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DEVELOPMENT AND CHARACTERIZATION OF NOVEL ILLUMINATION PYROTECHNIC FORMULATIONS

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Abstract: *This paper describes the investigations related to the development and characterization of various illumination pyrotechnic compositions based on polyurethane binders synthesized from commercial isocyanates and polyols, an oxidizer, two types of metallic powder and a burning catalyst. These types of binders improve the processability and minimize the risk associated with the manufacture process. The performance and safety characteristics of the novel pyrotechnic formulations were evaluated through various analytical techniques (DTA) and specific tests (rate of combustion, heat of combustion, specific volume, chemical stability, sensitivity to impact stimuli), according to NATO standards, providing promising preliminary results for further experimental investigations.*

Keywords: burning, illumination, pyrotechnics, polyurethane, safety

1. Introduction

Pyrotechnic compositions are heterogeneous mixtures of solid substances, comprising a fuel and an oxidizer [1-4]. When ignited, these compositions generate diverse effects like light, heat, smoke, and sound. Notably, the presence of an oxidizer enables the reaction to occur even without atmospheric oxygen. According to military standards, pyrotechnic compositions are substances or mixtures that undergo controlled combustion reactions upon ignition, generating specific effects, such as: heat, noise, light, or infrared radiation [4-5].

The fuel component can be organic (e.g., hydrocarbons) or inorganic (e.g., metallic alloys), with key attributes including heat release and oxidation byproducts [2-4]. Conversely, the oxidizer provides oxygen for the combustion reaction, influencing the composition's sensitivity, stability and compatibility. Common oxidizers include: salts, peroxides, and oxides, each fulfilling specific technical requirements to ensure optimal performance [2-4]. For instance, oxidizers must be solid, with a melting point above 80-100°C, minimal impurities, and resistance to decomposition in water. These stringent conditions ensure the effectiveness and safety of pyrotechnic compositions in various applications.

In practice, most pyrotechnic mixtures extend beyond simple fuel-oxidizer combinations, incorporating binders, stabilizers, catalysts and technological

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additives (shellac, polyvinyl chloride (PVC) etc.). These substances, whether organic or inorganic, serve to homogenize the mixture and to control or catalyze the burning process, enhancing plasticity and mechanical behaviour [2-4].

Binders maintain granular resistance and shape within pyrotechnic mixture and can act as organic fuel or intensify specific pyrotechnic effects. Typically, synthetic and natural resins, their derivatives, dried oils or glues serve as binders. Binders must meet strict criteria, including insolubility in water, solubility in organic solvents, adhesive ability, film-forming ability, and resistance to degradation. Generally, binders constitute 5-10% of the total composition, ensuring optimal pyrotechnic performance [2-4].

The inability of troops to operate effectively at night necessitated the development of pyrotechnic illumination systems and later night vision equipment. This disadvantage for night observation became an advantage for attacking troops. Pyrotechnic illumination is crucial for target observation, topography illumination, and initiating fire during nighttime operations. Historically, the first use of illumination systems dates back to 1583 in the conflict between the Ottoman and Persian Empires, where the Ottomans used lantern-like systems. In 1882, the British Royal Navy used spotlights to hinder Egyptian artillery deployment in Alexandria. World War II saw significant advancements, with British modifications to an M3 Grant tank, enhancing offensive capabilities.

Pyrotechnic illumination systems, extensively used in military contexts, have proven invaluable in resolving tactical challenges, spanning both World Wars to contemporary operations. Their development remains of paramount interest, vital for nocturnal military endeavors and tactical drills. Functionally, these systems serve to illuminate targets and terrain, with additional applications in igniting flammable targets in arid environments. Structurally categorized as munitions with special effects, they lack explosive impact on targets, facilitating in target identification at distances where observers cannot discern details. Pyrotechnic systems encompass various components, including compositions, structures, or accessories, tailored to fulfill specific operational functions. The establishment of system requirements typically involves two scenarios: either determining or verifying specifications for known systems or compositions, or designing and implementing systems or compositions to meet specific functions based on tactical or performance criteria.

The use of pyrotechnic compositions extends beyond simple mechanical and pyrotechnic integration, requiring specific modelling and loading methods to control firing rate, volume and mechanical strength. Homogeneity is crucial in this process, having a significant impact on the performance, stability and sensitivity of compositions. To ensure optimal performance, strict technical conditions are required, such as uniform combustion in various environments and long-term physico-chemical stability [4]. These reduce the risk of accidental ignition and the absence of toxic substances, while ensuring cost-effective production.

Thus, the purpose of this study is the development and characterization of various illumination pyrotechnic compositions by using various analytical techniques (DTA) and specific tests (rate of combustion, heat of combustion, specific volume, chemical stability and sensitivity to impact stimuli)[1, 5-8].

2. Materials and Methods

2.1 Materials

The following compounds were involved into the development of pyrotechnic compositions: barium nitrate ($Ba(NO_3)_2$, oxidizer, powder, average particle size 30 - 50 μm, purity >99%, FairPebTrade SRL, Romania), aluminium-magnesium alloy (PAM, metallic fuel, 1:1 weight ratio,

amorphous powder, particle size < 63 µm, FairPebTrade SRL, Romania), magnesium (Mg, metallic fuel, FairPebTrade SRL, Romania), Setathane D1160, (SET, hydroxyl content 5.4%, FairPebTrade SRL, Romania), Desmodur® 44V20L (MDI, -NCO content 31.5%, FairPebTrade SRL, Romania), iron oxide (Fe_2O_3, purity >99%, average particle size 50 µm, Sigma Aldrich), were used as received, except for the oxidizer which was vacuum dried for 24 h at 50 °C before use. *Figure 1* depicts the materials used in the development process.

Figure 1: Materials used in the development of pyrotechnic formulations

2.2 Methods

Preparation of the pyrotechnic mixture

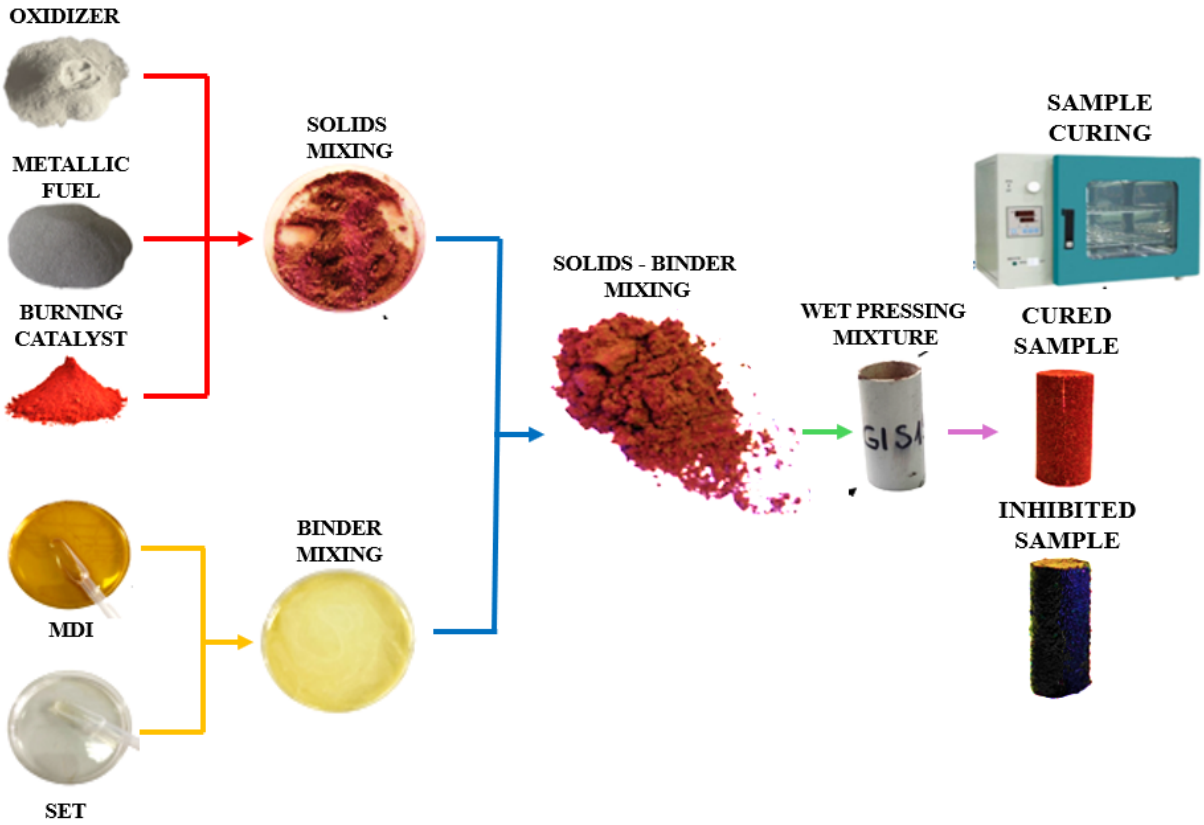
In general, the technological process of manufacturing an energetic material must be simple, allowing the development of new high-performance formulations with a low security risk for the personnel and equipment employed. Therefore, to obtain the proper homogeneity of the pyrotechnic mixture in order to provide adequate burning conditions, the development process is based on the following operations:

- *mass proportions establishment and component preparation (drying, grinding, sieving, weighing);*
- *pyrotechnic mixture development;*
- *pyrotechnic mixture moulding (wet pressing in this case).*

Considering the complexity of the process and the components involved, the development procedure was carried out in four directions, as follows:

i. ***solids mixing*** *(the oxidizer, metallic fuel and burning catalyst were mixed until visually homogeneous);*
ii. ***organic mixing*** *(solids mixture obtained above is mixed with the binder, by adding small amounts to the organic mixture based on MDI - 54% and SET - 46%);*
iii. ***molding and curing process*** *(the homogeneous mixture obtained is wet pressed into PVC tubes and cured for 24 hours at 60 °C, under atmospheric pressure);*
iv. ***cured sample preparation*** *(to obtain the proper burning control surface, the circular surface of the cured pyrotechnic samples was inhibited).*

For a better understanding the technological process steps are presented in *Scheme 1*, while in *Table 1*, the composition of the developed pyrotechnic formulations.



Scheme 1. Schematic representation of the pyrotechnic formulations development process

Table 1 The composition of the developed pyrotechnic formulations

Sample	Components [%]				
	$Ba(NO_3)_2$	PAM	Mg	PU	Fe_2O_3
C1S	72	24.50 (45µm)	-	3	0.5
C1B	72	24.50 (125µm)	-	3	0.5
C2S	72	22.50 (45µm)	-	5	0.5
C2B	72	22.50 (125µm)	-	5	0.5
C3S	72	20.50 (45µm)	-	7	0.5
C3B	72	20.50 (125µm)	-	7	0.5
C4S	72	-	24.50 (45µm)	3	0.5
C4B	72	-	24.50 (125µm)	3	0.5
C5S	72	-	22.50 (45µm)	5	0.5
C5B	72	-	22.50 (125µm)	5	0.5
C6S	72	-	20.50 (45µm)	7	0.5
C6B	72	-	20.50 (125µm)	7	0.5

3. Results and Discussion

3.1. Thermal Analysis

The thermal stability of the designed compositions is analysed using differential thermal analysis (DTA). An amount of 40 mg of composition was heated from 30˚C to 550˚C. The tests were carried out at a heating rate of 5˚C/min under standard atmospheric conditions according to STANAG 4515 [6]. According to STANAG 4515, the onset temperature is the temperature at which the decomposition process starts and corresponds to the exothermic peaks shown in *Figure 2*.

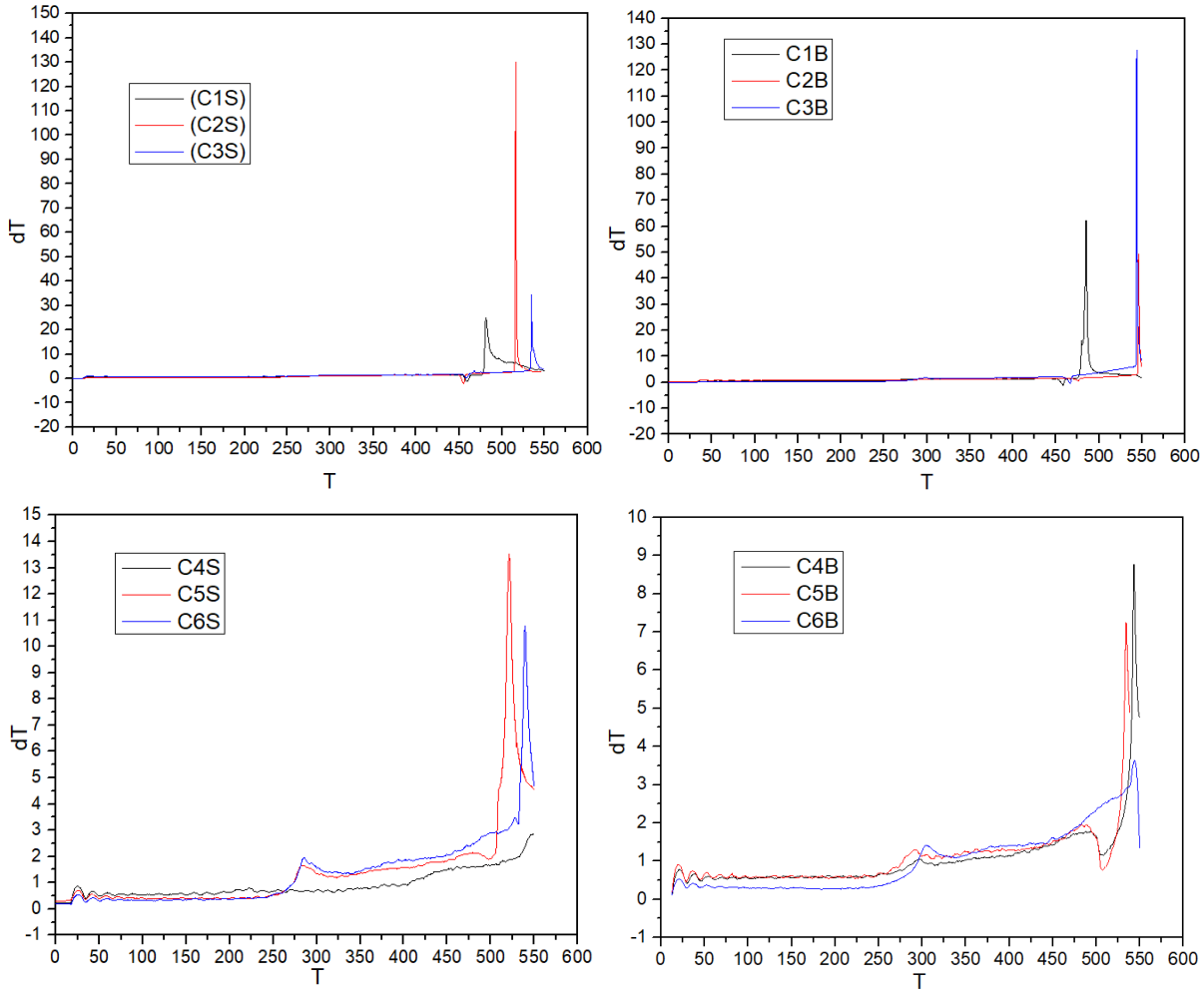


Figure 2: Thermal profiles of the developed pyrotechnic formulations

Table 2 DTA decomposition temperatures of designed pyrotechnic compositions

Sample	Temperature [°C]				Peak type
	Start	Onset	Top	Stop	
C1S	474.44	479.20	481.58	490.92	exothermic
C2S	514.18	519.96	520.60	544.77	exothermic
C3S	523.65	534.39	534.91	550	exothermic
C4S	550.01	-	-	-	exothermic
C5S	497.96	512.79	519.84	548.85	exothermic
C6S	531.20	534.56	538.93	550	exothermic
C1B	480.65	483.66	485.11	508.78	exothermic
C2B	514.79	525.54	526.11	550	exothermic
C3B	528.04	531.98	532.45	550	exothermic
C4B	517.81	540.02	543.29	550	exothermic
C5B	517.27	540.82	545.41	550	exothermic
C6B	546.92	547.42	550	550	exothermic

Characterization of pyrotechnic compositions through DTA analysis reveals a close relationship between thermal sensitivity and chemical composition. Polyurethane-based samples exhibit slightly lower but still acceptable

thermal stability compared to traditional mixtures employing iditol. Following STANAG 4515 guidelines [6], the onset temperature represnts the beginning of the decomposition process for energetic materials. The onset temperatures reported in *Table 2* align with the exothermic peaks depicted in *Figure 2*, indicating the decomposition process. Results from *Table 2* and *Figure 2* demonstrate that polyurethane-based pyrotechnic compositions maintain stability up to 200°C, with a subsequent low-intensity exothermic transition and energetic decomposition around 500°C. Literature suggests iditol-based compositions remain stable up to 480°C.

C1S, C2S, C3S, C1B, C2B, and C3B display similar thermal behavior in exothermic energy transformation, attributed to the aluminum-magnesium alloy fuel analyzed in the final step. Similarly, C4S, C5S, C6S, C4B, C5B, and C6B exhibit a comparable trend, with heightened peak sharpness near 200°C due to magnesium's high reactivity. Metallic fuel grain size minimally impacts thermal behavior, whereas mass variation and polyurethane substitution play significant roles. DTA analysis concludes that mass variation and substitution of the classical binder (iditol) with polyurethane influence decomposition temperature variation. The effects of polyurethane introduction will be further explored in subsequent analyses.

3.2. Friction Sensitivity

The purpose of the test is to determine the degree of risk associated with mechanical operations on pyrotechnic compositions. To determine the friction sensitivity of energetic materials, a BAM friction tester according to STANAG 4487 is used [1,7]. It consists of a cast steel base plate on which the friction device (porcelain plate and bolt) is mounted. The test results for the developed compositions are depicted in *Table 3*.

Table 3 – Friction sensitivity of the developed pyrotechnic compositions

Sample	**C1S**	**C1B**	**C2S**	**C2B**	**C3S**	**C3B**
Loading force [N]	216	216	252	252	360	360
Recorded results	*crackling; flash; smoke.*	*crackling; flash; smoke.*	*crackling; flash; smoke.*	*crackling; flash; smoke.*	*crackling; flash; smoke.*	*crackling; flash; smoke.*
Sample	**C4S**	**C4B**	**C5S**	**C5B**	**C6S**	**C6B**
Loading force [N]	120	120	160	168	216	216
Recorded results	*crackling; flash; smoke.*	*crackling; flash; smoke.*	*crackling; flash; smoke.*	*crackling; flash; smoke.*	*crackling; flash; smoke.*	*crackling; flash; smoke.*

Based on the data presented into the *Table 3*, the minimum force to which the samples under test reacted can be identified. It can be seen that samples containing magnesium as fuel have an increased sensitivity compared to those with aluminium-magnesium powder. At the same time, as the concentration of polyurethane increases, the sensitivity of the composition to friction decreases.

3.3. Combustion Analysis

The heat of combustion, the amount of gases and solid products resulting from the combustion and their temperature are the main thermodynamic characteristics of energy materials [1]. The high combustion rate ensures a high temperature of the reactants and their high pressure.

Combustion heat (Q_c) and specific volume (V_s) were determined using an AVL adiabatic calorimeter and a Julius Peters gasometer. For each measurement, 2 tests were performed for 2g of composition under vacuum conditions.
These characteristics were calculated using the following equations:
For combustion heat:

$$Q_c = \frac{K \times \Delta t - q}{\omega} \quad (1)$$

where: *K - caloric equivalent; Δt - burning time; q - combustion heat of ignition sample; ω - sample mass.*
For the specific volume:

$$V_s = \frac{W \times \Delta H \times 273.15}{\omega \times 760 \times (273.15 + t)} \quad (2)$$

where: *W - balloon volume + calorimeter bomb volume; ΔH – variation of mercury columns (Hi-Hf); t – ambient temperature.*

Table 4 Combustion heat and specific volume of the analysed samples

Sample	**C1S**	**C1B**	**C2S**	**C2B**	**C3S**	**C3B**
Combustion heat [kcal/kg]	1475.99	1479.47	1377.42	1378.47	1214.58	1210.88
Specific volume [l/kg]	118.5	118.43	204.17	203.6	229.14	230.09
Sample	**C4S**	**C4B**	**C5S**	**C5B**	**C6S**	**C6B**
Combustion heat [kcal/kg]	1407.19	1408.51	1288.25	1267.52	1078.5	1058.3
Specific volume [l/kg]	110.87	111.58	189.5	192.69	212.8	213.52

Based on results illustrated in *Table 4*, it can be seen that there is a direct corelation between the percentage of polyurethane contained in pyrotechnic compositions and the amount of heat released during the combustion process, but also between the same percentage and the resulting volume of gases. Thus, as the amount of polyurethane increases, the amount of heat released decreases and the volume of resulting gases increases. So, the thermally inert behaviour of the mixture of the two compounds is outlined.

3.4. Vacuum Analysis

The vacuum stability test is used to evaluate the thermal stability of designed compositions by measuring the volume of gases released when they are heated under specified conditions. The sample is heated for 40 hours in a heating bath maintained at 100˚C. The volume of gas obtained is determined using a piezoelectric transducer. The volume of gas V_{deg} (at a temperature of 273 K and a pressure of 1.013 bar) released during the test is calculated using the following equation:

$$V = \left[V_C + V_t - \frac{m}{d} \right] x \left[\frac{P_2 x 273}{273 + t_2} - \frac{P_1 x 273}{273 + t_1} \right] x \frac{1}{1{,}013} \quad (3)$$

where:
V - volume of gas released by the explosive sample (expressed in [cm^3] at standard temperature and pressure);
V_c - volume of the transducer and adapter [cm^3];
V_t - volume of the heating tube [cm^3];
m - mass of explosive sample tested [g];
d - density of the test sample [g/cm^3];
P_1 = pressure calculated at the start of the test [bar];
P_2 - calculated pressure at the end of the test [bar];
t_1 - room temperature at start of test [°C];
t_2 - room temperature at the end of the test [°C].

Table 5 Vacuum stability results of the analysed samples

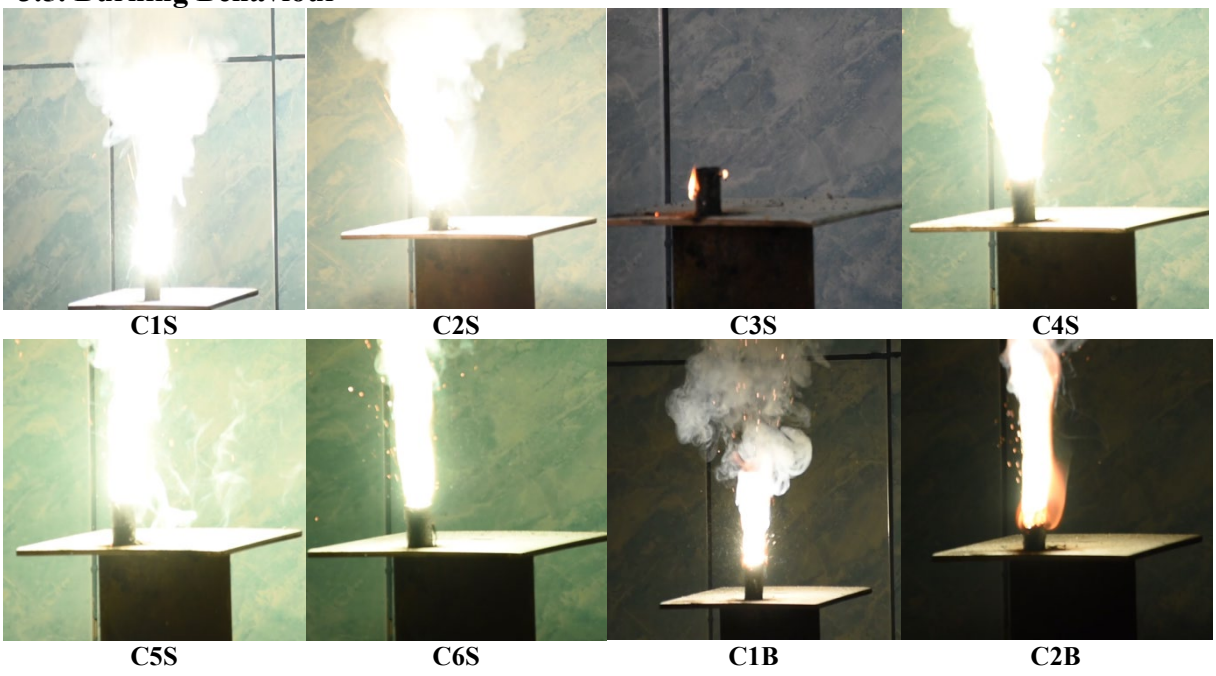
Sample	**C1S**	**C2S**	**C3S**
V_{deg} [cm^3/g]	0.1942	0.2032	0.2268
Sample	**C4S**	**C5S**	**C6S**
V_{deg} [cm^3/g]	0.2044	0.2268	0.2476

Vacuum stability analysis was performed only for samples containing metallic fuel with an small average particle size. It can been observed from *Table 5* that the volume released by the 6 compositions is less than $1 g/cm^3$, which is the required stability condition. According to STANAG 4556 [8], it can be affirmed that all the developed compositions present a proper stability and within the required limits. It should be pointed out that the volume of gas released during the analysis increases in proportion to the percentage of polyurethane added, and it can be seen that the instability of the compositions increases with the percentage of polyurethane added.

Further the behaviour of the designed compositions during combustion energy transformation will be analysed. Thus, with the thermal camera the flame temperature was analyzed, with the luxmeter the luminous intensity was measured and with a video camera the combustion rate was measured.

Based on the burning results of the the mixtures developed using PAM 20.5% and polyurethane 7% (C3S, C3B respectively) were not ignited by the igniter. The reason for non-initiation is the high amount of binder used which resulted in inhibition of the reaction.

3.5. Burning Behaviour



C1S **C2S** **C3S** **C4S**

C5S **C6S** **C1B** **C2B**

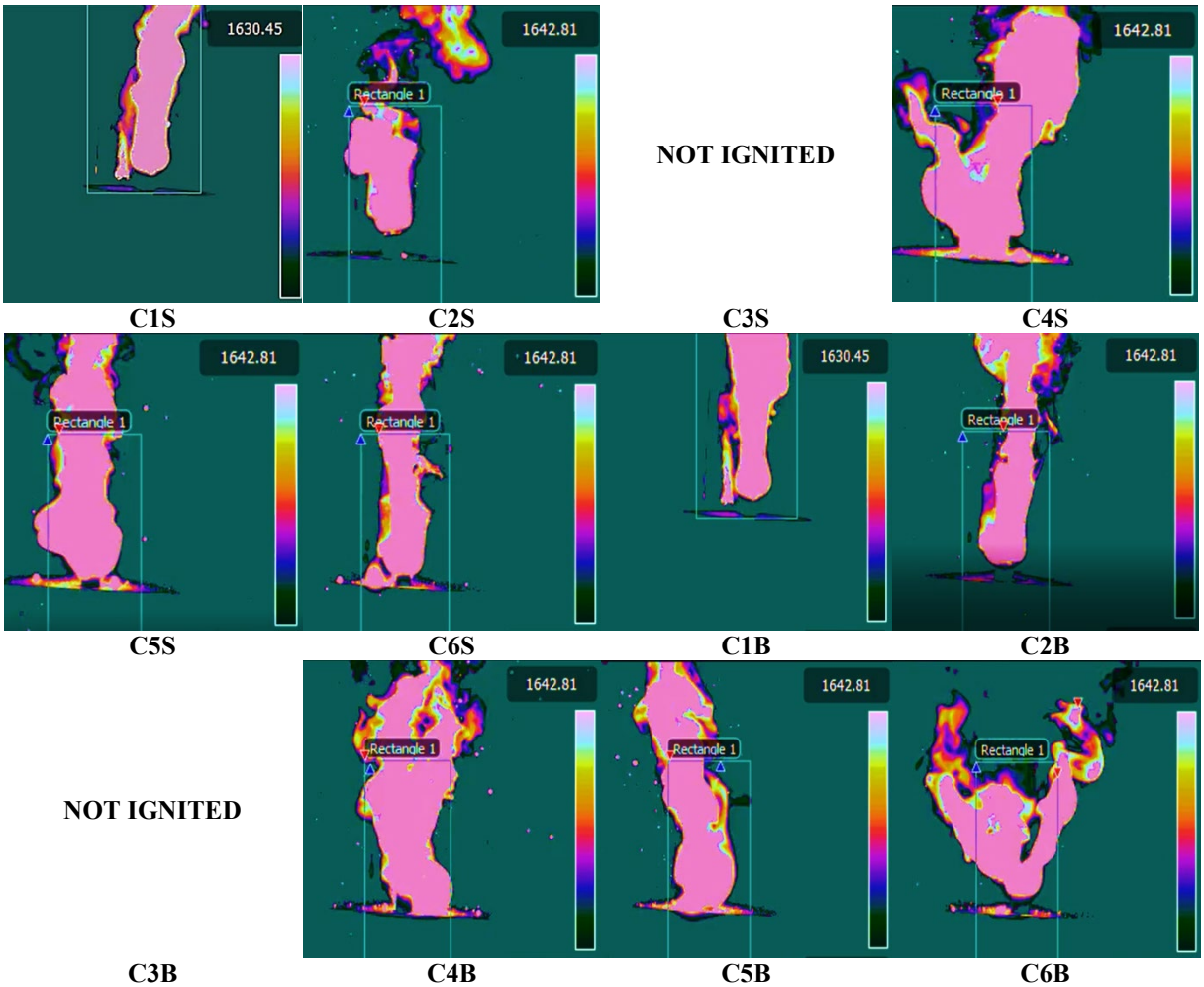
C3B **C4B** **C5B** **C6B**

Figure 3: Flame aspect of the developed pyrotechnic formulations

Based on thermal analysis the combustion temperature (T_c) of the compositions is higher than the maximum temperature that can be recorded by it, 1642,81 °C. Consequently, the combustion temperature was obtained using an infrared thermometer.

The burning rate (v_c) was determined from the ratio of the height of each layer of illumination composition to its burning time.

To perform the light intensity (Φ), measurement, the luxmeter was placed at a distance of 2 m from the composition. The values of all parameters mentioned above are listed in *Table 6.*



C1S **C2S** **C3S** **C4S**

C5S **C6S** **C1B** **C2B**

C3B **C4B** **C5B** **C6B**

Figure 4: Flame aspect of the developed pyrotechnic formulations recorded with thermal device

Table 5 Combustion parameters of the designed compositions

Sample	T_c [°C]	Φ [cd]	v_c [cm/s]
C1S	1944	56268.8	0.15
C2S	1928	70336	0.13
C3S	-	-	-
C4S	2010	163280	0.44
C5S	1851	139164.8	0.40
C6S	2000	108518.4	0.43
C1B	1952	58958.2	0.10
C2B	1921	72596.4	0.09
C3B	-	-	-
C4B	1942	133638.4	0.25
C5B	1980	98470.4	0.25
C6B	1962	72345.6	0.2

4. Conclusions and Perspectives

An experimental study was conducted to determine the performance and sensitivity characteristics of developed illimination pyrotechnic formulations based on polyurethanic binder, an oxidizer, two type of mettalic fuel powder and a burning catalyst. The new formulations were compared with regard to the amount of binder and type of mettalic powder used, in terms of safety and performance. The safety and performance characteristics were evaluated by performing tests and analyzes specific to these types of energetic materials: thermal and thermochemical analyzes, combustion experiments, sensitivity to friction with different loading forces and vacuum stability. These pyrotechnic formulations were designed to illuminate the tactical batle field during combat operations and it appears that the effects obtained from these analyzes meet the requirements of this type of material.

Thermal analysis showed that the pyrotechnic mixtures employing polyurethane posess a higher thermal sensitivity but the decomposition temperature is in all cases superior than 200 °C. In case of friction sensitivity the samples containing magnesium as fuel have an increased value compared to those with aluminium-magnesium powder. Also, as the amount of binder increases, the sensitivity decreases. Vacuum stability results indicated good chemical stability, being smaller than 1 cm^3/g.

In terms of luminous intensity, formulations which contain magnesium as fuel are more efficient and easier to ignite.

Combustion rate is influenced both by the type of metallic fuel used and its particles size. It has been observed that the combustion rate of compositions containing larger particles is significantly reduced. At the same time, compositions containing magnesium have twice the combustion rate of those containing aluminum.

To date, in terms of the manufacturing process, the safety and performance using polyurethane binders provide an ideal background for more comprehensive experimental studies to demonstrate their applicability in pyrotechnic systems.

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