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CHEMICAL ENGINEERING**



PHD THESIS

**PRACTICAL ASPECTS ON USING POLYVINYL CHLORIDE
AND POLYTETRAFLUOROETHYLENE IN
PYROTECHNICAL COMPOSITIONS**

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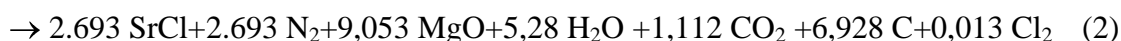
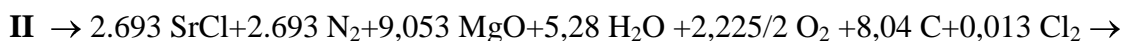
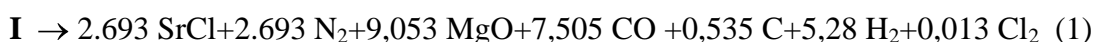
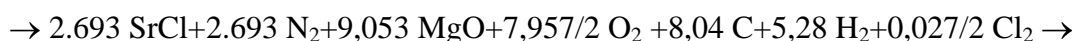
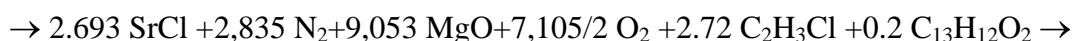
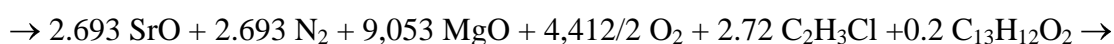
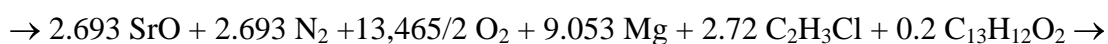
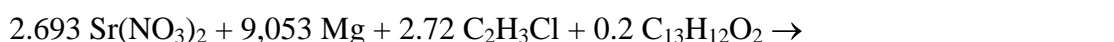
SECOND PART
ORIGINAL CONTRIBUTIONS ON THE DEVELOPEMENT AND
CHARACTERISATION OF PYROTECHNIC COMPOSITIONS
CONTAINING PVC AND PTFE

The experimental part of this doctoral thesis was started at SC Rompiro SA Orăștie and was continued in the laboratory of Military Technical Academy Bucharest. Materials were provided by SC Rompiro SA Orăștie except for polytetrafluorethylene (PTFE) obtained from the Scientific Research Center of the Naval Forces, Constanța.

3.5. Theoretical studies on the light, signaling and thermal traps pyrotechnic compositions.

3.5.1.2. Calculation of combustion heat and specific molar volume for the red pyrotechnic compositions

The molar equation of the combustion reaction for **CR1** is (for 1000 g of composition):



Combustion heat calculation for the red pyrotechnic compositions CR1, CR2 and CR3

Calculation of the combustion heat is according to equation no.1 [4,6].

$$H_e = \sum n_i \cdot H_{fp} - \sum n_i \cdot H_{fr} \quad (3)$$

Calculation of the combustion heat for path I of proposed combustion process.

$$\text{I. } H_e = 2.4 \cdot 97.87 + 0.67 \cdot 141.5 + 5.35 \cdot 143.8 + 9.35 \cdot 26.42 + 3.75 \cdot 57.5 - 3.07 \cdot 233.8 - 2.4 \cdot 23 - 0.35 \cdot 614.46 = \mathbf{813.648} \text{ kcal / kg [136]} \quad (4)$$

Calculation combustion heat for path II of proposed combustion process.

$$\text{II. } H_e = 2.4 \cdot 197.87 + 0.67 \cdot 141.5 + 5.35 \cdot 143.8 + 7.4 \cdot 26.42 + 5.7 \cdot 57.5 - 3.07 \cdot 233.8 - 2.4 \cdot 23 - 0.35 \cdot 614.46 = \mathbf{874.254} \text{ kcal / kg [136]} \quad (5)$$

Calculation of the molar volume

$$\text{I. } V = (3.07 + 1.95 + 9.35) \cdot 22.4 = \mathbf{321.888} \text{ l/ kg} \quad (6)$$

$$\text{II. } V = (3.07 + 7.4) \cdot 22.4 = \mathbf{234.528} \text{ l/kg} \quad (7)$$

These calculations have led to the theoretical values of the specific volume and specific combustion heat close to those reported in the literature [136].

3.5.1.3. Designing red color pyrotechnic compositions using NASA-CEA gui program

Beside the theoretical calculations presented previously, the same parameters have also been determined using CEAgui program developed by NASA for propergols.

Initial data have been programmed as follows.

problem

hp p,bar=1, t,k=3800

react

fuel=Mg wt=3.07 t,k=273.15

h,kj/mol=0 MG 1

oxide=SrN2O6 wt=5.35 t,k=273.15

h,kj/mol=233.8 SR 1 N 2 O 6

name=C2H3Cl wt=2.4 t,k=273.15

h,kj/mol=23 C 2 H 3 CL 1

name=C13H12O2 wt=0.35 t,k=273.15

h,kj/mol=614.46 C 13 H 12 O

output

The results are:

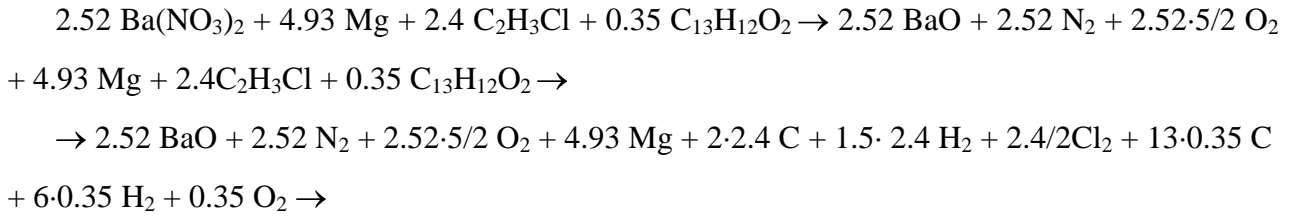
Thermodynamic properties

P, BAR	1.0000
T, K	2873.62
RHO, KG/CU M	1.4263-1
H, KJ/KG	712.71
U, KJ/KG	11.622
G, KJ/KG	-22403.2
S, KJ/(KG)(K)	8.0442

For these calculations 8 species were taken into consideration namely (SrCl, SrO, MgO, CO, C, N₂, H₂O, and H₂). One notice that CEA gui program takes into account 28 species, more than initially anticipated.

3.5.1.4. Calculation of the combustion heat and the specific molar volume for the green color pyrotechnic compositions

Chemical reaction equation for the green pyrotechnic composition:



Calculation of the combustion heat:

$$H_e = \sum n_i \cdot H_{fp} - \sum n_i \cdot H_{fr} \quad (10)$$

$$\text{I. } H_e = 2.4 \cdot 205.26 + 0.12 \cdot 131.12 + 4.93 \cdot 143.8 + 9.35 \cdot 26.42 + 1.42 \cdot 57.5 - 2.52 \cdot 236.9 - 2.4 \cdot 23 - 0.35 \cdot 614.46 = \mathbf{678.72} \text{ kcal / kg} \quad (11)$$

$$\text{II. } H_e = 2.4 \cdot 205.26 + 0.12 \cdot 131.12 + 4.93 \cdot 143.8 + 5.07 \cdot 26.42 + 5.7 \cdot 57.5 - 2.52 \cdot 236.9 - 2.4 \cdot 23 - 0.35 \cdot 614.46 = \mathbf{811.743} \text{ kcal / kg} \quad (12)$$

Calculation of the molar volume:

$$\text{I. } V = (2.52 + 9.35 + 4.28) \cdot 22.4 = \mathbf{361.76} \text{ l / kg} \quad (13)$$

$$\text{II. } V = (2.52 + 5.07) \cdot 22.4 = \mathbf{170.016} \text{ l / kg} \quad (14)$$

The values of the specific volume and combustion heat obtained from these calculations are consistent with the literature.

3.5.1.5. Designing green color pyrotechnic compositions by using NASA-CEAgui program

Example of CEAgui program for the green composition

Initial data are as follows:

problem

hp p,bar=1, t,k=3800

react

fuel=Mg wt=4.93 t,k=273.15

h,kj/mol=0 MG 1

oxide=BaN2O6 wt=2.52 t,k=273.15

h,kj/mol=233.8 BA 1 N 2 O 6

name=C2H3Cl wt=2.4 t,k=273.15

h,kj/mol=23 C 2 H 3 CL 1

name=C13H12O2 wt=0.35 t,k=273.15

h,kj/mol=614.46 C 13 H 12 O 2

output

Analyzing the components obtained it is noticed that there are more products than those considered in the previous calculations.

Molar fractions obtained by CEA gui program for the green pyrotechnic composition are presented in table 1.

Table 1 Molar fractions for the green pyrotechnic composition

BaCL	0.00028	*H2	0.17362
BaCL2	0.02447	*Mg	0.38059
CH4	0.00002	MgCL	0.01022
*CO	0.04687	MgCL2	0.01917
C2H2,acetylene	0.00009	MgH	0.00007
*H	0.00036	Mg2	0.00003
HCN	0.00084	*N2	0.02432
HCL	0.00080	C(gr)	0.20757
HNC	0.00004	MgO(cr)	0.1106

Thermodynamic properties

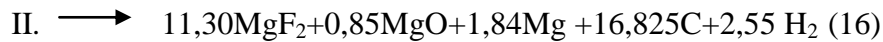
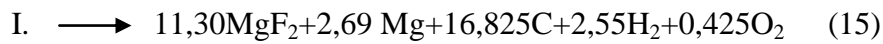
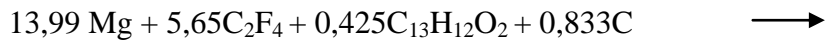
P, BAR	1.0000
T, K	1936.44
RHO, KG/CU M	2.3855-1
H, KJ/KG	412.92
U, KJ/KG	-6.2777
G, KJ/KG	-12330.6
S, KJ/(KG)(K)	6.5809

3.5.2 Calculation of combustion heat and molar volume for a magnesium-polytetrafluorethylene-identol-graphite pyrotechnic composition

A pyrotechnical composition based on magnesium, polytetrafluorethylene, identol and graphite was chosen for this study.

3.5.2.2. Calculation of the combustion heat and the specific molar volume for FLARE pyrotechnic compositions

Chemical reaction equation is presented for 1000 g of composition.



Calculation of the combustion heat for the proposed composition:

$$\text{I.} \Delta H_{\text{f products}} = 11,3 \times 268,94 + 2,69 \times 0 + 16,825 \times 0 = \mathbf{3039,02} \text{ kcal/kg} \quad (17)$$

$$\text{II.} \Delta H_{\text{f products}} = 11,3 \times 268,94 + 0,85 \times 146 + 1,84 \times 0 + 16,825 \times 0 + 2,55 \times 0 = \mathbf{3163,12} \text{ kcal/kg} \quad (18)$$

Combustion heat at constant pressure has been computed for the 2 cases:

$$\text{I.} \Delta Q_{\text{p combustion}} = 3039,02 - 1171,93 = \mathbf{1867,09} \text{ kcal/kg} \quad (19)$$

$$\text{II.} \Delta Q_{\text{p combustion}} = 3163,12 - 1171,93 = \mathbf{1991,19} \text{ kcal/kg} \quad (20)$$

Molar volume calculation:

$$\text{I.} V = 19 \cdot 22,418 = \mathbf{425,942} \text{ l/Kg} \quad (21)$$

$$\text{II.} V = 5 \cdot 22,418 = \mathbf{112,09} \text{ l/Kg} \quad (22)$$

3.5.2.3. FLARE pyrotechnic compositions' design using NASA-CEA gui program

The following results have been obtained using CEAgui program:

Thermodynamically properties:

P, BAR	1,0000
T, K	5295,99
H, KJ/Kg	7463,24
U, KJ/Kg	6721,02
M(1,n)	59,327

Molar fractions:

*CO2	0,00881
*F	0,18477
*H2	0,05284
MgF2	0,14950
C	0,36705
Mg	0,23704

We notice that the total number of products is the same as the one initially predicted.

**4. 4. Experimental studies on lighting, signaling and thermal traps
pyrotechnic compositions**

4.1 PVC containing pyrotechnic compositions

4.1.2. Red color pyrotechnic compositions development

Table 2 presents 6 red pyrotechnic compositions that were studied and launched into production at Orăștie. All of them contain PVC, having the same amount of chlorine as hexachlorobenzene, but the risks are diminished.

Table 2 Red color pyrotechnic compositions

Component/Percentage	Red 1	Red 2	Red 3	Red 4	Red 5	Red 6
Strontium nitrate	15-22	-	20-28	-	47-58	-
Strontium carbonate	-	19-25	-	-	-	15-25
Potassium perchlorate	24-33	21-32	33-47	33-47	-	-
PVC	7-12	8-15	9-15	9-15	4-9	7-12
Potassium nitrate	25-32	26-33	9-15	9-15	-	-
Dextrin	5-10	7-10	5-10	5-10	-	-
Strontium oxalate	-	-	-	25-32	-	-
Magnesium	-	-	-	-	21-27	-
Iditol	-	-	-	-	4-9	-
Shellac	-	-	-	-	4-9	-
Nitrocellulose	-	-	-	-	-	65-70

Based on previous results [52,137-139], the research continued at ATM on 3 red pyrotechnic compositions.

Table 3 Red color pyrotechnic compositions

Component/Percentage	CR-1	CR-2	CR-3
Strontium nitrate	57	60	65
Magnesium	22	17	13
PVC	17	18	15
Iditol	4	5	7

4.1.3. Green color pyrotechnic compositions development

Table 4 Green pyrotechnic compositions

Component/ Percentage	Green 1	Green 2	Green 3	Green 4	Green 5	Green 6	Green7
Barium nitrate	15-22	-	20-28	-	47-56	-	66
Barium carbonate	-	19-25	-	-	-	15-25	-
Potassium perchlorate	24-33	21-32	33-47	33-47	-	-	-
PVC	7-12	8-15	9-15	9-15	4-9	7-12	15
Potassium nitrate	25-32	26-33	9-15	9-15	-	-	-
Dextrin	5-10	7-10	5-10	5-10	-	-	-
Barium oxalate	-	-	-	25-32	-	-	-
Magnesium	-	-	-	-	21-27	-	12
Iditol	-	-	-	-	4-9	-	7
Shellac	-	-	-	-	4-9	-	-
Nitrocellulose	-	-	-	-	-	65-70	-

4.1.4. Blue-violet pyrotechnic compositions

Blue and violet pyrotechnic compositions studied and manufactured at Orăștie.

Table 5 Blue-colored pyrotechnic compositions

Component/Percentage	Blue 1	Blue 2	Blue 3	Blue 4	Blue 5	Blue 6
Potassium perchlorate	65-72	62-69	64-70	65-72	65-75	55-65
Copper oxide CuO	10-16	-	-	-	10-18	-
PVC	10-16	10-16	10-16	9-15	10-16	10-16
Dextrin	3-10	5-10	5-10	3-10	-	-
2CuCO ₃ Cu(OH) ₂	-	12-18	-	-	-	15-24
CuCO ₃ Cu(OH) ₂	-	-	12-17	-	-	-
Copper metal	-	-	-	10-16	-	-
Urotropine	-	-	-	-	3-10	-
Ammonium chloride	-	-	-	-	3-5	-
Sulfur	-	-	-	-	-	16-25

4.1.5. Yellow color pyrotechnic compositions development

Yellow-coloring flame salts have been used such as sodium nitrate, sodium oxalate and cryolite. Four yellow pyrotechnic compositions have been studied and launched into production at Orăștie.

Compositions 1-3 have dextrin as binder, while no. 4 has nitrocellulose both as binder and oxidant. All these compositions include 7-15% PVC acting as binder.

Table 6 Yellow color pyrotechnic compositions

Component/ Percentage	Yellow 1	Yellow 2	Yellow 3	Yellow 4
Potassium perchlorate	46-52	42-52	45-53	-
Sodium nitrate	25-33	-	-	-
PVC	7-12	9-12	9-15	7-12
Dextrin	5-10	5-10	5-10	-
Sodium oxalate	-	22-31	-	15-25
Cryolite	-	-	26-35	-
Nitrocellulose	-	-	-	65-70

4.2. PTFE containing pyrotechnic compositions for lighting and IR masking

4.2.1. The goal of the experimental studies for FLARE compositions

The research on FLARE type pyrotechnic compositions based on metallic fuel (magnesium, aluminum, titanium, aluminum-magnesium alloy) and polytetrafluorethylene have been coordinated by the Scientific Research Center of the Naval Forces Constanța; the pyrotechnic composition part was accomplished at SC Rompiro SA Orăștie.

Based on chemical calculation a pyrotechnic composition in which the magnesium would totally react with the fluorine from PTFE should contain contain 32.43% magnesium and the rest PTFE.

Based on the expertise obtained at Orăștie, 6 new thermic trap pyrotechnic compositions have been designed at ATM Bucharest.

Table 7 Pyrotechnic compositions with PTFE and iditol (% mass)

Code/Component	PTFE	Mg	Ti	Al	Al-Mg	Binder	C
CAP-1	56.5	34.0	-	-	-	9,5	-
CAP-2	56.5	34.0	-	-	-	8,5	1.0
CAP-3	70.0	-	-	24.0	-	6.0	-
CAP-4	70.0	-	-	24.0 sort Al PL5	-	6.0	-
CAP-5	64.0	-	30.0	-	-	6.0	-
CAP-6	64.0	-	-	-	30.0	6.0	-

For all of these compositions performance features have been determined: initiation temperature, combustion heat, specific volume, flame temperature for CAP-2, behavior at flame.

5. Studies on the physical, chemical, safety and performance characteristics of the pyrotechnic compositions

Ten pyrotechnic compositions have been studied at ATM Bucharest, three of red color, one green and 6 compositions based on polytetrafluorethylene. For these compositions physical, chemical, safety and performance features have been determined.

5.1 Determination of physical and chemical features of pyrotechnic compositions

In order to study the features of pyrotechnic compositions determinations of gravimetric densities, granulometry, higroscopicity, amount of moisture and volatile substances have been performed at ATM Bucharest. These determination are in strict conformity with the national and international standards [140-143,154].

Determination of the gravimetric density

Average gravimetric density varies between 1.540-1.544 g/cm³.

Granulometric determination

Granulometry determination for the 10 pyrotechnic compositions has been performed on a standardized apparatus according to the ATM procedure [141]. The granulometry of the pyrotechnic compositions is comprised between 0.2 and 0.8.

Higroscopicity determination

The goal of this measurement is the determination of the water content adsorbed on the oxidant.

Average results of the higroscopicity determinations on the 10 pyrotechnic compositions indicated an acceptable higroscopicity level of less than 1%.

Determination of moisture and volatile substances

Average results of the volatiles' determinations, performed on the ten pyrotechnic compositions indicate values under 0.9%.

5.2. Determination of the safety features of pyrotechnic compositions

The goal of these determination was the assessment of the risk level associated with the mechanical operations on the pyrotechnic compositions. Sensitivity to friction, sensitivity to impact, sensitivity to electrostatic discharges and the chemical stability of the pyrotechnic compositions under vacuum have been studied.

These determination have been performed in the ATM laboratory in the compliance with the national and international standard procedures.

5.2.1. Friction sensitivity. BAM apparatus method

The goal of this determination is to assess the risk level associated to the mechanical operations on pyrotechnic compositions.

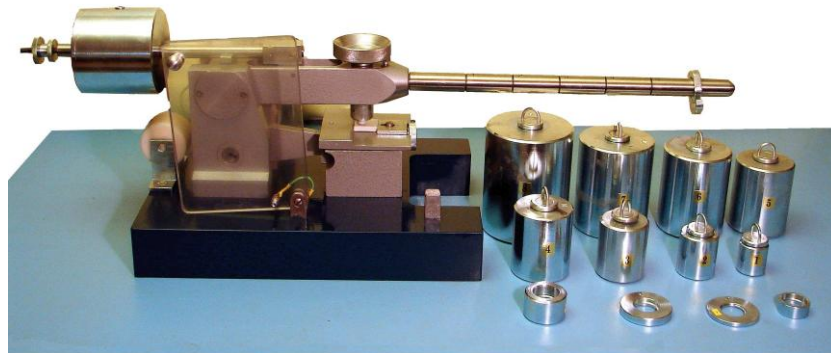


Figure 1. BAM apparatus for the determination of the friction sensitivity.

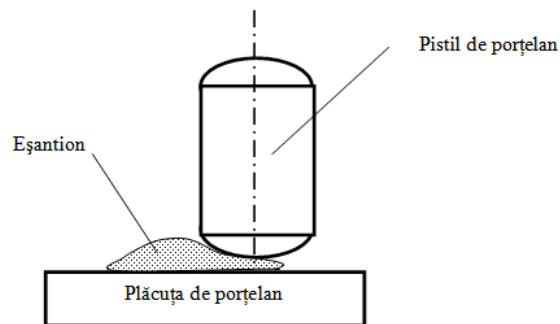


Figure 2. Testing configuration

The results indicate that all these ten compositions exhibit an extremely low sensitivity to friction (no reaction to pressing forces of 360N) indicating the fact that the degree of risk associated to mechanical operations on the pyrotechnic compositions is extremely low.

5.2.2 Experimental determination of the impact sensitivity

The goal of this test is to check the sensitivity of pyrotechnic compositions accidental mechanical shocks that could initiate the pyrotechnic composition.

Results show that all of these ten compositions exhibit an extremely low sensitivity to impact, indicating the fact that the degree of risk associated to the mechanical operations on pyrotechnic compositions is very low.

5.2.3. Experimental determination electrostatic discharge sensitivity

The goal of this test is the determination of the minimum discharge energy necessary to induce a reaction into an explosive material or into a pyrotechnic composition [146].

These tests were performed according to the SR EN 13938-2:2005 standard, representing the romanian version of the european standard EN 13938-2:2004 [147,148].

The results of this test indicate the fact that the ten pyrotechnic compositions exhibit a low sensitivity to electrostatic discharge, initiation energy is greater than 5 J.

5.2.4. Chemical stability of pyrotechnic compositions. Vacuum test

The goal of the test is the evaluation of the chemical stability by determining the pressure increase due to the artificial ageing during a certain period.

Chemical stability of the powders, explosives and pyrotechnic compositions is a very important feature from the safety perspective of transport, manipulation, storage and usage.

The temperature of the bath is represented in black, in brown is the variation of the environmental temperature, and in violet or blue the variation of the pressure in mbar.

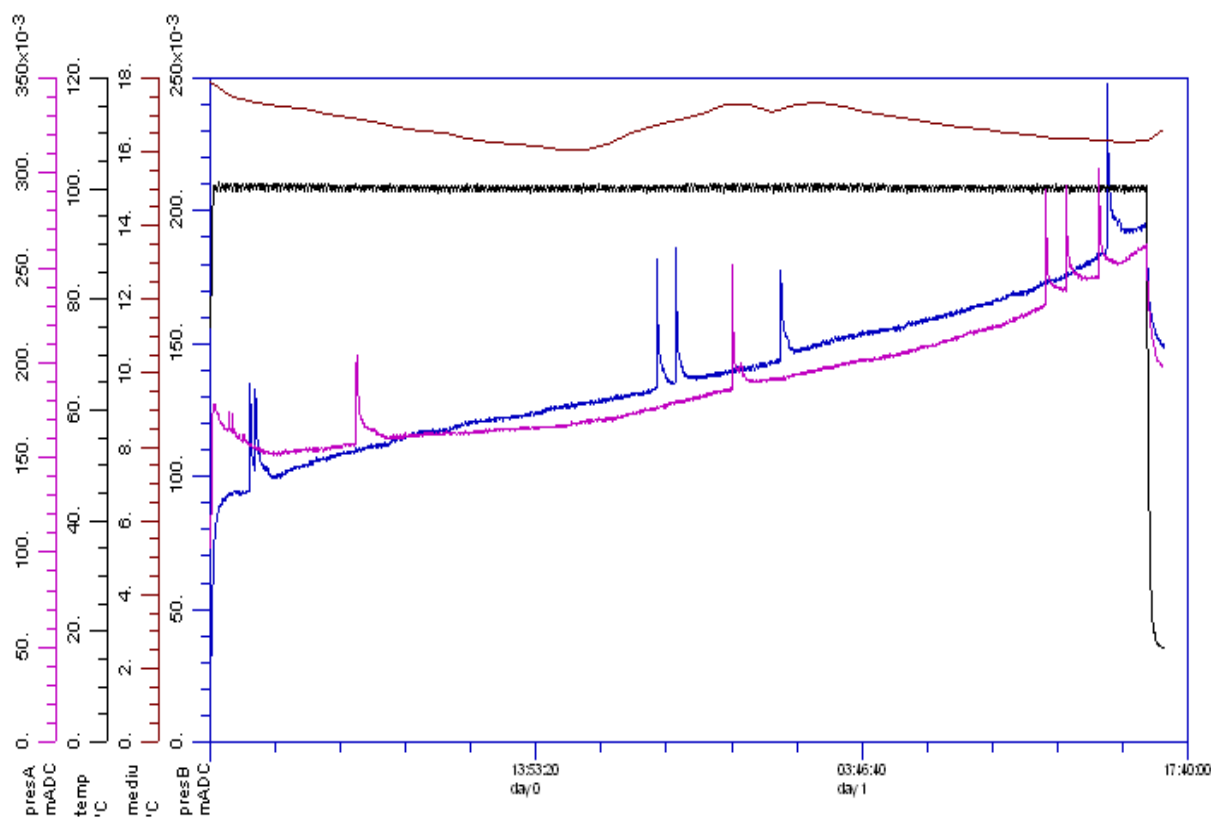


Fig.3 Chemical stability determination for the pyrotechnic composition CAP-2

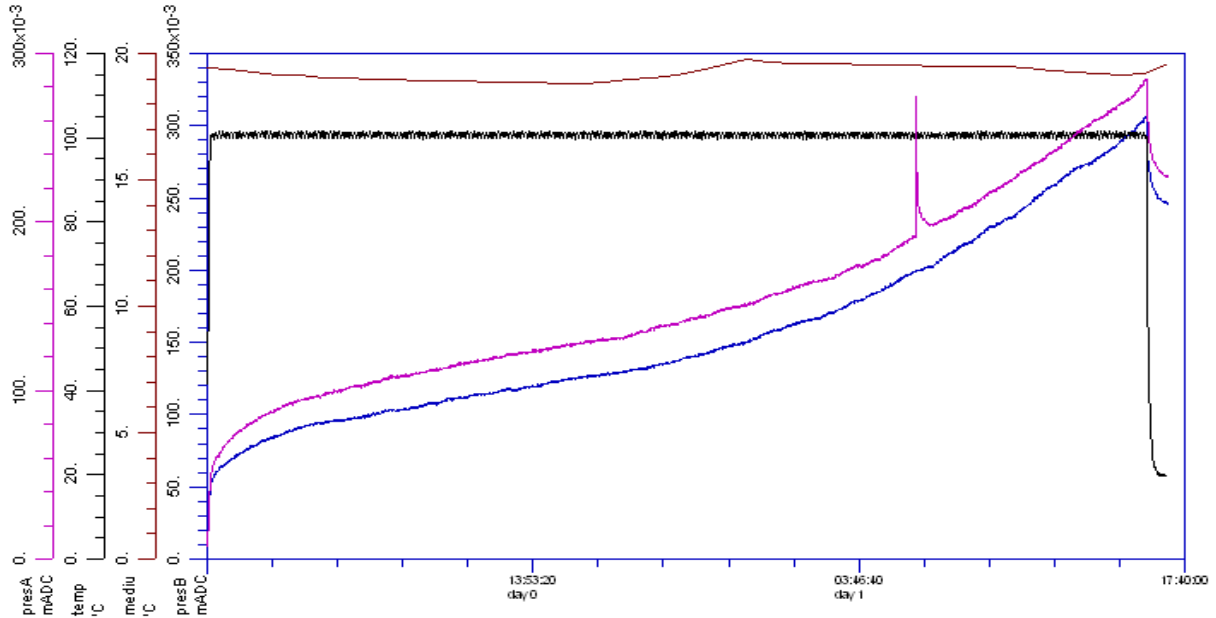


Figure 4 Chemical stability determination for the pyrotechnic composition V

Figure 3-4 present pressure variation during the 40 hours of test. Experimental results are presented in table 8.

Table 8 Chemical stability results for the pyrotechnic compositions

Nr.crt.	Compozitie	canal	Vc	Vt	m	d	P1	t1	P2	t2	Vsp	Vsp*(cm3/g)
1	CAP-1	B	21.8	2.75	5	1.54	0.004	20.85	0.216	20.27	4.15049	0.83009895
		A	21.35	2.75	5	1.54	0.008	17.94	0.1971	16.64	3.66991	0.73398235
2	CAP-2	B	21.8	2.75	5	1.54	0.002	17.94	0.14807	16.64	2.89562	0.57912424
												0.6565533
3	CAP-3	B	21.8	2.75	5	1.54	0.005	14.7	0.17	19.66	3.23526	0.64705137
4	CAP-4	A	21.35	2.75	5	1.54	0.00607	22.35	0.255	21.22	4.75552	0.95110467
5	CAP-5	B	21.8	2.75	5	1.54	0.008	22.92	0.2055	21.48	3.85135	0.77027045
6	CAP-6	A	21.35	2.75	5	1.54	0.002	17.31	0.1505	16.38	2.88414	0.57682895
7	CR-1	B	21.8	2.75	5	1.54	0.007	17.91	0.1326	16.81	2.48875	0.4977492
8	CR-2	A	21.35	2.75	5	1.54	0.0046	22.68	0.2182	21.53	4.07617	0.81523418
9	CR-3	A	21.35	2.75	5	1.54	0.002	18.54	0.24687	18.76	4.71682	0.94336416
		B	21.8	2.75	5	1.54	0.005	18.54	0.2331	18.76	4.48856	0.89771129
10	V											0.92053772
		A	21.35	2.75	5	1.54	0.003	19.45	0.2265	19.62	4.29253	0.85850535
		B	21.8	2.75	5	1.54	0.007	19.45	0.245	19.62	4.66961	0.93392181
												0.89621358

Where:

Vc-volume of the glass tube, Vt- traductor volume, m-mass of the pyrotechnic composition, d-density,

P1- initial pressure, T1 - initial temperature, P2- final pressure, T2 – final temperature

Vsp - gas volume from the sample, Vsp*- specific volume

Acceptance criterion is that the final value be less than 1 cm³/g European standard for 40 hours or less than 2 cm³/g USA standard for 48 ore, so the pyrotechnic compositions analyzed have passed the test, and are considered to be stable.

5.3 Determination of performance feature of pyrotechnic compositions

For the pyrotechnical compositions studied at ATM Bucharest the following performance parameters have been determined: initiation temperature, combustion heat, specific volume, combustion rate and flow, light intensity, autoignition temperature using DTA, and also their behavior on flame.

5.3.1. Determination of the initiation temperature

The procedure consists in determining the temperature to which a given mass of explosive material, or a pyrotechnic composition heated in a controlled thermic manner (20°C/min. or 5°C/min.), undergoes an explosive transformation (resulting in flames, smoke or noise) [150]. Initiation temperature of the explosive transformation is considered the minimal value of the temperature to which the explosive transformation occurs. The pyrotechnic composition with the lowest initiation temperature is the green one, with a value of 240°C.

The red signaling compositions, CR1, CR2 and CR3 have an initiation temperatures of around 450°C; this is due to the high decomposition temperature of the strontium nitrate. The pyrotechnical compositions for thermic traps CAP-1, CAP-2, CAP-3, CAP-4, CAP-5 and CAP-6 have the highest initiation temperatures, of around 480°C due to the polytetrafluorethylene decomposition.

Table 9 presents the average values for 2x3 samples for each type of composition.

Table 9 Initiation temperature determination results

crt.	Pyrotechnic composition %	Code	Sample	Initiation Temp (°C)	Reaction
1	Mg 24, PTFE 56.5, Iditol 9.5	CAP-1	2	498	Flame and smoke
2	Mg34,PTFE 56.5, Iditol 8.5, C1	CAP-2	2	521	Flame and smoke
3	Al 24, PTFE 70, Iditol 6	CAP-3	2	482	Flame and smoke
4	Al sort PL5 24, PTFE 70, Iditol 6	CAP-4	2	480	Flame and smoke
5	Ti 30, PTFE 64, Iditol 6	CAP-5	2	489	Flame and smoke
6	AlMg alloy 30, PTFE 64, Iditol 6	CAP-6	2	503	Flame and smoke
7	Mg22, Sr(NO ₃) ₂ 57, PVC 17, Iditol 4	CR1	3	485	Flame and smoke
8	Mg17, Sr(NO ₃) ₂ 60, PVC 18, Iditol 5	CR2	3	488	Flame and smoke
9	Mg13, Sr(NO ₃) ₂ 65, PVC 15, Iditol 7	CR3	3	491	Flame and smoke
10	Mg12, Ba(NO ₃) ₂ 66 , PVC15, Iditol 7	V	3	242	Flame and smoke

5.3.2. Determination of combustion heat

The experimental method for the determination of combustion heat is based on the measurement of the water temperature variation in the. The initiation of the transformation is performed in the calorimetric bomb, so that the reaction takes place at constant volume [151].

Table 10 Results obtained by combustion heat determination

Sample	Code	Q [kcal/kg]
Mg 24, PTFE 56.5, Iditol 9.5	CAP-1	1233,5
Mg34,PTFE 56.5, Iditol 8.5, C1	CAP-2	1401,6
Al sort PL5 24, PTFE 70, Iditol 6	CAP-4	1205,4
AlMg alloy 30, PTFE 64, Iditol 6	CAP-6	1435,8
Mg22, Sr(NO ₃) ₂ 57, PVC 17, Iditol 4	CR-1	1016,0
Mg17, Sr(NO ₃) ₂ 60, PVC 18, Iditol 5	CR-2	985,7
Mg13, Sr(NO ₃) ₂ 65, PVC 15, Iditol 7	CR-3	893,5
Mg12, Ba(NO ₃) ₂ 66 , PVC15, Iditol 7	V	865,1

The average values obtained by experimental determination of the explosion heats of the eight pyrotechnic compositions are presented in table 10.

It is noticed that CAP-6 has the highest heat of explosion value, followed by CAP-2. CR1 has the highest heat among the red compositions CR1, CR 2, CR3 as it has the highest content of magnesium.

5.3.3. Determination of the specific volume

The value of the specific volume determined experimentally differs from the theoretical value due to the water vapors formed in the bomb during the explosive decomposition that condense at the testing temperature.

Table.11 Specific volume

Sample	Sample	V _{osp} [l/kg]
Mg 24, PTFE 56.5, Iditol 9.5	CAP-1	170,9
Mg34,PTFE 56.5, Iditol 8.5, C1	CAP-2	132,0
Al sort PL5 24, PTFE 70, Iditol 6	CAP-4	144,5
Alms alloy 30, PTFE 64, Iditol 6	CAP-6	278,9
Mg22, Sr(NO ₃) ₂ 57, PVC 17, Iditol 4	CR-1	256,8
Mg17, Sr(NO ₃) ₂ 60, PVC 18, Iditol 5	CR-2	273,4
Mg13, Sr(NO ₃) ₂ 65, PVC 15, Iditol 7	CR-3	312,9
Mg12, Ba(NO ₃) ₂ 66 , PVC15, Iditol 7	V	329,2

5.3.4. Determination of the combustion temperature, rate combustion and flow

In order to determine the combustion temperature the measurement of the emitted radiation intensity 0,9 micron wavelength from a composition's surface in combustion is performed [153,154].

Combustion temperature determination has been performed with an IRCON ULTIMAX 50P pyrometer (Figure 5)

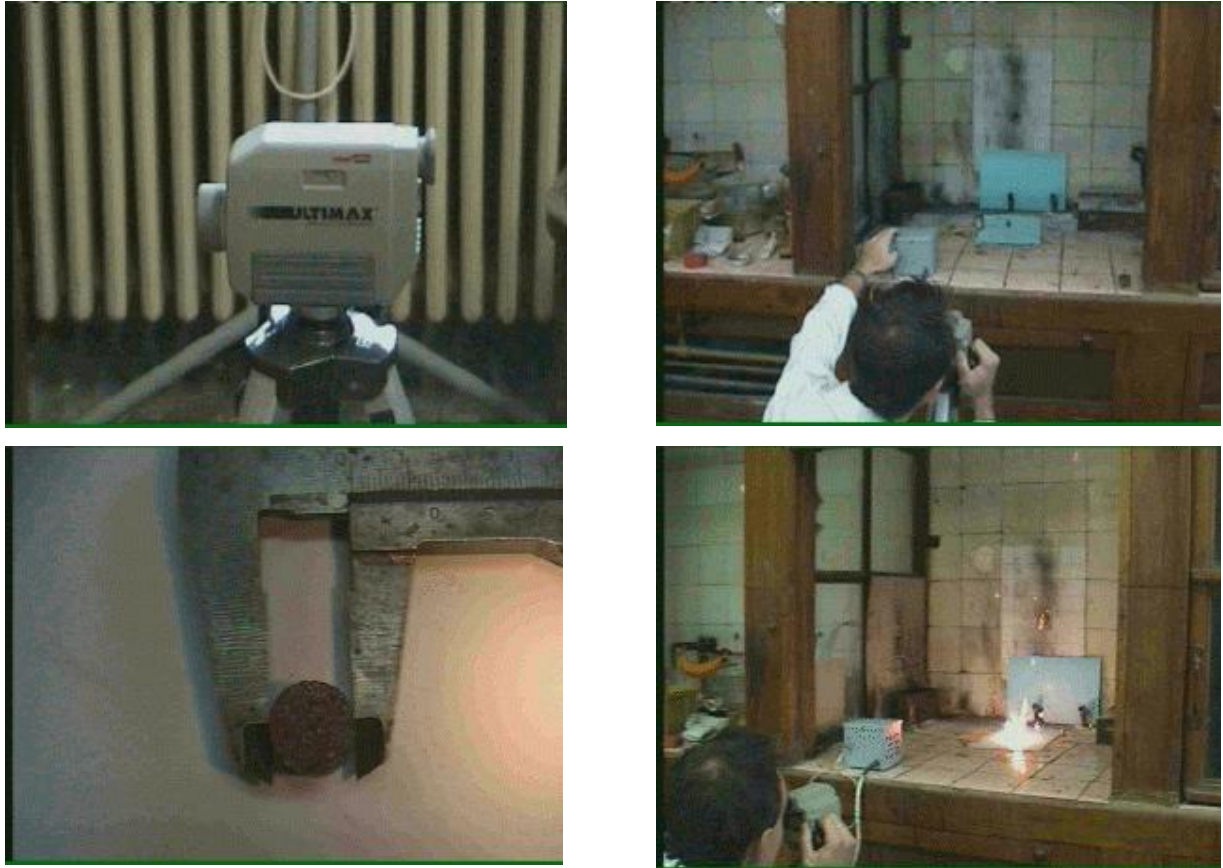


Figure.5 Combustion temperature experimental procedure

5.3.4.1. Determination of the combustion rate for the red pyrotechnic composition

14 cylinders of each pyrotechnic composition were pressed at two pressures: 751 bars and 1352 bar in order to determine and calculate the features of these pyrotechnic compositions. The cylinders have been weighted and their height and diameter was measured.

Table 12 - CR1 – values for the 751 bar pressing pressure

	p	h	Ø	m	S	V	ρ	Δt	u	Flow	D*
crt.	bar	mm	mm	g	cm²	cm³	g/cm³	s	mm/s	g/s	g/s
1	751	27.02	11.7	4.133	1.07	2.904	1.424	10.4	2.60	0.40	0.40
2	751	25.82	11.7	4.011	1.07	2.775	1.446	8.97	2.88	0.45	0.45
3	751	26.01	11.7	4.249	1.07	2.795	1.520	10	2.60	0.42	0.42
4	751	24.78	11.7	3.926	1.07	2.663	1.474	8.59	2.88	0.46	0.46
5	751	26.02	11.7	4.088	1.07	2.796	1.462	10.01	2.60	0.41	0.41
6	751	25.98	11.7	4.121	1.07	2.792	1.476	9.3	2.79	0.44	0.44
Avg	751	25.94	11.7	4.088	1.07	2.787	1.467	9.55	2.72	0.43	0.43

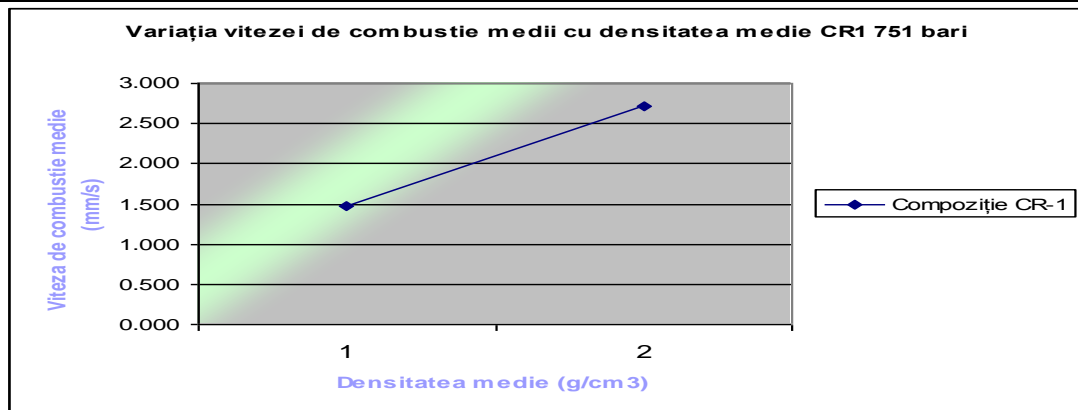


Figure 6 Combustion rate as a function of the density for the CR-1 composition

Table 13 CR1 – for the 1352 bar pressing pressure

	p	h	Ø	m	S	V	dens	Δt	u	Flow	D*
crt.	bar	mm	mm	g	cm²	cm³	g/cm³	s	mm/s	g/s	g/s
1	1352	22.87	11.7	4.228	1.07	2.458	1.720	8.8	2.60	0.48	0.48
2	1352	22.93	11.7	4.291	1.07	2.464	1.742	9.1	2.52	0.47	0.47
3	1352	23.07	11.7	4.299	1.07	2.479	1.734	9	2.56	0.48	0.48
4	1352	23.08	11.7	2.082	1.07	2.480	0.839	10	2.31	0.21	0.21
5	1352	23.63	11.7	5.316	1.07	2.539	2.094	8.8	2.69	0.60	0.60
6	1352	23.26	11.7	4.255	1.07	2.499	1.702	11	2.11	0.39	0.39
7	1352	23.93	11.7	4.310	1.07	2.571	1.676	10	2.35	0.42	0.42
Avg	1352	23.25	11.7	4.112	1.07	2.499	1.644	9.56	2.45	0.44	0.44

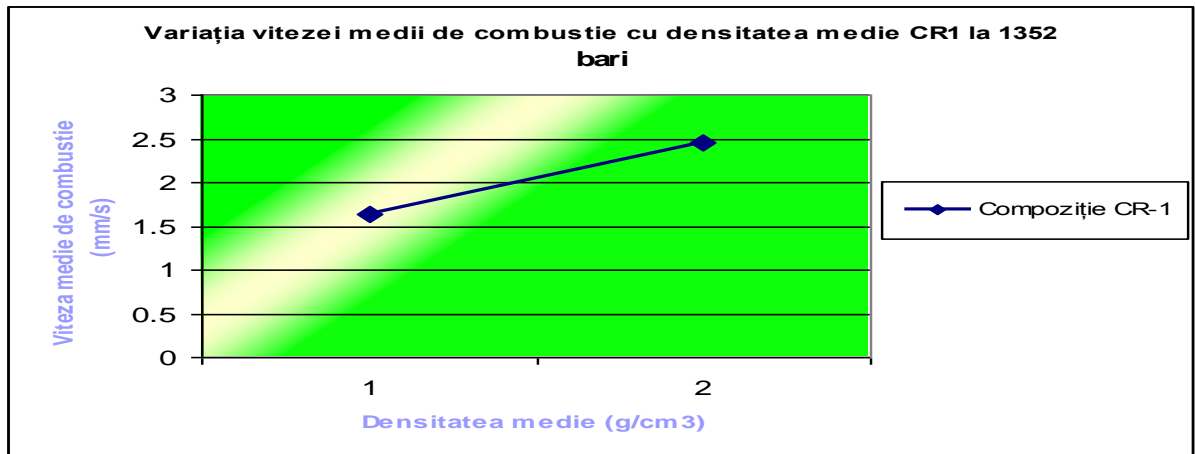


Figure 7 Combustion rate as a function of the density for the CR-1 composition

Table 14 – CR2 – for the 751 bar pressing pressure

crt.	p bar	h mm	Ø mm	m g	S cm ²	V cm ³	dens g/cm ³	Δt s	u mm/s	Flow g/s	D* g/s
1	751	21.59	11.7	3.883	1.07	2.320	1.674	10.6	2.037	0.37	0.37
2	751	22.05	11.7	3.598	1.07	2.369	1.518	12	1.838	0.30	0.30
3	751	22.49	11.7	3.533	1.07	2.417	1.462	13.2	1.704	0.27	0.27
4	751	22.78	11.7	3.677	1.07	2.448	1.502	10.2	2.233	0.36	0.36
5	751	22.83	11.7	3.514	1.07	2.453	1.432	13.7	1.666	0.26	0.26
6	751	22.39	11.7	3.645	1.07	2.406	1.515	11	2.035	0.33	0.33
7	751	22.93	11.7	3.486	1.07	2.464	1.415	11.4	2.011	0.31	0.31
Avg	751	22.44	11.7	3.619	1.07	2.411	1.503	11.7	1.932	0.31	0.31

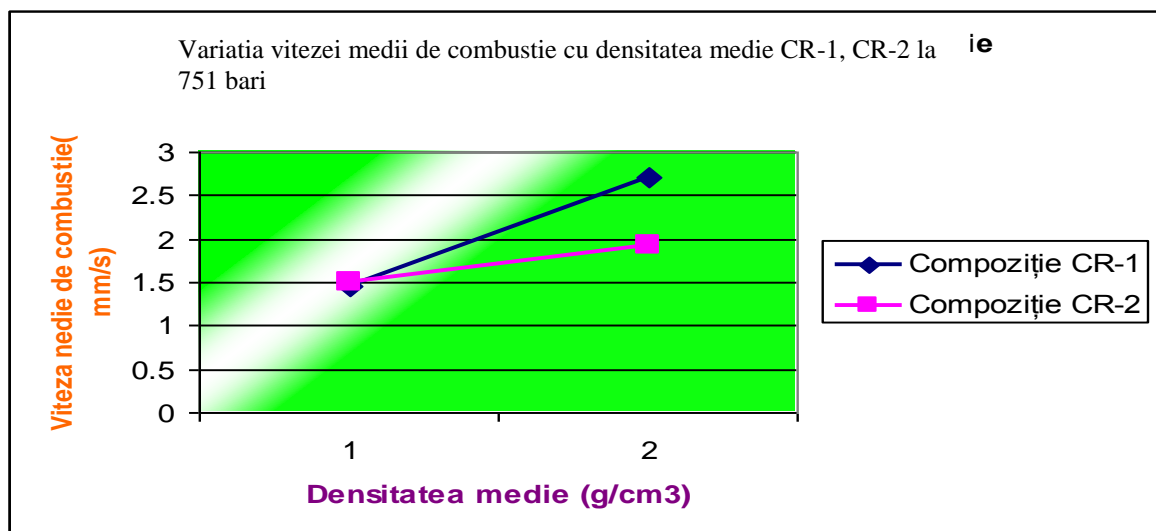


Figure 8 Combustion rate as a function of the density for CR-1, CR-2

Table 15 – CR2 – for the 1352 bar pressing pressure

	p	H	Ø	m	S	V	dens	Δt	u	Debit	D*
crt.	bar	Mm	mm	g	cm2	cm3	g/cm3	s	mm/s	g/s	g/s
1	1352	21.37	12	3.927	1.07	2.296	1.710	13	1.644	0.30	0.30
2	1352	21.5	12	3.681	1.07	2.310	1.593	12.7	1.693	0.29	0.29
3	1352	20.42	12	3.608	1.07	2.194	1.644	12.7	1.608	0.28	0.28
4	1352	20.67	12	3.975	1.07	2.221	1.789	12.1	1.708	0.33	0.33
5	1352	21	12	4.096	1.07	2.257	1.815	13.5	1.556	0.30	0.30
6	1352	21.63	12	3.918	1.07	2.324	1.686	12.5	1.730	0.31	0.31
7	1352	21.19	12	3.904	1.07	2.277	1.714	14	1.514	0.28	0.28
Avg	1352	21.11	12	3.873	1.07	2.269	1.708	12.93	1.636	0.30	0.30

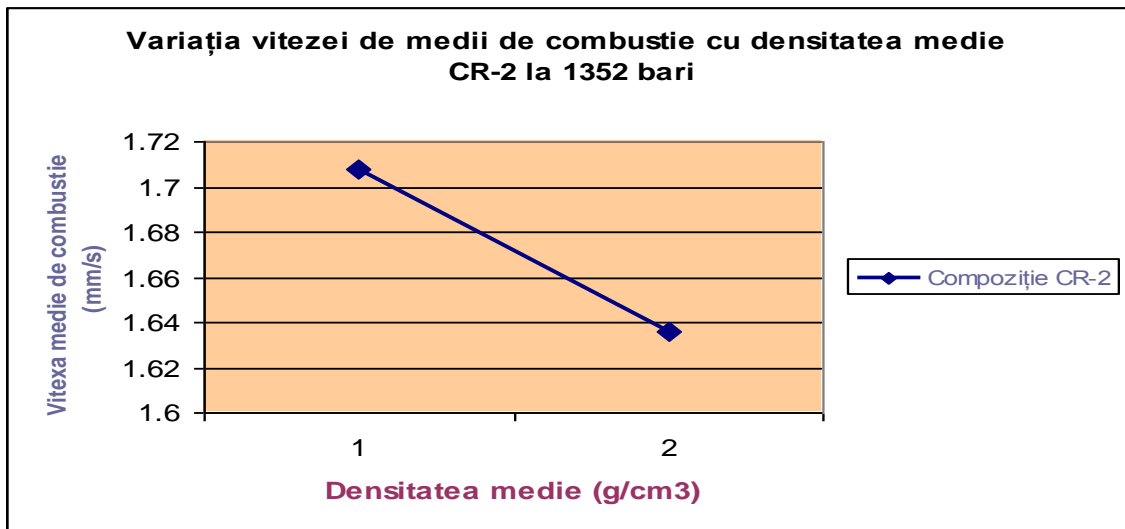


Figure 9 – Combustion rate as a function of the density CR2

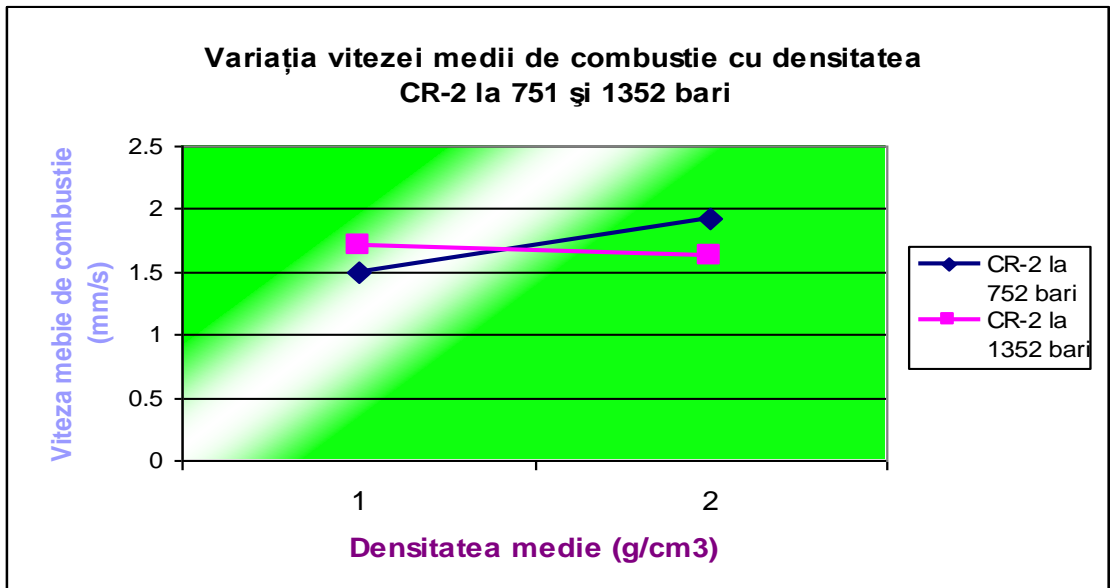


Figure 10- Average combustion rate as a function of the density

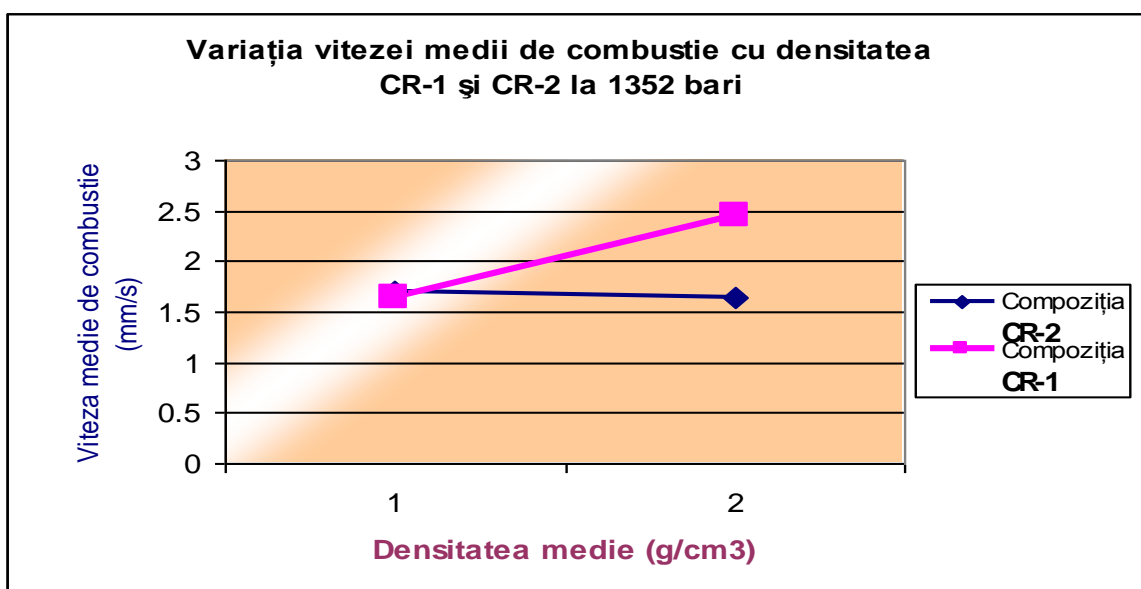


Figure 11 – Average combustion rate as a function of the density
 200g of red CR3 pyrotechnic composition have been produced of which 30,3g were turned into 14 cylinders.

Rate combustion determination chronometric method is based on measuring the combustion time and then computing the linear combustion speed.

The time was measured by a manual chronometer as the values were in a tens of seconds scale. A SONY camera was used to shoot the test.

5.3.4.2. Determination of the combustion rate for the green pyrotechnical composition

200g of green pyrotechnical composition have been obtained, of which 27.7g were used in series of 1.979 g, to get 14 cylinders.

The values of the combustion rate for the red CR-3 and the green V pyrotechnical compositions are presented in table 16.

Table 16 Comparative combustion rate of CR-3 and V compositions

Red	Δx [mm]	Δt [s]	u [mm/s]	Green	Δx [mm]	Δt [s]	u [mm/s]
1	55	43	1.279	1	49.17	36.49	1.347
2	54	50.1	1.077	2	49	29.3	1.672
Avg	-	-	1.178	Avg	-	-	1.50

The average computed value for a green cylinder of pyrotechnical composition was 1.0699 cm³, and the average density was 1.851g/cm³ [136].

Table 17 The features of the green V pyrotechnic cylinders

Height (mm)	Diameter (mm)	Volume (cm³)	Density (g/cm³)
9.6	11.76	1.042	1.899
9.82	11.77	1.068	1.853
9.96	11.76	1.081	1.831
9.98	11.75	1.082	1.829
10.17	11.75	1.102	1.796
9.55	11.78	1.040	1.903
9.69	11.77	1.054	1.878
9.89	11.77	1.076	1.839
9.68	11.81	1.060	1.867
10.13	11.77	1.102	1.796
9.85	11.76	1.069	1.851
9.82	11.78	1.070	1.850
9.35	11.76	1.015	1.950
10.19	11.82	1.118	1.770

Two burning shapes were created in order to determine the combustion rate: one of 49.17 mm, and the other 49 mm that have burned for 36.49s 29.3s respectively.

From the comparative analysis of the combustion rate of the pyrotechnical CR-3 and V compositions, the Green composition has the greatest speed and this is due to the fact that the barium nitrate decomposes to a lower temperature as compared to strontium nitrate so that the oxygen that has been released interacts with the magnesium leading to light and heat emission.

5.3.4.3. Determination of the combustion rate for the thermal trap pyrotechnic composition

Pyrotechnic thermal trap compositions, namely CAP-1 and CAP-2 were compacted separately in multiple molds.

Two test have been performed using a $\Phi 19$ mm diameter mold. The applied pressure was 25 bar for the first test and 50 bar for the second. Two ignition relay were inserted after pressing and the height of the column was measured and a 2mm level difference has been noticed.

Table 18 Results obtained for the $P_{\text{pres}} = 252$ bar test

crt.	p	H	Φ	m	S	V	ρ	Time	u	m	m*
	[bar]	[mm]	[mm]	[g]	[cm ²]	[cm ³]	[g/cm ³]	[s]	[mm/s]	[g/s]	[g/s]
1	252	14.6	18.9	5.74	2.8	4.088	1.4041	13.5	1.081	0.43	0.43
2	252	14.7	18.9	5.6	2.8	4.116	1.3605	13.9	1.058	0.40	0.40
3	252	13.9	18.9	5.52	2.8	3.892	1.4183	14.9	0.933	0.37	0.37
4	252	14.4	18.9	5.65	2.8	4.032	1.4013	12.5	1.152	0.45	0.45
Avg.Val.	252	14.4	18.9	5.628	2.8	4.032	1.39606	13.7	1.056	0.412633	0.412633

Combustion rate calculation:

$$t_{1\text{med}} = 13,7\text{s}$$

$$t_{2\text{med}} = 13,02\text{s}$$

$$h_{\text{med}} = 14,4 \text{ mm}$$

$$h_{\text{med}} = 12,4 \text{ mm}$$

$$v_{1\text{med}} = 1,056 \text{ mm/s}$$

$$v_{2\text{med}} = 0,95 \text{ mm/s}$$

Table 19 Results obtained for the $P_{\text{pres}} = 504$ bar test

crt.	p	H	Φ	m	S	V	ρ	Time	u	m	m*
	[bar]	[mm]	[mm]	[g]	[cm ²]	[cm ³]	[g/cm ³]	[s]	[mm/s]	[g/s]	[g/s]
1	504	12.5	18.9	5.49	2.8	3,5	1,40	12.5	1.000	0,44	0,44
2	504	12.57	18.9	5,42	2.8	3,51	1,39	12,3	1,02	0,44	0,44
3	504	12.4	18.9	5.48	2.8	3.47	1,41	13,8	0,89	0,39	0,39
4	504	12.15	18.9	5.75	2.8	3,402	1,40	13.5	0.900	0,42	0,42
Avg.Val.	504	12.41	18.9	5,54	2.8	3,47	1,4	13,02	0.95	0,42	0,42

5.3.4.4. Determination of the flame temperature for the CAP-2 pyrotechnic composition

The temperatures of the flames have been measured with a ULTIMAX optic pyrometer and the results have been recorded in a computer.

Table 20 Measured temperatures for the CAP-2 at $p=252$ bar

crt.	p	Temperature	p	Temperature
	[bar]	[⁰ C]	[bar]	[⁰ C]
1	252	1849-1525	504	1601-1525
2	252	1808-1592	504	1748-1491
3	252	1732-1206	504	1897-1632
4	252	1844-1467	504	1844-1667

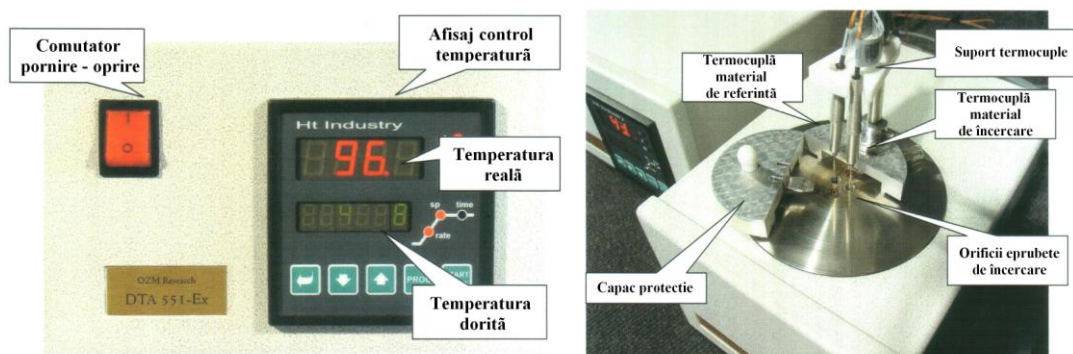
Temperature values obtained using ULTIMAX optical pyrometer are shown in table 20. It is noticed that the temperatures are high between 1206 and 1849⁰C for the pressed composition at 252 bar and between 1491-1897⁰C for the ones pressed at 504 bar.

5.3.5. Differential thermal analysis of pyrotechnic compositions

The goal of this test was the determination of the materials' behavior while heated at 20°C – 550°C temperature, checking the for the selfinflaming. Controlled heating speed of 5°C/min., 10°C/min., 15°C/min. or 20°C/min., is a parameter of the test. Selfinflaming temperature is a characteristic of the material's sensitivity to the temperature and represents an important safety feature to thermal acts [154].

DTA records the temperature difference between the studied sample and a thermically inert reference sample in the moment when both of them are placed in the same thermic conditions. The heating source is programmed, so that the heating speed is constant: for example 5°C/min, 10°C/min, 15°C/min etc.

Figure 12 Functioning scheme for the DTA equipment



Two heating speeds have been chosen 5 and 20 °C/min.

In the case of the red signaling pyrotechnic compositions graphics, we notice that the self decomposition temperature is high, of approximately 450°C, indicating a low thermal sensitivity. DTA data for the red pyrotechnical composition indicates: Sr(NO₃)₂ 65%, Mg 13%, PVC 15%, iditol 7%, as presented in Figure 13.

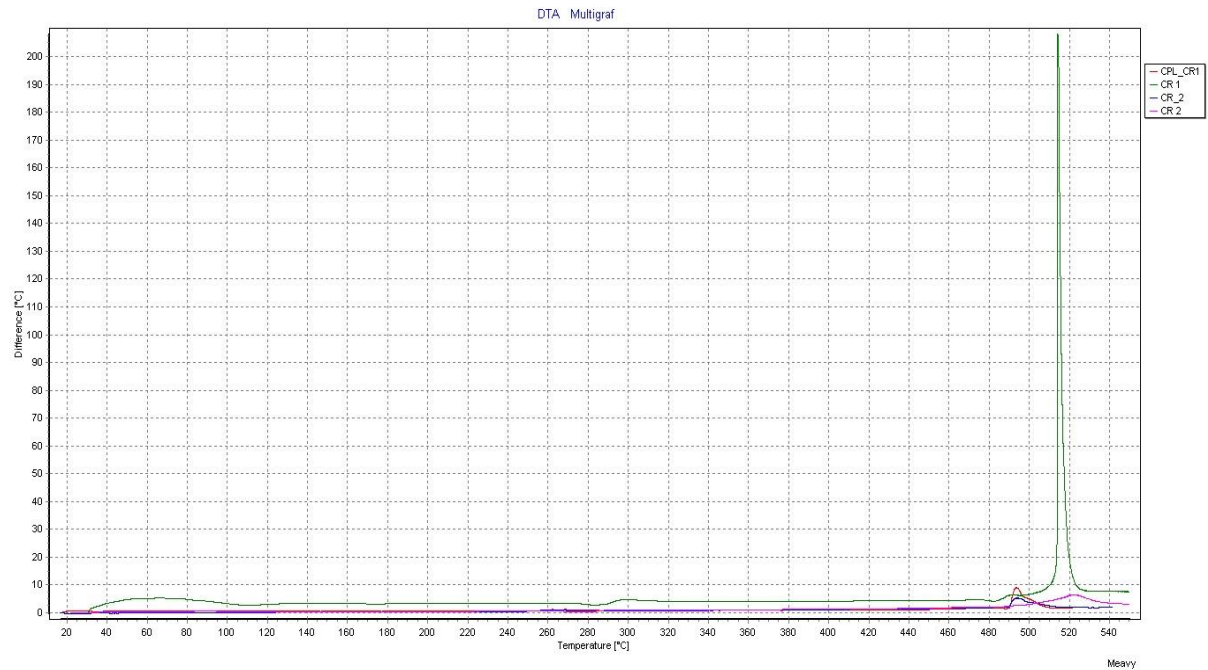


Figure 13 Comparative DTA for the pyrotechnic compositions CR-1, CR-2

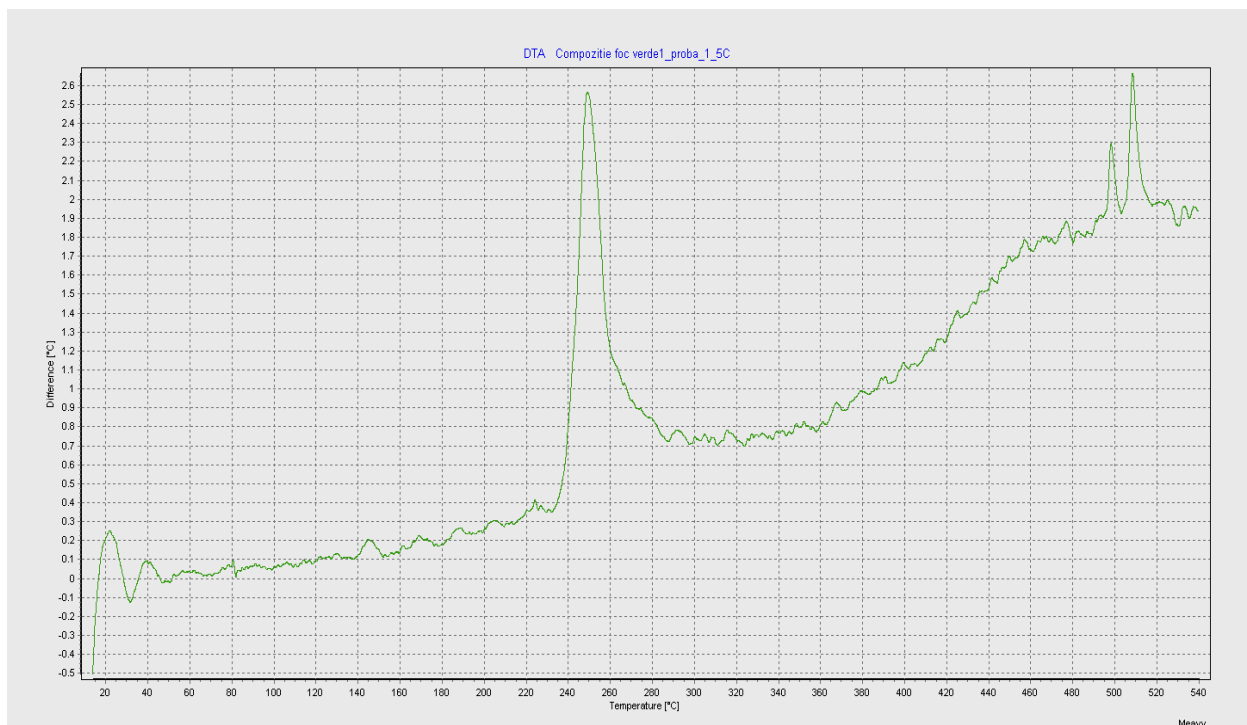


Figure 14 DTA of the green composition

The green composition graphics indicate a self decomposition temperature of 250 °C, lower than for the red case, by almost a half. We conclude that is more sensitive to the temperature [137]. Comparative termogramme for the thermal trap pyrotechnic compositions is presented in figure 15.

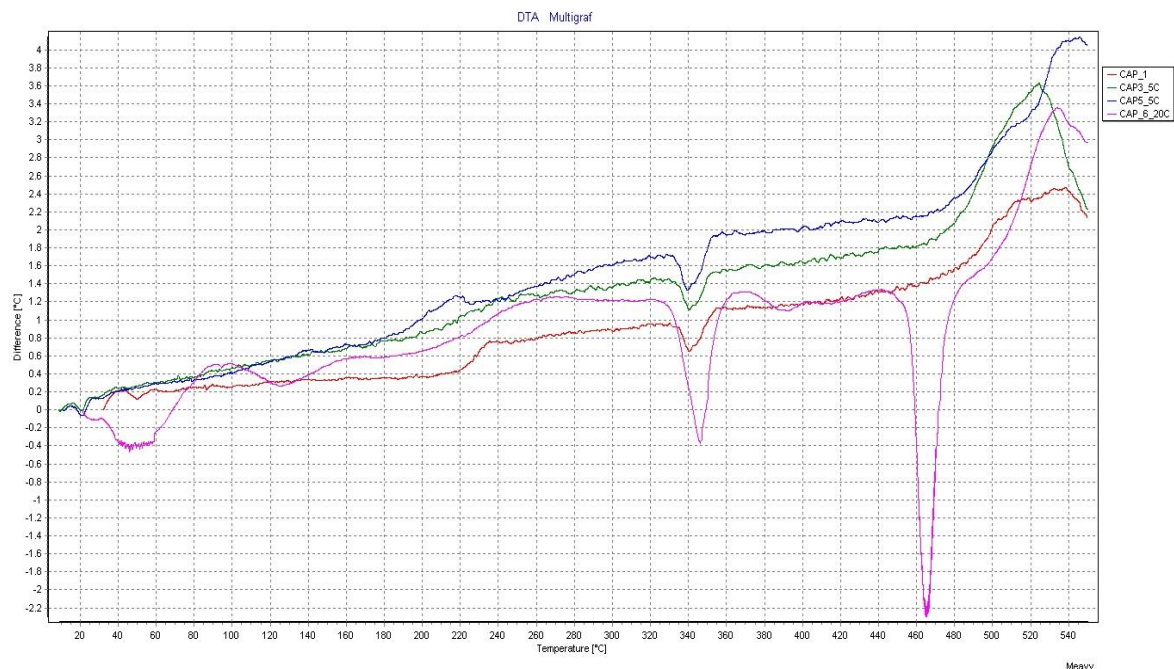


Figure 15 DTAs for the thermal traps pyrotechnic compositions

It is noticed that at 342.0 °C the teflon undergoes a phase change from solid to liquid. This endothermic transformation is encountered to all these compositions (CAP1-CAP6).

In the case of the CAP 6 pyrotechnical composition an endothermic transformation is noticed at 465°C probably due to the phase change (solid to liquid) of the aluminum-magnesium alloy, followed by a strongly exothermic transformation during the fluorine's reaction with aluminum and magnesium leading to metal fluorides [135].

5.3.6. Pyrotechnic compositions behavior study on flame action

After producing the magnesium-polytetrafluorethylene pyrotechnic compositions, the major problem was the initiation of the mixture. Classical triggers such as RW1 and RR4 have been tested

The flame behavior of all of these pyrotechnic compositions has been tested at Orăștie. No problems were encountered while transferring the fire from the wick or from the black powder to the pyrotechnic composition.

This study has been continued to ATM Bucharest for all of the thermic traps pyrotechnic compositions code-named CAP1, CAP2, CAP3, CAP5 and CAP 6, and the results are presented in table 22.

Table 22 Flame action behavior study

Crt.	Code	Components	Flame action result
1	CAP1	Mg34%, PTFE 56.5%, Iditol 9.5%	Positive
2	CAP2	Mg34%, PTFE 56.5%, Iditol 9.5% Graphite 1%	Positive
3	CAP3	Al 24%, PTFE 70%, Iditol 6%	Positive
4	CAP4	Al tip PL5 24% ,PTFE 70%, Iditol 6%	Positive
5	CAP5	Ti 30%, PTFE 64%, Iditol 6%	Negative
6	CAP 6	Ti 30%, PTFE 64%, Iditol 6%	Negative
7	CR1	Mg22%, Sr(NO ₃) ₂ 57%,PVC 17%, Iditol 4%	Positive
8	CR2	Mg17%, Sr(NO ₃) ₂ 60%,PVC 18%, Iditol 5%	Positive
9	CR3	Mg13%, Sr(NO ₃) ₂ 65%,PVC 15%, Iditol 7%	Positive
10	V	Mg12%, Ba(NO ₃) ₂ 66%,PVC 15%, Iditol 7%	Positive

For the CAP 5 and CAP 6 thermic traps the results are negative, as the triggering was not successful. The flame did not succeed in initiating the composition. This may be due to the fact that the granulation of the powders used for these pyrotechnic compositions was too high.

CONCLUSIONS

The goal of this research was to obtain and characterize new pyrotechnic compositions with civilian and military applications, using nonconventional comburants such as halogenated polymers like polyvinyl chloride (PVC) and polytetrafluorethylene (PTFE).

To achieve this general goal the following objectives have been proposed:

- Performing a literature study on the actual status of the pyrotechnic compositions with light effect (light, signaling, thermic traps, etc);
- Calculation and design of new pyrotechnic compositions with light effect for civilian and military applications;
- Obtaining new pyrotechnic compositions with light effect using halogenated comburants (PVC and PTFE);
- Determination of physical and chemical features of the new pyrotechnic compositions;
- Determination of safety features of the new pyrotechnic compositions;
- Determination of performance features of the new pyrotechnic compositions;
- Using the new pyrotechnic compositions for designing new pyrotechnic systems for civilian and military applications.

The first part represents a detailed literature study of the PVC and PTFE based pyrotechnic compositions. Chapter 1 introduces in pyrotechnics and presents the ingredients and the properties

of pyrotechnic compositions. When preparing the pyrotechnic compositions a compromise is necessary to be achieved between a high level of safety and an effective ignition for usage.

Chapter 2 presents the literature data on the polyvinyl chloride and polytetrafluorethylene containing pyrotechnic compositions and other high energy materials being developed at the border between pyrotechnics and detonics.

The second part of the thesis containing the original contributions is divided into three chapters. Designing the pyrotechnic compositions is presented in chapter 3 together with the computational method for calculating the heat of explosion and the specific volume for their new pyrotechnic compositions.

Chapter 4 presents the experimental studies performed at SC Rompiro SA Orăștie and ATM Bucharest on novel pyrotechnical compositions containing polyvinyl chloride and polytetrafluorethylene.

31 pyrotechnical compositions have been developed at Orăștie most of them containing polyvinyl chloride with the aim of producing economically efficient fireworks.

Six red, six blue, one violet, four yellow, four cold flame, two gold and silver, one comet-like and one noisy pyrotechnical compositions have been tested and manufactured on large scale. Fireworks of different sizes for individual usage have been developed based on these compositions. National approval was obtained and manufacturing process developed.

Based on the experimental tests the best results were noticed for the pressed pyrotechnic compositions. Compaction is required for numerous reasons. First is the fact that the pyrotechnic load has to have a well-established shape: a certain geometry and a burning surface. Its accidental change can turn worse the pyrotechnic effect, alter the burning time and even destroy the pyrotechnic system.

Secondly, compacting is a method of regulating the burning speed of the composition, increasing the pressing pressure diminishes the burning speed so that burning itself is more homogenous.

A technological process for manufacturing flare pyrotechnical compositions has been developed and 10 pyrotechnical compositions have been prepared three red and one green for signaling and six thermic traps (flare).

Flare pyrotechnic compositions have been used to manufacture military cartridges 1" x 1" x 8" Flare, 1" x 2" x 8" Flare and 1" x 1" x 8" Chaff.

These pyrotechnic compositions went through an extensive testing-evaluation process in order to determine a series of physical, chemical, safety and performance features in compliance

with the national and international standards regarding the approval of energetic materials (pyrotechnical compositions, powders). The results of these tests are presented in chapter 5.

Physical and chemical features analyzed were the gravimetric density, granulometry, higroscopicity and the moisture and volatile substances content.

The higroscopicity, moisture and volatile content of the polyvinyl chloride and polytetrafluorethylene containing pyrotechnic compositions are low.

The main advantage of using iditol-polyvinyl chloride and iditol-polytetrafluorethylene mixtures is their humidity strength leading to a long life span.

Safety feature have been determined for the pyrotechnical compositions containing polyvinyl chloride and polytetrafluorethylene. Friction and impact sensitivities have been determined by BAM method, and also electrostatic discharge sensitivity and the vacuum chemical stability.

Results show that all of these ten compositions exhibit a very low friction and impact sensitivity (no reaction to pressing forces $> 360\text{N}$), indicating the fact that the risk associated to mechanical operations on pyrotechnic compositions is very low. Tests indicate that the ten pyrotechnic compositions have a low sensitivity to electrostatic discharge. All the values are lying within the accepted limits for the pyrotechnic compositions.

The acceptance criterion for a chemical stability test is that the value of the emitted gases during thermal stress be less than $1\text{ cm}^3/\text{g}$ in 40 hours european standard or less than $2\text{ cm}^3/\text{g}$ in 48 hours USA standard. All the pyrotechnic compositions analyzed have passed the test, so they are considered as stable.

For the pyrotechnic compositions studied at ATM Bucharest the following performance parameters have been determined: initiation temperature, heat of explosion, specific volume, temperature, combustion rate and flow, light intensity, self inflammation using DTA, and also the behavior in flame.

The highest combustion heat belongs to CAP-6 composition, followed by CAP-2. Among the red CR-1, CR-2, CR-3 compositions the highest heat was determined for the CR-1 mixture due to the higher amount of magnesium.

The low difference between the combustion heat for the red CR-3 composition and the green V, is due to the almost similar magnesium content (12-13%).

The highest specific volume corresponds to the green signaling composition, and among the thermic trap compositions category to the CAP-6 based on aluminum-magnesium alloy.

Experimental values both for the combustion heat and for the specific volume are close to the computed values.

It is notice that at 342.0 °C teflon undergoes a phase change: it passes from the solid state to liquid. This endothermic transformation is encountered for all this series (CAP1-CAP6).

For the CAP 6 pyrotechnic composition an endothermic transformation at 465°C is noticed probably due to the phase change of the aluminum-magnesium alloy, followed by a strongly exothermic reaction of fluorine with aluminum and magnesium with the formation of metallic fluoride.

Pyrotechnic composition CR-3, with a high content of strontium nitrate, generates during combustion a high amount of strontium chloride, which positively influences the flame's color.

DTA graphics of the green composition shows us that the self decomposition temperature (250 °C) is lower than the red one. It is thus much more sensitive to the temperature than the red one.

The flame action behavior study has positive results for 8 of the pyrotechnic compositions, while for the CAP 5 and CAP 6 thermal traps the results were negative.

Flare magnesium-polytetrafluorethylene-identol pyrotechnic compositions have superior IR emission performances as compared to magnesium-barium nitrate-naphthalene pyrotechnic composition.

PVC and identol light signaling pyrotechnic compositions exhibit light properties resembling to hexachlorobenzene but the technological process and the mechanical resistance of the pressed pyrotechnic mixtures is better than using the PVC-identol mixture.

I consider that the goal of this thesis has been achieved by fulfilling all of the proposed objectives. The pyrotechnic compositions that have been designed and tested can be successfully incorporated into applicative systems for both civilian and military purposes.

Results of this thesis have been published in two scientific papers in the Revista de Chimie and presented in various national conference.

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