

## INFLUENCE OF HEAVY METAL ION ON THE THERMAL EXPLOSION OF HYDROGEN PEROXIDE

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Hydrogen peroxide containing impurities has caused a lot of explosion accidents. In this study, a simple device that using a glass vessel was made, cupric chloride was added into hydrogen peroxide, and properties of runaway reaction of hydrogen peroxide were evaluated. As a result, when copper ion exists over 0.04%, 50 g of 30%-hydrogen peroxide has caused runaway reaction. Besides, it has been confirmed that the shape of the reactor and initial temperature influence runaway reaction.

**Keywords:** heavy metal ion, hydrogen peroxide, runaway reaction, thermal explosion

### Introduction

Though 30%-hydrogen peroxide now on the market is stable at room temperature and is hardly decomposed under normal storage conditions, it is rapidly decomposed with the existence of a few impurities. When a self-heating rate by the decomposition exceeds a heat radiation rate toward the outside of the container, thermal storage occurs. Rising temperature accelerates the decomposition, leads to a thermal explosion after an induction period. On October 29, 1999, an explosion accident of a tank lorry carrying hydrogen peroxide occurred on the Tokyo Metropolitan Expressway. The tank lorry was destroyed by the explosion, and the body of the tank and its splinters were scattered around the scene. The cause of the accident is supposed that cupric chloride, which was left in the tank, accelerated catalytic decomposition of hydrogen peroxide and led to a runaway reaction [1]. Not only this case, hydrogen peroxide containing impurities has caused a lot of explosion accidents [2, 3]. It is well known that a heavy metal ion accelerates the decomposition of hydrogen peroxide [1, 4]. However, few researches have been made so far on the properties of runaway reaction and the intensity of thermal explosion.

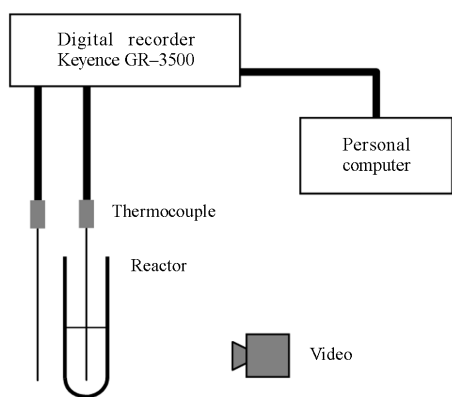
In this study, properties of runaway reaction of hydrogen peroxide at the presence of heavy metal ions were investigated. In general, when thermal hazards of reactive chemicals are evaluated, a differential scanning calorimeter (DSC) [5], an adiabatic calorimeter such as an accelerating rate calorimeter (ARC) or

a Dewar flask type [6, 7], and a reaction calorimeter (RC1) [8] are used. However, in these devices, materials of sample containers accelerate the decomposition of hydrogen peroxide, therefore the results are influenced by those container materials. Moreover, it takes rather a long time for measurement. In this study, a simple device using the glass vessel was made, for evaluation.  $\text{Cu}^{2+}$  ion was added into hydrogen peroxide and the change of the temperature was measured. The concentration of  $\text{Cu}^{2+}$  ion, the shape of the reactor and the initial temperature are changed, which are expected to have effect on the decomposition, and the amount of heat generated by the decomposition was measured. Based on the results, conditions under which hydrogen peroxide causes runaway reaction are examined.

### Experimental

The outline of the measuring device used for the experiment is shown in Fig. 1. The glass container was filled with the sample, and the time change of the temperature of the central part of the sample and the atmosphere was measured with a K-type thermocouple (made by Chino, Japan, protected tube diameter: 1.0 mm). SUS316, which is used for the protected tube of the thermocouple, accelerates the decomposition of hydrogen peroxide. Therefore measurement was conducted with covering the surface of the protected tube by a Teflon-made thermal contraction tube. Signals from the thermocouple were converted

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**Fig. 1** Scheme of measurement

into digital data by a digital recorder (made by Keyence, Japan, GR-3500) time resolution (100 msec), and they were put in the personal computer. Besides, the state of the runaway reaction was observed with a video camera.

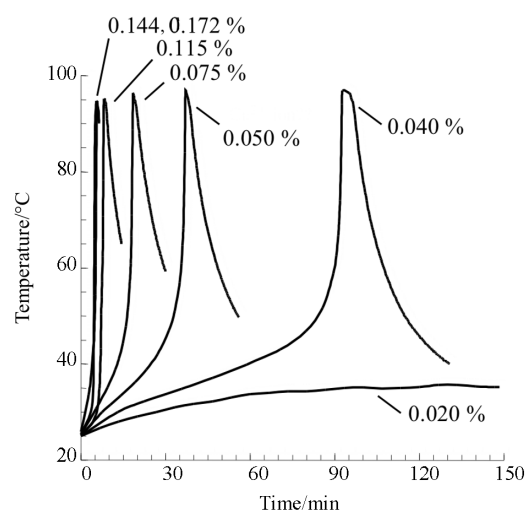
The experiment was carried out in the fume hood kept at a constant temperature. Aqueous solution of cupric chloride (Kanto Chemical, Japan) was added, after the temperature of stabilizer-free hydrogen peroxide (Wako Chemical, Japan) reached the predetermined retention temperature, and it was stirred to get uniformity. The concentration of hydrogen peroxide was set to be 30%, and the atmosphere temperature was kept at 25, 30 and 35°C, and using a 100 mL test tube and a cylindrical container made of glass as a reactor vessel, the measurement was carried out.

## Results and discussion

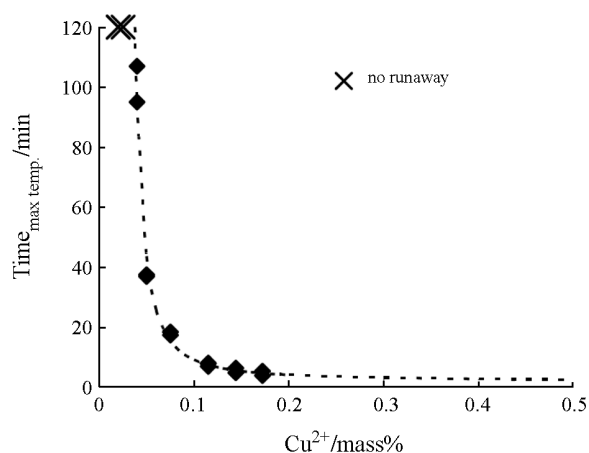
### Concentration of $\text{Cu}^{2+}$ ion dependence

The concentration of  $\text{Cu}^{2+}$  ion in hydrogen peroxide was changed, and the temperature change was measured up to the runaway reaction happens. In Fig. 2, behavior of the temperature and elapsed time is shown. When the  $\text{Cu}^{2+}$  ion was added, the decomposition of hydrogen peroxide was accelerated and the temperature of the sample gradually rose by heat of decomposition. With the rise in the temperature, the decomposition was more accelerated, and the maximum temperature was recorded, when the solvent water intensely boiled. In this paper, the time from the start of the experiment to the attainment of the maximum temperature is called time to maximum temperature ( $t_{\text{MAX}}$ ).

The concentration of  $\text{Cu}^{2+}$  ion dependence of  $t_{\text{MAX}}$  is shown in Fig. 3.  $t_{\text{MAX}}$  shortened with the increase in the concentration of  $\text{Cu}^{2+}$  ion, especially when the concentration was over 0.250%, it became bumping on adding the ion. When 0.025% or less, it



**Fig. 2** Time to temperature at various concentration of  $\text{Cu}^{2+}$  ion (0.020, 0.040, 0.050, 0.075, 0.115, 0.144 and 0.172 mass%) Concentration of  $\text{H}_2\text{O}_2$ : 30.0 mass%, initial temperature: 25 °C, test tube



**Fig. 3** Concentration of  $\text{Cu}^{2+}$  ion dependence of time to maximum temperature

did not reach runaway and decomposition ended. It is supposed that thermal equilibrium has been attained as the decomposition rate of hydrogen peroxide is small, and heat of decomposition and quantity of heat released into the surroundings became equal. Under conditions of this experiment, it was confirmed to get thermal equilibrium in about 120 min. However, even if the concentration of the  $\text{Cu}^{2+}$  ion is 0.025%, in the case in which the concentration of hydrogen peroxide is higher, or the sample approaches the thermal insulation condition, it is considered that runaway reaction would happen.

Inside diameter and scale dependence

$t_{MAX}$  was measured using cylindrical glass containers of which inside diameters differed, and the result is shown in Fig. 4. It was confirmed that  $t_{MAX}$  had the minimum value at 4–5 cm inside diameter. In the case where the container is 4–5 cm in inside diameter and the scale is 50 g, inside diameter and height of the container become equal, and the heat transfer area decreases. Therefore, heat of decomposition is not released into the surroundings, and it is considered that  $t_{MAX}$  has the minimum value. Furthermore, when inside diameter and height are changed,  $t_{MAX}$  was lengthened. Heat radiation of the sample is considered from two directions: a wall surface direction and a level direction. Heat radiation of the wall surface direction is heat transfer. In the level direction, heat radiation is promoted by heat transfer and convection generated by rise of oxygen in the system, which was

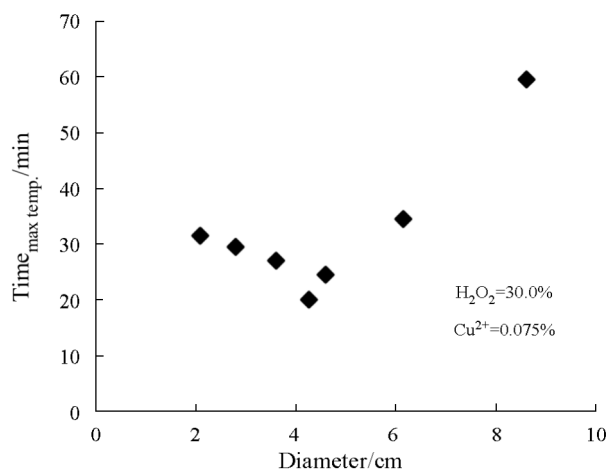


Fig. 4 Inside diameter dependence of time to maximum temperature, initial temperature: 25°C, shape of reactor: cylinder

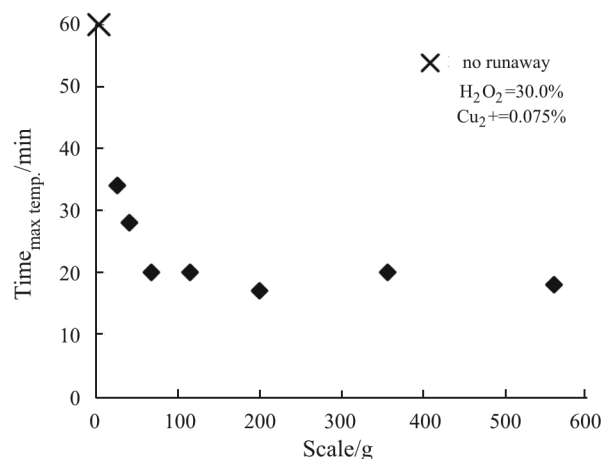


Fig. 5 Scale dependence of time to maximum temperature, initial temperature: 25°C, shape of reactor: cylinder

Table 1 Unit heat transfer area at various scale

| Scale/g | Inside diameter/cm | Unit heat transfer area/cm <sup>2</sup> g <sup>-1</sup> |
|---------|--------------------|---|
| 4.1     | 1.67               | 3.2   |
| 26.2    | 3.10               | 1.7   |
| 41.0    | 3.60               | 1.5   |
| 68.0    | 4.26               | 1.3   |
| 85.1    | 4.59               | 1.2   |
| 115.3   | 5.08               | 1.1   |
| 200.0   | 6.14               | 0.9   |
| 356.4   | 7.40               | 0.7   |
| 559.5   | 8.60               | 0.6   |

produced by decomposition. Therefore,  $t_{MAX}$  is lengthened in the containers of which inside diameter and height are long.

Subsequently, using the cylindrical containers, determining the shape of the sample so that inside diameter and height may become equal,  $t_{MAX}$  in which the reaction scale changed was measured. The result was shown in Fig. 5. When 68 g or less, it tended to lengthen  $t_{MAX}$ , and when 4 g, it did not reach the runaway. The heat transfer area per weight is obtained by Table 1, and the relation too  $t_{MAX}$  was examined. The unit heat transfer area increases with the decrease in the scale. Over 1.5, the effect of the heat radiation becomes remarkable, and  $t_{MAX}$  is lengthened. Besides,  $t_{MAX}$  showed constant value over 68 g. Therefore, when properties of runaway reaction of hydrogen peroxide is evaluated by to some extent scale, the effect of the heat released into the surroundings decreases, and it is shown that reproduction of large-scale runaway reaction is possible.

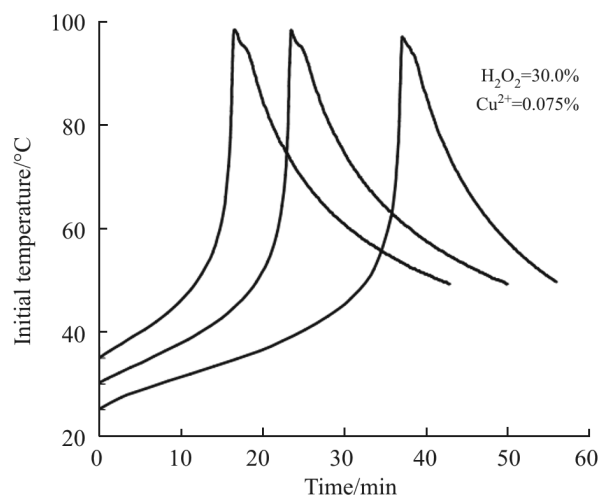
Temperature dependence

$t_{MAX}$  in which the temperature of the surroundings, in short the initial temperature, changed was measured, and the result was shown in Fig. 6. Even if the initial temperature changed, the temperature curve was similar (Fig. 7).

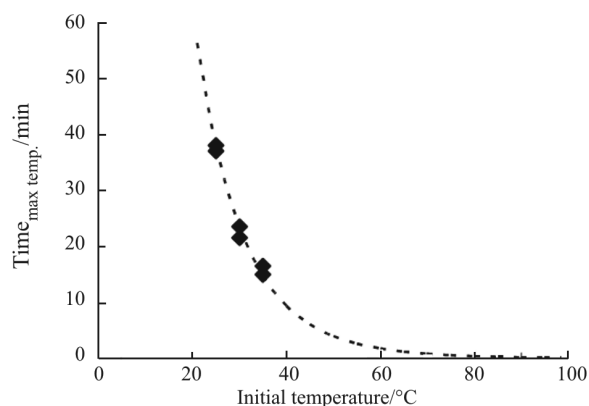
Generally, rate of reaction follows Eq. (1) under the isothermal condition.

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \tag{1}$$

According to Eq. (1),  $\alpha$  shows reaction rate in time  $t$ , and  $f(\alpha)$  is reaction model function.  $f(\alpha)$  is decided according to the rate-determining step.  $k(T)$  is rate constant, and it is dependent only on the temperature. Equation (2) is the Arrhenius equation.



**Fig. 6** Time to temperature at various initial temperature Reactor: 100 mL test tube



**Fig. 7** Initial temperature dependence of time to maximum temperature

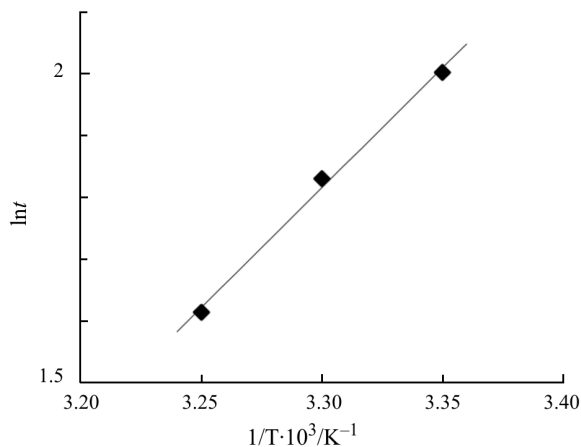
$$k(T) = A \exp\left(-\frac{E_A}{RT}\right) \quad (2)$$

In this experiment, the time until it reached the temperature which increases 5°C from initial temperature was defined as an induction period. If that the temperature rise of the interval does not influence reaction rate is assumed,  $k(T)$  is a constant. Then, Eq. (3) is obtained, when both sides of Eq. (1) is integrated.

$$\begin{aligned} t &= \frac{1}{k} \int_0^\alpha (1/f(\alpha)) d\alpha \\ &= A^{-1} \int_0^\alpha (1/f(\alpha)) d\alpha \exp\left(\frac{E_A}{RT}\right) \end{aligned} \quad (3)$$

Equation (4) is obtained, when both sides of Eq. (3) is integrated.

$$\ln t = \frac{E_A}{RT} + \ln \left\{ A^{-1} \int_0^\alpha (1/f(\alpha)) d\alpha \right\} \quad (4)$$



**Fig. 8** A linear regression according to the Arrhenius plot results in an activation energy of 32.3 kJ mol<sup>-1</sup>

The activation energy  $E_A$  can be determined by an Arrhenius plot according to Eq. (4). An Arrhenius plot showed good linear regression. (Fig. 8) By the way, calculated activation energy was 32 kJ mol<sup>-1</sup>.

## Conclusions

In runaway reaction in entrapping cupric chloride in hydrogen peroxide, the following were examined: concentration of Cu<sup>2+</sup> ion dependence, shape of container dependence and initial temperature dependence for  $t_{MAX}$ .

On the concentration of Cu<sup>2+</sup> ion dependence,  $t_{MAX}$  shortened with the increase in the concentration of Cu<sup>2+</sup> ion. When 0.025% or less, it reached the thermal equilibrium. The time which reached the thermal equilibrium was about 120 min.

On the shape of container dependence, in cylindrical container in which the inside diameter differs,  $t_{MAX}$  of the container in which the heat transfer area was small shortened. Besides,  $t_{MAX}$  was lengthened, when inside diameter and height changed.  $t_{MAX}$  in which the reaction scale changed was compared. When 68 g or less, it tended to lengthen  $t_{MAX}$ , and when 4 g, it did not reach the runaway. Moreover, the  $t_{MAX}$  showed constant value over 68 g.

On the initial temperature dependence, even if initial temperature changed, the temperature curve was similar. An Arrhenius plot showed good linear regression, activation energy was 32 kJ mol<sup>-1</sup>.

## Acknowledgements

The authors are grateful for support of staff of the Research Center for Explosion Safety at AIST.

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DOI: 10.1007/s10973-006-7636-9