

# Effect of industrial water components on thermal stability of nitrocellulose

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**Abstract** In order to prevent the spontaneous ignition of nitrocellulose (NC), NC is stabilized by washing with industrial water in its synthesis process. However, there is a possibility that the components in industrial water contribute to the thermal stability of NC. In this way, the purpose of this study is to clarify the effect of industrial water components on the thermal stability of NC. In experiments, a heat flux calorimeter was used to observe the thermal behavior of NC with the residue of vaporized industrial water. The induction period of heat release of NC with 2-mass% residues was approximately 2–5 h shorter than that of NC alone whose induction period was observed at 7 h. Those results indicate that the residue destabilized NC. On the other hand, when the additive amount of the residue was increased, the induction period gradually increased as well. Based upon these results, we assume that inorganic salts contributing to stabilization and destabilization competitively coexist in the industrial water components. The same thermal analysis was performed on NC with CaCO<sub>3</sub>, CaSO<sub>4</sub>, CaCl<sub>2</sub>, ZnSO<sub>4</sub>, NaCl, and CuCl. Those salts are predicted to exist in the industrial water. In the results, the induction period of NC with 2-mass% CaCO<sub>3</sub> was approximately 15-h longer than that of NC alone, while the induction period with the inorganic salts

CaSO<sub>4</sub>, CaCl<sub>2</sub>, ZnSO<sub>4</sub>, NaCl, and CuCl was 4–5-h shorter. Therefore, when the industrial water components accumulate in NC, the destabilization by inorganic salts such as CaSO<sub>4</sub>, CaCl<sub>2</sub>, ZnSO<sub>4</sub>, NaCl, and CuCl and the stabilization by compounds such as CaCO<sub>3</sub> are thought to counteract against each other.

**Keywords** Nitric acid ester · Industrial water · Self-ignition · Thermal stability

## Introduction

Nitrocellulose (NC) is widely used as an ingredient for propellants and explosives despite its unstable characteristics, including spontaneous ignition. When any errors are made during treatment or storage, NC can spontaneously ignite and cause serious accidents. In Japan, accidents resulting from the spontaneous ignition of NC or nitric acid ester have occurred in recent years [1, 2]. From this, the spontaneous ignition of NC is one of the most important issues that propellant and explosives industry are still facing today.

The mechanism of NC's spontaneous ignition was investigated for a long time. Generally, it is caused by a reaction between NC and NO<sub>2</sub> formed by the scission of O–NO<sub>2</sub> bonds and hydrolysis [3, 4]. The hydrolysis is accelerated by acid remaining after the synthesis process. In previous studies [5, 6], we reported that NO<sub>2</sub> accelerates the chain reaction of O<sub>2</sub> with radical species from NC. Kimura et al. [7, 8] reported that peroxyradicals are generated from the reaction between alkoxyradicals and NO<sub>2</sub>. They also suggested that the decomposition of hydroperoxides and more active species cause the ignition of NC. From those studies, NO<sub>2</sub> and acid play an important role in NC's stability. These findings indicate that the removal of

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$\text{NO}_2$  and acid from NC by washing it with water is thought to be an effective stabilization method based upon the reaction mechanisms.

Kawaguchi et al. [9] confirmed the stabilizing effects of washing of NC by the experiments using pure water. However, these results do not clarify the stabilizing effect of the substance-laden industrial water that is used in the actual process. When the industrial water components accumulate by repeating washing processes of NC, they may contribute to stability of NC.

The purpose of this study is to clarify the effect of industrial water components on the thermal stability of NC. The thermal behavior of NC with the residue remaining after vaporization of the industrial water was observed using the heat flux calorimeter. By performing the same thermal analysis on NC with pure chemicals, which are thought to exist in the industrial water, we investigated the effects of the each component of the industrial water.

## Experiment

NC in 2-propanol (12-mass% nitrogen; Sigma–Aldrich Corp.) was dried in a vacuum at approximately 298 K for 3–4 days. Particles with diameters of 75–106  $\mu\text{m}$  were separated by sieving. This was dried once again under the same conditions for 1–2 days. The NC was used as the experimental sample.

For calorimetric measurement, 50 mg of NC or NC with several mass% of additives, such as the residue of evaporated industrial water or a single inorganic salt, was placed in a 4-cm<sup>3</sup> steel ampoule. The air in the ampoule was removed by vacuum pump and then replaced with a dry gas such as  $\text{O}_2$ . This process was repeated 4–5 times to ensure complete replacement. The sample was stored in a C80 calorimeter (SETARAM Instrumentation) at 120 °C, and the thermal behavior was observed.

The induction period for heat release and maximum heat rate was used for the index of stability. The term induction period mentioned in this article means the induction period of heat release. The induction period indicates the intersection of a tangent for the maximum inclination point of heat flow and the baseline. The maximum heat rate is the heat flow value at the top of the exothermic peak.

## Results and discussion

Thermal behavior of NC with the residue of evaporated industrial water

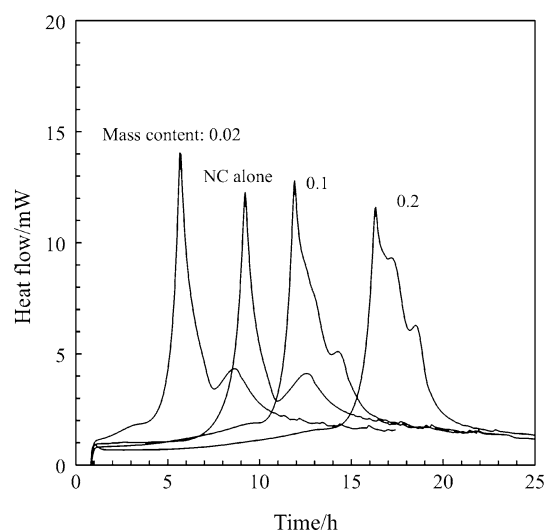
In order to ascertain whether substances in industrial water affect the thermal stability of NC, thermal analysis was

conducted for NC containing the residue of evaporated industrial water. Three kinds of evaporate residue were prepared by completely vaporizing the industrial water from Ibaraki prefecture in Japan, the same filtrated industrial water, and the filtrated industrial water from Miyazaki prefecture. The obtained residues were added to respective NC samples.

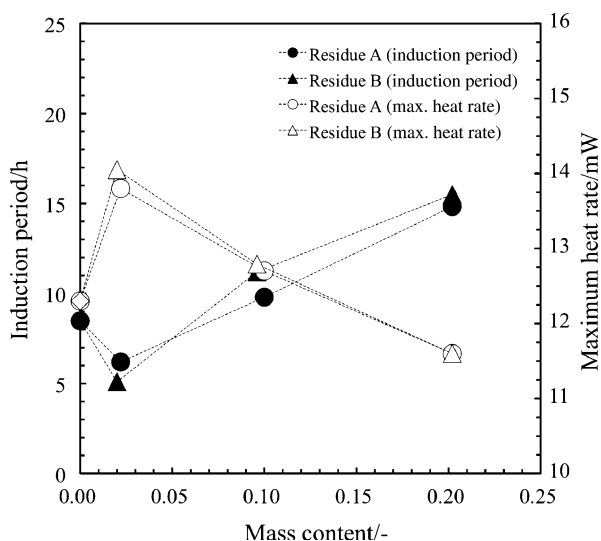
### Industrial water of Ibaraki prefecture

When observing the thermal behavior of NC with the residue from the Ibaraki industrial water (residue A) in an  $\text{O}_2$  atmosphere, the induction period for heat release and the maximum heat rate was found to depend upon the amount of residue A. The calorimetric curve, the induction period, and the plot of the maximum heat rate against the mass of residue A are shown in Figs. 1 and 2, respectively. As can be seen from these figures, when the residue was less than approximately 5 mass%, the induction period shortened and the maximum heat rate increased. On the other hand, when the residue was more than 5 mass%, the induction period prolonged and the maximum heat rate decreased as the amount of residue A increased. This behavior indicates that lower amounts of residue A destabilize NC and higher amounts stabilize it.

The thermal behavior of NC with residue A in an  $\text{N}_2$  atmosphere shows that heat was not released during 60 h of measurement time. In previous studies [5] on the plural peaks observed in NC alone as shown in Fig. 1, we suggested that the first peak concerned the oxidation of NC with atmospheric  $\text{O}_2$  because the heat amount of first peak depended on the partial pressure of  $\text{O}_2$  and the heat conversion corresponded to the  $\text{O}_2$  conversion. And, the



**Fig. 1** Calorimetric curve of NC and NC with residue A. Temperature: 120 °C (isothermal), atmosphere:  $\text{O}_2$

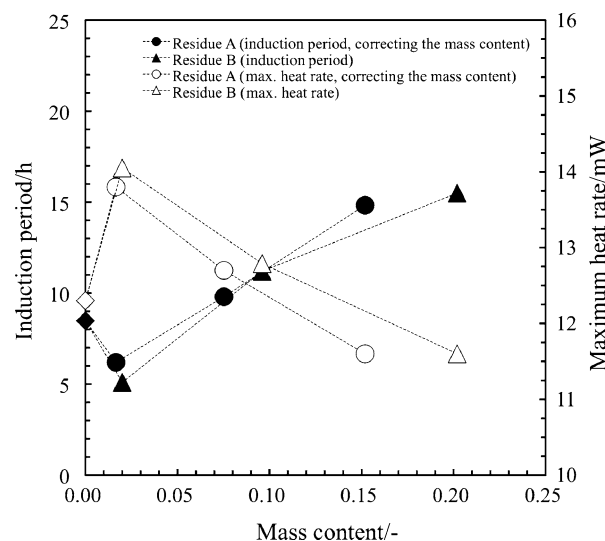


**Fig. 2** Induction period and maximum heat rate against mass content of residues A and B. Temperature: 120 °C (isothermal), atmosphere: O<sub>2</sub>

second one may result from the carbonization because the color of NC changed from white to black for second heat release. From this mechanism and the result in N<sub>2</sub> atmosphere, one possibility is arisen that residue A did not directly react NC, and reactions between NC, residue A, and O<sub>2</sub> would contribute.

#### Filtrated industrial water of Ibaraki prefecture

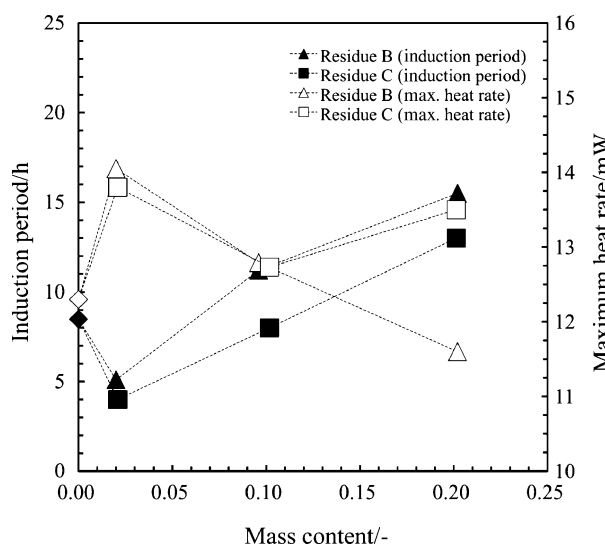
When observing the thermal behavior of NC with the residue of the filtrated industrial water of Ibaraki prefecture (residue B) in an O<sub>2</sub> atmosphere, the sample had roughly the same tendencies as NC with residue A. As shown in Fig. 2, amounts less than approximately 5 mass% of residue B destabilized NC, while higher amounts stabilized NC. However, the destabilizing and stabilizing effects on the induction period were slightly higher than those of residue A. The difference between residues A and B was whether the original industrial water was filtrated or not. This means that residue A contained insoluble substances such as organic compounds. Comparing the residue amounts obtained from industrial waters, residue A included approximately 25 mass% of insoluble substances. The plot of residue A in Fig. 3 shows the induction period versus the mass content multiplied by 0.75, meaning the plot is only of the expected soluble substances. In Fig. 3, the plots of the induction period for residues A and B almost overlapped. These plots suggest that the insoluble substances such as organic compounds hardly contributed to the NC thermal stability, and the soluble substances such as inorganic salts mainly affect the stability.



**Fig. 3** Comparison between residue A commuting the mass content and residue B. Temperature: 120 °C (isothermal), atmosphere: O<sub>2</sub>

#### Industrial water of Miyazaki prefecture

When observing the thermal behavior of NC with the residue of the Miyazaki-filtrated industrial water (residue C) in an O<sub>2</sub> atmosphere, the induction period for heat release and maximum heat rate depended upon the mass of residue C as shown in Fig. 4. In terms of the dependence on mass content, NC with residue C had roughly the same thermal behavior as NC with residues A and B. However, a detailed comparison between the samples with residues B and C, which were both obtained from filtrated industrial waters, shows that residue C had a higher destabilizing effect with lower mass content and a lower stabilizing



**Fig. 4** Induction period and maximum heat rate against mass content of residues B and C. Temperature: 120 °C (isothermal), atmosphere: O<sub>2</sub>

effect with higher mass content. The difference between residues B and C is due to the composition since the original industrial waters for residues B and C were different. Therefore, the difference in composition would result in differences in thermal behavior.

Based upon the above-mentioned results, we assume that inorganic salts contributing to the stabilization and the destabilization of NC coexist competitively in the residue of the each industrial waters.

#### Thermal behavior of NC with inorganic salts

In order to ascertain which salts contributed to the stabilization or destabilization of NC, we attempted to observe the thermal behavior of NC containing individual inorganic salts expected to exist in industrial water.

Prior to the thermal analysis, an analysis of components in the filtrated industrial waters from Ibaraki and Miyazaki prefecture was conducted using ion chromatography (Shimadzu Corp.; detector: CDD-6A, Column: Shim-pack IC-A3). The results are summarized in Table 1. From the ions in Table 1,  $\text{CaSO}_4$  (Alfa Aesar, 99.0%),  $\text{CaCl}_2$  (Wako Pure Chemicals Corp., 95.0%),  $\text{ZnSO}_4$  (Wako Pure Chemicals Corp., 95.0%),  $\text{NaCl}$  (Wako Pure Chemicals Corp., 99.5%),  $\text{NaNO}_2$  (Wako Pure Chemicals Corp., 98.5%), and  $\text{CuCl}$  (Wako Pure Chemicals Corp., 95.5%) were selected as they are easy to use and purchase. These salts were used as the experimental additives.  $\text{CaCO}_3$  (Wako Pure Chemicals Corp., 99.5%) was also used as an experimental additive because we obtained information that industrial water contains carbonate [10].

When the thermal behavior of NC with 2 mass% of the selected inorganic salt was observed in an  $\text{O}_2$  atmosphere, the results shown in Table 2 were obtained.

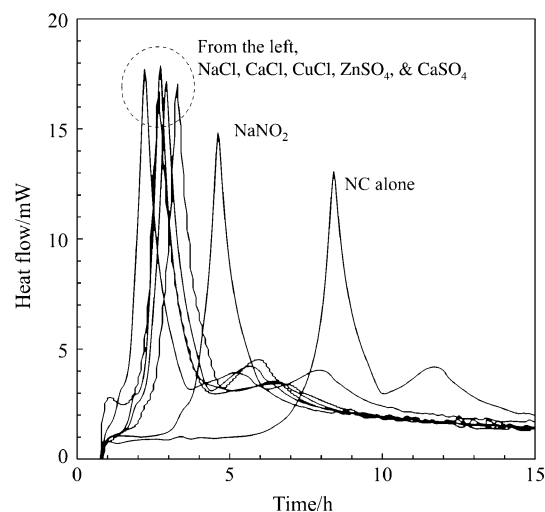
With the addition of  $\text{CaSO}_4$ ,  $\text{CaCl}$ ,  $\text{ZnSO}_4$ ,  $\text{CuCl}$ ,  $\text{NaCl}$ , and  $\text{NaNO}_2$ , the induction period was 2–4-h shorter than that of NC alone, and the maximum heat rate was higher. From these results, these inorganic salts can be shown to destabilize NC. Figure 5 indicates the calorimetric curve of NC with  $\text{CaSO}_4$ ,  $\text{CaCl}$ ,  $\text{ZnSO}_4$ ,  $\text{CuCl}$ ,  $\text{NaCl}$ , and  $\text{NaNO}_2$ . This figure shows that the destabilizing effect and the shape of the exothermic peak do not depend on the kind of inorganic salt, whereas the induction period for  $\text{NaNO}_2$  is slightly longer than that of the other salts.

**Table 1** Components of the filtrated industrial water

	$\text{Ca}^{2+}/$ $\text{mg L}^{-1}$	$\text{Mg}^{+}/$ $\text{mg L}^{-1}$	$\text{Na}^{+}/$ $\text{mg L}^{-1}$	$\text{Cu}^{2+}/$ $\text{mg L}^{-1}$	$\text{Zn}^{2+}/$ $\text{mg L}^{-1}$	$\text{SO}_4^{2-}/$ $\text{mg L}^{-1}$	$\text{NO}_2^{-}/$ $\text{mg L}^{-1}$	$\text{NO}_3^{-}/$ $\text{mg L}^{-1}$	$\text{Cl}^{-}/$ $\text{mg L}^{-1}$
Ibaraki prefecture	17.7	5.4	20.0	<1	<1	27.9	<1	13.5	23.1
Miyazaki prefecture	11.8	3.0	7.4	<1	<1	16.6	<1	3.1	4.8

**Table 2** Induction period and maximum heat rate of NC with inorganic salt

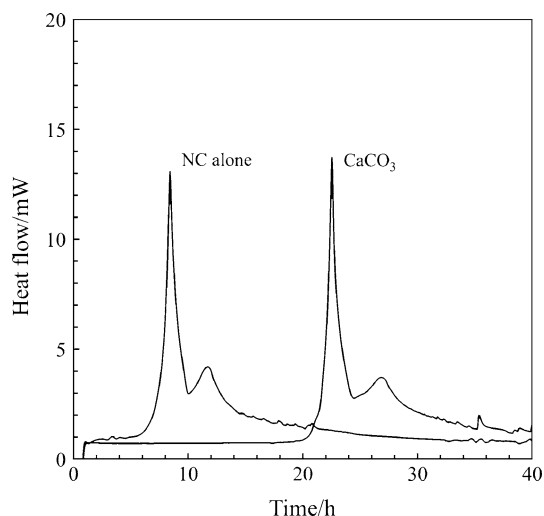
	Induction period/h	Maximum heat rate/mW
Control (NC alone)	6.7	14.3
$\text{CaCO}_3$	21.9	13.7
$\text{CaSO}_4$	2.7	16.9
$\text{CaCl}$	2.2	16.5
$\text{ZnSO}_4$	2.4	17.0
$\text{NaCl}$	1.6	17.4
$\text{NaNO}_2$	3.9	14.7
$\text{CuCl}$	2.2	17.8



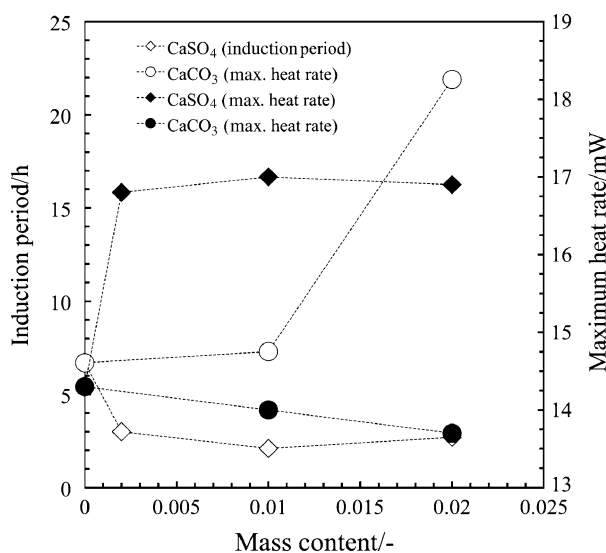
**Fig. 5** Calorimetric curve of NC alone and NC with  $\text{NaCl}$ ,  $\text{CaCl}$ ,  $\text{CuCl}$ ,  $\text{ZnSO}_4$ ,  $\text{CaSO}_4$ , or  $\text{NaNO}_2$ . Temperature: 120 °C (isothermal); atmosphere:  $\text{O}_2$

The induction period of NC with  $\text{CaCO}_3$  was approximately 15-h longer than that of NC alone, and the maximum heat rate lower (Fig. 6). This indicates that  $\text{CaCO}_3$  has a stabilizing effect on NC.

When the same experiment for  $\text{CaCO}_3$  and  $\text{CaSO}_4$  was carried out with different additive amounts, the results shown in Fig. 7 were obtained. As for NC with  $\text{CaCO}_3$ , the induction period became longer with an increase in additive amount. As for NC with 0.1-mass%  $\text{CaSO}_4$ , the induction period was approximately 4-h shorter than of NC



**Fig. 6** Calorimetric curve of NC alone and NC with  $\text{CaCO}_3$ . Temperature: 120 °C (isothermal), atmosphere:  $\text{O}_2$



**Fig. 7** Induction period and maximum heat rate against mass content of  $\text{CaCO}_3$  and  $\text{CaSO}_4$ . Temperature: 120 °C (isothermal), atmosphere:  $\text{O}_2$

alone. Even when further amounts of  $\text{CaSO}_4$  were added, the induction period did not show significant change. As mentioned in the previous section, the plot of induction period against the amount of industrial water residue showed the V-shaped dependence. When the residue contained more amounts of the destabilizing salts than that of the stabilizing salts, the V-shaped dependence can be explained by the stabilizing effect of compounds such as  $\text{CaCO}_3$  and the destabilizing effect of substances such as  $\text{CaSO}_4$ ,  $\text{CaCl}_2$ ,  $\text{ZnSO}_4$ ,  $\text{NaCl}$ , and  $\text{NaNO}_2$ .

In this stage, as for  $\text{CaSO}_4$ ,  $\text{CaCl}_2$ ,  $\text{ZnSO}_4$ ,  $\text{NaCl}$ , and  $\text{NaNO}_2$ , we assumed that common reactions contribute to the destabilization because the induction period and shape of the exothermic peak are barely affected by the kind of inorganic salt. As a conceivable destabilization mechanism by inorganic, we assume that water absorbed in NC was involved in the destabilization. Namely, because in the presence of inorganic salts, the boiling point of the water in NC is elevated, NC with inorganic salt contains more water than NC alone during the thermal analysis. Water is known as the substance that destabilizes NC [6]. Thus, such an effect of water is thought to contribute to destabilization by the inorganic salts.

For the stabilization by  $\text{CaCO}_3$ , we assume that a decrease in the acidity of water in NC was conducive to stabilization. Water saturated with  $\text{CaCO}_3$  (0.0014-g  $\text{CaCO}_3$ /100-g water at room temperature [11]) has a pH of 9.0–9.5. If 1–2 mass% of water remained in NC, the acidity of NC sufficiently decreases with the addition of a few milligrams of  $\text{CaCO}_3$ . By the decrease of acidity, acid-accelerated hydrolysis is suppressed. From this, the thermal stability of NC with  $\text{CaCO}_3$  may increase. In Fig. 5, the induction period for  $\text{NaNO}_2$ , which indicates a pH of 8.7–9.0 in the saturated aqueous solution [12], was slightly longer than for the other inorganic salts. This result is thought to be able to support the assumption of NC's stabilization by neutralization.

## Conclusions

In order to clarify the effect of industrial water components on the thermal stability of NC, NC thermal behaviors with the residue of vaporized industrial water and with individual inorganic salts were observed using the heat flux calorimeter. The following conclusions can be drawn:

- Lower amounts (<5 mass%) of residue from industrial water destabilized NC, and higher amounts (>5 mass%) stabilized it.
- It is assumed that insoluble substances in the industrial water barely contributed to the stability of NC.
- In  $\text{N}_2$  atmosphere, the heat release of NC was not observed with or without the residue from industrial water. From this, it is assumed that it was not a direct reaction between NC and residue, but a reaction to which NC, residue A, and  $\text{O}_2$  contributed.
- Inorganic salts such as  $\text{CaSO}_4$ ,  $\text{CaCl}_2$ ,  $\text{ZnSO}_4$ ,  $\text{NaCl}$ ,  $\text{NaNO}_2$ , and  $\text{CuCl}_2$  in the industrial water contributed to the destabilization of NC. Compounds such as  $\text{CaCO}_3$  contributed to the stabilization of NC.
- Since industrial water is thought to contain such inorganic salts, the behavior of NC with the residue

can be explained by the stabilizing effect of compounds such as  $\text{CaCO}_3$  and the destabilizing effect of substances such as  $\text{CaSO}_4$ ,  $\text{CaCl}_2$ ,  $\text{ZnSO}_4$ ,  $\text{NaCl}$ , and  $\text{NaNO}_2$ .

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