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Calorimetric studies on the thermal hazard of methyl ethyl ketone peroxide with incompatible substances

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Abstract

In Taiwan, Japan, and China, methyl ethyl ketone peroxide (MEKPO) has caused many severe thermal explosions owing to its thermal instability and reactivity originating from the complexity of its structure. This study focused on the incompatible features of MEKPO as detected by calorimetry. The thermal decomposition and runaway behaviors of MEKPO with about 10 wt.% incompatibilities, such as H_2SO_4, HCl, NaOH, KOH, $FeCl_3$, and $FeSO_4$, were analyzed by dynamic calorimeter, differential scanning calorimetry (DSC) and adiabatic calorimeter, vent sizing package 2 (VSP2). Thermokinetic data, such as onset temperature, heat of decomposition, adiabatic temperature rise, and self-heat rate, were obtained and assessed. Experimental data were used for determining the incompatibility rating on hazards.

From the thermal curves of MEKPO with assumed incompatible substances detected by DSC, all the onset temperatures in the other tests occurring earlier advanced, especially with alkaline or ferric materials. In some tests, significant incompatible reactions were found. Adiabatic runaway behaviors for simulating the worst case scenario were performed by using VSP2. These calorimetric data led to the same results that the alkaline or ferric solution was the most incompatible with MEKPO.

Keywords: Methyl ethyl ketone peroxide (MEKPO); Thermal instability; Thermal decomposition; Incompatible reactions; Adiabatic runaway behaviors

1. Introduction

In the last century, many thermal explosions in Taiwan, Japan, and China were caused by methyl ethyl ketone peroxide (MEKPO) being subjected to external fires and other igniting sources. Yeh et al. [1] used differential scanning calorimetry (DSC) and vent sizing package 2 (VSP2) with the techniques of thermal analysis to assess the thermal hazards and thermokinetic data. The exothermic onset temperature of MEKPO is determined to be about 110 °C. Tseng et al. [2] indicated that MEKPO is highly hazardous when mixed with H_2SO_4, NaOH, Fe_2O_3, in corroborating the thermal decomposition and runaway behaviors of MEKPO with specific incompatibilities. We used about 10 wt.% contaminant, such as H_2SO_4, HCl, NaOH, KOH, $FeCl_3$, and $FeSO_4$, to investigate the incompatible hazards of MEKPO with mixed materials.

Table 1 gathers statistical accidents caused by MEKPO in Taiwan, Japan, and China. In Taiwan, five selected accidents killed 55 and injured 156 people; one of the most catastrophic accidents was the Yung-Hsin plant explosion, which killed 10 people and injured 47 during the fire fighting [3]. The fire was originally caused by a runaway oxidation reaction in a reactor unit that then spread to the tank yard, thus resulting in a disaster. In Japan, from 1953 to 1978, MEKPO was involved in 14 accidents. In particular, in 1964 in Tokyo, about 3600 kg of MEKPO exploded, killing 19 and wounding 114 people [4]. In recent years in China, there have also been several severe accidents resulting from MEKPO.

MEKPO, which is widely used in polymerization in the plastic industry, is produced by the reaction of methyl ethyl ketone (MEK) and hydrogen peroxide (H_2O_2) with various catalysts [5]. In general, MEKPO has seven different structures; for

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Nomenclature

ΔH	heat of reaction ($J\,g^{-1}$)
ΔH_d	heat of decomposition ($J\,g^{-1}$)
P_{final}	final pressure (psig)
P_{max}	maximum pressure (psig)
$(dP\,dt^{-1})_{max}$	maximum pressure-rise rate (psi min^{-1})
t	time (min)
T	temperature (°C)
$dT\,dt^{-1}$	self-heat rate (°C min^{-1})
$(dT\,dt^{-1})_{max}$	maximum self-heat rate (°C min^{-1})
T_0	exothermic onset temperature (°C)
ΔT_{ad}	adiabatic temperature rises (°C)
T_{max}	maximum temperature (°C)

Greek symbols

Φ	thermal inertial

commercial purposes, the supplier often delivers the monomer and dimer structures. Due to the inherently reactive hazards of MEKPO, many organizations have established regulations during the preparation, manufacturing, storage, and transportation stages, such as OSHA 1910.119 [6], National Fire Protection Association (NFPA) 43B [7], Department of Transportation (DOT) [8], and HSE of Control of Industrial Major Accident Hazards Regulations [9], to name a few.

Regarding the accidents that have occurred in Taiwan, there are still several reasons, which cannot be confirmed. Generally, the accidents were considered as fire-induced thermal explosions. Yeh et al. [1] conducted calorimetry tests and found the onset temperature of MEKPO is about 110 °C, which could be interpreted as the hidden reason for the thermal explosions from an initial fire accident. However, if incompatibilities exist, these mixtures may result in exothermic phenomena under lower temperature, and then entail ensuing thermal hazards, thermal runaways or even thermal explosions. This is the exact reason that incompatible substances should be taken into account with respect to the influence of the thermal runaway reaction of MEKPO. These contaminants are possibly being encountered in process, storage, and transportation units.

Numerous studies of induced hazards by organic peroxides have been performed worldwide. The United Nations has even suggested that an organic peroxide supplier must make a precise test of self-accelerating decomposition temperature (SADT) in any specific commercial package [10]. TNO in the Netherlands has devoted considerable efforts to the testing and classification of organic peroxides. MEKPO has been recognized as a flammable type or class III or IV by the code of NFPA 43B. The members of Design Institute for Emergency Relief Systems (DIERS) have emphasized research on the characteristics of pressure relief for organic peroxides [11,12]. The exothermic threshold temperature of many organic peroxides is usually around 50–120 °C. However, for some runaway incidents caused by MEKPO, the reaction or storage temperatures have even been as low as ambient temperature [1]. To date, the reactive and incompatible hazards of MEKPO have not been clearly identified, and more efforts are needed for the study of its hazardous properties.

Table 1
Major accidents caused by MEKPO in Taiwan, Japan and China

Era	Country	Number of cases	Injuries	Fatalities
1979–2001	Taiwan	5	156	55
1953–1978	Japan	14	115	23
1980–2003	China	13	6	9

The emergency relief area of a safety relief valve or rupture disk of a reactor or storage tank is nearly proportional to the adiabatic self-heat rate at the blowdown conditions using DIERS methodology [11,12]. Most thermal runaway reactions caused by organic peroxides will be accompanied by violent heat-releasing rates and thermal explosions. The maximum self-heat rate is larger than 100 °C min^{-1} for many runaway reactions of organic peroxides. The self-heat rate or thermokinetics are affected by temperature, pH value, and metal of containers, ions, and other impurities. The aim of this research was to identify the incompatible characteristics of mixtures with MEKPO. Both DSC and VSP2 or other adiabatic calorimetries were used for thermal analyses in order to acquire thermal runaway data. Data, such as exothermic onset temperature (T_0), adiabatic time to maximum heat rate (TMR_{ad}), adiabatic temperature rise (ΔT_{ad}), and self-heat rate ($dT\,dt^{-1}$), etc., were employed for evaluating the hazard rating of incompatibility [13,14]. In summary, this study addressed the following objectives: identification and assessment of the effect of incompatibilities on the liability or stability MEKPO and the applicability of calorimetry to incompatibilities of hazardous materials.

2. Experimental

2.1. Samples

MEKPO of 31 wt.% diluted in dimethyl phthalate (DMP) was purchased directly from the Aldrich Co., and then stored in a refrigerator at 4 °C. Incompatible substances, such as H_2SO_4, HCl, NaOH, KOH, $FeCl_3$, and $FeSO_4$, which could be encountered in process or storage conditions, were deliberately selected to be prepared at approximately 5 and 10 wt.% relative to MEKPO in both DSC and VSP2 experiments, respectively.

2.2. DSC

Temperature-programmed screening experiments were performed on a Mettler TA8000 system DSC821^e; the test cell (Mettler ME-26732) could withstand high pressure until about 100 bar. The scanning rate selected for the temperature-programmed ramp was 4 °C min^{-1} to maintain better thermal equilibrium [15]. About 5 mg of MEKPO was used for testing samples, followed by adding different incompatible substances. The test cell was sealed manually, and the dynamic scanning test was conducted by using DSC.