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RESEARCH REGARDING THE PROPERTIES AND COMBUSTION PERFORMANCE OF A THERMAL DECOY PYROTECHNIC COMPOSITION

Ovidiu IORGA*, Cristiana EPURE*, Alexandru MARIN*, Dănuț-Eugeniu MOȘTEANU**

***Research and Innovation Center for CBRN Defense and Ecology, Bucharest, Romania**
****"Nicolae Bălcescu" Land Forces Academy, Sibiu, Romania**
iorga_ovidiu@yahoo.com, cristiana.epure@nbce.ro,
alexandrumarin41@yahoo.com, dmosteanu@gmail.com

Abstract: *The present research focuses on the characterisation of a new formulation for thermal decoy pyrotechnic composition, as an alternative to magnesium-teflon-viton (MTV) formulations. The oxidant used in the composition is potassium perchlorate, given its good thermal stability and high percentage of available oxygen. The fuel of choice is magnalium (alloy of Al-Mg 50-50 % wt.), as an higher energy alternative to magnesium. The binder used in the composition is a blend of solvent free polyurethane and a chlorinated rubber. The main advantages of this composition are related to the high thermal stability, the ease of processing, by squeeze casting method and its good combustion performance (temperature and burn rate profile). The use of chlorinated rubber in the composition is beneficial, as a sensible increase in the burn rate and combustion temperature is observed. The morphological properties and chemical composition of the material is evidenced by SEM-EDS analysis while the burn rate and combustion temperature is recorded with a high speed thermal camera. The combustion heat and specific volume is calculated with a dedicated thermochemical code while the results are validated in experimental determinations. The presented formulation can represent a more safe and cost effective material to be used in thermal countermeasure ammunitions.*

Keywords: countermeasure, flare, chlorinated rubber, combustion

1. Introduction

Flare pyrotechnical compositions are designed to burn at atmospheric pressure, with a constant rate, being optimized to emit radiation in either visible or IR spectrum. In the composition, the fuel is represented by a metal powder like aluminium or magnesium. This maximizes the emitted light. The oxidants used are diverse, and can be nitrate based or perchlorate based. In the infrared decoy flares, the oxidant used, polytetrafluoroethylene (PTFE) is used in conjunction with magnesium in a Viton matrix to provide a maximized IR radiation [1]. The use of polyurethane as binder for pyrotechnic compositions has been studied extensively [2]. The advantages of a such formulation is related to the good chemical and moisture resistance of the binder and the easy formation, by casting or squeeze casting of large grains with complex geometries [3]. The use of a solvent free formulation of polyurethane is an advantage when a thick grain has to be obtained [4].

The main disadvantage of using polyurethane flare compositions is related to the slow burning rate of the resulting formulation [5]. To overcome this limitation, a new composition has been developed, where the binder matrix is

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composed of solvent free polyurethane formulation and a chlorinated rubber. By this addition, we expect an improvement in both flame temperature and implicit radiation and also in the burn rate.

2. Formulation of the composition and thermo chemical calculations

The composition of the pyrotechnical material was design based on a polymer matrix obtained from a mixture of castor oil-based polyol (Setathane D1150) with diphenylmethane diisocyanate (Desmodur VL) in a ratio of 2:1 by weight, an oxidant –potassium perchlorate, fuel – alloy of Al-Mg (Magnalium), powdered chlorinated rubber (Parlon) and a plasticizer – mixture of dioctylphthalate (DOP) and solvent (acetone). The detailed chemical compositions are presented in Table 1.The fabrication method involved multiples phases such as drying the powdered materials for 24 hours at 60^{o}Cand mixing of components in a specific order. Subsequently, the composition was pressed with a force of 20 kN into polylactic acid-3D printed tubes with a10 mm internal diameter and 100±1 mm length, each tube having 30±0.5 g of pyrotechnic material. A layer of 0.2g of ignition composition was added in order to prime the tube. The detailed fabrication method is presented by EPURE et al.[1].

Table 1. Pyrotechnic formulation of the flare compositions

Flare	Potassium perchlorate [%]	Parlon [%]	Desmodur VL [%]	Sethatane D1150 [%]	Dioctyl phthalate [%]	Magnalium [%]
F5	50	0	2.5	5	5	37.5
F6	50	7.5	2.5	5	5	30

2.1. Thermo chemical calculations

Thermo chemical calculation were made in order to determine the combustion products of the pyrotechnical composition. Explo5® V6.06.02 software was used for the calculations. Both isochoric calculations were made in order to compare the results with calorimetric determinations and also isobaric (atmospheric) calculations were made, considering the experimental flame temperature measured. The isochoric combustion was performed using virial equation of state for gas products. The loading density was 0.05g/cm^3, in order to replicate calorimeter conditions. Initial guess temperature was set to 3700K. Isochoric cooling was implemented in the calculation with the freeze out temperature set to 500K and end temperature was set to 298K. The number of calculation steps for isochoric cooling was set to 20. The results of the calculations are presented in Table 2 and the calculated concentration of the combustion products are presented in Table 3.

Table 2. Results of thermochemical calculation obtained from Explo5® V6.06.02 software

Calculated parameter	F5	F6	Unit
Oxygen balance	-35.75	-36.91	%
Enthalpy of formation (at 298.15 K)	-1898.72	-2333.63	kJ/kg EM
Relative molar mass	52.23	60.93	g/mol EM
Q combustion (at 298.15 K)	-7819.64	-6966.26	kJ/kg EM
Specific volume(at 298.15 K)	215.65	281.97	L/kg EM
Adiabatic flame temperature (K)	2867.19	3217.19	K
Number of moles of gas(at 298.15 K)	8.70	11.37	1/kg EM
Mass of gaseous products(at 298.15 K)	148.09	188.10	g/kg EM

Mass of solid products (at 298.15 K)	851.77	811.80	g/kg EM
Mean molecular weight of products (at 298.15 K)	36.48	35.47	g/mol

Table 3. Calculated concentration of the combustion products

Composition of combustion products [mol/kg EM]			
F5		F6	
H_2	0.305	H_2	0.413
C	0.282	C	0.312
MgO	0.258	MgO	0.280
Al_2O_3	0.170	CO	0.214
Mg	0.131	KCl	0.176
KCl	0.129	Al_2O_3	0.161
CO	0.068	Mg	0.053
K	0.024	$MgCl_2$	0.035
AlCl	0.016	K_2Cl_2	0.016
Others	0.049	Others	0.058

The formulation containing Parlon (F6) is slightly less oxygenated and because the fuel is less, the calculated heat of combustion is 10% lower than standard polyurethane composition (F5). The chlorine addition in the brute formula caused by the use of Parlon in the formulation charges the combustion products equilibrium. The concentration of CO molecules is three times higher in composition F6 combustion products, while the Al_2O_3 concentration is slightly lower. This explains the lower heat of combustion but the 31% higher specific volume. The calculated flame temperature is also higher in case of composition F5.

3. Differential thermal analysis and calorimetric determinations

DTA analysis were performed on a DTA 551 Ex made by OZM Research. The heating rate was set to 5°C/min and the measurement domain was set to 50-550°C. Samples weighted (approximate 20mg) and loaded in glass vials. The DTA graphs are shown in figure 1.

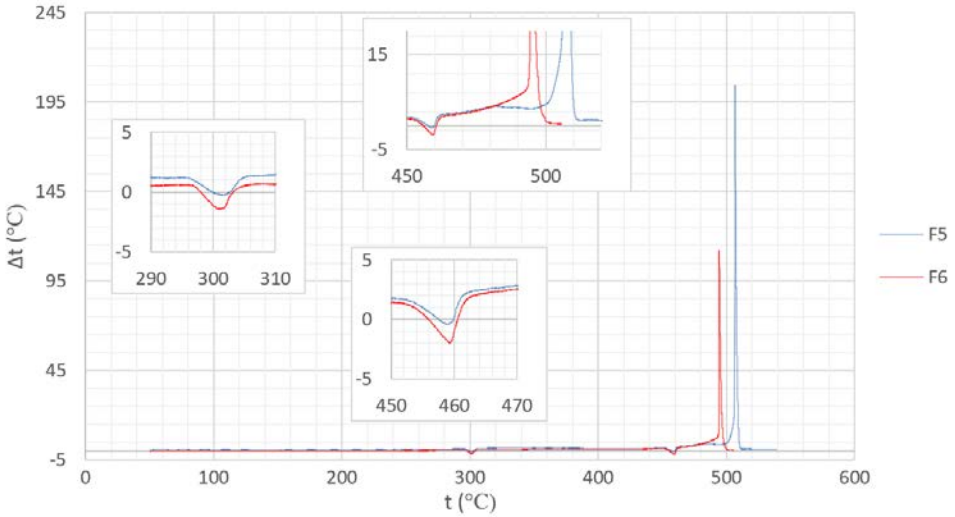


Figure 1: DTA graphs corresponding to the analyzed materials

The DTA analysis shows a similar thermal decomposition for both the formulations. The main difference is the self-ignition temperature of composition F6 (with

Parlon) which is about 10°C lower than standard formulation. After the endotherm peak recorded at 455°Can exotherm reaction starts, which undergoes self-ignition at 495°C for F6 and later for F5. Further analysis is needed, for single components in order to identify each physical transition or decomposition reaction.

The calorimetric measurements were performed with the equipment and the procedure described by Paraschiv et al.[6]. The samples were kept at 40°C for 24 hours in order to eliminate the moisture. The measurements were made in triplicate and the results presented in Table 4 are the averaged calculated values. The error is represented as a percentage of the difference between computation and experiments relative to the measured value. The difference is calculated relative to the polyurethane formulation (F5).

Table 4. Calorimetric measurements of the combustion of flare pyrotechnic material

Sample	Computed heat of combustion (kJ/kg)	Measured heat of combustion (kJ/kg)	Error (%)	Computed specific volume (L/kg)	Measured specific volume (kJ/kg)	Error (%)
F5	7819	7568	3.32	215.00	219.00	-1.83
F6	6966	6485	7.42	281.00	298.00	-5.70
Difference (%)		-14.31	Difference (%)		36.07	

The experiments made validate in an accepTable error the computations made with the computer software. The higher heat of combustion of F5 is expected to develop a higher flame temperature also.

4. SEM-EDS analysis

The SEM-EDS analysis (Scanning Electron Microscopy – Energy Dispersive X-ray Spectroscopy) allowed targeted analysis of sample surfaces F5, F6(fig. 2, 3, 4, 5). It was performed on a Tescan VEGA II LMU device coupled with a Bruker X-Flash 6 Detector. The magnification was set to 500X, obtained by manual focus and stigmators settings from a 15mm working distance. The peak current for analysis was set to 9 and the acquisition was made in 2 minutes for SEM and 15 minutes for EDS.

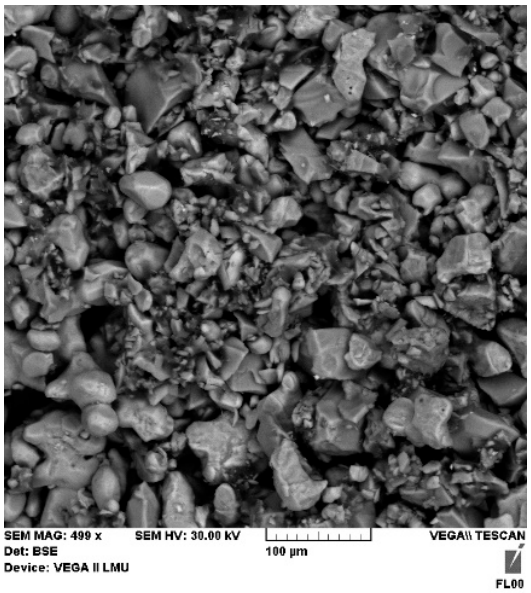


Figure 2: SEM micrograph of F5 formulation

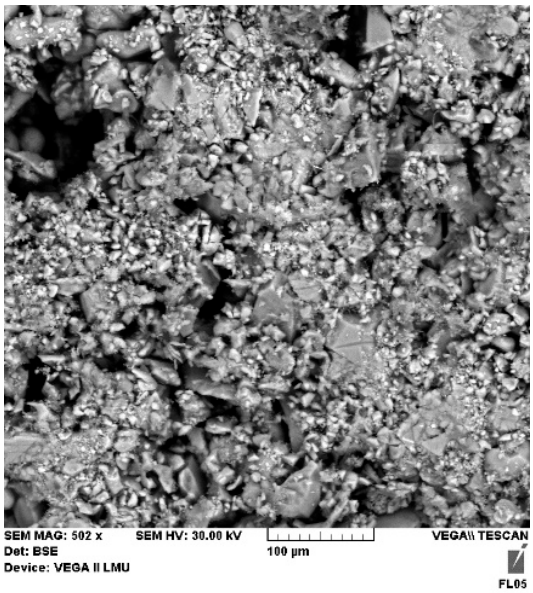


Figure 3: SEM micrograph of F6 formulation

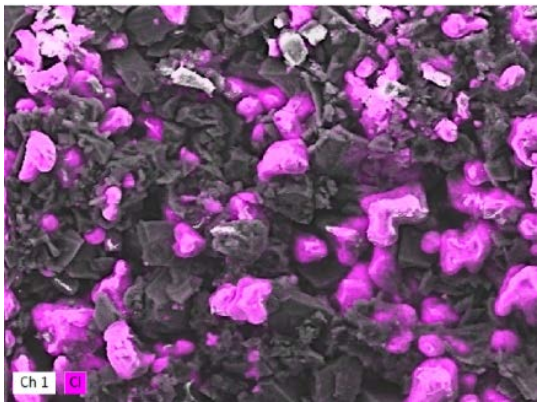


Figure 4: EDS Chlorine signal for composition F5

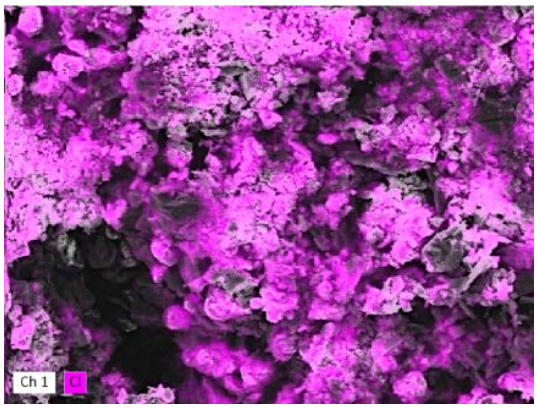


Figure 5: EDS Chlorine signal for composition F6

As it can be observed in the images acquired, the composition is homogenously prepared for both compositions. In case of F6, the polymer has a better contact with both fuel and oxidant particles. The back-scattered electron image show a compact material in case of F6 while in case of F5 the $KClO_4$ crystals and the Mg-Al particles can be clearly observed. The EDS signal show that the material covering the solid particles is Parlon.

5. Combustion rate and flame temperature determination

The equipment used for measurements and the setup of experiments is extensively described by Epure et al [1]. The temperature profile was measured for the whole burning period of the pyrotechnic grain but the average flame temperature in isobaric conditions was calculated only for the steady burning regime of the composition (excluding the recordings caused before full ignition and after combustion has ended (cooling combustion products are recorded), like shown in Figure 6 (these measurements are made with emissivity factor of 1, but were reprocessed to a factor of 0.7). The burning rate was calculated by the dividing the length of the grain to the burning period. Every experiment was repeated at least 3 times for each formulation in order to average the resultant average flame temperatures. For one of the F5 composition, a transient peak temperature was recorded and the burn time was significantly shorter. This could be caused by a non-steady burn. The results from these experiments were discarded. The resulting burn rate, flame temperature and radiative energy compared to the heat of combustion are represented in Table 5.

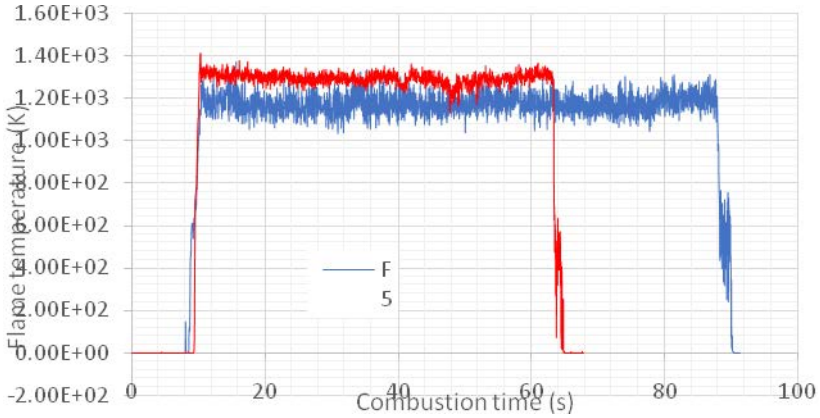


Figure 6: Temperature-time plot of the burning of pyrotechnic formulations

Table 5. Comparative combustion parameters of the pyrotechnic formulations

Sample	Burn rate [mm/s]	Flame temperature [K]	Radiative energy [kJ]	Heat of combustion (computed in isobaric conditions) [kJ]
F5	1.31	1310	2300	7500
F6	1.86	1450	4300	6400

6. Conclusion

This paper investigated the potential advantages of using Parlon as an additive in the binder matrix, to be used in polyurethane based pyrotechnic compositions. The thermochemical calculations, validated trough calorimetric determinations show a increase in the specific volume of gases of combustion, in case of Parlon additive composition. The heat of combustion is lower, as the combustion products have a lower heat of formation. The IR measurements show a higher burn rate (+41%) and a higher flame temperature (+10%). The reason can be explained, as it can be seen also in SEM-EDS analysis by the morphological aspect of additive containing compositions. The chlorine containing material can act both as a fuel and as oxidizer for particles in the composition, in the proximity of these particles, thus enhancing the burn rate.

Acknowledgement

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