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Praca doświadczalna / Research paper

Effect of vibration and stirring on 90% and 98% hydrogen peroxide **Wpływ wibracji i mieszania na 90% i 98% nadtlenek wodoru**

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Abstract: The influence of vibration and stirring of 90% and 98% hydrogen peroxide (high test peroxide – HTP) of two different purity levels in accordance with MIL-PRF-16005F, was determined. Testing was conducted in order to evaluate safety of use of highly concentrated solutions of hydrogen peroxide. The influence of vibration on HTP was tested at different frequencies up to 100 Hz. Further testing investigated the influence of stirring HTP, at three different speed values: 2000 rpm, 4000 rpm and 6000 rpm. During both tests, decomposition was determined by measuring concentration loss using density assay. Liquid during the tests was visually inspected for visible signs of decomposition such as: foaming, gas emission, turbidity.

Streszczenie: Określono wpływ wibracji i mieszania na 90% i 98% nadtlenek wodoru klasy HTP o dwóch poziomach czystości zdefiniowanych w normie MIL-PRF-16005F. Badanie przeprowadzono w celu oceny bezpieczeństwa stosowania roztworów nadtlenu wodoru o wysokim stężeniu. Został zmierzony wpływ wibracji o częstotliwości do 100 Hz na HTP. W ramach kolejnego badania sprawdzono wpływ mieszania na HTP, gdzie zastosowano trzy różne prędkości mieszania: 2000 rpm, 4000 rpm i 6000 rpm. Rozkład nadtlenu wodoru mierzony był poprzez pomiar stężenia roztworu przy zastosowaniu metody densymetrycznej. Dokonano wizualnych obserwacji roztworu podczas badań pod kątem występowania widocznych oznak rozkładu, jak: pienienie, emisja gazów, zmętnienie.

Keywords: hydrogen peroxide, HTP, stirring, vibration

Słowa kluczowe: nadtlenek wodoru, HTP, mieszanie, wibracje

1. Introduction

Over the last several years a special interest in seeking new “green” propellants, as an alternative to current ones, has been shown. Propellants such as hydrazine and its derivatives are toxic and show mutagenic and carcinogenic properties [1]. For this reason, research of environmentally friendly compounds which could replace hydrazine, has been performed. One of these could be highly concentrated hydrogen peroxide (HTP – high test peroxide). Hydrogen peroxide (H₂O₂) was discovered in 1818. At first it was used as a bleaching agent for fabrics. During World War II, Germany applied hydrogen peroxide as a military propellant [2]. Nowadays, it is widely used in a variety of areas [3]:

- a) pulp and paper bleaching,
- b) waste treatment,
- c) electronics production,
- d) chemical synthesis,

e) metals manufacturing.

Hydrogen peroxide is a colourless liquid (highly concentrated may be slightly blue), easily miscible with water at each proportion. Its vapour pressure at room temperature is low, which makes handling much easier than other commonly used strong oxidizers such as nitrogen tetroxide or fuming nitric acid. In general, hydrogen peroxide is odourless but it may be slightly sharp or acidic. It is an irritant but it is non-toxic as it decomposes to water vapour and oxygen according to the following equation:



Decomposition of hydrogen peroxide is increased by heat, UV radiation (sunlight) or contact with some metals and their compounds (*e.g.* manganese or iron). HTP is a relatively stable product. Increases in temperature raise rates of decomposition by a factor of 2.2 *per* 10-degree rise. The presence of trace amounts of impurities such as organic compounds, iron, manganese *etc.* may significantly increase decomposition rates. Normally, concentration loss of HTP is less than 1-2% *per* year, when stored under proper conditions [4, 5].

Hydrogen peroxide is not classified as an explosive, but it may violently decompose releasing large amount of steam, oxygen and heat. Because safe handling of hydrogen peroxide is an important issue, many extensive studies have been carried out in terms of explosion hazards and sensitivity to different conditions. Research has shown that it may exhibit explosive properties but only under certain conditions (*i.e.* hot vapors in contact with catalytically active materials). The liquid may decompose explosively when heated above 130 °C. On the other hand hydrogen peroxide does not show impact or friction sensitivity. Shock sensitivity depends on concentration and temperature, but such sensitiveness may be the result of contamination with non-compatible materials. Appropriate design of hydrogen peroxide systems and containers, selection of proper materials and their passivation as well as sustaining appropriate cleanliness, eliminates danger during handling [6]. Nevertheless, it is important to study its behavior indifferent environments in order to enable data for a proper design of propellant systems, to be obtained. In this study, the influence of vibration and stirring on was investigated.

2. Test Item

Hydrogen peroxide of two different concentration and two different purities (in accordance with standard [7]) was produced by Jakusz Sp. z o.o.:

- a) 90ES,
- b) 98ES,
- c) 90HP,
- d) 98HP,

where 90 and 98 refers to the concentration (mass percent); ES (extra stabilized) and HP (high purity) refers to the purity level according to [7] (Table 1).

Hydrogen peroxide, produced by Jakusz Sp. z o.o. was stabilized prior to testing. ES types of HTP were additionally contaminated with anions (chloride, sulphates) and metals in the form of salts (aluminum, chromium, manganese, iron, copper, nickel and zinc in the form of nitrates and chlorides). The amount of contamination did not exceed allowable levels for the ES grade in the case of anions and the HP grade in the case of metals. Such treatment was introduced in order to simulate hydrogen peroxide of lower purity, for example following long term contact with fairly compatible materials. HP grade hydrogen peroxide was not contaminated, only stabilized.

All grades of hydrogen peroxide were subjected to quality control. Chemical analysis was performed in order to confirm compliance with [7]. HTP grade HP met all the requirements of the standard. HTP Grade ES met all of the requirement beside stability. Nevertheless, less stable products were introduced during vibration and mixing testing in order to compare the behaviour of stable and less stable products.

Table 1. Allowable limits of chemical properties of hydrogen peroxide [7]

Properties		Limit	
		ES	HP
a) Anions:			
Chloride	[mg/kg]	2	0.5
Nitrate	[mg/kg]	7.5	5
Phosphate	[mg/kg]	0.5	0.2
Sulfate	[mg/kg]	5	0.5
b) Ammonium ion	[mg/kg]	3	3
c) Stability (24h/100°C)	[% oxygen loss]	2	2
d) Evaporation residue	[mg/kg]	-	20
e) Total Carbon	[mg/dm ³]	105	40
f) Metals:			
Aluminum (Al)	[mg/dm ³]	1	0.35
Tin (Sn)	[mg/dm ³]	0.7 - 7	1 - 4
Chromium (Cr)	[mg/dm ³]	-	0.03
Lead (Pb)	[mg/dm ³]	-	0.03
Manganese (Mn)	[mg/dm ³]	-	0.03
Iron (Fe)	[mg/dm ³]	-	0.03
Copper (Cu)	[mg/dm ³]	-	0.03
Nickel (Ni)	[mg/dm ³]	-	0.03
Antimony (Sb)	[mg/dm ³]	-	0.03
Arsenic (As)	[mg/dm ³]	-	0.03
Gold (Au)	[mg/dm ³]	-	0.03
Zinc (Zn)	[mg/dm ³]	-	0.03
Titanium (Ti)	[mg/dm ³]	-	0.03

According to [7], stability of hydrogen peroxide is expressed as percent Active Oxygen Loss (%AOL) parameter. The concentration and weight of hydrogen peroxide sample before and after conditioning at 100 °C for 24 h, is measured. These conditions are equivalent to storage for 1 year at room temperature. Mass difference ($W_1 - W_2$) refers to mass loss of oxygen in the sample due to decomposition reaction of hydrogen peroxide.

$$AOL = \frac{100(W_1 - W_2)}{0,47CW_1} \quad (2)$$

where: %AOL – percent active oxygen loss, W_1 – initial net weight, W_2 – final net weight, C – weight fraction of sample (concentration/100).

Stability of hydrogen peroxide may be also expressed as concentration loss (%) or relative concentration loss (%) which is concentration loss divided by the initial concentration of sample:

$$\% \Delta C = \frac{C_i - C_f}{C_i} \cdot 100\% \quad (3)$$

where: %ΔC – relative concentration loss, C_i – initial concentration of sample, C_f – final concentration of sample. Stability of HTP test items is presented in Table 2.

Table 2. Stability of HTP test items in regard to [7], expressed in different parameters

HTP type	Stability – 24 h at 100 °C		
	concentration loss [%]	%AOL (according to [7])	relative concentration loss [%]
90ES	48.5	184 ^a	57
98ES	59.1	152 ^a	60
90HP	0.1	1	0.1
98HP	0.2	1	0.2

^aResults may vary due to significant evaporation of unstable test liquid.

The %AOL parameter is sensitive to mass loss which, beside oxygen mass loss, may be a result of liquid evaporation (especially for unstable liquids) or splashing, which could occur during the stirring test. Therefore, the concentration loss parameter was applied in order to express influence of vibration and stirring. Concentration assay of hydrogen peroxide was done by density and temperature measurement. The results allowed the concentration of hydrogen peroxide to be calculated [5].

3. Test methods and results

3.1. Vibration influence

Vibration influence on hydrogen peroxide was evaluated by means of visual observation and determination of the loss of concentration.

3.1.1. Equipment

A vibrating table, VIBRAX Renfert of two modes of frequency (50 Hz and 100 Hz) and four modes of amplitude (1.5-15 G) was used as a source of vibration. Concentration determination was performed by means of density assay using densitometer Densito 30PX Mettler Toledo of reading accuracy 0.0001 g/cm³. Automatic pipette HTL Labmate Pro 1-10 ml was used for measuring test portions into 50 ml sterile polypropylene test tubes.

3.1.2. Scope of research

The influence of vibration on HTP was tested by measuring its density and visual observation. The test was conducted at a frequency of 100 Hz and 15 G amplitude during different 8-10 h time cycles. For comparison, 24 h cycle tests were conducted at different amplitudes and frequencies. These were conducted in an air conditioned room at a controlled temperature of 17.0-17.5 °C.

3.1.3. Test procedure

- The concentration of samples of hydrogen peroxide collected in 1 L polypropylene bottles was determined, based on density measurement.
- 20 ml of HTP was poured into a 50 ml sterile polypropylene pot using the automatic pipette.
- The pots were placed in clamps attached to the plate of the vibrating table.
- The frequency and amplitude of vibration was set and the vibrating table switched on.
- The duration of the test was divided into 8 h cycles.
- After the test, the density of the tested samples was measured and the concentration determined.

3.1.4. Results

During the test, bubbling and foaming of liquid was observed in all the types of tested hydrogen peroxide. It quickly stopped once the vibrating table was turned off. Gas bubbles were visible inside the test tubes but this is also typical behavior of hydrogen peroxide during storage. No uncontrolled decomposition or pressure

build-up was observed. No significant concentration loss of hydrogen peroxide was determined even after 55 h of the test. Results of the determination of concentration loss are presented in Tables 3 and 4.

Table 3. Results of vibration influence testing during 8-10 h cycles

HTP sample type	Frequency [Hz]	Amplitude [G]	Time [h]	Initial concentration [%]	Final concentration [%]	Concentration loss [%]
90ES	100	15	8	90.2	90.1	0.1
98ES				98.6	98.6	0.0
90HP				91.7	91.7	0.0
98HP				98.8	98.8	0.0
90ES	100	15	22	90.2	90.1	0.1
98ES				98.6	98.5	0.2
90HP				91.7	91.6	0.1
98HP				98.8	98.7	0.0
90ES	100	15	55	90.0	90.0	0.0
98ES				98.5	98.5	0.0
90HP				91.2	91.4	-0.3
98HP				98.2	98.3	-0.1

Table 4. Results of vibration influence testing during single 24 h cycles

HTP sample type	Frequency [Hz]	Amplitude [G]	Time [h]	Initial concentration [%]	Final concentration [%]	Concentration loss [%]
90ES	50	15	24	90.2	90.2	0.0
98ES				98.6	98.6	0.1
90HP				91.7	91.5	0.2
98HP				98.8	98.7	0.1
90ES	100	1,5	24	90.2	90.1	0.1
98ES				98.6	98.7	0.0
90HP				91.7	91.6	0.1
98HP				98.8	98.6	0.2
90ES	100	15	24	90.2	90.1	0.1
98ES				98.6	98.6	0.0
90HP				91.7	91.6	0.0
98HP				98.8	98.7	0.0

Vibration at the tested conditions does not increase decomposition of hydrogen peroxide. Small changes of HTP concentration are random and result from density measurement uncertainty. No pressure build-up was observed in the pots of HP Grade HTP. When opening pots containing Grade ES HTP, the sound of escaping gas was noticed. This effect was also present in storage containers of Grade ES HTP which were not subjected to vibration. Another visible effect was foaming and bubbling, which stopped shortly after turning off the vibrating table. The same effect was observed at initial testing using water instead of hydrogen peroxide. Based on the observations and measurements it can be concluded that vibrations up to 100 Hz frequency do not induce uncontrolled decomposition of hydrogen peroxide.

3.2. Stirring influence

The influence of stirring on hydrogen peroxide was evaluated by visual observation and the determination of loss of concentration.

3.2.1. Equipment

An IKA EUROSTAR 20 high speed digital stirrer with a speed range under nominal load of 0-6000 rpm and speed setting accuracy ± 1 rpm, was used. Determination of the loss of concentration was performed using densitometer Densito 30PX Mettler Toledo with a reading accuracy of 0.0001 g/cm^3 . Weight scale Fawag ONYX OX 3100 of reading accuracy to 0.01 g was used to weigh test samples.

3.2.2. Scope of research

The influence of stirring on HTP was determined by measuring concentration loss (assay by density measurement) of hydrogen peroxide due to decomposition, and visual observations. Tests were conducted at three different stirring speed values: 2000 rpm, 4000 rpm and 6000 rpm. Samples of tested liquid were collected every 2 h. The full test at a given stirring speed took 8 h for each type of hydrogen peroxide. Testing was conducted in an air conditioned room at a constant temperature of $20 \text{ }^\circ\text{C}$.

3.2.3. Test procedure

- Prior to testing, a stainless steel stirrer had been passivated in accordance with NASA TM-2004-213151 [6]. A clean stirrer was immersed in 65% nitric acid for 5 h, then rinsed with deionized water and immersed in approx. 90% hydrogen peroxide for 4 h. The stirrer was then rinsed with deionized water and dried.
- 1.5 L of hydrogen peroxide were poured into a clean, nitric acid passivated, 3 L borosilicate glass flask. The sample was weighed. Efforts were made to maintain similar sample quantities.
- The filled flask was clamped and the stirrer immersed in the liquid.
- The stirring speed was set and the stirrer switched on.
- Stirring continued for 8 h. Every 2 h about 25 cm^3 of liquid was collected using a glass pipette and transferred into a polypropylene beaker.
- The temperature and density of the collected samples was measured using a densitometer and the concentration of hydrogen peroxide calculated in accordance with [5].
- After each test, a fresh portion of hydrogen peroxide was used. Prior to pouring fresh liquid, the equipment was flushed five times with deionized water and a portion of fresh hydrogen peroxide.

3.2.4. Results

During the experiment, foaming of the liquid (Fig. 1) in all four types of hydrogen peroxide was observed. The foaming disappeared on turning off the stirrer, but gas bubbles were still visible in the liquid. Bubbles in Grade HP hydrogen peroxide disappeared quickly, so density measurement could be performed immediately after sample collection. Less stable Grade ES hydrogen peroxide had more gas bubbles remaining, so density measurements had to be performed after a while, as their presence caused disruption of the measurement. Averaged results are presented as graphs in Figures 2-5.

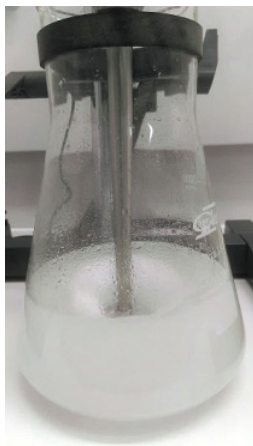


Figure 1. Foaming of liquid during test

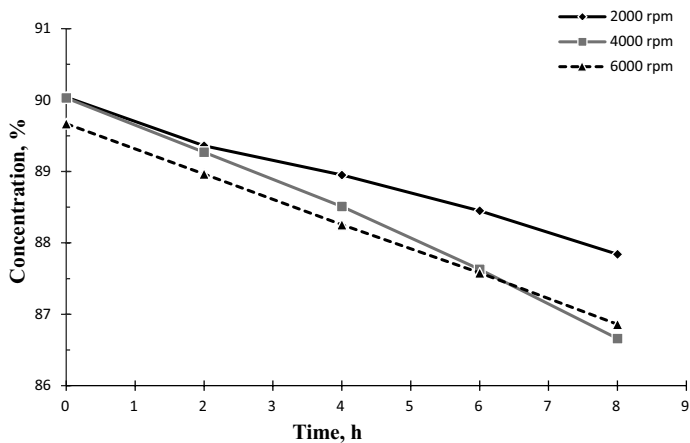


Figure 2. Concentration change of 90ES HTP during stirring

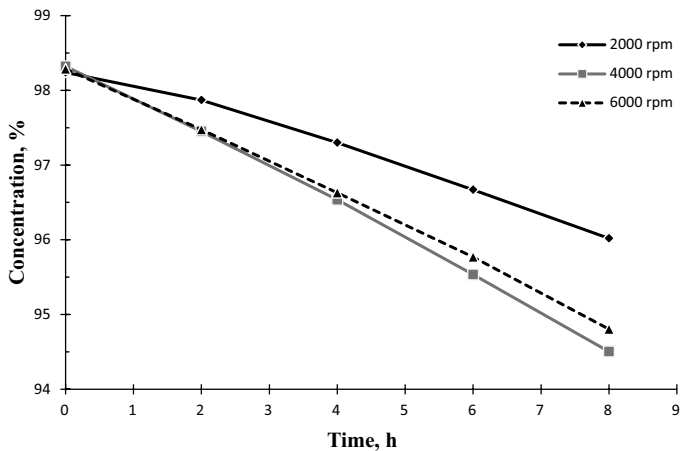


Figure 3. Concentration change of 98ES HTP during stirring

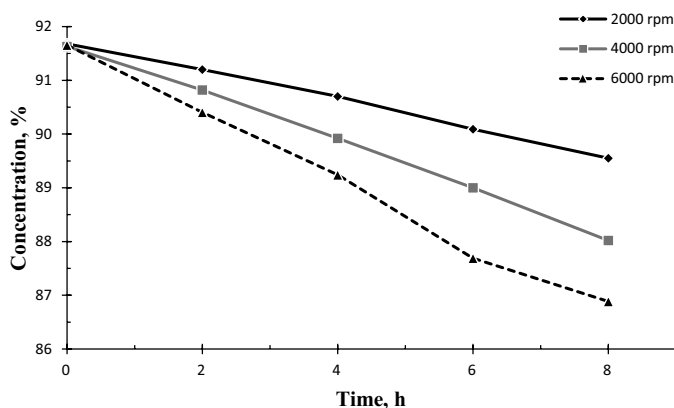


Figure 4. Concentration change of 90HP HTP during mixing

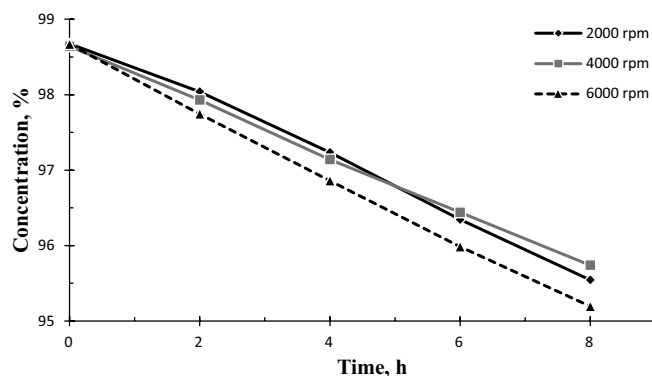


Figure 5. Concentration change of 98HP HTP during stirring

In order to confirm that the concentration loss of hydrogen peroxide was a result of stirring and not storage or material incompatibility, verification was performed. When the test was finished, liquid was left in the flask with the stirrer immersed for 16 h. After that time the concentration of the liquid was determined. No loss of concentration was noted. This confirmed that storage in a glass flask and contact with a passivated stainless steel stirrer does not affect the measured concentration. Results of testing are presented in Table 5.

Table 5. Comparison of test results

Stirring speed [rpm]	Concentration loss per hour [%]			
	90ES	98ES	90HP	98HP
2000	0.28	0.28	0.27	0.39
4000	0.42	0.48	0.36	0.35
6000	0.35	0.44	0.60	0.33
2000	0.28	0.28	0.27	0.39

For three types, 90ES, 98ES and 90HP, increasing the stirring speed from 2000 rpm to 4000 rpm increased the decomposition rate. Further speed increases from 4000 rpm to 6000 rpm decreased the decomposition rate of Grade ES but increased that of 90HP. A near linear relation between concentration loss and stirring speed was observed for 90HP. Higher purity grades of hydrogen peroxide showed slightly better stability, but only at 4000 rpm. This could mean that stirring speed itself is not the most important factor affecting hydrogen peroxide decomposition, but that other factors, such as temperature fluctuation, may play a role.

Higher stirring speeds cause higher shear forces and higher heating. Discrepancies in the results might be due to temperature changes occurring during the experiment *e.g.* the stirrer heats up while working, causing a temperature increase in the tested liquid. Hydrogen peroxide is very sensitive to temperature changes, which increase its decomposition rate. During stirring it was observed that the temperature of a collected sample had increased both with time and higher stirring speeds. Moreover, it was observed that samples which had a lower initial temperature before the test, had a higher decomposition rate during the first hours of the test than at the end. Nevertheless, beside changes of ambient temperature, heating of the stirrer may be an issue. It has direct contact with liquid, leading to temperature differences.

4. Conclusions

Stirring hydrogen peroxide significantly speeds up its decomposition rate but does not cause violent or uncontrolled decomposition. No significant difference was observed between the very stable and less stable types. However, depending on conditions, hydrogen peroxide loses 0.25% to 0.5% of its concentration *per* hour of intense stirring. Also, stirring causes foaming and bubbling of the liquid. It should be kept in mind that during decomposition, oxygen is released. This can cause an increase in pressure in a closed container. It follows that for higher stirring speeds (in a closed container) additional safety measurements should be adopted. Moreover, stirring hydrogen peroxide may cause a temperature increase as a result the raised decomposition rate. Hydrogen peroxide is very sensitive to temperature fluctuation, thus the heating effect during stirring is a very important factor which needs to be considered.

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