**Research paper**

# Study on degradation of a mixture of guanidine nitrate and basic copper nitrate during water absorption

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## Abstract

The degradation of a mixture of guanidine nitrate (GN) and basic copper nitrate (BCN), which is used as a gas generant, was studied under the application of heat and water. The degradation that occurs was observed using an ultraviolet-visible absorption spectrometer and X-ray diffraction (XRD) analysis. The results showed a change in the chemistry of BCN and the generation of cupric oxide (CuO). The chemical reaction produced the degradation of BCN at 75 °C. In addition, the GN/BCN exhibited deliquescence, implying that the mixture contained a large amount of water when it reacted with humid air; it was also observed that GN reduces the rate of degradation of BCN. The mechanism for reduction was considered and confirmed by adding nitrate or guanidine salts to an aqueous solution of BCN, which was subjected to heat. The results of XRD showed that the rate of degradation decreased because of the presence of nitrate ion, while the guanidine ions did not produce any effects of reduction. This study has revealed that the effect of the reduction of GN originated from the nitrate ions and depended on the quantity of GN.

***Keywords***: guanidine nitrate, basic copper nitrate, aging, water absorption, humidity

## 1. Introduction

Airbags are one of the most important safety devices in modern vehicles. When vehicles are struck during accidents, airbags decrease the possibility of people dying or becoming injured. Normally, the system in the devices uses energetic materials such as gas generants because they can help in expanding the airbag to such an extent that they can absorb the impact induced during accidents. One of the requirements for the proper functioning of an airbag is that it should be stable enough to withstand environmental conditions that are hot and humid. Recently, the lifetime of vehicles has increased; also, the importance of their stability has increased. Vehicles are used all around the world, and the environments that affect the stability of gas generants are becoming more severe. With regard to the stability of gas generants, an accident in which gas generants that consisted of ammonium nitrate absorbed moisture was reported[1)]. The compounds that made up the gas generants absorbed moisture at a high temperature and humidity, and the water produced an unexpected level of degradation in the composition, which affected combustion.

In general, the existence of harsh environmental conditions over a long period of time, is the cause of degradation. Each gas generant has its own degradation mechanism that is determined by the type of ingredients, shape, temperature, humidity, and so on.

Some compositions are common among gas generants. In this study, the gas generant consisted of a mixture of guanidine nitrate (GN) and basic copper nitrate (BCN), which is a major composition of gas generants; the hygroscopic property of this mixture was given due attention in order to investigate its behavior under degradation. Information about degradation mechanisms and conditions for mixing GN and BCN, contributes to the safety of vehicles. This study aims at revealing the condition of degradation that will be beneficial in elucidating the problem of combustion that is caused by degradation, and estimating the lifetime of gas generants in airbags.

GN is a well-known energetic material and has been used as gas generant[2)−9)]. This material provides a large quantity of gases because it contains four nitrogen atoms per molecule, and no atoms that are metals. The lack of metallic atoms is beneficial: it makes GN to produce a lower quantity of residue. Some materials added to GN-based gas generants enhance the combustion performance, with BCN exhibiting a high level of performance[4), 5)]. The effect of BCN on temperature during the decomposition of GN was reported. The balance of oxygen has been related with the effects of temperature on decomposition[6)]. GN/BCN decreased the initial temperature of a thermal decomposition from that of each component[6), 9)]. The decomposition temperature of the mixture was above the boiling point of water. This implies that any mixture that has a temperature that is not up to its boiling point, is not expected to decompose in water. In the midst of available literature, details on the degradation of GN/BCN in the presence of moisture have not been clarified.

In this study, the products of degradation in hot water were observed by an ultraviolet-visible absorption spectrometer (UV-vis) and X-ray diffraction analysis (XRD). The experiment was conducted as an accelerated aging test. A product of degradation was measured using XRD. In order to simulate the behavior in usage environments, the hygroscopic performance was measured by weight variation under conditions of controlled temperature and humidity. The effects of the nitrate and guanidine salts on the degradation of BCN were observed using XRD. The experiments conducted aim at observing the degradation that occurred in GN/BCN with water.

## 2. Experimental

### 2.1 Reagents

All of the samples obtained for the study were purchased and used without further purification. Guanidine nitrate, GN, had a purification level that was at least 97.0%; basic copper nitrate, BCN, had at least 99.9%; copper (II) nitrate trihydrate, $Cu(NO_3)_2$, had a minimum of 99.0%; copper (II) oxide, CuO, had a minimum of 95.0%; potassium nitrate, $KNO_3$, had 99.0%; strontium nitrate, $Sr(NO_3)_2$, had 98.0%, while guanidine carbonate, GC, had 98.0%; sodium chloride, NaCl, had 99.0%; potassium sulphate, $K_2SO_4$, 99.0%.

### 2.2 Preparation of a sample for UV-Vis

An aqueous solution containing GN, BCN, aged GN, aged BCN, and aged GN/BCN, was prepared for the UV-vis. A solution of GN or BCN was formed by dissolving them in 100 mL of water in a volumetric flask at a concentration of 1 g $L^{-1}$ for each sample. A solution of GN/BCN in a mixed ratio by volume of 1:1 was obtained by mixing a solution of GN with a solution of BCN. The aged solutions of GN, BCN, and GN/BCN were prepared by heating each unprocessed solution at 75 °C in glass bottles. The heated solutions were cooled after 1 h, so as to prevent any reactions; thereafter, they were subjected to a UV-vis.

### 2.3 Preparation of a sample for XRD

In order to study how the GN functions, two samples with different amounts of GN were aged for the XRD. Thirty milliliters of deionized water was added to 0.3 g of BCN in a test tube that had a flat bottom. In addition, 0.03 g of GN was mixed with 0.3 g BCN and 30 mL deionized water. In order to observe the effects of the nitrate salts and guanidine salts, GN, $KNO_3$, $Sr(NO_3)_2$, and GC were mixed with 0.3 g BCN and 30 mL of deionized water. The mole ratio of BCN to nitrate ions, and BCN to guanidine ions, was controlled at 1:2.

The aged samples were prepared by heating them for 1 h at 75 °C. The BCN samples were heated at 75 °C, for 0.5 h, 1 h and 2 h. Heated samples were cooled in ice water, and the cooling process quelled the reaction. Cooled samples were filtered with filter paper (qualitative filter paper, in which the retention of the particle is 5 μm), and the residue was collected. The residues were dried at room temperature.

### 2.4 Hygroscopicity test

The samples GN, BCN, and GN/BCN, were prepared. The mix mole ratio of GN to BCN in the mixture was 5:4. Each sample (weighing 0.3 g) was set on a plastic tray, and stored for 144 h in a sealed vessel that was under a state of controlled temperature and humidity. The temperature of 50 °C was controlled by an incubator, and the humidity (about 75% relative humidity (RH), and 95% RH) was controlled using the saturated salt solution method[10)]. In this study, NaCl and $K_2SO_4$&shy; were used as saturated salts. The hygroscopic behavior of the samples was shown by a variation in weight which can be measured using an electric scale. The durations for storage were 24, 48, 96, and 144 h.

### 2.5 Conditions for taking measurements

A UV-Vis was used to detect degradation. UV/visible spectra were recorded using V560 (JASCO). The samples were placed in a cell that consisted of quartz, and the range for the measurements taken, was between 900 nm and 200 nm, while the integration number was 2 times, and the scanning speed was 200 nm $min^{-1}$. A resolution of 0.5 nm, and a bandwidth of 1 nm, were applied. The sample obtained after aging test was the mixture of liquid and black degradation product.

XRD was used as a method for identifying the products that were produced during degradation. Powder XRD was measured using SmartLab (Rigaku Corporation); Copper k-alpha ($CuK\alpha$) radiation was used at 40 kV and 50 mA, while the scanning speed was 5 deg. $min^{-1}$. In the measurements recorded using XRD, the relationship between the molar ratio of BCN and the degradation product, and their integrated intensity ratio, were established.

## 3. Results and discussion

### 3.1 Detection of degradation using UV-vis

With regard to solubility, blue BCN particles dispersed in water and remained undissolved while water dissolved GN. After the aging test, both BCN samples, and the samples containing GN/BCN, turned black due to black precipitate. The results of the UV-vis are shown in Figure 1. There is no difference between the spectra of the unaged GN and that of the aged GN. The peak that was observed to be around 300 nm, was attributed to nitrate ion[11]. The spectra of copper nitrate showed a peak of nitrate ion at around 300 nm and one of copper ion at around 750 nm. A change in the UV-vis absorption spectra was observed in the results of the aged samples that contained BCN. The peak around 300 nm was observed both aged BCN and GN/BCN. These differences in UV-vis spectra indicate chemical change of BCN.

### 3.2 Determination of the products of degradation associated with water

The XRD result of the peaks obtained from residue is shown in Figure 2. The figure shows that some peaks increased as the heating duration increased, and each of the peaks at 32.5 °, 35.5 °, 38.7 °, and 48.7 °, were similar with the peaks obtained for the CuO produced. There were smaller peaks for BCN in the aged sample that was heated at 75 °C for 2 h. These results indicate that CuO, which is a product of degradation, is generated from BCN, and that BCN decomposed in water at 75 °C.

The decomposition of BCN was studied as reported in previous papers, and one of the products of decomposition is CuO. If heat is applied at a temperature of 230 °C, it will create a reaction that can be expressed as shown in equation[12];

$$Cu_2(OH)_3NO_3 \rightarrow 2CuO+HNO_3+H_2O \qquad (1)$$

The Equation (1) for decomposition describes the reaction occurred at a higher temperature than that used in our experiments; an end product of decomposition was found in our experiments. In the GN/BCN, CuO was reported as a product of thermal decomposition in the test that was also carried out at an elevated temperature[9]. CuO is one of the end products of heating GN/BCN.

The XRD peak area ratios of BCN to CuO were plotted as a function of the mix ratio of BCN to CuO, as shown in Figure 3. The regression curve was obtained as y. The ratio of BCN to CuO for each aged sample was estimated with the curve, as shown in Figure 4. The quantitative result shows that an increasing amount of CuO was being generated by the aging test.

### 3.3 Hygroscopic behavior of GN/BCN

Moisture easily penetrates into materials; this is a well-known cause of the degradation process, especially in hygroscopic materials. Hygroscopicity was observed by the variation of weight in humid air, by applying the hygroscopicity test.

The result of the hygroscopicity test is shown in Figure 5. The weight of BCN was unchanged in the humid air,

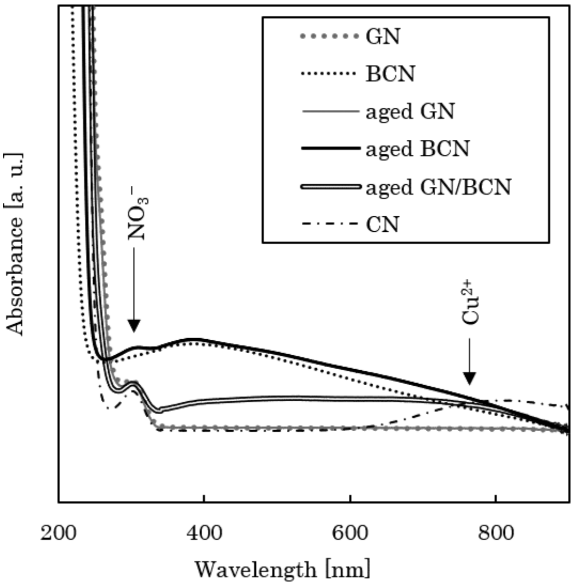

Figure 1 UV-vis results of aged samples (CN; 0.05 mmol L−1 Cu(NO3)2 solution).

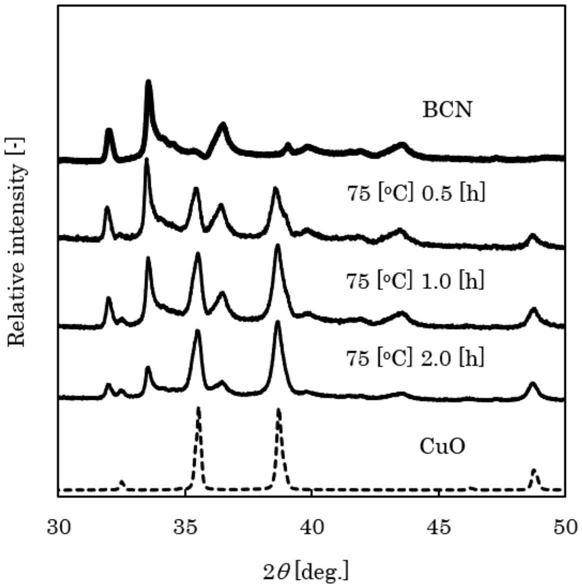

Figure 2 XRD patterns of aged BCN samples.

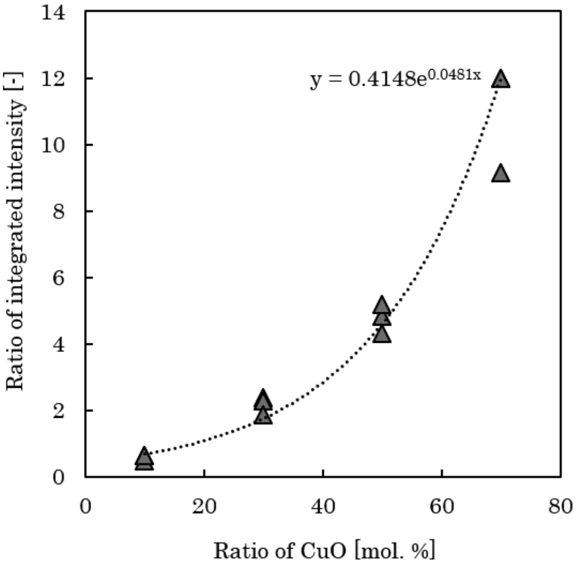

Figure 3 Calibration curve of CuO/BCN (Ratio of integrated intensity; the peak at 35.6 ° [CuO]/ the peak at 32.1 ° [BCN]).

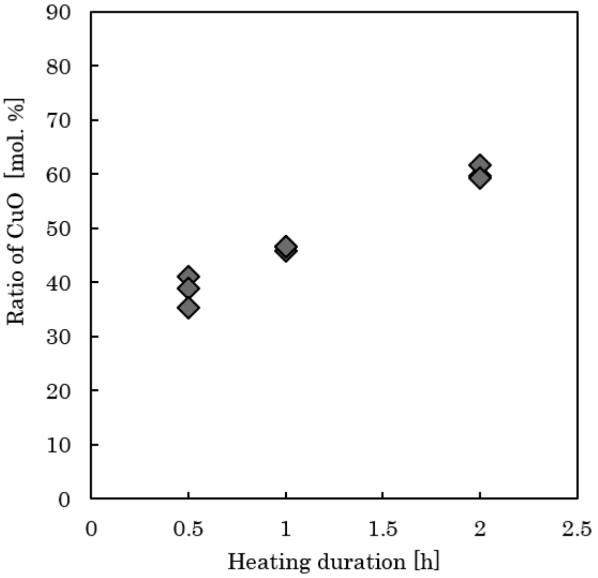

**Figure 4** Ratio of CuO in the residue of aged BCN after aging test.

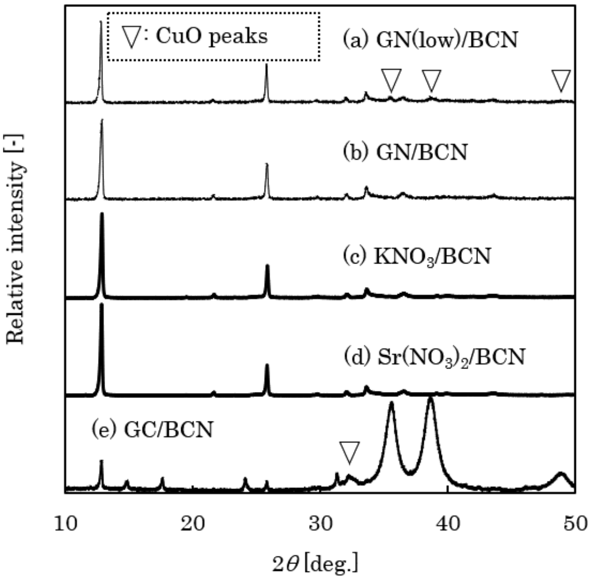

**Figure 6** Effects of additives on degradation of BCN (1 h, 75 °C) [GN(low)/BCN = 1/10 wt. ratio, Inverted triangle means CuO peaks].

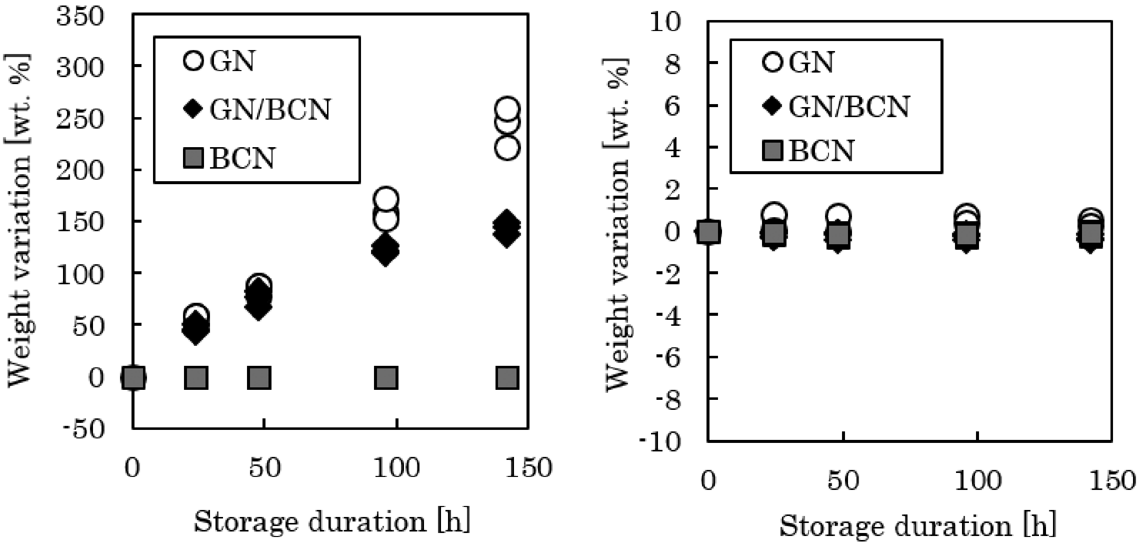

**Figure 5** Weight variation of the samples in the constant humidity (Left; 95% RH, Right; 75% RH).

and the results show that BCN is low in hygroscopic materials. The variation in the weight of the GN and GN/BCN, were scarcely observed. But at 95% RH, their weights obviously increased in the humid air. The implication of this increment is that the GN absorbed large amount of moisture at 95% RH. Moreover, the GN exhibited deliquescence at 95% RH, while BCN was stable around moisture. The deliquescence could produce water for BCN in the GN/BCN.

### 3.1 Effects of nitrate salts and guanidine salts on the degradation of BCN that had contact with water

The products of degradation of the GN/BCN that was immersed in water at 75 °C were measured using XRD in order to determine the effects of the GN on the degradation of BCN. The results of XRD are shown in Figure 6 (a). A product of degradation, CuO, was detected in the results of the mixture of aged GN(low)/BCN in which the weight ratio of BCN to GN was controlled at 10:1. The ratio of product that was calculated using a calibration curve, was about 25.4 mol.%, which is about five -ninths that of the aged BCN. In addition, the results showed that the rate of reaction in the solution of GN is lesser than that in pure water, and it indicated that the degradation to change BCN into CuO was inhibited by the existing GN in the solution. The residue obtained from a high concentration solution of GN showed no peak of the CuO appear (where the molar ratio of GN/BCN = 2:1) as is shown Figure 6 (b). These results show that the effects of GN in suppressing the degradation of BCN, depends on the concentration of GN in water. The mechanism for the reduction of the degradation was considered on the basis of these results and previous studies.

CuO, which is a product of the degradation of BCN, was observed in a residue using XRD (Figure 2). Nitrate ion was observed in aged BCN by UV-vis (Figure 1). From the results, the simple mechanism for degradation can be expressed through the following equation:

$$Cu_2(OH)_3NO_3 \xrightleftharpoons{k} 2Cu^{2+}+3OH^{-}+NO_3^{-} \quad (2)$$

$$Cu^{2+}+2OH^{-} \rightleftharpoons CuO+H_2O \quad (3)$$

The concentration of nitrate ion affects the solubility of BCN because the solubility of a material depends on the concentrations of ions dissolved in a solvent, which are based on the solubility product constant, $k$. When nitrate ion is produced from other materials, the ratio of dissolution of BCN is efficiently decreased, due to the lesser degree of solubility of BCN. Thus, the nitrate ion included in the GN was expected to inhibit degradation.

If $NO_3^-$ is the cause of the effects from the degradation of BCN, then the effects of inhibition of other nitrate salts can be observed. For the sake of determining the effects of nitrate ion, soluble nitrate salts (guanidine nitrate, potassium nitrate and strontium nitrate) and guanidine salts (guanidine nitrate and guanidine carbonate) were added to BCN, and water was poured into the mixtures. The XRD results of the residue of aged samples are shown in Figure 6. Only insoluble materials, such as BCN and CuO, appeared in the residue of aged samples. In Figure 6, the XRD patterns for a mixture of nitrate salts and BCN, contains BCN peaks without any CuO peaks. The results indicate that nitrate ion causes a reduction in the degradation of BCN. In the XRD pattern for aged GC/BCN, large CuO peaks appeared. These results indicated that the effect of GN on the degradation of BCN did not originate from the guanidine ion, but from the nitrate ion.

## 4. Conclusion

In order to reveal degradation of GN/BCN with water, accelerated aging test and hygroscopicity test were conducted in this study.

The results of the UV-vis showed a change of spectra in BCN at 75 °C. In the UV-vis spectra, the absorption of nitrate ions continued, even after heating, while the absorption was quite different for the aqueous solution of BCN, and the GN/BCN. The results of the XRD analysis showed a product of degradation of BCN at 75 °C; the product was CuO. The quantity of CuO increased, depending on the duration of heating.

The hygroscopicity test showed deliquescence of GN. And GN/BCN absorbed moisture at about 95% RH. The absorption of the moisture shows that there is contact between BCN and water.

The effect of GN on the rate of degradation of BCN was expected, and it was believed that the nitrate ions affected the dissolution process of the degradation of BCN. In consideration of this, the nitrate ions were expected to act as an agent that could reduce the rate of reaction of BCN in producing CuO, and the effect of the reduction was determined. The identification of products by XRD reveals the fact that the effect of GN on the rate of degradation of BCN depends on the quantity of nitrate ions. This result revealed that aging rate depends on quantity of guanidine nitrate, and the fact contributes to estimating aging rate and the lifetime of gas generants in airbags.

BCN has been considered to be very stable, these results reveal that water and heat degrade BCN. This finding can contribute to improving the safety performance of gas generants from the viewpoint of prediction of degradation problems. By searching extensively, it can be observed that the effects of degradation on combustion have not been reported. The effects of degradation on the combustion and decomposition mechanisms of GN/BCN, should be clarified in the near future.

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