FORMULATION AND SEVERAL CHARACTERISTICS OF THE SMOKE COMPOSITIONS BASED ON RED PHOSPHORUS

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Abstract

Red phosphorus is an important ingredient in the manufacture of pyrotechnic smoke and is likely to be in service for many years. One of the most effective ways to use smoke screens is to protect special vehicles from laser and infrared guidance systems. In this work, the formulation, obscurant and emission characteristics of the smoke composition in smoke devices used in special vehicles were determined and evaluated. Research results show that the smoke composition comprises red phosphorus, sodium nitrate, Al-Mg alloy, and fluorine-containing polymers. The outcomes also demonstrated that the smoke screen has a high attenuation capability to 1.064 µm laser radiation and strong infrared emission in both wavelength ranges of 3 - 5 µm and 8 - 14 µm.

Keywords: Smoke composition; obscurant; infrared radiation; red phosphorus.

1. Introduction

Some special vehicles such as warships and combat vehicles play an important role in modern combat. Therefore, these vehicles are potential targets for threats [1-3]. Many measures have been deployed to protect special vehicles, in which camouflage and countermeasures using smoke screens are considered effective in protecting vehicles against guidance systems [3-8].

There are many methods of creating a camouflage smoke screen, including dispersing liquid mist or using pyrotechnic mixtures. In the first instance, a mist-like smoke screen is created by spraying the liquid via specialized equipment. The C4 combination (i.e., SO_3 and HSO_3Cl), metal chlorides (i.e., $TiCl_4$, $SiCl_4$, $SnCl_4$) and the mixes of vaporized condensed oils are typical for this type. These smoke screens mainly obscure and attenuate radiation, allowing them to hide the vehicles only [9, 10]. Meanwhile, creating smoke screens by burning pyrotechnic compositions in grenades to protect special vehicles is more commonly used because of its camouflage ability as well

as its infrared emission. The smoke devices were fired in the needed direction and produced a smoke screen at a distance of 100 to 300 m from the vehicles covering the vehicles themselves for several minutes. HC compositions (based on hexachloroethane and hexachlorobenzene) were applied to the smoke devices and showed superiority over vaporized oil mixtures [11, 12]. However, C_2Cl_6/C_6Cl_6 and their combustion products (i.e., chlorinated organic compounds) are toxic (possibly carcinogenic) [13-15], so there was a need for less toxic alternatives.

Smoke compositions based on red phosphorus, rely on atmosphere burning to produce phosphorus pentoxide, which is further hydrolyzed to form an aerosol cloud [16, 17]. These compositions have been widely used on modern combat vehicles due to their high Yield factor (i.e., the ratio between the aerosol mass and the unit mass of the pyrotechnic payload) in comparison to other components [18, 19]. It is noteworthy that the smoke particles emanating from the combustion of these compositions attenuate not only the visible region but also infrared radiation. The use of red phosphorus-based formulations has been used since sophisticated electro-optic instruments using laser and infrared sensors as target detection tools [16, 20, 21]. Besides, with the presence of metal powder in the composition, modern smoke mixtures can camouflage (for laser-guided systems) and countermeasure decoy (for infrared-guided systems in the range of 3.0 - 5.0 μm and 8.0 - 14.0 μm). Therefore, smoke devices using these compositions have a compact structure and more features. As a result, red phosphorus-based smoke formulations gained worldwide attention.

This work focuses on determining the formulation and several characteristics (i.e., the combustion heat, the mass burning rate, the obscurant and the infrared radiation) of smoke compounds based on metal, red phosphorus and fluorinated polymers used in the smoke devices on the special vehicles (Russia). The infrared radiation characteristics (i.e., the infrared spectra distribution and the infrared radiance in the range of 3.0 - 5.0 μm and 8.0 - 14.0 μm) were determined using a spectroradiometer. Besides that, the absorption and scattering of screening smoke at 1.064 μm laser radiation were also determined.

2. Materials and methods

2.1. Materials

Smoke composition blocks obtained from smoke devices in the special vehicles (manufactured in 2018, Russia). Red phosphorus powder (170 - 270 mesh), sodium nitrate and manganese dioxide (MnO_2, 350 - 400 mesh) were provided by Xilong Scientific Co., Ltd. The Mg-Al alloy powder (i.e., the Mg/Al ratio of 50/50 by weight, 230-325 mesh) was provided by Sichuan Hermus Industry Co., Ltd. Viton A rubber (i.e., the fluorine

content of 66%) and PTFE (polytetrafluoroethylene, mean particles size of 10 μm) powder were obtained commercially from Chengguang Fluoro and Silicone Elastomers Co., Ltd.

2.2. Methods

- Formulation determination: The formulation of the Russian smoke composition was determined using traditional instrumental analysis methods combined with infrared and EDX spectroscopy. The analysis diagram is presented in Fig. 1.

- Sample preparation: Viton rubber was dissolved in acetone with the rubber/solvent ratio of 1/15 (w/v) and kept overnight to obtain a homogeneous solution. Homogeneous mixtures of Mg-Al, sodium nitrate, PTFE powder and manganese dioxide were obtained by dry mixing on a 0.5 mm sieve. Then, this mixture and red phosphorus powder were mixed into the adhesive solution using a stirrer at 700 rpm for around 30 min. The final mixture was dried for 30 min. in the air and then granulated through a 1.25 mm sieve. After that, the mixtures were vacuum-dried at 60°C for 3 hours to remove the solvents.
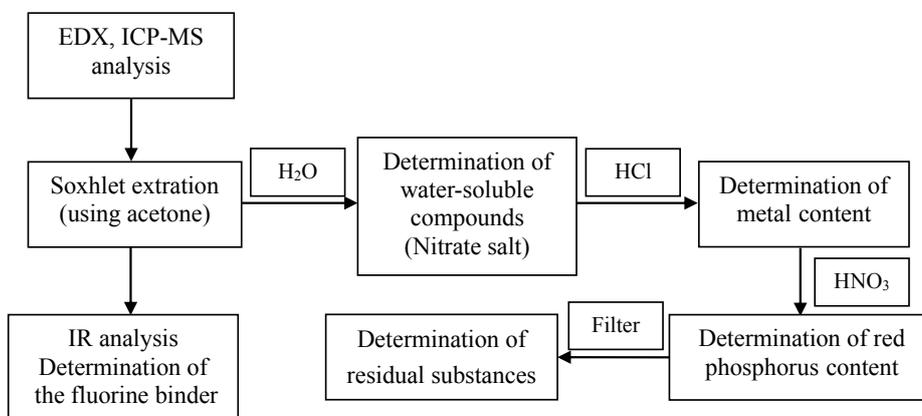
Fig. 1. Analytical diagram to determine the formulation of smoke composition.

The heat of combustion Q was determined using the Parr 6200 calorimeter (Parr Instrument Company, US). The mass of each sample was 1.0 g, ignited by an electric igniter in the bomb containing excess oxygen (i.e., the oxygen pressure in the bomb is about 2 atms), ensuring that the reducing agents in the bomb were completely oxidized. The ignition temperature was measured by the DT-400 (Germany): heating of 150 mg sample at a heating rate of 5.0 and 20.0 K.min^{-1} until the point of ignition was reached.

The obscurant properties of a smoke screen can be evaluated by the degree of transmission (i.e., the transmittance), which is determined by the absorption and scattering of a 1.064 μm-laser beam. The experimental setup used to measure the attenuation of the

laser radiation is shown in Fig. 2. A continuous-wave laser source (with an output power of 20.0 mW and a beam diameter of 2.0 mm) was passed through the chamber and recorded by a laser power meter. The total path length through the screening smoke was 600 mm. To eliminate the influence of weather conditions, the test chamber was arranged in a covered tent.
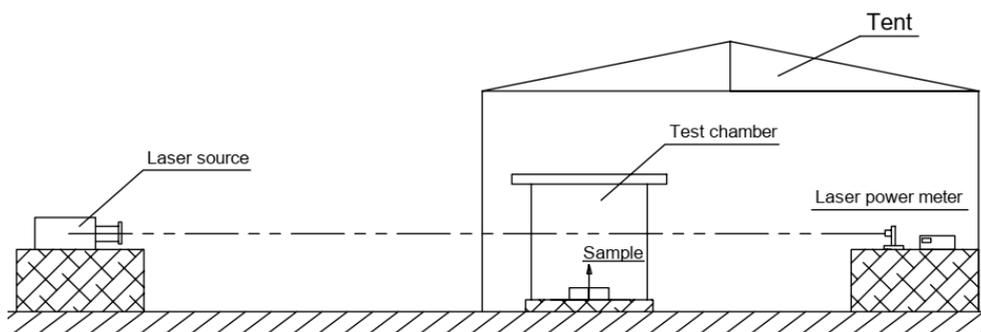

Fig. 2. The experimental setup used to measure the transmittance.

The degree of transmission T was determined by:

$$T = \frac{I_{\min}}{I_0} \tag{1}$$

where I_0 and $I_{\min}$ are the initial laser intensity without smoke and the minimum laser intensity after passing through the screening smoke, respectively.

The infrared emission characteristics of the smoke screen were determined by the SR-5000N spectroradiometer (CI systems, US) in the wavelength ranges of 3 - 5 µm and 8 - 14 µm. The experimental setup to determine the intensity and distribution of the infrared radiation is presented in Fig. 3. For each measurement, a smoke composition block (with a sample mass of 14.0 g and a density of 1.75 g.cm^{-3}) was ignited in the test chamber using an electric igniter. The distance between the lenses of the spectroradiometer and the test chamber is about 5.0 m. The intensity, distribution and radiance of infrared radiation of the smoke screen in the wavelength ranges of 3 - 5 µm and 8 - 14 µm were determined using built-in software.

The average mass burning rate of the smoke composition block (e.g., the triangular block with the sample mass m) was determined along with the infrared radiation characterization measurement (Fig. 3). The high-speed digital camera Fastcam SA 1.1 RV (Photron, Japan) was used to determine the time interval (t) from the start to the end of the combustion process of the block. Then, the mass burning rate (ω) is calculated by:
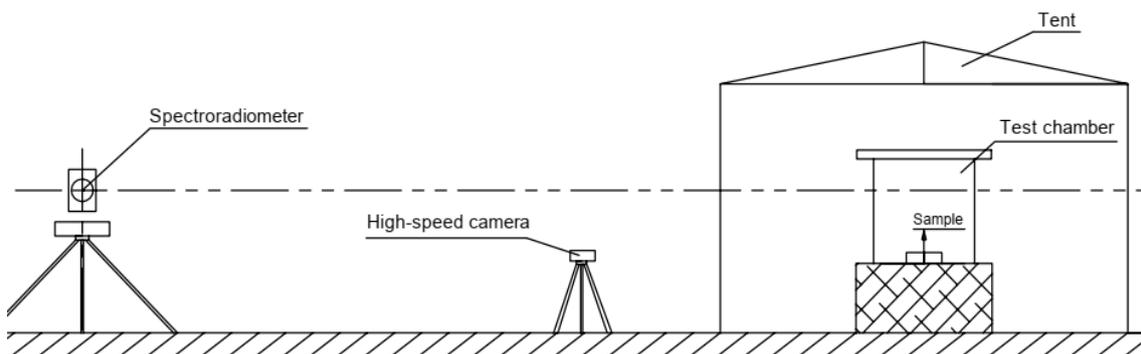
$$\omega = \frac{m}{t} \tag{2}$$

Fig. 3. The experimental setup used to measure the infrared radiation and the mass burning rate.

3. Results and discussion

3.1. Determination of the formulation

The results of analyzing the smoke formulation of the Russian sample according to the diagram in Fig. 1 reveal that the main ingredients include Mg-Al alloy, red phosphorus, sodium nitrate, PTFE, and fluorine rubber. Other additives in small content (e.g., MnO_2) are used as a combustion catalyst, which appears in the EDX spectrum (Fig. 4), but have not been determined. Based on the analysis of Russian samples, another formulation was proposed to evaluate the accuracy of the analysis process.
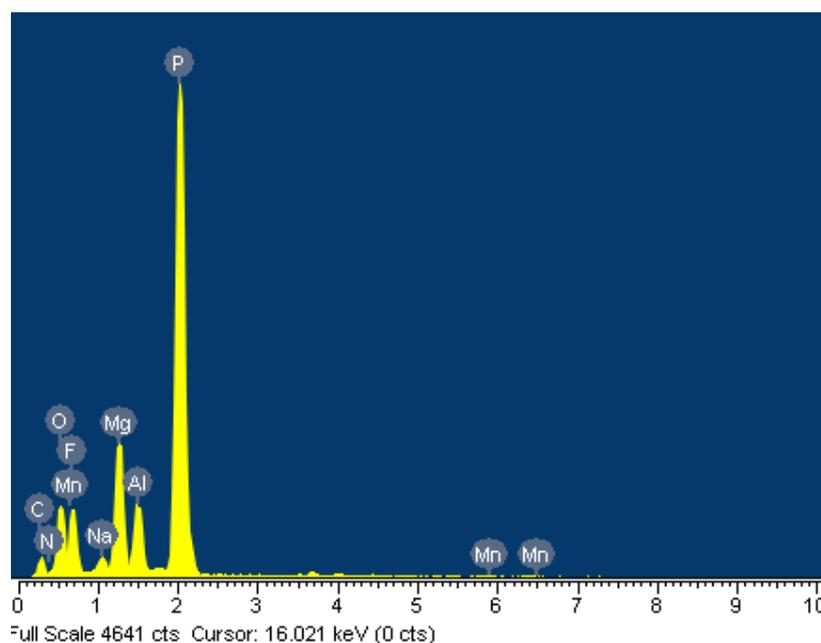

Fig. 4. The EDX spectrum of the Russian smoke composition.

The composition of Russia's smoke formulation (according to analysis results) and the proposed smoke formulation (named VN formulation) are presented in Table 1.

Table 1. The formulations of Russian sample and the proposed smoke composition

Ingredients	Content of ingredients, %	
	Russian sample	*Proposed smoke composition*
Mg-Al alloy (Mg$_4$Al$_3$)	15.6 ± 1.8	15.0
Red phosphorus	62.4 ± 2.8	63.5
Sodium nitrate (NaNO$_3$)	5.9 ± 1.2	7.0
PTFE	6.8 ± 1.0	6.0
Fluorine rubber	7.7 ± 1.1	8.0 (Viton A)
Manganese dioxide (MnO$_2$)	-	0.5

3.2. Combustion characteristics

The combustion characteristics of a smoke composition affect the obscurant and infrared emission characteristics of a smoke screen as well as its performance. Particularly, the component of combustion products directly affects the absorption and scattering of electromagnetic radiation. In addition, the combustion product, the combustion heat, the mass burning rate determine the infrared emission of the smoke screen. The results are summarized in Table 2.

Table 2. Combustion characteristics of the smoke compositions

Combustion characteristics	Russian sample	VN sample
The ignition temperature, °C	315.0 ± 1.2 (at 20.0 K.min^{-1}) 303.5 ± 0.7 (at 5.0 K.min^{-1})	312.2 ± 0.8 (at 20 K.min^{-1}) 302.4 ± 0.5 (at 5.0 K.min^{-1})
The heat of combustion, kcal.kg^{-1}	4450 ± 250	4515 ± 220
The average mass burning rate, g.s^{-1}	0.74 ± 0.03	0.74 ± 0.02
The main component of the combustion product (by REAL thermodynamic code)	Soot particles (C); H$_3$PO$_4$; MgO; MgF$_2$	

The ignition temperature, heat of combustion, and the average mass burning rate of the Russian and VN smoke compositions are all extremely similar, demonstrating the correctness of the Russian smoke formulation analysis process. Because of the higher ignition temperature, the Russian samples appear to have slightly higher heat stability than the VN ones, but not significantly. This can be explained by the differences in technical specifications of the components used to prepare the smoke composition.

3.3. Obscurant characteristics

From Table 2, it can be seen that the main constituents of the smoke screen are soot particles (i.e., carbon), H$_3$PO$_4$, MgO and MgF$_2$ particles. The obscurant characteristic (or transmittance) was evaluated by burning a certain amount of smoke compositions (e.g.,

0.3, 0.5, 0.7, and 1.0 g) in a test chamber (Fig. 3). After 5 seconds (to obtain a uniformly dispersed smokescreen in the test chamber), 1.064 µm-laser intensity values were recorded every 5 seconds, for approximately 120 seconds. The minimum value of the recorded laser intensity will be used to calculate transmittance according to (1). The experiments were conducted at 30°C and 70% RH. The dependence of transmittance on the mass of smoke composition and time is shown in Fig. 5.
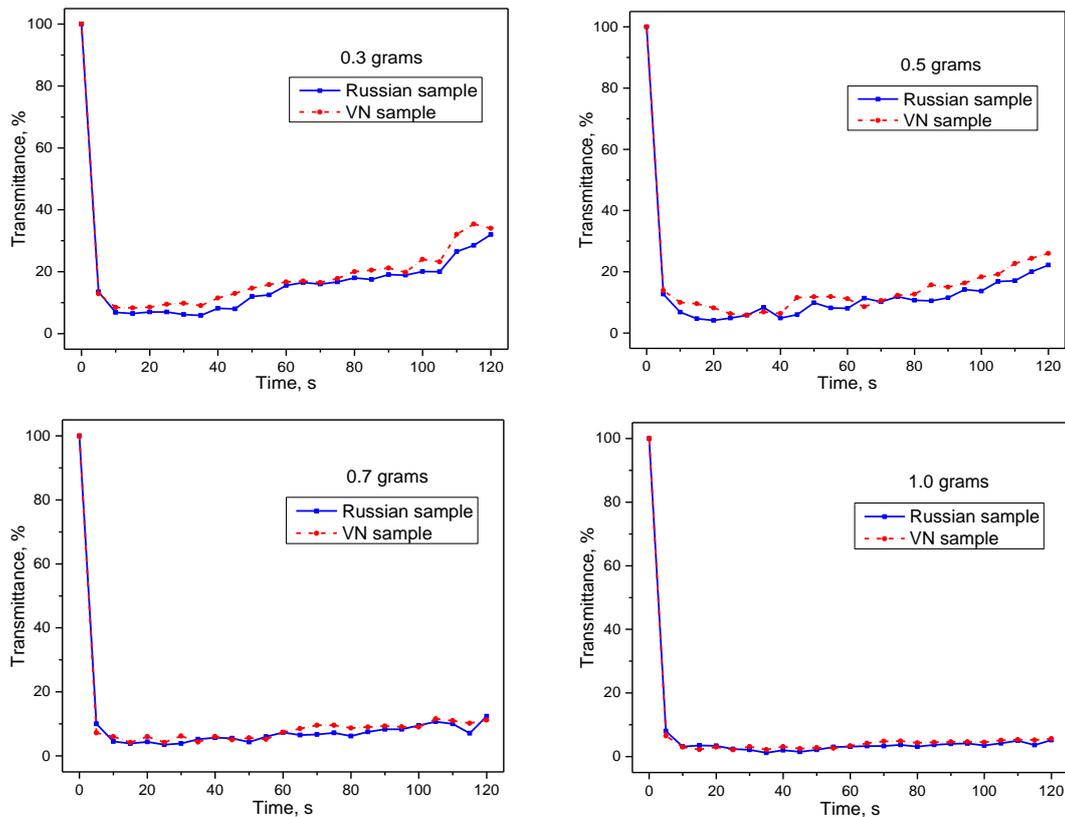

Fig. 5. Transmittance of smoke screen of the samples.

A smoke screen is considered effective in camouflage when its transmittance does not exceed 15% (i.e., its attenuation to radiation is greater than 85%). As seen in Fig. 5, the transmittance of the smoke screen decreases with the increasing smoke composition mass. For a sample weight of 0.3 g, the smoke screen maintains its camouflage effect for about 40 seconds. Besides, these times for 0.5, 0.7, and 1.0 g samples are always greater than 90 seconds (counting from the first 10 seconds after the ignition). In particular, the transmittance values of 1.0 g samples are consistently higher than 5%. When considering the Yield factor, smoke compositions with a mass of 0.5 to 0.7 g all

achieved the required coverage effect. On the other hand, the Russian and proposed smoke compositions both had similar transmittance, although the Russian samples were slightly more effective, but not significantly.

3.4. Infrared emission characteristics

The infrared emission characteristics (i.e., the spectral distribution, the radian intensity and the radiance) of smoke compositions were measured using the SR-5000N spectroradiometer and the results are presented in Table 3 and shown in Fig. 6. While the smoke clouds based on red phosphorus and fluorine polymers emit mainly in the wavelength range of 8.0 - 14.0 µm (FIR band) and the MTV-like mixtures perform high infrared emission in the wavelength range of 2.5 - 5.0 µm (MIR band), the smoke screens of mixtures based on Mg-Al alloy, red phosphorus and fluorocarbon emit strongly in both of the above wavelength ranges.

Table 3. Infrared radiance of smoke screens

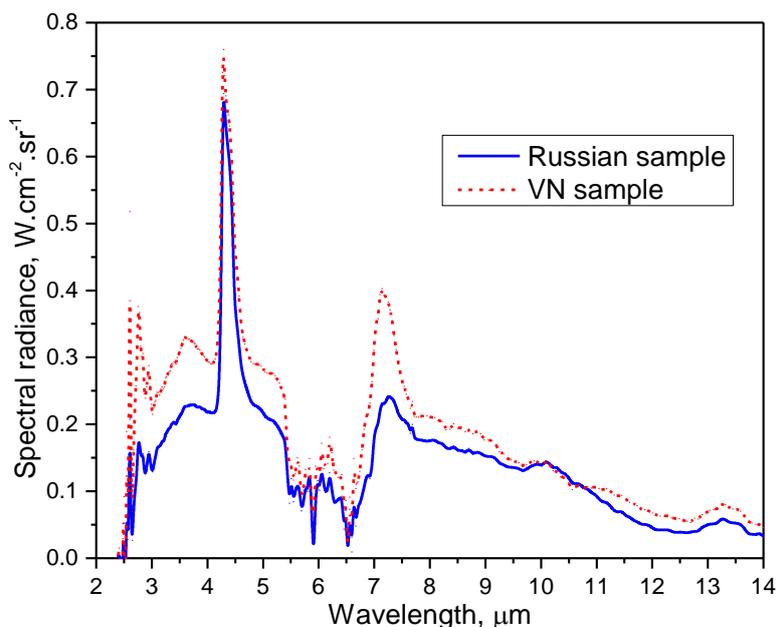| Sample	Infrared radiance, 10^{-2} W.cm^{-2}.sr^{-1}		Ratio of radiance in MIR/FIR band
	MIR band	FIR band	
Russian sample	2.52	3.24	0.78
VN sample	2.59	3.70	0.70

Fig. 6. Infrared emission of the smoke compositions.

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Smokescreens emit strong radiation in the 3 - 5 µm region with the peak intensity at a wavelength of 4.5 µm. On the other hand, in the range of 8 - 14 µm, the emission of both smokescreens tends to be evenly distributed. Figure 5 also reveals that the infrared emission distribution and radiance of the smoke screens of both the Russian and VN samples are similar.

4. Conclusion

The analysis of the formulation study reveals that Mg-Al alloy, red phosphorus, polytetrafluoroethylene powder, sodium nitrate, and fluorine rubber are the main components of the smoke composition utilized on Russian vehicles.

The similarity between the combustion characteristics (i.e., the ignition temperature, the heat of combustion, the mass burning rate), the obscurant (to the 1.064 µm laser) and the emission characteristics (in the wavelength ranges of 3 - 5 µm and 8 - 14 µm) of the Russian and VN samples proves that the proposed smoke formulation can be used in smoke devices to protect special vehicles against the electro-optically guided precision systems.

Further work needs to be carried out to assess the effect of environmental conditions on the stability, obscurant, and emission performance of smoke composition.

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THÀNH PHẦN VÀ MỘT SỐ ĐẶC TRƯNG CỦA THUỐC TẠO KHÓI SỬ DỤNG TRÊN CƠ SỞ PHỐT PHO ĐỎ

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Tóm tắt: Phốt pho đỏ là thành phần quan trọng trong chế tạo các hỗn hợp tạo khói, được sử dụng trong nhiều năm nay. Một trong những cách hiệu quả sử dụng màn khói là để bảo vệ các phương tiện đặc biệt khỏi các hệ thống dẫn đường bằng laze và hồng ngoại. Trong nghiên cứu này, thành phần, các đặc trưng ngụy trang và đặc trưng phát xạ hồng ngoại đã được khảo sát và đánh giá. Kết quả nghiên cứu cho thấy thành phần chính của thuốc tạo khói sử dụng trên xe chiến đấu của Nga bao gồm hợp kim Mg-Al, phốt pho đỏ, $NaNO_3$ và các polyme chứa flo. Kết quả nghiên cứu cũng cho thấy đám mây khói tạo ra có khả năng che phủ tốt đối với tia laze bước sóng 1,064 μm và phát xạ hồng ngoại mạnh ở cả hai dải bước sóng 3,0 - 5,0 μm và 8,0 - 14,0 μm.

Từ khóa: Thuốc tạo khói; ngụy trang; phát xạ hồng ngoại; phốt pho đỏ.

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