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ASSESSING CONTAMINATED HYDROGEN PEROXIDE FOR SAFE STORAGE AND TRANSPORTATION USING THE FTAI

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Hydrogen peroxide is a very versatile oxidizing agent, and it is also environmentally compatible considering that the products of its exothermic decomposition are oxygen and water. When kept in a clean temperature-controlled environment, the self-reaction (decomposition) rate is extremely low. However, it is well known that even a small amount of contamination will dramatically increase the reaction rate. This paper describes the use of the fast thermal activity interpreter (FTAI) instrument to examine the chemical reactivity of commercially available 50% hydrogen peroxide at two different temperatures (30 and 40°C) both with and without contamination. The results show that at 30°C a small amount of rust (330 ppm) increases the reaction rate of 50% hydrogen peroxide by a factor of 50. When the temperature is increased to 40°C, the reaction rate is further increased by almost a factor of four. The implication for reactivity management is that at this contamination level most practical vessel sizes would require emergency venting capability.

An evaluation was then performed to determine the emergency venting requirement for the safe transportation or storage of the contaminated hydrogen peroxide. It was determined that for quantities of the material less than 5 gallons, conventional breather vents would be sufficient to accommodate the gas evolved. However, for larger quantities, a safety relief device would be needed. For example, for a 400-gallon tote bin at 40°C the required minimum vent area is estimated to be 4.3 in^2, corresponding to a minimum vent diameter of 2.3 inches.

Keywords: *analysis, contamination, emergency venting, FTAI, hydrogen peroxide, isothermal, pressure measurement, safe, storage, testing, thermal activity, transportation, vent sizing*

Introduction

Hydrogen peroxide is a common industrial chemical that is used as an oxidizing agent for organic and inorganic chemical processing as well as in semi-conductor applications, as a bleaching agent for textiles and pulp, and as a treatment for municipal and industrial waste. The versatility of hydrogen peroxide is evidenced by the variety of oxidation potentials and pH conditions over which it can act as an oxidizer [1]. Under controlled conditions the reaction rate of hydrogen peroxide is known and quantified.

Contamination (or confinement) of hydrogen peroxide is generally to be avoided, and purity is carefully controlled during processing and transportation. However in a non-controlled environment the possibility for contamination can exist. Contamination can occur by accident (e.g. a rusty tool or pipe falling into a container) or by improper cleaning, conditioning or passivation of equipment. The amount of contamination that is necessary to dramatically increase the decomposition rate of hydrogen peroxide can be rather small, as illustrated below.

FTAI background info

Hydrogen peroxide, both contaminated and uncontaminated, is just one of a variety of gas generating (or consuming) systems that have been studied using the recently developed Fast Thermal Activity Interpreter (FTAI) [2]. The FTAI instrument uses an isothermal fluid bath, precision pressure transducers and a 24 bit A/D converter to measure pressures on the order of 100 Pa (~0.015 psi). The instrument interprets thermal activity (TA) on the order of 1 $\mu\text{W g}^{-1}$ and/or a self-heat rate on the order of 10^{-5}°C min^{-1}. The FTAI pressure transducer has an accuracy of better than ±0.0025 psi g (±17.2 Pa) with the fluid bath at room temperatures, so small pressure changes can be accurately measured.

A typical FTAI test comprises two stages. During the first stage, the Heatup phase, the pressure within the test cell will increase rapidly due to the heating of the material to the desired fluid bath temperature. Once the material is heated in the test cell, always within 1 h and typically within 20 min, the pressure rise rate will moderate and stabilize. The (isothermal) test phase, typically 1 h in duration, automatically follows the heatup phase. During the test phase, the pressure rise rate reflects only the gas generation rate of the material. Figure 1 shows the heatup and test phases for uncontaminated ('pure') 50% hydrogen peroxide at 30°C.

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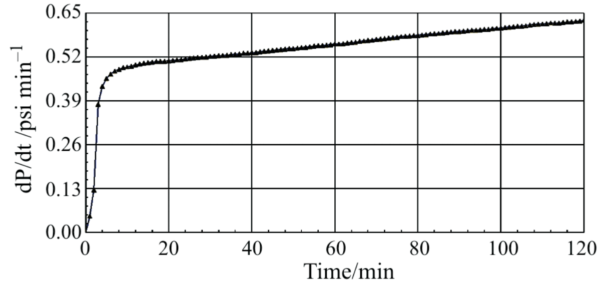

Fig. 1 FTAI heatup and test phase sample data

Test results

Prior to running each test, the FTAI glass test cells were cleaned and passivated according to established procedures for handling hydrogen peroxide. Then for the uncontaminated tests each 23 mL glass test cell was filled with 11.5 mL of 50% hydrogen peroxide (i.e. 50% fill fraction). Ordinary rust was the contaminant used for the evaluations presented in this paper. The rust was obtained by simply scraping a rusty pipe, so the rust particle size distribution was not characterized. For the contaminated tests the pure test setup was also followed, but 330 ppm of rust was added to each test cell. A series of FTAI tests were then performed to evaluate the influences of contamination and temperature effects as compared to uncontaminated hydrogen peroxide. The plot shown in Fig. 2 provides a summary of the results. Table 1 summarizes the pressurization rate of the rust contaminated hydrogen peroxide at 30 and 40°C.

The results show that at 30°C a small amount of rust contamination (330 ppm) increases the decomposition rate of 50% hydrogen peroxide by a factor of 50. When the contaminated hydrogen peroxide temperature is increased to 40°C, the self-reaction rate is increased by another factor of four, or a total increase of almost 200 times as compared to uncontaminated hydrogen peroxide at 30°C.

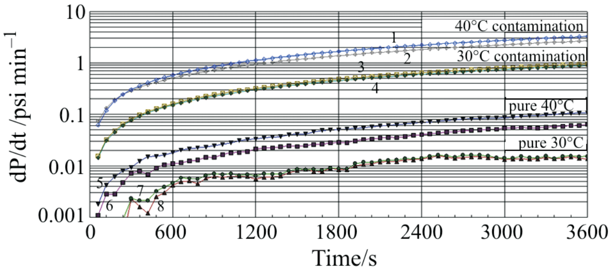

Fig. 2 FTAI results for pure and contaminated 50% hydrogen peroxide; 1, 2 – rust contamination 40°C, 3, 4 – rust contamination 30°C, 5, 6 – pure 40°C, 7, 8 – pure 30°C

Table 1 Summary of results

Material	Temperature/°C	Pressure rate (dP/dt)/psi min^{-1}
50% H_2O_2 with 330 ppm rust	30	0.014
	40	0.052

Given the measured pressurization rates for the contaminated hydrogen peroxide, an evaluation can be performed to determine if it can be safely stored or transported. The primary concern is whether the contamination will result in a runaway decomposition reaction, as would be expected if the heat generated by the accelerated decomposition exceeds heat losses from the container or vessel.

The measured pressure rates at 30 and 40ºC are 0.014 psi min^{-1} (100 Pa min^{-1}) and 0.052 psi min^{-1} (360 Pa min^{-1}), respectively, based on a sample mass of 13.4 g and a test freeboard volume of 11.5 mL. Assuming a 0th-order reaction model, the expressions for the self-heat rate dT/dt and the pressure rate dP/dt are

$$dT/dt=A\exp(-B/T) \qquad (1)$$

$$dP/dt=C\exp(-B/T) \qquad (2)$$

where B is the activation temperature and A and C are pre-exponential factors. Using the reported data, Eq. (2) can be solved to get B=12400 K, corresponding to an activation energy E_a=25 kcal g^{-1} mol^{-1}. The pre-exponential factor for the FTAI gas generation rate is then C=9.6·10^{15} psi min^{-1} (6.6·10^{19} Pa min^{-1}). This value can be scaled to represent other test equipment, as for example the ARSST [3], in which case the scaling factor is (11.5/350)(10/13.4)=0.0245 based on a 10 g sample and a 350 mL containment volume. For the ARSST the Arrhenius expression for the pressure rate (psi min^{-1}) is then

$$dP/dt=2.36\cdot10^{14}\exp(-12400/T) \qquad (3)$$

The pre-exponential factor for the self-heat rate expression can be estimated based on Fauske's observation [4] that for ARSST conditions the hydrogen peroxide self-heat rate dT/dt (ºC min^{-1}) is about four times larger than the pressure rise rate dP/dt (psi min^{-1}) independent of H_2O_2 and catalyst (contaminant) concentration. Thus we conclude that A=4C and arrive at the Arrhenius expression for the self-heat rate (ºC min^{-1})

$$dT/dt=9.44\cdot10^{14}\exp(-12400/T) \qquad (4)$$

With the above information in hand we can address the safe transport and storage of 50% hydrogen peroxide based on the assumed level of contamination. A quick check on the potential for a runaway gas-generating reaction can be performed using the stability criterion recently developed by Fauske [5].

$$d<10^{-3}\frac{T_0^2}{dP/dt(T_0)} \qquad (5)$$

appropriate for convective (non-viscous) fluids, where the pressure rate $\mathrm{d}P/\mathrm{d}t$ (T_0) [Pa min^{-1}] is measured in the FTAI at the test temperature conditions T_0 [K] and d [m] is the characteristic dimension or diameter to prevent a runaway at temperature T_0 [K]. In the present case a storage temperature of 40ºC would require that the container have a characteristic dimension less than 27 cm (11 inches) in order to prevent a runaway. Of course even under non-runaway conditions the generation of gas (as quantified using the FTAI) would need to be relieved by a conventional breather vent or similar device.

For the contamination level considered here, any vessel larger than about 5 gallons would need to be designed to accommodate a runaway reaction. The required vent capacity can be estimated using Fauske's general vent sizing equation [5]

$$A_\mathrm{v} = \frac{3.5\cdot10^{-3}}{P\left(1+\dfrac{1.98\cdot10^{3}}{P^{1.75}}\right)^{0.286}} \frac{V(\dot{T}+\dot{P})}{C_\mathrm{D}} \tag{6}$$

where A_v [m^2] – vent area, P [psi g] – relief set pressure or peak relief pressure, V [m^3] – volume of reactant, C_D – discharge coefficient, $\dot{T}$ [°C min^{-1}] – rate of temperature rise, $\dot{P}$ [psi min^{-1}] – rate of pressure rise resulting from a 10 g test sample in the ARSST.

Considering a relief set pressure of 5 psi g, the relief temperature is about 107ºC and the corresponding pressure and self-heat rates (from Eqs (3) and (4)) are about 1.6 psi min^{-1} and 6.4ºC min^{-1}, respectively. The ideal vent requirement is then A/V=0.0014 m^{-1}. For a 400-gallon tote bin at 80% fill, and assuming a discharge coefficient of 0.6, the required minimum vent area is 4.3 in^2, or a minimum diameter of 2.3 inches. Results using Fauske's Eq. (6) are consistent with large scale experience [4] if not always with DIERS two-phase flow methodology. For example, the homogeneous flow assumption yields a 6.5 inch diameter vent (i.e. more than seven times the vent area) even allowing 40% overpressure (absolute). Calculations of this type are readily implemented using the RMS (Reactivity Management Software) program [6].

Conclusions

The FTAI provides a fast and effective means for measuring small pressurization rates resulting from self-reactive gassy materials. Based upon these results, additional precautions for their safe handling, storage and transportation can easily be made part of good Reactivity Management practice.

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