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Enhancements of Slow-propagation Tungsten-Based Delay Compositions for Blasting and Propulsion Systems

Ahmed Hawass^{*}, Mohamed M. Elwany^{**}, Sahar Elmarsfy^{**}, Ehab Fouad Abadir^{**} *Cairo Higher Institute for Engineering, Computer Science and Management. **Department of Chemical Eng., Cairo University, Giza, Egypt hawass2000@yahoo.com

Abstract

Applications for controlled energetic timed events in both the military and civilian sectors highlight the critical function of delay compositions. The widespread usage of tungsten delay systems in space industry and other components motivates academic research aimed at enhancing the performance and reliability of these materials. Different delay compositions are created for this purpose based on varying amounts of tungsten (W) fuel modified with graphite (C). The major components of delay systems included polyvinyl acetate (PVA), BaCrO₄, KClO₄, and a graphite weight fraction that ranged from 2% to 10%. The compositions are made by combining, granulating, and then loading them into aluminum tubes. This study illustrates the impact of 2% to 10% graphite fuel added to tungsten-based delay composition. The heat of production and density for each constituent were computed and presented as part of thermochemical calculations using the ICT code to forecast the performance of the delay element. Schaffler Company's ignition static test for the delay element using the central testing unit (CTU) revealed an improvement in burning rate of 9% to 47%. Utilizing digital visual imaging systems, the burning behavior is observed, and SEM apparatuses are used to analyze changes in the composition's outer surface. The sensitivity tests (impact, friction, ignition, electrostatic discharge (ESD), and thermal analysis test utilizing DSC and TAM apparatus) are used to characterize the prepared compositions. All of the results from the evaluated delay compositions guarantee safe handling, production, transportation, and storage.

Keywords: Tungsten delay; Graphite; Sensitivity test; Thermal analysis; ICT code.



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1-Introduction

Gasless pyrotechnic mixtures have been employed in the past to create regulated heat and time delays in ordnance devices [1]. Numerous gasless compositions are alternately employed as fast delays, delay igniters, and heat powders. Additionally, some of the techniques created for producing and analyzing heat materials can be used for applications that delay. The required firing time delays are fabricated using different metals fuels and binder compositions. The delay elements take the shape of a blend of oxidants and fuels grains that can propagate an extremely exothermic propagated reaction [2]. The resulted delays should easily ignitable but safe to handle during storage and transportation [2]. Exothermic, self-sustaining, and self-contained are requirements for the delay combustion reaction, which must also operate at a steady, predefined rate unaffected by variations in the surrounding temperature [3].

In order to reduce the influence on burning rate caused by pressure because the main charge is completely closed, ignition response must be low gas produced [2]. After burning, the wave resulted from ignition moves steadily, ensuring that the main charge receives the initiating impulse in a precisely controlled amount of time. If all of these conditions are satisfied, the resulted burning time should be constant in value and the relation with the tube length should be linear.

The compositions fabricated are frequently pressed to produce exact time delays for different timing applications and maintaining high values of reliability and safety [4,5]. Such mixes' combustion properties play a key role in regulating this precise time delay. Even now, the basic propagations reactions for delay elements are not well examined. The resulted condensed phase reaction which represented by chemical and physical change are the principal causes of this reactions [6,7].

The conventional delay compositions based on (W), (SiO₂), (BaCrO₄) and (KClO₄), has been the most widely employed pyrotechnic composition in a variety of fields [8]. Studies from the past have discussed the combustion velocities, burning properties, and response processes of this delay composition [9-11].



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Delay compositions typically anticipated for extended working time due to their prolonged storage prior to use. Numerous studies have examined how different delay materials age subjected to different aging conditions as humidity and temperature to increase their shelf life [12]. Carbon is deposited into the crystal structure of graphite and play as a heat transfer promoter used to enhance the thermal conductivity of the materials [13].

Along with its excellent heat conductivity, expandable graphite also has unusual qualities like appearance and resistance against different applied load. Inflammability, thermal conductivity, and stability of paraffin and expandable graphite mixes have all been investigated by Mochane and Luyt [14]. Hahma has tested the burning delay elements made of metal and fuel powder and he found that adding 1% graphite significantly increased the burning rate [15].

This study's primary goal is to examine the burning behavior of tungsten-based compositions with slow propagating gasless delays. In all compositions, the percentage of graphite in the delay composition has the biggest impact on the burning rate.

Using two different types of experimental techniques, the burning behavior of slow propagating gasless delay compositions was examined in this study. All of the tested delay compositions' burning behavior was captured on video using an ultra-high-definition camera, and the CTU by Shaffer was used to measure the burning rate.

The produced delay element was additionally evaluated for sensitivity and temperature analysis for processing, handling, and storage. For the safe and dependable design of selfdestructive fuses, electro explosive devices, and mining applications, it is crucial to analyze all the results that were collected.

2- Theoretical Calculations

Additives have different effects on the performance of delay compositions as it affects both burning rate and fabrication, so studying the effect of additives as graphite was studied through preparation of different compositions using as in table (1).



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Preparation of gasless delay compositions is based on different percentage of graphite (2%, 4%, 6%, 8%,10%) at expense of fuel while maintaining binder, and burning rate modifier at optimum percentage.

Ingredients Wt.%	S1	S2	S3	S4	S5	S6
W	40	38	36	34	32	30
BaCrO ₄	35	35	35	35	35	35
KClO ₄	15	15	15	15	15	15
PVA	10	10	10	10	10	10
Graphite	-	2	4	6	8	10

Table 1 Formulation of delay compositions based on different graphite percentage

This study demonstrates different main performance parameter for selected delay elements. Pyrotechnic delay compositions were tested by using ICT thermodynamic code which depends on chemical properties of the compositions and the surrounding pressure.

It is clear from figures (1-3) that the density, oxygen balance and heat of formation of the delay formulations changes by using different percentage of graphite (C) with respect to respect to fuel (W) at constant oxidizer / burning rate modifier ratio.

The heat of formation increases with increasing the percentage of additive graphite from (2% to 10 %), while the oxygen balance decreases from (14.88% to 39.78%). This is due to the carbon content in the composition increases from (4.54 to 12.8 mole) on the other hand the tungsten content decreases from (2.17 to 1.63 mole). The delay composition density goes down from (4.235 to 3.631 g/cm³) with the increase of graphite percentage. This mainly due to Tungsten higher density value of (19.3 g/cm³) compared to that of graphite (2.25 g/cm³).



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Figure 1. Heat of formation and percentage of graphite (C) relation.



Figure 2. Loading density and percentage of graphite (C) relation.







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Figure 3. Oxygen balance and percentage of graphite (C) relation.

3- Experimental Part

3.1 Materials and Fabrication

All the chemicals used in this experimental work were provided by Kaha Company for chemical industries (Military factory 270) and Abu Zaabal company for specialist industries (Military factory 300). These chemicals were used directly without any purification or treatment. The choice of these chemical was based on the recent research work related to pyrotechnic gasless delay compositions. The selected chemicals are safe in handling and reliable the preparation procedures for gasless delay compositions can be described as follows:

- 1. The required percentage of fuel, burning rate modifier and oxidizer was mechanically mixed.
- 2. Preparation of the binder liquor through dissolving in acetone.
- 3. Addition of the binder liquor to the dry mixture and granulate.
- 4. Dry the granules on a tray in an open air for minimum 4 hours.
- 5. Drying the compositions in an oven at 37°C for 3 days.

Also, the Fabrication of delay element process as the following:



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- 1. Preparation of gasless delay compositions S1, S2, S3...etc.
- 2. Drying the prepared composition in Vacuum Furnace for 24 hours.
- 3. Meshing to achieve the required particle size using Mechanical Screening.
- 4. Loading the composition in Al Tube-Housing.
- 5. Pressing the loaded compositions using hydraulic pressing system model parker.
- 6. Assembling initiator Electric Squib (Ignition Source).

The final delay elements final product is shown in figure (4).



Figure 4. (a) Schematic diagram of fabricated delay element: (b) Real digital image for fabricated delay element.

3.2 - Experimental Apparatus for testing

The burning time testing by Schaffler company was used as shown in figure (5).



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Figure. 5 Schematic diagram of burning measurements.

The thermal analysis qualifications for delay compositions was carried out using (DSC-TAM) apparatus.

The ability of delay composition for ignitions which includes (impact, friction, ignition and ESD) have been done using the Czechoslovakia (BAM type IN 10455) for impact, BAM friction tester Reichel & Partner GmbHis, heating block tester DT- 400 and SESD 2900 By Schloder for Electrostatic Discharge.

4- Results and Discussion

The effect of different applied physical and chemical parameter on the performance of delay composition, while the effect of changing this parameter on the burning layers was examined using SEM.

The fabricated tungsten-based delay compositions were characterized by different sensitivity and thermal analysis tests.



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4.1 Effect of different percentage of additive (graphite)

Figure (6) illustrate the burning rate measurement of tungsten delay composition based on different percentage of graphite varying from 2 to 10% at expense of fuel while maintaining oxidizer, binder, and burning rate modifier at optimum percentage.

The graphite substituted tungsten composition increases the burning rate from 1.02 to 1.47 mm/sec by increasing the percentage of graphite from 2 to 10 %.

The enhancement of the burning rate obtained was related to the combined effect of both the higher thermal conductivity and the higher energy by the addition of graphite to the tungsten delay mixture.



Figure 6. Different percentage of graphite (C) with respect to fuel.

New relation was obtained between the theoretical heat of formation and the experimental burning rate measurements from the CTU testing unit.



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The demonstration of this novel relationship was represented in figure (7), where the experimental burning rate increased as the theoretical heat of formation increased.

This conducted relation represents a useful tool for prediction of the expected burning rate depending on the theoretical heat of formation.



Figure 7. Heat of formation and burning rate relation.

4.2 Thermal stability test Differential scanning calorimeter (DSC)

DSC features as shown in figures (8-12) endotherm at 106 °C is due to loss of moisture while endotherm at 305 °C is likely KClO₄ phase transition.

No chemical reaction has been observed between binder, tungsten, graphite, BaCrO₄ and KClO₄ up to 340°C. This result reveals and confirms the thermal stability of all compositions during storage.



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Figure 9. DSC result for delay composition containing 4%(C) additive







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Figure 11. DSC result for delay composition containing 8%(C) additive





4.3 Thermal stability test using heat flow calorimetry (TAM 3)

The measurements resulted from (HFC) calorimetry was conducted for the first 3-4 days measured at 90°C. All the tested delay samples show a good thermal stability property where no heat release was observed during all measurements.





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Therefore, the HFC obtained results predict that the all delay compositions are valid and stable for 10 years of storage conditions. These results were agreed with DSC results which confirmed the thermal stability.

4.4 Sensitivity test (Impact-Friction-Ignition-ESD)

For qualification and safety consideration of tungsten delay compositions, all the tests must have acceptable results. Sensitivity tests according to military standards (impact, friction, ignition, and ESD) have been carried out. All the results were satisfactory and no evidence of initiation (sound, spark, smoke) was noticed. The PVA binder eliminates friction energy between sharp edges. The use of insulating materials such as PVA in pyrotechnic compositions minimizes the hazard of initiation due to ESD as in the delay element industry. The high thermal resistance of the binder layer coating the delay composition grains, decreases heat transfer, as a result eliminating the chance of ignition.

4.5. Scanning electron microscope (SEM) imaging

As shown in figure 13 (a, b), the addition of graphite from 2% to 10% enhances the thermal conductivity between layers of delay compositions, causing more pores and cambers on the outer surface, which proves the thermal decompositions of the PVA layer that coats the composition grains. This in turn increase the internal surface area for decomposition reaction to take place, thus increasing the overall burning rate.



Figure 13. SEM micrograph for delay composition having a weight ratio of graphite from 0-10% respectively (a) before burning: (b) after burning.



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5- Conclusion

The influence of graphite addition on expense of tungsten on the burning properties of the tungsten delay compositions was investigated. The theoretical calculation conducted by ICT code shows increasing heat of formation values as the weight percentage of graphite increases from 2 to 10 %, also the density decreases from 4.2 to 3.6 g/ cm³. Different percentage of graphite substituted tungsten had remarkable effect on enhancing the burning rate by 9% to 47%, this due to the high thermal conductivity of graphite and the resulting increasing of heat of formation from 3000 to 4600 KJ/Kg. The imaging methods including ultra-high-resolution video camera and SEM imaging confirmed the role of graphite enhancements during burning propagation. A novel relation between the theoretical heat of formation and burning rate represent a useful tool for prediction the performance of tungsten delay elements design applied in self-destructive fuses, rocket systems and space industry. A series of thermal analysis tests (DSC, TAM 3) and sensitivity tests such as impact, friction, ignition and ESD were conducted for all the tested delay samples show good stability and safety proprieties during fabrication, handling as well as storage and field operation.

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