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DESIGN OF SUITABLE PYROTECHNIC DELAY COMPOSITION WITH WIDELY USED COMPONENTS

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Abstract: *The development of time delay pyrotechnic elements represents an important part of improving a new fuse and ammunition. This study aims to show an optimization of the ratio in the fuel oxidant mixture and how this ratio influences the burning properties of pyrotechnic compositions. In compositions observed in this research, sulfur and charcoal react as fuels, potassium nitrate reacts as an oxidant and phenol-formaldehyde resin operates as a binder. The stochiometric ratios were determined by using the oxygen balance (OB) and pyro valence (PV) values. The linear burning rate was measured using a VOD 811 system for some typical compositions which were pressed into aluminium tubes. The calorimetric bomb was used in the experiments with an inert gas supply to determinate the heat of reaction and the closed-vessel test was used to measure the production of gaseous products.*

Keywords: *Pyrotechnic, time delay, charcoal, sulfur, burning rate,*

1. INTRODUCTION

Among the variety of energy-intensive compositions, delay pyrotechnic compositions are of great interest, which serve to create time delays of the required duration. The need to ensure a time delay in the operation of pyrotechnic products arose with the appearance of black powder and the first powder bombs, hand grenades and rockets. The delay was necessary to have time to move away to a safe distance, and to detonate the charge at the right moment [1]. Pyrotechnic delay compositions can be considered gasless or gas-producing depending on the quantity of gas generated during the combustion. Typically, gasless delays are used in sophisticated projectiles and gas-producing delays are used for inexpensive munitions such as hand grenades and signal devices, considering the quantity of gas upon ignition (approximately 50% of the reaction products are gaseous) [2]. The advantages of gas producing delay compositions over gasless systems are their ability to provide accurate delay time, long-term storage stability, and available ingredients. The disadvantage of the system lies in the effect of external pressure on their burning rate which can be overcome by providing an adequate design of a fuze [3]. Black powder composition designed in a manner of time delay device in this paper typically consists of 65-80 wt.% potassium nitrate, 5-25 wt.% charcoal, 5-10 wt.% sulfur with rest comprising of phenol-formaldehyde resin. Some of the important characteristics of these delay compositions are gaseous combustion behaviour, constant burning time, economically acceptable and widely used ingredients and long-term storage stability. Charcoal is a natural solid fuel. It is produced by pyrolysis or carbonization of wood. The precise definition of chemical composition and physical appearance is hard to define. It depends on the degree of carbonization, temperature and pressure in which the process takes place. This natural material contains carbon, moisture, ash-generating minerals, and a large number of different hydrocarbons that volatilize when combustion is initiated.[4] It has properties like large surface area, approximately 1-3m^2/mg, heat conductivity and adsorption. [5] Thus, black powder has a high burning rate and charcoal is used as a catalyst. The pyrotechnic behaviour of charcoal may vary, depending on which wood is used to prepare the material.

[2,5] A similar observation has been reported previously by [2], [6-9] and thermodynamic code EXPLO5 has predicted charcoal formula as shown in Table 1. This implies that charcoal contains largely of carbon, and for easier determination of OB, PV and theoretical maximum density (TMD) in this paper was used carbon as an approximation in calculations. The charcoal used in this paper has a willow tree (Salix) origin.

Table 1. Charcoal formulations from different sources

Number	Charcoal formula	Source
1	C_6H_{2O}	Sidlovski [6]
2	$C_{16}H_{10}O_2$	Maksimovic[7], Cokling[2]
3	$C_{20}H_7O$	Orbovic [8]
4	$C_{42}H_{60}O_{28}$	Koch [9]
5	$C_{7,2}H_{4,99}O_{0,52}$	EXPLO5
6	$C_{10}H_{4,77}N_{0,04}O_{1,23}Ca_{0,003}$	EXPLO5

Eight compositions were selected to determinate OB, PV and TMD, and they are presented in Table 2. The $\Omega(CO_2)$ of all compositions lies in the range of -63.08% to +34.3%. Pyro valence was calculated for all compositions and it is noticeable that PV approach has a similar trend when it comes to assuming the products of reaction as OB method. The theoretical maximum density (TMD) is calculated using the mass fraction and density of each ingredient in the mixture.

Table 2. Selected formulations of time delay pyrotechnic compositions

	TD-1	TD-2	TD-3	TD-4	TD-5	TD-6	TD-7
KNO_3	65	70	75	80	85	75	75
C	25	20	15	10	5	5	10
S	5	5	5	5	5	15	10
$C_{13}H_{12}O_2$	5	5	5	5	5	5	5
OB[%]	-63.08	-52.6	-37.3	-12.55	+34.3	-9	-25.8
PV	+7.22	+5.05	+3.4	+1.47	-0.42	+1.36	+2.32
TMD [g/cm^3]	2.734	2.602	2.471	2.339	2.208	2.201	2.335

2. EXPERIMENTAL DETAILS

2.1. Ingredients and Preparation

2.1.1 Mixing process

The following substances were used to prepare the abovementioned formulations and perform the experimental study: potassium nitrate as an oxidizer, charcoal and sulfur as fuel and phenol-formaldehyde resin as a binder. The method of preparation consists of the following operations:

1) weighting of ingredients;
2) drying of oxidizer and fuels in an oven at 60°C for 3h;
3) dissolving the phenol-formaldehyde resin in a solvent;
4) dry homogenization is performed in several phases. The first phase was performed by mixing fuels until all components were evenly dispersed, then was added oxidizer and all compounds were well-mixed together
5) wet homogenization was performed with well mixed ingredients from dry homogenization with the addition of dissolved binder
6) mashing phase consists of manual sieving of the wet mixture through a sieve
7) drying in an oven at 60°C for 4h to remove remaining moisture content
8) the last operation was packing into hermetic containers. [10]

The present study focuses on experimentally investigating the impact of the ratio in the fuel oxidant mixture and how this ratio influences the burning properties of pyrotechnic compositions with widely used components. All ingredients were delivered by Trayal Corporation AD (commercial quality) and formulations TD-1, TD-3, TD-4, TD-6 and TD-7 from Table 2 were selected to determinate linear burning rate, the heat of reaction and predict the burning behaviour of formulations by the closed-vessel system. These mechanical mixtures are used in powder form for calorimetric bomb and closed-vessel experiments. Further, these mechanical mixtures were pressed with a hydraulic press into aluminium tubes for burning rate tests.

2.2. Techniques

2.2.1 Heat of reaction

The calorimetric bomb analysis was performed using the IKA-Calorimeter C 2000 model. Experiments were performed in the absence of oxygen with an inert gas supply to determinate the heat of reaction value. A mechanical mixture of 3 g was used in powder form to determinate the value of heat released during the reaction. Heat of reaction is defined as the amount of heat released through the combustion of 1 g of pyrotechnic composition in an inert atmosphere.

2.2.2 Linear Burning rate

Burning characteristics of any multicomponent solid fuels depend on many significant parameters such as overall composition, fuel and oxidizer particle size, adequate inter-particle contacts between reactants, an adequate technique of mixing, bulk thermal conductivity and heat of reaction of the mixture, reaction rate progress, reaction zone temperature and pressure. [11] It is a self-propagating reaction in solid mixtures with a strongly exothermic reaction when a considerable amount of heat is evolved in the chemical charge. The linear burning rate can be determined based on the physicochemical property of the ingredients and their relative proportion. The purpose of this time delay composition is to be able to provide a specific time between two events and also has a role to ignite the next mixture in the pyrotechnic line. Therefore, it is important to define the precise time and flux of gaseous products so they can fulfil their required function. For each composition, five tubes were tested. A specific amount of each pyrotechnic composition was measured and pressed into an aluminium alloy tube (height 15mm, radius 8mm and thickness of wall tube 2mm) with 20 MPa of pressure on the "DUNKES" hydraulic press (Figure 1.). The linear burning rate was determined with VOD 811 system with specially adjusted software for the correct display of lower combustion velocities.

Figure 1. "DUNKES" vertical press

2.2.3 Closed vessel system

The selection of an oxidizer, fuel and binder for pyrotechnic composition and their weight ratio determines the heat output as well as the gas output for the mixture under consideration. [2] For time delay compositions, considered in this paper, is very important to have first information on gas generating possibilities especially how many gas products are going to be produced in a function of time. The pressure of combustion products is a very distinctive characteristic of every pyrotechnic composition and it is strongly influenced by the nature of ingredient's oxygen/fuel ratio. The pressure of combustion products was measured in a closed vessel. Every sample prepared for the experiment consisted of 3g of pyrotechnic composition in powder form placed in polyethylene containers and fitted with an electric igniter. The polyethylene containers were then placed in a bomb and an electric igniter was connected onto connectors on the bomb cover. The Tektronix DPO 4054 Digital Phosphor Oscilloscope (500MHz-2ns) (Figure 2.) was used to measure data.

Figure 2. Tektronix DPO 4054 Digital Phosphor Oscilloscope

3. RESULTS AND DISCUSSION

3.1. Heat of reaction

For each pyrotechnic composition, three measurements were performed and an average value is presented in Figure 3. The first property to notice in Figure 3 is that the value of energy potential is the highest with the composition TD-4 (3051.8 J/g). It contains the highest content of oxidizer from 80 wt.% and OB has a -12.55% value. It is interesting to note that composition TD-6 has the second highest value of energetic potential, the highest content of sulfur and smallest OB value -9% of all compositions. This result can be explained by the dual nature of sulfur. Depending on conditions, sulfur can behave as an oxidizer or as a fuel in the combustion process.

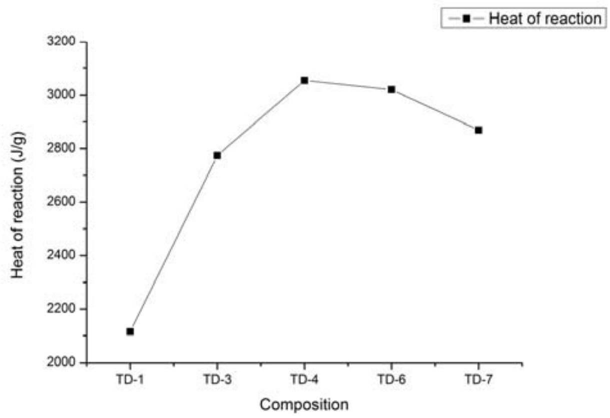

Figure 3. Selected compositions and their heat of reactions values

3.2. Determination of gas producing characteristic

The gas-producing characteristic was measured in a manometric bomb. For each composition, three measurements were taken and an average value was calculated. The results are shown in Figure 4.

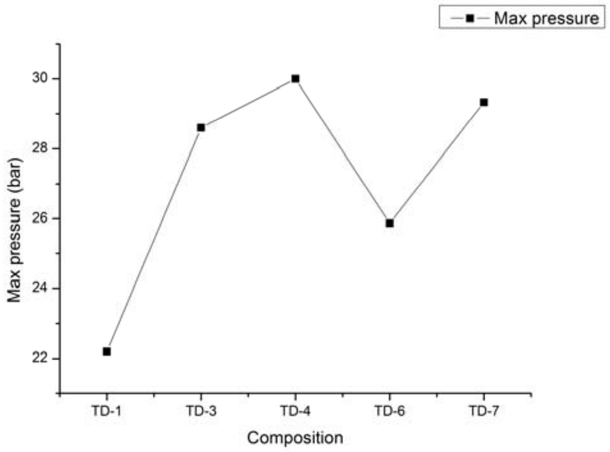

Figure 4. Selected compositions and their maximum pressure

Results in Figure 4 and Table 3 show that compositions TD-3, TD-4, TD-6 and TD-7 have relatively small scattering values in both maximum pressure of combustion products (P_{max}) and time to reach P_{max} (t_{max}), so they have similar behaviour when it comes to gas-producing characteristic.

Table 3. Measured time (t_{max}) to reach maximum pressure (P_{max}) for selected compositions

Composition	TD-1	TD-3	TD-4	TD-6	TD-7
P_{max} [bar]	22.2	28.6	30	25.87	29.33
t_{max} [ms]	121.73	47.27	39.87	51.53	36.2

Pyrotechnic composition TD-1 has a huge drop compared to the four mentioned in both maximum pressure of combustion products (P_{max}) and time to reach P_{max} (lowest t_{max}). This is attributed to the presence of a high mass percentage of charcoal which implies that due to its nature, charcoal has an affinity to "suffocate" combustion process. Furthermore, this implies that incomplete combustion has occurred with TD-1 composition.

3.3. Linear burning rate

Data from the linear burning test are shown in Figure 5. For each composition, five tubes were tested, and an average value was calculated. Results in Figure 5 reveal that the fastest burning belongs to composition TD-1 and from that point there is a decreasing trend of burning time which follows until composition TD-6. It is interesting to note that the pyrotechnic composition TD-1 has the highest OB value, the lowest value of heat of reaction and poorest, substandard values of gas-producing characteristic, this implies that burning characteristic depends on properties like inter-particle contacts between reactants, heat conductivity increases if the pyrotechnic composition is in compressed form.

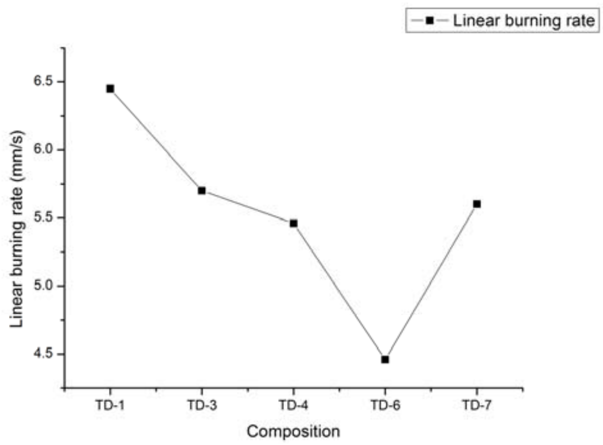

Figure 5. Average linear burning rate for selected pyrotechnic composition

4. CONCLUSION

The main focus of this work was to incorporate widely used and acceptable ingredients to produce desired time delay effect. In this work, a four-component pyrotechnic system of potassium nitrate (KNO_3), charcoal, sulfur and phenol-formaldehyde resin were analyzed and compared. Any change in the ratio of the pyrotechnic composition essentially affects the equilibria. For gaseous, time delay pyrotechnic composition is important to have a well-balanced combination of gaseous and condensed products of combustion. The obtained data shows that combustion of pyrotechnic compositions is a complex thermodynamic process and that it changes with a slight change in oxidant-fuel ratio. Therefore, the primary functions of gaseous time delay compositions are satisfied with compositions TD-3, TD-4, TD-6 and TD-7. Those pyrotechnic compositions can be used in different types of ammunition depending on the required effect. The composition TD-1 does not satisfy the minimum of performed tests. However, for a more precise determination of time delay compositions, more tests must be performed for full characterization. For some future work, it would be interesting to perform an analysis with active carbon and carbon black instead of charcoal.

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