

## **PREDICTION OF SPONTANEOUS IGNITION BEHAVIOR OF POWDERY ORGANIC PEROXIDE: EFFECT OF TEMPERATURE DEPENDENCE OF THERMAL CONDUCTIVITY**

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### **Summary**

A method for predicting the hazard of spontaneous ignition of an organic peroxide in powder form stored in a certain temperature environment is proposed. This method is that wherein the thermal ignition theory is simulated through numerical calculation by means of the finite difference approximation. The parameters concerning heat generation and heat removal needed for this method are obtained by measuring temperature rising rate through the adiabatic storage test and thermal conductivity through a transient heat wire method. With this prediction method, the influence of the sample consumption due to an exothermic reaction and the dependency of thermal conductivity on temperature and apparent density can be taken into consideration. It has been verified through comparison of the result of this method with the result of the isothermal storage test that more correct prediction can be made, if those factors are taken into consideration.

### **1. Introduction**

The chemical industry in recent years has been aiming at manufacture of substances having high added value, and for that purpose, the industry is heading for production of fine and many kinds of products. As a result, numerous substances which are unstable and highly reactive are synthesized and handled. It is very important, therefore, to assess the hazard related with these substances. Particularly in cases where large quantities of chemical substances are to be handled, transported or stored, making assessment of their thermal behaviors in advance is indispensable for prevention of deterioration of their quantities and for assurance of safety.

The test that is most generally practiced to identify the thermal behavior of chemical substances is thermal analysis. For the explosive substances such as explosives, a stability test method to examine their thermal stability for security reasons has long been used.

For the chemical substances also, various test methods have been developed and used to assure the safety of storage and transportation. They include the spontaneous ignitability test [1], Koenen test [2], pressure vessel test [3], adiabatic storage test [4], isothermal test [5], self-heating decomposition temperature test (SADT) [6] and 75°C stability test [7].

In using the data of these tests for the assessment of hazard, the following two methods are generally used. One is the method to use the test data for relative assessment in comparison with the data of other hazardous substances which have been used over many years. The other is the method to use the test data as the input data of the model for making assessment of hazard by simulating the thermal behavior in the actually used state [8]. The latter method is not so popularly practiced because it is generally difficult to construct a model or to process the test data into input data. Nevertheless, this method must be developed to a higher level, in view of its utilization value, as it is by far superior to the former method for the assessment of heat sensitivity or hazard of spontaneous ignition.

Examined in the present study is a method for predicting the thermal ignition behavior, as a method to assess the hazard of spontaneous ignition of an organic peroxide powder by putting the exothermic data obtained from an adiabatic storage test and the heat removal data obtained from the thermal conductivity test using a fine-wire heating method into the thermal ignition model.

## 2. Model using thermal ignition theory

Typical of thermal ignition theory are Semenov's theory [9], Frank-Kamenetskii's theory [10] and Thomas's theory [11]. These theories were originally proposed to obtain the limit of thermal ignition by analytical solutions [12]. For that purpose, the steady state disregarding the sample consumption is assumed. However, in case the adiabatic self-heating is not sufficient, application of the assumption of steady state poses a problem. Consequently, a theory to analytically obtain the thermal ignition limit with respect to an unsteady state model taking the sample consumption as a more general theory into consideration has been studied [13]. However, today when computers allow easy operation, simulation by numerical calculation may be an effective means to assess the hazard of spontaneous ignition.

Examined in the present study is the method to simulate the thermal behavior of an organic peroxide in powder form by numerically calculating the formula of the thermal ignition theory with respect to an unsteady state model by using the finite difference approximation based on Crank-Nicolson's implicit solution [14].

The dimensionless basic set of equations of one-dimensional thermal ignition theory may be given by the following equations [15].

$$\frac{\partial \theta}{\partial \tau} = \frac{\partial^2 \theta}{\partial Z^2} + \frac{J}{Z} \frac{\partial \theta}{\partial Z} + \delta \omega^n \exp\left(\frac{\theta}{1 + \epsilon \theta}\right), \quad (1)$$

$$\frac{d\omega}{d\tau} = -\frac{\delta}{B} \omega^n \exp\left(\frac{\theta}{1 + \epsilon \theta}\right) \quad (2)$$

Boundary conditions are

$$\begin{aligned} -\frac{d\theta}{dZ} &= B_1 \theta_2 \quad \text{at } Z = \pm 1 \quad \text{if } J=0, \\ &\quad \text{at } Z=1 \quad \text{if } J=1 \text{ or } 2, \\ \frac{d\theta}{dZ} &= 0 \quad \text{at } Z=0. \end{aligned} \quad (3)$$

Initial conditions are

$$\begin{aligned} \theta &= 0 \\ \omega &= 1 \end{aligned} \quad \text{at } \tau=0, \quad (4)$$

where dimensionless parameters are given by the following equations.

$$\theta = \frac{E}{RT_a^2} (T - T_a), \quad \tau = \frac{\lambda t}{C_v \rho r^2}$$

$$Z = X/r, \quad \omega = C/C_0$$

$$\delta = \frac{EQ A_0 r^2 C_0^n}{\lambda RT_a^2} \exp\left(-\frac{E}{RT_a}\right)$$

$$B = \frac{EQ C_0}{C_v \rho RT_a^2}, \quad \epsilon = RT_a/E$$

$$\theta_s = E(T_s - T_a)/RT_a^2, \quad Bi = hr/\lambda,$$

where  $Q$  denotes the heat of reaction,  $A_0$  frequency factor of reactant,  $C$  concentration of reactant,  $n$  order of reaction,  $E$  apparent activation energy of reaction,  $R$  gas constant,  $T$  sample temperature,  $T_s$  surface temperature of sample,  $T_a$  ambient temperature,  $h$  heat transfer coefficient,  $r$  sample radius,  $Bi$  Biot number,  $\lambda$  thermal conductivity of a bulk of powdery material,  $C_v$  apparent specific heat of powdery material,  $X$  distance from the center of the sample,  $t$  time, and  $J$  shape parameter (0: infinite flat plate, 1: infinite cylinder, 2: sphere).

The spontaneous ignition process was simulated by finite difference-approximation equations (1) and (2) according to Crank–Nicolson's implicit solution.

### 3. Determination of parameters concerning heat generation and removal rates

To carry out the calculation of the simulation described in the preceding section, it is necessary to know the accurate value of the parameters concerning heat generation and heat removal. In the present study, the methods to determine these parameters were the adiabatic storage test for the heat generation measurement and the thermal conductivity test using a hot wire method for heat removal measurement within the sample.

#### 3.1 Determination of parameters concerning heat generation

It is possible to obtain all of the parameters concerning heat generation needed for the simulation of thermal ignition process by the adiabatic storage test. Furthermore, since this test is conducted using a large amount of sample compared with other test methods, it has the merit of absorbing slight thermal noises to the extent in which the test result is little affected.

##### 3.1.1 Testing equipment and method

The adiabatic storage test was devised by TNO of the Netherlands [4]. We used this method with a slight modification. As is evident from Fig. 1, the equipment consists of the main body, temperature controller and temperature recorder. Installed at the center of the main body is a cylindrical sample vessel

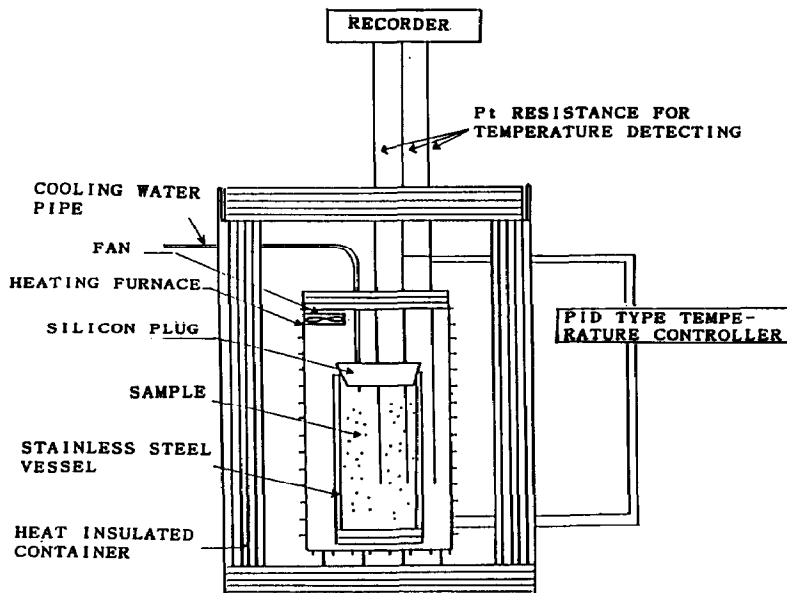


Fig. 1. Experimental setup schematic of adiabatic storage test.

made of stainless steel with a size of 80 mm dia.  $\times$  150 mm (depth), and this vessel is encompassed by a cylinder equipped with a heater for heat insulation, which in its turn is installed in a container insulated with heat insulating material.

Platinum resistance temperature sensors were installed at three places, i.e. the core part of the sample vessel, the side wall and outside the side wall. Through the use of PID temperature controller and heat-insulating heater, it was possible to control the temperature outside the sample at all times and to maintain the sample in adiabatic state.

The test procedure was as follows: One litre of dry sample was filled into the sample vessel and the temperature sensor in the core was set to a prescribed level. The ambient temperature of the sample vessel was held at the pre-set temperature, and when the sample temperature rose to the pre-set temperature, control mode was turned to adiabatic control.

In this state, the temperature of the core part of sample and that of the side wall part are automatically recorded. From this recording, the parameters concerning heat generation are obtained from using the analysis described in the next section.

On the other hand, this test equipment is also used to measure the specific heat. In this case, a Dewar flask is used as the sample vessel, with a heater provided inside the sample. In the adiabatic control mode, the energy is slowly supplied from the heater to the sample, and the specific heat is obtained from the supplied energy and temperature rise of the sample.

### 3.1.2 Analytical method

Assuming that heat will be generated as a result of a reaction of the Arrhenius type under adiabatic conditions and disregarding sample consumption, the following equation will hold:

$$C_v \rho \frac{dT}{dt} = QA_0 \exp\left(-\frac{E}{RT}\right), \quad (5)$$

where  $C_v$ : specific heat of sample (J/g K),  
 $\rho$ : apparent density of sample (g/cm<sup>3</sup>),  
 $T$ : temperature of sample (K),  
 $t$ : time (min),  
 $Q$ : molar reaction heat of sample (J/mol),  
 $A_0$ : frequency factor (mol/cm<sup>3</sup> min),  
 $E$ : apparent activation energy of reaction (J/mol),  
 $R$ : gas constant (J/mol K).

Here, supposing that  $dT/dt$  takes a constant value in a very narrow temperature range near  $T$ (K), we can rearrange the above equation as follows:

$$\ln \frac{\Delta T}{\Delta t} = -\frac{E}{R} \left(\frac{1}{T}\right) + \ln \frac{QA_0}{C_v \rho} \quad (6)$$

Reading  $\Delta T/\Delta t$  from the adiabatic temperature rising curve obtained from the adiabatic storage test and plotting the value versus  $1/T$ , we obtain the empirical formula

$$\ln \frac{\Delta T}{\Delta t} = -\frac{a}{T} + b, \quad (7)$$

where  $a$ ,  $b$  are constants.

Comparing eqn. (6) and eqn. (7) side by side, we obtain

$$a = \frac{E}{R} \quad (8)$$

$$b = \ln \frac{QA_0}{C_v \rho}$$

In other words, since  $R$  is a constant, we can obtain  $C_v$  from measurement and we can actually measure  $\rho$ , so that we can calculate  $QA_0$ .

### 3.2 Determination of thermal conductivity

There are many methods to measure thermal conductivity, and in the present study we used a non-steady-state fine-wire heating method [16,17]. With this method, a result with considerably high accuracy can be obtained by using relatively simple testing equipment.

#### 3.2.1 Testing equipment and method

In Fig. 2 the testing equipment is shown, which consists of a stainless steel sample vessel, a fine wire of 3.2 mm dia. for heating and an oven. And, as shown in Fig. 3, the fine wire for heating is equipped with alumel–chromel thermocouples to measure the temperature of the fine wire, and a platinum resistance is used as the temperature sensor for controlling the temperature of the oven. The test procedure is as follows: A sufficiently dry sample is put into the sample vessel, and the fine wire for heating is installed at the position of center axis. Then, the oven is set to a prescribed temperature. When the temperature of the core part of sample has reached a fixed equilibrium value, a fixed electric power is supplied to the fine wire for heating, and the changes in temperature are automatically recorded.

#### 3.2.2 Analytical method

Let us suppose that there is a uniform substance having infinite degree of uniform temperature, inside which is installed a heating wire of infinite length with radius,  $r$ , and that a fixed amount of heat (with the heat generation,  $q$ , per unit length) is discharged. Also let us suppose that a formula,  $r^2 \ll 4 \alpha t$  holds, where the time taken after the start of heat generation is assumed as  $t$  and diffusivity of heat as  $\alpha$  and that heat will propagate to the surroundings

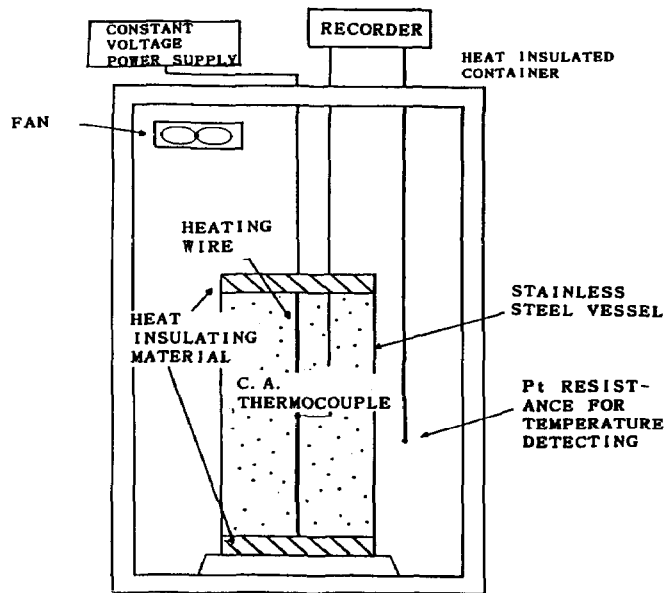


Fig. 2. Experimental setup schematic of thermal conductivity measurement.

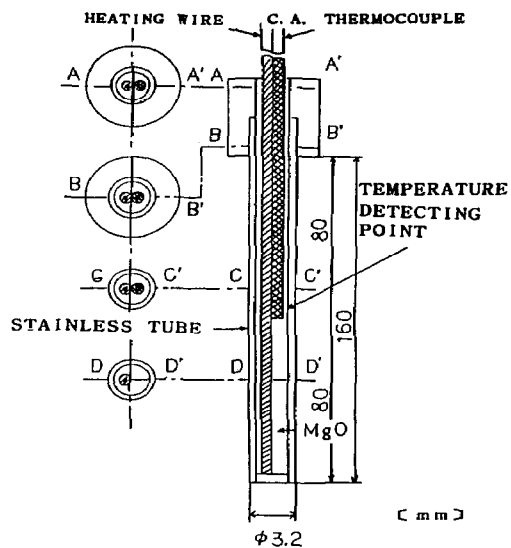


Fig. 3. Schematic of heating wire.

through conduction only. The, the rise in the surface temperature,  $\Delta T$ , of the heating wire can be approximately given by

$$\Delta T \approx \frac{q}{4\pi\lambda} \left( \ln \frac{4\alpha t}{r_0^2} - 0.572 \right) \quad (9)$$

From this, thermal conductivity,  $\lambda$ , can be obtained from the following equation.

$$\lambda = \frac{q}{4\pi} \frac{\Delta(\ln t)}{\Delta(\Delta T)} \quad (10)$$

The relation between the natural logarithm of time and the temperature was plotted from the time-course changes in fine-wire temperature obtained from the fine-wire heating method. Thermal conductivity can be obtained by substituting the gradient obtained by the plotting,  $\Delta(\ln t)/\Delta(\Delta T)$  into eqn. (10).

#### 4. Evaluation examples

The thermal behavior of the sample in the isothermal storage test of an organic peroxide was simulated using this method and the simulation result was compared with the test result. Used as the sample was bis(*p-tert*-butylcyclohexyl)peroxydicarbonate (hereinafter called TCP), which is used as a polymerization initiator for vinyl chloride or a hardener for unsaturated polyesters. The structural formula of the sample is given in Fig. 4.

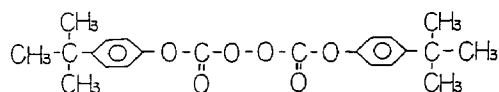


Fig. 4. Bis(*p-tert*-butylcyclohexyl)peroxydicarbonate.

#### 4.1. Simulation

##### 4.1.1 Parameter measurement

The adiabatic temperature-rise curve obtained from the adiabatic storage test is shown in Fig. 5. With this analysis,  $\Delta t$  is set to 10 minutes, and  $\Delta T/\Delta t$  at each temperature is obtained from Fig. 5. Then, the reciprocal temperature vs.  $\ln(\Delta T/\Delta t)$  is plotted, with the result as shown in Fig. 6. Arranging this result by using the least squares method, we obtain

$$\ln \frac{\delta T}{\Delta t} = \frac{24,200}{T} + 73.5 \quad (11)$$

From eqns. (8) and (11), we obtain

$$\frac{E}{R} = 24,200 \quad (12)$$



$$\ln \frac{QA_0}{C_v \rho} = 73.5$$

Specific heat was obtained from the aforementioned test method, i.e.  $C_v = 1.67$  (J/g K). And, since  $R = 8.314$  (J/mol K), these values were substituted into eqn. (12) and the following values were obtained

$$QA_0 = 6.00 \times 10^{30} \text{ (J/cm}^3\text{min)} \quad (13)$$

$$E = 201 \text{ (kJ/mol)} \quad (14)$$

On the other hand, the data obtained by the fine-wire heating method were arranged into a graph, where the natural logarithm of time,  $\ln t$  is taken in the abscissa and the rise in temperature,  $\Delta T$  in the ordinate, as shown in Fig. 7.

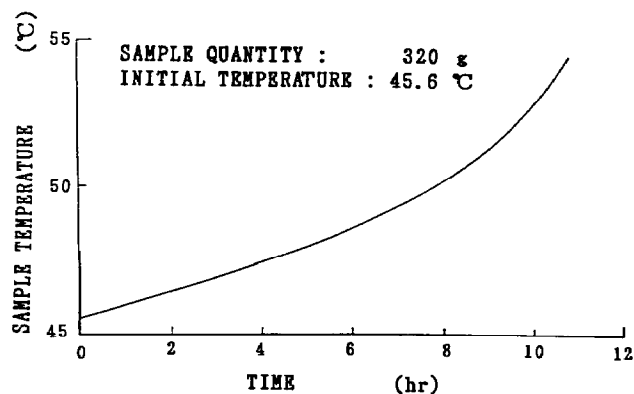


Fig. 5. Adiabatic storage test result.

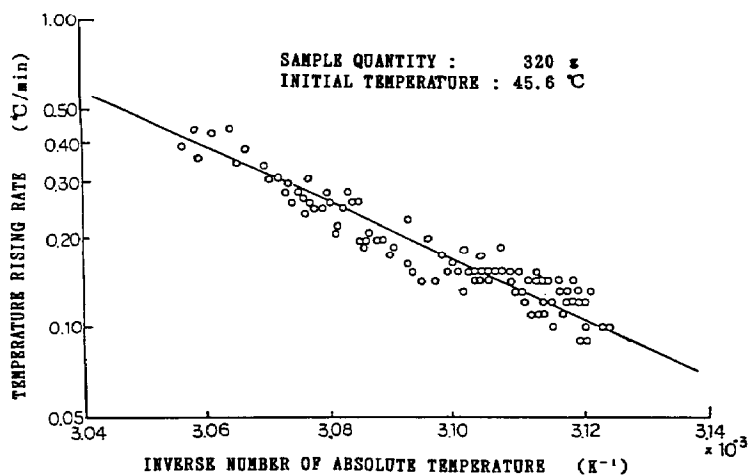


Fig. 6. TCP Arrhenius plot.

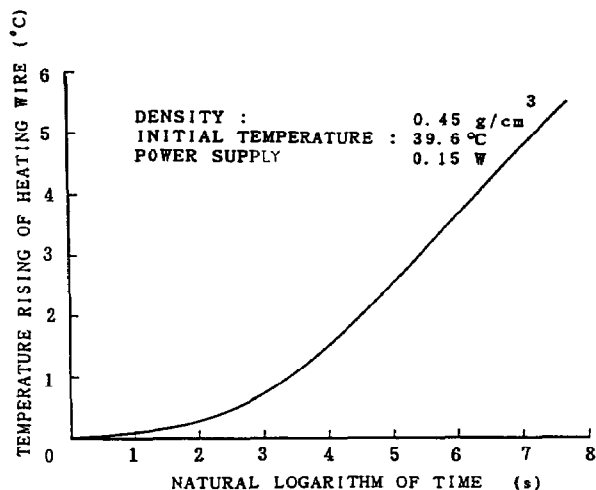


Fig. 7. Temperature rise of heating wire vs. heating time.

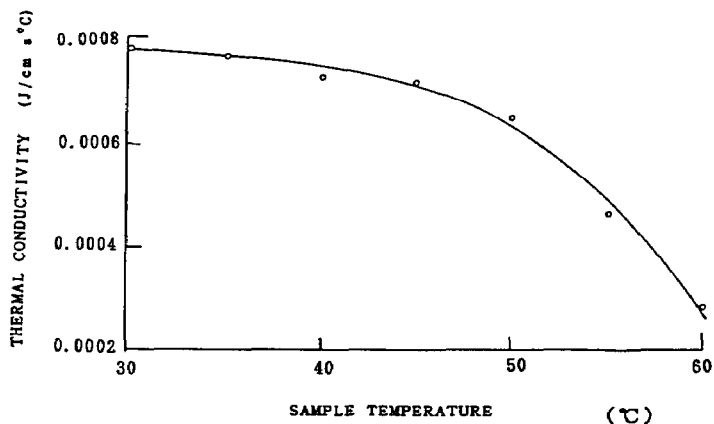


Fig. 8. Thermal conductivity as function of sample temperature ( $\rho=0.45 \text{ g/cm}^3$ ).

The portion of the graph where time  $t$  is small does not form a straight line. This may be attributed to the influence of specific heat of the heating wire.

In deriving eqn. (9), the sample size was assumed infinite, but a sample of finite size is used in the actual test. The error due to this influence appears where  $t$  is large, i.e. the rising of temperature deviates from the straight line shown in eqn. (9) and gradually approaches a fixed value. In the time range of data shown in Fig. 7, the influence of sample radius is not seen. Thermal conductivity can be obtained by substituting the gradient of the straight line part shown in this figure into eqn. (10). The relation between the thermal conductivity measured and the initial temperature of sample is shown in Fig. 8.

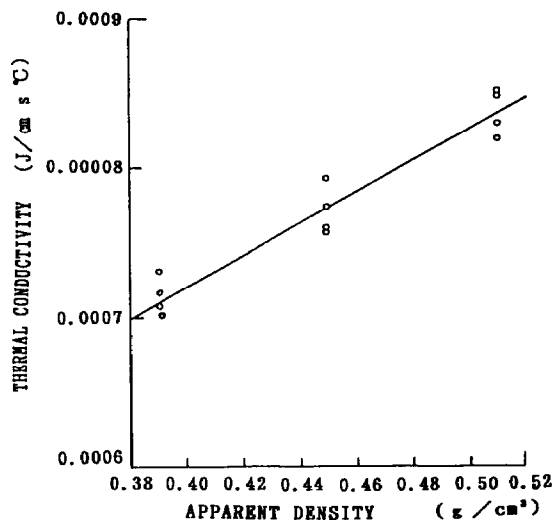


Fig. 9. Relation between thermal conductivity and sample apparent density ( $T=30^{\circ}\text{C}$ ).

Figure 8 clearly shows a trend in which thermal conductivity decreases as sample temperature increases. However, this trend does not mean that the thermal conductivity decreased so much as shown in the figure, but that it is the result of a measurement error resulting from heat generation caused by self-decomposition of the sample. Since it was thought that there would be no heat generation leading to the said measurement error for the portion lower than  $45^{\circ}\text{C}$ , the relation between thermal conductivity and temperature was obtained from the measured data for the  $30\text{--}45^{\circ}\text{C}$  range as:

$$\lambda = -5.59 \times 10^{-6} T + 9.43 \times 10^{-4} \quad (\text{J/cm s K}) \quad (15)$$

Furthermore, by arranging the measured results of thermal conductivity with respect to a sample temperature of  $30^{\circ}\text{C}$  and a sample apparent density of  $0.39\text{--}0.51 \text{ g/cm}^3$  for the purpose of examining the dependency of thermal conductivity on apparent density (Fig. 9), the following relation was obtained.

$$\lambda = 1.03 \times 10^{-3} \rho + 3.08 \times 10^{-4} \quad (\text{J/cm s K}) \quad (16)$$

#### 4.1.2 Simulation of thermal behavior

Simulation was conducted with respect to isothermal storage models using the parameters obtained in the preceding section. Supposing that an infinite cylindrical TCP (of 8 cm diameter) is placed in an atmosphere of constant temperature, numerical calculations were conducted with respect to the five models described below.

(a) Model disregarding the consumption of the sample caused by reaction;

- (b) Model taking the consumption of the sample caused by reaction into consideration (first-order reaction);
- (c) Model taking the dependency of thermal conductivity on density into consideration in addition to (b);
- (d) Model taking the dependency of thermal conductivity on temperature into consideration in addition to (b);
- (e) Model taking the dependency of thermal conductivity on temperature and apparent density into consideration in addition to (b).

The reason why Model (b) is referred to as first-order reaction is because through the analysis of the results of differential thermal analysis and vacuum stability test (Farmer test), the reaction of decomposition in the temperature range considered for this sample is thought to be a first-order reaction.

Examples of the time-course changes in the sample's internal temperature obtained from the simulation are shown in Fig. 10 with respect to Model (b) and in Fig. 11 with respect to Model (e). Both are the results obtained through calculation on the assumption that the temperature of the sample side wall is identical with the ambient temperature, being 52°C and 54°C for the both cases, resp. These results predict that at the ambient temperature of 52°C, no run-away reaction will take place leading to an ignition in the case of Model (e). However, no run-away reaction is predicted in the case of the model where thermal conductivity is constant, even when ambient temperature is 54°C. From this, it is clear that accurate data of thermal conductivity are necessary to accurately predict the critical temperature of ignition.

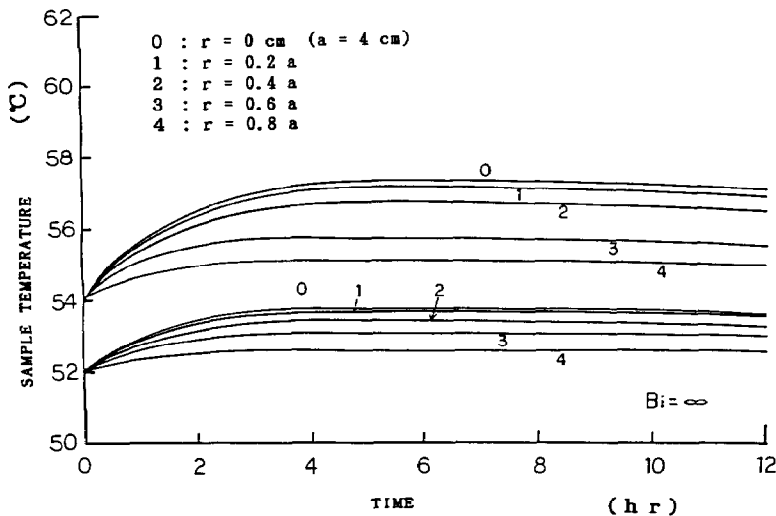


Fig. 10. Model (b) calculation result.

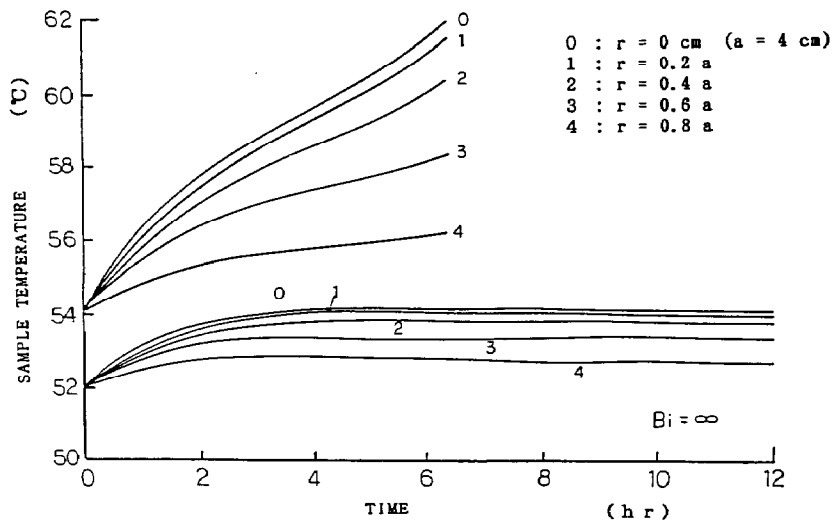


Fig. 11. Model (e) calculation result.

## 4.2 Comparison with isothermal storage test result

### 4.2.1 Isothermal storage test method

The isothermal storage test equipment shown in Fig. 1 was used. The testing procedure was as follows: One litre of sample is filled into the sample vessel and a heat insulating material is set to the top and bottom ends of the sample. And, a temperature detector is inserted into the sample core and into the part 5 mm aside to the sample's outer boundary. This sample vessel is installed at a prescribed position in the testing equipment. Keeping the ambient temperature in the equipment constant, the time-course changes in sample internal temperature are recorded.

### 4.2.2 Comparison of test and simulation results

In the simulation, a cylindrical sample of 8 cm diameter and infinite length was supposed, and in this model, the flow of heat is only considered in the radial direction. On the other hand, in the isothermal storage test, the sample had the same radius of 4 cm as used in the simulation model, but its length was finite (15 cm), so that an axial heat flow might be present.

However, if we assume that the axial heat flow can be neglected in view of the fact that the sample length is sufficiently long compared with its diameter and that a heat insulating material is set to its top and bottom ends, the said simulation model may be used for predicting the changes in the internal temperature of the sample used for the isothermal storage test.

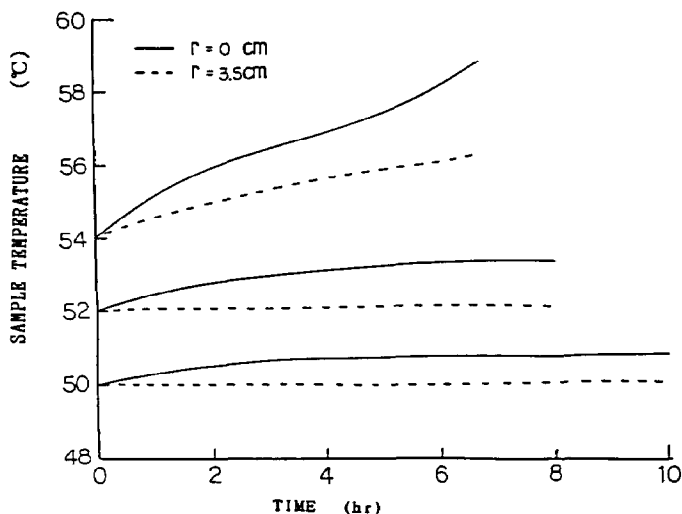


Fig. 12. Isothermic storage test result.

The results of the isothermal storage test are shown in Fig. 12; no sign of run-away reaction is observed when the ambient temperature is 50 °C and 52 °C, but when the ambient temperature is raised to 54 °C it shows the onset of run-away reaction.

On the other hand, from the simulation results described above, the onset of a run-away reaction at of 54 °C, as in the test, appears only in Model (e), where the dependency of thermal conductivity on both temperature and apparent density is taken into consideration in addition to sample consumption due to reaction.

And, the time elapsed before the onset appears is 5 to 6 hours in both the test and the simulation, showing a good coincidence. However, comparison of the rise in temperature during this lag phase shows that the simulation yields a higher temperature. So, the model accuracy needs improving, a point of further study.

From the aforementioned, it has become known that the hazard of spontaneous ignition of powdery organic peroxide TCP stored in a certain temperature environment and the time it takes before a run-away reaction leading to an ignition may be predicted by using the mathematical model (e) of thermal ignition examined in the present study.

## 5. Conclusion

A method to predict the hazard of spontaneous ignition of a powdery organic peroxide stored in a certain temperature environment was proposed.

With this method, the thermal ignition theory is simulated through numerical calculation by finite difference approximation. The parameters concerning

heat generation and heat removal needed for this simulation are obtained by measuring temperature rising rate through the adiabatic storage test and thermal conductivity through the fine-wire heating method.

A model of an isothermal storage test with respect to organic peroxide TCP was developed, and a simulation was conducted. This simulation result compared well with the test result, which is proof of the fact that accurate prediction can be made by taking into consideration the influence of sample consumption caused by the exothermic reaction and the dependency of thermal conductivity on temperature and density. Furthermore, good matching was observed between the numerical simulation and the test results with respect to the lowest environment temperature at which a spontaneous ignition could take place and the time duration before a run-away reaction started.

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