



# Explosion characteristics of mixtures containing hydrogen peroxide and working solution in the anthraquinone route to hydrogen peroxide



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## ABSTRACT

The explosive properties of mixtures of aqueous hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) and working solution (WS), and the main components of the working solution (1, 3, 5-trimethyl benzene(TMB), trioctylphosphate (TOP)) were investigated by the drop weight test. The explosion range was interpreted by thermal calculation, and the calculated results agreed well with the experimental test. The explosion mechanism of the TMB/H<sub>2</sub>O<sub>2</sub> mixture is the partial oxidation of TMB by H<sub>2</sub>O<sub>2</sub>, which is qualitatively obtained by analyzing the gaseous and liquid products of the TMB/ H<sub>2</sub>O<sub>2</sub> mixture after explosion. Finally, a proposed explosion mechanism was suggested.

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## 1. Introduction

Hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) is a green inorganic chemical product, the decomposition product of which is water. It is widely used in various areas of industry, such as chemical synthesis, bleaching of pulp, and environmental protection (Hage and Lienke, 2005; Bilińska et al., 2017; Xiang et al., 2010; Corma et al., 2001; Malakootian and Moridi, 2017; Khan et al., 2015). H<sub>2</sub>O<sub>2</sub> is used in the paper pulping and water treatment industries where it is being used as an environmentally friendly alternative to chlorine, the use of which as a bleaching agent/disinfectant has been prohibited by law in some parts of the world.

With the increasing awareness of environmental protection, H<sub>2</sub>O<sub>2</sub> gradually replaces some of the chemicals that pollute the environment. As such the demand of H<sub>2</sub>O<sub>2</sub> is increasing rapidly. Specially, H<sub>2</sub>O<sub>2</sub> with high concentration (50–70 wt.%) is used more widely because of its high oxidation capacity (Lu et al., 2018).

The main industrial process currently used for the production of H<sub>2</sub>O<sub>2</sub> is the anthraquinone process. 2-Ethylanthraquinone (EAQ) is dissolved in a solvent mixture of C9–C10 aromatics (the main component is 1, 3, 5-trimethyl benzene (TMB)) and trioctylphosphate (TOP) to form a working solution (WS) (Chen, 2008). The WS is always used because the anthraquinone (AQ) and anthrahydro-

quinone (AHQ) have different solubility. AQ dissolves in nonpolar, aromatic solvents, and AHQ dissolves well in polar solvents (TOP). The primary reactions are represented in Fig. 1, where the AQ is hydrogenated into AHQ, and AHQ is then oxidized into H<sub>2</sub>O<sub>2</sub> and AQ. The produced H<sub>2</sub>O<sub>2</sub> is usually extracted from the WS with water. The WS separated from H<sub>2</sub>O<sub>2</sub> is recycled to the reduction process. Thus, the anthraquinone process efficiently produces H<sub>2</sub>O<sub>2</sub> from H<sub>2</sub> and O<sub>2</sub> in very high yield.

The concentration of H<sub>2</sub>O<sub>2</sub> extracted from the oxidized working solution, using demineralized water in liquid-liquid sieve tray columns, is usually 27.5 wt.% to 35 wt.%. It is more energy efficient to raise the concentration of H<sub>2</sub>O<sub>2</sub> to 50~70 wt.% during extraction. However, the higher the concentration, the more H<sub>2</sub>O<sub>2</sub> becomes susceptible for forming explosive mixtures (Goor et al., 2007; Othmer, 2018).

It is well documented that there is a H<sub>2</sub>O<sub>2</sub>-organic-water explosion zone upon extraction of H<sub>2</sub>O<sub>2</sub> from the organic working solution using water. The concentration of H<sub>2</sub>O<sub>2</sub> should not exceed a maximum of 44 wt.% (Othmer, 2018). The limit of this explosion zone depends on the nature of the organic material (in this case, the components of the WS) and the operating conditions. With the progress of the technology, the composition of the WS has changed and different factories use different WS. So it is necessary to develop a method to test the explosion range of the liquid system and investigate the mechanism of the explosion to ensure the safety of the process.

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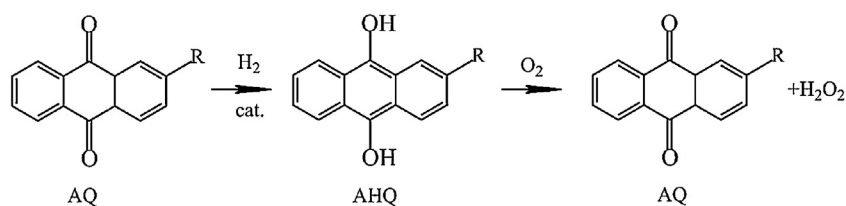


Fig. 1. The scheme of the anthraquinone process.

In open literature, the explosion ranges of the H<sub>2</sub>O<sub>2</sub>/organic mixtures are mainly restricted to the organics that are soluble to H<sub>2</sub>O<sub>2</sub> (Bretschger and Shanley, 1947; Shanley and Greenspan, 1957; Shanley and Perrin, 1958; Monger et al., 1961; Schreck et al., 2004; Chi et al., 2012). Schreck et al. (2004) investigated the thermal explosion hazard of mixtures of 2-propanol (2-PropOH), 2-methyl-2-propanol (TBA), 2-methyl-2-butanol (TAA) and 2-methyl-2-pentanol (THA) with aqueous H<sub>2</sub>O<sub>2</sub> in various ratios by heating the mixtures under confine mentor by exposing them to a shock wave. They compared the range of the explosion limits of different organics using different experimental methods. Chi et al. (2012) investigated the influence of acetone on the thermal stability of H<sub>2</sub>O<sub>2</sub> by Differential Scanning Calorimetry (DSC) and Vent Size Package 2(VSP2). Details of the explosive properties of mixtures of aqueous H<sub>2</sub>O<sub>2</sub> and insoluble organics are hardly known.

To determine the explosive properties of such types of dangerous mixtures, various methods are described. Frequently used test methods are the drop weight test (Schreck et al., 2004), the BAM 50/60 test (Koenen et al., 1961), the TNO 50/70 steel tube test (Groothuizen et al., 1974), and the USA GAP test (Mason and Aiken, 1972; Conner, 1974). In this work, the explosion range of the WS/H<sub>2</sub>O<sub>2</sub>, TMB/H<sub>2</sub>O<sub>2</sub> and TOP/H<sub>2</sub>O<sub>2</sub> mixtures was determined by the drop weight test (Recommendations on the transport of dangerous goods, 2009). To investigate the explosion mechanism of the TMB/H<sub>2</sub>O<sub>2</sub> mixtures, the explosion experiment was conducted in a closed bomb test. A reaction mechanism was proposed based on the gaseous and liquid products formed during this test.

## 2. Test procedure

### 2.1. Drop weight test

In the industrial process, the organic phase and the water phase are mixed well in an extraction column, but in the sample cell in the drop weight test, the organic phase and the water phase are layered. In order to simulate the situation in the working conditions, a surfactant (Sodium dodecylbenzenesulphonate, SDBS) was added to the WS/H<sub>2</sub>O<sub>2</sub> mixtures to enable a good contact between the two phases, and the results were compared with the system without surfactant. The amount of surfactant was so little (0.1 wt.%) that the reaction of the surfactant with H<sub>2</sub>O<sub>2</sub> can be ignored.

The drop weight test was carried out with a falling weight machine (UN Test A.1) as shown in Fig. 2 (Recommendations on the transport of dangerous goods, 2009). 40 mm<sup>3</sup> of the sample was confined in a steel cylinder beneath a piston. The freely falling 5 kg weight was dropped from a height of one meter directly on the piston. The effect was judged by the sound, which was a very loud noise upon explosion produced by the sample. On a certain given composition, take the first test. If the result is positive, finish the experiment, and the result is taken as positive. If the result is negative, the test is continued until a positive result arises, and the result is taken as positive. If the result of the fourth test is still negative, finish the experiment, and the result is taken as negative.



Fig. 2. The drop weight test device.

### 2.2. Closed bomb test

The sample amount of the drop weight test is so small (40 mm<sup>3</sup>) that the amounts of gaseous and liquid products are not sufficient for analysis. In order to collect and analyze the gas and liquid products, the closed bomb test is (Recommendations on the transport of dangerous goods, 2009) carried out. The closed bomb test device was shown in Fig. 3.

The apparatus consisted of a cylindrical steel pressure vessel of 89 mm in length, 60 mm in external diameter and 50 mm in internal diameter. Two flats are machined on opposite sides, and the firing plug was fitted on the bottom plug while the bursting disc was fitted on the above plug. The mixtures were ignited under confinement.

For liquid samples, the ignition system consisted of a 25 cm long Ni/Cr wire with a diameter 0.6 mm and a resistance of 3.85Ω/m. The wire was wound, using a 5 mm diameter rod, in the shape of a coil and was attached to the firing plug electrodes. The distance between the bottom of the vessel and the underside of the ignition coil should be 20 mm. The wire was heated by a constant power supply able to deliver 10 A.

The TMB, TOP, EAQ and SDBS used in the experiment had a purity of 99.7% and were purchased from the Aladdin Industrial Corporation (Shanghai, China), and high-purity water with an electrical

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