Preparation and Characterization of Magnesium/Teflon/Viton Mixtures for Tracking Flares

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Abstract:
This article examines the influence of fuel/oxidizer ratios and particle sizes of the fuel on combustion characteristics of the pyrolant based on magnesium, polytetrafluoroethylene, and Viton such as heat of explosion, the specific volume of gaseous products, burning rate, and IR intensity. Based on the theoretical and experimental analysis, an appropriate ingredient and particle sizes of components were chosen to meet the requirement for tracking flares. The pyrolant has a medium autoignition temperature and a low sensitivity to friction. It means that the pyrolant is quite safe in transportation, storage, and use.

Keywords:
combustion, MTV mixtures, infrared radiation, tracking flares

1. Introduction
The pyrolants based on magnesium, polytetrafluoroethylene, and Viton (so-called MTV) were developed in the 1950s and applied in many military fields, such as decoy flares [1-3], tracking flares [4], igniter of rocket motor [5], signaling applications [6], incendiary devices [7], solid rocket fuels [8], etc.

Currently, most anti-aircraft missiles can detect targets due to infrared radiation emitted by jet engine streams. In order to train missile shooters, tracking flares capable to emit infrared radiations, such as jet engine streams, were produced. Compared to old-style pyrolants, MTV mixtures have higher radiation intensity in the middle IR range. However, the detailed studies of these pyrolants are not widely available. Therefore, the objective of this study is to successfully prepare an MTV mixture and to apply it to tracking flares.

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2. Materials and Methods

2.1. Materials
The powder polytetrafluoroethylene (PTFE) has the particle size in a range of 3-5 µm and the density of 2.0 g/cm$^3$. The powder magnesium (Mg) has the density of 1.8 g/cm$^3$ and its particle size is in the ranges of 45-55, 55-65, 65-75, 75-85, 85-100, 100-125, and 125-150 µm. Viton is a copolymer of vinylidene fluoride (VDF) and hexafluoropropylene (HFP), which has the fluor content of 66% and the density of 1.78-1.83 g/cm$^3$. All materials were made by Xilong Co., Ltd. Other properties of the raw materials are shown in Table 1 [9].

| Materials | Formula | Molecular weight [g/mol] | Enthalpy of formation [kJ/kg] |
|-----------|---------|--------------------------|-----------------------------|
| PTFE      | C$_2$F$_4$ | 100.02                   | 8099.9                      |
| Viton     | C$_{10}$H$_7$F$_{13}$ | 374.14                   | 7451.7                      |
| Magnesium | Mg      | 24.31                    | 0                           |

2.2. Preparation of MTV Mixtures
The powder PTFE and magnesium were dried in the temperatures ranging between 80-90 °C and 50-60 °C, respectively, in 2 hours. The required quantities of different ingredients of PTFE and Mg powders were weighed and dried-mixed by brushing them from 5 to 7 times through 0.25 mm sieves. Viton was being dissolved in acetone for 5 hours with a concentration of 0.1 g/cm$^3$. After that, the viscous solution was kneaded with the PTFE-Mg mixture. The amount of acetone and Viton were used in such a way that the acetone/pyrotechnic mixture ratio equals to 1 cm$^3$/g and the Viton content in the pyrotechnic samples closed to 10% by weight. The wet pyrotechnic mixtures were preliminarily dried in the air for 30 minutes and then passed through the 0.60 mm sieves. Finally, the pyrotechnic samples were dried at the temperature ranging between 55-60 °C for 4 hours.

2.3. Characterization
The heat of the explosion was determined using a Parr-6200 calorimeter (Parr Instrument Company, USA) with 2 grams of the sample. Thereafter, the pressure in the calorimeter bomb was measured on a Lutron-9017 manometer (Lutron Electronic Enterprise, Taiwan) and the volume of gaseous products was calculated as follows:

$$ V = \frac{0.273}{T_c} \cdot \frac{\Delta P V_b}{m} \tag{1} $$

where $V$ – the volume of gaseous products; $\Delta P$ – the difference between the values of pressure in the combustion chamber before and after measurement; $T_c$ – the temperature of the combustion chamber, which equals to the room ambient temperature; $V_b$ – the volume of the combustion bomb equals to 334 ml; $m$ – the mass of the sample [g], 0.273 – the constant equal to 273 (the standard temperature in Kelvin) divided by 1000 (1 000 mbar).
The burning rate was obtained as a ratio between the traveling distance of the combustion front and the corresponding time interval determined by using a digital camera (Fig. 1). To measure the burning rate, the pyrotechnic mixture was pressed into a steel tube with 17 mm in inner diameter to 1.8 g/cm³ of density with 100 MPa of the pressure. The distance between the starting and ending points on the steel tube is 30 mm. The autoignition temperature was determined by an AET-402 Automatic Explosion Temperature Tester (OZM Research, Czech Republic) according to STANAG 4491. Tracking flares were steel tubes (34 mm in outer diameter, 30 mm in inner diameter, and 200 mm of length) loaded with pyrotechnic mixture at 1.8 g/cm³. The radiation intensity of the tracking flare was recorded on the Spectral Master 12-550 Mark III Radiometer (Infrared Systems Development Corporation, USA), so that the distance between end close of the tube and the Radiometer was 300 m (Fig. 2). The friction sensitivity was carried out by a BAM Friction Tester (Reichel & Partner GmbH, Germany) according to STANAG 4487 [10].

3. Results and Discussion

3.1. Prediction of Combustion Characteristics of MTV Mixtures

It is difficult to determine experimentally several combustion characteristics of MTV mixtures such as enthalpy of reaction $\Delta H_c$, adiabatic temperature $T_c$, and composition of combustion products. Thus, we used the REALWIN software [11] to predict the characteristics of MTV mixtures with different Mg/PTFE weight ratio ranging from 20/70 to 60/30 and with Viton content of 10% in mass. In calculation, two equilibrium parameters are the internal energy considered as constant and the loading specific volume of reaction products that equals to 0.167 m³/kg. Predicted values of $T_c$, $\Delta H_c$, and several main combustion products at solid [s] and gaseous [g] states of MTV mixtures are given in Tab. 2.

The maximum theoretical adiabatic temperature (3623 K) and enthalpy of reaction (4176 kJ/kg) were obtained at the Mg/PTFE ratio of 30/60. The ratio closes to the stoichiometric formulation, as shown in a simple reaction of the mixture predicted by REALWIN software:

$$12.75 \text{Mg} + 5.9 \text{C}_2\text{F}_6 + 0.27 \text{C}_{10}\text{H}_7\text{F}_{13} \rightarrow 12.75 \text{MgF}_2 + 14.39 \text{C} + 1.56 \text{HF} + 0.08 \text{CH}_4$$

At Mg/PTFE ratios of 20/70 and 25/65, magnesium did not appear in combustion products. Thus, secondary reactions will not occur between magnesium and oxygen in
the air, which leads to rising IR intensity, whereas at Mg/PTFE ratios of 55/35 and 60/30 the flame temperature was sufficiently low to decrease the IR radiation. Therefore, Mg/PTFE ratios in a range of 30/60-50/40 were selected for experimental studies.

3.2. Influence of Fuel/Oxidizer Ratio on Heat of Explosion, Volume of Gaseous Products, and Burning Rate

In order to assess the influence of fuel/oxidizer content on combustion characteristics of the MTV mixture, we prepared samples with PTFE/Mg ratios as shown in Tab. 2. Contents of Viton are 10 wt.% and particle sizes of PTFE and Mg are 3-5 µm and 85-100 µm, respectively.

The experimental values of the essential combustion characteristics of the MTV mixture samples, i.e. the heat of explosion $Q_v$, the gaseous volume $V$, the burning rate $u$ at the pressed density of 1.8 g/cm$^3$, are shown in Fig. 3.

As shown in Fig. 3, the heat of explosion $Q_v$ increases and reaches the maximum value at the Mg/PTFE ratio of 35/55 closing to the stoichiometric formulation. Therefore, variations of theoretically calculated enthalpy of reaction and experimental heat of explosion are similar. Nevertheless, the volume of gaseous products is declined by rising Mg contents. In addition, low values of gaseous products ($< 50$ cm$^3$/g) indicate that combustion products of MTV mixtures are almost in condensed states at the ambient temperature, for example C, MgF$_2$, and Mg$_{\text{residual}}$. In contrast to the volume of gaseous products, the rise of Mg concentration leads to an increasing burning rate. It is explained by increasing thermal conductivity of pyrotechnic mixtures.

3.3. Influence of Fuel/Oxidizer Ratio on IR Intensity

IR intensity is the most important characteristic of MTV mixtures for tracking flares. In general, MTV mixtures burn with air oxygen. The secondary reaction of residual magnesium with oxygen causes an increase in combustion heat and IR intensity. Hence, we determined the IR intensity of four MTV mixtures with Mg/PTFE ratios of 40/50, 45/45, 50/40, and 55/35 at the pressed density of 1.8 g/cm$^3$. IR spectra of MTV
mixtures are indicated in Fig. 4. The IR intensity in the wavelength range of 2.5-5 µm is shown in Fig. 5.

Fig. 4. IR intensity in the wavelength range of 2.5-5 µm. (a) IR intensity of Mg/PTFE mixtures. (b) IR intensity of Mg/PTFE/Viton mixtures.

It can be clearly seen in Fig. 5 that the rising magnesium content leads to raising IR intensity. The increase of IR intensity is caused by the increase in combustion rate. Infrared emission intensity reaches the maximum value at the Mg/PTFE ratio of 50/40. The continually increased Mg content will not be reasonable because the radiation intensity of the tracking flares starts to decrease (Fig. 5) and the radiation intensity within a wavelength zone of 8-10 µm zone increases (Fig. 4). On the other hand, comparing IR intensity of four MTV mixtures at different distances to the sensitivity of three photoresistors (Tab. 3) indicated that all mixtures meet the requirements for tracking flares of training missile guidance systems equipped with the above photoresistors at distance 5 000 m.

Tab. 3 Comparing IR intensity of MTV mixtures at different distances with the sensitivity of several photoresistors

| Mg/PTFE | IR intensity (λ = 4 µm) at different distances [W·sr⁻¹·cm⁻²] | Sensitivity of photoresistors at λ = 4 µm [W·Sr⁻¹·cm⁻²] |
|---------|----------------------------------------------------------|----------------------------------------------------------|
|         | 300 m | 3000 m | 4000 m | 5000 m | PbS | PbSe | PbTe |
| 40/50   | 0.283 | 8.1 × 10⁻⁴ | 4.6 × 10⁻⁴ | 2.9 × 10⁻⁴ | 2.0 × 10⁻¹⁰ | 1.8 × 10⁻⁹ | 2.0 × 10⁻¹⁰ |
| 45/45   | 0.336 | 9.6 × 10⁻⁴ | 5.4 × 10⁻⁴ | 3.5 × 10⁻⁴ | 2.0 × 10⁻¹⁰ | 1.8 × 10⁻⁹ | 2.0 × 10⁻¹⁰ |
| 50/40   | 0.339 | 9.7 × 10⁻⁴ | 5.5 × 10⁻⁴ | 3.5 × 10⁻⁴ | 2.0 × 10⁻¹⁰ | 1.8 × 10⁻⁹ | 2.0 × 10⁻¹⁰ |
| 55/35   | 0.345 | 9.7 × 10⁻⁴ | 5.6 × 10⁻⁴ | 3.6 × 10⁻⁴ | 2.0 × 10⁻¹⁰ | 1.8 × 10⁻⁹ | 2.0 × 10⁻¹⁰ |

3.4. Influence of Magnesium Particle Sizes on Burning Rate

In order to examine the effect of Mg particle size on burning rate, we classified Mg into seven groups and prepared samples with an Mg/PTFE/Viton ratio of 50/40/10. The values of burning rate at a density of 1.8 g/cm³ are shown in Fig. 6.
Fig. 4 IR spectral intensity of MTV mixtures with different Mg/PTFE ratios

Fig. 5 Variation of IR intensity of MTV mixtures by fuel/oxidizer ratios

Fig. 6 Influence of Mg particle size on burning rate
It can be clearly observed in Fig. 6 that the smaller the particle size, the higher the burning rate is, because, when the particle size is smaller, the contact surface area of fuel and oxidizer particles is larger, so, as a result, chemical reactions occur faster. The MTV mixture using Mg 85-100 mm in size was selected because it ensures meeting the burning rate requirement, as well as it has better economic efficiency.

3.5. Autoignition Temperature and Friction Sensitivity of MTV Mixtures
The autoignition temperature of the MTV mixture with an Mg/PTFE ratio of 50/40 measured by AET-700 Automatic Explosion Temperature Tester is 540 K. This value is similar to the decomposition temperature of PTFE. It indicates that the chemical reaction of Mg occurs immediately after the decomposition of PTFE.

In addition, we conducted a measurement of friction sensitivity of the MTV mixture by a Friction sensitivity Tester BAM. The obtained result pointed out that no initiation was observed in 10 trials at a maximum load of 36 kg. In other words, the friction sensitivity of the MTV mixture is very low. Thus, it could be concluded that the MTV mixture is relatively safe to friction action.

4. Conclusion
The MTV mixture for tracking flares was successfully designed and produced. The reasonable composition and particle size of magnesium, PTFE, and Viton were determined. The pyrolant contains 50 wt.% of Mg, 40 wt.% of PTFE, and 10 wt.% of Viton. Particle sizes of Mg and PTFE were 3-5 µm and 85-100 µm, respectively. The pyrolant has the heat of explosion of 6385 kJ/kg, volume of gaseous products of 20.8 cm$^3$/g, and the burning rate of 6.27 mm/s at 1.80 g/cm$^3$ of density. The IR intensity of the tracking flares using the MTV mixture was greater than the sensitivity of three common photo resistors at 5000 m of distance. It demonstrates that the MTV mixture meets the requirement for tracking flares. In addition, the autoignition temperature of 540 K and low friction sensitivity of this pyrolant was measured. The values are appropriate for the production, storage and use of tracking flares.

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