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THERMAL ACCIDENT INVESTIGATION OF METHYL ETHYL KETONE PEROXIDE BY CALORIMETRIC TECHNIQUE

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ABSTRACT

Methyl ethyl ketone peroxide (MEKPO) has highly reactive and unstable exothermal features. In recent years, it has caused many thermal explosion and runaway reaction accidents in manufacturing processes. Hydrogen peroxide (H_2O_2), dimethyl phthalate (DMP), and methyl ethyl ketone (MEK) were applied to manufacture MEKPO. To prevent casualties from runaway reactions and thermal explosion events from occurring, the goal of this study was to simulate a process for an emergency response. Differential scanning calorimetry (DSC) was employed to integrate thermal hazard development. Results indicated that MEKPO decomposed at lower temperature (30–40°C) and exploded on exponential development. Temperature of no return (T_{NR}), time to maximum rate (TMR), self-accelerating decomposition temperature (SADT), maximum of temperature (T_{max}), etc., were necessary and useful to study emergency response procedure in terms of industrial applications. In view of loss prevention, corporations with reactive chemicals must have an emergency response plan.

Key words: Methyl ethyl ketone peroxide (MEKPO), Thermal explosion, Differential scanning calorimetry (DSC), Time to maximum rate (TMR)

INTRODUCTION

The behavior of thermal explosions or runaway reactions has been widely studied for many years. In a reactor with an exothermic reaction, it is very easy to accumulate energy and temperature, when the heat generation rate exceeds the heat removal rate by Semenov theory[1].

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Methyl ethyl ketone peroxide (MEKPO) is usually applied as initiators and cross-linking agents for polymerization reactions. One reason for accidents involves the peroxy group (–O–O–) of organic peroxides, due to its instability and high sensitivity for thermal sources. Many thermal explosions and runaway reactions have been caused globally by MEKPO resulting in a large number of injuries and even death, as shown in Table 1[2–6]. Table 1 displays three accidents for MEKPO in Australia and UK from Major Hazard Incident Data Service (MHIDAS)[6].

Table 1. Thermal explosion accidents caused by MEKPO globally.

Year	Nation	Frequency	Injuries	Fatalities	Worst case
1953–1978	Japan	14	115	23	114 (Injuries) 19 (Fatalities) in Tokyo
1980–2004	China	14	13	14	8 (Injuries) 5 (Fatalities) in Honan
1984–2001	Taiwan	5	156	55	49 (Injuries) 33 (Fatalities) in Taipei
2000	Korea	1	11	3	11 (Injuries) 3 (Fatalities) in Yosu
1973 – 1986	Australia[6]	2	0	0	Not applicable
1962	UK[6]	1	0	0	Not applicable

A worst-case investigation in Taiwan in 1996

A thermal explosion and runaway reaction of MEKPO occurred at Taoyuan County (the so-called Yung-Hsin explosion) that killed 10 and injured 47 people in Taiwan in 1996. Figures 1 (a) and 1 (b) show the accident damage situation from the Institute of Occupational Safety and Health in Taiwan.

Accident development was investigated by a report from the High Court in Taiwan. Unsafe actions (wrong dosing, dosing too rapidly, errors in operation, cooling failure) caused an exothermic reaction and the first thermal explosion of MEKPO. Simultaneously, a great deal of explosion pressure led to the top of the tank bursting and the hot concrete broken and shot to the 10-ton hydrogen peroxide (H_2O_2) storage tank (d = 1, h = 3). Under this circumstance, the 10-ton H_2O_2 storage tank incurred the second explosion and conflagration that caused ten people to perish (including employers, fire fighters) and forty-seven injuries. Many plants near Yung-Hsin Co. were also affected by the conflagration caused by the H_2O_2 tank. H_2O_2, dimethyl phthalate (DMP), and methyl ethyl ketone (MEK) were applied to manufacture the MEKPO product. To prevent any casualties from runaway reaction and thermal explosion events from occurring, the aim of this study was to simulate an emergency response process.

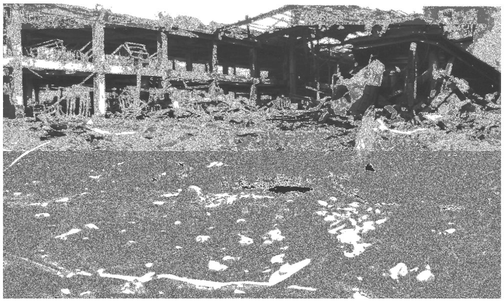

Fig. 1(a): The aftermath of the Yung-Hsin explosion which devastated the entire plant, including all buildings within 100 m

Fig. 1(b): Reactor bursts occurred by thermal runaway

Differential scanning calorimetry (DSC) was employed to integrate thermal hazard development. Processing of experimental data and kinetics evaluation was implemented by applying the TDPro and For K software developed by CISP Ltd. The method is thoroughly described by Kossoy and Akhmetshin[7] for the creation of a kinetic model and the algorithms that are utilized. Due to MEKPO decomposing at low temperature (30–40°C)[7–8] and exploding with exponential development, developing or creating an adequate emergency response procedure is very important for preventing it. The safety parameters, such as temperature of no return (T_{NR}), time to maximum rate (TMR), self-accelerating decomposition temperature (SADT), maximum temperature (T_{max}), etc., were necessary and useful for studying emergency response procedure in terms of industrial applications. In view of loss prevention, emergency response plan is mandatory and necessary for corporations to cope with reactive chemicals under upset scenarios.

EXPERIMENTAL

Methods

Fundamental thermal detection by DSC

DSC has been employed widely for evaluating thermal hazards[9–10] in various industries. It is easy to operate, gives quantitative results, and provides information on sensitivity (exothermic onset temperature, T_0) and severity (heat of decomposition, ΔH_d) at the same time. DSC was applied to detect the fundamental exothermic behavior of 31 mass% MEKPO in DMP that was purchased directly from the Fluka Co. Density was measured and provided directly from the Fluka Co. ca. 1.025 g cm^{-3}. It was, in turn, stored in a refrigerator at 4 °C. DSC, as shown in Figures 2(a) and (b), involved two thermocouples, gold of test crucible (100 bar), STAR^{e} software, and so on. According to Figure 2 (b), the S side put on sample crucible and the R side detects the blank crucible.

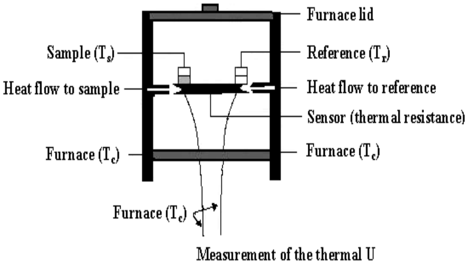

Fig. 2(a): Measurement principle of a heat flux DSC sensor with a singlethermocouple[11]

Fig. 2(b): Measurement principle of the FRS 5 interchangeable heat flux DSC sensor with 56 thermocouples[12]

RESULTS AND DISCUSSION

Thermal decomposition analysis of 31 mass% MEKPO for DSC

Fig. 3 demonstrates a comparison of thermal curves of decomposition of 31 mass% MEKPO with four types of β (β = 1, 2, 4, and 10°C min^{-1}) by DSC.

Table 2 summarizes the thermodynamic data by the DSC STAR^{e} program for the runaway assessment. MEKPO could decompose slowly at 30–32°C, as disclosed by our previous study for monomer. We surveyed MEKPO decomposing at 30°C, shown in Fig. 3.

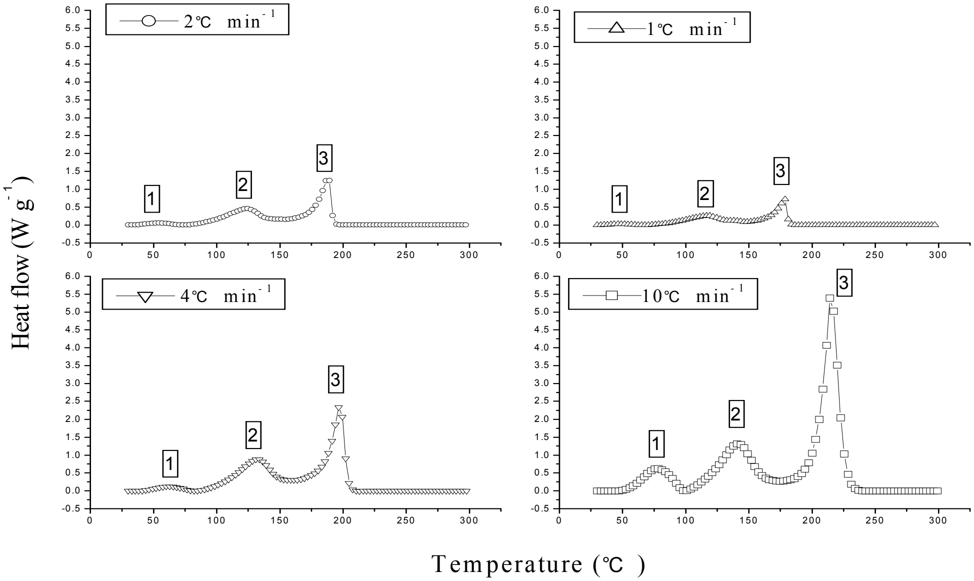

Fig. 3: Heat flow *vs.* temperature of MEKPO 31 mass% under dynamic various scanning rates by DSC

Table 2. Thermokinetics and safety parameters of 31 mass% MEKPO by DSC under various scanning rates.

β (°C min^{-1})	Mass (mg)	Initial decomposition		Mainly thermal decomposition						
		1st peak		2nd peak			3rd peak			
		T_1 (°C)	ΔH_d (J g^{-1})	T_2 (°C)	T_{max} (°C)	ΔH_d (J g^{-1})	T_3 (°C)	T_{max} (°C)	ΔH_d (J g^{-1})	ΔH_{total} (J g^{-1})
1	4.00	30	29.16	70	115	382.76	142	180	825.29	1,237.51
2	3.72	35	35.85	75	125	324.11	152	187	768.95	1,128.91
4	4.00	42	41.35	83	135	304.05	160	200	768.13	1,113.53
10	4.90	47	96.87	100	140	250.82	175	220	584.00	931.69

Various scanning rates by DSC were used to survey the initial decomposition circumstances. Under the scanning rate of 10°C min^{-1} situation, the T_0 was measured at about 47°C and ΔH of the first peak was evaluated at about 96.87 J g^{-1}. As a result, a quick temperature rise may cause violent initial decomposition (the first peak) of MEKPO under external fire condition. Table 2 shows thermokinetic parameters, such as T_0, ΔH, T_{max}, of 31 mass% MEKPO by DSC under various scanning rates. The initial decomposition peak usually releases little thermal energy, so it is often disregarded. The T_2 of mainly decomposition was about 80°C. The total heat of reaction (ΔH_{total}) was about 1,200 J g^{-1}. DSC was applied to evaluate the E_a and frequency factor (A). The E_a under DSC dynamic test was about 168 kJ mol^{-1} and A was about $3.5.10^{19}$ (s^{-1}).

Thermal decomposition analysis of 20 mass% H_2O_2 for DSC

Fig. 4 displays the exothermic reaction of 20 mass% H_2O_2 under 4°C min^{-1} of β by the DSC.

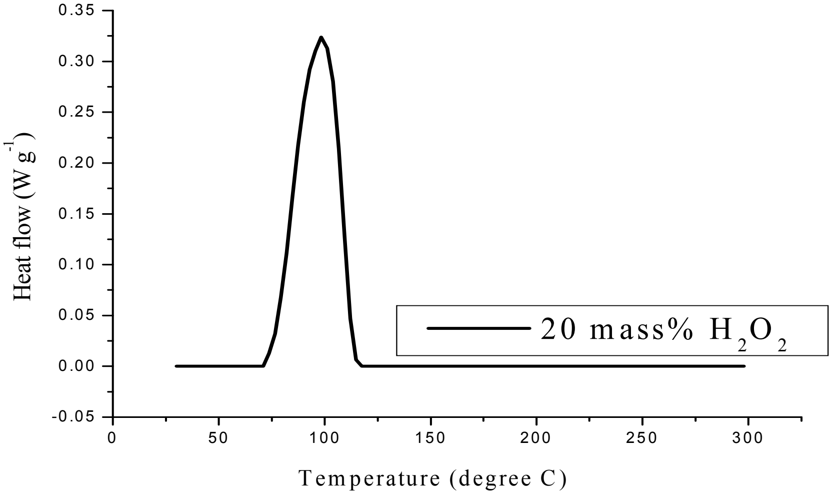

Fig. 4. Heat flow *vs.* temperature of 20 mass% H_2O_2 under 4°C min^{-1} scanning rate by DSC

Table 3. Thermokinetics and safety parameters of 20 mass% H_2O_2 by DSC under various scanning rates.

Chemical	Mass (mg)	T_0 (°C)	T_{max} (°C)	ΔH_d (J g^{-1})
H_2O_2	2.47	67	105.0	395.0
Reference[13]	2.20	69	99.6	409.7

Due to H_2O_2 being a highly reactive chemical, operators must carefully control flow and temperature. H_2O_2 was controlled at 10°C, when it precipitated the reaction. H_2O_2 exothermic decomposition hazards are shown in Table 3.

Evaluation of safety parameters

We used DSC parameters, including E_a, A, and ΔH, to set up the Semenov equation. SADT for a 25 kg package was calculated by using a wetted surface area (S), S = 0.48124 m^2, and heat transfer coefficient (U), U = $1.7034.10^{-1}$ (kJ m^{-2} $^{o}C^{-1}min^{-1}$). SADT for a 0.51 Dewar vessel was evaluated as S = 0.0303 m^2, and U = $8.7402.10^{-2}$ (kJ m^{-2} °C^{-1} min^{-1}). The SADT for a 5 and 55 gallon drum was evaluated as S = 0.137 m^2, S = 1.51 m^2, respectively, and U = 11.34 (J m^{-2} °C^{-1}). The SADT of various vessels was determined as demonstrated in Table 4.

Table 4. T_{NR} and SADT for safety storage and transportation by various vessel situations

Vessel type	T_{NR} (°C)	SADT (°C)
5 gallon drum	78.0	72.0
55 gallon drum	97.9	84.5
UN 25 kg package	62.7	54.2
UN 0.51 L Dessel vessel	55.0	50.0
Adiabatic test by VSP 2	100.0	80.0

Kinetic–based curve–fitting

There are several well known methods for evaluating simple autocatalytic models, i.e., for estimating the model parameters. One can derive complex multi-stage kinetic models that depict autocatalytic phenomena in more detail, but special numerical optimization methods are required to estimate parameters of such models as discussed by Kossoy and Koludarova[14], for a complex model of two consecutive reactions where the second stage is autocatalytic.

The reaction mechanism of MEKPO could be represented by the following kinetic model:

$$\text{Initiation reaction: } A \rightarrow B + C + \ldots;\ \text{stage } r_1 \qquad \ldots(1)$$

Autocatalytic reaction: A + B→2B + C + …; stage r_2 …(2)

$$\frac{d\alpha}{dt} = r_1 + r_2 \quad \ldots(3)$$

$$r_1 = (1-\alpha)^{n1} k_{01} \exp(-\frac{E_1}{RT}) \quad \ldots(4)$$

$$r_2 = \alpha^{n21}(1-\alpha)^{n2} k_{02} \exp(-\frac{E_2}{RT}); \quad \frac{dQ}{dt} = Q_1^{\infty} r_1 + Q_2^{\infty} r_2 \quad \ldots(5)$$

According to Eqs. (1) and (2), it might be noted that two reaction mechanisms without initial catalyst (B) exist in the incipient stage, indicating that the reaction rate was proportional not only to the reactant concentration, but also to the product concentration. Fig. 5 apply the TDPro and ForK to simulate the TMR versus temperature. We used 31 mass% MEKPO of DSC experimental data (scanning rate is 4°C min^{-1}) to fit the thermal curve and to simulate the TMR model. Under 100°C situation, the TMR of MEKPO was calculated as about three minutes.

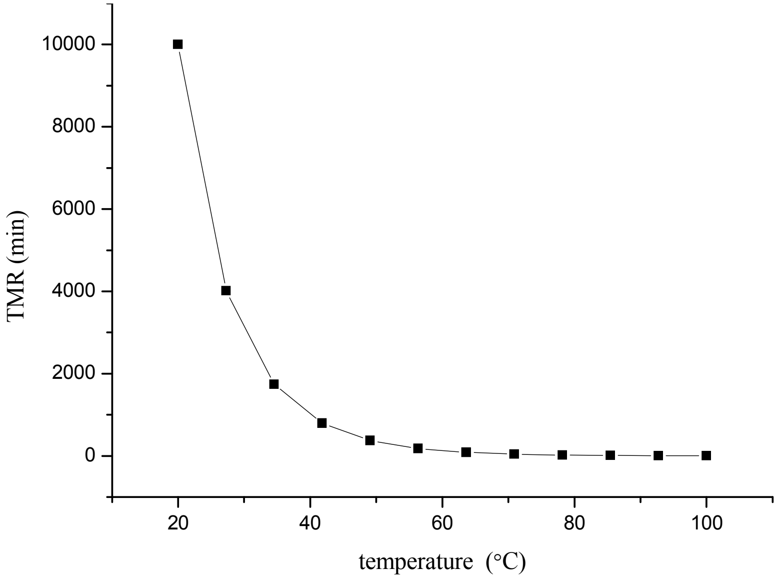

Fig. 5: TMR *vs.* temperature (kinetic–based curve–fitting) for 31 mass% MEKPO by DSC for 4°C min^{-1} of heating rate

CONCLUSIONS

According to the DSC experimental data, MEKPO decomposes at 30–40°C. If the β is high, the initial exothermic temperature could be delayed and ΔH would cause its temperature to rise quickly. Under external fire circumstances, MEKPO can decompose quickly and cause a runaway reaction and thermal explosion. During storage and transportation, a low concentration (< 40 mass%) and a small amount of MEKPO should be controlled. Under differential storage and transportation vessels, for the SADT there was a disparity. This study, with a view of predicting the SADT of a 55 gallon drum in Taiwan, came up with a value of about 85°C. H_2O_2 was controlled 10°C, when it joined a MEKPO manufacturing reaction. This is very dangerous for the MEKPO manufacturing process, so the reaction was a concern and controlled at less than 20°C in the reactor.

Thermokinetics determined by an autocatalytic thermal curve could be used to assess the thermal explosion hazard for organic peroxides and to determine useful parameters such as T_0, SADT, temperature of no return (T_{NR}), and adiabatic time to maximum rate (TMR_{ad}). In practice, these data are necessary for the proper choice of safe conditions for application, storage, and transportation in terms of chemical products.

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