Study on the spontaneous combustion risk and thermal decomposition characteristics of nitrocellulose

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Abstract. Nitrocellulose (NC) is an important raw material for industrial products and is widely used in military and civilian industries. However, accidents of nitrocellulose burning and explosion are common. In order to test the thermal hazards of NC and guide its safe production, storage, transportation and use, an auto-ignition temperature tester was used to study the effects of different factors (quality, heating rate, nitrogen content) on NC spontaneous combustion. And differential scanning Calorimetric method was used to test the heat flow curve of nitrocellulose at a heating rate of 5 ℃/min after adding different content of diphenylamine (DPA) to determine the thermal kinetic characteristics of the initial reaction exotherm temperature, maximum peak temperature, reaction enthalpy change, etc. The results show that after adding 1%, 2%, and 3% DPA, the ΔT of NC increases sequentially by 4, 3.12, and 3.10℃. DPA as a stabilizer has good compatibility with NC, which can effectively slow down the thermal decomposition speed of NC and prolong the storage life of NC.

1. Introduction
On August 12, 2015, a fire and explosion accident occurred in the dangerous goods warehouse of Ruihai Company in Tianjin Port, Binhai New Area, Tianjin, causing more than 900 casualties and huge economic losses[1]. After investigation, the direct cause of the accident was that the nitrocellulose was partially dry due to the loss of the wetting agent. Under the action of high temperature (weather) and other factors, the heat was accelerated to release the heat, and the accumulated heat spontaneously ignited, which caused an explosion.

Nitrocellulose (NC) usually forms a double-based system with nitroglycerin and is used as the main energy component for gun, gun launch, or rocket and missile propulsion[2][3]. Because it is prone to intramolecular oxidation-reduction reaction and is a polymer material, high molecular weight causes its poor thermal conductivity, it is easy to form heat accumulation thus causing thermal spontaneous combustion accident[4]. In order to suppress the autocatalysis of NC and improve its storage performance, the most effective way is to add a small amount of weakly basic chemical stabilizers, mainly including aniline, phenylurea and phenol ether[5][6][7].

In order to explore the danger of NC, many scholars have conducted a lot of research on the thermal decomposition characteristics and thermal decomposition mechanism of NC. Hu and others conducted a detailed study on the kinetics of nitrocellulose autocatalytic reaction using thermal analysis[8]. Wang studied the thermal decomposition mechanism of NC and found that the thermal decomposition gas phase products of NC include NO2, HCHO, CO, CO2, HCOOH and NO[9]. Zhao and Liu studied the effect of nano-iron oxide particles on the thermal decomposition of nitrocellulose. Nano-Fe2O3 particles all played a catalytic role in the thermal decomposition of NC, which could
promote the breaking of O–NO₂ bonds and accelerate the secondary autocatalytic reaction of NC[10]. However, few studies have been conducted on the spontaneous combustion temperature of nitrocellulose. In order to study the risk of spontaneous combustion of NC and the effect of the addition of alkaline stabilizers on the thermal decomposition of NC, this article uses a spontaneous combustion temperature tester and a DSC test system to investigate the effects of different factors on the spontaneous combustion properties of nitrocellulose and study the stability of DPA on NC. The influence of thermal behavior brings guiding suggestions to the production, storage and transportation of NC.

2. Experimental

2.1. Materials
Nitrocellulose, the nitrogen content is NC (11.0%), NC (11.9%), NC (12.5%), provided by Hengshui Jianmin Cellulose Co., Ltd., NC (13.5%), NC (14.0%) by Xi’an Modern Chemistry Research Institute. Diphenylamine (DPA), provided by Shanghai Aladdin Biochemical Technology Co., Ltd., analytically pure.

2.2. NC-DPA mixtures preparation
The mixed sample of DPA and NC was prepared by solvent mixing method, in which the mass ratio of DPA was 1%, 2% and 3%, respectively.

First choose a volatile solvent, which has good solubility in DPA and does not dissolve NC. Therefore, this experiment used absolute ethanol as the solvent. Dissolve DPA in absolute ethanol, then remove a certain amount of the above solution separately, add it to a special reaction tube equipped with a constant weight dry NC (nitrogen content 12.5%), and ultrasonically disperse the solution evenly on the NC surface. Then, vacuum dry to constant weight to obtain NC/DPA mixed samples with different mass ratios[11].

2.3. Equipment

2.3.1. AIT400. The AIT400 solid spontaneous combustion temperature tester used in this article is shown in Figure 1. It is produced by the Edison company and is mainly composed of a heating furnace, an operation rack, a test vessel bracket, an air flow meter, and a temperature sensor.

![Figure 1. AIT400 solid spontaneous combustion temperature tester](image-url)

According to the United Nations "Recommendation on the Transport of Dangerous Goods-Manual of Tests and Standards" Test N.4 [12] and GB/T 21756-2008[13] Determination of the relative spontaneous combustion temperature of solid substances of chemical products for industrial use, place the sample in an oven The temperature is raised to 400 °C at a specific heating rate, and the temperature of the sample and the oven are measured separately. When the sample self-heats ahead of
the oven temperature to reach 400 °C, the oven temperature is the auto-ignition temperature of the sample.

2.3.2. **Differential Scanning Calorimeter.** Differential scanning calorimeter (DSC), as shown in Figure 2, measures the relationship between temperature and heat flow related to the internal thermal transition of the material.

![DSC](image)

Figure 2. Differential Scanning Calorimeter

3. **Results and discussion**

3.1. **Influence of quality on spontaneous combustion temperature of NC**

Weigh the nitrocellulose with a nitrogen content of 11.90%, and test the nitrocellulose with different qualities 0.1g, 0.2g, 0.3g, 0.4g, 0.5g respectively. The results are shown in Figure 3 below.

![Temperature vs Quality](image)

Figure 3. Auto-ignition temperature--quality relationship diagram

It can be seen from Figure 3 above that the spontaneous ignition temperature at 0.1g is 189.71°C, 189.66°C at 0.2g, 189.54°C at 0.3g, 189.42°C at 0.4g, and 189.27°C at 0.5g. The spontaneous ignition temperature of a substance is affected by its own physical and chemical properties on the one hand, and by its storage environment on the other hand. With the increase of quality, the spontaneous combustion temperature of nitrocellulose does not change much, but there is a tendency to decline slowly. Due to the spontaneous ignition temperature test, the space density of the sample with more mass becomes larger, the rate of heat absorption and release of objects is affected, and the temperature of the sample itself and the space temperature are not smoothly exchanged, so that the sample temperature is always higher than the test space temperature. It is more prone to spontaneous combustion. This is also in accordance with the regulations for nitrocellulose storage when ventilating and prohibiting large piles.
3.2. Effect of nitrogen content on spontaneous combustion temperature of NC

Put 20 mm cubes containing nitrocellulose with five different nitrogen contents (11.0%, 11.9%, 12.5%, 13.5%, 14.0%) into the oven, and set the oven temperature at a rate of 0.5°C/min up to 400 ℃, compare the spontaneous combustion temperature of different nitrogen content and different quality of nitrocellulose.

![Spontaneous combustion temperature diagram of different nitrogen content with quality](image)

It can be seen from Figure 4 that as the nitrogen content of nitrocellulose continues to increase, the temperature of its spontaneous ignition point gradually decreases. When the nitrogen content is 12.5%, there is a sudden change. When the mass reaches 0.2g, temperature fluctuations begin to appear. As the mass increases, the spontaneous ignition temperature also gradually decreases. For five types of nitrocellulose with different nitrogen contents and different qualities, the lowest spontaneous ignition temperature is 188.12°C and the highest spontaneous ignition temperature is 190.11°C. The overall difference is close to 2°C.

3.3. Effect of heating rate on spontaneous combustion temperature of nitrocellulose

Nitrocellulose will thermally decompose at a certain heating rate when subjected to external energy, and the change of external energy will affect the change of heating rate. When nitrocellulose is decomposed at different heating rates, its thermal characteristics will also be different. Weigh 0.2 g of nitrocellulose to conduct experiments at a heating rate of 2, 5, 10, and 20 °C/min. The experimental results are shown in Figure 5.

![Spontaneous combustion temperature--heating rate relationship diagram](image)

It can be seen from Figure 5 that as the heating rate increases, the spontaneous ignition temperature of NC tends to decrease slowly. NC has a clear limit on the maximum stacking volume during transportation and storage. This is mainly because the change of the sample volume within a certain volume of the sealed environment will have a great impact on the thermal decomposition.
characteristics of nitrocellulose. If the storage capacity of nitrocellulose, excessive heat will increase its own heat dissipation. When the heat dissipation is insufficient, heat accumulation will form and reduce the thermal safety of nitrocellulose.

3.4. DSC analysis

DSC is a common non-isothermal thermal analysis method.[14] Put the mixed samples of pure NC and DPA with a mass ratio of 1%, 2%, and 3% into the crucible respectively, seal them with a prototype and place them in the furnace, and conduct the test at a temperature of 5 °C/min. The DSC curve of the heat flux of the mixed samples with the mass ratios of 1%, 2% and 3% of pure NC and DPA obtained by the test as a function of temperature is shown in Fig. 6 below. Table 1 is the corresponding thermal decomposition characteristic data, where $T_0$ is the initial decomposition temperature, $T_m$ is the maximum peak temperature, $\Delta T$ is the difference between the maximum peak temperature and the initial decomposition temperature, and $\Delta H$ is the reaction enthalpy change. $\Delta T$ corresponds to the time required from the start of the reaction to the maximum reaction rate, so the speed of the reaction and the catalytic effect can be judged from this.

![DSC curve at 5 °C/min heating rate](image)

**Table 1.** Thermodynamic parameters of mixtures of DPA and NC in different ratios

| Sample         | $T_0$/°C | $T_m$/°C | $\Delta T$/°C | $\Delta H$/Wg⁻¹ |
|----------------|----------|----------|---------------|-----------------|
| NC             | 181.24   | 197.34   | 16.10         | 474.38          |
| NC/DPA (1%)    | 178.00   | 198.10   | 20.10         | 475.02          |
| NC/DPA (2%)    | 178.43   | 197.65   | 19.22         | 475.47          |
| NC/DPA (3%)    | 178.51   | 197.71   | 19.20         | 476.83          |

The test curve protrudes upward as an exothermic peak, and downward as an endothermic peak. It can be seen from Fig. 6 that the DSC curves of pure NC and NC/DPA mixtures with different mass ratios have an obvious exothermic peak. In addition, it can be seen from Table 1 that after the addition of 1%, 2%, and 3% DPA, the initial temperature $T_0$ of the NC is advanced to varying degrees, respectively, 3.24, 2.81, 2.73 °C, the maximum peak temperature $T_m$ of the NC Different degrees of lag, respectively lag 0.76, 0.31, 0.37°C. According to the NATO Standardization Agreement STANAG 4147, after adding DPA, the temperature change of the NC exothermic peak is less than 4°C, so it can be confirmed that DPA and NC have good compatibility.

It can be seen from Table 1 above that after adding 1%, 2%, and 3% DPA, respectively, the reaction enthalpy change $\Delta H$ of the NC increases slightly, but the change range is less than 2Wg⁻¹, which can be changed within the allowable range of the error. It is believed to be caused by the accidental nature of the experiment. In addition, the difference $\Delta T$ between the peak temperature and the initial temperature increases by 4, 3.12, and 3.10°C, respectively. It shows that DPA plays a catalytic role in the thermal decomposition process of NC, and can effectively slow down the thermal decomposition.
speed of NC, and there is no linear relationship between the reduction effect and the amount of DPA added.

4. Conclusion
In this paper, through the NC spontaneous combustion temperature test, it was found that the quality, nitrogen content, and different heating rates of the NC all have a certain effect on the spontaneous combustion temperature, which provides a reference for the storage of the NC.

The effect of adding DPA on the thermal decomposition of NC was further studied by DSC experiment. According to the data, after adding 1%, 2%, and 3% DPA, the $\Delta T$ of NC increases by 4, 3.12, and 3.10°C, respectively. It was found that DPA can effectively delay the thermal decomposition rate of NC, and there is no obvious linear relationship between the degree of delay and the amount of DPA.

The change of initial decomposition temperature and peak decomposition temperature can confirm that DPA has good compatibility with NC, which confirms the feasibility of DPA as a traditional stabilizer used to store NC.

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