Research on the Flame Retardant Effect of Super-porous Nitroguanidine Propellant Coated with Different Coating Contents of TiO$_2$

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Abstract. The flame-retardant effect of coating liquid with different titanium dioxide (TiO$_2$) content on the coating of super-porous nitroguanidine propellants is studied by closed bomb tests and X-Ray Diffraction (XRD) tests. Using three different proportions of insensitive coating liquid to make a single-hole propellant. Taking single hole propellant 20g respectively for constant volume combustion test, and analyses the p-t, u-p curve. Then, select 30% and 35% of TiO$_2$ coating propellant and uncoated propellant to do constant volume combustion experiments, and to analyze the p-t curves. By analyzing the results of experiments, we draw the following two conclusions: (i) When the content of TiO$_2$ in the coating liquid of the single hole propellant is 35%, at the same loading density, the maximum pressure reached is the minimum and the time required is the longest. (ii) As the content of TiO$_2$ in the coating layer increases, the insensitivity effect of the coating layer become more obvious, and the increasing explosiveness of the propellant will increase.

1. Introduction

To reduce the burning velocity of the super-porous nitroguanidine propellant. One can choose to add different proportions insensitive materials[1]. In this paper, we utilize 100nm anatase TiO$_2$ as the flame retardant material. TiO$_2$ is a metal oxide. TiO$_2$ is a type of coating agents. It can prolong the ignition time and slow down the burning speed of propellants in the combustion process[2]. After adding TiO$_2$ as a flame retardant material to the coating liquid, a super-porous nitroguanidine propellant is insensitively coated, and the obtained coating medicine has a good sense of low-temperature[3].

TiO$_2$ is evenly distributed in the coating liquid, which changes the coating liquid from the original homogenous system into a heterogeneous system[4]. At the same time, because TiO$_2$ itself has a certain specific heat capacity, part of the heat in the combustion process of the coating will be absorbed by TiO$_2$, which also plays a role in flame retardant[5].

In this paper, by doing constant volume combustion experiments, analyze the p-t, u-p curve to study the flame retardant effect of coating liquids coated with different TiO$_2$ contents on super-porous nitroguanidine propellants.

2. Experimental
2.1. Test Materials and Instruments.
Super-porous nitroguanidine propellant, Liaoning Qingyang Special Chemical Co., Ltd.; acetone, ethanol, chemical pure, Nanjing Chemical Reagent Co., Ltd.; 100nm anatase oleophilic TiO$_2$, purity 99.8%, Shanghai Aladdin Biochemistry Technology Co., Ltd.; Sanwa-15 absorption tablets, Liaoning Qingyang Special Chemical Co., Ltd.
X-ray diffractometer, XP205 German Bruker company, closed explosives, Zhangzhou North Chemical Industry Co., Ltd.; coating machine, Taizhou Liming Pharmaceutical Machinery Co., Ltd.; water bath oven, AHX safe oven, Nanjing University of Science and Technology.

2.2. Experimental Methods.
25%, 30%, and 35% of the TiO$_2$ content of the coating liquid were made into a single-hole propellant. Doing a constant volume combustion test, and the combustion powder was taken for XRD test[6].
Select 30% and 35% TiO$_2$ coating propellants and uncoated propellant sing closed bomb for constant-volume combustion experiments. Exact sampling is given in Table 1.

| Group number | Composition                                      | Quality/g |
|--------------|--------------------------------------------------|-----------|
| (1)          | Two 30% titanium dioxide coatings                 | 38.3984   |
| (2)          | Two 30% titanium dioxide coatings                 | 39.0252   |
| (3)          | Base + 30% titanium dioxide coating (mixed)       | 38.2097   |
| (4)          | Two 35% titanium dioxide coatings                 | 39.1608   |
| (5)          | Base + 35% Titanium dioxide coating (mixed)       | 38.7811   |
| (6)          | Base + 35% Titanium dioxide coating (mixed)       | 38.5079   |

3. Data Processing and Analysis

3.1 Coating solution preparation method
(1) Placing Sanwa-15 absorption tablets in a water bath oven, and set the oven temperature to 50°C. Placing in the oven for three days, and remove the absorbent tablets after the solvent is completely evaporated.
(2) Taking a certain amount of Sanwa-15 absorption tablets, and add different amounts of TiO$_2$ and acetone ethanol solvent into a 2500 mL measuring cup. Using a constant digital mixer to stir at 3000 r/min and stir for about 24 h. Preparation of the coating liquid as showed in Table 2:

| Group | Sanwa-15 absorbent content/g | TiO$_2$ content/g | Solvent content/g | Solvent ration |
|-------|------------------------------|-------------------|-------------------|---------------|
| 01#   | 75                           | 25 (25%)          | 550               | 1:5.5         |
| 02#   | 70                           | 30 (30%)          | 550               | 1:5.5         |
| 03#   | 65                           | 35 (35%)          | 550               | 1:5.5         |

The following “figure 1” shows the comparison of the super-porous nitroguanidine propellant coating.
3.2 Effect of TiO$_2$ as insensitive coating material on coating.

In order to study the effect of TiO$_2$ content on the combustion performance of the coating. Using three different proportions of insensitive coating liquid to make a single hole propellant. Taking single hole propellant 20g respectively for constant volume combustion test, and the p-t, u-p curve are shown in the “figure 2”, “figure 3”.

![Figure 1. Uncoated and coating](image)

**Figure 1.** Uncoated and coating

From Figure 2, it can be seen that the 35% TiO$_2$ of the coating liquid made the single hole propellant reaching the maximum pressure for the longest time, which increases the pressure plateau effect of the p-t curve. From Figure 3, it can be observed that under the conditions of loading density of 0.2g/L, the single hole propellant made from the coating solution with 35% TiO$_2$ content has the lowest combustion pressure and the lowest burning rate. Comparing with 25% TiO$_2$ content and 30% TiO$_2$ content of the coating solution. It can be concluded that when the TiO$_2$ content is 35%, it flame retardant effect is the best.

3.3 XRD analysis of residues after combustion of single hole propellant with different coating formulation

The 25%, 30% and 35% TiO$_2$ content coating liquids are made into a single-hole propellant, and doing the constant-volume combustion test. Taking the powder from this combustion for XRD test. Result diagram is shown in “Figure4”, “Figure5”, “Figure6”, “Figure7”.

![Figure 2. P-t curves](image)

**Figure 2.** P-t curves

![Figure 3. U-p curves](image)

**Figure 3.** U-p curves
From spectrum 4, it can be seen that the strongest diffraction peak of the sample correspond to the 101 crystal plane appearing at about 25°, which is anatase titanium dioxide. The spectrums 5, 6, and 7 are the strongest for the TiO$_2$ powder removed after the constant volume combustion test. The diffraction peak corresponds to the 110 crystal plane appearing at about 27°, which are rutile titanium dioxide. It can be proved that the TiO$_2$ crystal form has changed from anatase to rutile during constant volume combustion.

3.4 Constant volume combustion test of coating.
After sampling and burning in accordance with Table 1, p-t curves as showed in Figure 8.
Figure 8. Constant-temperature combustion test p-t curves

Table 3. Maximum pressure and maximum pressure occurrence time of constant volume combustion test

| Group number | Greatest pressure | Maximum pressure occurrence time |
|--------------|-------------------|----------------------------------|
| #1           | 537.36            | 20.756                           |
| #2           | 551.02            | 19.727                           |
| #3           | 532.48            | 17.906                           |
| #4           | 545.76            | 22.123                           |
| #5           | 550.06            | 18.215                           |
| #6           | 533.37            | 23.482                           |

Try to ensure that each group of experimental propellants has a similar quality. The quality of the propellant will mainly affect the maximum pressure generated by the combustion. From the comparison of curves #1 and #3 in Figure 8 and Table 3, it can be seen that under similar mass conditions, the maximum pressure of the pure coated propellant is 2.85ms later than the maximum pressure time of the coated and the uncoated propellant. The increase of the maximum pressure time indicates that the coating has a role in increasing the burning of the propellant. Comparing curves #2 and #4, #3 and #6. It can be illustrated that 35% TiO$_2$ to 30% TiO$_2$ is more effective in increasing the gradual increase in the combustion of the propellant.

4. Conclusion
(1) The addition of TiO$_2$ significantly reduces the energy density of the single hole propellant. When
the content of TiO$_2$ in the coating liquid of the single hole propellant is 35%, at the same loading density, the maximum pressure reached is the minimum and the time required is the longest. The burning speed is obviously affected by the TiO$_2$ content. And it has a good flame retardant effect.

(2) XRD analysis of residues after combustion of single hole propellant with different coating formulation. During the process TiO$_2$ has undergone a crystal transformation from anatase to rutile.

(3) The coating layer plays an important role in increasing the burning of the propellant. 35% TiO$_2$ works better, and it is more effective in improving the gradual increase of the propellant's combustion.

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