

Hydrogen peroxide decomposition in the presence of organic material. A case study

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Abstract

Hydrogen peroxide is widely used as a bleaching agent. An accident is reported which occurred during the treatment of a surfactant with a peroxide/water solution that is usually highly diluted. Due to several circumstances, a higher concentrated solution was applied at start-up of the unit. This caused a sudden pressure increase which burst a pipe, releasing large quantities of heating fluid, which caught fire. The fire destroyed the unit. The sudden pressure increase was investigated by thermochemical methods. It could be demonstrated in the laboratory that even concentrations of hydrogen peroxide as low as 10% by weight in a homogeneous solution with organic material can cause sudden pressure increases in excess of the regular rating of apparatus used in the chemical industry, and high rates of pressure increase.

1. INTRODUCTION

Traditionally, the main applications of hydrogen peroxide are in bleaching processes in which solutions of a few percent hydrogen peroxide are normally applied. Hydrogen peroxide is fairly stable at room temperature, showing a small decomposition of less than one percent per year under normal storage conditions. Raising the temperature accelerates the decomposition. However, at 100°C, the thermal stability is still in the order of several hours under conditions without any contaminant. The decomposition yields half a mole of oxygen per mole of hydrogen peroxide, the energy release being 96 kJ mol⁻¹ for 100% pure hydrogen peroxide [1].

In the accident reported here, hydrogen peroxide was being used to bleach a surfactant in a continuous process. Because the process required the dilution of the molten tenside by an equal amount of water, the bleaching was done in the same step as the solvation. To do this, the hydrogen peroxide was fed directly into the dilution water close to the suction point of the feeding pump. The concentration of hydrogen peroxide in the final solution was of the order of 0.1%. The hot molten surfactant and the cold water which contained less than 0.5% peroxide, were mixed thoroughly in a mixer resulting in an average temperature of approx. 150°C. The whole system was kept under a pressure of 4 bar to avoid flashing of

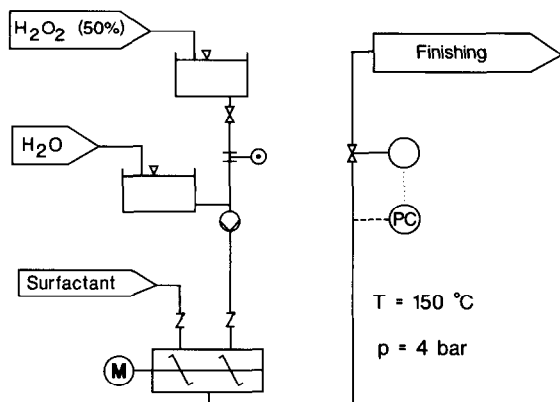


Fig. 1. Scheme of the bleaching process of a tenside using hydrogen peroxide.

steam. Downstream, after thorough mixing, the reaction solution was expanded to atmospheric pressure to evaporate dissolved gases. At this high temperature and due to the slight alkalinity of the mixture, the decomposition of the hydrogen peroxide is very fast and runs to completeness during residence time in the mixer. The scheme of the process is shown in Fig. 1.

2. ACCIDENT REPORT

On the day of the accident, the unit had been put in service again after a regular shut-down which was slightly prolonged due to unforeseen difficulties. The regular procedure is to start the production of the molten surfactant first and to fill the holding vessel up-stream of the mixer. In parallel, the mixer and the pipes connected up to the pressure regulator are filled with cold water for the dilution of the molten surfactant. Then the mixer and the flow regulators are put in service. When the level in the holding vessel reaches a set point, the pump to feed the mixer is started.

On the day of the accident, the operators followed the same procedure which was recorded in the control room. About 30 seconds after the start of the feeding pump for the molten surfactant, the pressure in the mixer rose very rapidly and a few seconds later a grumbling bang was heard followed by shaking of the building. The operators rushed to the production site and saw a large fire evolving from the area around the mixer. The fire brigade was called immediately. It took several hours to get the fire under control due to the runoff of large quantities of hot heating fluid in the bonded area which caught fire and spread the fire across the unit. The heating fluid was widely used in the unit to prevent the apparatus and the pipes from blocking. The fire caused glass tubes used in the reaction part to break, releasing the processed paraffins, which increased the damage. As there was no access to the isolation valves, the whole system was drained, pouring

several tons of heating fluid and paraffins into the unit. A catch pot for fast draining of the system was not available at that time.

The unit is divided into a main building, made of concrete, with the control room and the offices, and a production site which is partly sheltered against rain and cold by weak panels. None of the operators was close to the place where the explosion occurred so that nobody was injured. Nevertheless, the heat released by the fire damaged the construction so severely that the unit had to be pulled down and has to be totally rebuilt.

3. INVESTIGATION OF THE ACCIDENT

When the fire was extinguished and access to the unit was possible, the investigation of the cause of the explosion was started. This was impeded by the demolishing force of the fire to the construction, piping and apparatus. Nevertheless, the mixer and the connecting pipes were found in the debris. The mixer itself did not burst. Any mechanical damage prior to the accident could be excluded. The investigation of the flanges and the piping on the side of the two feed lines also gave no indication of a failure prior to the accident. Common to all parts, was the change in crystal structure typical of being pressurized to an excess pressure.

The pipe behind the mixer was ruptured along a length of 1.5 m between the mixer and the pressure regulator at the other end. This pipe was equipped with a jacket for the heating fluid to avoid condensation of the water solution by cooling and to keep the system at the required temperature during start-up and interruption in the process. This large opening in the heating jacket caused the release of heating fluid in the first step, which, according to the witnesses, was immediately ignited by an unidentified ignition source. The ignition may have been a consequence of the accident itself because the unit was equipped with explosion-proof electrical installations conforming to the German regulations for classified areas, here zone 1 [2].

Because the sudden pressure increase was connected with the feed of molten surfactant into the mixer, the next task was to identify the reason for the sudden decomposition of the mixture. The presence of excess hydrogen peroxide was the main focus of this investigation because the surfactant and its water solution are thermochemically stable up to the highest applied temperatures. An excess flow of hydrogen peroxide into the mixer prior to the feed of the molten surfactant into the apparatus had to be assumed. This was possible due to a slight change in the design over the years of operation. The intermediate storage tank for the 50% hydrogen peroxide solution was relocated on a higher platform to use normal gravity flow for the control of the flux. This flow was then fed directly into the ionized water pipe to avoid the risk of contamination of the concentrated hydrogen peroxide. The flow was controlled by an orifice for maximum flow and a

manually operated valve for disconnection during shut-down. It was never testified by an operator that the valve was not closed during the shut-down, but it must be assumed that a small flow of hydrogen peroxide into the deionized water formed a thin layer of enriched hydrogen peroxide solution at the bottom of the reservoir tank which was then fed into the mixer before the molten surfactant. When similar mistakes previously occurred, they were probably never combined with a prolonged-shut down, as in the reported case. The unforeseen difficulties during maintenance gave extra time for the required excess of hydrogen peroxide to accumulate in the main water basin, causing the rupture of the pipe.

But it was still not believed that an insignificant increase in the hydrogen peroxide concentration in the system could have caused such damage. From the mechanical damage to the piping, it was concluded that a minimum pressure of 150 bar was necessary to rupture the tube in the observed way.

4. THERMOCHEMICAL INVESTIGATION

Hydrogen peroxide becomes thermally unstable if it is heated to temperatures above 100°C. In addition, an increase in the alkalinity or the addition of heavy metal ions enhances the decomposition of the peroxide [1,3,4]. Therefore, the thermal stability of water solutions of the surfactant, containing increasing amounts of hydrogen peroxide were investigated using a differential scanning calorimeter a calorimeter with a large sample volume, adiabatic storage tests, and measurement of pressure and temperature of the decomposition reaction in a closed system.

Because the surfactant is fully soluble in water, only homogeneous mixtures were tested.

4.1. Heat of decomposition

The heat of formation of hydrogen peroxide is given in the literature as 96 kJ mol⁻¹. This value refers to a 100% pure sample of peroxide. Table 1 shows heats of decomposition measured and calculated from the temperature records of the individual runs, taking into account the inertness of the

TABLE 1

Heat of decomposition of hydrogen peroxide (50% solution) measured by different techniques and compared with the value for pure hydrogen peroxide given in the literature

Method	$\Delta H_{\text{decompos}}/\text{kJ mol}^{-1}$
DSC	106
Calorimeter [5]	89
Adiabatic storage test	70
Temperature measurement in a closed system	≈70
Literature	96

TABLE 2

Results of the DSC measurements of the heat of decomposition compared to the best value of Table 1

H ₂ O ₂ in %	R–SO ₃ in %	H ₂ O in %	$\Delta U_{\text{decom}}/\text{J g}^{-1}$	$\Delta U_{\text{decom}}/\Delta U_{\text{H}_2\text{O}_2}$
12	–	88	420	1.2
25	–	75	780	1.1
8	51	41	730	3.4
12	45	43	1150	3.2
25	30	45	2080	3.0

sample holders. All measured values refer to a 50% solution in water as delivered by the supplier.

Table 1 demonstrates that the applied techniques give the same range of values for the heats of decomposition although the precision and sensitivity are quite different. The most precise measurement is the one in the calorimeter [5]. Its slightly lower value compared to the accepted literature value may be due to the dilution in water.

Similar measurements were performed with mixtures of hydrogen peroxide and the surfactant using a differential scanning calorimeter (Mettler TA 2000) with a heating rate of 3 K min⁻¹. Sealed glass sample holders were used so that heat loss by evaporation was suppressed. The results of this investigation are listed in Table 2. A nearly tripled heat of decomposition was determined, as compared to the water solution without the tenside.

A typical DSC diagram is shown in Fig. 2. The onset temperature of the decomposition is shifted to lower temperatures compared to the thermal stability of the bulk material; this may be caused by the high surface-to-volume ratio in the DSC study and was not due to the addition of the surfactant, as will be demonstrated below. The pattern of the DSC diagram reveals a two-step process. A weak exothermic reaction starts at about 100°C, followed by a rapid decomposition at about 150°C. This behavior was also observed in the other measurement with lower peroxide contents, but was less pronounced.

The increase in the heat of decomposition of hydrogen peroxide in the presence of organic material is known from the literature. It can be explained by an oxidation reaction of the oxygen released by the organics. This is the process exploited in the application of hydrogen peroxide as a bleaching agent. The measured ratio of the increase in the total energy released is in remarkably good agreement with theoretical estimates, assuming the formation of CO₂ gas and water vapor as reaction products (factor 3.3). When non-volatile products are formed, the exothermicity can be even higher.

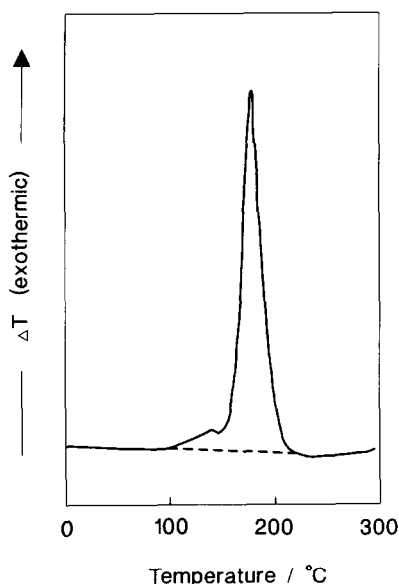


Fig. 2. DSC diagram of the decomposition of a water solution of 30% surfactant and 25% hydrogen peroxide.

4.2. Adiabatic storage tests

The pH value of the surfactant water solution is in the range of 6.5–7.5. The slight increase in pH compared to the guaranteed acidity of less than pH 5 should not have a significant influence on the thermal stability of the hydrogen peroxide. This was confirmed in a series of adiabatic storage tests using Dewar flasks which were stored in an autoclave at a total pressure of 10 bar of nitrogen. The temperatures of the autoclave and the sample were recorded, as well as the pressure [6].

Mixtures containing 7.5–50% hydrogen peroxide were tested, the latter without the addition of the surfactant. The measured times to maximum rate are plotted in Fig. 3 as a function of the inverse temperature. Although the scatter of the data is larger than normal for this type of test method, the measurements do not show a notable influence of the presence of surfactant or of the concentration of peroxide. The thermal stability can best be described by an activation energy of about 75 kJ mol^{-1} which is in acceptable agreement with literature values of $86\text{--}88 \text{ kJ mol}^{-1}$ [5, 7].

The influence of alkalinity on the thermal stability was also investigated. In the investigation of the accident, it could not be ruled out that the pH value of the water solution was alkaline. Again adiabatic storage tests were performed, this time at ambient temperature and pressure. A linear dependence of the rate of decomposition as a function of the sodium hydroxide concentration was observed, starting with a non-detectable rate for the normal water solution of surfactant and hydrogen peroxide, and

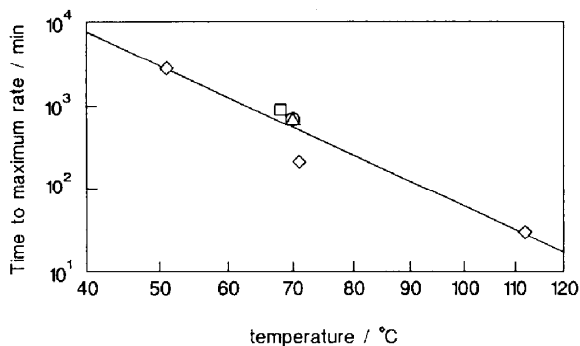


Fig. 3. Time to maximum decomposition rate of reaction mixtures containing: ○, 7.5% H₂O₂ and 51% R-SO₃; ◇, 13% H₂O₂ and 45% R-SO₃; □, 25% H₂O₂ and 30% R-SO₃; and △, 50% H₂O₂.

ending with a time of maximum rate of 40 min for a 1% sodium hydroxide concentration. Again no difference was observed for the pure peroxide solution and for the mixtures containing the surfactant. All measurements were made with a peroxide concentration of 12.5%.

4.3. Pressure increase

The pressure increase during decomposition of the reaction mixture was studied in an autoclave of 200 cm³ volume [8]. The autoclave was fitted with a glass inliner for thermal isolation of the sample. For each run, 60–110 g of the mixture were used, resulting in a filling level of 0.3–0.5 g cm⁻³. The autoclave with the sample was then heated up at a rate of about 2°C min⁻¹. Figure 4 displays the recorded pressure of the run with the highest

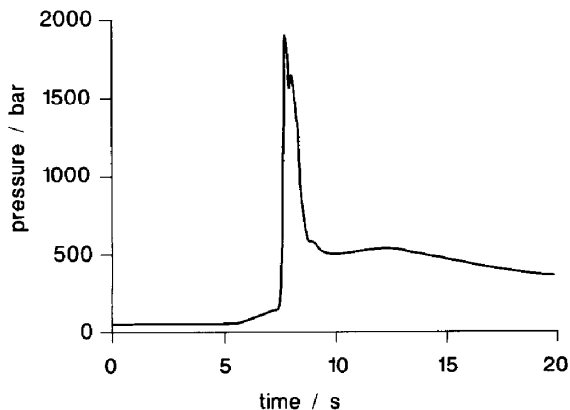


Fig. 4. Recorded pressure of the decomposition of 100 g of reaction mixture containing 25% H₂O₂ and 30% R-SO₃ in a 200 cm³ autoclave. The starting temperature of the decomposition was 100°C; the recorded peak temperature was 660°C.

concentration of hydrogen peroxide used. For all runs, the thermal decomposition started at about 100°C. The start of the decomposition raised the sample temperature above the autoclave temperature. The pressure increase is moderate at this stage of the decomposition, about 0.1 bar s⁻¹. A moderate heat release was also observed in the DSC measurements at the beginning of the decomposition. After this stage of moderate temperature and pressure increase, the decomposition suddenly accelerates yielding a peak pressure of 1900 bar in a second and a maximum rate of pressure increase of about 10 000 bar s⁻¹. The peak temperature was recorded as 655°C for the run shown in Fig. 4. The pressure collapses in a few seconds. To understand this rapid rise and fall in pressure, it must be considered that the released decomposition energy heated the mixture up to a temperature far above the critical point of water: $p_{crit.}$, 228 bar; $T_{crit.}$, 374°C. The thermodynamics of the critical gas is different from that under normal conditions and caused the unforeseen high pressure rise as well as the pressure drop. Nevertheless, all runs with hydrogen peroxide contents of 10% and above ended with a maximum pressure of more than 150 bar and a rate of pressure increase higher than 100 bar s⁻¹. This is documented in Fig. 5 which compares the rate of pressure increase for mixtures including the surfactant in excess of the peroxide with the results of measurements without an organic addition as a function of the peroxide concentration. There is evidence that not only is the heat of decomposition of hydrogen peroxide tripled in the presence of organics but the severity of the decomposition is also significantly amplified when the heat of decomposition exceeds about 500 J g⁻¹.

The analysis of the experiments, furthermore, proves that the decomposition of hydrogen peroxide does not yield volatile gases in the presence

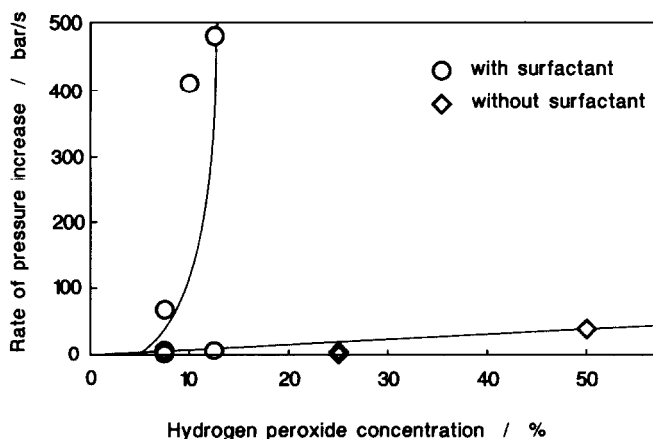


Fig. 5. Recorded maximum rate of pressure increase as a function of the hydrogen peroxide concentration for water solutions with and without surfactant.

of organics, in contrast to the runs without an organic addition. This confirms that the oxygen is absorbed by an oxidation reaction in the presence of the surfactant, yielding non-volatile products.

5. DISCUSSION AND CONCLUSION

The supposed enrichment of hydrogen peroxide in the water used to fill the mixture for start-up of the unit strongly implies that the bursting of the pipe was the primary cause of the accident. At the high temperature of the reaction mixture, the time to maximum rate is in the order of less than a minute and may have even been reduced by the residual basicity of the product. Because the system was totally filled with liquid, the decomposition may have taken place at a locally restricted volume. The observed pressure increase in the laboratory is too fast to be released by the pressure regulator for the expansion of the solution. The conclusion that even a local decomposition could have caused the accident is of some importance because the maximum flow of highly concentrated hydrogen peroxide water solution was estimated to be very small.

Although the measurements are limited to the studied mixture of a specific surfactant, comparable measurements in our laboratory have demonstrated that the results are common to mixtures with organics. The heat of decomposition was always greater by a factor of two than the value for hydrogen peroxide.

Hydrogen peroxide is widely used as a bleaching agent for many applications without spectacular accidents such as the one reported here. The risk of an uncontrolled decomposition is only real when higher concentrations are applied by mistake and the excess energy cannot be compensated for, for example by evaporation of water. Below a concentration of 2.5% peroxide, the risk of a pressure build-up can even be ruled out in a vented vessel. Fast rates of pressure increase have to be considered only above a hydrogen peroxide concentration of 5% by weight.

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