

Study on the spontaneous ignition of cellulose nitrate

Effect of the type of storage atmosphere (I)

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The effects of the type of storage atmosphere used on the spontaneous ignition of cellulose nitrate (NC) were investigated. Nitrogen dioxide, nitric oxide, oxygen, nitrogen, and dried air were used as storage atmospheres. Exothermic degradation was observed to be accelerated in oxygen. In contrast, no degradation was observed with nitrogen. These results indicate that exothermic degradation by oxygen is related to spontaneous ignition. In addition, when low concentrations of nitrogen dioxide were used, there was no exothermic degradation. These results suggest that nitrogen dioxide contributes little to the generation of heat.

1. Introduction

Cellulose nitrate (NC) is quite valuable when used as a propellant in rockets and ballistics. However, it is quite unstable and subject to spontaneous ignition. When NC is mishandled, spontaneous ignition may occur and cause serious accidents. There have been many accidental explosions caused by the spontaneous ignition of NC.¹⁾ In order to solve such problems, spontaneous ignition has been studied. However, accidents relating to the spontaneous ignition of NC continue to occur.¹⁾

In previous studies,^{2) 3)} it has been assumed that NC spontaneously ignites due to heat accumulation of degradation reactions with nitrogen dioxide produced by thermal O-NO₂ bond scissions. Recently, it was also suggested that NC spontaneously ignites in the presence of oxygen in air.^{4) 7)}

The spontaneous ignition mechanism is very complicated, and its clarification would be valuable to achieve the objective of safe storage.

The purpose of this study is to clarify the spontaneous ignition mechanism of NC and to suggest a method for stabilization and evaluation. In this paper, the effects of the reaction atmosphere used on the spontaneous ignition of NC are reported.

2. Experimental

2. 1 Preparation

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. NC was put in vessels made of stainless steel. The air in each vessel was removed *in vacuo* and then replaced by nitrogen dioxide, nitric oxide, oxygen, nitrogen, or dried air (Suzuki Shokan Co., Ltd). This procedure was repeated 4–5 times to ensure complete replacement.

2. 2 Measurement of the decomposition temperature

The decomposition temperature of NC prepared in 2.1 was measured by C-80 (0.2 K·min⁻¹).

2. 3 Storage at 60°C

The NC prepared in 2.1 was stored at 60 °C for 1–60 days. Fourier transformation infrared spectroscopy (FT-IR; Shimadzu Co., FT-IR 8000) was performed by the KBr method to analyze the structural change of NC after storage.

2. 4 Storage at 120 °C

The NC prepared in 2.1 was stored in C-80 (Setaram Co.) at 120 °C to observe thermal behavior during isothermal storage. In addition, the FT-IR spectrum was observed after storage.

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Table 1 Time period of the FT-IR spectrum change, color change, and decomposition temperature in various atmospheres.

Atmospheres	Time period of FT-IR spectrum change	Color change after storage	Decomposition temperature / $^{\circ}\text{C}$
Nitrogen	No change (60 days)	No change	162
Dried air	30~60 days	Black	158
Oxygen	4 days~	Black	147
Nitric oxide	No change (60 days)	No change	—
Nitrogen dioxide	Soon after storage	Pale yellow	—

3. Results and Discussion

3. 1 Effect of oxygen

3. 1. 1 Decomposition temperature

The decomposition temperature measured by C-80 ($0.2\text{ K}\cdot\text{min}^{-1}$) is shown in Fig. 1 and Table 1. The decomposition temperature in oxygen was $147\text{ }^{\circ}\text{C}$, and, in nitrogen, $162\text{ }^{\circ}\text{C}$. A comparison of the decomposition temperature in oxygen and nitrogen showed that the decomposition temperature was lower by 15 K than that in nitrogen. In addition, a small exothermic peak was observed at 150°C in dried air. This suggests that the decomposition temperature tends to become lower with oxygen.

3. 1. 2 Time required for the FT-IR spectrum and the color to change

The time required for the FT-IR spectrum and the color to change was observed at $60\text{ }^{\circ}\text{C}$. The results are summarized in Table 1. No change was observed in the FT-IR spectrum or in the color of the NC stored in nitrogen for 60 days. In contrast, an FT-IR spectrum change and the darkening of the NC were observed in oxygen in 4 days and, in dried air, within 60 days.

The thermal behavior was examined during storage at $120\text{ }^{\circ}\text{C}$ by C-80 to investigate the reaction between oxygen and NC. As shown in Fig. 2, the thermal behavior and FT-IR spectrum did not change in nitrogen for more than 23 hours. On the other hand, two exothermic peaks were observed for 2–8 hours in oxygen. Similarly, an exothermic peak was observed in dried air after approximately 10 hours. Exothermic behavior in oxygen was similar to that in dried air in terms of the 2-head peak. Therefore, the results suggest that the reaction with oxygen is more strongly related to the generation of heat.

3. 1. 3 FT-IR spectrum

NC in oxygen was stored in C-80 at $120\text{ }^{\circ}\text{C}$, and an

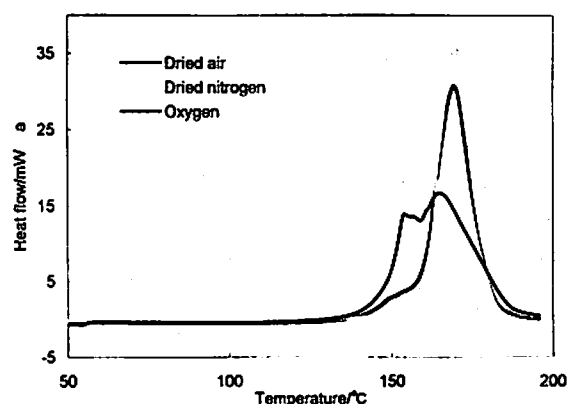


Fig.1 Thermal behavior in nitrogen, oxygen, or air
Heating rate: 0.2 Kmin^{-1} (C-80).

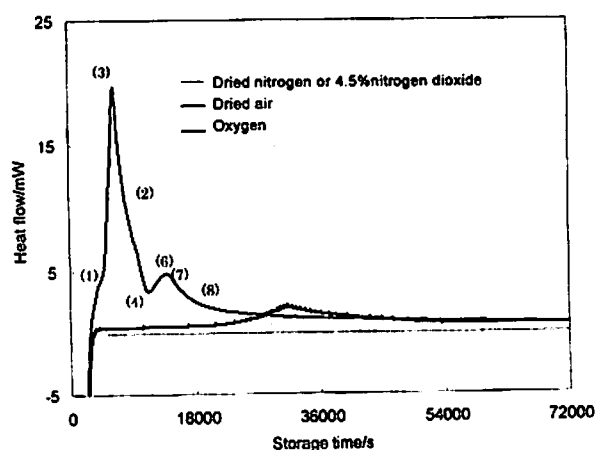


Fig.2 Thermal behavior in nitrogen, oxygen, air, or
nitrogen dioxide (4.5% nitrogen balance)
Isothermal storage: 120°C (C-80).

FT-IR spectrum change during exothermic degradation was then observed. This result is shown in Fig. 3. From those FT-IR spectra, the 1280 cm^{-1} and 1650 cm^{-1} absorption bands (O-NO₂ bond) and the 830 cm^{-1} absorption band (O-N bond) decreased, and the 1750 cm^{-1} absorption band (carbonyl group) and 3500 cm^{-1} absorption band (-OOH and -OH group) increased with

an increase in the storage time. These results suggest that the nitric group disappeared and that peroxide, or other OH groups and carbonyl groups, was formed.

The absorption band at 1400 cm^{-1} was attributed to nitrogen dioxide, which was released from NC and adsorbed on potassium bromide as a base matrix. To confirm this hypothesis, an FT-IR measurement was carried out for potassium bromide, which was exposed to nitrogen dioxide. As shown in Fig. 3, an absorption band at 1400 cm^{-1} was observed. Hence, the absorption band at 1400 cm^{-1} was considered to be characteristic of nitrogen dioxide, which was adsorbed on potassium bromide.

3. 1. 4 Effect of the partial pressure of oxygen

Thermal behavior was examined by C-80 during storage at $120\text{ }^\circ\text{C}$ in various partial pressures of oxygen to investigate the relationship between partial pressure of oxygen and the exothermic degradation of NC. As shown in Figs. 4 and 5, the time to reach the maximum rate decreased, and the maximum rate increased with an increase of the partial pressure of oxygen. This tendency was distinct at a low partial pressure of oxygen. For

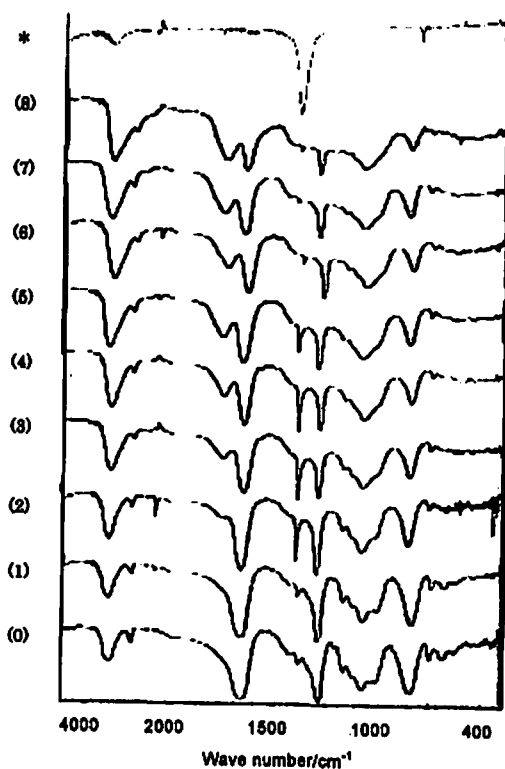


Fig.3 FT-IR spectrum after storage in oxygen. The number corresponds to that in Fig. 2. *Absorption of potassium bromide exposed to nitrogen dioxide.

instance, when the partial pressure of oxygen was lower than 5 %, no exothermic peak was observed for more than 23 hours, and no change was observed in the FT-IR spectrum of NC after storage. Hence, if the partial pressure is low enough, exothermic degradation of NC hardly occurs.

3. 2 Effect of nitric oxide

Previous studies^{5) 6)} suggested that the only gas evolved from NC is nitric oxide. Thus, an FT-IR spectrum was examined after storage in nitric oxide at $60\text{ }^\circ\text{C}$. No change in the FT-IR spectrum was observed for 60 days. The FT-IR spectrum in oxygen, as mentioned above, changed in 4 days, which suggests that the reactivity of nitric oxide to NC was much lower than that of oxygen.

3. 3 Effect of nitrogen dioxide

The FT-IR spectrum was observed after storage in

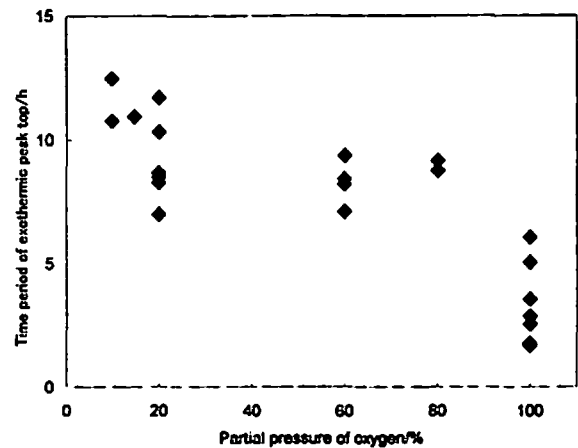


Fig.4 Time period up to the exothermic peak top for the partial pressure of oxygen.

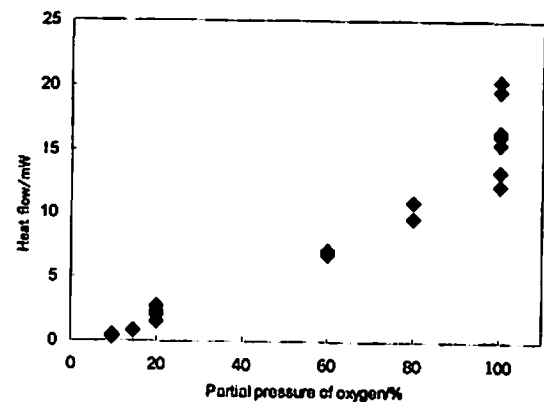


Fig.5 The maximum rate for the partial pressure of oxygen.

nitrogen dioxide at 60 °C. As a result, a change in the FT-IR spectrum was observed immediately after storage. Therefore, nitrogen dioxide may participate in the degradation NC. However, the concentration of nitrogen dioxide is very low in the case of initial degradation during actual storage. Therefore, storage in nitrogen dioxide at low concentration (4.5 % nitrogen balance) was carried out on the assumption of actual storage. No change in the FT-IR spectrum was observed for 60 days at 60 °C, indicating that NC is comparatively stable at such a low concentration of nitrogen dioxide.

In addition, the thermal behavior was examined during storage at 120 °C in nitrogen dioxide at a low concentration (4.5 % nitrogen balance). As shown in Fig. 2, the thermal behavior during storage did not change for more than 40 hours, and no change in the FT-IR spectrum was observed after storage. Therefore, it was concluded that nitrogen dioxide scarcely participates in the heat generation of NC.

3. 4 Effect of water

Storage was carried out in dried air and atmospheric air at 60 °C. A change in the FT-IR spectrum was observed after storage in dried air for 60 days. On the other hand, the FT-IR spectrum in atmospheric air changed after approximately 14 days. It was assumed that the degradation of NC was promoted by water. However, no change was observed for 14 days when distilled water was added although an FT-IR change was observed within 14 days in atmospheric air.

4. Conclusion

The effects of the storage atmosphere used on the spontaneous ignition of NC were investigated. Nitrogen dioxide, nitric oxide, oxygen, nitrogen, and dried air were used as storage atmospheres. FT-IR spectroscopy was performed after storage, and thermal behavior was observed by C-80 during storage.

No changes in the FT-IR spectrum or color were

observed for 60 days during the storage in nitrogen at 60 °C. In contrast, changes in the FT-IR spectrum were observed in oxygen after 4 days, and, in dried air, within 60 days. The thermal behavior during storage at 120 °C in nitrogen remained stable for more than 23 hours, and no change in the FT-IR spectrum was observed during that time. On the other hand, in nitrogen, two exothermic peaks were observed within 2–8 hours. These results indicate that the reaction with oxygen is related to spontaneous ignition. Additionally, the degradation of NC was also accelerated by nitrogen dioxide. However, when the concentration of nitrogen dioxide was low enough, the thermal behavior during storage did not change for more than 40 hours. No change in the FT-IR spectrum after storage was observed. Therefore, it can be concluded that nitrogen dioxide scarcely participates in the exothermic degradation. Similarly, it was observed that NC did not degrade in nitric oxide.

Other aspects of this study will be continued. The effects of water were barely considered in the current study. Therefore, more research will be required.

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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1報)

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ニトロセルロースの自然発火に及ぼす貯蔵雰囲気(二酸化窒素, 一酸化窒素, 酸素, 窒素, 空気)の影響を FT-IR スペクトル及び C-80 による熱分析により追跡した。その結果, 窒素雰囲気と比較して, 酸素及び乾燥空気雰囲気中で劣化は促進した。したがって, NC の自然発火は, 酸素が大きく寄与するものと考えられる。大過剰な二酸化窒素雰囲気中では, NC の劣化は, 促進するが比較的低濃度(4.5%)の場合には, 酸素及び乾燥空気雰囲気中よりも劣化は, 抑制され, 実際の貯蔵雰囲気における分解初期の段階では, 酸素の寄与が大きいものと考えられる。

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