



5th Annual Symposium, Mary Kay O'Connor Process Safety Center
"Beyond Regulatory Compliance: Making Safety Second Nature"
Reed Arena, Texas A&M University, College Station, Texas
October 29-30, 2002

Decomposition of Hydroxylamine/Water Solution added Iron Ion

Yusaku IWATA and Hiroshi KOSEKI
National Research Institute of Fire and Disaster
14-1 Nakahara 3-Chome Mitaka,
Tokyo 181-8633, JAPAN
E-mail: iwata@fri.go.jp

ABSTRACT

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

When the heat accumulation storage test was conducted using HA50wt.%/water solution without the addition of the iron ion, the self-accelerating decomposition temperature (SADT) was 80 °C. Therefore HA50wt.%/water solution was not classified in self-reactive substances following the United Nations recommendations on transport of dangerous goods. The concentration of the iron ion in HA50wt.%/water solution was not more than 1ppm.

The decomposition hazards of HA50wt.%/water solution with a very small amount of the iron ion were investigated. The range of the concentration of the iron ion in HA/water solution used in tests was between 1ppm and 6ppm. The thermal stability of HA50wt.%/water solution decreased by the addition of the iron ion in the heat accumulation storage test. HA50wt.%/water solution with the addition of the iron ion was classified in self-reactive substances following the United Nations recommendations on transport of dangerous goods. The Koenen test was conducted using HA50wt.%/water solution with the addition of the iron ion. The intensity of the thermal decomposition of HA50wt.%/water solution increased by the addition of the iron ion.

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

1. Introduction

In recent years, hydroxylamine (HA) was involved in two tragic accidents. One occurred in the United States of America in February 1999 [1]. The other occurred in Japan in June 2000. The chemical formula of HA is NH_2OH . HA100wt.% 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. HA is required as an organic agent in ϵ -caprolactam synthesis in the chemical 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, 4, 5]. We presented the 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 handling, use and storage. In the United Nations recommendations on transport of dangerous goods (Version 9), HA is classified as Class 8 (corrosive substances) dangerous goods though HA/water solution of high concentration involves high energy [7]. HA50wt.%/water solution is a candidate for a material of Division 4.1 in Class 4 (self-reactive substances) in the United Nations recommendations on 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 transport of dangerous goods, test and criteria manual (Version 2) 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 MkIII D test were conducted using HA50wt.%/water solution.

The decomposition of HA/water solution is accelerated by the catalytic effect of a metal ion. Reactivity of HA/water solution with an iron ion, a copper ion, a nickel ion, a chromium ion and a manganese ion was examined by measuring the weight reduction after the addition of the metal ion in another report [9]. The ignition automatically began when the 0.5wt.% (5,000 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 the iron ion. HA/water solution did not react with other ions.

This paper presents information about the influence of the iron ion on the decomposition of HA/water solution. The decomposition hazards of HA/water solution with a very small amount of the iron ion were evaluated by the United Nations recommendations tests. The decomposition hazards of HA/water solution with the addition of the 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 HA50wt.%/water solution with and without the addition to the iron ion. The decomposition hazards of HA/water solution with and without the addition of the 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

HA50wt.%/water solution was supplied by the HA manufacturer. This HA50wt.%/water

solution contains less than 1ppm iron and is distributed in the market.

Three kinds of samples were used in risk evaluation tests. HA50wt.%/water solution without the addition of the iron ion/water solution was used as sample A. HA50wt.%/water solutions with the addition of the iron ion/water solutions were used as sample B and sample C.

The concentration of the iron ion in sample A was within the range from 0.05 ppm to 1 ppm. The iron ion/water solution was added to HA50wt.%/water solution when sample B or sample C was made. The resulting solution was stirred so that the iron ion diffused uniformly in HA50wt.%/water solution after the iron ion water/solution was added to HA50wt.%/water solution.

Source of the ferric ion (Fe^{3+}) was ammonium ferric sulfate $[\text{Fe}(\text{III})\text{NH}_4(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}]$. The concentration of the iron ion in sample B was within the range from 1 ppm to 2 ppm. The concentration of the iron ion in sample C was within the range from 5 ppm to 6 ppm.

2.2. Risk evaluation test methods

The following seven kinds of tests were conducted using sample A, sample B and sample 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 MkIII D test

Table 1 shows hazards evaluated by these test methods. All tests were conducted following the United Nations recommendations on transport of dangerous goods, tests and criteria manual (Version 3).

2.3. Heat accumulation storage test

The Dewar with a grass rid 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 70 mW/kg/K was 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, which height was the same level as that of the thermocouple for the sample temperature.

The 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 30g. Heating was provided by four propane burners. The heating rate was 3.3 K/s. The heating rate was checked with dibutyl phthalate of 27 cm³ in the sample vessel.

The test criteria are as follows.

“Violent”: the limiting diameter is greater than or equal to 2.0mm.

“Medium”: the limiting diameter equal to 1.5mm.

“Low”: the limiting diameter is equal to or less than 1.0mm and the effect in any test is different from the tube unchanged.

“No”: the limiting diameter is less than 1.0mm and the effect in all tests is different from 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 cm³. 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 10g or 50g. Heating was provided by a propane burner. The heating rate was 3.3 K/s. The heating rate was checked with dibutyl phthalate of 10g in the pressure vessel.

The test criteria are as follows.

“Violent”: rupture of the disc with an orifice of 9.0mm or greater and a sample mass of 10.0g.

“Medium”: no rupture of the disc with an orifice of 9.0mm but rupture of the disc with an orifice of 3.5mm or 6.0mm and a sample mass of 10.0g.

“Low”: no rupture of the disc with an orifice of 3.5mm and a sample mass of 10.0 g but rupture of the disc with an orifice of 1.0mm or 2.0mm and a sample mass of 10.0g or rupture of the disc with an orifice of 1.0mm and a sample mass of 50.0g.

“No”: no rupture of the disc with an orifice of 1.0mm and a sample mass of 50.0g.

The limiting diameter was the diameter of the orifice with the largest diameter, 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 HA50wt.%/water solution

Results of the United Nations recommendations tests are shown in Table 1. Since The SADT of HA50wt.%/water was 80 °C, HA50wt.%/water solution was not classified in self-reactive substances following the United Nations recommendations. The intensity of the thermal

decomposition for HA50wt.%/water solution was found by the only Dutch pressure vessel test.

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

The greatest heat release was generated at the end of the test when the ambient temperature was 80 °C and 90 °C. One of the reasons for greatest heat release 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.

3.2. Koenen test and Dutch pressure vessel test for HA50wt.%/water solution

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

Details of the results of the Dutch pressure vessel test are shown in Table 4. The rupture disc operated once in twice runs when sample A of 50g and the disc with the orifice of 1.0mm was used in the Dutch pressure vessel test. On the other hand, when sample A of 10g was used, the rupture disc did not operate. This difference of results might be due to differences of the sample mass. Because water evaporated easier than HA in HA/water solution, HA/water solution with more than 50wt.% concentration was made. The decomposition of the concentrated HA/water solution might make operate 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 (40K/min) of the Japanese pressure vessel test was smaller than that of the Dutch pressure vessel test (200K/min). Sample A of 5g was used in the Japanese pressure vessel test. The rupture disc operated twice in ten runs in the Japanese pressure vessel test with the orifice of 1.0mm [6]. It was possibility that the HA concentration became more than 50wt.% in the heating rate of Japanese pressure vessel test before HA/water solution disappeared.

The intensity of the thermal decomposition of HA was investigated by the mini closed pressure vessel test (MCPVT) [6]. The volume of the pressure vessel was 6 cm³. The weight of the HA sample used was 5g. The intensity of the thermal decomposition was estimated by the $(dP/dt)_{max}$ in the MCPVT. The intensity of the thermal decomposition increased with increasing concentration of HA solution on the basis of the MCPVT results. The results by the MCPVT might support the results by the Dutch vessel test.

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

Heat accumulation storage tests of HA50wt.%/water solution added the iron ion were conducted at 75 °C only. Time history of ΔT between the sample temperature and the ambient temperature in the heat accumulation storage test for HA50wt.%/water solution with added the iron ion is shown in Figure 2. Time 0 was when the sample temperature became equal to the ambient temperature.

The SADTs of sample B and sample C were less than 75 °C. The addition of the iron ion was effective in the decrease of the SADT in the heat accumulation storage test. Both sample B

and sample C were classified in self-reactive substances following the United Nations Recommendations.

Sample B produced gradual heat release after the sample temperature reached the ambient temperature (75 °C). The maximum temperature difference from ambient temperature was approximately 11 °C.

Sample C produced great heat release after the sample temperature reached the ambient temperature (75 °C). The thermal stability of HA/water solution decreased with increasing concentration of the iron ion in HA/water solution. There was possibility that the SADT of sample C lowered compared with that of sample B. The temperature of sample C stopped increasing and made a plateau at approximately 100 °C. A possible explanation is that released heat of reaction was used to evaporate water. Most of the sample reacted and decomposed.

3.4. Comparison between heat accumulation test results and DTA results

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

The concentrations of the iron ion in HA/water solution were 10ppm and 30ppm. The heat-release onset temperature (T_{onset}) shifted to the low temperature side when the 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 the iron ion solution was added to HA/water solution. The heat of reaction hardly depended on the iron ion concentration. These experiment results suggested that the decomposition reaction of HA/water solution was accelerated due to the catalytic effect of the iron ion.

T_{onset} of HA/water solution, which contained the iron ion of 10ppm, was approximately 40 °C lower than that of HA/water solution. T_{onset} of HA/water solution, which contained 30ppm the iron ion, was approximately 60 °C lower than that of HA/water solution.

When the concentration of the iron ion in HA85wt.%/water solution was beyond 40ppm, heat release began at room temperature. DTA measurement could not be conducted when the concentration of the iron ion was more than 40ppm.

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

3.5. Koenen test for HA50wt.%/water solution added the iron ion

Results of the Koenen test for HA50wt.%/water solution added the iron ion are shown in Table 3. The sample vessel burst to several pieces once in twice runs for sample B when the orifice of 1.0mm was used in the Koenen test. when sample B.

The bottom of the sample vessel bulged out once in twice runs when the orifice of 1.0mm was used in the Koenen test for sample C. The intensity of the thermal decomposition increased when the iron ion was added to HA50wt.%/water solution.

3.6. Dutch pressure vessel test for HA50wt.%/water solution added the iron ion

Results of the Dutch pressure vessel test for HA50wt.%/water solution added the iron ion are shown in Table 4. The intensity of the thermal decomposition did not increase very greatly due to the addition of the iron ion in the Dutch pressure vessel test.

The rupture disc operated when the orifice of 1.0mm was used in the test for sample B of 10g. On the other hand, the rupture disc did not operate when the orifice of 1.0mm was used in the test for sample C of 10g.

The concentration of HA in sample C might be not concentrated by heating because HA was decomposed rapidly by the iron ion. It was elucidated from the MCPVT results that the intensity of the thermal decomposition increased as the concentration of HA solution 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 the iron ion.

The concentration of HA might play more important role in the intensity of the thermal decomposition than the concentration of the iron ion because the iron ion worked as the catalyst in the decomposition of HA.

4. CONCLUSIONS

The decomposition hazards of HA50wt.%/water solution and HA50wt.%/water solution added a very small amount of the iron ion were studied following the United Nations recommendations on transport of dangerous goods for the purpose of obtaining information for safe handling, use and storage of HA/water solution.

The following conclusions are made:

- (1) The SADT of HA50wt.%/water solution without the addition of the iron ion was 80 °C following the heat accumulation storage test. HA50wt.%/water solution was not classified in self-reactive substances following the United Nations recommendations on transport of dangerous goods. HA50wt.%/water solution with more than 1ppm of the iron ion was classified in self-reactive substances following the United Nations recommendations on transport of dangerous goods.
- (2) The heat accumulation storage test was conducted using HA50wt.%/water solution with the addition of the iron ion. The thermal stability of HA50wt.%/water solution decreased with increasing concentration of the iron ion in the heat accumulation storage test. The Koenen test was conducted using HA50wt.%/water solution with the addition of the iron ion. The intensity of the thermal decomposition increased by the addition of the iron.

REFERENCES

- [1] Hazardous Materials Safety Techniques Association, Report of investigation of explosive fire of hydroxylamine at a chemical plant in gunma prefecture, March 2001 (in Japanese).
- [2] N. Irving Sax, Richard J. Lewis, SR, Dangerous Properties of Industrial Materials, Seventh Edition, Volume III, Van Nostrand Reinhold, 1989.
- [3] L. Cisneros, W. J. Rogers, M. S. Mannan, Adiabatic calorimetric decomposition studies of 50wt.% hydroxylamine/water, Journal of Hazardous Materials, 82, 2001, pp. 13-24.
- [4] The National Institute of Industrial Safety, The National Institute of Industrial Safety Guide for explosion hazards of hydroxylamines and their safe handling, NIIS-SG-NO.1, 2001(in Japanese).
- [5] T. Uchida, M. Wakakura, Hazardous evaluation of hydroxylamine, Proceedings of 33rd Meeting of Japan Society for Safety Engineering, Yokohama, Japan, November 2000, pp. 141-142 (in Japanese).
- [6] Y. Iwata, H. Koseki, M. Yamada, K. Hasegawa, F. Hosoya, Risk evaluation of decomposition of hydroxylamine/water solution, Report of National Research Institute of Fire and Disaster, No.92, September 2001, pp. 37-48 (in Japanese).
- [7] The United Nations, Recommendations on transport of dangerous goods, Version 9, 1995.
- [8] The United Nations, Recommendations on transport of dangerous goods, manual and criteria, Version 2, 1995.
- [9] H. Koseki, Y. Iwata, Risk evaluation of hydroxylamine/water solution - Influence of metal ion -, Proceedings of 31st Symposium of Japan Society for Safety Engineering, Tokyo, Japan, July 2001, pp. 331-332 (in Japanese).
- [10] Y. Iwata, H. Koseki, K. Hasegawa, Risk evaluation of hydroxylamine/water solution by DTA, mini closed pressure vessel test and pressure vessel test, Proceedings of Asia Pacific Symposium on Safety, Kyoto, Japan, November 2001, vol.1, pp. 49-52.