Study on Risk Evaluation of Hydroxylamine/water Solution

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ABSTRACT

In order to find the cause of explosive fire which occurred in Japan in June 2000[1]?the decomposition hazards of hydroxylamine(HA) solution were studied experimentally. The thermal decomposition of HA solution was evaluated from calorimetric data obtained using deferential thermal analysis (DTA). The magnitude of the intensity of decomposition was investigated on the basis of the results of the mini closed pressure vessel test (MCPVT) and the pressure vessel test (PVT), the steel tube test and the burning test of HA.

The thermal analysis was conducted to evaluate the ease of thermal decomposition of the HA solution. The heating onset temperatures using the stainless steel cells were reduced more than 70 ?C compared with those measured using the gold-coated stainless steel cells. Therefore the heating onset temperature depended on the materials of sample cell. On the other hand, the heat of reaction did not depend on the materials of sample cell. The decomposition reaction of HA solution was enhanced due to the catalytic effect of iron ion came from the stainless steel surface. Burning test of mixture of HA and iron ion supported these data. Sudden fire was made when 85 % of HA and iron was mixed. These data were compared with APTAC data by Cisneros et al.[2] and it was found both data gave good agreement regarding the heating onset temperature.

The MCPVT, the PVT and the steel tube test were conducted for the purpose of evaluating the magnitude of the intensity of the thermal decomposition when HA solution decomposed. The intensity of the thermal decomposition of HA increased when the HA concentration reached 70 %. In addition, HA 85 % solution was easily detonated by a small detonator.

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Abstract

The risk evaluation of decomposition of hydroxylamine(HA) solution was studied experimentally. The thermal decomposition of HA solution was studied from the calorimetric data obtained using differential thermal analysis (DTA), and the magnitude of the intensity of decomposition was studied on the basis of the results of the mini closed pressure vessel test (MCPVT) and the pressure vessel test (PVT) in addition to the steel tube test.

The thermal analysis was conducted to evaluate the ease of thermal decomposition of the HA /water solution. The heating onset temperatures using the stainless steel cells were reduced more than 70 °C compared with those measured using the gold-coated stainless steel cells. The heating onset temperature depended on the materials of sample cell of DTA. On the other hand, the heat of reaction did not depend on the materials of sample cell. The thermal decomposition reaction of HA solution was accelerated due to the catalytic effect of the stainless steel surface.

The MCPVT, the PVT and the steel tube test were conducted to evaluate the magnitude of the intensity of the thermal decomposition when the HA solution decomposed. The intensity of the thermal decomposition of HA increased as the HA concentration increased in the MCPVT. The intensity of the thermal decomposition of HA increased greatly when the HA concentration was beyond 80% (wt.) in the MCPVT. It was evaluated that thermal decomposition of HA 70% solutions was very violent in PVT. In addition, HA solutions of more than 80% concentration could detonate in the steel tube test. HA 85 % solution was easily detonated by a small detonator in the steel tube test.

Keywords: Hydroxylamine; Thermal decomposition; Differential thermal analysis; Mini closed pressure vessel test; Pressure vessel test; Steel tube test

1. Introduction

Recently two tragic accidents occurred by hydroxylamine (HA)/water solution, one was in the United States of America in February 1999 and the other was in Japan in June 2000. HA is widely used in semiconductors, chemical and pharmaceutical industries. In the UN recommendations on the transport of dangerous goods, tests and criteria manual (version 3), HA is classified into class 8 (corrosive substances) dangerous good, and we have not paid attention so much on its explosion properties.

There are some papers about the hazards of the decomposition of HA [1, 2]. It is important to obtain more knowledge of the decomposition of HA for the purpose of safe handing, use and storage of HA. This paper presents the potential hazards of HA solution with two aspects. First one was the thermal decomposition of HA solution, which was evaluated from the calorimetric data obtained using differential thermal analysis (DTA). Second one was the magnitude of the intensity of the decomposition, which was investigated from the results of mini closed pressure vessel test (MCPVT) and the pressure vessel test (PVT) in addition to the steel tube test.

It is well known that the decomposition of HA solution is accelerated by the catalytic effect of a metal ion such as iron ion. The mixture hazards by adding an iron ion will be reported in another paper.

2. Summary of Accident of HA in Japan

An accident occurred on June 10, 2000 in a factory where HA solution was manufactured in Gunma prefecture, Japan [3]. The residential houses around the factory were damaged by the blast of the explosion to the range of 1,500m in radius around this factory. The panes of a convenience store and a restaurant, which were about 100m away from the factory, were broken by the blast of the explosion. In addition to the explosion, a fire occurred in this accident. Some of the facility in the factory were burnt down by the fire due to HA solution and hydroxylamine salts, for example hydroxylamine chloride and hydroxylamine sulphate. Huge amount of smoke occurred in the fire and prevented the fire fighting activity.

The explosion killed four people and injured fifty-eight people, and destroyed the facilities. The accident happened in the process of the re-distillation. A re-distillation tower was completely destroyed by the explosion. In this re-distillation tower, the refined HA 50% (wt.) solution was produced by the re-distillation of HA 85% solution. The refined HA 50% solution was a commercial product. Impurities such as a metal ion were hardly included in this refined HA 50% solution. HA 85% solution did not circulate in the market and existed only at this factory.

A vessel containing HA 85% solution in the re-distillation tower was completely destroyed and by the explosion. It was predicted that initial detonation occurred in HA 85% solution of 750- 800 L, which existed in the vessel and the piping connected to the vessel.

3. Experiment

The following five kinds of experiment were conducted;
(1) Thermal analysis of HA solution using differential thermal analysis (DTA)
(2) Accelerating rate calorimeter (ARC)
(3) Mini closed pressure vessel test (MCPVT)
(4) Pressure vessel test (PVT)
(5) Steel tube test

The thermal analysis was conducted to evaluate the ease of thermal decomposition of the HA solution. Stainless steel cells and gold-coated stainless steel cells were used in the experiments to investigate the effects of the types of the sample cells. ARC was used to measure the activation energy of the HA solution in the thermal decomposition.

The MCPVT and the PVT were conducted to evaluate the magnitude of the intensity of the thermal decomposition when HA solution decomposed. The experiment using the steel tube test was done to determine whether HA solution actually detonated and to evaluate the shock sensibility of the HA solution.

3.1. HA samples
HA 50 % and HA 90 % solution by weight were supplied by the HA manufacturer. Both of them contained proper stabilizers. HA solutions with other concentrations used in the experiments were made by diluting the HA 90 % solution. Each concentration of HA 50 % and HA 90 % solution was checked by oxidation- reduction titration.

3.2. DTA experiment
Old stainless steel cells, new stainless steel cells and gold-coated stainless steel cells were used in the experiments. Stainless steel cells were made of SUS 304 of Japanese Industrial Standard (JIS). Stainless steel of SUS 304 contained nickel, chromium and manganese in addition to iron. The old stainless cells were made more than five years ago. The new stainless steel cells were used in the DTA experiments within a month after they were made. All sample cells were sealed and were able to endure a pressure until 5MPa.

TAS-100, which was made by Rigaku Corporation, was used as DTA apparatus. The DTA measurements were conducted in air. The equipment constant for calculating heat of reaction was calibrated by In, Sn and Pb.

HA solution was placed into a sample cell using disposable plastic pipettes. The sample was weighted in a sample cell. The sample weights were 2.2 mg (± 0.4 mg). The sample cells were covered with caps and sealed by a cell sealer. The increase in temperature rate was 10°C /min in all DTA experiments. The weight change of the samples was measured by thermogravimetry (TG) to check leakage from the sample cells during the measurements. The number of tests was more than five times for each condition. The DTA data were excluded when sample cells leaked during the measurement or the baseline of DTA curves was not stabilized.

3.3. ARC experiment
ARC is an adiabatic calorimeter which measures exothermic behavior in adiabatic condition for hazardous evaluation of reactive chemicals. The activation energy of chemical substances can be obtained by measuring the relation of self-heat rate vs. temperature in adiabatic conditions.
ARC apparatus was made by Columbia Industries Scientific. ARC was used to measure the activation energy of the HA solution in the thermal decomposition. Sample cell was made of titanium. The amount of sample was 0.9 g (± 0.05 g). The measurement started from room temperature.

3.4. MCPVT experiment
The main components of the MCPVT apparatus were an electrical furnace, a pressure vessel, a temperature control unit, a data recorder and analysis software. Details of the MCPVT apparatus are shown in the literature [4, 5]. The heating rate was 10°C/min. The volume of the pressure vessel was

6cm^3. A sample vessel made of glass was placed inside the pressure vessel. The weight of HA sample used was 0.5 g (± 0.05 g) . The pressure rising inside the pressure vessel was measured.

3.5. PVT experiment
The PVT experiment was conducted according to the test method in the Japanese Fire Service Law. The pressure vessel of the PVT used in this paper was basically similar to those of USA, Dutch and German from the point of using an open pressure vessel with almost the same volume. The volume of the pressure vessel used in the PVT was approximately 200cm^3.

HA 50% and HA 70% were used as samples(see Table 1). The weight of HA sample used was 5 g (± 0.5 g). Sample vessels were made of aluminum or glass. The heating rate was 40.5°C/min. The measurements were finished when the bursting disc burst or all of the samples were evaporated and disappeared.

3.6. Steel tube test experiment
A glass tube containing the sample was placed inside a steel tube. The dimensions of the glass tube were 25 mm in diameter and 200 mm length. The volume of the HA samples was 40 cm^3. Volume of HA samples were measured by a mess cylinder and poured into the glass vessel. A stopper made of silicone rubber was put on the glass. The glass tube was placed into the steel tube. Trimethylene trinitroamine (RDX) agent was wrapped with the electric detonator by a transparent thin film. RDX was used as an initial explosive in the measurements except for No.2 test (see Table 2). The electric detonator with the RDX was attached to the outside of the glass tube. Initiation was conducted using an electric detonator #6. The experimental condition is described in detail elsewhere [6].

In addition, larger size of the stainless tube was used in the measurement (No.6 in Table 2). The dimension of the steel tube was 50mm in diameter and 500mm length. The volume of the HA sample was 980cm^3. HA sample was put into a bag made of polyethylene. The compressed RDX, which contained 5 % (wt.) wax, was used as the initial explosive.

4. Results and discussion
4.1. Thermal analysis by DTA
The thermal analysis was conducted to evaluate the ease of the thermal decomposition of the HA solution. The old stainless steel, the new stainless steel and the gold-coated stainless steel cells were used to investigate the effect of the types of the sample cells on the thermal decomposition of the HA solution.

4.1.1. DTA curve
DTA measurements of the HA solution with various concentrations (HA 20%- HA 85%) were conducted using the new stainless steel and the gold-coated stainless steel cells. The DTA curves of HA 50% solution measured using the new stainless steel cells and the gold-coated stainless steel cells are shown in Figure 1 and 2. The DTA curves measured using the new stainless steel cells had one peak in HA20% and HA30% solution. The DTA curves measured using the new stainless steel cells had two peaks in more than 40% concentrations.

The DTA curves were measured using the old stainless steel cells in addition to using the new stainless steel and the gold-coated stainless steel cells. The DTA curves measured using the old stainless steel cells had two peaks in HA 50% and HA85% solution. The configuration of the DTA curves of HA50% solution and HA85% solution measured using the old stainless steel cell was similar to that of HA solution of more than 40% concentration measured using the new stainless

steel cell. However, the first peak of DTA curves measured using the old stainless steel cell was on the lower temperature side, compared to the DTA curves measured using the new stainless steel cell. On the other hand, the DTA curves measured using the gold-coated steel cells had only one peak in all concentrations of HA.

4.1.2. Heating onset temperature (T_{onset}) and heat of reaction (H_R)

The relationship between the HA concentration and the heating onset temperature (T_{onset}) is shown in Figure 3. All data of T_{onset} using the gold-coated stainless steel cells were almost constant for different HA concentrations (136 ± 5°C). When the new stainless steel cells were used, T_{onset} decreased with an increasing of the HA concentration. When the HA concentration became more than 50%, T_{onset} became almost constant (63 ± 3 °C).

The relationship between the HA concentration and the heat of reaction (H_R) is shown in Figure 4. H_R increased proportionally with the HA concentration for both the new stainless steel cells and the gold-coated stainless steel cells. H_R values obtained by the new stainless steel cells were almost the same value as those of the gold-coated stainless steel cells. The chemical equation of the overall decomposition of HA might be the same in the new stainless steel cell and the gold-coated stainless steel cell.

H_R of HA 100 % was 4.3- 4.6 kJ/g assuming a proportional relationship between the HA concentration and H_R in Figure 4. The heat of decomposition in trinitrotoluene (TNT) is 5.1 kJ/g [7]. There is possibility that HA involves the potential great hazard like to TNT.

4.1.3. Influence of sample cell on T_{onset} and H_R

The reactions of decomposition in two types of sample cells were different because the configurations of two DTA curves were different (see Figures 1 and 2). T_{onset} of HA 50 % solution measured using the new stainless steel cell and the gold-coated stainless steel cell were 66 °C and 141 °C, respectively (see Figure 3). T_{onset} measured using the new stainless steel cell was lower than T_{onset} measured using the gold-coated stainless steel cells. The materials of the sample cells influenced the thermal decomposition of HA.

On the other hand, H_R measured using the new stainless steel cell were almost the same as the H_R measured using the gold-coated stainless steel cells (see Figure 4). One of the reasons that T_{onset} decreased when the stainless steel cells were used, might be the catalytic effect of the stainless steel because gold was not reactive and seldom reacted with other substances.

The activation energy of HA 50 % solution measured by ARC using titanium sample cell was 2.2 kJ/g. The decomposition reaction of the HA started at room temperature in ARC experiments. The activation energy of HA 50% solution measured by the Adiabatic Pressure Tracking Accelerating Calorimeter (APTAC) using the glass sample cell was 3.7- 4.3 kJ/g[8]. The heating onset temperature was 133-136 °C in APTAC experiments. This difference of the heating onset temperature indicated that the activation energy was reduced by the catalytic effect of the metal surface such as not only stainless steel but also titanium.

T_{onset} was different in the new stainless steel cell and the old stainless steel cell. T_{onset} of HA 50 % solution measured using the old stainless steel cell was 44°C (see Figure 3). T_{onset} measured using the old stainless steel cell was lower than T_{onset} measured using the new one (see Figure 3). The followings might be predicted as one of the reasons for the T_{onset} difference between the new stainless steel cell and the old stainless steel cell. Originally, the stainless steel surface reacted with

the HA solution. The surface of the stainless steel has been oxidized since the stainless steel cell was made. The surface of the stainless steel might have iron oxide and turn rough. As a result, the reaction rate of decomposition reaction rate of HA might become larger because of the wider surface area, which was in contact with the HA solution. The surface situation of the sample cell might influence the thermal decomposition of HA in addition to the materials of sample cell.

H_R measured using the old stainless steel cell was smaller than H_R measured using the other cells (see Figure 4). The generation of heat had already started from room temperature in the DTA curves of the old stainless steel cell. It was difficult that the baselines of DTA curves were stabilized when the old stainless steel cells were used. There was possibility that the reaction of decomposition of HA started before the measurements. Therefore H_R measured using the old stainless steel cell was smaller than those of the new stainless steel cells and the gold-coated stainless steel cells

4.1.4. Decomposition reaction
DTA curves measured using the gold-coated stainless steel cell had one peak. It is known that HA 100% (solid) starts decomposing violently at the temperature higher than approximately 130 °C [9]. It was considered that this peak measured with the gold-coated stainless steel cell was associated with the thermal decomposition of HA without influence of the stainless steel surface.

The chemical equation of the overall decomposition of HA did not depend on the catalytic effect. It was considered that final products in the stainless steel cell were the same as those in the gold-coated stainless steel cell when HA decomposed completely.

It is known that HA decomposes into ammonia and water and so on very fast with heat or the presence of a metal ion. Products of decomposed HA depend on the experimental conditions. An example of equations of the HA decomposition is as follows :

$$3NH_2OH_{(cryst)} \rightarrow NH_{3(gas)} + N_2 + 3H_2O_{(gas)} \qquad H_R = 4.3(kJ/g) \qquad (1)$$
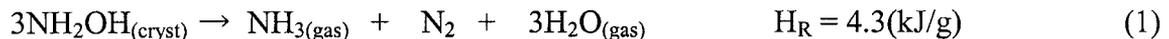
The H_R value of the chemical equation (1) was close to the H_R value of HA 100% estimated from the DTA experiment (see Figure 4). The chemical reaction in the chemical equation (1) might occur in the steel stainless and gold-coated stainless steel cell of DTA.

However the process of decomposition reaction of HA depended on the materials of the sample cell because the DTA curves obtained using the stainless steel cell were different from those obtained using the gold-coated stainless cell (see Figures 1 and 2).

4.2. MCPVT
The magnitude of the intensity of the thermal decomposition of HA can be estimated by the (dP/dt)max value in the MCPVT. The (dP/dt)max value is the maximum of the pressure rising rate. Relationship between the (dP/dt)max value and HA concentration is shown in Figure 5. The (dP/dt)max value increased with the concentration of HA solution increasing. The magnitude of the intensity of the thermal decomposition of HA increased greatly when the HA concentration was beyond 80%.

The bursting disc operated in the measurements of HA 90% solutions. The bursting disc used in the MCPVT was fitted as a safety valve. The bursting disc fitted with the pressure vessel of the MCPVT could endure with the pressure of 35 MPa. Generally, the bursting disc did not operate in

the measurements for organic peroxides when sample mass of organic peroxides was approximately 1g. The (dP/dt)max values of organic peroxides were generally less than 100 MPa/s when the sample of 1g was used in the MCPVT . The thermal decomposition of HA 90% concentration was very violent compared with those of organic peroxides. When the (dP/dt)max value was approximately 1,000 MPa/s, detonation might occur in the vessel.

4.3. PVT
The experiment result measured with the aluminum sample vessel is shown in Table 1. It is evaluated that the samples has hazardous properties in the Japanese Fire Service Law when the bursting disc operates more than five times in ten runs. The bursting disc fitted with the pressure vessel of the PVT could endure with the pressure of 600 kPa. The aluminum sample vessel was prescribed by the Japanese Fire Service Law.

When HA 50% solution was heated in the pressure vessel, the HA solution was concentrated due to water distillation. When a testing of HA 50% solution was done using the aluminum sample vessel, the decomposition gas of HA was emitted from the orifice of the pressure vessel. Therefore it was evaluated that was not so violent (see Table 1). In the measurements of HA 70% solutions, the glass sample vessel was used in addition to the aluminum sample vessel. The some measurements with the glass sample vessel were conducted before the measurements with the aluminum sample vessel because of the safety reason. When the glass sample vessels were used, they were crushed by the thermal decomposition of HA completely. In addition, the bursting disc operated. When the aluminum sample vessels were used, they were burst to several pieces by the thermal decomposition of HA. It was evaluated that thermal decomposition of HA 70% solutions was very violent (see Table 1). Because of the safety reason that there was possibility of detonation on the basis of the MCPVT results, the PVT measurements were not conducted using HA 80% samples.

4.4. Steel tube test
The hazards of HA were evaluated according to the appearance of the destruction of the steel tube. It was examined whether HA could detonate. In addition, the shock sensibility was evaluated with changing detonator in the steel tube tests.

The experiment result is shown in Table 2. When detonation occurred, the steel tube fragmented into six or more small pieces. It was clear that HA solutions of more than 80% concentration could detonate. Especially, HA 85% solution was easily detonated by a small detonator. It is necessary to examine whether HA 85% solution detonate by smaller energy or not.

5. CONCLUSIONS
The decomposition hazards of HA solution were evaluated on the basis of the results of the experiments with the DTA, the MCPVT, the PVT, and the steel tube test. The following conclusions were made:

(1) Regarding the results of the DTA, the ease of the thermal decomposition of the HA solution was studied. The heating onset temperature depended on the materials of the sample cell. The heating onset temperatures using the stainless steel cells were reduced more than 70 ˚C compared with those measured using the gold-coated stainless steel cells. The heat of reaction did not depend on the materials of sample cell. The decomposition reaction of HA solution was accelerated due to the catalytic effect of the stainless steel surface.

Table 1. Results of the pressure vessel tests

No.	HA concentration (wt%)	Orifice diameter (mm)	Number of runs	Number of burst discs
1	50	9.0	1	0
		1.0	10	2
2	70	9.0	5	5
		1.0	—	—

Table 2. Results of the steel tube tests

No.	HA concentration (wt.%)	Ignition method	Result
1	90	Detonator+ RDX 10g	Detonation
2	85	Detonator	Detonation
3	85	Detonator+ RDX 2g	Detonation
4	80	Detonator+ RDX 10g	Detonation
5	70	Detonator+ RDX 10g	No Detonation
6a	50	Detonator+ RDX 50g	No Detonation
7	0	Detonator+ RDX 10g (blank test)	No Detonation

a: stainless tube of 50mm in diameter and 500mm length, sample volume is 980cm^3. HA sample was put into a bag made of polyethylene. The compressed RDX was used as the initial explosive.
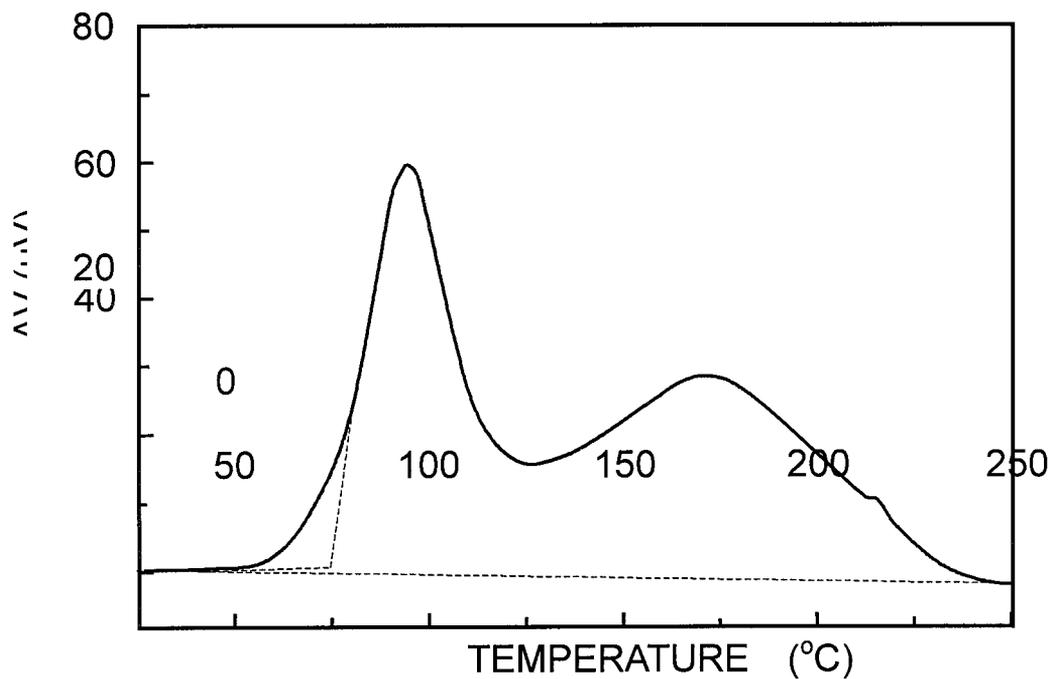
Figure 1.　DTA curve of HA 50 wt.% measured using the new stainless steel cell.
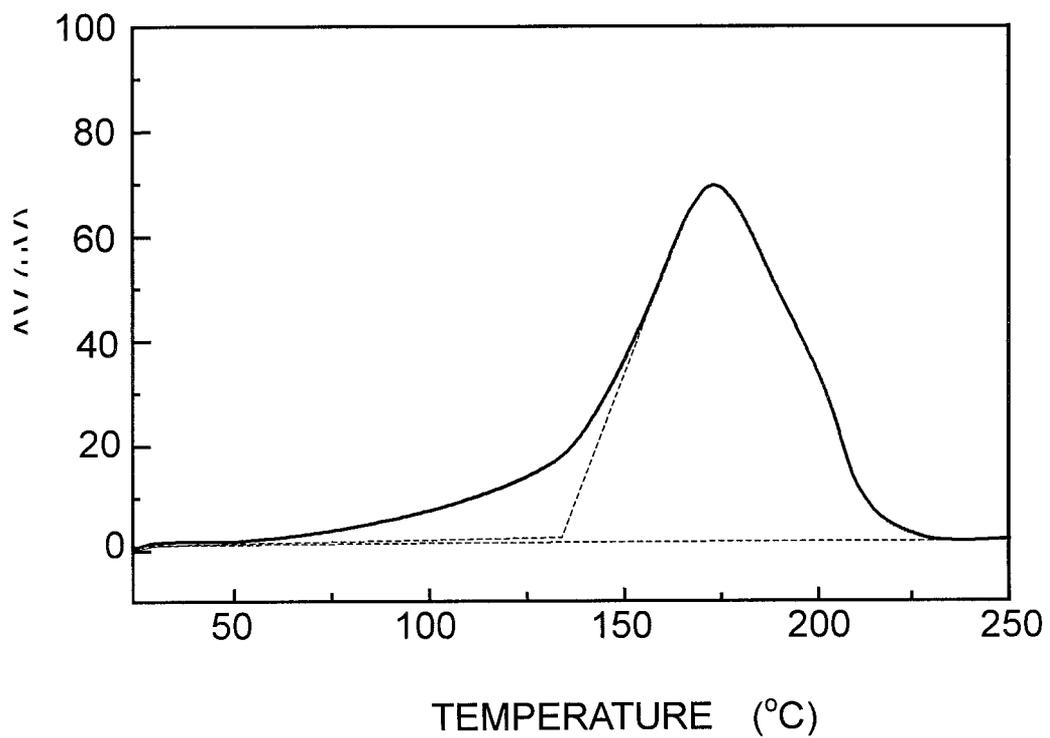
Figure 2.　DTA curve of HA 50 wt.% measured using the gold-coated stainless steel cell.
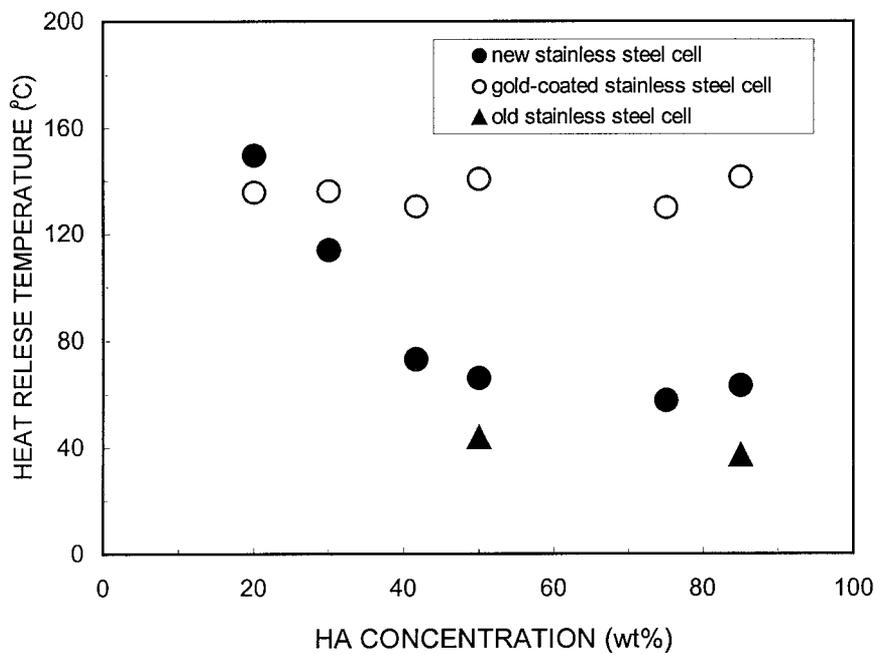
Figure 3.   Relationship between HA concentration and heat release onset temperature.
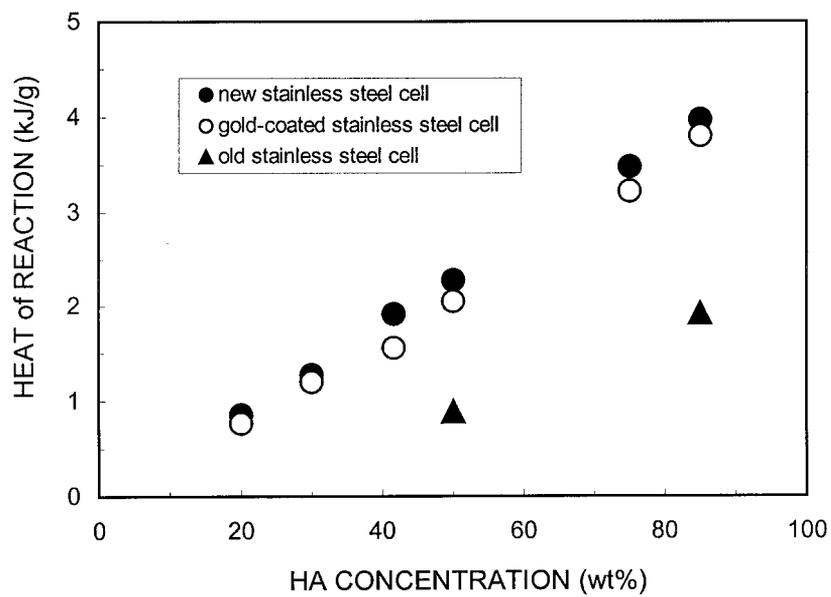
Figure 4.   Relationship between HA concentration and heat of reaction.
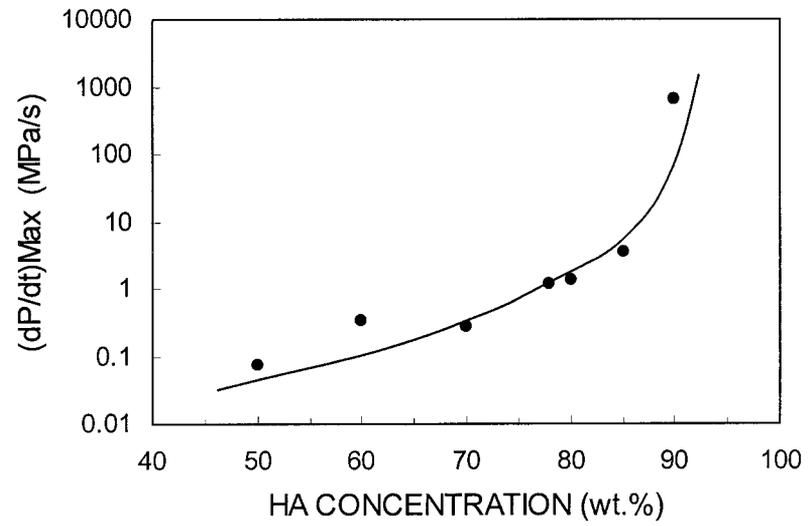
Figure 5. Relationship between HA concentration and the intensity of the thermal decomposition measured using MCPVT.

(2) Regarding the results of the MCPVT, the PVT and the steel tube test, the magnitude of the intensity of the thermal decomposition was studied when HA solution decomposed. The intensity of the thermal decomposition of HA increased as the HA concentration increased in the MCPVT. The intensity of the thermal decomposition of HA increased greatly when the HA concentration was beyond 80% in the MCPVT. It was evaluated that the thermal decomposition of HA 70% solutions was very violent in the PVT. In addition, HA 85% solution was easily detonated by a small detonator in the steel tube test.

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