Journal of Loss Prevention in the Process Industries 25 (2012) 142–147

Contents lists available at ScienceDirect

Journal of Loss Prevention in the Process Industries

journal homepage: www.elsevier.com/locate/jlp

Thermal hazard accident investigation of hydrogen peroxide mixing with propanone employing calorimetric approaches

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ARTICLE INFO

Article history:
Received 3 May 2011
Received in revised form
28 July 2011
Accepted 30 July 2011

Keywords:
Hydrogen peroxide (H_2O_2)
Incompatible reaction
Propanone
Thermal hazards
Differential scanning calorimetry (DSC)

ABSTRACT

Hydrogen peroxide (H_2O_2), historically, due to its broad applications in the chemical industries, has caused many serious fires and explosions around the world. Its thermal hazards may also be incurred by an incompatible reaction with other chemicals, and a runaway reaction may be induced in the last stage. This study applied thermal analytical methods to explore the H_2O_2 leading to these accidents by incompatibility and to discuss what might be formed by the upset situations. Thermal hazard analysis contained a solvent, propanone (CH_3COCH_3, so-called acetone), which was deliberately selected to mix with H_2O_2 for investigating the degree of thermal hazard. Differential scanning calorimetry (DSC) and vent sizing package 2 (VSP2) were employed to evaluate the thermal hazard of H_2O_2. The results indicated that H_2O_2 is highly hazardous while mixed with propanone, as a potential contaminant. The time to maximum rate (TMR) was used as emergency response time in the chemical industries. Therefore, TMR of H_2O_2 was calculated to be 70 min for runaway reaction (after T_0) and TMR of H_2O_2/propanone was discovered to be 27 min only. Fire and explosion hazards could be successfully lessened if the safety-related data are properly imbedded into manufacturing processes.

1. Introduction

Hydrogen peroxide (H_2O_2) has been used to bleach textiles, paper products, manufacture or process foods, minerals, petrochemicals, and consumer products (detergents) (Baciocchi, Boni, & Aprile, 2004; Liou & Lub, 2008; Poulopoulos, Arvanitakis, & Philippopoulos, 2006). It was used for pollution control on municipal wastewater applications in the 1970s, industrial waste/wastewater applications in the 1980s, and more recently, air applications since the 1990s. In practice, H_2O_2 is readily available throughout the world, in drums, wet tasks totes, mini-bulk, and bulk quantities in concentrations of 35 or 50 mass%.

The physical and chemical properties of H_2O_2 have the hazardous structure of H—O—O—H, and can be dissolved in water and alcohol, but not in petroleum ether (Barton & Nolan, 1989; Chen, Lin, Shu, & Kao, 2006; Duxbury, 1980; Fauske, 1984; Huff, 1982; Leung, 1986; Lu, Yang, & Lin, 2006; Schreck et al., 2004). Generally speaking, H_2O_2 could be solidly crystallized under low temperature (−261 to 0 °C).

Thermal explosions caused by H_2O_2 subjected to external fires and other igniting sources have frequently occurred in operating area worldwide. Yeh, Shu, and Duh (2003) used differential scanning calorimetry (DSC) and vent sizing package 2 (VSP2) with thermal analysis techniques to obtain thermokinetic data for which the exothermal onset temperature (T_0) of H_2O_2 is about 41–81 °C (Yeh et al., 2003). To understand the thermal decomposition and runaway behaviors of H_2O_2 with propanone (CH_3COCH_3), this study was used to determine the reactive hazards of H_2O_2 with a chemical of specific interest.

1.1. Thermal explosion accident investigation of H_2O_2

H_2O_2 is widely used as an oxidant and was used to provide the oxygen bond in polymerization process. A thermal explosion occurred at Taoyuan county in Taiwan and was investigated to be 10 people passed away and 47 injured in 1996 (Chi, Wu, & Shu, 2009). Accident investigation by the High Court in Taiwan was described as follows:

H_2O_2, dimethyl phthalate (DMP), and methyl ethyl ketone (MEK) were used to yield methyl ethyl ketone peroxide (MEKPO). Firstly, wrong dosing and cooling system failure has caused an exothermic reaction in the reactor and led to thermal explosion of

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doi:10.1016/j.jlp.2011.07.008

MEKPO. Hot concrete being broken by thermal explosion and propelled into the 10-ton hydrogen peroxide (H_2O_2) storage tank ($d = 1$ m, $h = 3$ m). Subsequently, the 10-ton H_2O_2 storage tank underwent a second explosion and conflagration that caused 10 people to perish (including employees and fire fighters) and 47 injuries.

In Taiwan, five selected accidents by peroxides killed 55 people and injured 156. One of the most serious accidents was the Yung-Hsin plant explosion, which perished 10 people and wounded 47 during the fire fighting (Duh, Lee, Hsu, Hwang, & Kao, 1997; Wu, Su, & Shu, 2008). In USA and Japan, from 1996 to 2005, H_2O_2 induced 11 accidents. Especially in 1999 in Tokyo, an accident wounded 19 people. In recent years, several accidents have resulted from H_2O_2 due to various causes in China. In general, the accidents have been considered as being triggered by the thermal hazard. However, incompatibilities may also result in an exothermic runaway under lower temperature, and then cause in a follow-up thermal explosion, if not mitigated properly. In this study, the incompatible substances have been taken into account concerning the influence of the thermal runaway reaction of H_2O_2.

From the test results of H_2O_2 with incompatible substances, all of the onset temperatures, 71–92 °C (Chen et al., 2006), were higher than the pure one. Furthermore, its heat of decomposition, 97.35–486.62 J g^{-1}, was lower than the pure one. Numerous studies on thermal hazards by organic peroxides have been performed worldwide. The United Nations (UN) suggested OPs must make a precise test for self-accelerating decomposition temperature (SADT) in any specific commercial package (Chen, Wu, Wang, & Shu, 2008; Recommendations on the Transport of Dangerous Goods, 2006; Wu, Shyu, I, Chi, & Shu, 2009). TNO in Netherlands has devoted considerable efforts to test and classify OPs. The members of the Design Institute for Emergency Relief Systems (DIERS) have emphasized studies on the characteristics for pressure relief of OPs. The exothermic threshold temperature of many OPs is usually 50–120 °C. However, H_2O_2 with incompatible substances is prone to cause runaway reactions: its reaction or storage temperatures could be as low as the ambient temperature. The reactive and incompatible hazards of incompatible substances have not been clearly identified until now, and more efforts are required for investigating the above-mentioned.

Most thermal runaway reactions caused by OPs will be accompanied by violent heat-releasing rates and thermal explosions (Chen, Wu, Lin, Hou, & Shu, 2008; Wang, Shu, Duh, & Kao, 2001; Weber, 2006; Wu, Wang, Wu, Hu, & Shu, 2008). The maximum self-heating rate $((\mathrm{d}T\,\mathrm{d}t^{-1})_{\max})$ is larger than 100 °C min^{-1} for runaway reactions of OPs. The self-heating rate and thermokinetics are influenced by temperature, Lewis acid (H^+), Lewis bases (OH^-) and metal of containers, ions, and other impurities.

Acetone, so-called propanone, was widely employed as a cleaner in the chemical industries. Propanone mixed with H_2O_2 was prohibited (Wu et al., 2010). To prevent chemical reaction and thermal explosion, this study was used to evaluate reactive characteristics of H_2O_2 with propanone under runaway reactions. To evaluate the runaway hazards, DSC and VSP2 were been adopted for thermal analyses, for acquiring thermal runaway data, such as T_0, adiabatic time to maximum rate ($\mathrm{TMR_{ad}}$), adiabatic temperature rise (ΔT_{ad}), and self-heating rate, etc.

In summary, this study was used to determine the inherent and relative instabilities of H_2O_2 while mixed with propanone, to identify and assess the effect of reactive hazard on H_2O_2 with propanone, and to mix with the pure H_2O_2.

Table 1
Fundamental parameters of various tank types for T_c calculation.

Type	a_0	a_1	a_2	c_1	c_2	α	γ
Flat	0.8865	0.0705	0.0508	5.59234	1.04562	0.1875	0.0360
Barrel	2.0189	0.1681	0.1201	4.72918	1.04565	0.1876	0.0359
Sphere	3.3539	0.2846	0.2037	4.19710	1.04567	0.1866	0.0359

2. Experimental method

2.1. Samples

Thirty-one mass% H_2O_2 was purchased directly from the Aldrich Co. A reactive substance, propanone (CH_3COCH_3) (100 mass%), that could be assumed to be encountered in process or storage conditions, was chosen to be in the DSC experiments. As planned, H_2O_2 samples with 10, 20, 31, and 45 mass% were chosen.

2.2. Differential scanning calorimetry (DSC)

Temperature-programmed screening experiments were performed on a Mettler TA8000 system DSC821^{e}: the test cell (Mettler ME-26732) could withstand high pressure of about 100 bar. Heating rate chosen for the temperature-programmed ramp was 4 °C min^{-1}, to maintain better thermal equilibrium. The tests were conducted between 30 and 300 °C with a series of incompatible materials. The test used a pipet to inject at about 5 mg, with 10, 20, 31, and 45 mass% H_2O_2 dripped for few different incompatible samples, respectively, and then was injected into the test cell. The test cell was sealed manually, and dynamic scanning by DSC tests was conducted (Fessas, Signorelli, & Schiraldi, 2005; Hou, Shu, & Duh, 2001; Liao, Wu, Su, Shyu, & Shu, 2006; Marti, Kaisersberger, & Emmerich, 2004; Miyake, Kimura, Ogawa, Satoh, & Inano, 2005; Sivapirakasam, Surianarayanan, Chandrasekaran, & Swaminathan, 2004).

2.3. Vent sizing package 2 (VSP2)

VSP2, a PC-controlled adiabatic calorimeter manufactured by Fauske & Associates, Inc. (Wang et al., 2001), was used to obtain thermokinetic and thermal hazard data, such as temperature and pressure traces versus time. The heat–wait–search (H–W–S) mode for detecting the self-heating rate was adopted for VSP2. If the self-heating rate was larger than 0.1 °C min^{-1}, the H–W–S and main heater would be immediately terminated for measuring the original phenomenon of self-exothermicity. The low heat capacity of the cell ensured that all the reaction heat released remained within the tested sample. Thermokinetic and pressure behavior in the same test cell (112 mL) usually could be tested, without any difficult extrapolation to the process scale due to the low thermal inertia factor (Φ) of about 1.05–1.32. The low Φ allows for bench scale simulation of the worst credible case, such as incorrect dosing, cooling failure, or external fire conditions.

2.4. Thermokinetics application for adiabatic system

The kinetic parameters of a single reaction can be evaluated from the equation derived by Townsend and Tou (1980) for an adiabatic process:

Table 2
Thermokinetic parameters of 20 mass% H_2O_2 by VSP2.

Property	Q (kJ mol^{-1})	A (s^{-1})	E_a (kJ mol^{-1})	λ (J cm^{-1} s^{-1} °C^{-1})	ρ (g cm^{-3})	M (g mol^{-1})
	97.5	9.74×10^{9}	128.9	8.75×10^{-3}	1.458	34