

THERMAL HAZARD EVALUATION FOR METHYL ETHYL KETONE PEROXIDE MIXED WITH INORGANIC ACIDS

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Methyl ethyl ketone peroxide (MEKPO) possesses complex structures which have caused many incidents involving fires or explosions by mixing with incompatible substances, external fires, and others. In this study, reactivities or incompatibilities of MEKPO with inorganic acids (HCl, HNO₃, H₃PO₄ and H₂SO₄) were assessed by differential scanning calorimetry (DSC) and vent sizing package 2 (VSP2). Parameters obtained by the above-mentioned devices could be readily employed to discuss the runaway reaction, such as onset temperature (T_0), heat of reaction (ΔH_4), time to maximum rate (TMR), maximum self heat rate $(dT/dt)_{\max}$, adiabatic temperature rise (ΔT_{ad}), maximum pressure of decomposition (P_{\max}) and so on.

Mixing MEKPO with hydrochloric acid resulted in the lowest T_0 among inorganic acids. Nitric acid not only lowered the T_0 but also delivered the highest heat releasing rate or self heat rate (dT/dt) , which was concluded to be the worst case in terms of contamination hazards during storage or transportation of MEKPO.

Keywords: DSC, inorganic acids, methyl ethyl ketone peroxide (MEKPO), runaway reaction, vent sizing package 2 (VSP2)

Introduction

In industry, methyl ethyl ketone peroxide (MEKPO) is normally employed as a radical source for initiation as a cross-linker during polymerization. In Taiwan, Japan, China and Korea, many kinds of accidents have occurred in the manufacturing process or storage area (Table 1) [1]. When an exothermic reaction takes place in a system, self heat tends to cause acceleration in the reaction rate. This inclination is opposed by both heat loss through the walls and by reactant consumption [2]. This study was planned with a view to evaluate the hazard during the period of mixing on MEKPO contacted with any one of the inorganic acids (HCl, HNO₃, H₃PO₄ and H₂SO₄). Via the calorimetric tests, the hazardous characteristics with respect to specific inorganic acids could be established precisely.

As for its potential hazards, the first peak of MEKPO is identified as first order reaction [3]. If, depending on various conditions, the heat and pressure are induced to emerge immediately, because MEKPO has very low stability [4], a reactor will overflow, and a fire or an explosion in the process may result. A chemical reactor, as one of the most important units in the chemical industry, should be paid tremendous attention, especially if it contains an unstable reactive chemical, such as MEKPO [5–7].

In practice, many manufacturing processes use MEKPO to conduct various types of reactions, but few workers are aware of the hazardous characteristics of MEKPO while dealing with the upset situations. Therefore, the related accidents have not been terminated until now. Specifically, when MEKPO is mixed with inorganic acids, the phenomenon of runaway reactions could be tested earlier. Through the results of these tests, we could provide information on the hazards and instruct the related staff to prevent and mitigate the accident before or during the period of runaways incurred by MEKPO along with the above-mentioned contaminants.

Experimental

Sample preparations

MEKPO 31 mass% was purchased directly from the Fluka Co., and then stored in a refrigerator at 4°C. Dimethyl phthalate (DMP) was used as the diluent solvent in preparing various concentrations of MEKPO with 10 and 15 mass% for differential scanning calorimetry (DSC), and vent sizing package 2 (VSP2) tests separately.

Four types of commonly used inorganic acids were selected to combine with MEKPO in this study for scru-

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Table 1 Selected severe thermal explosion accidents caused by MEKPO in Taiwan (ROC), Japan, Korea and China [1]

Date	Location	Injuries	Fatalities	Hazard
1979	Taipei (Taiwan, ROC)	49	33	explosion (Storage)
1996	Taoyuan (Taiwan, ROC)	47	10	explosion (Tank)
1964	Tokyo (Japan)	114	19	explosion
2000	Yosu (Korea)	11	3	explosion
2001	Jiangsu (China)	2	4	explosion
2003	Zhejiang (China)	3	5	explosion

tinizing its incompatible reactions, such as HCl (6 N), HNO₃ (6 N), H₃PO₄ (6 N) and H₂SO₄ (6 N), as the contaminants of interest. The original concentrations of H₂SO₄, HNO₃, HCl and H₃PO₄ were 96, 65, 37 and 85% separately, and then by using distilled water as the thinner for allocating the above-mentioned concentrations. HCl and H₃PO₄ were purchased from Baker in USA directly, H₂SO₄ had been purchased from Katayama Chemical Co., Ltd. in Japan, HNO₃ had been gotten from Hayashi pure chemical Ind., Co., Ltd. in Japan. The mixture reactions were stirred at room temperature, and then put it into the device for testing.

Differential scanning calorimetry (DSC)

Temperature-programmed screening experiments were performed (Mettler TA8000 system) and coupled with a measuring cell that can withstand relatively high pressure to approximately 100 bar (DSC 821^e). STAR^e software was employed to obtain thermal curves [8]. DSC has been calibrated with regard to both heat flux and temperature [9]. For better thermal equilibrium, the scanning rate chosen for the temperature-programmed ramp was 4°C min⁻¹ [10]. The range of temperature rise was chosen from 30 to 300°C for each condition of experiments. This apparatus could adequately obtain the heat flow, and then via experimental data to calculate the T_0 , T_{max} and ΔH_d in the interior function of DSC.

Vent sizing package 2 (VSP2)

As a PC-controlled adiabatic calorimeter system, the VSP2 manufactured by Fauske Associates, Inc. [11] was used to measure the thermokinetic and thermal hazard data such as temperature and pressure traces with respect to time. Essentially, the low heat capacity of the cell ensures that nearly all the reaction heat released remains within the test sample. Thermokinetics and pressure behaviors in the small test cell (112 mL) can therefore be extrapolated directly to the process scale due to the low thermal inertia of about 1.05 to 1.2 [12]. In the experimental conditions, if the self heat rate exceeds 0.1°C min⁻¹, the heat-wait-search mode is terminated and the instrument enters exotherm mode. In exotherm mode, the main heater (i.e., the heater cou-

pled directly to the test cell) is turned off and only the guard heater is operated to ensure negligible heat losses. This allows the self heat behavior of the sample to be measured. If the runaway reaction have been induced in the test cell, the self heat rate may larger than 100°C min⁻¹, in order to keep the adiabatic condition during experiment, guard heater has to be started completely by automatically interior function for heating to the same temperature between test cell and vessel. Adiabatic cotton had been employed to stuff between test cell and heater, which also was being treated as an important unit for maintaining adiabatic condition during VSP2 testing.

Results and discussion

Inorganic acids of HCl, HNO₃, H₃PO₄ and H₂SO₄ (6 N) were used as the contaminants, mixed with 10 and 15 mass% MEKPO for VSP2 and DSC tests, respectively. The experimental results are displayed in Tables 2–3 and Figs 1–13. In investigation, most of the mixing conditions possessed a strong phenomenon, inorganic acids had caused a highly degree of hazard during experiments.

Experimental analyses for DSC tests

Through the results from thermal curves in Fig. 1, pure MEKPO 15 mass% only had two consecutive exothermic peaks in the overall reactions. It means that its mechanism was much more complex than

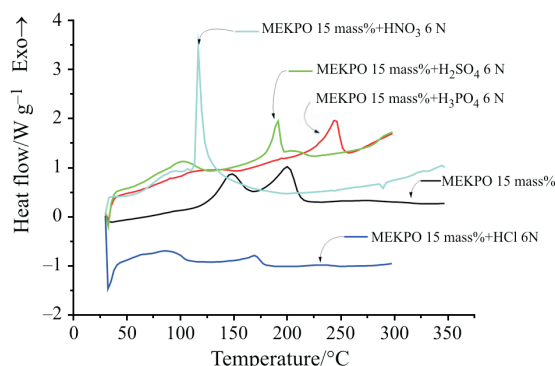


Fig. 1 Heat flow vs. temperature by the DSC experiments for MEKPO 15 mass% mixed with inorganic acids

Table 2 Calorimetric data from the dynamic scanning experiments of MEKPO 15 mass% and mixed with inorganic acids for the total peak of the reaction by DSC

Sample	<i>m</i> /mg	<i>r</i> /°C min ⁻¹	<i>T</i> _{max} /°C	<i>T</i> ₀ /°C	Δ <i>H</i> _d /J g ⁻¹	Total heat of reaction/mJ
MEKPO 15 mass%	4.7	4	200	126	600	2805
MEKPO 15 mass%+H ₂ SO ₄ (6 N, 0.9 mg)	3.0	4	190	56	477	1431
MEKPO 15 mass%+HNO ₃ (6 N, 1.3 mg)	3.6	4	116	61	875	3141
MEKPO 15 mass%+HCl (6 N, 0.9 mg)	6.5	4	86	50	251	1628
MEKPO 15 mass%+H ₃ PO ₄ (6 N, 1 mg)	3.6	4	244	64	485	1746

Table 3 Calorimetric data from the adiabatic experiments of MEKPO 10 mass% and mixed with inorganic acids by VSP2

Sample	Φ	<i>T</i> ₀ /°C	<i>T</i> _{max} /°C	<i>P</i> _{max} /psi	d <i>T</i> d <i>t</i> _{max} ⁻¹ / °C min ⁻¹	d <i>P</i> d <i>t</i> _{max} ⁻¹ / psi min ⁻¹
MEKPO 10 mass%, 50 mL	1.191	102	235	304	64	152
MEKPO 10 mass%, 50 mL+H ₃ PO ₄ (6 N), 5 mL	1.177	91	191	228	25	83
MEKPO 10 mass%, 50 mL+HNO ₃ (6 N), 5 mL	1.177	60	237	395	688	4030
MEKPO 10 mass%, 50 mL+HNO ₃ (2 N), 5 mL	1.177	64	182	201	61	80
MEKPO 10 mass%, 50 mL+H ₂ SO ₄ (6 N), 5 mL	1.177	53	200	280	471	1498

other peroxides, such as cumene hydroperoxide (CHP). The temperature to maximum peak (*T*_{max}) was about 200°C for pure MEKPO, the onset temperature (*T*₀) was tested in the point of 126°C, and the heat of reaction (Δ*H*_d) was about 600 J g⁻¹. From Table 2, all of the inorganic acids caused the *T*₀ to form earlier, and changed its original runaway configurations in the mixing reactions. Especially, when MEKPO was mixed with HNO₃ (6 N), it not only induced the *T*₀ to occur earlier but also formed a very high heat of reaction after the mini-exothermic reaction of the first peak, because MEKPO was very sensitive to H⁺ [13, 14]. After H⁺ attacked the structure of MEKPO, and then the NO₃⁻ contributed to this complex reaction for breaking the unstable structure, the second dangerous reaction had been triggered immediately. MEKPO affected by HNO₃ was very serious and prominent among other inorganic acids in this study, and compared with [15], HNO₃ was for the first time being discovered to undergo such consecutive and complex reaction during mixing with MEKPO in this study. The phenomena are demonstrated in Fig. 1.

In the process of producing MEKPO, a plant normally uses the H₃PO₄ to deal with the combining reaction. When MEKPO was mixed with H₃PO₄ in the experimental process, the reason behind the hazard was not clearly elucidated during an upset situation, but the *T*₀ also had occurred earlier than for the pure one. As for the effect on HCl, in the period of mixing reaction, HCl may have incurred a mini-exo-

thermic reaction the moment after MEKPO was mixed with it; the *T*₀ was earlier to 50°C, and clearly changed its original configuration. In addition, care must be taken with the experimental setup under this condition. Continually, another dangerous inorganic acid was H₂SO₄, which is also a common catalyst employed in plants. When MEKPO contacts H₂SO₄, the degree of hazard will be increased instantly from the test results in terms of *T*₀, *T*_{max} and Δ*H*.

Experimental analyses for VSP2 tests

For this section of experiments we used VSP2 to obtain various incompatible hazards. Related parameters, such as self heat rate (°C min⁻¹), pressure-rising rate (psi min⁻¹), and onset temperature could be accurately obtained on an adiabatic system. In view of the clear changes of temperature and pressure, the degree of hazard could be defined explicitly. This study employed MEKPO 10 mass% to mix with inorganic acids, such as HNO₃ (6 N), H₃PO₄ (6 N) and H₂SO₄ (6 N), for measuring the runaway phenomenon on adiabatic conditions.

The adopted function of VSP2 was the heat-wait-search mode. From Table 3, the results of pure MEKPO 10 mass% showed the *T*₀, maximum self heat rate, and maximum pressure-rising rate were about 102°C, 64°C min⁻¹ and 152 psi min⁻¹, respectively. Figures 2–13 reveal that when MEKPO was

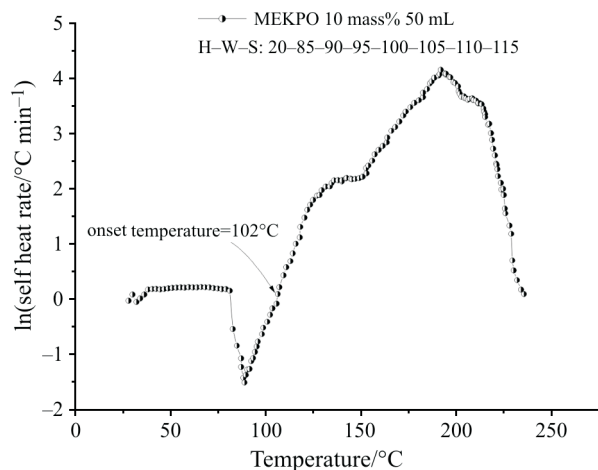


Fig. 2 Natural logarithm self heat rate vs. temperature by the VSP2 experiment for MEKPO 10 mass%

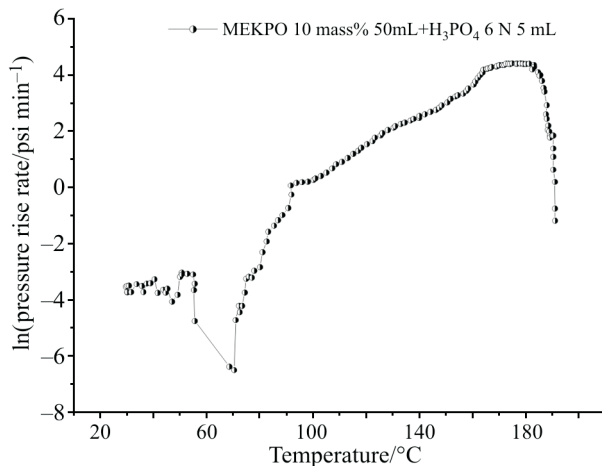


Fig. 5 Natural logarithm pressure rising rate vs. temperature by the VSP2 experiment for MEKPO 10 mass% mixed with H₃PO₄

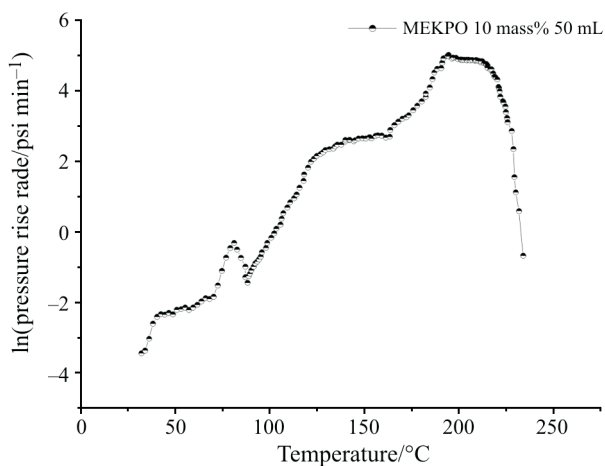


Fig. 3 Natural logarithm pressure rising rate vs. temperature by the VSP2 experiment for MEKPO 10 mass%

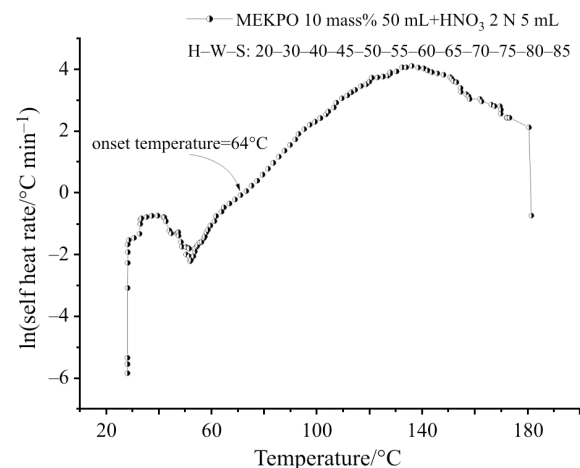


Fig. 6 Natural logarithm self heat rate vs. temperature by the VSP2 experiment for MEKPO 10 mass% mixed with HNO₃

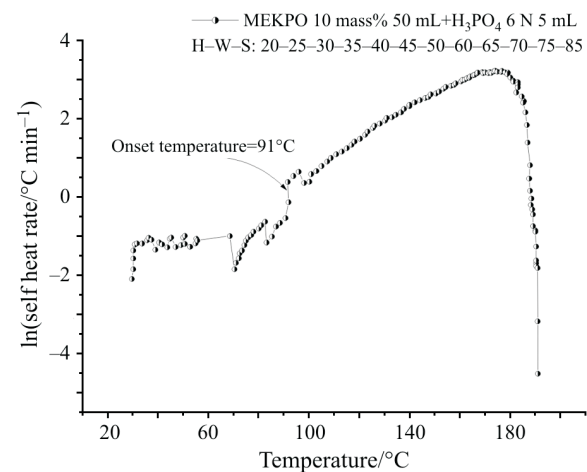


Fig. 4 Natural logarithm self heat rate vs. temperature by the VSP2 experiment for MEKPO 10 mass% mixed with H₃PO₄

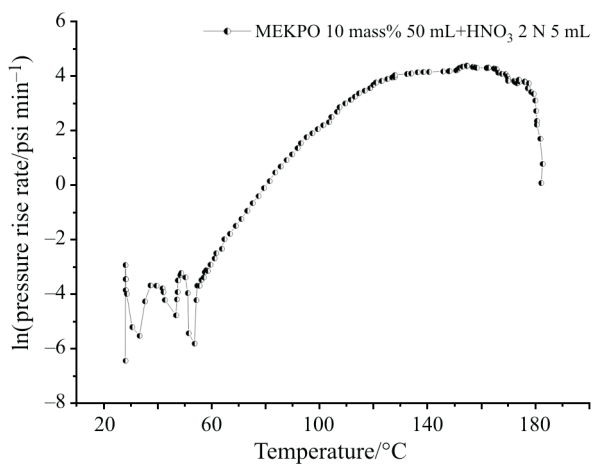


Fig. 7 Natural logarithm pressure rising rate vs. temperature by the VSP2 experiment for MEKPO 10 mass% mixed with HNO₃

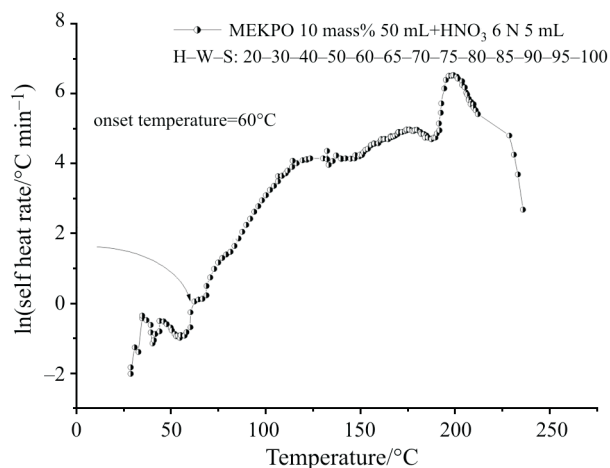


Fig. 8 Natural logarithm self heat rate vs. temperature by the VSP2 experiment for MEKPO 10 mass% mixed with HNO₃

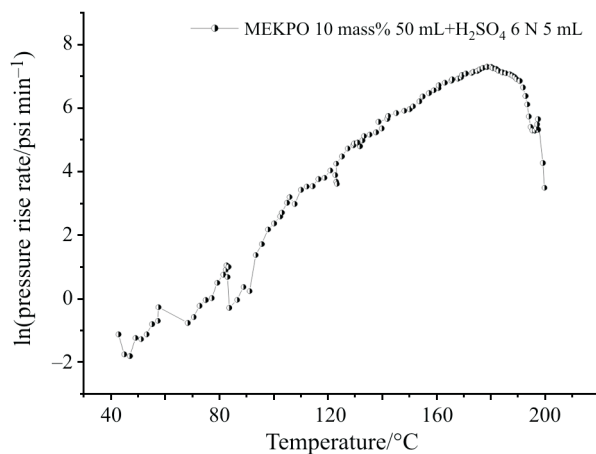


Fig. 11 Natural logarithm pressure rising rate vs. temperature by the VSP2 experiment for MEKPO 10 mass% mixed with H₂SO₄

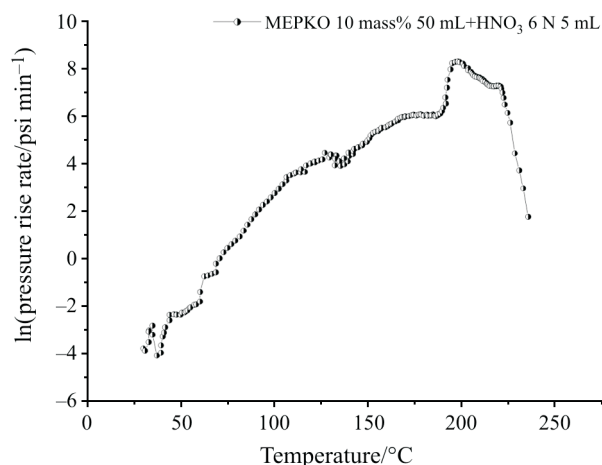


Fig. 9 Natural logarithm pressure rising rate vs. temperature by the VSP2 experiment for MEKPO 10 mass% mixed with HNO₃

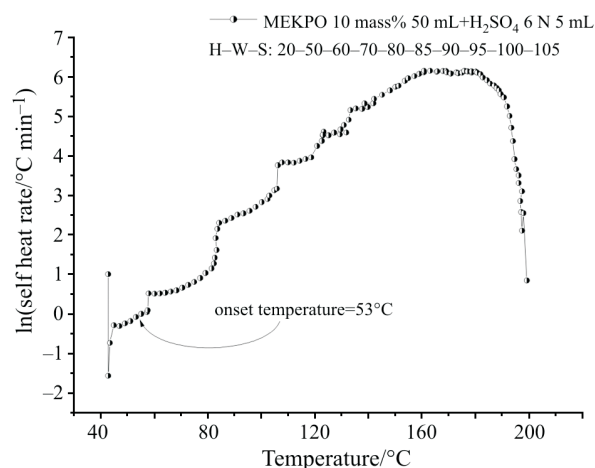


Fig. 10 Natural logarithm self heat rate vs. temperature by the VSP2 experiment for MEKPO 10 mass% mixed with H₂SO₄

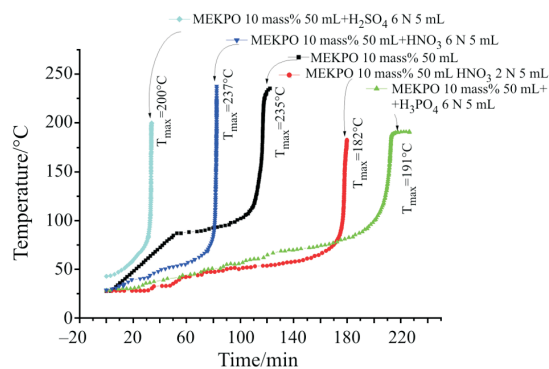


Fig. 12 Runaway reactions detected by the VSP2 for MEKPO 10 mass% mixed with inorganic acids

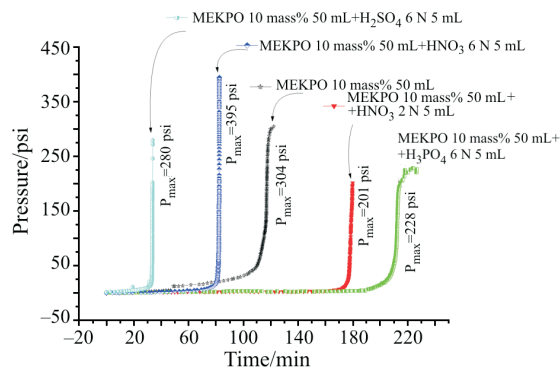


Fig. 13 Pressure behaviors under runaway reactions detected by the VSP2 for MEKPO 10 mass% mixed with inorganic acids

mixed with inorganic acids, the T_0 was earlier to occur than the pure one. Unusually, HNO₃ (6 N) caused the MEKPO 10 mass% to create an extremely dangerous situation in which the pressure-rising rate reached more than 25 times (4.030 psi min⁻¹) compared to the pure one, and the self heat rate could reach 688°C min⁻¹. The runaway situation was incredible in

terms of thermal hazards. When the concentration of HNO₃ (6 N) was decreased to HNO₃ (2 N), the degree of hazard was lessened significantly. It indicates that MEKPO must be attacked by high concentration of H⁺ in relative ratios, and then the unstable structure will be broken and release much more bond energy. H₂SO₄ also had a very interesting effect on MEKPO 10 mass%, by observing the variation of temperature and pressure. All results indicated that pure MEKPO 10 mass% was very sensitive to NO₃⁻ and SO₄²⁻.

Under the above-mentioned situations, when self heat rate reached to a limit point, the pressure would rise vertically. These results illustrated that if temperature exceeds the point of a ceiling temperature, the system will be swiftly jeopardized to a very dangerous stage.

Conclusions

MEKPO has been defined as a hazardous material, and has resulted in more than 30 critical accidents worldwide, with the hazard potential ascribed to its unstable and sensitive characteristics. This study focused on this material and specified inorganic acids for testing the specific reactive hazard. MEKPO was very sensitive to inorganic acids, in particular the HNO₃ at high concentrations (6 N); its extent of oxidizing ability was higher than other inorganic acids, such as H₃PO₄, HCl and H₂SO₄ via the observed phenomenon of self heat rate and pressure rising rate. In the DSC thermal curves, MEKPO had two consecutive exothermic peaks. If it is mixed with one of the inorganic acids in this study, the configurations of these two peaks will be changed during the decomposition process, and the *T*₀ induced in the earlier stage. It also means that the hazard of pure MEKPO was lower than incompatible reactions where MEKPO mixed with inorganic acids or other contaminants published in earlier papers.

According to the experimental results, the VSP2 could detect the *T*₀ beforehand compared with the efficiency of DSC, because VSP2 is an adiabatic system, where a tiny amount of heat could pass through this system to the environment in the confined space. Therefore, the minimum amount of heat of reaction could be tested in the wait stage settled from various conditions. By providing experimental results and hazardous information of the manufacturing process, related staff could prudently employ these data for increasing the sensitivity to hazardous vigilance, and meanwhile alleviating the degree of hazard, as for MEKPO.

Nomenclature

<i>m</i>	total mass of reactant/g
<i>P</i>	pressure/psi
<i>P</i> _{max}	maximum pressure/psi
<i>r</i>	scanning rate/°C min ⁻¹
<i>T</i>	temperature/°C
<i>T</i> _{max}	temperature at which the peak maximum occurs/°C
<i>T</i> ₀	exothermic onset temperature/°C
Φ	thermal inertia, dimensionless
Δ <i>H</i> _d	heat of reaction/J g ⁻¹
Δ <i>T</i> _a	adiabatic temperature rise/°C

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