Egyptian Journal of Chemistry
http://ejchem.journals.ekb.eg/

Novel Evaluation for the Effect of Binder Percentage on Tungsten-Based Delay Compositions

Ahmed Hawass[a*], Mohamed M. Elwany[b], Sahar Elmarsfy [b], Ehab fouad abadir[b]

[a]Technical Research Center, Cairo, Egypt

[b]Department of Chemical Eng, Cairo university, Giza, Egypt

Abstract

Tungsten delay systems widely used in mining and blasting operations which encourage the scientific research about improving the performance and reliability of these compositions. Binders' types and its percentage have a great effect in the performance of delay compositions. For this purpose, new research applied to different delay compositions which based on tungsten, $BaCrO_4$, $KClO_4$ and polyvinyl acetate (PVA) according to different percentage of (PVA). The PVA weight percentage varied from 5% to 15%. The compositions are fabricated by mixing, granulated and finally loaded in aluminium tube. Novel methods have been applied to predict the performance of delay element by ICT code. Which the resulted heat of formation and density have been illustrated. Ignition static test for delay element using central testing unit (CTU) by Schaffler company showed enhancement in burning rate by 7% to 37%. Characterization of the prepared compositions is carried out through sensitivity tests (impact, friction, ignition, electrostatic discharge (ESD) and thermal analysis test using DSC and TAM apparatus. All the obtained results from tested delay compositions ensure safety behaviour during handling, fabrication, transportation and storage.

Keywords:.Tungsten delay; Mining; Blasting Thermal analysis; ICT code.

1. Introduction

Delay compositions systems as fuses and electro explosive devices are a safe starting trigger for different applications as rocket launching systems and space industry [1,2]. Different types (gassy and gasless) delay compositions are mainly used to transfer the ignition from one stage to another at preordained time [3]. Simplicity in structure and low production cost makes delay compositions widely used in different military and civilian products [4]. In different confined design for military and civilian application the gasless delay is preferred. The gasless delay compositions main components are oxidizer, fuel and binder. The main role of oxidizer as chlorates and chromates is to supply the required amount of oxygen during combustion [5-7]. Large amount of heat can be secured during oxidation of fuel which considered one of the vital components of delay composition [8]. For reducing the sensitivity and improving the chemical stability against environmental condition binder can be used for coating fuel and oxidizer granules [9,10]. One of the

*Corresponding author e-mail: hawass2000@yahoo.com. (Ahmed Hawass)
Received date 06 November 2022; ;revised date 02 January 2023; accepted date 02 January 2023
DOI: 10.21608/EJCHEM.2023.173053.7157

most promising slow-propagation delay compositionssystems that based on heavy metal and oxidant is W/KClO4/BaCrO4[11]. Many researchers investigated the role of different additives in the modification of burning rate of delay compositions [12-14]. Kosanke et al studied different inert and chemically active additives impact on the in pyrotechnic delay composition [15]. The reduction of burning rate for delay composition caused by addition of inert material as Kaolin has been investigated by Brown, also he studied the effect of addition of thermal conductive material on increasing the burning rate of black powder [16]. Phanindra et al study the effect of thermal environmental on different compositions containing potassium perchlorate ($KClO_4$), aluminum (Al) and graphite (C) and they found the high percentage of oxidizer with respect to fuel produce more energetic compositions [17]. It is commonly used to add binders to pyrotechnic delay compositions due to granules formation which enhance the fabrication process. The two types of binders (organic or inorganic). which can be used including natural resins e. g. gum Arabic and gum and Inorganic binders
include gypsum, water glass and bentonite applied in this industry. The amount and type and of the binder have major effect in different performance parameter including burning rate and energy output [18]. On the other hand, polymeric binders play another role in pyrotechnic and explosive compositions as it enhances the mechanical performance and provide more protection against environmental condition which increasing shelf life. binder have a vital role for maintain the homogeneity of pyrotechnic mixture and also increasing the safety during pressing process [19-21].

The main objective of this research is to investigate in new approach the great effect of PVA percentage on the manufactured delay elements. The burning behavior of slow propagating gasless delay compositions based on tungsten with different PVA binder percentage. In all cases of compositions, the effect of PVA on the burning rate mainly depends on its percentage in the delay composition. In this research the burning behavior of slow propagating gasless delay composition were determined using two types of experimental methods. Ultra- high-resolution video camera and CTU by Shafflar company were used for recording the burning behavior and measuring the burning rate for all tested delay composition. The fabricated delay element was also characterized by sensitivity and thermal analysis testing for theapproval during processing, handling and storage. The analysis of all the obtained results is of great importance for safe and reliable design of self-destructive fuses, electro explosive device and mining applications.

2. Theoretical Calculations

Ignoring the effect air oxygen on the burning of delay compositions, the theoretical thermo chemical calculations have been carried out using ICT thermo dynamic code, produced by Fraunhofer Institute of Chemical Technology which calculates heat of formation and density based on the chemical formula of the elements. ICT code have been used for prediction of the output delay elements performance for different compositions based on changing the percentage of PVA to $BaCrO_4$, which are used for enhancing the burning rate as shown in table 1.

Table (1). Tungsten delay compositions with different percentage of PVA.

%	Comp1	Comp2	Comp3	Comp4	Comp5
W	40	40	40	40	40
$BaCrO_4$	40	37.5	35	32.5	30
$KClO_4$	15	15	15	15	15
PVA	5	7.5	10	12.5	15

Figure (1) represents the relation between the heat of formation of different delay mixtures based on various PVA weight percentage with respect to burning rate modifier $BaCrO_4$.

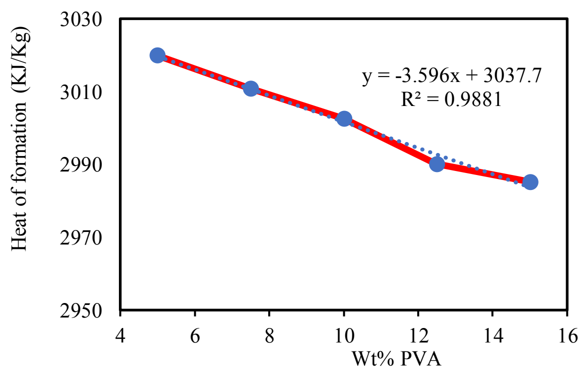


Figure 1. Effect of PVA percentage on the heat of formation of delay compositions.

Figure (1) demonstrated that as the PVA percentage increases, the heat of formation decreases. This phenomenon can be related to lower value of heat of formation of PVA with respect to $BaCrO_4$.

Density of the of delay composition is a very important aspect, not only during processing but also affect the rate of burning. Figure (2) shows the decrease of the delay composition density as the PVA percentage increases and this also related to decreasing the percentage of $BaCrO_4$.

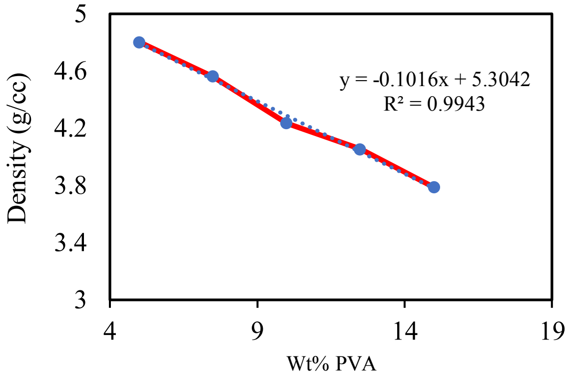


Figure 2. Effect of PVA percentage on the loading density of delay compositions.

3-Experimental Part

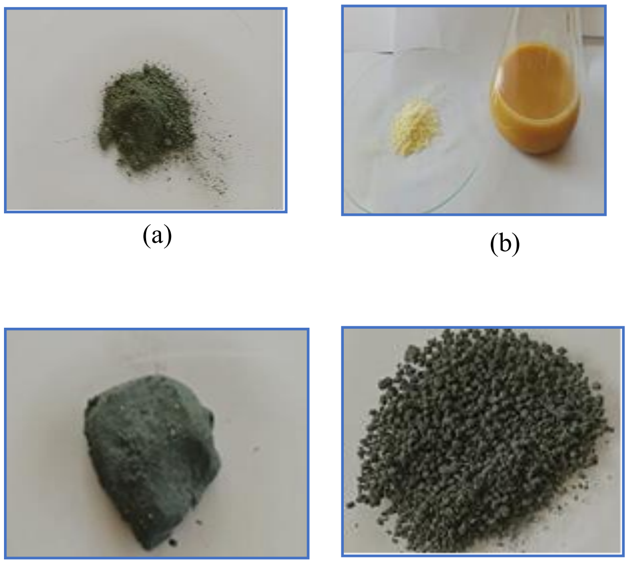
3.1. Materials and Fabrication

Tungsten powder supplied by Merck supplier with purity 99.9% and an average particle diameter range from10-12 µm. Potassium perchlorate reagent grade 99.2% and average particle size about 18-20µm, Barium chromate with purity 99% with an average diameter of about 1.8-2.4 µm were delivered from Nano chema zone.

Polyvinyl acetate (PVA) was used as binder commercially supplied as white powder below 4 µm. The basic experimental formulas for delay compositions as weight percentage was ($W/BaCrO_4/KClO_4$/PVA) 40:35:15:10, the weight percentage of PVA varied from 2% to 10% on expense of weight percentage of tungsten. While all the other ingredients were kept constant.

The delay compositions were prepared by dry mixing of ingredients tungsten (W), potassium perchlorate ($KClO_4$), barium chromate ($BaCrO_4$) and graphite(C) powders while (PVA) as a binder was dissolved in solvent.

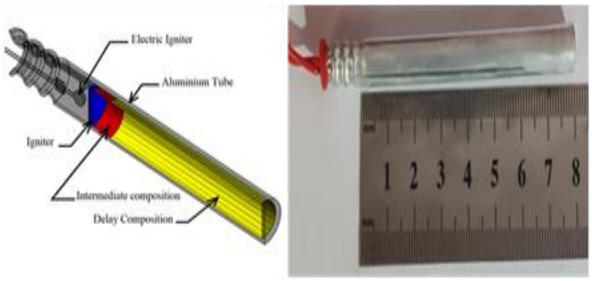
The dry mixture is then added to the PVA solution to form a paste then granulated and mechanically sieved to the required particle size. the procedure for the delay compositions fabrication are represented in Figure (3).



(a) (b) (c) (d)

Figure 3. procedure for the delay compositions fabrication. (a) (dry mixing) :(b) (binder dissolving) :(c) (paste): (d) (granulation).

The formulations of the delay compositions are shown in Table (1). The different delay compositions series were processed to produce delay element by drying, precisely weighing then loaded and pressed in a cylindrical aluminum tube as one pellet to measure their burning rate as shown in Figure (4). The compositions were loaded in 90 mm long aluminum tubes with an internal diameter of 4 mm and a wall thickness of 1.2 mm. The assembling process started with filling 5 g of delay composition and pressed with a 1 kN load. An intermediate composition of 0.5g composed of 0.25 g delay composition and 0.25 g igniter based on magnesium pressed with 0.5 kN. Finally, 0.2 g of igniter was added and pressed with 0.5 kN load. An electric squib was assembled as a source of ignition as shown in Figure 4 (a,b).



A B

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

3.2Experimental Apparatus

The central testing unit (CTU) by Schaffler company was used for measuring the burning rate of delay compositions. Digital imaging capture system using ultra-high-resolution video camera was used to observe burning phenomena. The delay compositions loaded in aluminum tube was ignited by the ignition system, all the phenomena of ignition, combustion, flame propagation and burning rate were recorded and measured by ultra-high resolution digital camera and CTU.

The delay compositions were characterized by thermal analysis using (DSC-TAM), while sensitivity tests including (impact, friction, ignition and ESD) are carried out. The detailed experimental set up and apparatus are described as follow:

3.2.1 Imaging systems

The digital visual imaging system include 108MPultra-high resolution Samsung HMX video camera and a digital processing device. The ultra-high-resolution camera can shot 960 fps which enhance the observation of flame propagation during delay burning. The arrangement set up for imaging system is shown in Figure (5).

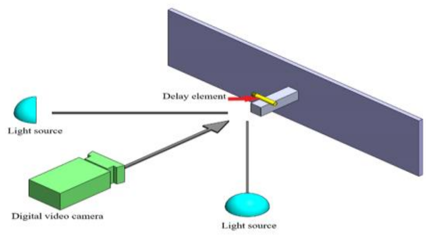


Figure 5. Schematic diagram of the visual-imaging set up.

3.2.2 Central testing unit (CTU)

The CTU system consists mainly from different sample holder (slots) for fixing the delay element during testing. The CTU firing system composed of a DC current source of 1000 mA connected to a current limiter and switch time gate to produce the required pulse for starting ignition. The CTU measuring and recording system consists of flash transducer for time measurement, signal conditioner to filter and amplify the received signals and data acquisition system with maximum range of 20 sec and accuracy of 10 µsec. The schematic set up for burning time measuring system as shown in figure (6).

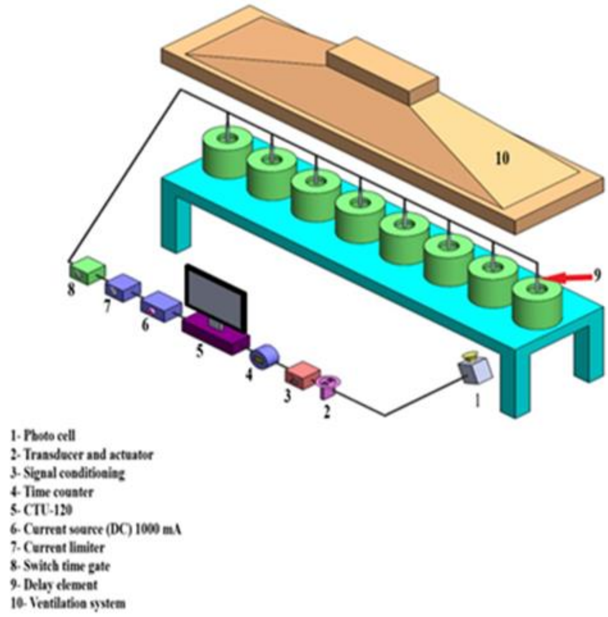


Figure 6. Schematic diagram of the CTU set up.

3.2.3Sensitivity tests

The Czechoslovakia (BAM type IN 10455) fall hammer is used for determination of the sensitivity to shock or an impact force for 50 mg delay compositions sample that may cause ignition. The BAM friction tester Reichel & Partner GmbHis was used to determine the sensitivity to friction of 50 mg of delay composition sample according to STANAG 4487.The porcelain plate moves, back and forth over a distance of about 10 mm with a speed of 141r min-1 causing friction of the sample with the porcelain pin. The heating block tester DT- 400 is used to measure the response of 0.5 g of the delay composition sample to ignition. The sample to be tested is heated to 400 °C gradually with a heating rate of 20 °C/min. Electrostatic Discharge ignition Sensitivity for delay compositions have been carried out using SESD 2900 By Schloder EMV-system &komponenten. A sample of 50 mg is tested by electrostatic stimulus of various intensities according to the standard VG-Norm 95378-11.

3.2.4Thermal Analysis

The tungsten delay composition was thermally analyzed by the differential scanning calorimeter) DSC Q2000. A 2 mg sample was subjected to heating rate of 20°C/sec. to maximum temperature of 340

°C. Thermal analysis using Heat flow calorimetry (HFC)TAM3 have been used for predicting the delay compositions shelf life. Sample of 4 mg delay compositions was kept for 3.8 days at constant temperature of 90°C.

4-Results and Discussion

The burning properties of tungsten delay composition with different PVA percentage depends on a several parameters as grain size, stoichiometry, density, thermal conductivity, environmental temperature, pressure, and the applied design. Different delay elements based on tungsten modified with different percentage of PVA burning rate, was measured using CTU and ultra-high resolution digital camera to investigate the effect of PVA percentage on the performance of tungsten delay composition. The tungsten-based delay compositions based on different percentage of PVA were characterized by different sensitivity and thermal analysis test.

4.1. The burning rate measurement of tungsten delay composition based on different percentage of PVA.

The burning rate was measured by CTU for tungsten delay compositions with different percentage of PVA varied from 5 to 15 %. Figure (7) shows the effect of different PVA percentage on the measured burning rate.

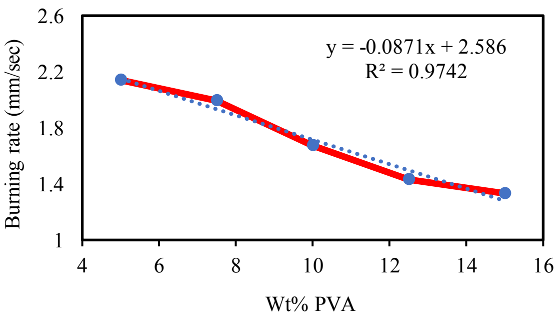


Figure 7. Effect of PVA percentage on the burning rate of delay compositions.

The burning rate obtained was related to Low density compositions provide more voids between layers of delay composition which increase the propagation of burning across the delay mixture. The PVA substituted BaCrO4composition increase the burning rate from 1.33 to 2.14 mm/sec with increasing the percentage of PVA from 5 to 15 %. The enhancement of the combustion events of delaycompositions were recorded and captured by means of108MPultra-high resolution Samsung HMX video camera to investigate the burning propagation along the delay element as shown in figure (8).

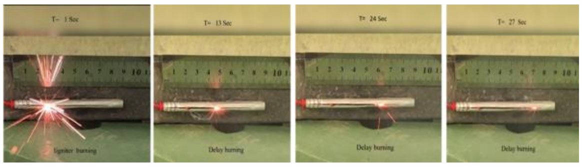


Figure 8. The combustion propagation for composition having a weight ratio W/$BaCrO_4$/$KClO_4$/PVA 40:35:15: 10.

Uniform burning propagation was observed all over the tested delay elements sample. the illuminating area transfer across the delay element with nearly constant burning rate of 1.4 mm/sec.

For saving both cost and time in different preparation and testing procedure for various compositions of tungsten delay elements a novel relation was obtained between theoretical heat of formation resulting from (ICT code) and the experimental burning rate from (CTU) testing unit. The demonstration of this novel relation was represented in figure (9), where the experimental burning rate increase as the theoretical heat of formation increases.

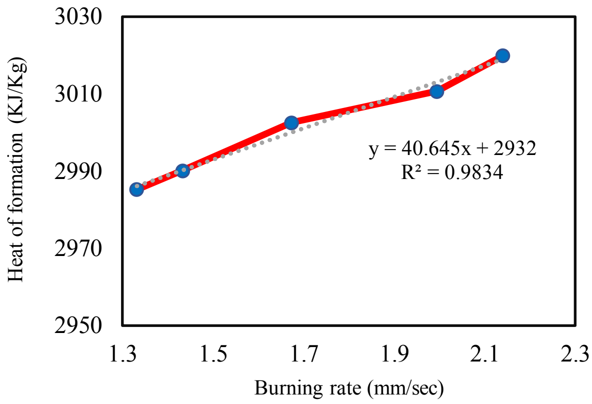


Figure 9. Relation between theoretical heat of formation and experimental burning rate of delay compositions.

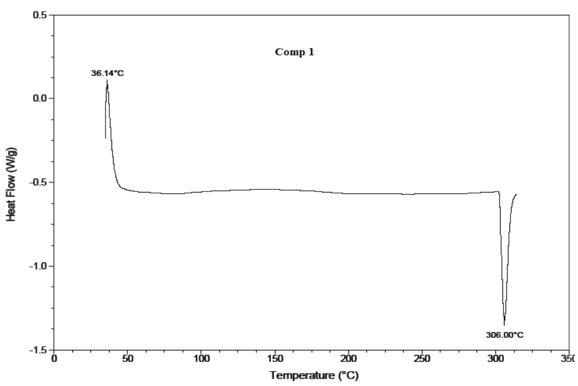
The resulted relation shows the burning rate increases from 1.33 to 2.14 mm sec^{-1} as heat of formation increases from 2985 to3019 KJ Kg^{-1} with PVA percentage, increases from (5 to 15 %). This novel relation represents a useful tool for prediction the of the expected burning rate depending on theoretical heat of formation.

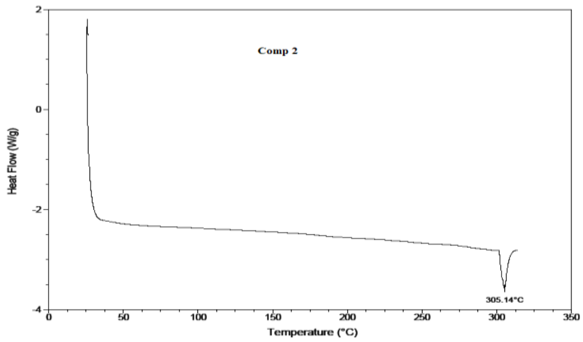
4.2. Thermal analysis for tungsten delay composition based on different percentage of PVA.

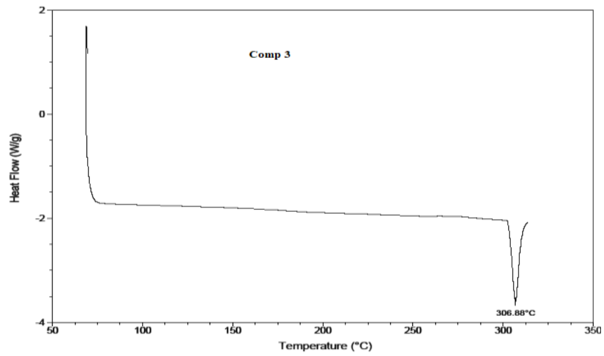
Thermal analysis using Differential scanning calorimetry (DSC) and Heat flow calorimetry (HFC)TAM 3 were carried out to characterize the thermal decomposition behavior for all tested tungsten delay compositions. This characterization will be useful for predicting the behavior of all tested samples during processing, fabrication and storage. Using DSC Q2000, a non-ignition condition was maintained by using nitrogen atmosphere to prevent the effect of air oxygen on fuel oxidation. This technique measures thermal changes in tested delay compositions and the resulted thermal analysis curves illustrates the rate of reaction as a function of temperature.

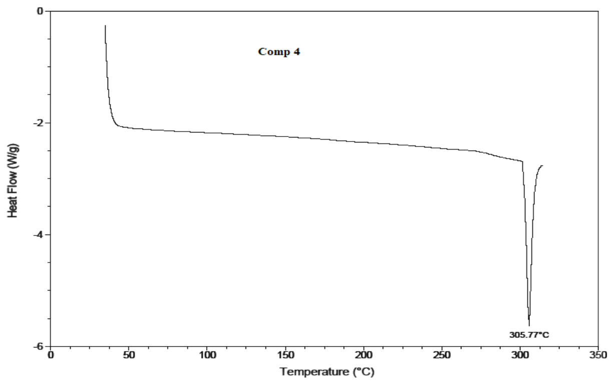
Figure (10) represent varied PVA percentage from 5 to 15 %, no chemical reaction has been observed between tungsten, PVA, $BaCrO_4$and $KClO_4$ up to 340°C. This result reveals and confirm the thermal stability of all compositions during storage.

Heat flow calorimetry (HFC) measurement was conducted according to STANAG 4582, on figure (11). The principal role of HFC is that all physical and chemical reactions that generate heat are recorded during the whole measuring time.
The decomposition rate is calculated from the recorded heat flow curve and yields information regarding the thermal stability of tested delay compositions as well as the prediction of their shelf life.









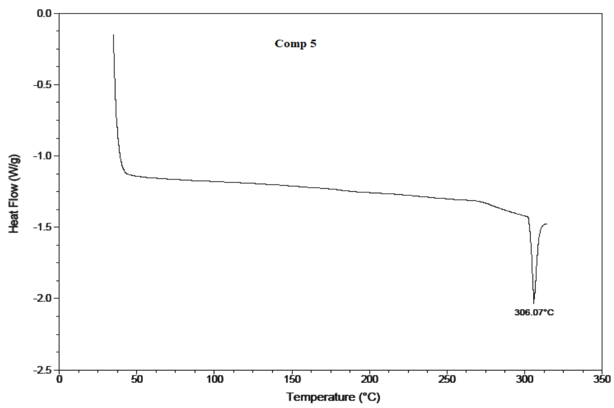


Figure10. DSC carves for tested delay compositions

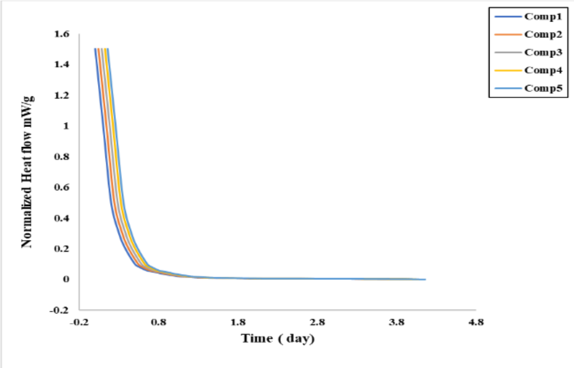


Figure11. HFC (TAM3) carves for tested delay compositions.

Figure (11) shows the first 3.4 days of micro calorimeter heat flow data from the sample measured at 90°C. All tested delay samples show a good thermal stability property measured using HFC where no heat flow released was observed for all six measurements. Therefore, the HFC obtained results predicts that tested sample will remain chemically stable for a minimum of 10 years of storage at ambient temperature (25°C). The HFC results were in agreement with DSC results that confirm the thermal stability and no decomposition of the analyzed samples.

4.3 Sensitivity analysis for tungsten delay composition based on different percentage of PVA.

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. The impact sensitivities of different tungsten delay samples kept at(25°C) were tested by standard Drop weight (2 Kg) at height 50 cm (9.8 J). No observed noise, sparks or any indication for initiation, ignition for all tested samples, and this result due to PVA layer surround the delay grain. Friction sensitivity is a hard stimulus to be eliminate, as it presented during handling, fabrication and at the storage of the energetic material. A 50 mg of all tested samples according to STANAG 4487 were subjected to a friction load from 60 to 360 N, all the results were satisfactory and no evidence of initiation (sound, spark, smoke) were noticed. The PVA binder that eliminate friction energy between sharp edges of delay ingredients that cause hot spot initiation. The use of insulating material as PVA in pyrotechnic compositions minimize the hazard of initiation due to ESD as in delay element industry. A sample of 50 mg of all Tungsten delay compositions were subjected to electrostatic stimulus of various intensities range from 15 mJ to 18 J according to the standard VG-Norm 95378-11. No positive evidence (initiation, ignition, spark, noise) was observed.

Delay elements assembled in different military and civilian products should maintain its performance and safety requirements during the entire storage time. For satisfying this requirement, an ignition temperature test was conducted to 50 mg of delay sample which subjected to temperature arising from 100 to 400°C with heating rate of 20 °C min $^{-1}$. No ignition reaction was observed for all tested samples and this related to the high thermal resistance of PVA layer coating the delay compositions grains, which decrease heat transfer between heating source and delay composition, eliminating the chance of ignition. All the obtained results can be used as a vital design constrains for self-destruction fuses, rocket lunched systems and energetic timing mechanism in space industry.

5-Conclusion

The novel influence of PVA addition on expense of $BaCrO_4$ on the burning properties of the tungsten delay compositions was investigated. The theoretical calculation conducted by ICT code shows decreasing in heat of formation values as the weight percentage of PVA increases from 5 to 15 %, also the density decreases from 4.8 to 3.7 gc^{-3}.

Different percentage of PVA substituted $BaCrO_4$ had remarkable effect on enhancing the burning rate by 7% to 64%, this due to the lower density which produce more voids permitted the propagation of burning across the delay element faster. The imaging methods including ultra-high-resolution video camera confirmed the role of PVA 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.

6-Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

7-Acknowledgements

This research has been fully supported by the GOE foundation. The authors would like to acknowledge department of chemical engineering, cairo university.

8-References

[1] Muravyev NV, Monogarov KA, Schaller U, Fomenkov IV, Pivkina AN. Progress in additive manufacturing of energetic materials: Creating the reactive microstructures with high potential of applications. Propellants, Explosives, Pyrotechnics. 2019Aug;44(8):941-69, https://doi.org/10.1002/prep.201900060

[2] Poret JC, Shaw AP, Csernica CM, Oyler KD, Vanatta JA, Chen G. Versatile boron carbide-based energetic time delay compositions. ACS Sustainable Chemistry & Engineering. 2013 Oct 7;1(10):1333-8, https://doi.org/10.1021/sc400187h

[3] Gerlich MM, Wojewódka AT. Study of gasless compositions used in time-delay elements. Journal of Thermal Analysis and Calorimetry. 2020 Mar;139(6):3473-9, 10.1007/s10973-019-08721-8.

[4] Lu KT, Yang CC, Ko YH. investigation of the burning properties of slow-propagation tungsten type delay compositions. Propellants, Explosives, Pyrotechnics: An International Journal Dealing with Scientific and Technological Aspects of Energetic Materials.2008Jun;33(3):219-26, https://doi.org/10.1002/prep.19970220405

[5] Focke WW, Tichapondwa SM, Montgomery YC, Grobler JM, Kalombo ML. Review of gasless pyrotechnic time delays. Propellants, Explosives, Pyrotechnics.2019Jan;44(1):55-93, https://doi.org/10.1002/prep.201700311

[6] Khan A, Malik AQ, Lodhi ZH, Badshah G. Study of effect of binders and loading pressures on the performance of the time delay pyrotechnic compositions. Journal of Energetic Materials. 2018 Oct.2;36(4):386-97, 10.1080/07370652.2018.1441925

[7] Steinhauser G, Klapötke TM. “Green” pyrotechnics: a chemists' challenge. AngewandteChemie International Edition. 2008 Apr 21;47(18):3330-47, http://doi.org/10.1002/anie.200704510

[8] Comet M, Martin C, Schnell F, Spitzer D. Nanothermites: A short review. Factsheet for experimenters, present and future challenges. Propellants, Explosives, Pyrotechnics. 2019 Jan;44(1):18-36, https://doi.org/10.1002/prep.201800095

[9] Talawar MB, Sivabalan R, Mukundan T, Muthurajan H, Sikder AK, Gandhe BR, Rao AS. Environmentally compatible next generation green energetic materials (GEMs). Journal of Hazardous Materials. 2009 Jan 30;161(2-3):589-607, 10.1016/j.jhazmat.2008.04.011

[10] Shachar E, Gany A. Investigation of Slow-Propagation Tungsten Delay Mixtures. Propellants, explosives, pyrotechnics. 1997 Sep;22(4):207-11, https://doi.org/10.1002/prep.19970220405

[11] Miklaszewski EJ, Shaw AP, Poret JC, Son SF, Groven LJ. Performance and aging of Mn/MnO2 as an environmentally friendly energetic time delay composition. ACS Sustainable Chemistry & Engineering. 2014 May 5;2(5):1312-7, https://doi.org/10.1021/acssuschemeng.7b02579

[12] Swanepoel D, Del Fabbro O, Focke WW, Conradie C. Manganese as fuel in slow-burning pyrotechnic time delay compositions. Propellants, Explosives, Pyrotechnics. 2010 Apr;35(2):105-13, https://doi.org/10.1002/prep.200900005

[13] Beck MW, Brown ME. Modification of the burning rate of antimony/potassium permanganate pyrotechnic delay compositions. Combustion and flame. 1986 Oct 1;66(1):67-75, https://doi.org/10.1016/0010-2180(86)90033-7

[14] Tichapondwa SM, Focke WW, Del Fabbro O, Labuschagne G. The Effect of Additives on the Burning Rate of Silicon-Calcium Sulfate Pyrotechnic Delay Compositions. Propellants, Explosives, Pyrotechnics. 2016 Aug;41(4):732-9, https://doi.org/10.1002/prep.201500243.

[15] Miklaszewski EJ. Microchannel combustion dynamics of low gas, environmentally friendly time delay compositions (Doctoral dissertation, Purdue.University). https://docs.lib.purdue.edu/dissertations/AAI3636473/

[16] Brown, M. E., and R. A. Rugunanan. "A temperature-profile Study of the Combustion of Black Powder and its constituent binary mixtures." *Propellants,explosives,pyrot.* 14.2(1989):6975. https://doi.org/10.1002/prep.19890140205

[17] Phanindra KH, Sivapirakasham SP, Balasubramanian KR, Surianarayanan M. Thermal and impact sensitivity of pyrotechnic compositions containing the potassium perchlorate, aluminium and Graphite. InMaterials Science Forum 2019 (Vol. 969, pp. 146-151). Trans.Tech.PublicationsLtd.https://doi.org/10.4028/www.scientific.net/MSF.969.146

[18] B. Berger. Parameters Influencing the Pyrotechnic Reaction, Propellants Explos. Pyrotech.2005,30,2735. https://doi.org/10.1002/prep.200400082

[19] Zhang Y, Pan J, Zhu Y, Bani S, Lu Q, Zhu J, Ren H. The effect of embedded high thermal conductivity material on combustion performance of catalytic micro combustor. Energy Conversion and Management. 2018 Oct 15;174:730-8. 10.1016/j.enconman.2018.08.085.

[20] Wissa, D. A., Ward, A. A., Gad, S. A., Rozik, N. N., Nassar, A., Abd-El-Messieh, S. L., &Khairy, S. A. http://ejchem. journals. ekb. e.g.. 65, (11),Nov.2022,10.21608/EJCHEM.2022.142955.6242.

[21] Hawass, Ahmed, Hosam Mostafa, and Ahmed Elbeih. "Multi-layer protective armour for underwater shock wave mitigation." *Defence Technology* 11.4(2015):338-343.https://doi.org/10.1016/j.dt.2015.04.006.