



## Applications of thermal hazard analyses on process safety assessments



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### ARTICLE INFO

#### Article history:

Received 5 December 2013

Received in revised form

11 November 2014

Accepted 14 November 2014

Available online 15 November 2014

#### Keywords:

Runaway reaction

Thermal explosion

Azo compounds

Organic peroxides

Process safety practices

### ABSTRACT

In 2011, a large petrochemical complex in Taiwan incurred several fire and explosion accidents, which had considerable negative impact for the industry on both environmental and safety issues. Reactive substances are widely used in many chemical industrial fields as an initiator, hardeners, or cross-linking agents of radical polymerization process with unsaturated monomer. However, the unpredictable factors during the process having risk to runaway reaction, thermal explosion, fire, and exposure to harmful toxic chemicals release due to the huge heat and gas products by thermal decomposition could not be removed from the process. This study used differential technology of thermal analysis to characterize the inherent hazard behaviors of azo compounds and organic peroxides in the process, to seek the elimination of the source of the harmful effects and achieve the best process safety practices with zero disaster and sound business continuity plan.

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### 1. Introduction

Rapid industrial expansion has led to an increase in the diversity and the huge quantity of chemicals that are used; however, the reactivity and variability of many of these chemicals are two major causes of accidents. Therefore, to avoid industrial accidents caused by fire and explosion, the evaluation of the hazards and reactivities of chemicals has become a major focus in modern chemical production. On the morning of September 9, 2002, an explosion and resulting fire broke out in the INEOS phenol plant in Mobile, Alabama, USA. The main cause of the disaster was a failure in the emergency shutdown system, which caused the cumene hydroperoxide (CHP) feeding valve to remain open. Subsequently, an excessive amount of CHP mixed with acid, resulting in runaway reactions (Hsu et al., 2012; Iwata et al., 2006). On April 13, 2011, at approximately 10:00 PM at the FuXin chemical plant in Daqing city, Heilongjiang province, China, an explosion and fire occurred during the process of manufacturing 2,2'-azodi-isobutyronitrile (AIBN). A total of fourteen workers were on site, nine of whom died immediately. According to the hazard information, AIBN decomposes promptly at 100 °C and can cause explosions and fires, and the

released nitrogen and organic cyanide are also harmful to the human body.

In addition, hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) is widely used as an oxidant or bleach. Mixing high-purity H<sub>2</sub>O<sub>2</sub> solutions with ammonia solution (NH<sub>4</sub>OH), sulfuric acid (H<sub>2</sub>SO<sub>4</sub>), and hydrochloric acid (HCl) in various proportions also plays a key role in improving the semiconductor wet cleaning technology. However, H<sub>2</sub>O<sub>2</sub> is a strong oxidant and presents fire and explosion hazards (Casson et al., 2012). When the concentration of the H<sub>2</sub>O<sub>2</sub> solution is greater than 65 mass%, the spontaneous reactions can easily occur. Moreover, when the solution concentration is greater than 90 mass %, particularly in the presence of catalysts or cross-linking agents, it is even more prone to swift decomposition and the release of tremendous quantities of heat, thus causing a fire hazard (Lu et al., 2006).

Organic peroxides and azo compounds are highly thermally sensitive and can readily cause extended thermal hazards, as their thermal decomposition generates large quantities of heat and gaseous pollutants (Maschio et al., 1992). According to the definitions of the 27 Globally Harmonized System of Classification and Labeling of Chemicals (GHS) hazard classes, organic peroxides have highly hazardous characteristics of exothermic decomposition and thermal explosion and are classified as explosive substances. Azo compounds are compounds bearing the functional group R–N=

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## Nomenclature

A	pre-exponential factor ( $s^{-1}$ )
C	concentration of the reactant
$E_a$	apparent activation energy ( $kJ\ mol^{-1}$ )
k	reaction rate constant
$k_0$	pre-exponential factor
n, m	reaction orders of a specific stage
$P_{max}$	maximum pressure (psig)
R	gas constant ( $J\ mol^{-1}\ K^{-1}$ )
SADT	self-accelerating decomposition temperature ( $^{\circ}C$ )
$T_i$	temperature of sample (K), $i = 1, 2$
$T_{max}$	maximum temperature (K)
$T_0$	exothermic onset temperature ( $^{\circ}C$ )
$T_f$	final temperature (K)
U	heat transfer coefficient ( $J\ min^{-1}\ m^{-2}\ K^{-1}$ )
z	autocatalytic constant
$\Delta H$	heat of decomposition ( $J\ g^{-1}$ )
$\Delta T_{ad}$	temperature from initial to final reaction under the adiabatic condition (K)
$(dP\ dt^{-1})_{max}$	maximum pressure rise rate (psig $min^{-1}$ )
$(dT\ dt^{-1})_{max}$	maximum self-heating rate ( $^{\circ}C\ min^{-1}$ )

N–R', in which R and R' can be either aryl or alkyl. Azo compounds are widely used in dyes, pigments, blowing agents, and initiators. Unfortunately, these compounds contain the bivalent –N–N– composition which might be cleaved readily even under high ambient temperature. The self-accelerating decomposition might cause a runaway reaction and lead to a fire or explosion when the cooling system fails or other upsets occur (Dubikhin et al., 2012). Azo compounds are classified as self-reactive substances, which include unstable liquids, solids, or mixed materials that can undergo a strongly exothermic decomposition even without the participation of oxygen or air. Most of the organic peroxides undergo exothermic decomposition under 120 °C or even at approximately room temperature, and azo compounds can undergo exothermic decomposition in environments with a temperature higher than 40 °C. Therefore, the United Nations (UN) transportation regulations recommend that the temperature during the transportation of samples should not exceed the self-accelerating decomposition temperature (SADT), and that reliable experimental methods should be used to obtain the SADT of packaged samples during the storage and transport processes (Kotoyori, 1999; U.N., 2003).

A series of studies have investigated and assessed the thermal hazards and reaction incompatibilities of organic peroxides (Hou et al., 2012; Miyake et al., 2005; Yeh et al., 2003; Duh et al., 2008; Li and Koseki, 2005; Hou et al., 2001) and performed preliminary thermal analyses of azo compounds (Li and Koseki, 2004). Various studies have shown that due to the diverse reactivity of organic peroxides, both macroscopic and microscopic methods are required to fully understand the hazards of organic peroxides and to thereby obtain the optimal process conditions, establish reliable intrinsic material safety parameters, and take prudent preventive measures (Casson and Maschio, 2012; Maschio et al., 2010).

In this study, the thermal decomposition and runaway behaviors of organic peroxides and azo compounds with incompatible chemical, such as acid and base, were analyzed by DSC and TAM III thermal analysis and VSP2 adiabatic calorimetry. The thermokinetic data obtained via calorimetry, such as apparent exothermic onset temperature, heat of decomposition, adiabatic temperature

rise, and self-heating rate, were also compared with those of organic peroxides and azo compounds. The aim of this research was to verify the thermal decomposition behaviors and to establish a thermal analytic model by the hazard analytic case of organic peroxides and azo compounds. The results of these tests have proven helpful in establishing safe handling, storage, transportation, and disposal procedures.

## 2. Thermal hazard analysis techniques

The commonly used thermal hazard analysis techniques and equipment can be divided into five categories: thermal analysis technology (DSC, DTA), isothermal calorimetric technology (TAM III), adiabatic calorimetric technology (VSP2, ARC), reaction calorimetric technology (RC1, C80), and emergency relief control technology (VSP2, RSST). These techniques can be used to experimentally measure the intrinsic hazard data of hazardous or unknown substances used in manufacturing processes, including the thermal stability, incompatibility, lowest exothermic temperature, and hazardous consequence analysis, to determine the hazardous properties and to provide references for protective process safety design.

We investigated and described here the thermal stability analysis techniques (thermal analysis technology and isothermal calorimetric technology) and adiabatic calorimetry that are used frequently in current research worldwide (Maschio et al., 1999).

### 2.1. Thermal analysis technology: differential scanning calorimetry (DSC)

A DSC measures the heat flow that occurs in a sample when heated, cooled, or held isothermally at constant temperature. DSC can detect endothermic and exothermic effects by using small samples (a few mg), and show the heat flow phenomenon of the process material or the thermal decomposition of the raw materials. In addition, n-order reaction, autocatalytic reaction, and single thermal curve can be executed by the preliminary thermal screening tests to obtain the thermokinetics. DSC measurement is a method of ASTM specification for the determination of substances in the heat of reaction, apparent activation energy, frequency factor and reaction rate constant and kinetic parameters, in order to evaluate the appropriateness of substances potentially harmful and process operation (ASTM E698, 2011).

#### 2.1.1. Experimental setup

DSC experiments were conducted with a Mettler DSC governed by a TA8000 thermal analyzer. A high pressure crucible that can withstand pressures up to 100 bar and temperatures up to 600 °C was employed. Temperature and heat flow measurements obtained via DSC were calibrated with high-purity indium and zinc (Mettler, 2014). It is an instrument to achieve a better state of thermal equilibrium, for research selectable 1–10 °C  $min^{-1}$  as a dynamic scanning rate.

In this case, a series of sealed high pressure crucibles previously filled with organic peroxides and azo compounds were employed into the 4 °C  $min^{-1}$  dynamic scanning process.

DSC can be applied to scan for thermal hazards in the production process, using small amounts of samples to rapidly obtain information about the hazardous nature of the substance. The extrapolated exothermic onset temperature of chemicals can be acquired from the intersection of the exothermic peak slope and the baseline level. More strict detection methods rely on the sensitivity of the individual calorimeter, where the detection limit is set as three times the noise of the calorimeter and the rate of the heat release of the reaction must be greater than the detection limit

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