

Stabilization of nitrocellulose by diphenylamine and phenol compound

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Abstract

The thermal behavior of nitrocellulose containing diphenylamine (DPA) or 1,1,3-tri-(2-methyl-4-hydroxy-5-tert-butyl-phenyl)-butane (BP_{less}) was observed during the isothermal storage at 393 K using C80. The result indicated that each stabilizer decreased the maximum heat release rate and increased the induction period of the heat release of NC. And the maximum heat release rate and the induction period were dependent on the amount of the stabilizer.

Keywords: Nitric ester, Nitric acid ester, Antioxidant, Self-ignition, Autoxidation

1 Introduction

Nitrocellulose (NC) is widely used as an ingredient of propellants and dynamites in spite of its unstable characteristic such as spontaneous ignition. The spontaneous ignition of NC has caused serious accidents, which have been reported even in recent years¹⁾.

The spontaneous ignition mechanism of NC has been investigated for a long time. Some reviews^{2), 3)} suggested that the spontaneous ignition was caused by the reaction between NC and NO₂. The NO₂ originated from the O-NO₂ bond scissions or the hydrolysis.

In order to stabilize NC, the stabilizer such as diphenylamine (DPA), its derivatives, or ethyl centralite (EC) is added. As for DPA stabilization mechanism, it is described that DPA traps NO₂ and terminates the exothermic reaction since DPA is easy to react with NO₂ and that produces its nitro or nitroso- derivatives²⁾⁻⁴⁾. However, it was thought that its reaction mechanism is not fully understood yet since even the heat release mechanism of sole NC was quite complicated. In addition, the previous study suggested that there was possibility that DPA has comparatively low stabilization effect on the smokeless

powder^{5), 6)}. Therefore, not only the stabilization mechanism but also the stabilization effect on the heat release of NC is not fully understood yet. In this way, the investigation of the NC stabilization effect by the existing stabilizer is required.

On the heat release mechanism of NC, we recently reported that an exothermic reaction of NC hardly took place without O₂⁷⁾⁻⁹⁾ during the isothermal storage of NC. The results implied that O₂, rather than NO₂, directly contributed to the exothermic reaction. From this, we proposed the spontaneous ignition mechanism of NC as shown in the reaction scheme. In this reaction scheme, NO₂ and RO·, which is generated in R. 1-5, abstract the hydrogen from NC (R. 6 and 7)¹⁰⁾⁻¹⁵⁾. The generated R· and atmospheric O₂ start the propagation called autoxidation (R. 8 and 9)^{16), 17)}. It is considered that the autoxidation (R. 8 and 9) and the subsequent termination process (R. 10) are quite conducive to heat release since each reaction in those processes releases more reaction heat than that in initiation process.

When autoxidation contributed to the heat release of NC based on our previous research, phenol compound are

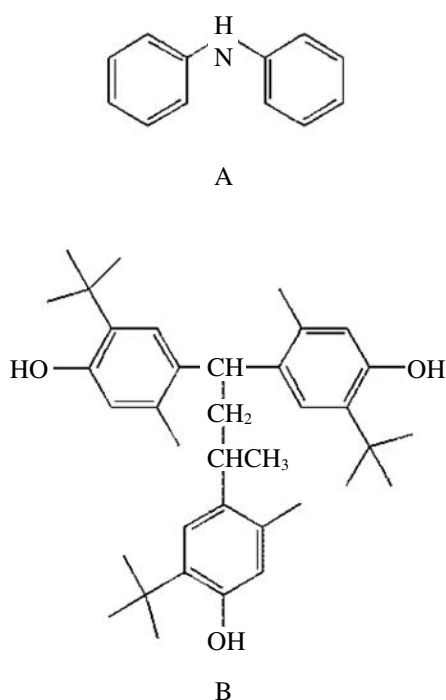
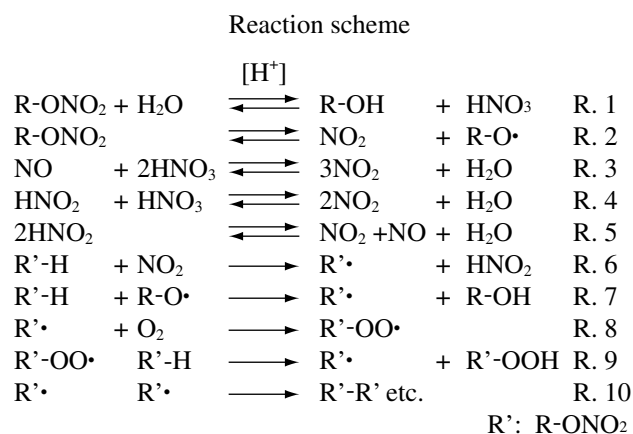


Fig. 1 Chemical structures of DPA and BP_{1ess} .
A: DPA, B: BP_{1ess}

expected to stabilize NC since it interfere with the autoxidation. These antioxidants are anticipated to be a novel stabilizer for preventing the spontaneous ignition of NC.

The purpose of this study is to estimate the effects of existing stabilizers and phenol compounds on the NC stability. In the experiments, the thermal behavior was monitored using C80 during isothermal storage.

2 Experimental

2.1 Samples

NC in 2-propanol (nitrogen content, 12 wt.%; Sigma-Aldrich Corp.) was dried under vacuum at approximately 298 K for 3-4 days. Particles with a diameter of less than 75-106 μm were prepared by sieving, and then the NC was again dried under the same conditions for 1-2 days. As a stabilizer, DPA (Sigma-Aldrich Corp.) or 1,1,3-tri(2-methyl-4-hydroxy-5-tert-butyl-phenyl)-butane (BH_{1ess} ;

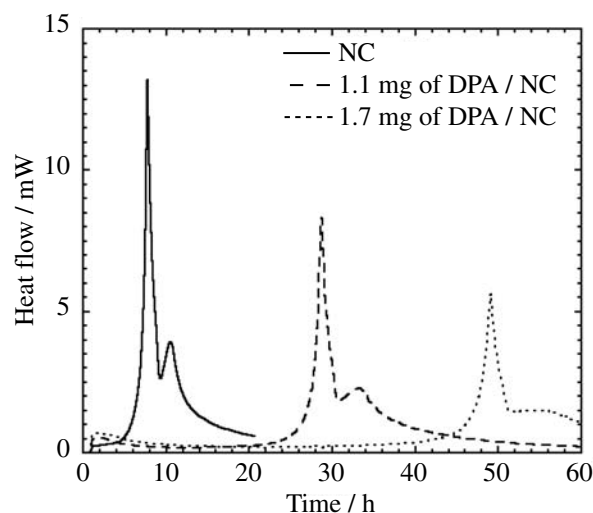


Fig. 2 Thermal behavior of DPA / NC.
NC: 50 mg, temperature: 393 K (isothermal),
atmosphere: O_2

Asahi Denka Corp., Ltd) was used without further purification. The chemical structures of these stabilizers are shown in Fig. 1.

2.2 Thermal analysis

The NC with the stabilizer was placed in the 4 cm^3 of vessels, respectively. The air in the vessel was removed under vacuum and then replaced by O_2 (Suzuki Shokan Corp., Ltd.). This procedure was repeated 4-5 times to ensure complete replacement. The sample was stored in C80 (SETARAM) at 393 K to observe the thermal behavior during the isothermal storage.

As the evaluation of stabilizer, the induction period and the maximum heat release rate were used. The induction period is expressed by the intersection of a tangent on the maximum inclination point of heat flow and the base line of it. The maximum heat release rate is the value of the heat flow on the exothermic peak top.

3 Results

3.1 DPA

The NC stability increased with increase in the content of DPA and its derivatives. Figure 2 shows the thermal behavior for NC with the different content of DPA. From this, the induction period increased with increase in the amount of DPA. The induction period of NC without DPA, with 1.1 mg of DPA, and with 1.7 mg of DPA was observed at approximately 7-10 h, 27 h, and 48 h, respectively. In addition, the maximum heat release rate also decreased with increase in the amount of those stabilizers. NC without DPA, with 1.1 mg of DPA, and with 1.7 mg of DPA had the maximum heat release rate of 13.0-13.6 mW, 8.3 mW, and 5.7 mW.

3.2 Phenol compound

The NC stability increased with increase in the content of BP_{1ess} . Figure 3 shows the thermal behavior of different content of BP_{1ess} / NC. The values of the induction period of 1.1 mg of BP_{1ess} / NC, 1.9 mg of BP_{1ess} / NC, and 3.9 mg

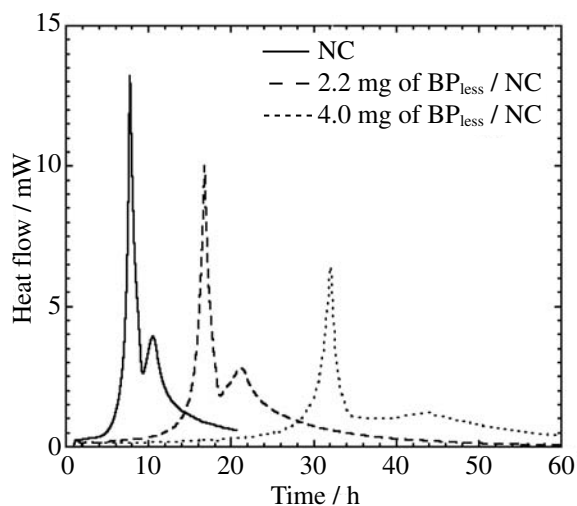


Fig. 3 Thermal behavior of BP_{less} .
NC: 50 mg, temperature: 393 K (isothermal),
atmosphere: O_2

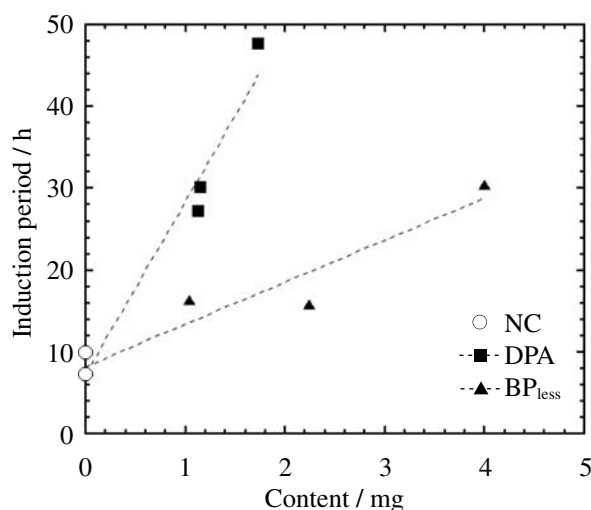


Fig. 4 Induction period against stabilizer content.
NC: 50 mg, temperature: 393 K (isothermal),
atmosphere: O_2

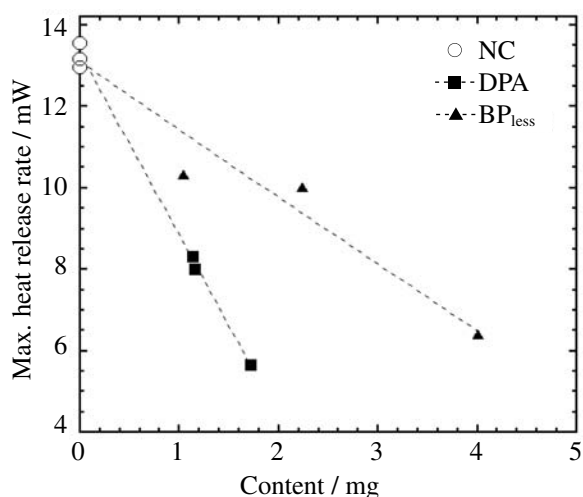


Fig. 5 Maximum heat release rate against stabilizer content.
NC: 50 mg, temperature: 393 K (isothermal),
atmosphere: O_2

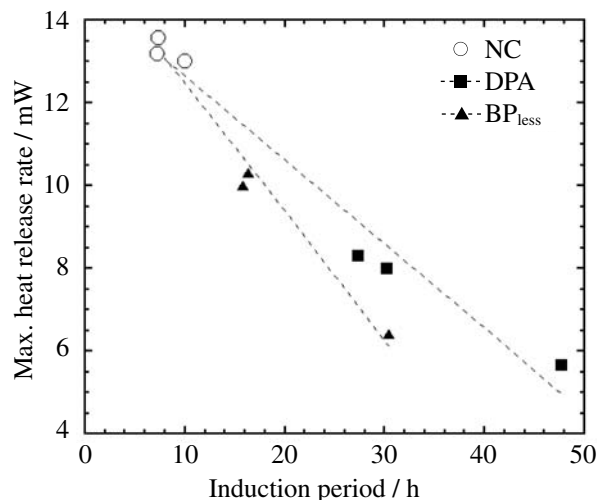


Fig. 6 Maximum heat release rate against induction period.
NC: 50 mg, temperature: 393 K (isothermal),
atmosphere: O_2

of BP_{less} / NC were observed at approximately 13 h, 20 h, and 26 h whereas that of NC without BP_{less} was observed at 7-10 h. And 1.1 mg of BP_{less} / NC, and 1.9 mg of BP_{less} / NC, and 3.9 mg of BP_{less} / NC had the maximum heat release rate of 11.7 mW, 9.8 mW, and 9.0 mW whereas NC without BP_{less} had the maximum heat release rate of 13.3 mW.

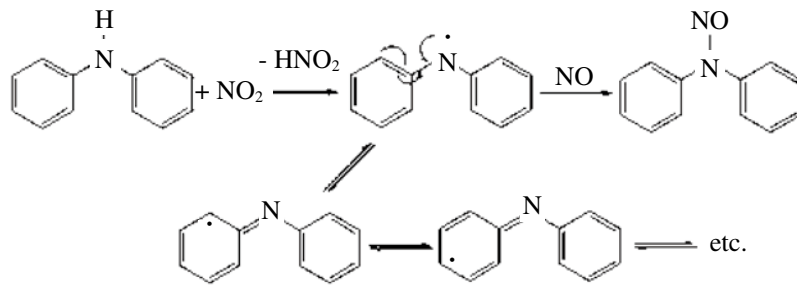
4. Discussion

On the experiment in this study, the thermal behaviors of NC with DPA and BP_{less} were different from another in terms of relationship between the induction period and the maximum heat release rate. Plots of maximum heat release rate and induction period against the stabilizer content are shown in Figs. 4 and 5. And, Fig. 6 shows the plot of the maximum heat release rate against the induction period. The result indicated that in comparison with the phenol compound, DPA was less effective on the decrease of the maximum heat release rate of NC than on the increase of

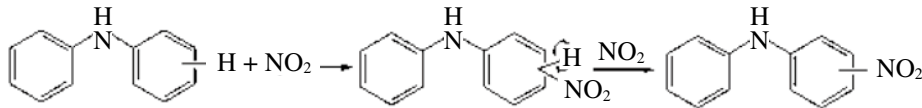
the induction period of NC. The difference of the thermal behavior would show the difference of reaction mechanism between amine compounds and phenol compounds.

As stabilization mechanism of DPA, R. 11⁴⁾ and R. 12^{18), 19)} were reported. By these reactions, DPA would trap NO and NO_2 , and its hydrogen on phenyl group was selectively substituted by NO and NO_2 molecules.

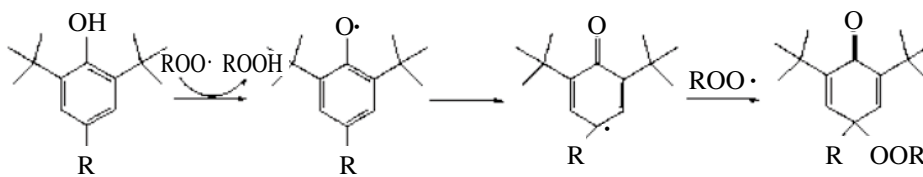
Contrary to the reaction of DPA with NO or NO_2 , it was considered that the phenol compound reacted with the $ROO\cdot$, and $ROO\cdot$ was deactivated to $ROOH$ which is more stable than $ROO\cdot$ as shown in R. 13^{17), 20)}. These reactions are well known as a mechanism of autoxidation of polymer, and they will be applied to NC. Phenol compounds tend to react with NO_2 existing in the atmosphere. However, K. C. Smeltz suggested R. 14 as the reaction mechanism of 2,6-tert-butyl-3-methyl-phenol (BHT) with NO_2 ²¹⁾. This reaction indicated that the reaction site of BHT was few, and NO_2 was consequently released as nitrous acid. Therefore, there is a possibility that the action



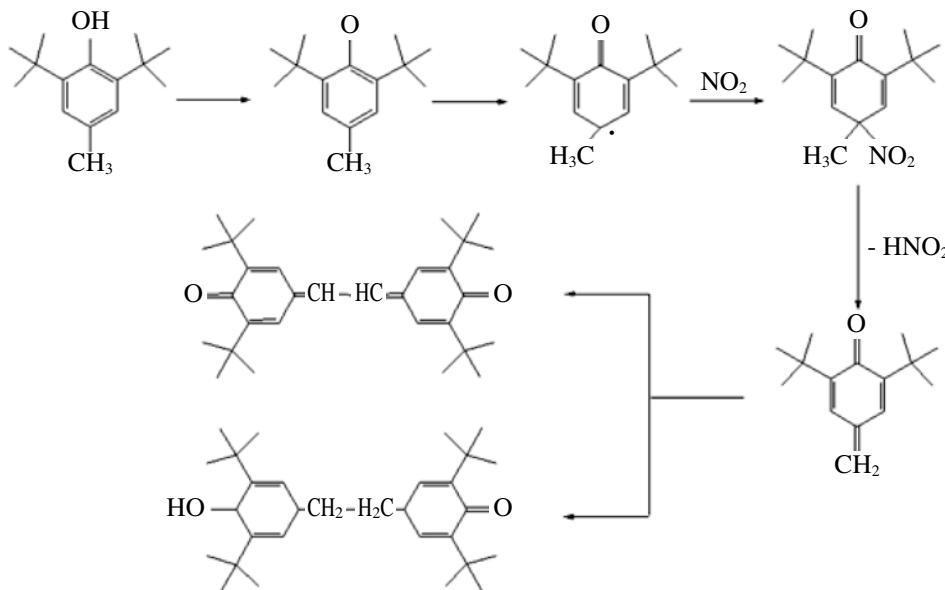
R. 11



R. 12



R. 13



R. 14

between DPA and phenol compounds was different in NC.

When the actions of DPA and phenol compound were applied to the reaction mechanism of NC, a likely explanation of difference of thermal behavior was that the DPA had the effect on trapping NO_2 generated in R. 1-5 and on preventing the initiation process which hardly contributed to the heat release. On the other hand, the phenol compound more decreased the maximum heat release rate with increase in the induction period. From this, There is a possibility that the phenol compound trapped $\text{ROO}\cdot$ generated in the autoxidation (R. 8 and 9) and, the phenol compound, thus, prevented the autoxidation which contributed to the heat release.

5 Conclusion

The thermal behavior of NC containing DPA or BP_{less} was observed during the isothermal storage at 393 K using C80. And, the conclusions are shown below:

- DPA or BP_{less} decreased the maximum heat release rate and increased the induction period of the heat release of NC, which was suggested that not only existing stabilizer but also the phenol compound stabilized NC.
- The induction period was increased, and the maximum heat release rate was decrease with increase in the amount of DPA or BP_{less} within a measured range.
- The relationship between the maximum heat release rate and the induction period was different between DPA and BP_{less} . This behavior might result from difference of the stabilization mechanisms.

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ジフェニルアミンおよびフェノール化合物による ニトロセルロースの安定化

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ジフェニルアミン (DPA) およびフェノール化合物 (1,1,3-tri- (2-methyl-4-hydroxy-5-tert-butyl-phenyl) -butane (BP_{less})) を含有したニトロセルロース (NC) の等温貯蔵下 (120℃) における熱的挙動を熱流束型熱量計C80を用いて観察した。その結果、これらの安定剤を添加することにより、発熱に至るまでの誘導期が延長し、最大発熱速度が低下することが分かった。また、その効果は、安定剤含有量に依存した。以上の結果から、DPA および BP_{less} はそれぞれNCを安定化させる可能性があることが示唆された。

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