Research paper

The effects of conventional stabilizers and phenolic antioxidants on the thermal stability of nitroglycerine

Katsumi Katoh*†, Masaru Nakahama**, Shuhei Kawaguchi***, Yuji Wada****,
Yuji Ogata****, and Mitsuru Arai*****

*Department of Chemical Engineering, Faculty of Engineering, Fukuoka University, 8-19-1,Nanakuma, Jonan,
Fukuoka 814-0180, JAPAN
TEL : +81-92-871-6631 FAX : +81-92-865-6031
†Corresponding address : kkatoh@fukuoka-u.ac.jp

**Graduate School of Frontier Sciences, University of Tokyo, 7-3-1 Hongo, Bunkyo, Tokyo 113-0033, JAPAN

***Taketoyo Plant, NOF Corp. 61-1, Kitakomatsudani, Taketoyo, Aich 470-2379, JAPAN

****Research Institute of Science for Safety and Sustainability (RISS), AIST 16-1,Onogawa, Tsukuba, Ibaraki
305-8569, JAPAN

*****Environmental Science Center, The University of Tokyo, 7-3-1Hongo, Bunkyo, Tokyo 113-0033, JAPAN

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Abstract

To estimate the effects of conventional stabilizers and phenolic antioxidants on the thermal stability of nitroglycerine (NG), the thermal behaviors of mixtures of NG with diphenylamine (DPA), ethyl centralite (EC), Akardite II (AKII), (2-nitrophenyl) phenylamine (2-NO_2-DPA), two commercial hindered phenolic compounds (BP_{hin}) and (BP_{semi}) used as antioxidants for polymers, 2,6-di-*tert*-butyl-4-methylphenol (BHT), and hydroquinone (HQ) were monitored during isothermal storage by using a C80 microcalorimeter. The effect of these compounds in prolonging the induction period of the main exothermic reaction was AKII > DPA ≈ EC > 2-NO_2-DPA ≈ BHT ≈ BP_{hin} > BP_{semi} > HQ, whereas the order in decreasing the maximum rate of heat release was DPA ≈ BHT > AKII > 2-NO_2-DPA ≈ EC ≈ BP_{hin} > BP_{semi} > HQ. However, NG with DPA or BHT released small amounts of heat before the main exothermic reaction. We therefore consider that AKII is most effective stabilizer for NG. In addition, BP_{hin} has a stabilizing effect that is almost identical to that of 2-NO_2-DPA. Further investigation may reveal that phenolic compounds could be used as stabilizers for nitric acid esters.

Keywords : Self-ignition, Spontaneous ignition, Nitric acid ester, Antioxidant, Stabilizer

1. Introduction

Nitroglycerine (NG) is widely used as an ingredient of propellants and explosives, despite its unstable characteristics, such as spontaneous ignition. The mechanism of spontaneous ignition of nitric acid esters has been the subject of investigation for a considerable time. As a common mechanism, some studies[1, 2] suggest that spontaneous ignition is caused by the reaction between the nitric acid esters and NO_2 formed by scission of O-NO_2 bonds and hydrolysis. To stabilize nitric acid esters, stabilizers such as *N*-phenylaniline (DPA) are added. With regard to the mechanism of stabilization by DPA, it has been revealed that DPA traps NO_2 and prevents the exothermic reaction, since DPA reacts readily with NO_2 to form its nitro and nitroso derivatives[1-3]. However, more research is needed on the stabilization mechanism, as it is not clear how effective the trapping of NO_2 is in stabilizing nitric acid esters, and the spontaneous-ignition mechanism itself is not yet completely understood. In addition, the previous studies have indicated that DPA is effective with single-base propellants, but is less effective with a propellant containing nitroglycerine[4]. Therefore, not only is the stabilization mechanism incompletely understood, but also the effect of stabilizers has not been fully elucidated.

In addition, because some conventional stabilizers are toxic to humans[5], there is a need to develop alternative stabilizers for the sake of industrial hygiene. It has recently been reported that phenolic compounds that are widely used as antioxidants for polymers prolong the induction period for heat release and decrease the maximum rate of heat release for nitrocellulose (NC)[6]. Accordingly, these phenolic compounds could be useful as new stabilizers for preventing the spontaneous ignition of NG.

The purpose of this study was to estimate the effects of conventional stabilizers and phenolic antioxidants on the thermal stability of NG. As conventional stabilizers, we chose DPA, ethyl centralite (EC ; 1,3−diethyl−1,3−diphenylurea), Akardite II (AKII ; 3−methyl −1,1−diphenylurea), and *N*−(2−nitrophenyl)aniline (2−NO_2−DPA). As phenol compounds, we chose two hindered phenolic compounds (BP$_{hin}$ and BP$_{semi}$), which are used as polymer antioxidants ; 2,6−di−*tert*−butyl−4−methylphenol (BHT), which used as an antioxidant for foods and cosmetic products ; and hydroquinone (HQ), which is used as an antioxidant for rubber.

We monitored the thermal behavior of NG containing each stabilizer under isothermal conditions at 393 K in an O_2 atmosphere by using a C80 microcalorimeter.

2. Experimental

2.1 Materials

Distilled water (2.5 mL) was added to 0.5 mL of a 10 wt.% solution of NG in ethanol (NOF Corp.) in a glass vessel. The mixture was allowed to stand until highly pure NG separated. The NG was extracted into another glass vessel by using a microsyringe. A small amount of residual water and ethanol in the NG were removed under a vacuum to give dry NG that was used as the experimental sample.

As stabilizers, DPA (Sigma−Aldrich Corp.), EC (provided by NOF Corp.), AKII (provided by NOF Corp.), 2−NO_2−DPA (provided by NOF Corp.), octadecyl 3−(3,5−di−*tert*−butyl−4−hydroxyphenyl) propanoate (BH$_{hin}$; Adeka Corp.), 2,4,8,10−tetraoxaspiro [5.5] undecane− 3,9−diyldipropane−2,2−diyl bis [3−(3−*tert*−butyl−4−hydroxy−5 −methylphenyl) propanoate (BH$_{semi}$; Adeka Corp.), BHT (Wako Pure Chemical Industries Corp.), and HQ (Wako Pure Chemical Industries Corp.) were used without further purification. Each stabilizer was added directly to NG. The chemical structures of the stabilizers are shown in Figure 1.

2.2 Procedure

The NG alone or NG with the stabilizer was placed in a glass vessel in order to avoid the reaction with metals. The glass vessel was then placed inside a 4−mL metal vessel. The air in the metal vessel was evacuated and replaced by O_2 (Suzuki Shokan Corp., Ltd.) : this procedure was repeated 4−5 times to ensure complete replacement. The sample was placed in a C80 microcalorimeter (Setaram) and its thermal behavior was examined during isothermal storage at 393 K. The amount of used NG was fixed at 50 mg and various amounts of the stabilizer were added as required.

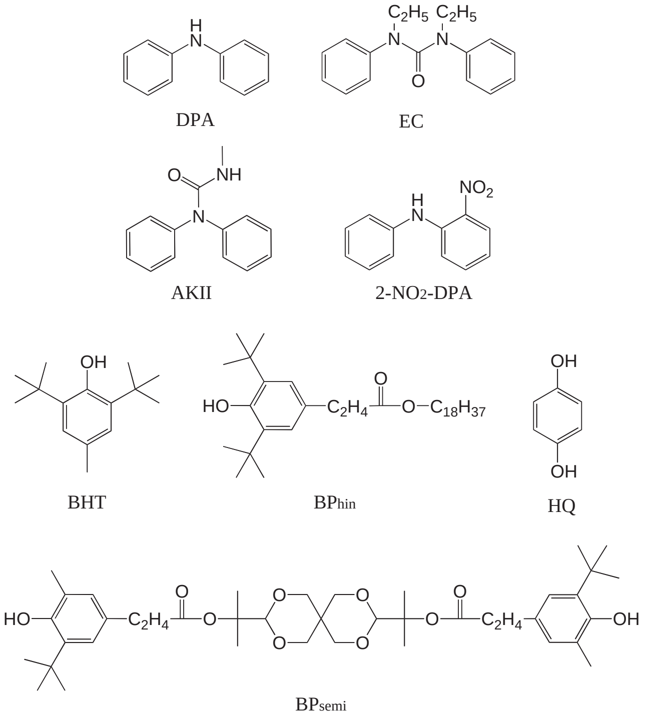


Fig. 1 Chemical structure of the stabilizers

2.3 Evaluation of the stability

To evaluate the efficiency of the stabilizers, we measured the induction period before the exothermic peak and the maximum rate of heat release at the exothermic peak. The induction period is taken as the intersection between a tangent at the point of maximum inclination of the heat flow curve and the baseline. The maximum heat release rate is the value of the heat flow at the top of the exothermic peak.

3. Results

3.1 Thermal behavior of DPA/NG

Comparison between NG alone and NG with DPA shows that DPA prolonged the induction period of the main exothermic peak of NG, and it decreased the maximum rate of heat release. Figure 2 shows the thermodiagram of NG alone and of NG with DPA for storage at 393 K under O_2. The induction periods were 5.8, 10.6, and 13.8 h for 2, 4, and 6 wt.% of DPA, respectively, whereas the induction period of NG alone was 4.6 h. The maximum rates of heat release were 17.1, 12.7, and 10.6 mW for 2, 4, and 6 wt.% of DPA, respectively, whereas that of NG alone was 37.6 mW. Those results indicate that DPA reduced the heat release from NG.

Although DPA suppressed the main heat release from NG, NG with DPA released a small amount of heat before the main exothermic peak. We suggest that this small release of heat is caused by reactions of DPA with NG or its degradation products, because the amount of heat released depended on the amount of DPA, and the small release of heat did not occur with NG alone. The heats of reaction for the exothermic peak were 32, 100, 152 J per

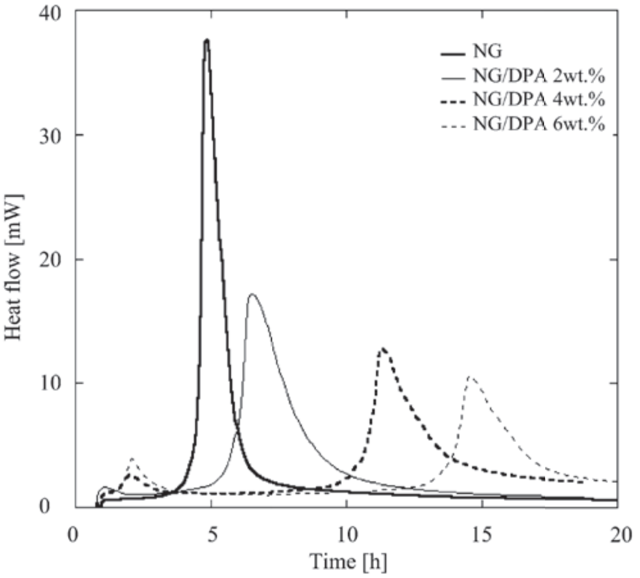


Fig. 2 Thermodiagram of NG with DPA

gram of NG for 2, 4, and 6 mg of DPA, respectively. From these results, we consider that this small exothermicity may account for the instability of NG reported in a previous study, which found that DPA had hardly any stabilizing effect on double−base propellants[4].

3.2 Thermal behavior of EC/NG

When the thermal behavior of NG with EC was examined, EC was found to delay the induction period and to decrease the maximum rate of heat release. This effect depended on the amount of EC, as shown in Figure 3. The induction periods were 7.0, 8.5, and 14.2 h for 2, 4, and 6 wt.% of EC, respectively, whereas the induction period for pure NG was 4.6 h. The addition of 2, 4, or 6 wt.% of EC decreased the maximum rate of heat release from 37.6 mW for NG alone to 29.8, 16.8, and 12.7 mW, respectively. No release of heat before the main peak was observed, in contrast to the case of DPA.

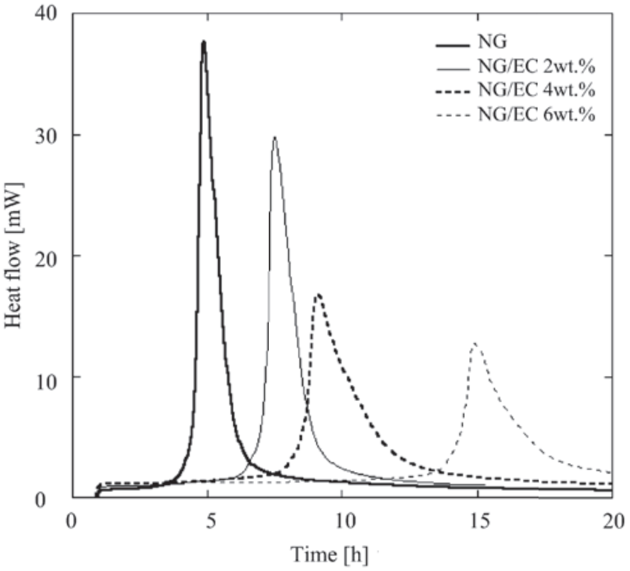


Fig. 3 Thermodiagram of NG with EC

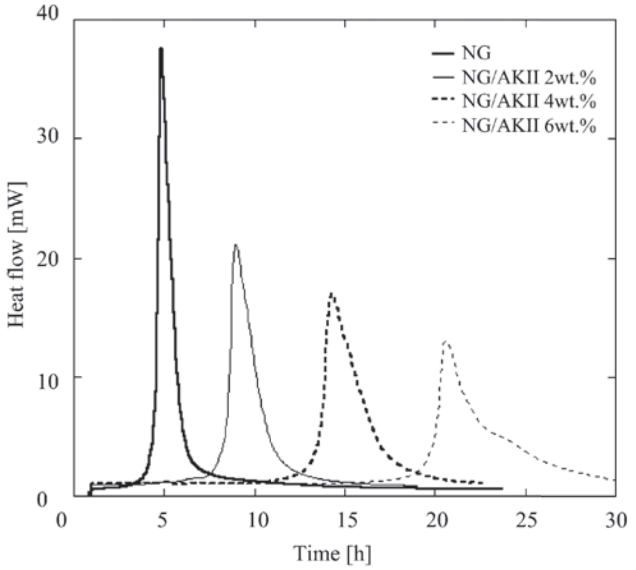


Fig. 4 Thermodiagram of NG with AKII

3.3 Thermal behavior of AKII/NG

AKII prolonged the induction period and decreased the maximum rate of heat release. The thermodiagram is shown in Figure 4. The induction period increased from 4.6 h for NG alone to 8.4, 13.6, and 19.9 h in the presence of 2, 4, and 6 wt.%, respectively, of AKII. The corresponding maximum rate of heat release rate decreased from 37.6 mW for NG alone to 21.1, 17.0 and 12.9 mW for 2, 4, and 6 wt.%, respectively, of AKII. No release of heat before the main peak was observed, in contrast to the case of DPA.

3.4 Thermal behavior of 2–NO_2–DPA/NG

2−NO_2−DPA prolonged the induction period and decreased the maximum rate of heat release, as shown in Figure 5. The induction period increased from 4.6 h for NG alone to 6.7, 9.1, and 12.4 h in the presence of 2, 4, and 6 wt.%, respectively, of 2−NO_2−DPA. The corresponding maximum rate of heat release decreased from 37.6 mW for NG alone to 20.5, 19.7, and 12.7 mW for 2, 4, and 6 wt.%, respectively, of 2−NO_2−DPA. No release of heat before the main

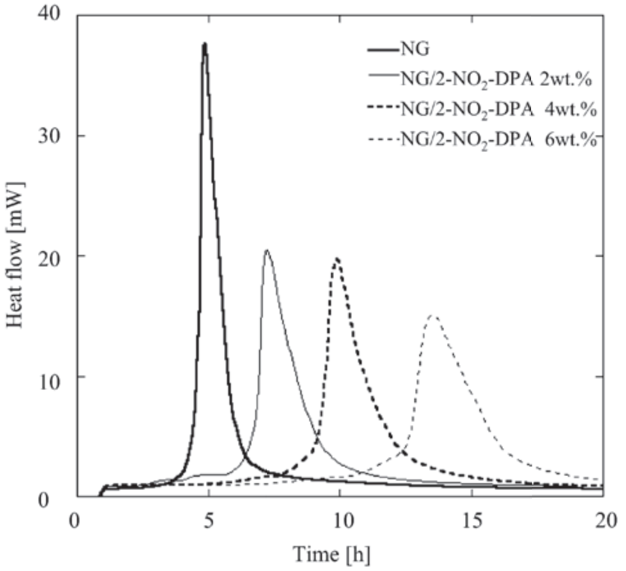


Fig. 5 Thermodiagram of NG with 2−NO_2−DPA

peak was observed, in contrast to the case of DPA.

3.5 Thermal behavior of $\mathrm{BP}_{\mathrm{semi}}$/NG

In the case of NG with a small amount of $\mathrm{BP}_{\mathrm{semi}}$ (~ 4 wt.%), the induction period was shortened in comparison with NG alone, whereas in the case of a higher content (6 wt.%), it was prolonged. The maximum rate of heat release tended to be decreased slightly for all content ranges. The thermodiagram is shown in Figure 6. This figure shows that the induction periods were 3.9, 3.6, 2.3, 4.2, and 8.0 h for 0.2, 1, 2, 4, and 6 wt.%, respectively, of $\mathrm{BP}_{\mathrm{semi}}$, whereas the induction period for NC alone was 4.6 h. Because the induction period of NG with 2 wt.% of $\mathrm{BP}_{\mathrm{semi}}$ was the shortest, NG was most destabilized at that content of $\mathrm{BP}_{\mathrm{semi}}$.

The maximum rates of heat release decreased with increasing content of $\mathrm{BP}_{\mathrm{semi}}$. The maximum heat release rates were 28.4, 27.6, 29.0, 20.5, and 19.7 mW for 0.2, 1, 2, 4, and 6 wt.%, respectively, of $\mathrm{BP}_{\mathrm{semi}}$, whereas that of NG alone was 37.6 mW.

3.6 Thermal behavior of $\mathrm{BP}_{\mathrm{hin}}$/NG

$\mathrm{BP}_{\mathrm{hin}}$ prolonged the induction period and decreased the maximum rate of heat release. The thermodiagram of NG alone and of NG with $\mathrm{BP}_{\mathrm{hin}}$ is shown in Figure 7. The induction period increased from 4.6 h for NG alone to 7.0, 8.6, and 11.4 h in the presence of 2, 4, and 6 wt.% of $\mathrm{BP}_{\mathrm{hin}}$, respectively. The corresponding maximum rate of heat release decreased from 37.6 mW for NG alone to 22.8, 18.6, and 14.4 mW for 2, 4, and 6 wt.%, respectively, of $\mathrm{BP}_{\mathrm{hin}}$. No release of heat before the main peak was observed, in contrast to the case of DPA.

3.7 Thermal behavior of BHT/NG

BHT prolonged the induction period and decreased the maximum rate of heat release. The thermodiagrams of NG alone and NG with BHT is shown in Figure 8. The induction period increased from 4.6 h for NG alone to 6.2, 8.7, and 12.1 h in the presence of 2, 4, and 6 wt.% of BHT, respectively. The corresponding maximum rates of heat release decreased from 37.6 mW for NG alone to 17.5, 15.8, 11.3 mW for 2, 4, and 6 wt.%, respectively, of BHT.

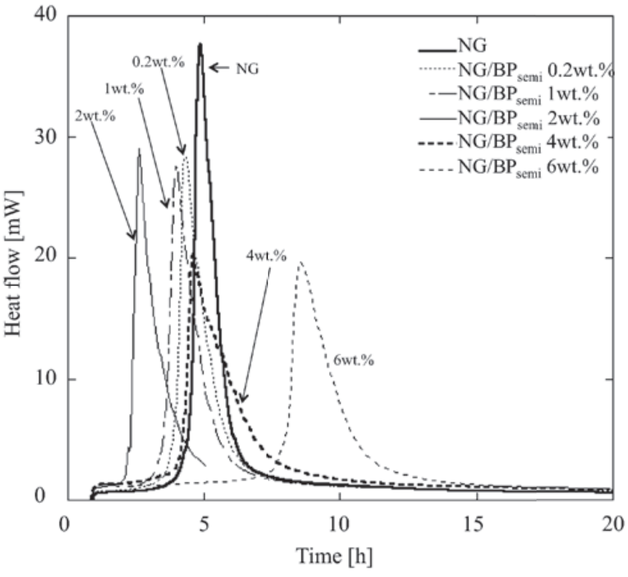


Fig. 6 Thermodiagram of NG with $\mathrm{BP}_{\mathrm{semi}}$

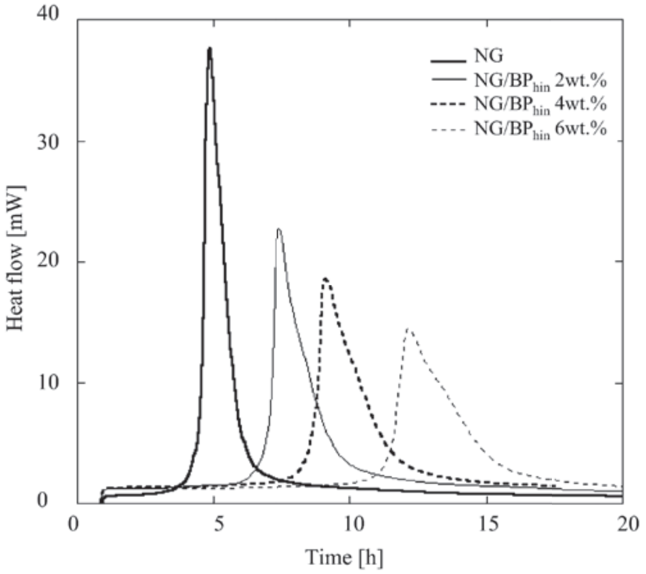


Fig. 7 Thermodiagram of NG with $\mathrm{BP}_{\mathrm{hin}}$

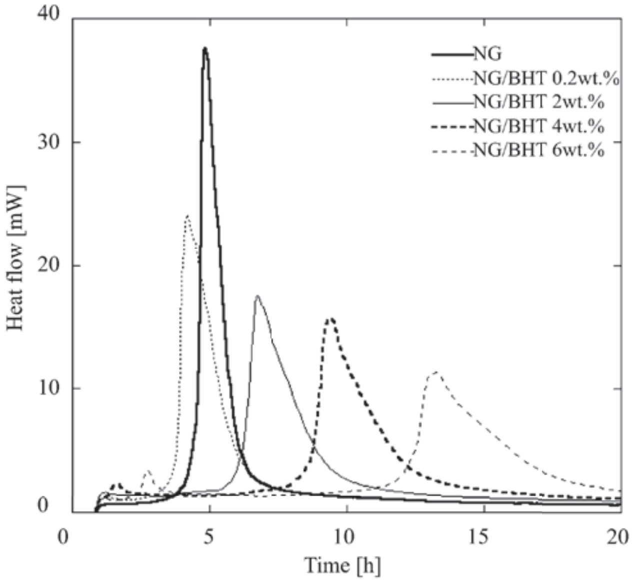


Fig. 8 Thermodiagram of NG with BHT

Although BHT suppressed the main heat release from NG, NG with BHT showed a small release of heat before the main exothermic peak, as in the case of DPA.

3.8 Thermal behavior of HQ/NG

The induction period for NG decreased with increasing HQ content, although the maximum rate of heat release fell, indicating that HQ destabilized NG. The thermodiagram of NG with HQ is shown in Figure 9. The induction period decreased from 4.6 h for NG alone to 2.7, 1.9, and 1.2 h for 2, 4, and 6 wt.%, respectively, of HQ. The maximum rate of heat release decreased from 37.6 mW for NG alone to 22.7, 23.0, and 30.7 mW for 2, 4, and 6 wt.%, respectively, of HQ. These results show that HQ is not an effective stabilizer for NG, because NG with HQ released heat soon after commencement of storage.

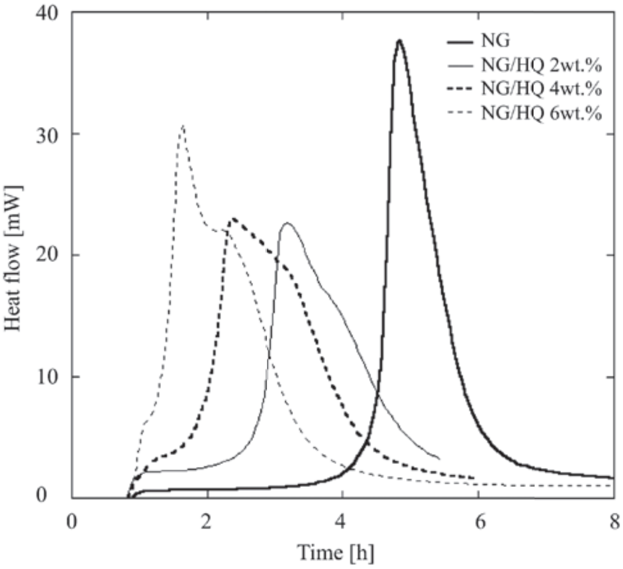


Fig. 9 Thermodiagram of NG with HQ

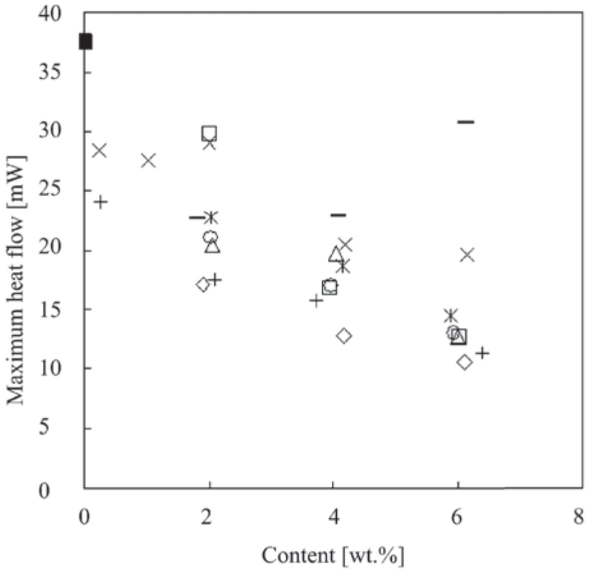


Fig.11 Relationship between the maximum heat release rate and the stabilizer content (wt.%)
■ : NG alone, ◇ : DPA, □ : EC, ○ : AKII, △ : $2\text{-}NO_2\text{-}DPA$, × : BP_{semi}, ∗ : BP_{hin}, + : BHT, − : HQ

4. Discussion

4.1 Comparison of the stabilizers

Plots of the induction period and the maximum rates of heat release of the main exothermic peak against the stabilizer content are shown in Figures 10 and 11. If the slope of the approximate straight line for each plot is defined as the stabilization effect for the corresponding stabilizer, the order of the stabilization effect on the induction period is AKII > DPA ≈ EC > $2\text{-}NO_2\text{-}DPA$ ≈ BHT ≈ BP_{hin} > BP_{semi} > HQ, and the order for the maximum rate of heat release is DPA ≈ BHT > AKII > $2\text{-}NO_2\text{-}DPA$ ≈ EC ≈ BP_{hin} > BP_{semi} > HQ.

DPA showed a comparatively high stabilization effect both on the induction period and the maximum rate of heat release. However, it might be necessary to be cautious about using DPA for energetic materials containing NG, because in the presence of DPA, NG releases a small amount of heat before the main heat release : this also applies to BHT. Other than DPA and BHT, AKII was the most effective stabilizer in increasing the induction period and decreasing the maximum rate of heat release, and EC was next in terms of effectiveness. Therefore, AKII and EC could be used as effective stabilizers of energetic materials containing NG.

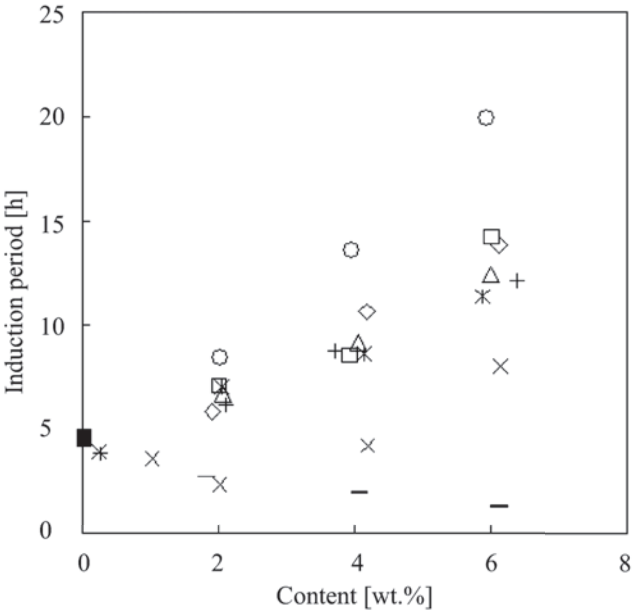


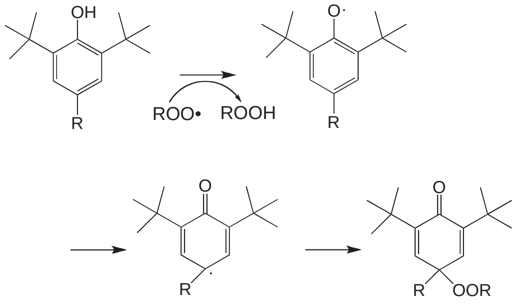
Fig.10 Relationship between the induction period and the stabilizer content (wt.%)
■ : NG alone, ◇ : DPA, □ : EC, ○ : AKII, △ : $2\text{-}NO_2\text{-}DPA$, × : BP_{semi}, ∗ : BP_{hin}, + : BHT, − : HQ

In terms of both the induction period and the maximum rate of heat release, BP_{hin} had an equivalent effect to $2\text{-}NO_2\text{-}DPA$. Therefore, further investigation may reveal that phenolic compounds could also be used as stabilizers for nitric acid esters.

4.2 Reaction mechanism

In a previous study[7], it was observed that peroxide is generated during storage of NG. Figure 12 shows that the relationship between the amount of peroxide generated during the experimental storage of NG and the heat released. These results suggest the possibility that the generation of peroxide or peroxy radicals may contribute to the release of heat from NG.

Because the induction period for heat release in the presence of a phenolic compound was prolonged, the generation of peroxide may have been prevented. Therefore, it is possible that the phenolic compounds stabilized NG by means of the reactions shown in R.1, in which peroxide radicals are trapped to form aryl peroxides.



· · · R.1

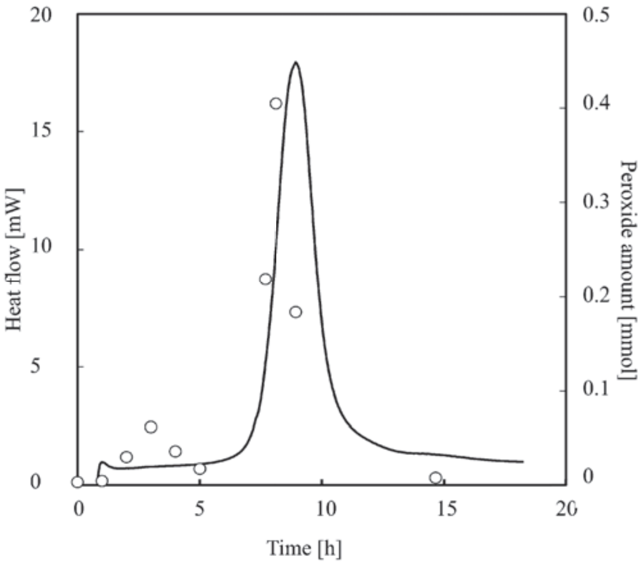


Fig.12 Relationship between the heat release and amount of peroxide [7]
− : Heat flow, ○ : peroxide amount

This is well known as a general stabilization mechanism for polymers[8].Furthermore, the reverse reaction occurs with more difficulty when the ***ortho***−position of the phenolic compound is sterically hindered, so that the thermal stability of the substance increases[9]. Also, in this study, unlike BP_{hin}, BP_{semi}, or BHT, HQ was found to destabilize NG. HQ has hydrogen atoms in the ***ortho***−positions, whereas BP_{hin}, BP_{semi}, and BHT have *tert*−butyl groups or methyl groups.

With regard to the most common action of phenyl amines such as DPA and its derivatives, it is known that phenyl amines stabilize nitric acid esters by trapping NO_2[1−3]. Also, AKII reacts with NO_2[10]. Nitrogen oxides are trapped at a carbon atom of the phenyl group or at the nitrogen atom of the amine group.

Furthermore, it has also been reported that a reaction may occur between a phenolic compound and nitrogen oxides[11], and between a phenyl amine and a peroxy radical or peroxide[8, 12, 13]. Our previous study on NC showed that phenyl amines contributed mainly by trapping nitrogen oxides, because an amine−containing stabilizer was more effective in prolonging the induction period than were phenolic compounds[6]. In the case of NG, it is not possible to estimate which mechanism is more effective in the reaction between NG and phenyl amine because, in addition to autoxidation, other reactions may also contribute to heat release from NG[14].

5. Conclusion

To estimate the effects of conventional stabilizers and phenolic antioxidants on the stability of NG, by using a C80 microcalorimeter, we monitored the thermal behaviors of NG containing DPA, EC, AKII, 2−NO_2−DPA, BP_{hin} BP_{less}, BHT, and HQ subjected to isothermal storage at 393 K. We drew the following conclusions.

(1)AKII, EC, 2−NO_2−DPA, and BP_{hin} prolonged the induction period and decreased the maximum rate of heat release. Each of these stabilizers exerted a stabilizing effect on NG that was proportional to the content of the stabilizer.

(2)DPA and BHT with NG showed a small release of heat before the main exothermic peak of NG although they both prolonged the induction period and decreased the maximum rate of heat release of the main exothermic peak of NG in a content−dependent manner.

(3)In the case of BP_{less}, the stability of NG was dependent on the content of stabilizer. A low content of BP_{less} (~4 wt. %) shortened the induction period in comparison with NG alone, whereas a high content (6 wt. %) prolonged the induction period.

(4)In the case of HQ, the stabilizer reduced the induction period of NG in a manner that depended on its content, indicating that it destabilized NG.

(5)In comparing the stabilizers, we found that the order of the stabilization effect for the induction period of the main exothermic peak was AKII > DPA ≈ EC > 2−NO_2−DPA ≈ BHT ≈ BP_{hin} > BP_{semi} > HQ, whereas that for the maximum rate of heat release was DPA ≈ BHT > AKII > 2−NO_2−DPA ≈ EC ≈ BP_{hin} > BP_{semi} > HQ.

6. References

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ニトログリセリンの熱安定性に及ぼす安定剤および フェノール系酸化防止剤の効果

加藤勝美*†，中浜優，川口周平***，和田有司****，緒方雄二****，新井充*******

ニトログリセリン（NG）の熱安定性に及ぼす既存の安定剤およびフェノール系酸化防止剤の効果を評価することを目的として，ジフェニルアミン（DPA），エチルセントラリット（EC），アカルダイトII（AKII），(2－ニトロフェニル）フェニルアミン（2－NO_2－DPA），および２種類のフェノール系酸化防止剤（BP_{hin}およびBP_{semi}），2,6-di-*tert*－ブチル－4－メチルフェノール（BHT），およびヒドロキノン（HQ）をそれぞれ添加したNGの120°C等温貯蔵下における熱的挙動を熱流束型反応熱量計C80により観察した。発熱に至るまでの誘導期は，AKII > DPA ≈ EC > 2－NO_2－DPA ≈ BHT ≈ BP_{hin} > BP_{semi} > HQの順に増加した。また，最大発熱速度は，DPA ≈ BHT > AKII > 2－NO_2－DPA ≈ EC ≈ BP_{hin} > BP_{semi} > HQの順に減少した。一方，NG/DPAおよびNG/BHTでは，主たる発熱の前に微小な発熱が観察された。これらの結果から，NGの安定剤としてAKIIが最も効果を有するものと推測した。また，BP_{hin}においては，2－NO_2－DPAと同程度の効果を有することから，今後の更なる研究により安定剤としての使用の可能性があるものと考えた。

*福岡大学工学部化学システム工学科　〒814-0180　福岡県福岡市城南区七隈8-19-1
TEL：092-871-6631　FAX：092-865-6031
†Corresponding address：kkatoh@fukuoka-u.ac.jp

**東京大学大学院新領域創成科学研究科　〒113-0033　東京都文京区本郷7-3-1

***日油株式会社武豊工場　〒470-2379　愛知県知多郡武豊町字北小松谷61-1

****独立行政法人産業技術総合研究所安全科学研究部門　〒305-8569　茨城県つくば市小野川16-1

*****東京大学環境安全研究センター　〒113-0033　東京都文京区本郷7-3-1