THE PREPARATION AND CHARACTERIZATION OF THE RED FLAME COMPOSITION BASED ON STRONTIUM NITRATE, MAGNESIUM, AND POLYVINYL CHLORIDE

Quang Sang Dam[1,*], Van Tuan Nguyen[1], Trung Huu Hoang[1], Van Bo Nguyen[2]

[1]*Le Quy Don Technical University, Hanoi, Vietnam*

[2]*Institute of Tropical Durability, Russian - Vietnamese Tropical Center, Hanoi, Vietnam*

Abstract

This paper presents the influence of oxidizer/fuel ratios on several energetic characteristics (the heat of combustion, gaseous volume, burning rate) of the red flame pyrotechnic containing strontium nitrate, magnesium, polyvinyl chloride, and novolac resin. Based on the received experimental data and theoretical calculation results, the reasonable strontium nitrate/magnesium ratio of 58/15 is determined. The pyrotechnic mixture has the heat of combustion of 921 cal/g, a gaseous volume of 260 ml/g, a burning rate of 2.02 mm/s at a pressed density of 1.60 g/cm^3, a color purity of 89%, a decomposition temperature of 481.5^{o}C, and less sensitive to friction and impact.

Keywords: *Pyrotechnic; strontium nitrate; magnesium; polyvinyl chloride.*

1. Introduction

Signal flame composition is a type of pyrotechnic mixtures, which can burn and form a flame with characteristic color. It is used to send signals when military operations occur on lands or at seas. Currently, the signal color system is mainly used red, yellow, and green. The flame color is generated by the radiation of molecules, atoms, and ions in combustion products. For example, the red color is due to the radiation of the SrCl molecule, the yellow color - the Na atom, etc. Signal flame pyrotechnics often include oxidizers (strontium nitrate, barium nitrate, potassium nitrate, potassium perchlorate), fuels (magnesium, PAM-3), colorants (polyvinyl chloride - PVC, sodium oxalate, copper oxide), binders (novolac resin, colophony) [1].

In the military, signal flame pyrotechnics are loaded into signal missiles, signal bullets, signal mines, etc. [2]. Among the colored flame pyrotechnics, red flame mixtures are widely used by the characteristically colored flame, which is easily recognizable at long distances. To make red flame compositions, the mixture of strontium nitrate and magnesium is commonly used because it produces the “clean” signal flame color and has a strong radiation intensity. Several red flame compositions are presented in Tab. 1 [3].

* Email: damquangsang@lqdtu.edu.vn

The mechanism for creating the red flame of the pyrotechnic mixture is as follows: Firstly, $Sr(NO_3)_2$ is decomposed to release oxygen, then which reacts with Mg according to the respective equations.

$$Sr(NO_3)_2 \rightarrow SrO + N_2 + 2.5O_2 \quad (1)$$

$$2Mg + O_2 \rightarrow 2MgO + Heat \quad (2)$$

Tab. 1. Several red flame compositions

№	Composition	% by Weight	Use
1	Strontium nitrate, $Sr(NO_3)_2$ Magnesium 30/50 mesh, Mg Polyvinyl chloride, PVC Potassium periodate, KIO_4 Epoxy binder	43 32 15 5 5	"Green pyrotechnics" perchlorate-free red illuminant, replacement for U.S. military M662
2	Strontium nitrate, $Sr(NO_3)_2$ Magnesium, 30/50 mesh, Mg Polyvinyl chloride, PVC 5-aminotetrazole, CH_3N_5 Epon 813/Versamid 140 (binder)	33.3 41.4 14.7 3.8 6.8	"Green pyrotechnics" perchlorate-free red illumant based on 5-aminotetrazole

Due to a large amount of heat released from the combustion of Mg, SrO reacts with chlorinated compounds such as Cl_2, HCl… (the decomposition of the colorants PVC) to produce $SrCl^*$, which gives a red flame according to the respective equations.

$$2SrO + Cl_2 \rightarrow 2SrCl^* + O_2 \quad (3)$$

$$2SrO + 2HCl \rightarrow SrCl^* + H_2 + O_2 \quad (4)$$

The studies on the preparation and characterization of colored flame pyrotechnics, in general, and red flame mixtures, in particular, are less published [4, 5]. This paper presents some research results on the preparation and determination properties of the red flame pyrotechnic based on strontium nitrate, magnesium, and polyvinyl chloride.

2. Experiment

2.1. Materials

Chemicals used to prepare pyrotechnic mixtures are presented in Tab. 2.

Tab. 2. Chemicals used to prepare red flame pyrotechnic mixtures

№	Chemicals	Formulas	Requirements	Sources
1	Strontium nitrate	$Sr(NO_3)_2$	Purity ≥ 98.0%	Himedia, India
2	Magnesium	Mg	Purity ≥ 99%	Xilong, China

№	Chemicals	Formulas	Requirements	Sources
3	Polyvinyl chloride	$(C_2H_3Cl)_n$	SG-3 grade	Shanxi, China
4	Novolac resin	$C_{13}H_{12}O_2$	Softening temperature > 90°C; Phenol content: 0.1-3.0%.	Anti-aircraft and airforce Technical Institute, Vietnam
5	Ethanol	C_2H_6O	Ethanol > 96%	Xilong, China

2.2. Preparation of pyrotechnic mixture samples

- Preparation of components: $Sr(NO_3)_2$ was dried at 60 ÷ 70°C in 2 hours; Mg, PVC, novolac resin were dried at 40 ÷ 50°C in 2 hours. $Sr(NO_3)_2$, Mg, and PVC were separated by the 38 #/cm sieves (particle size is smaller than 0.153 mm). The novolac solution with 40% of weight concentration was prepared by dissolving novolac resin in 96% ethanol.

- Mixing, granulation, and drying: The required quantities of different ingredients ($Sr(NO_3)_2$, Mg, and PVC) were weighed and mixed by brushing them from 3 to 4 times through 15 #/cm sieves. The achieved mixture was blended thoroughly in the novolac solution in such a way that the content of novolac resin in the pyrotechnic samples is 10% [1, 2, 6]. The wet pyrotechnic mixtures were preliminarily dried in the air in 8 ÷ 10 min and then passed through the 9 #/cm sieves. Finally, the pyrotechnic samples were dried in the air for 2 hours, then at a temperature range of 55 ÷ 60°C for 2 hours.

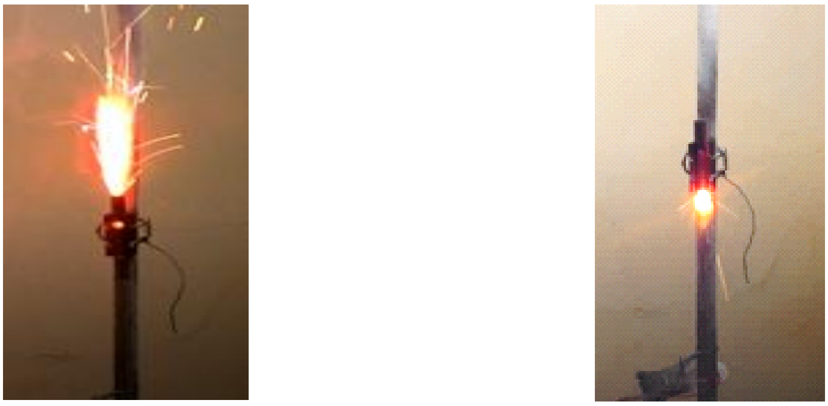
2.3. Characterization

The heat of combustion was determined on the PARR 6200 apparatus (USA) with 2 grams of the sample weight. The volume of gaseous products was measured on the Lutron 9017 manometer and calculated by the formula:

$$V = \frac{0.273\Delta P V_b}{T_c m} \tag{5}$$

where V is the volume of gaseous products, ml/g; ΔP is the difference between values of pressure in the combustion chamber before and after measurement, mbar; T_c is the temperature of the combustion chamber, which equals to the room ambient temperature, K; V_b is the volume of the combustion chamber equals to 334 ml; m is the sample weight, which equals to 2 grams.

The burning rate is obtained as a ratio between the distance traveled of the combustion front and the corresponding time interval determined by using a digital camera [6]. To measure the burning rate, the red flame pyrotechnic was loaded (5 times) into a steel tube 4.2 mm in inside diameter, the wall thickness of the tube is 0.15 mm. The distance between the starting and ending points on the steel tube is 19.3 mm. Ignition is carried out by a Bickford fuse. Each measuring was carried out three times then calculating the average value. The test to determine the burning rate is illustrated in Fig. 1.



(*a*) (*b*)

Fig. 1. The test to determine the burning rate: the starting (a) and ending (b) points.

The color purity of flame is calculated as the ratio between the area of the red light spectrum (λ = 620 ÷ 760 nm) and the area of the visible light spectrum (λ = 400 ÷ 760 nm) [6]: In calculations, *E* can be expressed both in units of luminous flux - lumens and in a value proportional to the lumen, i.e. in candles.

$$p = \frac{E(620 \div 760 \text{ nm}) \cdot 100}{E(400 \div 760 \text{ nm})} \tag{6}$$

The decomposition temperature was determined by thermogravimetric analysis (TGA) performed on a Netzsch STA 409 PC using the dynamic method with about 15 mg of powder samples. The temperature was scanned from 50 to 700^{o}C at a rate of 10^{o}C/min. The friction sensitivity was carried out by a BAM Friction Tester according to STANAG 4487 [7]. The impact sensitivity was carried out by KAST equipment according to GOST 4545-88 [8].

3. Results and discussion

3.1. The effect of $Sr(NO_3)_2$/Mg ratio on the characteristics of the pyrotechnic mixture

In the pyrotechnic mixtures, $Sr(NO_3)_2$ is the oxidizer and Mg is the fuel. The $Sr(NO_3)_2$/Mg ratio determines energy characteristics and pyrotechnic effects. The concentrations of PVC and novolac resin are fixed and equal to 17%, and 10%, respectively [1, 2, 6]. In this study, the ratio of $Sr(NO_3)_2$/Mg was changed from 63/10 to

53/20. Results of the theoretical calculation of oxygen balance K_b (by COMBUS software [9]) and experimental data of the heat of combustion Q_v, specific volume of gaseous products V, burning rate u are presented in Tab. 3.

Tab. 3. The effect of $Sr(NO_3)_2$/Mg ratio on energetic characteristics of the red flame pyrotechnic samples

Samples	Content, %		K_b, %	Q_v, cal/g	V, mL/g	u, mm/s
	$Sr(NO_3)_2$	Mg				
M1	63.0	10.0	-28.50	862 ± 14	297± 10	1.97 ± 0.18
M2	60.5	12.5	-31.09	913 ± 05	275 ± 15	2.00 ± 0.20
M3	58.0	15.0	-33.68	921 ± 18	260 ± 14	2.02 ± 0.15
M4	55.5	17.5	-36.27	997 ± 16	247 ± 12	2.25 ± 0.11
M5	53.0	20.0	-38.86	1052 ± 12	231 ± 13	2.50 ± 0.17

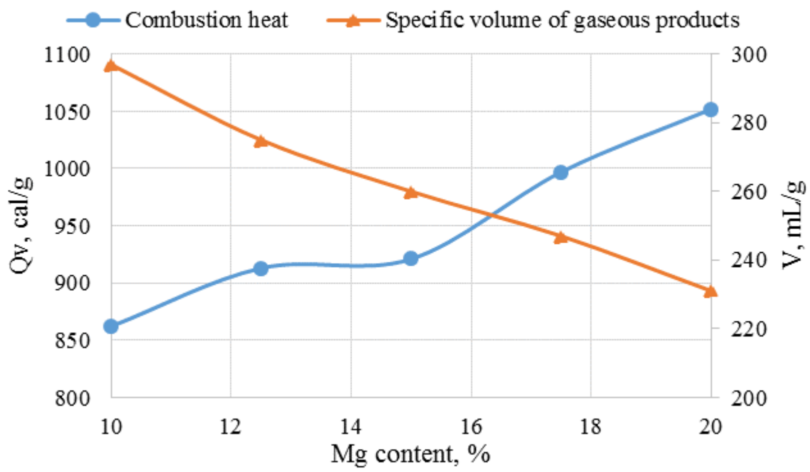


Fig. 2. The effect of Mg content on the heat of combustion and specific volume of gaseous products.

From the results in Tab. 3 and Fig. 2, when the $Sr(NO_3)_2$/Mg ratio decreases from 63/10 to 53/20 (corresponding to increasing Mg content), the oxygen balance decreases, the combustion heat increases, and the specific volume decreases. This is explained by the fact that the combustion of Mg is a strongly exothermic reaction with other combustion products to form condensed chemicals as follows:

$$2Mg + O_2 \rightarrow 2MgO \quad (7)$$

$$CO_2 + 2Mg \rightarrow 2MgO + C \quad (8)$$

$$CO + Mg \rightarrow MgO + C \quad (9)$$

$$H_2O + Mg \rightarrow MgO + H_2 \quad (10)$$

The higher the heat of combustion is, the higher the combustion temperature is, and the higher the $SrCl^*$ content is. However, when the heat of combustion is too high, the decomposition of $SrCl^*$ begins to cause the flame to become bright, gradually losing its red color [1, 2, 6]. Therefore, the Mg content should not be too low but also should not be too high. With this mixture, a reasonable ratio of strontium nitrate/magnesium is 58/15.

Besides, the thermodynamic characteristics, the burning rate is also a particularly important parameter affecting the burning time of stars. The burning rate of samples was measured at a pressed density of 1.60 g/cm^3. The change of the burning rate according to the Mg content ($Sr(NO_3)_2$/Mg ratio respectively) is shown in Fig. 3. It is clear that, when increasing the Mg content, the burning rate increases. This is due to the increase in the heat of combustion and the thermal conductivity of pyrotechnic samples. Experimental data indicated that sample M3 has a high enough heat of combustion but the burning rate is significantly lower than that of M4, M5 samples, so it is suitable for applications that need to extend the signal transmission time.

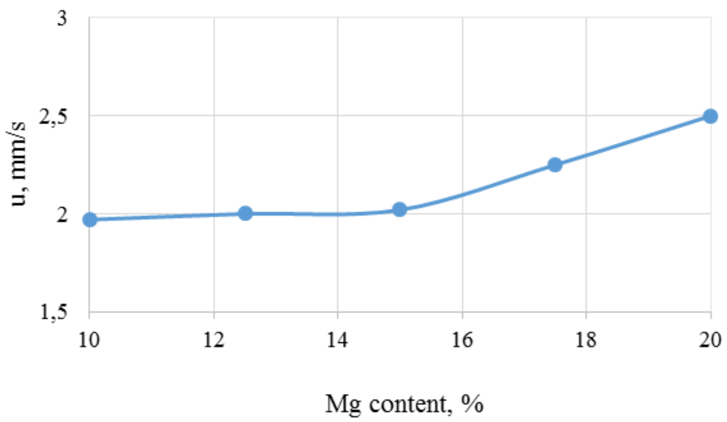


Fig. 3. The effect of Mg content on the burning rate.

Other important technical characteristics of the M3 sample were determined such as spectroscopy, color purity of flame, thermal behavior, and friction and impact sensitivities.

3.2. Technical characteristics of the M3 sample

3.2.1. Spectrum and color purity of flame

The spectrum of the flame of the M3 sample is shown in Fig. 4. The red color of the flame is generated by the radiation of SrCl and SrOH molecules [5]. The color purity of flame is calculated by Formula (II) equal to 89% (the technical requirements for color purity of flame is greater than 70 ÷ 75% [1]). Thus, the flame has a characteristically red color, meeting the technical requirements.

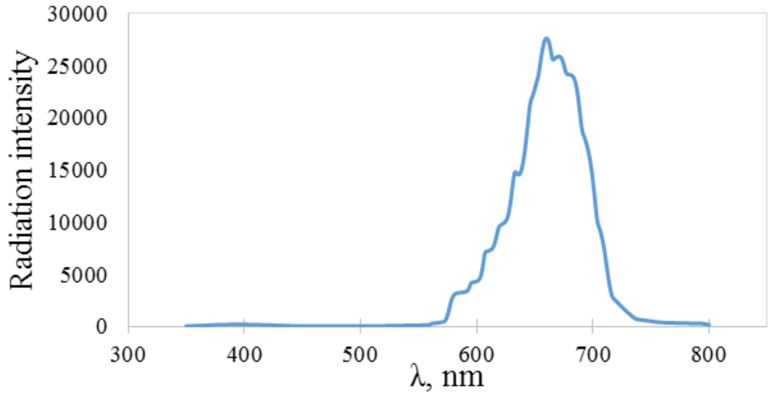


Fig. 4. The spectrum of the flame of the M3 sample.

3.2.2. The thermal behavior

The TG curve of the M3 sample indicates a mass loss in two steps. The M3 sample loses 10% weight in the first step corresponding to the thermal decomposition of novolac resin. In the second step, the M3 sample loses 38% weight more corresponding to the thermal decomposition of PVC and strontium nitrate (Eq. 1). According to DTG curve, there are two peaks of temperature (Fig. 5).

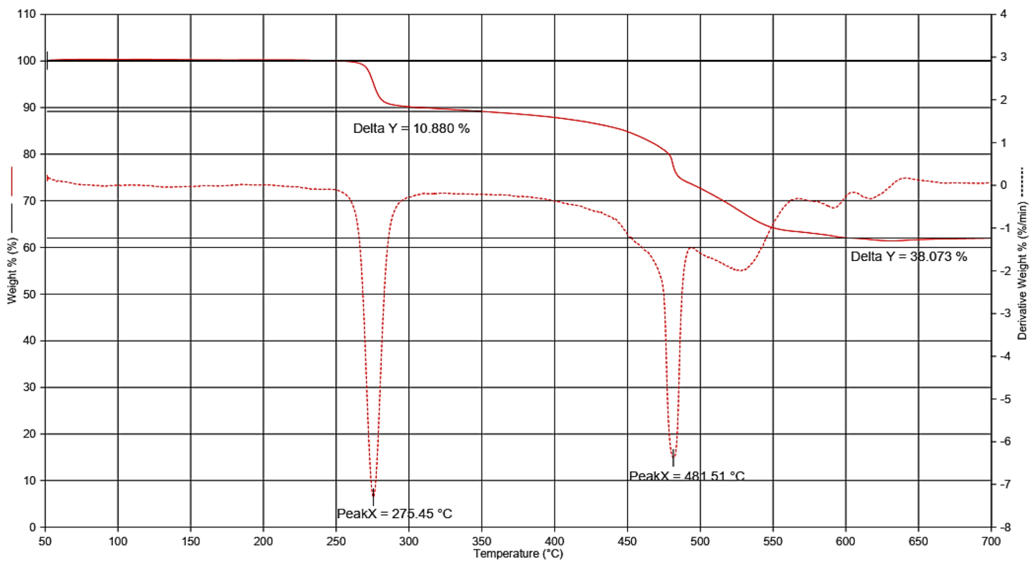


Fig. 5. TGA diagram of the M3 sample with $Sr(NO_3)_2$/Mg ratio of 58/15.

The peaks in DTG curve were observed at the temperature closing to 275.5°C and 481.5°C, respectively. The residue mass of the M3 sample is the solid products such as

MgO, SrO or SrCl. Mass loss at high temperatures was also demonstrated when the M3 sample was measured for its flash point on the DT-400. The value of the flash point is beyond the measuring limit of the apparatus (i.e. above 400°C).

3.2.3. The friction sensitivity

The recorded value of friction sensitivity of the red flame pyrotechnic was 324 N according to STANAG 4487 (no one explosion among six tests). While, friction sensitivity of other explosives such as RDX - one explosion among ten tests at 124 N; HMX - one explosion among ten tests at 116 N of weight; PETN - one explosion among 10 tests at 64 N of weight; LX-11-0 - one explosion among ten tests at 324 N. Thus the red flame pyrotechnic is relatively safe to friction action in manufacturing, storage, transport, and using.

3.2.4. The impact sensitivity

The results of the impact test on the KAST equipment [8] showed that the impact sensitivity of the pyrotechnic M3 sample is 12%. It is only slightly higher than the impact sensitivity of TNT explosives (8%) under the same test conditions. Thus, it can be assessed that this pyrotechnic mixture has a very low sensitivity to impact.

4. Conclusions

The $Sr(NO_3)_2$/Mg ratio strongly affects the combustion heat, the specific volume of the gaseous product, and the burning rate of the red flame pyrotechnic mixture. Exist a reasonable $Sr(NO_3)_2$/Mg ratio is 58/15 to give a high quality of the red flame and low burning rate (2.02 mm/s at a pressed density of 1.60 g/cm^3). The pyrotechnic mixture has technical characteristics such as the high color purity of the flame (89%). In addition, its small friction and impact sensitivities indicate that it is quite safe in production, transport, storage, and use.

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ĐIỀU CHẾ VÀ XÁC ĐỊNH CÁC ĐẶC TRƯNG CỦA THUỐC HỎA THUẬT TẠO LỬA MÀU ĐỎ TRÊN CƠ SỞ STRONTI NITRAT, MAGIE VÀ POLYVINYL CLORUA

Đàm Quang Sang, Nguyễn Văn Tuân, Hoàng Trung Hữu, Nguyễn Văn Bộ

Tóm tắt: *Bài báo trình bày ảnh hưởng của tỉ lệ chất ôxi hóa/chất cháy tới một số đặc trưng năng lượng (nhiệt lượng cháy, thể tích sản phẩm khí, tốc độ cháy) của thuốc hỏa thuật tạo lửa màu đỏ chứa stronti nitrat, magie, polyvinyl clorua và nhựa novolac. Dựa trên số liệu thực nghiệm và kết quả lý thuyết, đã xác định được tỉ lệ stronti nitrat/magie hợp lý là 58/15. Hỗn hợp hỏa thuật này có nhiệt lượng cháy 921 cal/g, thể tích sản phẩm khí 260 mL/g, tốc độ cháy 2,02 mm/s ở mật độ nén 1,60 g/cm^3, độ sạch của màu ngọn lửa là 89%, nhiệt độ phân hủy là 481,5^{o}C, kém nhạy với xung ma sát và va đập.*

Từ khóa: Hỏa thuật; stronti nitrat; magie; polyvinyl clorua.

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