TECHNOTES
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A Study Monitoring the Hydrogen Peroxide Stability for Shelf-Life Determination

Using a Permanganate Titrate Test Method

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Introduction

Texwipe's Hydrogen Peroxide solutions (TexP) are a mixture of 35% weight percent hydrogen peroxide diluted with USP-deionized water to concentrations of 4% and 7.5% by weight solutions. During the manufacturing process, the solution is submicron filtered, filled into clean bottles, capped, and double-bagged. All bottles are individually lot coded and have an expiration date for easy recordkeeping. TexP offers no VOCs and is nonflammable, making it safer for the personnel and regulatory compliance. The product leaves no residue, is completely biodegradable, decomposing into water and oxygen. It offers a low toxicity profile and is noncorrosive on most surfaces. The product offering is found in Appendix 1.

Hydrogen peroxide solutions are intended to be used for cleaning and residue removal:

- Cleaning general surfaces, tables, equipment, walls and floors,
- Pre-cleaning before disinfectant application, or
- Removing residues after disinfectant application.

Bottles of hydrogen peroxide solution are sometimes stored for years from the manufacturing process through distribution to its final use. Hydrogen peroxide is inherently unstable being easily degraded by light and contaminants including organic compounds and various metal ions. Because of this property, a heat-aged shelf-life experiment was performed to determine the shelf-life of our TexP products.

Purpose

Since end users need a consistent product for their use, it is important to document the hydrogen peroxide concentration stability as a function of time. A study was implemented to monitor the hydrogen peroxide concentration over a period of time at an elevated temperature of 50°C to simulate storage at room temperature for three years. A recommended shelf-life is intended to provide assurance of the appropriate quality of the hydrogen peroxide product throughout its storage after manufacturing and throughout distribution by demonstrating the consistency of the hydrogen peroxide concentration over time.

Experimental

The development of the accelerated aging theory is found in A.S. Maxwell, *et. al.* at the UK National Physical Laboratory (1). Whenever chemical reactions are thought of, Arrhenius rate equation is used to describe the relationship of the reaction rate with temperature. The Arrhenius equation is shown below.

$$K(T) = A^* e^{\left(\frac{-E_a}{RT}\right)}$$

Where:
K(T) = reaction rate for the reaction
A = Arrhenius constant
E_a = barrier reaction energy
R = gas constant, and
T = absolute temperature in Kelvin

Taking the natural logarithm of both side results in $Ln\,K(T) = \frac{-E_a}{RT} + C$
Where: C is a constant.

A plot of natural log of the rate, Ln K(T), against 1/T should result in a straight line with slope $-E_a/R$. Sometimes, the reaction rate can be modeled better with a similar equation shown below since E_a may not be a single value. The new equation is

$$Ln\,K = ln\,K_0 + \frac{B(T_0-T)}{10}$$

Where: K_0 is the reaction rate at T_0, and B is a constant.
This equation can be modified to

$$B = \frac{10}{T_0-T} * \ln \frac{K}{K_0}$$

and by rearranging,

Taking the antilog of both sides of the equation yields the equation shown below:

$$B = \ln\left(\frac{K}{K_0}\right)^{\frac{10}{T_0-T}}$$

Where Q_{10}, is a unitless quantity, which expresses the temperature dependence of a process.

$$Q_{10} = \left(\frac{K}{K_0}\right)^{\frac{10}{T_0-T}}$$

For first order chemical reactions like the degradation of hydrogen peroxide into water and oxygen, Q_{10} is known to be two, a conservative value. This implies that the reaction rate doubles for every ten-degree temperature increase.

To determine the number of days at an elevated temperature that represents aging at room temperature, the above equation through a similar process shown above changes to the equation below.

$$Q_{10}^{\frac{(T_0-T)}{10}} * \frac{Weeks}{year}\ at\ T_0 = Weeks\ at\ elevated\ temperature,\ T$$

Using Q_{10} equal to 2, To equal to 22°C, test temperature T = 50°C, and 52 weeks in a year, we find that 7.5 weeks at 50°C is equivalent to one year at room temperature.
Several bottles of 4% and 7.5% hydrogen peroxide solution (TX684, TX687, TX684G, TX687G) were placed in a 50°C oven for accelerated aging using heat for at least 22.5 weeks to determine if there is a three year shelf-life at room temperature. The hydrogen peroxide level in the bottles was periodically measured using the test method described below.

Test Method

The reaction between the hydrogen peroxide in testing solution and potassium permanganate in a standardized solution is used to determine the concentration of hydrogen peroxide in testing solution. The overall, balanced reaction equation is:

$$KMnO_4 + 5H_2O_2 + 4H_2SO_4 \rightarrow 2KHSO_4 + 2MnSO_4 + 8H_2O + 5O_2\,(g)\uparrow$$

Where:

$KMnO_4$ = potassium permanganate
H_2O_2 = hydrogen peroxide
H_2SO_4 = sulfuric acid, a supply of acid
$KHSO_4$ = potassium hydrogen sulfate
$MnSO_4$ = manganese (II) sulfate, one product of the permanganate-peroxide reaction originating from the potassium permanganate
H_2O = water, and
O_2 = molecular oxygen, the second reaction product from the permanganate-peroxide reaction originating from the hydrogen peroxide.

The potassium permanganate solution is standardized using sodium oxalate according to the reaction:

$$2MnO_4^- + 16H^+ + 5C_2O_4^{2-} \rightarrow 2Mn^{2+} + 8H_2O + 10CO_2\,(g)\uparrow$$

Where:

MnO_4^- = permanganate ion
$C2O_4^{2-}$ = oxalate ion
Mn^{2+} = manganese (II) ion, the manganese containing reaction product of the permanganate-oxalate reaction
CO_2 = carbon dioxide, the carbon containing reaction product of the permanganate-oxalate reaction.

The permanganate solution is standardized by the following steps. One gram of dried sodium oxalate is dissolved in 100 ml of 5 N sulfuric acid solution while heating to 75°C. When the solid is dissolved and the solution temperature is at 75°C, the potassium permanganate solution is added through a burette until a faint pink color remains in the solution. Using the amount of sodium oxalate and the volume of potassium permanganate solution used, the concentration of the potassium permanganate solution is determined.

The concentration of hydrogen peroxide in solution is determined by the following steps. Approximately one gram of solution is weighed into an Erlenmeyer flask. Fifty milliliters of 5 N sulfuric acid solution is added to this flask. The solution is titrated with standardized potassium permanganate solution until a faint pink color remains in the solution. Using the amount of hydrogen peroxide solution and the volume of potassium permanganate solution used, the concentration of the hydrogen peroxide solution is determined.

The results of the accelerated aging using elevated temperature of the hydrogen peroxide samples are described next.

Results

Hydrogen peroxide is a thermodynamically unstable molecule. The rate of its decay is impacted by the solution concentration, the storage temperature, and the solution pH. A hydrogen peroxide solution that is dilute, stored at cool temperatures and acidic conditions is the most stable.

The products presented here are at concentration where decomposition is expected.

The decomposition of the hydorgen peroxide concentration can be observed in the stability charts (Figures 1, below, for a 4% hydrogen peroxide solution and Figure 2, next page, for a 7.5% hydrogen peroxide solution).

Hydrogen Peroxide Stability (4%) Study Results

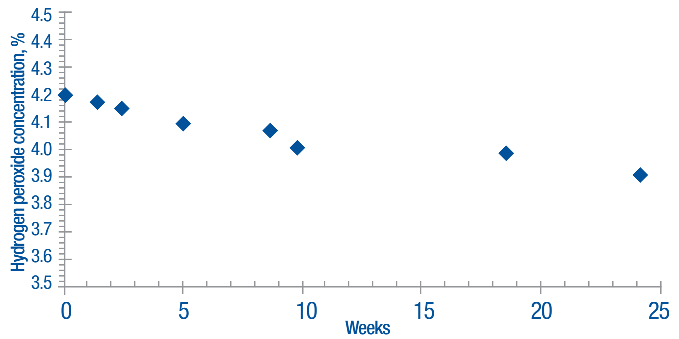

Figure 1. The results of the accelerating aging study for a 4% hydrogen peroxide solution. Notice the gradual decay of the hydrogen peroxide activity. The solution concentration of 4.2% at the beginning of the study decreased to 4.05% by the eighth week of the study representing one year of aging in real time, decays to 3.97% at the 18-19th week of study (which represents 2.4 years in real time), and to 3.87% at the 24th week, which represents three years in real time.

Hydrogen Peroxide Stability (7.5%) Study Results

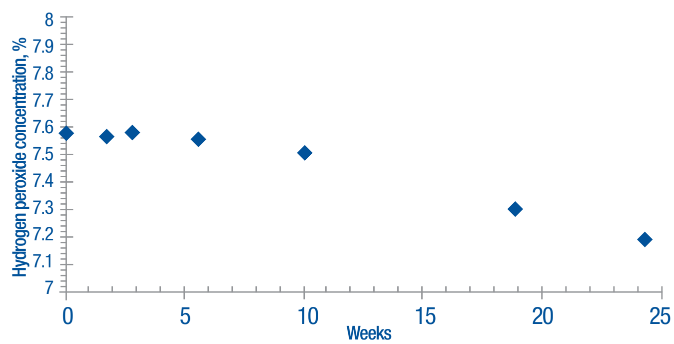

Figure 2. The results of the accelerated aging study for a 7.5% hydrogen peroxide solution. Notice the gradual decay of the hydrogen peroxide activity. The solution concentration of 7.57% at the beginning of the study decreased to 7.49% at the 10th week of the study (which equals to 1.3 years in real time) falling to 7.34% at the 18-19th week of study (which equals to 2.4 years in real time), and ends at 7.23% at the 24th week (that equals to 3 years in real time).

Discussion

The target (the acceptable) range of 4% hydrogen peroxide solution is from 4.5% to 3.5% concentration. The percentage decrease was from 4.2% to 3.87% (or by 0.33%) in three years that complies with the targeted range.

The target (the acceptable) range of 7.5% hydrogen peroxide solution is from 7.9% to 6.8% concentration. The percentage decrease was from 7.57% to 7.23% (or by 0.34%) in three years that complies with the targeted range.

The data shown in the stability charts were not smooth. Some points seemed to have a slightly higher value than expected. Measuring the hydrogen peroxide level in solution is a must step process where errors may occur. Sources of error are:

- The sodium oxalate not being dried completely,
- Weighing error for the sodium oxalate,
- A burette reading error when standardizing the potassium permanganate solution,
- A bubble in the burette impacting the volume of solution used,
- An error weighing the hydrogen peroxide sample,
- A burette reading error when titrating the hydrogen peroxide solution, and
- A bubble in the burette impacting the volume of potassium permanganate solution used.

Even with these sources of error, the data show that the product does decompose.

Conclusion

The study data shows that the 4% hydrogen peroxide solution has decomposed from 4.2% to 3.87% (or by 0.33%) in three years that complies with the targeted concentration range of 4.5%-3.5%.

The 7.5% hydrogen peroxide solution has decomposed from 7.57% to 7.23% (or by 0.34%) in three years that complies with the targeted concentration range of 7.9%-6.8%.

The slow decomposition rate of both hydrogen peroxide solutions and their compliance with the targeted range at the end of the study permit to the justification their shelf life of three years. The mentioned solutions demonstrated the consistency of the hydrogen peroxide concentration over time and may be stored and used within the three year time frame without concerns about the quality and stability of products.

Reference

1. Maxwell, A.S., Broughton, W.R., Dean, G. and Sims, G.D., Review of accelerated ageing methods and lifetime prediction techniques for polymeric materials, National Physical Laboratory, Report DEPC MPR 016, March 2005, http://www.npl.co.uk/upload/pdf/depc_mpr_016.pdf (July 29, 2014) pages 24 – 25.

For additional information, please contact Texwipe Customer Service at the number listed below.

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