

# Study on the spontaneous ignition of cellulose nitrate

## Effect of the type of storage atmosphere (II)

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### Abstract

On the spontaneous ignition of NC, the effect of water and oxygen and that of nitrogen dioxide and oxygen were investigated by observing the thermal behavior and structural change. As the result, it was observed that hardly any exothermic degradation took place only by nitrogen dioxide nor water; hardly any exothermic degradation took place in atmospheres without oxygen. From this, it was suggested that exothermic degradation was due to oxygen and it was promoted by nitrogen dioxide and water. The results indicated that auto-oxidation caused by atmospheric oxygen could explain the spontaneous ignition mechanism of NC.

### 1. Introduction

Cellulose nitrate (NC) is a very valuable material that is used for rocket propellants, ballistics, and dynamite, among other uses. However, it is one of the most unstable energetic materials in terms of spontaneous ignition. If it is mishandled, spontaneous ignition may occur and cause a terrible accident.

In previous studies<sup>1,2)</sup>, it has been believed that NC spontaneously ignites due to the accumulation of heat in the degradation reaction with nitrogen dioxide produced by thermal O-NO<sub>2</sub> bond scissions or hydrolysis by water which existed in NC. However, after observing the FT-IR spectrum change and the thermal behavior in nitrogen, dried air, oxygen, nitrogen dioxide, and nitric oxide, we reported<sup>3-5)</sup> that hardly any exothermic degradation took place in atmospheres without oxygen. These results indicated that the auto-oxidation in which oxygen participated could not be disregarded and that it, rather than the reaction with nitrogen dioxide, directly contributed to spontaneous ignition. Thus, the spontaneous ignition mechanism of NC is very complicated and is not yet fully understood. Therefore, its clarification is necessary for the purposes of safe storage.

The purpose of this study is to clarify the spontaneous ignition mechanism of NC and suggest a stabilization method and an evaluation method based on it. In this paper, we report the effect of water and oxygen and that of

nitrogen dioxide and oxygen by observing the thermal behavior and structural change.

### 2. Experimental

#### 2.1 Preparation

##### 2.1.1 Drying of NC

NC in 2-propanol (nitrogen content, 12 w%; Aldrich Co.) was dried *in vacuo* at 25 °C for 3-4 days. Particles with a diameter of less than 50-100 μm were prepared with a sieve.

##### 2.1.2 NC in 4.5%nitrogen dioxide/air

NC prepared in Section 2.1.1 was put in vessels made of stainless steel. The air in the vessel was removed *in vacuo* and then replaced by 4.5%nitrogen dioxide/air (Suzuki Shokan Co., Ltd.). This procedure was repeated 4-5 times to ensure complete replacement. Figure 1a is an illustration of this concept.

##### 2.1.3 NC in air/water

The NC prepared in Section 2.1.1 was allowed to stand for more than 6 hours in a glove box under a condition of relative humidity of 100%, and NC was saturated with moisture. Inside the glove box, the NC that had absorbed moisture was put in a vessel made of stainless steel, and the vessel was sealed. Figure 1b is an illustration of this concept.

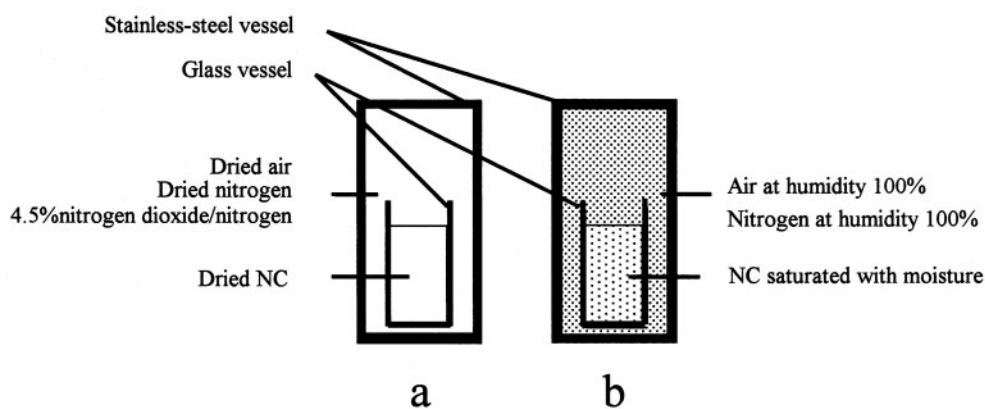


Fig. 1 Basic concept of samples.

### 2.1.4 NC in nitrogen/water

Using an impinger, the atmosphere in the glove box was made to have a condition of relative humidity of 100% in the nitrogen atmosphere. Inside the glove box, the NC prepared in Section 2.1.1 was saturated with moisture, as in Section 2.1.3. The NC that had absorbed moisture was put in the vessel made of stainless steel, and the vessel was sealed. Figure 1b is an illustration of this concept.

### 2.1.5 Control sample

The NC prepared in Section 2.1.1 was put in vessels made of stainless steel. The air in the vessel was removed *in vacuo* and then replaced by dried nitrogen and dried air (Suzuki Shokan Co., Ltd.). This procedure was repeated 4-5 times to ensure complete replacement. This vessel was used as the control sample. Figure 1a illustrates this concept.

### 2.2 Measurement of decomposition temperature

The decomposition temperature of NC (50mg) prepared in Section 2.1.3-5 in each atmosphere was measured by C-80 (Setaram Co.; heating rate:  $0.2 \text{ K}\cdot\text{min}^{-1}$ ).

### 2.3 Storage at 60°C

The NC (100mg) prepared in Section 2.1.3-5 was stored at 60 °C for 1-60 days. Fourier transform infrared spectroscopy (FT-IR; Shimadzu Co., FT-IR 8000) was performed by the KBr method to analyze the structure change of NC after storage.

### 2.4 Storage at 120°C

The NC (50mg) prepared in Section 2.1.2-5 was stored in C-80 at 120 °C to observe the thermal behavior during isothermal storage. In addition, the FT-IR spectrum was observed after storage.

## 3. Results and discussion

### 3.1 Effect of nitrogen dioxide and oxygen

The thermal behavior during storage was observed in both 4.5% nitrogen dioxide/air and dried air. As shown in Fig. 2, the time to reach an exothermic peak was approximately 4 hours in 4.5% nitrogen dioxide/air, compared with approximately 7-9 hours in dried air. From this result, it was suggested that NC in 4.5% nitrogen dioxide/air was less stable than that in dried air.

Furthermore, in a previous paper<sup>3)-5)</sup>, we reported that an exothermic peak was not observed in 4.5% nitrogen dioxide/nitrogen for more than 23 hours under similar condition. These results indicated that exothermic degradation was caused by oxygen and was accelerated by nitrogen dioxide.

### 3.2 Effect of water and oxygen

#### 3.2.1 Amount of moisture absorption

As shown in Fig. 3, NC absorbed 2.7 % of its weight in moisture, and no further moisture absorption was observed. The moisture content, 2.7%, was neither influenced by the amount of NC nor the configuration of the vessel in which NC was put. It was experimentally known that the degree of moisture absorption (W%) was a function of the nitrogen content (N%) and it was represented in  $W\% = 14.6 \cdot N\%^2$ . The degree of moisture absorption observed in this study agreed well with the degree estimated by the function.

#### 3.2.2 Decomposition temperature

The decomposition temperature in nitrogen/water and

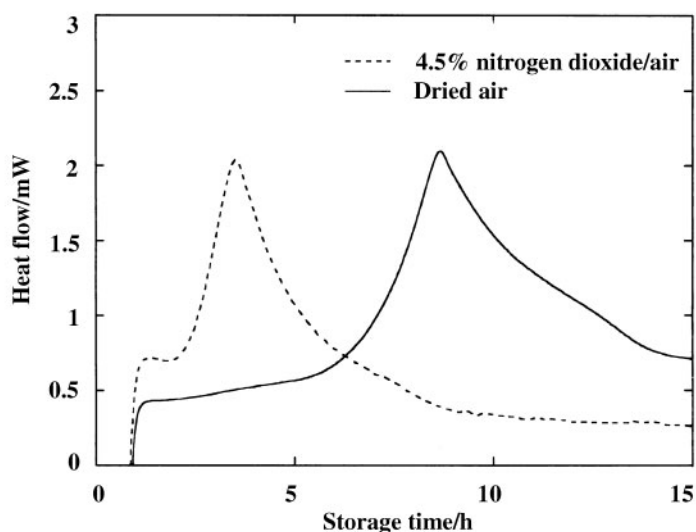


Fig. 2 Thermal behavior of NC during isothermal storage in various atmospheres (Storage temperature: 120 °C).

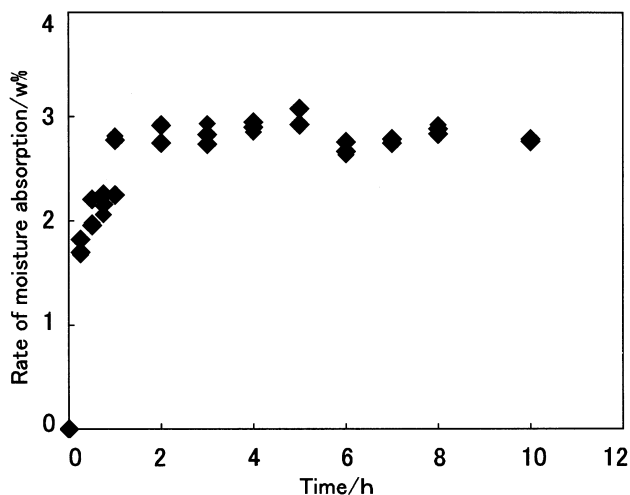


Fig. 3 Moisture content with time.

air/water atmospheres was measured by C-80 (heating rate: 0.2K·min), and the results were compared with those in dried nitrogen and dried air.

As shown in Fig. 4, since the decomposition temperature in a nitrogen/water atmosphere was 163 °C, it is similar to that in the case of dried nitrogen. This indicated that exothermic degradation was not promoted solely by water. On the other hand, two exothermic peaks were observed in the air/water atmosphere. The decomposition temperature of the first peak was 80 °C, and that of the second peak was 103 °C. The decomposition temperature, which was 158 °C in dried air, extraordinarily decreased with the addition of water. From this, it was suggested that exothermic degradation was caused by oxygen in air and was accelerated by water.

### 3.2.3 Isothermal storage

The thermal behaviors in nitrogen/water and air/water atmospheres were measured by C-80 (isothermal storage: 120 °C) and were compared with that in dried nitrogen and dried air.

As mentioned above, NC in air/water decomposed before reaching 120 °C. On the other hand, the thermal behavior did not change in nitrogen/water for more than 23 hours (Fig. 5).

Urbanski<sup>6)</sup> reported that the pH of nitric esters became lower with storage time. Moreover, Nakamura<sup>7) 8)</sup> et al. reported that the acid content became higher with storage time. From such previous studies, it was expected that the nitric ester group would be hydrolyzed by water in NC or atmosphere. However, the results of this study suggested

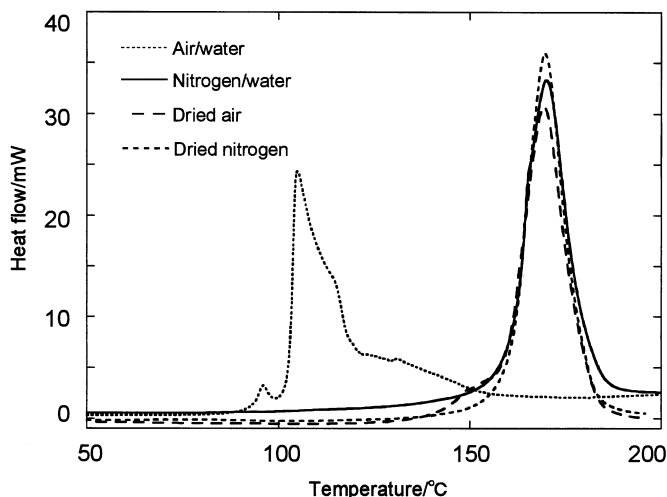


Fig. 4 Thermal decomposition behavior of NC in various atmospheres (Heating rate:0.2Kmin<sup>-1</sup>).

that hardly any exothermic degradation took place by hydrolysis solely and that it was accelerated by a reaction related to oxygen and water.

Subsequently, the FT-IR spectra after storage in nitrogen/water and air/water atmospheres were measured and were compared with those in dried nitrogen and dried air.

As shown in Table 1, while no change in the FT-IR spectrum was observed for more than 14 days in nitrogen/water, it was observed within 7 days in an air/water atmosphere. Additionally, the FT-IR spectrum did not change for 30 days in dried air. These results indicated that the degradation by oxygen was, as in the case of storage at 120 °C, accelerated by water in spite of storage

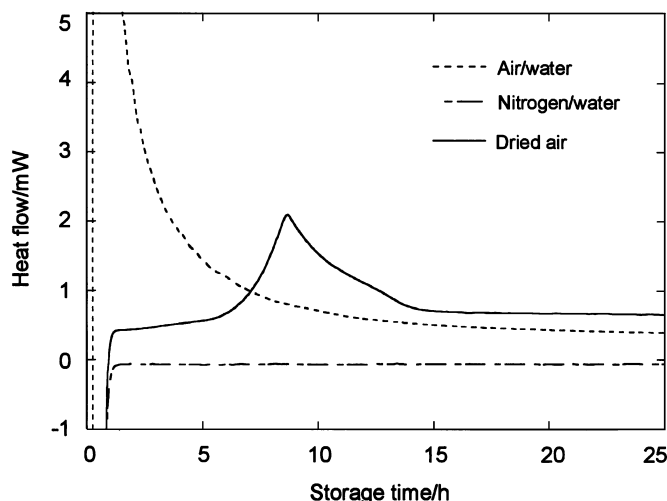


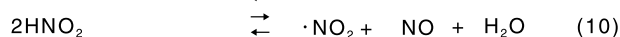
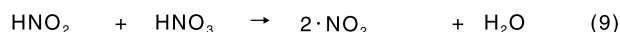
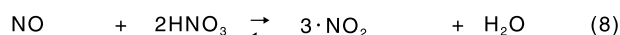
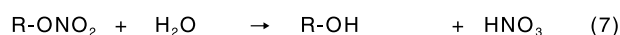
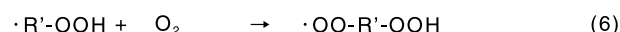
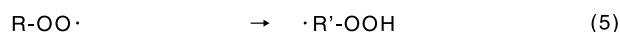
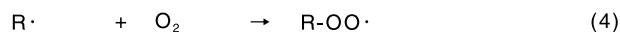
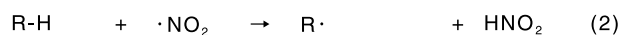
Fig. 5 Thermal behavior of NC during isothermal storage in various atmospheres (Storage temperature:120 °C).

Table 1 Decomposition temperature and results of the 60 °C -storage experiment.

Storage atmospheres	Time up to the FT-IR spectrum change	Color change after storage	Decomposition temperature/
Dried nitrogen	No change (60 days)	No change	162
Dried air	30 ~ 60 days	Black	158
Nitrogen/water	No change (60 days)	No change	163
Air/water	~7 days	Pale yellow	80 and 103

at low temperature.

### 3.3 Estimation of the spontaneous ignition mechanism



In previous study<sup>9)10)</sup>, the decomposition mechanism of nitric ester was estimated. In this mechanism, nitric esters first decompose, and nitrogen dioxide and the alkoxy radical are generated following formula 1. Subsequently, nitrogen dioxide and the alkoxy radical abstract hydrogen in intramolecular reaction, and an alkyl radical is generated, as shown in formulae 2 and 3. In the auto-oxidation mechanism<sup>11)12)</sup>, when oxygen exists within the system, an oxygen molecule reacts with the alkyl radical generated in formulae 2 and 3, and an alkyl peroxy radical is generated, as shown in formula 4. The alkyl peroxy radical, as shown in formula 5, abstracts intramolecular hydrogen, and a hydroperoxy alkyl radical is generated. Chain propagation is caused by such reactions, and ignition consequently occurs. The reactions described in formulae 1, 2, and 3 do not participate in ignition, but they occur before the ignition and cause to accumulate alkyl radicals. Chain propagation occurs by the reactions shown in formulae 4-6, and the chain propagation causes ignition.

In a previous study<sup>3)5)</sup> and this study, it was observed that hardly any exothermic degradation took place in atmospheres without oxygen, and that exothermic degradation was not caused in a nitrogen dioxide/nitrogen atmosphere and was accelerated in a nitrogen dioxide/air atmosphere. In addition, Nakamura<sup>8)</sup> et al. suggested that peroxide was generated during storage. In consideration of these results, the spontaneous ignition mechanism of NC may be explained by the auto-oxidation mechanism.

Additionally, when water exists within the system, the nitric ester group is hydrolyzed by water in NC or atmosphere, and nitric acid is generated (formula 7). With regard to oxidation with nitric acid<sup>13)</sup>, nitrogen dioxide is remarkably generated by the reactions described in formulae 8, 9, and 10. When the concentration of nitrogen dioxide is higher, the reaction described in formula 2 is accelerated, and the subsequent chain propagation is also accelerated. Similarly, the results of this study indicated that exothermic degradation was accelerated when both water and oxygen were present. The effect of water on the spontaneous ignition of NC may be explained by the oxidation mechanism with nitric acid.

## 4. Conclusion

The purpose of this study was to clarify the spontaneous ignition mechanism of NC. In this paper, we reported the effect of water and oxygen and that of nitrogen dioxide and oxygen by observing the thermal behavior and structural change.

Degradation in 4.5%nitrogen dioxide/air was more accelerated than that in dried air. Additionally, a previous study also reported that hardly any exothermic degradation took place in 4.5%nitrogen dioxide/nitrogen<sup>3)5)</sup>. These results indicate that exothermic degradation was caused by oxygen and was promoted by nitrogen dioxide.

No change in thermal behavior was observed during 120°C-isothermal storage in a nitrogen/water atmosphere, as in the case of that in dried air. In addition, the decomposition temperature in a nitrogen/water atmosphere was similar to that in dried air. These results suggested that hardly any exothermic degradation took place by hydrolysis or acid catalytic activity alone.

The decomposition temperature in an air/water atmosphere was lower than that in dried air or dried nitrogen, and exothermic degradation in air/water was accelerated even at low temperature. These results indicated that exothermic degradation was caused by oxygen and was promoted by water.

Consequently, it was suggested that the spontaneous ignition mechanism of NC may be explained by the auto-oxidation mechanism, and effect of water, which promoted the ignition, may be explained by the oxidation with nitric acid.

This study is now in progress. We confined discussion of the mechanism to qualitative evaluation in this paper. So it will be necessary that the mechanism be kinetically investigated.

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## ニトロセルロースの自然発火に関する研究 貯蔵雰囲気の影響 第2報

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4.5%二酸化窒素/空気, 窒素/水, 空気/水雰囲気中でのニトロセルロースの構造の変化及び熱的挙動を追跡し, ニトロセルロースの自然発火に及ぼす水と酸素の相互作用及び二酸化窒素と酸素の相互作用について考察した。4.5%二酸化窒素/空気雰囲気では, 発熱ピークに達するまでの時間が若干短くなり, 二酸化窒素は, 酸素による発熱分解を促進させる効果があることが確認された。また, 酸素が存在しない場合, ニトロセルロースが十分に吸湿していても熱的变化は観察されず, また分解開始温度も乾燥窒素雰囲気と同程度であった。このことから, 加水分解ひいては, 酸による触媒作用のみでは発熱しないことが示唆された。空気/水雰囲気中では, 乾燥窒素或いは乾燥空気と比較して分解開始温度が大幅に低下し, かつ60℃という比較的低温でも分解が促進した。以上の結果から自動酸化反応によりニトロセルロースの自然発火も説明できる可能性が示唆された。

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