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Decomposition of hydroxylamine/water solution with added iron ion

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Abstract

Decomposition hazards of hydroxylamine (HA)/water solution with and without the addition of iron ion were studied in this paper. Tests were conducted to obtain information about decomposition hazards of HA/water solution following the United Nations recommendations on the transport of dangerous goods.

When the heat accumulation storage test was conducted using HA50 wt.%/water solution without the addition of iron ion, the self-accelerating decomposition temperature (SADT) was 80 °C. Therefore, HA50 wt.%/water solution was not classified with self-reactive substances following the United Nations recommendations on the transport of dangerous goods.

Decomposition hazards of HA50 wt.%/water solution with added iron ion were investigated. The concentration of iron ion in sample of HA50 wt.%/water solution without the addition of iron ion was below 1.0 ppm. The range of the concentration of iron ion in sample of HA50 wt.%/water solution with added iron ion was between 1.0 and 5.4 ppm. The thermal stability of HA50 wt.%/water solution decreased by the addition of iron ion in the heat accumulation storage test. HA50 wt.%/water solution with the addition of iron ion was classified with self-reactive substances following the United Nations recommendations on the transport of dangerous goods. The intensity of the thermal decomposition of HA50 wt.%/water solution increased by the addition of iron ion in the Koenen test.

Keywords: Hydroxylamine; Thermal decomposition; Heat accumulation storage test; Self-accelerating decomposition temperature (SADT); Iron ion contamination

1. Introduction

In recent years, hydroxylamine (HA) was involved in two tragic accidents. One occurred in the USA in February 1999. The other occurred in Japan in June 2000 [1]. The chemical

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formula of HA is NH_2OH. HA100 wt.% is a colorless crystal at room temperature. HA is widely used as a flaking off agent and a metallic surface treatment agent in the semiconductor industry.

It is well known that HA decomposes by heat and metal ion contamination [2]. Some studies exist on the thermal decomposition of HA/water solutions. The thermal behavior was studied to evaluate the potential hazards of HA/water solutions on the basis of the calorimetric data [3–5]. We presented risk evaluation of the decomposition of HA/water solution in the previous work [6]. In that work, information regarding thermal properties and the intensity of the thermal decomposition was obtained by thermal analysis and the pressure vessel test.

It is important to obtain more knowledge of the decomposition of HA/water solution for the purpose of safe handing, use and storage. In the United Nations recommendations on the transport of dangerous goods, model regulations (Version 12), HA is classified as Class 8 (corrosive substances) dangerous goods though HA/water solution of high concentration involves high energy [7]. HA50 wt.%/water solution is a candidate for a material of Division 4.1 in Class 4 (self-reactive substances) in the United Nations recommendations on the transport of dangerous goods. The decomposition hazards of HA/water solution were evaluated by the test methods, which were prescribed in the United Nations recommendations on the transport of dangerous goods, test and criteria manual (Version 3) in this paper [8]. The heat accumulation storage test, the BAM50/60 steel tube test, the time pressure test, the deflagration test, the Koenen test, the Dutch pressure vessel test and the ballistic mortar MkIIID test were conducted using HA50 wt.%/water solution. Detailed descriptions of these tests are given in [8].

The decomposition of HA/water solution is accelerated by the catalytic effect of a metal ion. Reactivity of HA/water solution with iron, copper, nickel ions, chromium and manganese ions were examined by measuring the weight reduction after the addition of the metal ion in another report [9]. The ignition automatically began when the 0.5 wt.% (5000 ppm) iron ion was added to HA85%/water solution. In contrast, the decomposition reaction of HA85%/water solution with the copper ion was calm compared to that of iron ion. HA/water solution did not react with other ions.

This paper presents information about the influence of iron ion on the decomposition of HA/water solution. The decomposition hazards of HA/water solution with a very small amount of iron ion were evaluated by the United Nations recommendations tests. The decomposition hazards of HA/water solution with the addition of iron ion were found by the heat accumulation storage test, the Koenen test and the Dutch pressure vessel test. The thermal stability and the intensity of the thermal decomposition of HA/water solution were discussed on the basis of the results of the heat accumulation test, the Koenen test and the Dutch pressure vessel test.

2. Experiment

The risk evaluation tests for self-reactive substances were conducted following the United Nations recommendations [8]. Samples were HA50 wt.%/water solution with and without the addition of iron ion. The decomposition hazards of HA/water solution with and without the addition of iron ion were discussed on the basis of the results of the heat accumulation storage test, the Koenen test and the Dutch pressure vessel test.

2.1. Samples

HA50 wt.%/water solution was supplied by Wako Pure Chemical Industries, Ltd. This HA50 wt.%/water solution contains iron below 1 ppm according to its product information and is distributed on the market. This HA50 wt.%/water solution has the added stabilizer to prevent the decomposition of HA.

Three kinds of samples were used in risk evaluation tests. HA50 wt.%/water solution without the addition of iron ion/water solution was used as sample A. HA50 wt.%/water solutions with the addition of iron ion/water solutions were used as sample B and sample C.

The concentration of iron ion in sample A was within the range 0.1–1.0 ppm on the basis of the measurement results by inductively coupled plasma (ICP) spectrometry. The iron ion/water solution was added to HA50 wt.%/water solution when sample B or sample C was made. Source of ferric ion (Fe^{3+}) was ammonium ferric sulfate [$Fe(III)NH_4(SO_4)_2\cdot12H_2O$]. The resulting solution was stirred so that iron ion diffused uniformly in HA50 wt.%/water solution after the iron ion water/solution was added to HA50 wt.%/water solution. The concentration of iron ion in samples B and C were 1.2 (±0.2) ppm and 5.2 (±0.2) ppm, respectively, on the basis of the measurement results of ICP analysis.

2.2. Risk evaluation test methods

The following seven kinds of tests were conducted using samples A–C:

(1) Heat accumulation storage test,
(2) BAM50/60 steel tube test,
(3) Time pressure test,
(4) Deflagration test,
(5) Koenen test,
(6) Dutch pressure vessel test,
(7) Ballistic mortar MkIIID test.

Table 1 shows hazards evaluated by these test methods. All tests were conducted following the United Nations recommendations on the transport of dangerous goods, tests and criteria manual (Version 3) [8]. Decomposition hazards of HA/water solution without and with iron ion were discussed on the basis of the results of the heat accumulation storage test, the Koenen test and the Dutch pressure vessel test. Outlines of these test methods are described as follows.

2.3. Heat accumulation storage test

The Dewar with a glass lid was used in the heat accumulation storage test. The sample mass used was 0.43 (±0.01) kg. A Dewar vessel with a heat loss of 69.2 mW/kg/K was

Table 1
Hazards measured by test methods

Test method	Hazards evaluated
Heat accumulation storage test (SADT)	Thermal stability
BAM50/60 steel tube test	Propagation of detonation
Deflagration test	Propagation of deflagration
Time pressure test	Propagation of deflagration
Koenen test	Intensity of heat decomposition
Dutch pressure vessel test	Intensity of heat decomposition
Ballistic mortar Mk. IIID test	Explosive power

used in tests. The sample temperature was measured by a thermocouple, which was put into a glass tube. The thermocouple for the sample temperature was placed 60 mm above the bottom of the Dewar vessel.

The Dewar vessel was put in a drying oven. The air temperature in the oven was controlled at the desired temperature. The thermocouple for the ambient temperature was set in the middle point between the wall of the oven and the Dewar vessel, whose height was the same level as that of the thermocouple for the sample temperature. The sample temperature and the ambient temperature were measured every 2 min. Mass reduction was measured at the end of the test.

The self-accelerating decomposition temperature (SADT) is reported as the lowest temperature at which the sample exceeds the test chamber temperature by 6 K or more within a week. The substance should be considered to be a self-reactive substance if the SADT is 75 °C or less.

2.4. Koenen test

The sample vessel was 24 mm in internal diameter and 75 mm in length. The orifice plate was fitted with the sample vessel using the nut. The diameters of the orifices used in the Koenen test were 1.0, 1.5 and 2.0 mm.

The sample mass was 30 g. Heating was provided by four propane burners. The heating rate was 3.3 K/s. The heating rate was checked with 27 cm^3 volume of dibutyl phthalate in the sample vessel.

The test criteria are as follows:

Violent	the limiting diameter is greater than or equal to 2.0 mm,
Medium	the limiting diameter is equal to 1.5 mm,
Low	the limiting diameter is equal to or less than 1.0 mm and the effect in any test is different from the tube unchanged,
No	the limiting diameter is less than 1.0 mm and the effect in all tests is the same as the tube unchanged.

The limiting diameter of a substance is the largest diameter of the orifice when the sample vessel burst to several pieces at least once in three tests. The intensity of the thermal decomposition was classified by the deformation of sample vessel.

2.5. Dutch pressure vessel test

The volume of the pressure vessel was 234 cm^3. The diameters of the orifices used in the Dutch pressure vessel test were 1.0, 2.0, 3.5, 6.0 and 16.0 mm. The rupture disc was made of aluminum and endured about 520 kPa.

The sample mass was 10 or 50 g. Heating was provided by a propane burner. The heating rate was 3.5 K/s. The heating rate was checked with 10 g of dibutyl phthalate in the pressure vessel.

The test criteria are as follows:

Violent	rupture of the disc with an orifice of 9.0 mm or greater and a sample mass of 10.0 g,
Medium	no rupture of the disc with an orifice of 9.0 mm but rupture of the disc with an orifice of 3.5 mm or 6.0 mm and a sample mass of 10.0 g,
Low	no rupture of the disc with an orifice of 3.5 mm and a sample mass of 10.0 g but rupture of the disc with an orifice of 1.0 mm or 2.0 mm and a sample mass of 10.0 g or rupture of the disc with an orifice of 1.0 mm and a sample mass of 50.0 g,
No	no rupture of the disc with an orifice of 1.0 mm and a sample mass of 50.0 g.

The limiting diameter was the diameter of the orifice with the largest diameter with which the rupture disc was broken at least once in three tests. The intensity of the thermal decomposition was classified by the limiting diameter.

3. Results and discussion

3.1. Heat accumulation storage test for HA50 wt.%/water solution

Results of the United Nations recommendations tests are shown in Table 2. Since the SADT of sample A was 80 °C, HA50 wt.%/water solution was not classified with self-reactive substances following the United Nations recommendations. The intensity of the thermal decomposition for sample A was found only by the Dutch pressure vessel test.

Heat accumulation storage tests for sample A were conducted at 70, 75, 80 and 90 °C. Time history of ΔT between the sample temperature and the ambient temperature in the heat accumulation storage test is shown in Fig. 1. Time 0 was when the sample temperature became equal to the ambient temperature.

Sample A produced a heat release after the sample temperature reached the ambient temperature. The released heat of reaction was used to evaporate water and elevate the sample temperature. The temperature of sample A stopped increasing when time elapsed. The heat release with the greatest heat release rate was generated at the end of the test when the ambient temperature was 80 and 90 °C. One of the reasons for the greatest heat release rate was that HA might be concentrated because water evaporated easier than HA in HA/water solution. During the test, the sample volume decreased gradually due to evaporation of water.

Table 2
Decision results measured by test methods

Test method	Iron ion concentration[a] (ppm)		
	0.1–1.0 (sample A[b])	1.2 ± 0.2 (sample B[c])	5.2 ± 0.2 (sample C[c])
Heat accumulation storage test (SADT)	80 °C	70 °C	55 °C
BAM50/60 steel tube test	No	No	No
Deflagration test[d]	No	No	No
Time pressure test	No	No	No
Koenen test	No	Low	Low
Dutch pressure vessel test	Low	Low	Low
Ballistic mortar Mk. IIID test	No	No	No

[a] The iron ion concentration in HA50 wt.%/water solution.

[b] HA50 wt.%/water solution without the addition of iron ion.

[c] HA50 wt.%/water solution with the addition of iron ion.

[d] Sample temperature for: sample A was 20 and 50 °C; sample B was 50 °C and sample C was 23 °C.

3.2. Koenen test and Dutch pressure vessel test for HA50 wt.%/water solution

Results of the Koenen test for sample A are shown in Table 3. No vessel deformations occurred when sample A of 30 g and the disc with the orifice of 1.0 mm was used in the Koenen test.

Results of the Dutch pressure vessel test for sample A are shown in Table 4. The rupture disc operated once in two runs when sample A of 50 g and the disc with the orifice of 1.0 mm was used in the Dutch pressure vessel test. On the other hand, when sample A of 10 g was used, the rupture disc did not operate. This difference of results might be due to differences in the sample mass. Because water evaporated easier than HA in HA/water solution, HA/water solution with more than 50 wt.% concentration was made. The more the mass of HA/water solution the higher HA might be concentrated before HA/water solution

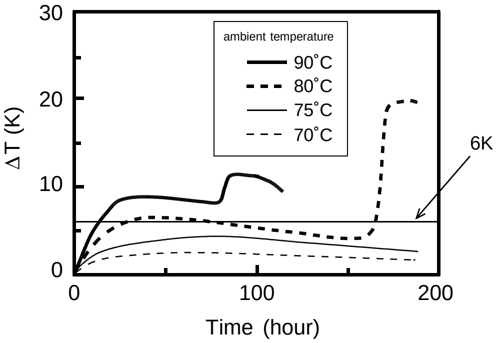

Fig. 1. Time history of ΔT in the heat accumulation storage tests at the various ambient temperatures. Sample is HA50 wt.%/water solution without the addition of iron ion water solution (sample A). ΔT indicates the temperature difference between the sample temperature and the ambient temperature.

Table 3
Results by the Koenen test

Sample	Sample mass (g)	Orifice diameter (mm)	Number of runs	Number of vessels changed
A	30	1.0	3	0
A	30	2.0	1	0
B	30	1.0	2	1
B	30	1.5	3	0
C	30	1.0	3	1

disappeared. The decomposition of the concentrated HA/water solution might result in operation of the rupture disc.

The pressure vessel following the Japanese Fire Service Law is basically similar to the pressure vessel test of the Dutch pressure vessel test from the point of using an open pressure vessel with almost the same volume. However, the heating rate (40 K/min) of the Japanese pressure vessel test was smaller than that of the Dutch pressure vessel test (210 K/min). The weight of sample was 5 g in the Japanese pressure vessel test. When HA50 wt.%/water solutions without added iron ion were used as samples, the rupture disc operated twice in 10 runs in the Japanese pressure vessel test with the orifice of 1.0 mm [6]. It was a possibility that the HA concentration increased more than 50 wt.% in the heating rate of Japanese pressure vessel test before HA/water solution disappeared.

The intensity of the thermal decomposition of HA/water solution without added iron ion was investigated by the mini closed pressure vessel test (MCPVT) [6]. The volume of the pressure vessel was 6 cm^3. The weight of sample was 0.5 g. The heating rate was 10 K/min. HA/water solutions with various concentrations were used as samples in the MCPVT. The pressure rise inside the pressure vessel was measured by the pressure transducer and recorded in the data acquisition system. The intensity of the thermal decomposition was estimated by the $(\mathrm{d}P/\mathrm{d}t)_{\max}$ in the MCPVT.

Table 4
Results by the Dutch pressure vessel test

Sample	Sample mass (g)	Orifice diameter (mm)	Number of runs	Number of burst discs
A	10	1.0	3	0
A	10	2.0	1	0
A	10	6.0	1	0
A	10	16.0	1	0
A	50	1.0	2	1
B	10	1.0	1	1
B	10	2.0	3	0
B	10	3.5	1	0
C	10	1.0	3	0
C	10	2.0	1	0
C	50	1.0	3	1

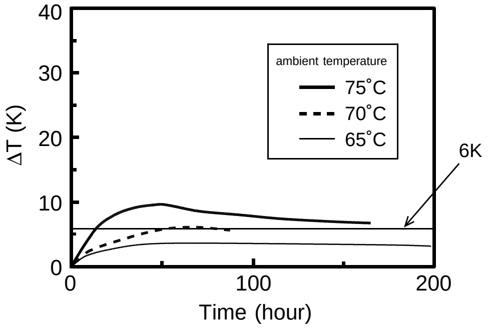

Fig. 2. Time history of ΔT in the heat accumulation storage tests at the various ambient temperatures. Sample is HA50 wt.%/water solution with the addition of iron ion (0.9 ppm) water solution (sample B). ΔT indicates the temperature difference between the sample temperature and the ambient temperature.

The intensity of the thermal decomposition increased with increasing concentration of HA solution on the basis of the MCPVT results [6]. For example, the $(dP/dt)_{max}$ of HA70 wt.%/water solution was approximately 17 times greater than that of HA50 wt.%/water solution. The results by the MCPVT might support the results by the open pressure vessel test such as the Dutch pressure vessel test.

3.3. Heat accumulation storage test for HA/water solution with added iron ion

Heat accumulation storage tests for HA50 wt.%/water solution with added iron ion were conducted at various temperatures. Time history of ΔT between the sample temperature and the ambient temperature in the heat accumulation storage test for HA50 wt.%/water solution with added iron ion is examined. Experimental results of samples B and C are shown in Figs. 2 and 3. Time 0 was when the sample temperature became equal to the ambient temperature in both the figures.

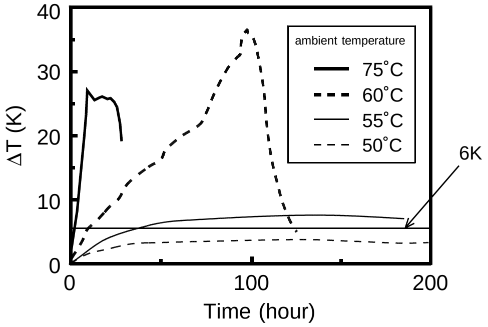

Fig. 3. Time history of ΔT in the heat accumulation storage tests at the various ambient temperatures. Sample is HA50 wt.%/water solution with the addition of iron ion (4.9 ppm) water solution (sample C). ΔT indicates the temperature difference between the sample temperature and the ambient temperature.

The SADTs of samples B and C were 70 and 55 °C, respectively. They were less than 75 °C. The addition of iron ion was effective in the decrease of the SADT in the heat accumulation storage test. Both samples B and C were classified as self-reactive substances following the United Nations recommendations. The SADT of sample C lowered compared with that of sample B. The thermal stability of HA/water solution decreased with increasing concentration of iron ion in HA/water solution. Weight reduction of samples B and C at each SADT was 26 and 19 g at the end of test. It was caused by the decomposition reaction and evaporation.

Sample B produced a heat release after the sample temperature reached the ambient temperature. The temperature of sample B stopped increasing as well as sample A when time elapsed. The maximum temperature difference from the ambient temperature was approximately 10 °C when the ambient temperature was 75 °C.

Sample C produced a heat release after the sample temperature reached the ambient temperature. The temperature of sample C in 50 and 55 °C of the ambient temperature stopped increasing as well as samples A and B when time elapsed. Sample C produced a great heat release when the ambient temperature was 60 and 75 °C. The temperature of sample C stopped increasing at approximately 100 °C when the ambient temperature was 60 °C. The temperature of sample C stopped increasing and made a plateau at approximately 100 °C when the ambient temperature was 75 °C. Most of the sample decomposed and evaporated at the end of test when the ambient temperature was 75 °C.

3.4. Comparison between heat accumulation test results and DTA results

The mixture hazards by adding iron ion were investigated by differential thermal analysis (DTA) experiment in another report [10]. The thermal stability of HA85%/water solution with iron ion was discussed on the basis of the heat-release onset temperature.

The concentrations of iron ion in HA/water solution were 10 and 30 ppm. The heat-release onset temperature (T_{onset}) shifted to the low temperature side when iron ion concentration increased. An intersection point of the baseline and the maximum slope of the peak was used as T_{onset} in DTA. T_{onset} decreased when iron ion solution was added to HA/water solution. The heat of reaction hardly depended on iron ion concentration. These experimental results suggested that the decomposition reaction of HA/water solution was accelerated due to the catalytic effect of iron ion.

T_{onset} of HA/water solution, which contained iron ion of 10 ppm, was approximately 40 °C lower than that of HA/water solution. T_{onset} of HA/water solution, which contained 30 ppm of iron ion, was approximately 60 °C lower than that of HA/water solution. When the concentration of iron ion in HA85 wt.%/water solution was beyond 40 ppm, heat release began at room temperature. DTA measurement could not be conducted when the concentration of iron ion was more than 40 ppm.

The decrease of T_{onset} per iron ion concentration was 2–4 K/(Fe^{3+}) ppm in the DTA experiment when the HA concentration was 85 wt.%. The decrease of the SADT per iron ion concentration was 5–10 K/(Fe^{3+}) ppm in the heat accumulation storage test though the HA concentration of the heat accumulation storage test (50 wt.%) was lower than that of DTA (85 wt.%).

3.5. Koenen test for HA50 wt.%/water solution with added iron ion

Results of the Koenen test for HA50 wt.%/water solution added iron ion are shown in Table 3. The sample vessel burst to several pieces once in two runs for sample B when the orifice of 1.0 mm was used in the Koenen test. The bottom of the sample vessel bulged out once in three runs when the orifice of 1.0 mm was used in the Koenen test for sample C. The intensity of the thermal decomposition increased when iron ion was added to HA50 wt.%/water solution.

3.6. Dutch pressure vessel test for HA50 wt.%/water solution with added iron ion

Results of the Dutch pressure vessel test for HA50 wt.%/water solution with added iron ion are shown in Table 4. The intensity of the thermal decomposition did not increase very greatly due to the addition of iron ion in the Dutch pressure vessel test.

The rupture disc operated when the orifice of 1.0 mm was used in the test for sample B of 10 g. On the other hand, the rupture disc did not operate when the orifice of 1.0 mm was used in the test for sample C of 10 g. The concentration of HA in sample C might be not concentrated by heating because HA was decomposed rapidly by iron ion. It was elucidated from the MCPVT results that the intensity of the thermal decomposition increased as the concentration of HA increased.

This explanation could be applied to the Koenen test results. Sample B decomposed more violently than sample C in the Koenen test. The concentration of HA in sample B was concentrated by heating. The concentration of HA in sample C might be not concentrated by heating because HA was decomposed rapidly by iron ion. The concentration of HA might play a more important role in the intensity of the thermal decomposition than the concentration of iron ion because iron ion worked as the catalyst in the decomposition of HA.

4. Conclusions

The decomposition hazards of HA50 wt.%/water solution and HA50 wt.%/water solution with the addition of a very small amount of iron ion were studied following the United Nations recommendations on the transport of dangerous goods for the purpose of obtaining information for safe handing, use and storage of HA/water solution.

The following conclusions are made:

(1) The SADT of HA50 wt.%/water solution without the addition of iron ion was 80 °C following the heat accumulation storage test. HA50 wt.%/water solution was not classified with self-reactive substances following the United Nations recommendations on the transport of dangerous goods. HA50 wt.%/water solution with more than 1.0 ppm of iron ion was classified with self-reactive substances following the United Nations recommendations on the transport of dangerous goods.

(2) The heat accumulation storage test was conducted using HA50 wt.%/water solution with the addition of iron ion. The thermal stability of HA50 wt.%/water solution decreased with increasing concentration of iron ion in the heat accumulation storage test. The

Koenen test was conducted using HA50 wt.%/water solution with the addition of iron ion. The intensity of the thermal decomposition increased by the addition of the iron.

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