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Long Term Storability of Hydrogen Peroxide

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Hydrogen peroxide is a currently used storable propellant which is finding use in various emerging systems. It is commonly misunderstood that hydrogen peroxide cannot be stored for long periods of time. Existing data and current research clearly shows the opposite, with significant improvements in long term storability being demonstrated. The various physical phenomenon and quantitative data, both historical, and modern are summarized and compared to show that the storability of hydrogen peroxide meets most of the needs of the propulsion community with little risk, and in fact major improvements to the storability of hydrogen peroxide have been recently made. Further improvements are possible and it is likely that all foreseeable applications for hydrogen peroxide can be easily accommodated with the stability and storability of the chemical.

Nomenclature

AOL = active oxygen loss
C = concentration or degrees centigrade
C_1 = initial concentration
C_2 = final concentration
lb_m = mass, pounds
ppb = parts per billion
ppm = parts per million
ppt = part per trillion
W_1 = initial mass
W_2 = final mass

ρ = density

I. Introduction

Near the end of World War II, hydrogen peroxide began to be used as a rocket propellant both in monopropellant applications and as an oxidizer in bipropellant rockets. This use was expanded through the years up to approximately 1960 to 1970 when the favor for storable propellant applications began to shift to other chemicals, such as various types of hydrazine; some as monopropellants and some as the storable fuel in bipropellant systems with nitrogen tetroxide as an oxidizer. The use of hydrazine and nitrogen tetroxide progressively reduced the use of hydrogen peroxide to fewer platforms. Manufacturing of rocket grade hydrogen peroxide diminished and it was eventually no longer used as a rocket propellant or oxidizer. In the 1990's, with the emerging desire for non-toxic propulsion and power applications, the popularity of hydrogen peroxide began to return. The usage of hydrogen

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peroxide has progressively increased over the past ten years and there are now several organizations and applications are using hydrogen peroxide as a propellant and working fluid.

Hydrogen peroxide is commonly believed to be unstable such that it is unsuitable to be stored for any extended period of time. This assertion is incorrect and hydrogen peroxide has in fact, demonstrated successful long term storage in several applicable systems. Current work and advancements in technology in the past 40 years have been in the direction of improving the long term storage of hydrogen peroxide. This paper discusses the historical and current research and development to illustrate the storability of propellant grade hydrogen peroxide.

II. Long Term Storability Requirements

The typical applications for storable rocket propellants are when the user wants to transfer the propellant into the system and leave the system for extended periods of time either in service or in a holding condition waiting to be used. Applications include long life spacecraft, weapons systems such as missiles, emergency auxiliary power systems, and launch platforms. The long term storability requirement for each of these applications varies, but in general the industry standard for long term storability is set by the use of hydrazine when used as a spacecraft propellant. Other applications, such as weapon systems and launch platforms can have vastly differently storability requirements and as such, need to be considered on a case by case basis. For example, many weapon applications have very severe environmental and storage requirements which are most easily met with solid propellants. Large performance constrained launch platforms commonly use cryogenics which are inherently non-storable. Launch platforms based on Intercontinental Ballistic Missiles (ICBM) have used storable propellants to permit long term storage of the weapon in a silo as in the example of the Titan family of rockets.

In general, for launch vehicle platforms it is desirable for a storable propellant to be loaded and left alone for periods of weeks to months. Note that many launch platforms use solids (very long term storage) and cryogenics (essentially no long term storage capacity). In launch vehicle applications it would be advantageous for a storable propellant to be similar to the existing storable propellants of the hydrazine family and nitrogen oxide propellants.

For satellite and spacecraft applications, the propellant must remain stored in a sealed container in a spacecraft for many years; a reasonable value is 15 years or more. The propellant is stored in a pressurized tank which is not normally vented. The need for reliability in these types of applications is paramount. Significant efforts have been made to test and prove the long term storability of hydrazine[1], and conferences have been dedicated to the discussion of hydrazine compatibility. A comparable effort has not been made for hydrogen peroxide and as such, test data for hydrogen peroxide is not as voluminous and as detailed as it is for hydrazine. For the intents of reasonable consideration, it will be assumed that the requirement for hydrogen peroxide storability for propulsion applications will be greater than 15 years in a sealed and pressurized containment system. There will be other applications, such as short life spacecraft, launch vehicles, and others, where shorter term storage such as several weeks to a few years would be more than adequate.

Note that a comparison of hydrogen peroxide to hydrazine for satellite applications may be a somewhat moot consideration because of the overall system level trade considerations one makes when converging a spacecraft design. Most modern spacecraft are very expensive and have considerable life times on the order of 10 years or more. The overall cost to build, launch and insure these assets is sizeable in comparison to the cost of the spacecraft propulsion system. A typical risk consideration would heavily favor existing flight proven systems with very long life times. At a programmatic level, hydrazine has a very significant advantage over hydrogen peroxide for long life high end spacecraft, however since hydrazine sets the standard for long term storability, these basic requirements will be considered as a point of comparison.

The most common applications of hydrogen peroxide are for systems which have specific requirements which preclude or discourage the use of cryogenics or conventional storable propellants. These applications normally involve regular exposure of the system to humans where low toxicity concerns are important (reusable launch vehicles, man operated weapon systems), low cost launch platforms which try to reduce operations by not using cryogenics, and low cost propulsion systems which try to reduce costs by eliminating conventional storable toxic propellant operations.

Hydrazine storability can be defined as a metric of the rate of decomposition of the hydrazine when exposed to a material. A reasonable rate of decomposition of hydrazine is in the range of $10^{15.791}$ to $10^{16.857}$ molecules per square centimeter per 1000 hours[1]. Decomposition rates for hydrogen peroxide use different units, but in comparison, these rates of decomposition of hydrazine are much lower than what has been demonstrated for hydrogen peroxide. This does not preclude the use of hydrogen peroxide, but it does reinforce the position that for very long life spacecraft, hydrazine has a programmatic advantage.

The long term storage requirements for hydrogen peroxide can be summarized as:

Propellant is capable of being safely stored in a sealed vessel for extended durations of time.
Storage durations for launch vehicles is weeks to months.
Storage for spacecraft is on the order of years.

III. Stability of Hydrogen Peroxide

The stability of hydrogen peroxide is normally defined by two parameters: the Active Oxygen Loss (AOL) and a term called the Stability. The AOL parameter is normally defined as a value based upon a test at a specific temperature and duration for a combination of specific fluid properties (concentration, purity, and stabilizer content) and a specific material with any or no surface treatment or processing. A common test is an elevated temperature test at 66 deg. Celsius for 1 week. This is a type of an accelerated exposure test.

These are quantitative means of defining how fast the hydrogen peroxide is decomposing based upon standard test criteria[2]. For a given material, the AOL and stability of the combination of the propellant and material can be best determined quantitatively via test. Industry guidelines for a semi-quantitative grading system for hydrogen peroxide compatibility has been in use which scales materials from a Class 1 (the best material choice for long term exposure) to a Class 4 material which is unsuitable for hydrogen peroxide exposure or is a potentially good choice as a catalytic material. In general, the most important issue for hydrogen peroxide and material compatibility is the effect of the material on the hydrogen peroxide because more often than not, the material will have a deleterious effect on the hydrogen peroxide long before the hydrogen peroxide will begin to degrade or damage the material. In some cases the effect of the hydrogen peroxide on the material is a concern and with long term exposure, this behavior becomes more significant. Many other factors can also influence and effect the compatibility of hydrogen peroxide with a material including: pH, hydrogen peroxide concentration, hydrogen peroxide purity, hydrogen peroxide stabilizers, hydrogen peroxide lot variation, temperature, surface contamination, container surface to volume ratio, surface finish, surface passivation, surface coatings, and surface fabrication effects (heat effected weld zones, local stresses, honing/grinding operations, heat treating, and others).

The requirement for long term storability essentially assumes the consideration of Class 1 materials only; therefore this paper will only address issues with Class 1 materials. Consideration of Class 2 and 3 materials will not be discussed as these are not technically suitable for long term exposure.

Reference 2 defines the criteria for Class 1 as shown in figure 1.

The method for testing for classification starts by making a sample coupon 3 inches X 0.5 inches X 0.0625 inches which is cleaned, treated, and processed as closely as possible to the actual material being used. It is useful to investigate processes such as welds when making these coupons. Since there are part to part variations and test dispersions, it is also useful to make several coupons and select some random pieces for test. This coupon sample size has a surface to volume ratio of approximately 0.33 in^{-1} when tested in 75 ml of hydrogen peroxide. This simulates the surface to volume ratio of a typical hydrogen peroxide drum.

The procedure to test this coupon is summarized as: The sample is placed in a clean and passivated 100 ml glass flask and weighed to an accuracy of $\underline{+}$ 0.01 grams. Hydrogen peroxide of a known initial concentration (C_1) is added to the flask and the flask is weighed again. The difference between these two measurements is the initial mass of hydrogen peroxide: W_1. The flask neck is covered with a 10 ml beaker.

The flask is placed in a constant temperature bath for specific test temperature and duration, such as 66 deg. Celsius for 1 week. At the end of the test, the flask is removed and cooled. The 10 ml beaker is removed and the flask and contents are weighed again and the final concentration of the hydrogen peroxide is determined: C_2. The final hydrogen peroxide mass is found from the difference between the final mass of the flask, fluid and sample from the initial dry mass of the flask and sample as: W_2.

The AOL is calculated as:

$$AOL = 100\% \times \frac{W_1 C_1 - W_2 C_2}{W_1 C_1}$$

After the AOL test, a sample of the final hydrogen peroxide is subject to a stability test. A cleaned and passivated 50 ml volumetric flask is filled to 50 ml with hydrogen peroxide from the AOL test. The flask is weighed to ± 0.01 grams giving the initial mass: W_1 . The flask is covered with a 10 ml beaker and immersed in a constant temperature bath at 100 deg. Celsius for 24 hours. After 24 hours, the flask is removed and allowed to cool. The 10 ml beaker is removed and the flask is re-weighed to determine the final mass W_2. The stability is defined as:

$$Stability = 100\% \times \frac{(50 * \rho * C * 0.47) - (W_1 - W_2)}{(50 * \rho * 0.47)}$$

where,

ρ – density of the hydrogen peroxide

C – Concentration of the hydrogen peroxide at the beginning of the test

IV. Class 1 Materials with Hydrogen Peroxide

Numerous sources are available which claim various compatibilities of materials with hydrogen peroxide. Most of these sources derive their data from very early sources and the specific test data is sometimes unclear. This data should also be considered carefully, especially if several sources suggest or show a conflict. Examples of recent test data will be discussed to highlight this type of concern. Some recent compatibility data has been conducted in the past few years and some of this information will also be discussed to show areas of improvement.

The best collection of compatibility data is in reference 2. Other sources[3,4] also have useful tables of compatibility data which may contain data not found in reference 2. A partial summary of literature Class 1 material is shown in figures 2, 3, and 4.

This data shows that the best AOL is 0.1% for 1060 aluminum. Reference 3 reports that under very specific test conditions using Pyrex glass, stabilized 90% hydrogen peroxide, at room temperature, an AOL of 0.04% was achieved.

A note of caution is prudent when considering these lists of data. Much of this data is old and some of it is traceable to dates before 1965, perhaps as early as the 1940's. The chemical manufacturing process of hydrogen peroxide has changed progressively over time and some of the materials have also changed. The author has experienced degradation of commercially available Viton when exposed to hydrogen peroxide for several months. Other materials have also been found to be in disagreement with these older literature values. These data should be considered as guides in selecting materials.

A material not shown in the above tables is Aluminum 6061 which is normally considered a Class 2 material. Reference 2 shows that this material has an AOL of 4.8% at 66 deg. Celsius for 1 week and a stability of 98.7%. This actually qualifies as a Class 1 material per figure 1, but there is a note in reference 2 that 6061 aluminum is a Class 2 material because of corrosion. Corrosion of materials when in contact with hydrogen peroxide is very sensitive to the trace impurities in the hydrogen peroxide. For example chlorine impurities which are introduced into the hydrogen peroxide during the manufacturing process from water or are introduced by water used in handling operations, can make hydrogen peroxide significantly more corrosive. To counteract this corrosive nature, nitrates are sometimes added to act as a corrosion inhibitor. Advances in the manufacturing technology of hydrogen peroxide can and have reduced the chlorine level, thereby reducing the corrosive behavior of hydrogen peroxide. It possible that modern propellant grade hydrogen peroxide may not have the corrosive effects on 6061 aluminum that it had had in the past.

Note that the list of polymers is old and some of the trade names are now rarely used. Several common fluoropolymers are not shown which are being used in the commercial hydrogen peroxide industries and may be superior to these polymers. As previously stated, most of the literature compatibility data is at least 40 years old and significant progress has been made since then in polymer science. Polymers such as PFA, PTFE, and Halar are potentially excellent choices for Class 1 considerations.

Also note a lesser know item with zirconium and a zirconium/hafnium alloy. Zirconium is a commonly used metal in the nuclear power, medical, and chemical industries and while it is not as common as stainless steel and aluminum, it is not prohibitively exotic either. It is interesting to see that the alloy of zirconium and hafnium is better than zirconium alone. Research with zirconium alloys may produce new materials for hydrogen peroxide usage. A standard alloy of zirconium and hafnium is commercially made.

V. Effect of Water Content on Stability of Hydrogen Peroxide

A common understanding by persons familiar with hydrogen peroxide is that as the concentration gets lower, the stability decreases. This phenomenon is sometimes used to test the compatibility of large hydrogen peroxide containers by exposing them, not to high concentration hydrogen peroxide, but to low concentration hydrogen peroxide, as this is a more stressing test of the compatibility of the tank. If the tank is passive with low concentration hydrogen peroxide, the compatibility will improve as the concentration increases. This is somewhat counter intuitive in that it suggests that very high concentrations of hydrogen peroxide, such as 98% or anhydrous hydrogen peroxide are more stable than 90% or 70% and therefore potentially safer to store. Most people would assume that as the concentration increased, the stability would decrease and the propellant would be more dangerous to handle. Some hazards do increase as the concentration increases, such as auto-ignition with flammables, hypergolic reactions, and self-sustained thermal decomposition, however the stability of hydrogen peroxide does improve as the concentration increases. So in terms of the storability of hydrogen peroxide, hydrogen peroxide is more stable as the concentration increases. 98% is more stable than 90% which is more stable than 70% hydrogen peroxide. This can be visually seen if one compares identical glass receptacles containing the three concentrations. One will see more "bubbles" in 70% hydrogen peroxide in comparison to 90% or 98% hydrogen peroxide. The physical explanation for this behavior is that water actually acts as a destabilizing contaminant with the hydrogen peroxide. A possible reason for this could be the way in which the hydrogen peroxide and water weakly bond with each other and thereby the slightly different structure of the water molecule versus the hydrogen peroxide molecule stresses the hydrogen peroxide molecule and increases the opportunity for the hydrogen peroxide molecule to decompose. Reference 3 suggests that this is caused by different propellant purity from the different amounts of water and a change in surface tension at different concentrations. Reference 4 shows this effect and this data suggests that anhydrous hydrogen peroxide is essentially the most stable, as shown in figure 5.

Investigation of anhydrous hydrogen peroxide could potentially show significant improvements in storability as well as offer system performance improvements.

VI. Surface to Volume Effect on Stability of Hydrogen Peroxide

The decomposition of hydrogen peroxide and therefore its storability is dependent on the surface to volume ratio of the system containing the hydrogen peroxide. In general when the surface to volume ratio decreases, the storability improves. This means that larger systems or systems with more spherical shaped tanks have better storability than smaller systems or tanks with longer aspect ratios. A common bench mark for surface to volume ratio for hydrogen peroxide test data is 0.33 in^{-1}. This corresponds to the surface to volume ratio of a typical hydrogen peroxide drum containing 250 lb_m of fluid. Systems smaller than a typical peroxide drum would have a larger surface to volume ratio, where as larger systems would be expected to have smaller surface to volume ratios.

Reference 5 quantified the surface to volume effect for a highly compatible combination of PFA in fused Pyrex. This graph shows that the best storability is achieved with systems that have surface to volume ratios less than 0.5 cm^{-1} and as is obvious, as the surface to volume ratio approaches zero, the heterogeneous decomposition of the hydrogen peroxide contacting the container walls will also approach zero. An important conclusion, is that the propellant stability is primarily driven by surface decomposition, so systems with small surface to volume ratios will have significantly reduced decomposition and inherently improved storability.

VII. Material Surface Treatment Effect on Propellant Stability

Materials can and often are processed to render them more suitable for service with hydrogen peroxide. Typically theses processes are cleaning, chemical passivation, and a propellant exposure process called conditioning. These processes try to make the surface as clean as possible to remove potential surface catalysts and to create a chemically inert barrier which resists interaction with the fluid. Other processes such as surface polishing and annealing can also alter the surface characteristics either at a macro or micro scale. In general, smoother surfaces have less effective surface area and would have better compatibility. In some cases heat treating surfaces can decrease compatibility such as in hardening of some stainless steels or improve compatibility in the case of annealing Pyrex glass. Various processes have been developed in the past which can alter the compatibility of Class 1 materials thereby improving their compatibility. Examples of these improvements can be found in references 2 and 3. These processes have not been rigorously optimized using a methodology like a design of experiments. It is postulated that further improvements in material compatibility is possible through a passivation process optimization.

The existing literature data is limited for the effect of surface finish and the quantitative effect of surface finish is not clear. High quality surface finishes should improve compatibility as by definition, they reduce the exposed surface area. In this regard, surface finish processes such as electro-polishing can be especially helpful because they smooth the surface finish at very small scales which cannot be easily smoothed by mechanical polishing.

Two examples of how surface treatments can improve compatibility illustrate this effect: In Table 2 for the AOL of 1060 aluminum with 90% hydrogen peroxide at 66 deg. Celsius for 1 week. The AOL for this material changed from 1.5% to 0.1% by using a nitric acid passivation[2]. Reference 3 shows a six times reduction in AOL for 1260 aluminum when the passivation fluid is changed from stearic acid to 1% disodium ethylene diaminetetraacetic acid in 35% nitric acid followed by a repeated exposure to 90% propellant hydrogen peroxide. Various other examples of varying chemistry, temperature, durations, and process steps can be found in several sources. These examples show that the AOL can be reduced by a factor of 5 to 10 times by the proper form of passivation. The investigation and optimization of a passivation process can be assumed to improve the compatibility of a material several times and upwards of one order of magnitude and perhaps more.

VIII. Modern Propellant Stability

Recent work[5] has shown that the apparent stability of hydrogen peroxide in contact with Class 1 materials is most likely being driven by the surface effect of the material causing a heterogeneous decomposition reaction of the hydrogen peroxide. The apparent stability of the chemical itself appears to be much greater than when it is contacting a surface. This is very important, in that it identifies that the source of the material compatibility effect is primarily an effect of the material and that the propellant is inherently highly stable. Material research is then a strong source for improvements to material compatibility and thereby a major advancement in propellant storage could be realized through materials research.   It also calls into question much of the material compatibility data in that, the data may be biased based upon the materials of the equipment which was used in the test. Most of the literature material compatibility data is old or is pulled from reference material which is even older. Since the origination of much of the material compatibility data (most of this data is from before 1965), materials technology has changed and materials themselves have changed as well as new materials have been created.

The work in reference 5 demonstrated hydrogen peroxide stabilities between 99.56 to 99.97 with various Class 1 materials and associated AOL values of 0.014 to 0.202 % at a temperature of 100 deg. C for 24 hours. These tests were performed in Pyrex, fused Pyrex and PFA. The notable result of this work was to demonstrate that the hydrogen peroxide was extremely stable and that the surface effect of the material was a driving factor. It is also note worthy that the actual levels reported are significantly lower than the values shown in the prior table of historical compatibility values for both AOL and stability. This work also tested the materials at a different temperature than most of the literature data. Reference 5 proposes that the acceleration of the compatibility test correlates as: 24 hrs at 100 deg. Celsius is equal to 2 weeks at 66 deg. Celsius which is equal to 1 to 2 years at 25 deg. Celsius. So for a simple comparison, this data is conservatively comparable to the condition of 66 deg. C for 1 week.

The quality of the hydrogen peroxide has improved since the bulk of the compatibility test data was generated. It is important to note that hydrogen peroxide is a common industrial chemical which is produced in extremely large quantities to support such businesses as the paper and pulp industry and the electronics manufacturing industries. The latter of these two, the electronics industry, is a relatively new industry which requires very high purity hydrogen peroxide, at much higher purities than were required in the past by the propellant users. For example, prior propellant grade specifications for hydrogen peroxide typically impose part per million (ppm) levels of contamination. Electronics manufacturing requires hydrogen peroxide with parts per billion (ppb) or parts per trillion (ppt) contamination levels. If this high purity hydrogen peroxide material is used as the raw feed stock for the propellant grade hydrogen peroxide, one can see that there is a potential improvement in purity of 1000 to 1,000,000 times. The overall stability of the propellant should have some positive improvement. Existing literature data shows that over time that the manufacturing of hydrogen peroxide has improved the stability and storability.

This data, shown in figure 7, indicates that over time the apparent stability of hydrogen peroxide has improved. In fact the modern hydrogen peroxide may be ten times more stable than the material made in 1965, which suggests that systems built today could have significantly longer storage durations than systems built in 1965 simply due to the improvement in the propellant. An estimated AOL data point of 0.078% for 2 years at 66 degrees Celsius for a modern circa 2003 propellant was found as the average of the AOL's reported in Table 3 of reference 5. Note that the comparison of this current data with the historical data is difficult as the specific test conditions of the historical data are unclear. The intent is to show that there may be a trend whereby as the propellant purity has improved over time, that the propellant stability has improved as well. It is very important to note that the propellant made in 2003 is not the highest purity hydrogen peroxide which can be made.

This 2003 propellant is being made to the current industry propellant specification MIL-P-16005F which is a derivative specification which is traceable to the 1965 grade propellant. The FMC version of MIL-P-16005F hydrogen peroxide has a purity level which is equivalent to 50 ppb grade hydrogen peroxide used in the electronics industry. Current propellant suppliers can make more pure propellant grade hydrogen peroxide than required by MIL-P-16005. Existing commercial needs for higher purity hydrogen peroxide have created an industrial capability for very high purity hydrogen peroxide. Currently the biggest electronics grade market for high purity hydrogen peroxide is a 100 ppt grade. This 100 ppt grade means that any metal contaminant in the hydrogen peroxide is less than 100 ppt. Note that for some electronics fabrication companies, ppb grade hydrogen peroxide is unacceptable. In addition, known purification processes, such as fractional crystallization, could take standard propellant grade hydrogen peroxide and make an Ultra-High Purity (UHP) version of hydrogen peroxide, in a like manner to the UHP hydrazine developed by the hydrazine community. As seen by figure 7, improvements in propellant purity have improved stability. Further developments in propellant purity (which are currently possible) could further improve the stability of hydrogen peroxide beyond what is seen in figure 7.

IX. Current Class 1 Materials Research

Work has been done on various programs to investigate and characterize materials with various classifications. Most of this work has dealt with Class 1 and Class 2 materials. While much of this data is not currently available due to the nature of the work, some information is available which shows that modern materials research and renewed compatibility testing with hydrogen peroxide can provide important and useful information.

Recent work by Lee[6] has developed and demonstrated several new higher strength aluminum alloys (see figure 8). It is assumed that these materials were tested with 90% hydrogen peroxide at 66 deg Celsius for 1 week.

When compared to figure 2, this suggests that either these alloys are superior to prior aluminum alloys, or the propellant stability improved, or a combination of both items. In either case, data is becoming available which suggests that stability is comparable or superior to what was known in roughly 1965. High strength aluminum alloys are necessary for various aerospace applications especially large light weight propellant tanks in pump fed systems or as liners for composite tanks in pressure fed systems. A common perception of hydrogen peroxide is that while suitable materials are available, these materials (such as Al 1060 or 1160) are too weak for efficient light weight pressure vessels. Figures 8 and 9 show viable Class 1 materials with mechanical properties which are significantly better than aluminum 1060 and 1160 and are comparable to the more common high strength aluminum alloys, like 2219.

Figure 9 illustrates that high strength aluminum alloys are available which can provide Class 1 compatibility and have mechanical properties suitable for light weight low pressure tanks or for liners for composite pressure vessels. This allows systems to be built in which hydrogen peroxide can be loaded into flight weight tanks and left for long periods of time without the need for de-tanking.

Recent work by the author tested high purity tantalum with 90% hydrogen peroxide at 66 deg. Celsius for 1 week. This material was found to be a Class 4 when tested in this condition. This was initially thought to be unusual since tantalum is commonly believed to be a highly compatible material with hydrogen peroxide. This belief stems from the inheritance of the compatibility data from prior sources without the knowledge of how that rating was established. In reviewing reference 2 one sees that there actually is no data for the AOL or stability for tantalum and that the assessment is based upon a cryptic note titled “Based on service experience”. The current data which shows tantalum as a Class 4 material at 66 deg. Celsius is probably valid and the prior classification was made by other means. It is also possible that the currently available tantalum is different than the tantalum which was made in the past.

Tantalum is a high chemically inert material, but it is also a refractory metal and like other refractory metals it has the propensity to undergo catastrophic oxidation at elevated temperatures. Normally this occurs at many hundreds of degrees when exposed to the oxygen in air. It is postulated that this oxidation behavior may occur at lower temperatures when exposed to the oxidizing environment of liquid hydrogen peroxide. Further compatibility tests with tantalum at different temperatures could help illustrate this behavior. Note that tantalum has been used in the past as a heater element to boil hydrogen peroxide.

X. Case Study – Demonstrated Long Term Storability: Syncom II, Syncom III, and Early Bird

Several of the very early US spacecraft[7] used hydrogen peroxide as the primary propellant for orbit trim burns, maneuvering, and attitude control. Notably, the Syncom II (see figure 10), Syncom III, and Early Bird spacecraft all used a mono-propellant hydrogen peroxide based propulsion system made by Walter Kidde. These systems were all very similar in the means by which they achieved long term storability. Various incremental changes to the designs were made to improve the life time of the spacecraft and in general the spacecraft hydrogen peroxide system design features improved from the Syncom II to the Syncom III and further with the Early Bird. Technical features of the Early Bird will be discussed as this is the most mature of these platforms deployed.

Early Bird had a design life of 3 years, but was estimated to have a useful life of 5 years. The hydrogen peroxide tanks held 5.45 lb_m of propellant and the propulsion system was a blow down pressurization system. The spacecraft was spin stabilized such that positive displacement devices were not used. The materials of construction were 1060 H-12 aluminum for the tank shells, 1060 F aluminum bar stock for components, and the lines were 1060 aluminum. Other components were Kel-F and Teflon coated stainless steel for some minor exposure of valve parts. The worst material was a 17-7 PH stainless steel pressure transducer which was protected from the hydrogen peroxide by a Kel-F insert. The propellant valve seat was sapphire. The aluminum was cleaned with sodium hydroxide, passivated with nitric acid, rinsed with deionized water and checked with hydrogen peroxide for compatibility.

Other spacecraft deployed with hydrogen peroxide propulsion systems were: HS303A and ATS. Based upon the various early spacecraft which were deployed using hydrogen peroxide, it can be assumed that the technology of 1960's was capable of fielding hydrogen peroxide systems for long term storage of at least 3 years and upwards of 5 years. Other platforms which were also deployed which used hydrogen peroxide in similar applications but with lesser demonstrated storage durations were: the Mercury capsule, X-15, X-1B, Little Joe II, Burner, SATAR, ASSET, 122Y, LLRV, and the Astronaut Maneuvering Unit (AMU) from the Gemini program.

Flight systems using hydrogen peroxide for long term storage in sealed flight spacecraft have been deployed in the 1960's. These spacecraft were successes and hydrogen peroxide has demonstrated its suitability for what are now considered relatively short life spacecraft (less than 5 years).

XI. Demonstrated Long Term Storage of Hydrogen Peroxide in Vented Containers

Much of the historical data on the storage of hydrogen peroxide is with vented containers. While this is of lesser utility in demonstrating long term storage in sealed containers, it does show some indications of what types of long term storage tests were conducted. For some applications, such as booster vehicles or upper stages which may permit tank venting, this data would be highly appropriate in that it could define reasonably expected hold times.

A common method of storing hydrogen peroxide is in aluminum 30 gallon drums similar or identical to the US DOT 42D specification. Reference 3 provides some long term storage test data for these types of drums which is shown in figure 11. This data provides clear examples that for systems which can tolerate venting, such as launch vehicles waiting to be launched, that long term storage of several months to years has been demonstrated.

Other data points worth considering are a single drum a 90% propellant grade hydrogen peroxide which has been in storage at FMC for over 17 years. The concentration of this drum started at 90% to 91% and after 17 years is now at approximately 84%, which is just less than 0.4% drop in concentration per year. This drum has been stored outdoors in the ambient conditions of Texas. In addition, a second set of drums containing 90% hydrogen peroxide have been in storage at 5 deg. Celsius for over 17 years and have been recently measured at 90.5%[8]. This demonstrates that at 5 deg. Celsius that essentially no decomposition occurred for 17 years.

XII. Ideal Long Term Storage of Hydrogen Peroxide and Technologies to Enhance Hydrogen Peroxide Storability

Existing data show that numerous means exist to demonstrate and or show improvements to the long term storage of hydrogen peroxide. If one were to try and make a system to have the maximum long term storability, the general design criteria would be:

Surface to Volume Ratio	Less than 0.5 cm^{-1}.
Hydrogen Peroxide Concentration	Higher is better, anhydrous may be the best.
Temperature	Lower is better, preferably less than 100 deg. Fahrenheit.
Hydrogen Peroxide Purity	Cleaner is better. Ppb or ppt purity may offer improvements.
Materials	Compatibility similar to or better than Syncom (i.e.1060 Aluminum). AOL < 1.5% at 66 deg. Celsius for 1 week Stability > 98.8%

Various technologies are readily available and can be easily investigated to show improvements to the storability of hydrogen peroxide. Many of these improvements may have already been made due to the development of technologies in general since 1965 when most of the technology for hydrogen peroxide was matured. Areas to expect improvements or where improvements can be investigated are:

Improvement of hydrogen peroxide purity
Investigate materials which have been developed in the last 40 years (i.e. PFA, Halar, etc…)
Investigate more pure versions of existing materials
Higher concentration hydrogen peroxide, including anhydrous
Optimize passivation techniques
Investigate new passivation processes
Investigate alternate stabilizers
Improve purity of stabilizers

XIII. Conclusions

Hydrogen peroxide has previously demonstrated long terms storage of several years in deployed spacecraft applications using technology from roughly 1965. Subsequent to that date, significant advancements have been made in the propellant purity and materials technology which should enhance the actual long term storage capability. Improved propellant purity suggests that the storability of hydrogen peroxide is 2 to 10 times better than it was in 1965. The prior demonstrated long term usage of 3 years in a spacecraft could be easily extended to 15 years or more based upon the improvements in propellant and materials made since 1965. Advancements made since most of the literature data was created have been in the direction of improving the long term storability of hydrogen peroxide. Numerous opportunities exist for research and development which can further support and demonstrate improved long term storage, such as materials research, passivation process research and development, propellant purification, and the characterization of anhydrous hydrogen peroxide. Recent successes in some of the areas show that further improvements are likely. The ability to store hydrogen peroxide for several weeks to several years is currently possible using existing technology and as such is acceptable for immediate use in applications such as short life spacecraft, re-useable launch vehicles, expendable launch vehicles, and upper stages.

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Material	Max. AOL/week		Min. Stability	Notes
	30 deg. C	66 deg. C		
Metals	0.2	5	95%	No other effect on H2O2 or material. Non-impact sensitive to a 3 kg-meter impact at 212 deg. F
Plastics for drums and liners	0.2	5	95%	No other effect on H2O2 or material. Non-impact sensitive to a 3 kg-meter impact at 212 deg. F
Plastics for gaskest, tubing, etc..	0.4	6	95%	No other effect on H2O2 or material. Non-impact sensitive to a 3 kg-meter impact at 212 deg. F
Oils and Greases	1	10	95%	No other effect on H2O2 or material. Non-impact sensitive to a 3 kg-meter impact at 212 deg. F

Figure 1. Class 1 Criteria

Metals	AOL	AOL Condition	Stability
Aluminum 1060, wrought	1.5	Assumed 90% H2O2 , 66 deg C, 1 week	98.8
Aluminum 1060, wrought	1.5	90% H2O2, 66 deg. C, 1 week	---
Aluminum 1060, wrought	0.1	90% H2O2, 66 deg. C, 1 week	---
Aluminum 1060, wrought	0.4	90% H2O2, 30 deg. C, 4 weeks	---
Aluminum 1060, wrought	1.5	98% H2O2, 66 deg. C, 1 week	---
Aluminum 1100, wrought	3	Assumed 90% H2O2 , 66 deg C, 1 week	---
Aluminum 1160, wrought	1.5	Assumed 90% H2O2 , 66 deg C, 1 week	98.9
Aluminum 1160, wrought	1.5	90% H2O2, 66 deg. C, 1 week	---
Aluminum 1160, wrought	0.4	90% H2O2, 30 deg. C, 4 weeks	---
Aluminum 1160, wrought	1.5	98% H2O2, 66 deg. C, 1 week	---
Aluminum 1260, wrought	1.5	Assumed 90% H2O2 , 66 deg C, 1 week	98.8
Aluminum 1260, wrought	1.5	90% H2O2, 66 deg. C, 1 week	---
Aluminum 1260, wrought	1.5	98% H2O2, 66 deg. C, 1 week	---
Aluminum 5254	1.7	98% H2O2, 66 deg. C, 1 week	---
Aluminum 5254-O	0.3	90% H2O2, 66 deg. C, 1 week	---
Aluminum 5254-H34	0.3	90% H2O2, 66 deg. C, 1 week	---
Aluminum, 6063	4	90% H2O2, 66 deg. C, 1 week	---
Aluminum, 6063	0.2	90% H2O2, 30 deg. C, 4 weeks	---
Aluminum 7072, wrought	2.1	Assumed 90% H2O2 , 66 deg C, 1 week	---
Aluminum 7072	2.1	90% H2O2, 66 deg. C, 1 week	---
Aluminum B356, cast	2.8	Assumed 90% H2O2 , 66 deg C, 1 week	98
Aluminum B356	2.8	90% H2O2, 66 deg. C, 1 week	---
Tantalum	---	N/A	---
Zirconium	3.2	Assumed 90% H2O2 , 66 deg C, 1 week	---
Zirconium (2% Hafnium)	1.3	Assumed 90% H2O2 , 66 deg C, 1 week	---

Figure 2. Class 1 Metals

Polymers	AOL	AOL Condition	Stability
Aclar 22C, 15 mil	1.2	90% H2O2, 66 deg. C, 1 week	---
Aclar 22C, 15 mil	0.7	90% H2O2, 30 deg. C, 4 weeks	---
Aclar 22C, 15 mil	0.5	98% H2O2, 66 deg. C, 1 week	---
Aclar 22C, 15 mil	0.4	98% H2O2, 30 deg. C, 4 weeks	---
Fairprene 80-080	3.94	90% H2O2, 66 deg. C, 1 week	---
Fairprene 80-080	1.06	90% H2O2, 30 deg. C, 4 weeks	---
Flourel 2141	0.3	90% H2O2, 66 deg. C, 1 day	---
Flouroflex T-TP1001	3.6	Assumed 90% H2O2 , 66 deg C, 1 week	---
Kel-F (unplasticized)	3.5	Assumed 90% H2O2 , 66 deg C, 1 week	---
Kel-F	3.2	90% H2O2, 66 deg. C, 1 day	---
Kel-F	1	90% H2O2, 30 deg. C, 4 weeks	---
Kel-F F800	4.5	Assumed 90% H2O2 , 66 deg C, 1 week	97.8
25% 5500 Kel-F - 75% 800 Kel F	3.5	90% H2O2, 66 deg. C, 1 day	---
25% 5500 Kel-F - 75% 800 Kel F	1.5	90% H2O2, 30 deg. C, 4 weeks	---
50% Kel-F 5500 - 50% Kel F F 800	3.6	Assumed 90% H2O2 , 66 deg C, 1 week	97.7
Mylar A	5	Assumed 90% H2O2 , 66 deg C, 1 week	---
Mylar B	1.7	Assumed 90% H2O2 , 66 deg C, 1 week	---
Teflon	2.8	Assumed 90% H2O2 , 66 deg C, 1 week	95
Teflon, virgin	2.2	90% H2O2, 66 deg. C, 1 week	---
Teflon, virgin	0.4	90% H2O2, 30 deg. C, 4 weeks	---
Teflon, tape	2.8	90% H2O2, 66 deg. C, 1 week	---
Teflon, tape	0.3	90% H2O2, 30 deg. C, 4 weeks	---
Teflon, welded	2.7	90% H2O2, 66 deg. C, 1 week	---
Teflon, welded	2	90% H2O2, 30 deg. C, 4 weeks	---
Omni (Viton A)	2.9	90% H2O2, 66 deg. C, 1 week	---
Omni (Viton A)	0.5	90% H2O2, 30 deg. C, 4 weeks	---
Omni (re-inforced)	2.9	90% H2O2, 66 deg. C, 1 week	---
Omni (re-inforced)	0.5	90% H2O2, 30 deg. C, 4 weeks	---
Viton B	0.6	90% H2O2, 66 deg. C, 3 days	---
Viton B	3.3	90% H2O2, 50 deg. C, 1 week	---
Viton B	1	90% H2O2, 30 deg. C, 4 weeks	---
Viton B	3.1	98% H2O2, 50 deg. C, 1 week	---

Figure 3. Class 1 Polymers

Other	AOL	AOL Condition	Stability
Synthetic sapphire (polished)	0.8	Assumed 90% H2O2 , 66 deg C, 1 week	---
Pyroceram (9608)	3.9	Assumed 90% H2O2 , 66 deg C, 1 week	---

Figure 4. Class 1 Other Materials

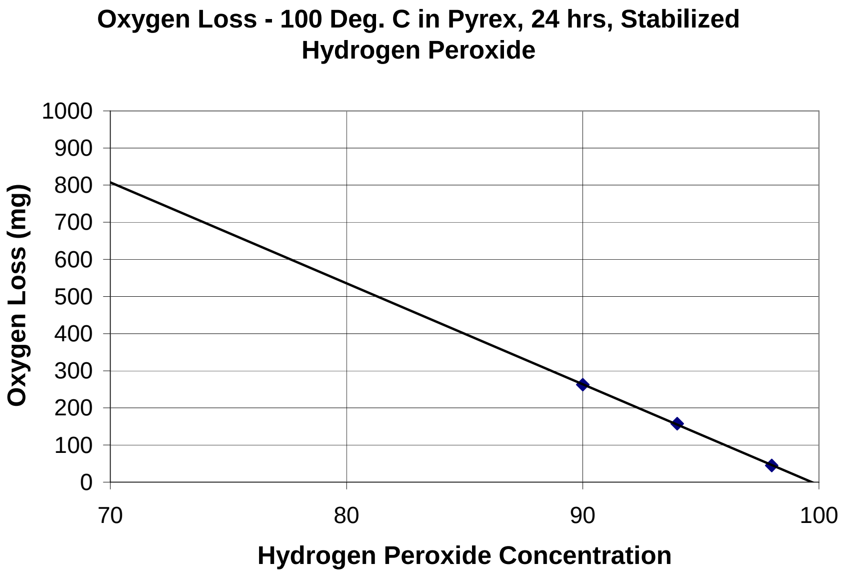

Figure 5. Effect of Water on the Stability of Hydrogen Peroxide[4]

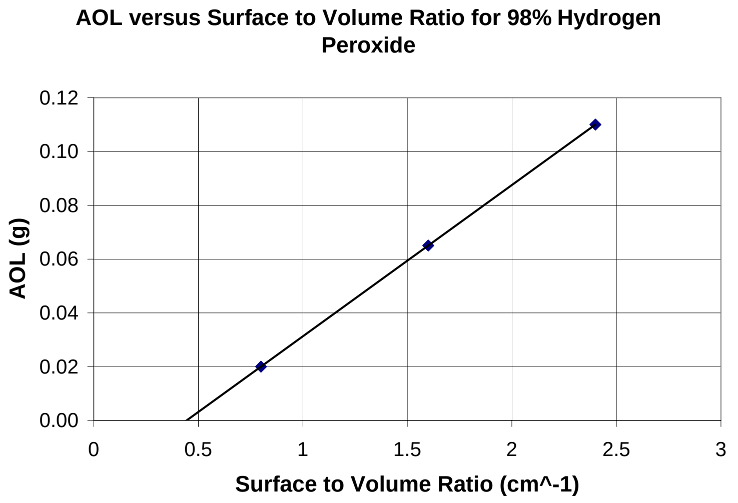

Figure 6. Effect of Surface to Volume Ratio on Decomposition

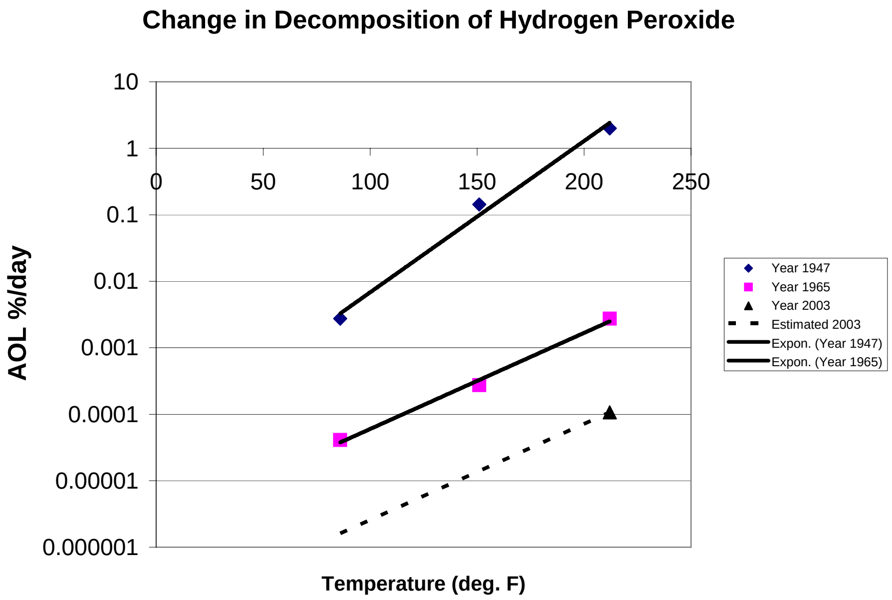

Figure 7. Comparison of AOL with Year Hydrogen Peroxide was Made[3,5]

Alloy	AOL (%)	Stability
RX 5000	0.276	99.16
C557	0.8845	98.24
7X0X	0.3405	99.51
7X11	0.3395	99.29

Figure 8. New Class 1 Alloys

Alloy	Yield Strength (ksi)
1060-T6	11.0
2219-T87	57.0
5254-H112	17.0
5254-H34	33.0
7X11-T6	82.3
7X0X-T6	78.5
RX 5000-H112	42.0

Figure 9. Comparison of Aluminum Alloy Yield Strengths

Figure 10. **Syncom Spacecraft**

Fluid	Duration (months)	AOL/year (%)
90% unstabilized hydrogen peroxide	36	Average 0.24, Range of 0.169 to 0.381
90% unstabilized hydrogen peroxide	13	Average 0.31, Range of 0.039 to 0.60
90% unstabilized hydrogen peroxide	33	Average 0.076, Range of 0.021 to 0.125
90% Torpedo grade hydrogen peroxide	62	Average 0.19, Range of 0.12 to 0.26
70% Torpedo grade hydrogen peroxide	76	0.088

Figure 11. **Long Term Storage of Hydrogen Peroxide In Drums**