers except the first are the same and equal to $T_{ambient}$.
- As the radii decrease in the course of time they may become zero and even negative. To prevent negative radii it is postulated that, as the relative radius in any layer becomes zero, the layer does not exist anymore and the layer below it only produces heat by its chemical reaction and loses heat to the layer below it.
- The maximum temperature that can be reached is 2700 K because it is the boiling point of aluminum. It corresponds to $(2700/T_{ambient})$ and at this temperature no particles are present anymore and the layer has disappeared.

In the modeling, values based on literature data have been used to estimate the parameters. k_1 was varied from 10 to 15 which corresponds to activation energies

between 25 and 37.5 kJ/mole. Reliable numbers for the activation energy of magnesium or aluminum oxidation are not available in the literature, however a high activation energy is necessary to ensure that the reaction does not occur at ambient temperature, but can be initiated at ignition temperature T_1 . Values for k_2 can be estimated from the literature values for the standard heat of formation Q and heat capacity c_p which are 600 kJ/mole and 25 J/(mole.K), respectively, for magnesium and 1670 kJ/mole and 24 J/(mole.K), respectively, for aluminum yielding values for k_2 equal to 80 (Mg) and 230 (Al). For the magnalium composite, values for k_2 will be in between these boundaries and in our simulations values for k_2 were varied between 100 and 200. The value for the parameter k_3 is difficult to estimate. The strobe consists of a highly conductive medium (magnalium) and poorly conducting salts. The heat transfer between adjacent layers is however crucial for the observation of strobe behavior which depends on a balance between heating of the fuel particles and heat transfer to subsequent layers. The variation of k_3 in the simulations described demonstrates the sensitivity of the strobe behavior on k_3 (heat transfer in the composition).

Figure 5.10 shows the temporal evolution of the temperature in 15 layers for different values of k_3 . For low values of k_3 (slow heat transport between layers) only the first layer burns. Increasing k_3 to 1.5 or 2.5 produces the experimentally observed strobe effect. Faster heat transfer results in a higher strobe frequency. For $k_3 = 3.5$ heat transfer is so efficient that no heat can build up to start the avalanche flash reaction. The model beautifully reproduces the strobe behavior and demonstrates that the present model can explain oscillating strobe behavior in a homogeneous medium consisting of a fuel and an oxidizer. Longer initial time intervals for smaller k_3 values are also consistent with experiments. Furthermore, the model quantitatively reproduces the observed size dependence of the strobe frequency. The time interval between flashes is inversely proportional to r_0 , the initial particle size radius due to the larger surface area for smaller particles for the same weight fraction. The predicted linear relation between particle size and time interval between flashes shown in Figure 5.10(E) is in agreement with the results in Figure 5.8(A). The effect of adding more magnalium is mainly on k_3 . Heat transfer becomes more efficient with the fraction of conductive metal particles. If we assume that the heat transfer parameter k_3 is proportional to the metal content, a linear increase in frequency with magnesium content is predicted (Figure 5.10(E)), in agreement with the observations of Figure 5.8(B).

In Figure 5.11 the strobe behavior is plotted for fixed values of k_1 and k_2 and different values for k_3 in the regime where strobe behavior is observed. In all cases the experimentally observed linear dependence is reproduced.

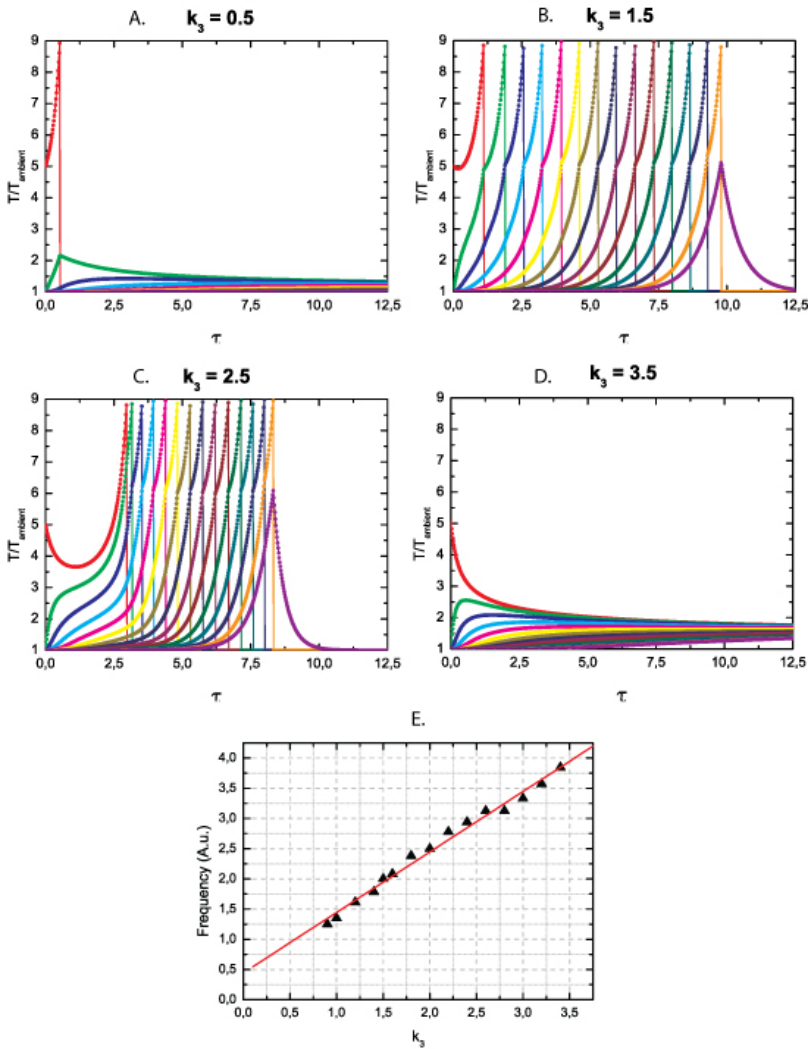


Figure 5.10 – Graph representing the evolution of the temperature $T/T_{ambient}$ of magnalium particles in the successive layers for $k_1 = 15$ and $k_2 = 100$. The parameter k_3 , representing heat transfer between layers, is varied from 0.5 (A) to 3.5 (D). The temperature in different layers is presented by different colors from the top (red) to the bottom (purple) layer. Graph E represents the evolution of the frequency calculated from the model (in arbitrary unit) with k_3 .

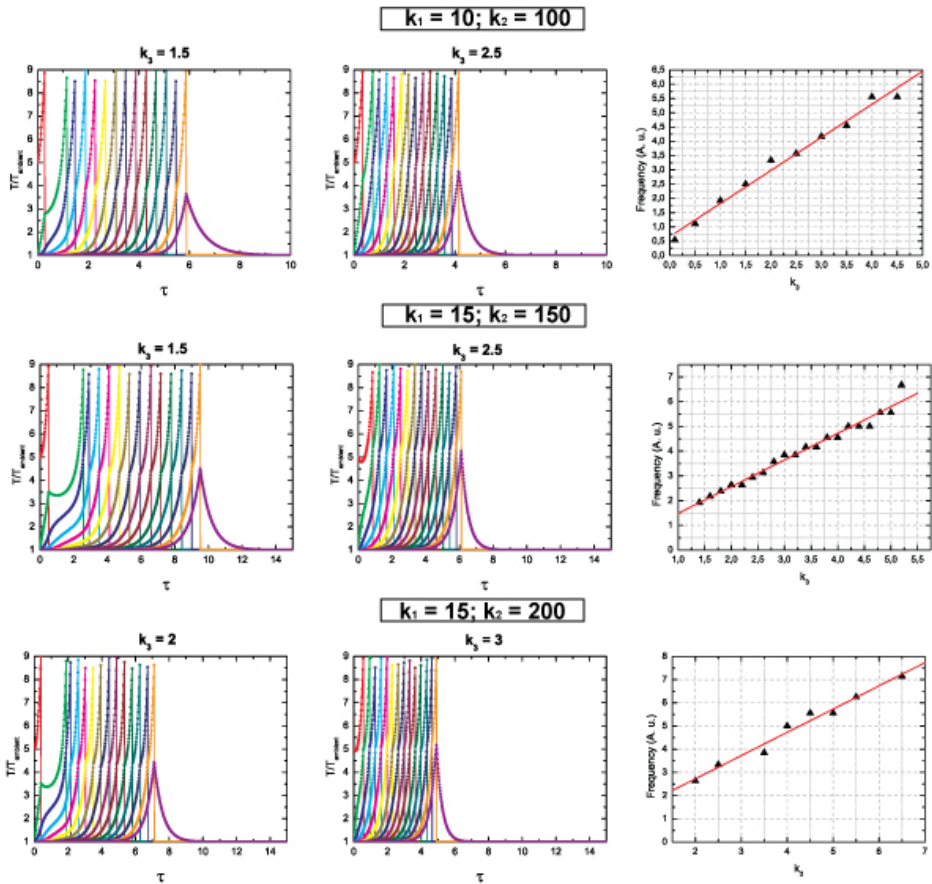


Figure 5.11 – Relation between strobe frequency and the heat transfer coefficient k_3 for $k_1 = 10$, $k_2 = 100$ (top), $k_1 = 15$, $k_2 = 150$ (middle) and $k_1 = 15$, $k_2 = 200$ (bottom). In all three panels, the two figures on the left give examples of the time evolution of the temperature for $k_3 = 1.5$ and $k_3 = 2.5$. The right-hand figure gives the frequencies determined from the simulations as a function of k_3 over a wider range.

5.5 CONCLUSION

A simple model is shown to accurately describe strobe behavior in pyrotechnic compositions. The model explains the observation of periodic flashes in a homogeneous medium consisting of an oxidizer and metal (fuel) particles. A good quantitative agreement is found between experimental results and the model for the relation between flash frequency and both metal particle size and content, providing strong support for the model. The present results give detailed insight into the mechanism behind the intriguing and well-known phenomenon of the brightly flashing fireworks. In addition it enables the design of strobe compositions with well-defined flash frequencies for military applications and crowd control.

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APPENDIX: MATHEMATICAL DESCRIPTION OF THE STROBE BEHAVIOR MODEL

To model the Strobe reaction, a simple reaction is assumed on a spherical object for which the change in volume is proportional to the surface area where the reaction takes place. For the oxidation of the magnalium particles this gives:

$$\frac{dV}{dt} = -k \times A \times p_{O_2} \quad (5.6)$$

Where V is the volume of one particle and A its surface area, k the rate constant of the oxidation reaction of magnalium and p_{O_2} is the oxygen pressure. It assumed that the presence of oxidizer is not rate limiting and so p_{O_2} is taken constant and independent of time. By replacing V and A by their expressions as function of the radius r , Equation (5.6) can be rewritten as:

$$\frac{dr}{dt} = -k \times p_{O_2} \quad (5.7)$$

Thus, the radius decreases with time according to:

$$r = r_0 - k \times t \times p_{O_2} \quad (5.8)$$

If the reaction rate is temperature dependent, it can be written in an Arrhenius form and the time dependence of the radius of the magnesium sphere now becomes:

$$r = r_0 - k_0 \times p_{O_2} \times \exp\left(-\frac{E_{act}}{RT}\right) \times t \quad (5.9)$$

The heat released by the heating of dN mol of magnesium $dQ_{heating}$ is balanced by the heat transferred to the environment dQ_{loss} so the resulting heat Q from the burning of dN mol of magnalium is:

$$Q \times (-dN) = dQ_{heating} + dQ_{loss} \quad (5.10)$$

$$-Q \times dN = c_p \times \rho \times V \times dT = \chi \times A \times (T - T_{ambient}) \times dt \quad (5.11)$$

where c_p is the specific heat of magnalium at constant pressure ($J.K^{-1}.mol^{-1}$), ρ is the molar density of magnalium ($mol.m^{-3}$), V is the volume of the magnalium

particle (m^3), T the temperature of the magnalium particle (K), $T_{ambient}$ is the temperature of the atmosphere (K), χ is the heat transfer coefficient ($\text{J.K}^{-1}.\text{m}^{-2}.\text{s}^{-1}$) and A is the surface of the magnalium sphere.

Dividing Equation (5.11) by dt to obtain a differential equation and by N , V and A to obtain their expressions depending on particle radius, the following expression is obtained:

$$\frac{dT}{dt} = -\frac{Q}{c_p \times \rho \times \nu \times r} \times \frac{dr}{dt} - \frac{3\chi}{c_p \times \rho \times r} \times (T - T_{ambient}) \quad (5.12)$$

ν being the molar volume. The product $\rho\nu$ must equal 1. Using the time dependence equation of the radius of magnalium sphere, the following two differential equations are obtained:

$$\begin{cases} \frac{dT}{dt} = \frac{k_0 \times p_{O_2} \times Q}{c_p \times r} \times \exp\left(-\frac{E_{act}}{R \times T}\right) - \frac{3\chi}{c_p \times \rho \times r} \times (T - T_{ambient}) \\ \frac{dr}{dt} = -k_0 \times p_{O_2} \times \exp\left(-\frac{E_{act}}{R \times T}\right) \end{cases} \quad (5.13)$$

The variable t is replaced by the dimensionless variable $\tau = (k_0 p_{O_2} t)/r_0$ to reach:

$$\begin{cases} \frac{dT}{d\tau} = \frac{k'_2}{(r/r_0)} \exp\left(-\frac{k'_1}{T}\right) - \frac{k_3}{(r/r_0)} (T - T_{ambient}) \\ \frac{(r/r_0)}{d\tau} = -\exp\left(-\frac{k'_1}{T}\right) \end{cases} \quad (5.14)$$

The assumption is made that the strobe burns layer by layer. The system is supposed homogeneous: particles are present in all layers as the same density. Except for the top et bottom layers, any layer n gains heat from layer $n - 1$, produces heat from a chemical reaction, heat the particles in it and transfers heat to $n + 1$. The relative particles radius in layer n is then described by:

$$\frac{(r_n/r_0)}{d\tau} = \exp\left(-\frac{k'_1}{T_n}\right) \quad (5.15)$$

Where the subscript n refers to the layer n with particle radius r_n and temperature T_n , τ is the dimensionless time, inversely proportional to the initial particle radius

r_0 . The change of temperature is given by:

$$\frac{T_n}{d\tau} = \frac{k'_2}{(r/r_0)} \times \exp\left(\frac{k'_1}{T_n}\right) - \frac{k_3}{(r_n/r_0)} \times (T_n - T_{n+1}) + \frac{k_3}{(r_n/r_0)} \times (T_{n-1} - T_n) \quad (5.16)$$

The first term on the right hand side describes the heat produced by the chemical reaction. The second term on the right hand side represents the heat loss from layer $n + 1$ and the last term the gain of heat in layer n from the layer above it, layer $n - 1$.

A dimensionless temperature θ_n is defined by $T_n/T_{ambient}$ so parameters k'_1 and k'_2 are replaced by $k_1 = E_{act}/RT_{ambient}$ and $k_2 = Q/C_p T_{ambient}$, respectively. The two coupled differential equations obtained are:

$$\begin{cases} \frac{\theta_n}{d\tau} = \frac{k_2}{(r/r_0)} \times \exp\left(\frac{k_1}{\theta_n}\right) - \frac{k_3}{(r_n/r_0)} \times (\theta_n - \theta_{n+1}) + \frac{k_3}{(r_n/r_0)} \times (\theta_{n-1} - \theta_n) \\ \frac{(r_n/r_0)}{d\tau} = -\exp\left(-\frac{k_1}{\theta_n}\right) \end{cases} \quad (5.17)$$

6

Summary and Outlook

6.1 STROBE MECHANISMS

Strobes are self-sustained oscillatory combustions that have various applications in the fireworks industry and also in the military area (signaling, missile decoys and crowd control). However, most of the strobe compositions were discovered using trial and error methods. The fundamental mechanisms involved in strobe remain unclear. A few oscillatory chemical systems are reviewed in Chapter 1 and compared to strobe reactions. First, the oscillatory behavior observed in some of the systems (BZ type reactions and cool flames) was explained by the presence of intermediate species that are created and consumed by two chemical pathways. Those chemical reactions often involved autocatalysis. They compete with each other and it results in an oscillation of the concentration of the intermediate species. Then, to explain the oscillatory behavior observed in some SHS combustion, the assumption made was that the reactions occurring are very fast and the heat transfer in the composition is very slow. Consequently, while a part of the composition reacts very quickly, the rest is slowly ignited resulting in a oscillating combustion. Those two features were considered in the analysis of strobe reaction.

The classical ternary strobe composition made of ammonium perchlorate / magnalium / barium sulfate was studied in this thesis. The following physical mechanisms were observed (see Chapter 2). After ignition of the composition, there is the formation of a layer on top of the pellet. This layer is heated up by a reaction and begins to melt. When the flash is imminent, parts of the surface layer are ejected indicating the formation and rapid expansion of gas below the surface. A bright flash follows after which the process is repeated. The pellet is consumed almost linearly, layer by layer. In Chapter 2, some of the chemical mechanisms of this strobe were identified. The decomposition of ammonium perchlorate present in the layer ignited produces the heat and the oxygen molecules necessary for the strobe reaction to proceed. Then the magnalium begin to melt and decomposes into aluminum and magnesium. Finally, the oxidation of liquid and gaseous aluminum and magnesium is observed. The same reactions occur in the next layer.

Parameters that influence the strobe effect are discussed:

- In Chapter 2 the effect of potassium dichromate is studied. A small amount of this compound in the compositions has an important impact on the regularity and sharpness of flashes. It was hypothesized that the decomposition of this compound during the dark phase absorbs part the energy released, restraining the increasing reaction rate.
- Chapter 3 studies the influence of the melting point of the metal sulfates or nitrates used. It appears that the compositions containing high melting point metal sulfates (barium and strontium sulfates) produce sharper and more

regular flashes. Those compositions also have a lower flash frequency.

- The temperature evolution during the strobe reaction is reported in Chapter 4. No strong influence of the composition and atmosphere on the maximum temperature reached during the flash phase is observed.
- Chapter 5 studies the influence of the heat transfer of the composition on the strobe behavior by varying the fuel weight fraction and its particle size. It appears that compositions with a lower heat transfer in the composition results in a lower flash frequency.

Based on the observations made for other chemical oscillating systems and on the results of the experiments performed in this thesis, a strobe model was built (see Chapter 5). It is based on a layer-by-layer combustion and a delicate balance between heat generation in one layer and heat transfer to the next layer. The first layer containing magnalium is ignited, initiating the decomposition of ammonium perchlorate and the oxidation reaction of magnesium and aluminum, thermally activated exothermic reactions. As the temperature rises due to the reaction heat, the reaction rate increases causing an avalanche reaction culminating in a flash of light. Most of the heat released by the first layer is dissipated and only a small part is slowly transferred to the next layer and the processes repeat. The model can explain the various observations for the strobe behavior qualitatively and quantitatively.

6.2 HOW TO CONTROL THE STROBE FREQUENCY

A control of the frequency of flashes of a strobe composition is achieved by a control of the heat transfer in the composition. The conductivity of a solid composition can be changed by varying the porosity of the composition (or density), the reactant particle sizes, the diameter or shape of the composition, the dilution of the reactants by an inert material, change the metal content, etc. In this thesis, the heat transfer of the ternary composition studied was varied by changing the particle size of magnalium and the weight fraction of magnalium. Smaller particle size of magnalium and higher weight fraction of magnalium increases the heat transfer in the composition and also increases the frequency of flashes.

6.3 OUTLOOK

It is of paramount importance to find a more accurate method to measure the evolution of the temperature of the strobe composition and check if the variation of parameters such as the metal sulfates used or heat transfer of the composition affects the temperature.

Some of the gaseous species were identified thanks to emission spectra recorded during the flash phases. More accurate methods should be used to identify the gaseous species produced the flash phases but also the dark phases. This knowledge may yield to a better understanding of the chemical reactions involved in this strobe reaction and improve the existing model for strobe reaction.

Only one type of strobe compositions was studied in this thesis based on the couple ammonium perchlorate / magnalium and the model built is based on the burning of magnalium particles. Magnalium is very often the preferred fuel for strobe compositions but other metal can be used such as copper. Ammonium perchlorate can easily be replaced by for instance sulfur, guanidine nitrate, potassium perchlorate or nitrate. The various strobe compositions must be tested to verify if the model can be applied to other strobos.

Finally, strobe compositions currently in existence use oxidizers like metal sulfates, nitrates, perchlorates and additives such as dichromates. No environmentally friendly strobing compositions are known at this time. The development of environmentally friendly strobe compositions, in particular the replacement of potassium dichromate, is an area of potential interest.

Samenvatting in het Nederlands

Strobes zijn oscillerende verbrandingen die leiden tot een opeenvolging van flitsen worden toegepast in de vuurwerkindustrie en de defensiewereld (markering, raketafleiding en niet-dodelijke wapens). De meeste composities (samenstellingen van chemische ingrediënten) die strobegegedrag vertonen zijn gevonden door heel pragmatisch veel verschillende samenstellingen uit te proberen. Het fundamentele mechanisme achter het strobegegedrag is echter onduidelijk. Enkele in de literatuur genoemde verklaringen zijn verwant aan bekende voorbeelden van oscillerende chemische systemen. Deze worden in dit proefschrift nader bekeken en vergeleken met het gedrag van een strobe. Een vorm van oscillerend gedrag dat wordt waargenomen in sommige systemen (zogenaamde BZ-type reacties en koude vlammen) kan worden verklaard aan de hand van een intermediair dat wordt gecreëerd en tegelijkertijd geconsumeerd door twee chemische reacties. Doordat deze reacties met elkaar concurreren ontstaat er een oscillatie in de concentratie van het intermediair. Een andere type oscillerend gedrag wordt waargenomen in SHS (Self-propagating High Temperature Synthesis) verbranding en voor dit type reactie wordt het oscillerend gedrag verklaard door een reactietijd die concurreert met de karakteristieke tijd voor warmteoverdracht. Beide mechanismen voor oscillerend gedrag worden meegenomen in de analyse van het gedrag van strobes.

De klassieke strobe bestaande uit perchloraat / magnalium / barium sulfaat vormt de basis voor dit proefschrift. Tijdens de verbranding van deze strobe worden de volgende waarnemingen gedaan: Na ontsteking van de compositie wordt er een laag gevormd aan de bovenkant van de cilindrische pil. Deze laag warmt op door de vrijkomende reactiewarmte en begint te smelten. Vlak voor een flits komen gedeeltes los van de oppervlaktelaag wat een indicatie is voor de formatie en snelle expansie van gassen onder het oppervlak van deze laag. Hierna volgt een heldere flits waarna het proces opnieuw begint in een volgend laagje. De cilindrische pil verbrandt bijna lineair, laag voor laag, van boven naar beneden. Verschillende chemische reacties die bijdragen aan het strobe-mechanisme zijn geïdentificeerd. De ontleding van de ammoniumperchloraat in de ontstoken laag produceert de warmte en de zuurstof die nodig zijn voor de voortgang van de strobe-reactie. De magnalium smelt en scheidt in aluminium en magnesium. Tot slot wordt de oxidatie van het vloeibare en gasvormige aluminium en magnesium waargenomen waarbij zeer veel energie vrijkomt in de vorm van warmte en licht. Al deze reacties vinden plaats in opeenvolgende lagen tot de strobe is opgebrand.

Enkele parameters die het strobe-gedrag beïnvloeden zijn in meer detail bestudeerd. Als eerste is het effect van kaliumdichromaat bestudeerd. Een kleine toevoeging van

deze stof aan de compositie heeft een sterk positief effect op de reproduceerbaarheid en scherpte van de flitsen. De hypothese in de literatuur is dat deze stof door decompositie een gedeelte van de vrijkomende energie tijdens de donkere periode voor de flits absorbeert en zo de reactiesnelheid tempert. Daarnaast is de invloed van het smeltpunt van metaalsulfaten en nitraten bestudeerd. Hieruit kwam naar voren dat composities die een metaalsulfaat met een hoog smeltpunt bevatten (barium- en strontiumsulfaat) een scherpere en meer reproduceerbare flits produceren. Deze composities hebben ook een lagere flitsfrequentie. Tot slot is de invloed van warmteoverdracht op het gedrag van een strobe bestudeerd door het variëren van de brandstofhoeveelheid in de compositie en de deeltjesgrootte van de brandstofdeeltjes (magnalium). Hieruit kon worden geconcludeerd dat composities met een lagere warmteoverdracht een lagere flitsfrequentie opleveren. Daarnaast is er geconstateerd dat geen van deze parameters een sterke invloed heeft op de eindtemperatuur die bereikt wordt tijdens de verbranding.

Gebaseerd op de al eerder gemaakte waarnemingen voor andere chemisch oscillerende systemen en de resultaten van de experimenten in dit proefschrift is een model voor het verklaren van het strobegedrag opgesteld. Dit model is gebaseerd op een laag voor laag verbranding en een subtiële balans tussen het vrijkomen van warmte in een laag en warmteoverdracht naar de volgende laag. Het ontsteken van de eerste laag, die magnalium bevat, initieert de decompositie van ammoniumperchloraat en de oxidatiereactie van magnesium en aluminium, beide thermisch geactiveerde exotherme reacties. Met het stijgen van de temperatuur door de vrijkomende warmte uit de exotherme reacties stijgt de reactiesnelheid exponentieel wat uiteindelijk leidt tot een lawine-effect en een flits. Het grootste gedeelte van de warmte die vrijkomt door de verbranding van de eerste laag verdwijnt uit het systeem in de vorm van straling. Slechts een klein gedeelte wordt via warmteoverdracht doorgegeven naar de volgende laag waar het proces van verbranding geïnitieerd wordt. Dit proces herhaalt zich totdat er geen laag / compositie meer beschikbaar is. Als een consequentie hiervan kan de frequentie van de strobe worden gecontroleerd door de warmteoverdracht en warmteproductie in de compositie te beïnvloeden. Dit kan door één of meer van de volgende parameters te veranderen: porositeit (dichtheid) van de compositie, de grootte van de deeltjes, de diameter en vorm waarin de compositie is geperst, toevoeging van een inert materiaal, veranderen van het metaalaandeel in de compositie, etc. In dit proefschrift is de warmteoverdracht van de strobecomposities veranderd door het variëren van de deeltjesgrootte van het magnalium en het percentage van het magnalium in de compositie. Een kleinere deeltjesgrootte en hogere gewichtsfractie verhogen de warmteoverdracht in de compositie en verhogen daardoor ook de frequentie van de flitsen.

De nieuwe inzichten in strobereacties die tijdens het onderzoek verkregen zijn vormen een belangrijke doorbraak in het begrip van stobes. In het laatste hoofdstuk

worden de belangrijkste conclusies samengevat en worden uitdagingen geschetst voor verder onderzoek. Beter inzicht in de diverse chemische reacties die bijdragen aan het strobe effect en alternatieve (milieuvriendelijke) strobe-samenstellingen vormen uitdagingen voor verder onderzoek.

Résumé en Français

Les “Strobes” ou “Clignotants” sont des compositions pyrotechniques produisant des flashes de lumière blanche ou colorée par intermittence. Ces compositions sont utilisées principalement dans l’industrie des feux d’artifices. Elles sont appliquées dans le domaine militaire au travers de fusées de signalement ou de leurres aériens. La majorité des compositions stroboscopiques ont été découvertes de manière empirique et les mécanismes physiques et chimiques responsables des oscillations restent incompris. Il existe actuellement de nombreux systèmes chimiques présentant des oscillations d’une ou plusieurs variables telles que la température, la pression ou les concentrations de certaines espèces chimiques. Dans cette thèse, plusieurs de ces systèmes sont décrits: les réactions de Belousov-Zhabotinski, les flammes froides, les combustions “Self-propagating High-temperature Synthesis” (SHS). Ils sont ensuite comparés aux mécanismes observés durant la combustion de plusieurs compositions stroboscopiques. Les comportements périodiques des réactions de Belousov-Zhabotinskii et des flammes froides sont souvent expliqués par la présence d’espèces chimiques intermédiaires qui sont successivement produites et consommées. Dans ces systèmes chimiques, deux réactions sont en compétition pour créer et consommer les espèces intermédiaires. Ainsi, leurs concentrations varient de façon périodique. Des variations en température sont souvent observées dans les compositions de type SHS. Elles sont le plus souvent attribuées à des paramètres physiques liés au coefficient de transfert de chaleur. Ces observations ont été prises en compte dans l’étude des compositions stroboscopiques.

Le mélange contenant du perchlorate d’ammonium, du magnalium (un alliage 50/50 d’aluminium et de magnésium) et du sulfate de baryum est considéré comme une composition stroboscopique classique. Les différents mécanismes physiques et chimiques responsables du comportement périodique sont étudiés dans cette thèse. Après ignition, une fine pellicule se forme à la surface de la composition. Une réaction exothermique dégage de la chaleur dans cette couche et se met à fondre. Quand le flash est imminent, cette pellicule en partie liquide se morcèle et certains fragments se détachent de la composition. Cela indique la formation et l’expansion rapide de gaz en dessous de la surface. Après la formation d’un flash de lumière intense, le cycle recommence. La composition se consume presque linéairement, couche après couche. Certains des mécanismes chimiques ont pu être identifiés. La décomposition du perchlorate d’ammonium dans la pellicule qui se forme sur la surface dégage de la chaleur et produit les molécules d’oxygène nécessaires aux réactions d’oxydation de l’aluminium et du magnésium. Ensuite, le magnalium fond permettant la dissociation des molécules de magnésium et d’aluminium. Enfin,

ces deux espèces chimiques sont oxydées, créant ainsi de l'oxyde de magnésium et d'aluminium sous forme liquide ou gazeuse. La chaleur dégagée par les diverses réactions est majoritairement dissipée dans l'atmosphère. Seulement une petite partie de cette énergie est transmise au reste de la composition où une nouvelle pellicule se forme et le cycle recommence.

Plusieurs paramètres influencent l'effet stroboscopique. Tout d'abord, l'ajout de dichromate de potassium en petite quantité a un effet manifeste sur la régularité et la séparation des flashes. L'hypothèse avancée expose que la décomposition de cette espèce chimique, pendant les phases sombres, absorbe une partie de l'énergie libérée par les diverses réactions, restreignant ainsi l'accélération rapide de la vitesse de réaction. Par la suite, il a été constaté que le point de fusion des sulfates ou nitrates de métaux a une influence importante sur l'effet stroboscopique. Les résultats d'expériences ont montré que les compositions contenant des sulfates de métaux ayant des points de fusion élevés (sulfates de baryum et de strontium) produisent des flashes plus réguliers et la séparation entre les flashes est également plus nette. Puis, l'influence du coefficient de transfert de chaleur de la composition a été étudiée. Le pourcentage massique de fuel (magnalium) et sa taille de particules sont deux paramètres liés à la conductivité de la composition. Une étude de corrélation est effectuée entre ces paramètres et la fréquence de flashes. Les intervalles de temps entre deux flashes successifs sont plus longs pour les compositions ayant un coefficient de transfert de chaleur moins élevé. Enfin, l'évolution de la température de différents stroboscopes a été évaluée dans cette thèse. Aucun des paramètres cités précédemment ne semble avoir une influence perceptible sur la température.

En s'inspirant des mécanismes observés pour les différents systèmes chimiques oscillatoires décrits dans cette thèse et les résultats d'expériences réalisées, un modèle théorique a pu être construit. Il est basé sur une combustion couche par couche et un équilibre fragile entre la production de chaleur et son transfert aux couches inférieures. La première couche se forme après ignition de la composition. Le perchlorate d'ammonium se décompose, libérant de l'énergie nécessaire aux réactions d'oxydation du magnésium et de l'aluminium. Tandis que la température dans la couche supérieure augmente, la vitesse de combustion s'accélère créant des réactions en chaîne responsables du flash de lumière. La majeure partie de chaleur dégagée par les réactions dans la couche supérieure est dissipée dans l'environnement. Seulement une petite partie est lentement transférée à la couche suivante et le cycle recommence dans celle-ci.

La fréquence de flashes d'un stroboscope est contrôlée par le coefficient de transfert de chaleur de la composition. La conductivité d'une composition peut être changée en variant sa porosité (ou sa densité), la taille des particules, le diamètre ou la forme de la composition, la dilution des réactifs dans un matériau inerte, la proportion de métal dans la composition, etc. Dans cette thèse, l'influence du coefficient

de transfert de chaleur de la composition classique contenant du perchlorate d'ammonium, du magnalium et du sulfate de baryum sur l'effet stroboscopique a été étudiée en changeant la taille de particules de magnalium et son pourcentage massique. La fréquence de flash peut être diminuée en augmentant la taille des particules de magnalium ou en diminuant le pourcentage massique de magnalium.

Une nouvelle approche des réactions stroboscopiques est développée dans cette thèse et représente une avancée importante dans la compréhension de cette combustion oscillatoire. Le dernier chapitre récapitule les principales conclusions de cette thèse et propose des directions de recherche pour de futures études. Une meilleure compréhension des nombreuses réactions chimiques qui contribuent à l'effet stroboscopique et le remplacement de certaines espèces chimiques (compositions moins polluantes) sont des défis pour le futur.

List of publications

Journal Publications

'Strobe: pyrotechnic compositions that show a curious oscillatory combustion'; Justine M. L. Corbel, Joost N. J. van Lingen, John F. Zevenbergen, Onno L. J. Gijzeman, Andries Meijerink; *Angewandte Chemie International Edition; in press* (Chapter 1).

'Study of a classical strobe composition'; Justine M. L. Corbel, Joost N. J. van Lingen, John F. Zevenbergen, Onno L. J. Gijzeman, Andries Meijerink; *Propellants, Explosives, Pyrotechnics; in press* (Chapter 2).

'Strobe: an oscillatory reaction'; Justine M. L. Corbel, Joost N. J. van Lingen, John F. Zevenbergen, Onno L. J. Gijzeman, Andries Meijerink; *Journal of physical chemistry B*; **2012**; 116(16); 4967-4975 (Chapter 3).

'Strobes: an Intriguing Oscillating Combustion Phenomenon'; Justine M. L. Corbel, Joost N. J. van Lingen, John F. Zevenbergen, Onno L. J. Gijzeman, Andries Meijerink; *to be submitted* (Chapter 5).

Oral presentations in conferences

'**New Insight into strobe reactions**'. *12th International Symposium on Fireworks*, October 11-15, 2010, Porto/Gaia (Portugal)

'**Understanding Strobe Reactions**'. *8th Workshop on Pyrotechnic Combustion Mechanisms*, May 14, 2011, Reims (France)

'**The use of Sulfates in Strobe Compositions**'. *Europyro 2011 - 10th International GTPS Seminar - 37th IPS event*, May 12-19, 2011, Reims (France) (Chapter 3).

'**Strobes: an Intriguing Oscillating Combustion Phenomenon**'. *38th International Pyrotechnic Seminar*, June 10-15 2012, Denver, Colorado (USA). (Chapter 5), **Young Scientist award**.

Poster presentations

'**Understanding Strobe Reactions**'. *36th International Pyrotechnic Seminar*, August 23-28, 2009, Rotterdam (The Netherlands)

'**Influence of the initial composition on strobe reactions**'. *NWO Scientific meeting on Chemistry related to Physics & Material Sciences / Dutch Polymer Days*, March 14-15, 2011, Veldhoven (The Netherlands)

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Curriculum Vitae

The author of this thesis was born on November 12th 1985 in Brest, France. She obtained her “Baccalauréat” in 2003 with honors at the High School Iroise in Brest (France). The same year, she started a two-years post-secondary school preparation in advanced Mathematics and Physics for the competitive entrance examinations to French Graduate Engineering Schools (Classes préparatoires MPSI/MP*) in the High School Kerichen in Brest (France). In 2005, she got accepted in the general engineering school ENSTA Bretagne (former ENSIETA) in Brest (France) where she specialized during her last year in Energetic Materials Engineering. She obtained her engineer diploma (Equivalent of Master Science degree) in 2008. During her studies, she did a few internships. In 2006, she went to Burkina Faso for an humanitarian internship (Funding and Fabrication of identity papers and birth certificates for the women and children). In 2007 she did a technical internship as an assistant engineer in the “Pyrotechnie Saint-Nicolas” in Relecq Kerhuon (France) and performed a security study on ammunitions transportation inside the military base. In 2008, she did her final internship in TNO (Netherlands Organization for Applied Research) in the Netherlands where she modeled a prototype launch vessel for a low smoke lifting of shell.

After the completion of her studies, she left France in November 2008 to start her PhD research at the Utrecht University in the Faculty of Science in the group Condensed Matter and Interfaces (CMI) in collaboration with TNO Defence Security and Safety under the supervision of Professor Andries Meijerink (Utrecht University), Dr. Onno Gijzeman (Utrecht University), Dr. Joost van Lingen (TNO) and Dr. John Zevenbergen (TNO). During the course of the PhD studies, the author supervised two master students in the course of their project.

During the PhD research, the author attended numerous international conferences and workshops, where she presented results of her research in the form of posters and oral presentations. The international meetings included the 36th International Pyrotechnic Seminar (IPS 2009) in Rotterdam, The Netherlands, the 12th International Symposium in Fireworks (ISF 2010) in Porto/Gaia, Portugal, The NWO scientific meeting on Chemistry related to Physics (2011) in Veldhoven, The Netherlands, The 8th Workshop in Pyrotechnic Combustion Mechanisms (IPS Workshop 2011) in Reims, France, the EuroPyro 2011 in Reims, France and the 38th International Pyrotechnic Seminar (IPS 2012) in Denver, USA where the author received the IPS Young Scientist Award. She also attended the Pyrotechnics Course in the Department of Applied Science, Security and Resilience of Cranfield University given by Dr. Nigel Davies in England.

