Research paper

Aging characteristics of the energetic oxidizer ammonium dinitramide

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Received : January 7, 2011 Accepted : May 26, 2011

Abstract

Aging can change the performance of energetic materials. The present study aimed to characterize the effects of aging on ammonium dinitramide (ADN, $NH_4N(NO_2)_2$), a promising new oxidizer for solid rocket propellants due to its high energy content and low environmental impact.

Freshly synthesized ADN (ADN(2009)) was compared with a sample that had been stored in the dark for 11 years (ADN(1998)). Characterization was conducted using infrared (IR), Raman and ultraviolet (UV) spectroscopy, sealed cell differential scanning calorimetry (SC-DSC), and a thermal activity monitor (TAM).

The results of IR, Raman and UV spectroscopy, and SC-DSC suggested that ADN(1998) had an altered composition and was a mixture of ADN and ammonium nitrate (AN), showing that some of the ADN had degraded to AN during storage. The amount of ADN in ADN(1998) was 57 wt.% in the surface region and 89 wt.% in the bulk region, showing that more aging had occurred at the surface than in the bulk region.

The results of DSC and TAM analysis showed the influence of aging on the thermal decomposition of ADN. It appeared that the presence of AN generated by the aging of ADN mainly caused the difference of thermal properties.

Keywords : oxidizer, ammonium dinitramide, aging, thermal decomposition

1. Introduction

Environmental problems associated with propellants and enhancement of the performance characteristics of propellants have been the subject of much recent research and technological development. The goal of this research is to find new eco-friendly propellants with high energy content[1)-5)]. In a rocket propellant, solid oxidizers generate high temperatures and oxidized gases by thermal decomposition. Ammonium perchlorate (AP, NH_4ClO_4) is currently the main solid oxidizer for solid propellants because of its superior oxygen balance, energy content, stability, and mechanical properties[1)]. However, AP contains Cl, and HCl is generated as a reaction product.

One promising new oxidizer is ammonium dinitramide (ADN, $NH_4N(NO_2)_2$), which consists of NH_4^+ and $N(NO_2)_2^-$ (Fig. 1)[6)]. The main physical properties of ADN are summarized in Table 1. ADN has both a high oxygen balance and high energy content, and does not contain halogen atoms[7)-9)]. However, since ADN is a reactive substance, it might degrade upon storage, resulting in changed chemical and physical properties. We therefore studied the effects of aging by comparing the composition and performance of newly synthesized ADN with a sample of ADN synthesized in 1998 (ADN(1998)); the aging products are identified, the extent of aging is quantified, and the effect of aging on the thermal decomposition of ADN are discussed.

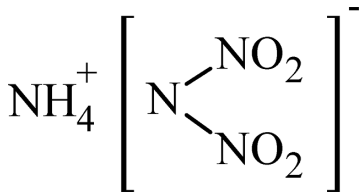

Fig. 1 Molecular structure of ADN.

Table 1 Physical properties of ADN.

Molecular weight	124.07[6]
Density [g cm^{-3}]	1.82–1.84[6]
Melting point [°C]	91.5–92.5[6]
Heat of formation [kJ mol^{-1}]	−148[10]
Solubility in 100 g water at 20.0 °C [g]	78.1[11]

2. Experimental

ADN(2009) and ADN(1998) (Hosoya Pyro–Engineering Co., Ltd.) were used as samples. ADN(1998) had been stored for 11 years in the dark. The effects of light, heat, moisture and other factors on the samples will vary depending on the area of the sample tested. Therefore, ADN(1998) was separated into a surface region and a bulk region, which were characterized separately (Fig. 2). To understand the difference qualitatively, the region assumed sufficient contact with atmosphere (until approximately 2 mm deep) was defined as surface region. Commercially available powdered ammonium nitrate (AN, >99 % pure) was used as a reference.

The surface of ADN(2009) and ADN(1998) was examined by scanning electron microscopy (SEM) using a Shimadzu SUPERSCAN–220. The chemical structure of the samples was confirmed by infrared (IR), Raman and ultraviolet (UV) spectroscopy. The KBr method was used for IR spectroscopy, conducted on a JASCO FT/IR–420.

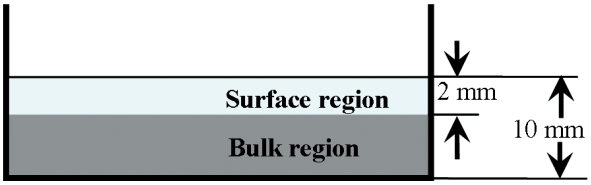

Fig. 2 Definition of the surface region and the bulk region of ADN(1998).

For Raman spectroscopy, a Kaiser Raman RXN system coupled to a 785 nm semiconductor laser was used. The sample was directly illuminated by the focused laser beam. UV spectroscopy on ADN aqueous solutions was carried out on a Shimadzu UV–1800.

The thermal behaviour of ADN was characterized using sealed cell differential scanning calorimetry (SC–DSC, Mettler Toledo HP DSC 827e) and a thermal activity monitor (TAM, TA Instruments TAM III). For DSC measurements, approximately 1.5 mg of sample was loaded into a SUS303 cell and sealed in air, then heated from 30 to 350 °C at 5 K min^{-1}. For TAM measurements, approximately 100 mg of sample was loaded into a SUS ampoule in air and was then maintained at 110 °C.

3. Results and discussion

3.1 The surface condition of ADN(2009) and ADN (1998)

Figure 3 shows SEM images of ADN(2009) and ADN (1998). ADN(2009) particles are plate–shaped, whereas the ADN(1998) particles are small, needle–like, and form aggregates. ADN(1998) particles are larger than ADN (2009) particles due to aggregation of the small crystals.

3.2 Identification of aging products from ADN

Figures 4 and 5 show the IR and Raman spectra of ADN (2009), ADN(1998), and AN. IR absorption of NO_3^- at 1380 cm^{-1}, and Raman scatterings of NO_3^- at 1040 and 710 cm^{-1}, were observed in ADN(1998), whereas no NO_3^- was detected in ADN(2009), showing that compounds containing NO_3^- are present in ADN(1998). The origin of NO_3^- is not clear, although it may be due to AN, since AN is composed of NH_4^+ and NO_3^-.

ADN(1998) was separated into its components by filtration using acetone. Figure 6 shows the IR spectra of ADN(2009), ADN(1998), AN, and the residue remaining after separation. Infrared absorption due to NH_4^+ at 3150 cm^{-1} and to NO_3^- at 1380 cm^{-1} was observed in the residue and in AN. Figure 7 shows the SC–DSC curves obtained for the residue and for AN. In the DSC curve of AN, heat absorption due to phase transitions was observed at around 55, 130 and 170 °C, and heat generation from the decomposition of AN was evident at

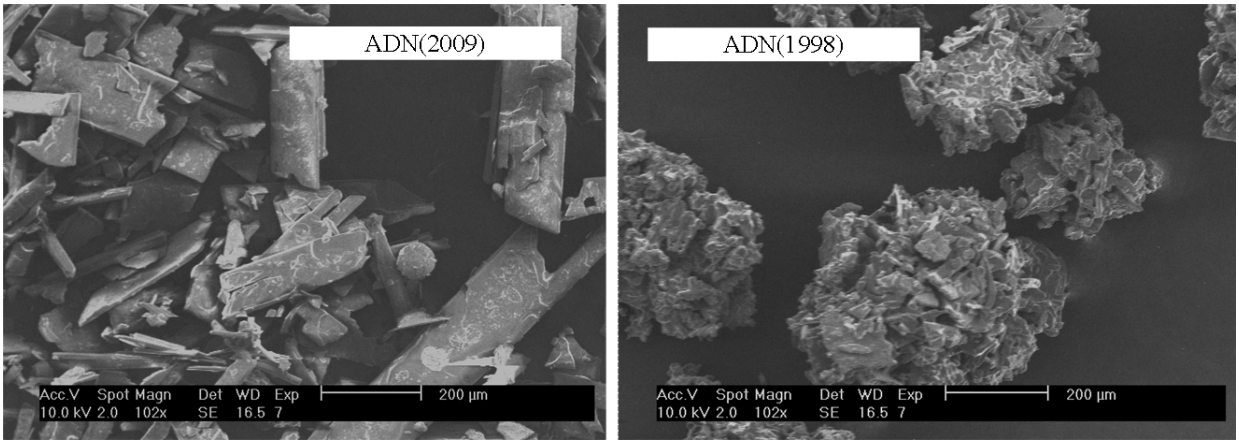

Fig. 3 SEM images of ADN(2009) and ADN(1998).

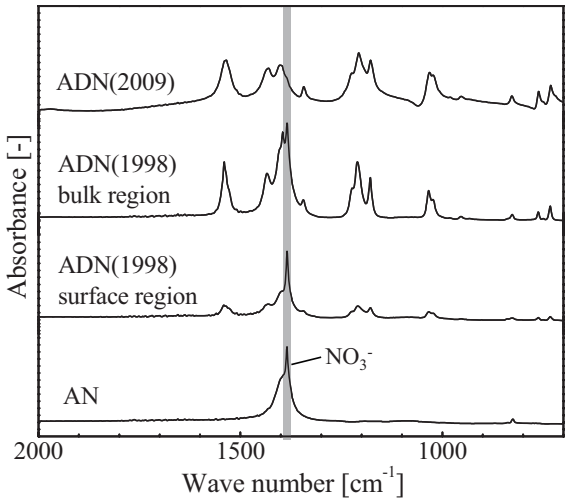

Fig. 4 IR spectra of ADN(2009), ADN(1998), and AN.

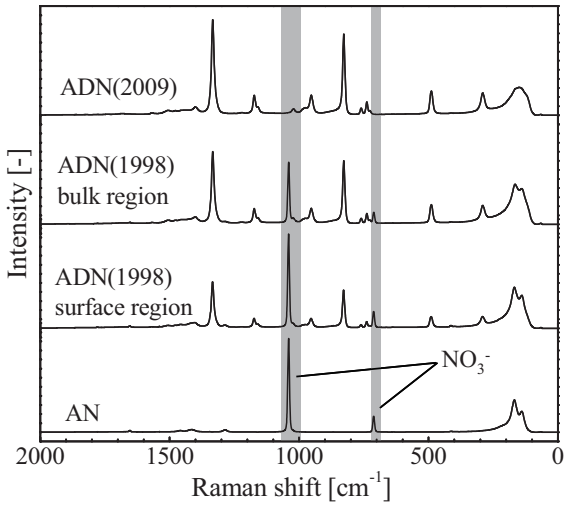

Fig. 5 Raman spectra of ADN(2009), ADN(1998), and AN.

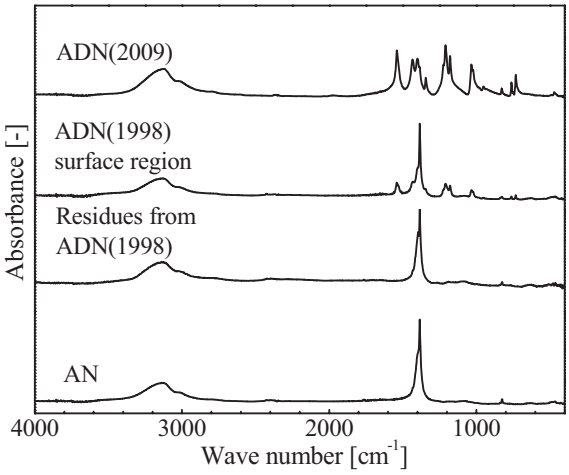

Fig. 6 IR spectra of ADN(2009), ADN(1998), residues from ADN(1998), and AN.

approximately 260 to 300 °C. These heat absorption and heat generation were also observed in the residue, indicating that the heat absorption in the residue are the phase transitions of AN, and the heat generation in the residue is due to the decomposition of AN. Spectroscopic and thermal analyses of the residue therefore show that ADN(1998) contained ADN and AN, and that ADN had degraded to AN during storage.

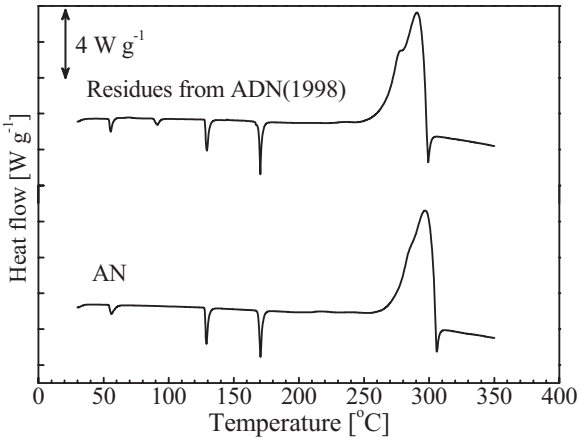

Fig. 7 DSC curves of the residue from ADN(1998), and AN.

3.3 The quantification of the aging

An aqueous solution of ADN(2009) absorbed UV at 284.8 nm. Assuming that ADN(2009) consisted entirely of ADN, the amount of ADN in ADN(1998) was determined by absorbance at 248.8 nm and was determined to be 57 wt.% at the surface and 89 wt.% in the bulk region (Fig. 8). Thus, the extent of aging at the surface is greater than that in the bulk region.

3.4 Comparison of the result of spectroscopy with that of thermal analysis

Figure 9 shows the DSC curves of ADN(2009), ADN (1998), and AN. Two heat generation events are evident at approximately 130 to 220 °C (first exothermic peak) and 220 to 290 °C (second exothermic peak) in ADN(2009) and ADN(1998). The temperature range of the second exothermic peak is identical to the thermal decomposition of AN. The thermal decomposition of ADN is believed to produce AN and N_2O[12], as shown in the reaction formulae in equations (1) and (2). During the first heat generation event, ADN decomposes to AN and N_2O, and during the second heat generation event, AN is further decomposed to N_2O and H_2O.

$$NH_4N(NO_2)_2 \rightarrow NH_4NO_3 + N_2O \quad (1)$$

$$NH_4NO_3 \rightarrow N_2O + 2H_2O \quad (2)$$

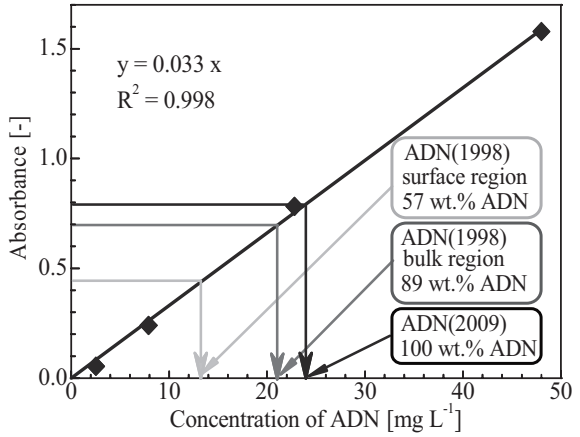

Fig. 8 The amount of ADN in aqueous ADN(2009) and ADN (1998).

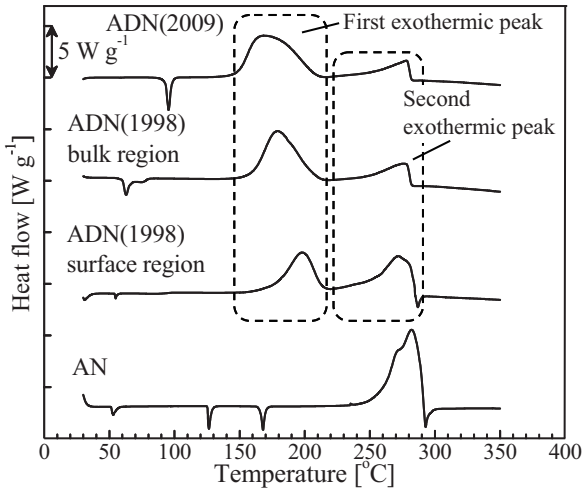

Fig. 9 DSC curves of ADN(2009), ADN(1998), and AN.

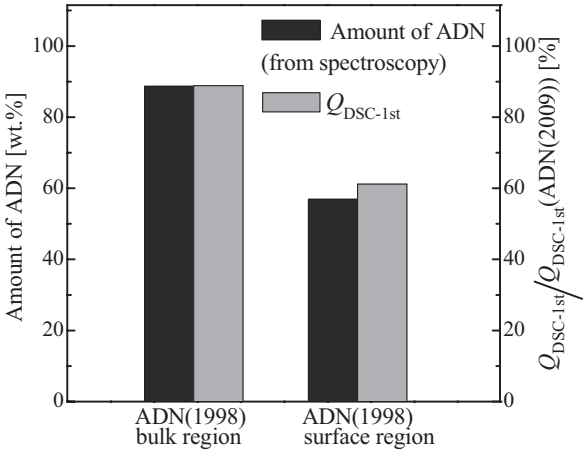

Fig.10 Amount of ADN in ADN(1998) determined by SC–DSC and UV spectroscopy.

The first exothermic peak of ADN(1998) showed lower heat generation than that of ADN(2009), whereas ADN (1998) released more energy than ADN(2009) at the second exothermic peak. Figure 10 shows the $Q_{DSC-1st}$ ratio for ADN(2009) and the ADN ratio as determined by UV spectroscopy, in which $Q_{DSC-1st}$ is the heat value of the first heat generation event. Compared to ADN(2009), the $Q_{DSC-1st}$ of ADN(1998) was 89 % in the bulk region and 61 % at the surface. Thus, $Q_{DSC-1st}$ decreased as the ADN ratio decreased. In addition, the ratio of decrease in $Q_{DSC-1st}$ was approximately equal to that in the amount of ADN.

These results indicate that the first heat generation event is due to the decomposition of ADN, and that the second heat generation event is due to the decomposition of AN generated by the thermal decomposition or aging of ADN. Thermal analysis also indicated that aging decreases the amount of ADN and increases the amount of AN, showing that the aging of ADN can be quantified by thermal analysis.

3.5 Influence of aging on thermal decomposition of ADN

The melting point T_m, the onset temperature, and the heat value of the first heat generation event, $T_{DSC-1st}$ and $Q_{DSC-1st}$, from DSC are summarized in Table 2. The DSC

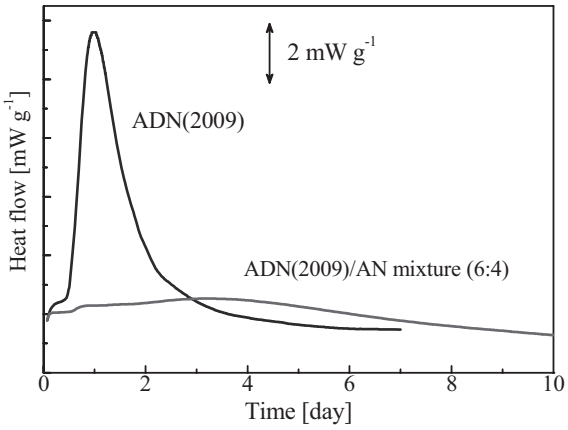

Fig.11 Heat flow from ADN(2009) and an ADN(2009)/AN mixture (6 : 4) at 110°C.

Table 2 DSC results for ADN(2009) and ADN(1998).

Sample	ADN amount [wt.%]	T_m [°C]	$T_{DSC-1st}$ [°C]	$Q_{DSC-1st}$ [kJ g^{-1}]	$Q_{DSC-1st}$ [%]	$Q_{DSC-2nd}$ [kJ g^{-1}]
ADN(2009)	100	94	132	1.8	100	0.6
ADN(1998) bulk region	89	62	136	1.6	89	0.7
ADN(1998) surface region	57	56	150	1.1	61	1.2

results for ADN(1998) showed a lower T_m, higher $T_{DSC-1st}$, and a lower $Q_{DSC-1st}$ than for ADN(2009). AN significantly reduces the melting point of ADN[13]. It appears that the observed changes in the thermal properties are due to a decreased amount of ADN and an increased amount of AN due to aging.

Figure 11 shows the results of an isothermal experiment at 110 °C for ADN(2009) and an ADN(2009)/AN mixture (6 : 4) on a TAM. From Chapter 3.2 to 3.4, ADN was degraded to AN, and the amount of ADN in ADN(1998) at the surface was approximately 60 wt.%. In this experiment, the ADN(2009)/AN mixture was prepared as a sample for reproduction of ADN(1998) at the surface. In ADN(2009), rapid heat generation was observed after approximately 1.2 days, whereas only moderate heat generation was observed from the ADN(2009)/AN mixture, after about 3.3 days. It is likely that these heat generation events result from the thermal decomposition of ADN, since the start of heat generation is at approximately 130 °C in the DSC curves of ADN(2009) and ADN(1998). These results suggested aging curtails the thermal reactivity of ADN.

4. Conclusion

The surface characteristics of ADN(2009) and ADN (1998) were investigated using SEM, and showed that ADN(1998) particles are largely aggregates.

The composition of ADN(1998) was investigated using IR, Raman and UV spectroscopy, and DSC. AN was found in ADN(1998), showing that ADN had degraded to AN during storage. The amount of ADN in ADN(1998) was 57 wt.% at the surface and 89 wt.% in the bulk region,

indicating that the extent of aging at the surface is greater than in the bulk region.

The DSC and TAM results showed the influence of aging on the thermal decomposition of ADN. The thermal properties of ADN(2009) and ADN(1998) differed, mainly due to the presence of AN generated by the aging of ADN. Thus, aging can change the physical properties of ADN, which affects its performance as a rocket propellant.

Acknowledgements

The authors are grateful to Dr. Yuji Wada and Dr. Yusuke Wada belonging to National Institute of Advanced Industrial Science and Technology for supporting our research.

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高エネルギー酸化剤アンモニウムジニトラミドの経時変化特性

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経時変化はエネルギー物質の性能を変化させる可能性がある。本研究ではアンモニウムジニトラミド（ADN，$NH_4N(NO_2)_2$）の経時変化特性を明らかにすることを目的とした。ADNは高エネルギーかつ環境影響が小さいことから，固体ロケット推進薬の新規酸化剤として期待されている。

最近合成されたADN（ADN(2009)）と暗所にて11年間保存された試料（ADN(1998)）を比較した。特性の測定は赤外（IR），ラマン，紫外（UV）分光分析，密封セル示差走査熱量測定（SC−DSC）および高感度熱量計（TAM）を用いて行った。

IR，ラマン，UV分光分析およびSC−DSCによりADN(1998）の組成は変化しており，ADNと硝酸アンモニウム（AN）の混合物であることが示唆され，ADNの一部が硝酸アンモニウム（AN）に分解していることが示された。ADN(1998）中のADN量は，表面では57 wt. %，内部では89 wt. %であり，経時変化は内部よりも表面の方が進行していることが示された。

DSCとTAMの結果より，ADNの熱分解に及ぼす経時変化の影響が示された。経時変化により生じたANが熱特性の変化の主な原因であると考えられた。

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