

Rocket Grade Hydrogen Peroxide (RGHP) for use in Propulsion and Power Devices - Historical Discussion of Hazards

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Common historical anecdotal negative characteristics for propellant grade hydrogen peroxide are described and reviewed. Supporting evidence, analysis, historical technical data, recent test data, prior experience, current experience, modern and literature test data are provided to address the issues and perceived concerns and to provide referenced and established scientific data and evidence which can be used to make informed decisions.

Nomenclature

ASTM	=	American Society of Test and Materials
H ₂ O ₂	=	Hydrogen Peroxide
H ₂ O ₂	=	Hydrogen Peroxide
Hg	=	Mercury
ID	=	Internal Diameter
IRFNA	=	Inhibited Red Fuming Nitric Acid
ISTAR	=	Integrated Systems Test of an Airbreathing Rocket
lbm	=	pounds, mass
lbs	=	pounds
LO ₂	=	Liquid Oxygen
m	=	meters
ml	=	milliliter
MMH	=	Monomethylhydrazine
mm	=	millimeter
MON	=	Mixed Oxides of Nitrogen
N ₂ H ₄	=	Hydrazine

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NIOSH	= National Institute for Occupational Safety and Health
NRA	= National Research Announcement
NTO	= Nitrogen Tetroxide
O/F	= Oxidizer to Fuel Ratio
PETN	= Pentaerythritol tetranitrate
ppm	= parts per million
RBCC	= Rocket Based Combined Cycle
RGHP	= Rocket Grade Hydrogen Peroxide
Sch	= schedule
sec	= seconds
SS	= Stainless Steel
UDMH	= Unsymmetric Dimethyl Hydrazine
UHP	= Ultra High Purity

I. Introduction

High concentration or “rocket grade” hydrogen peroxide has a long history of application to aerospace propulsion and power systems due to its high density, its monopropellant characteristics, its low toxicity and ease of handling. Numerous applications on both manned and unmanned systems can be cited from the 1930’s to the present time^{1,2,3,4}. The development of Shell 405 catalyst and higher purity hydrazine in the 1960’s led to a decreased use of hydrogen peroxide due to the superior performance and long-term stability characteristics of hydrazine. In the current environment where systems are cost and safety driven, the expense of handling highly toxic propellants is becoming undesirable. For this reason, hydrogen peroxide had been receiving a renewed interest; however historical ideas and arguments from the period of transition from hydrogen peroxide usage to hydrazine still linger in ill-defined terms. This recollection of mostly anecdotal historical accounts creates many perceptions that are based on a lack of knowledge and inaccurate or unsubstantiated data. Since hydrogen peroxide is still only used in limited applications for propulsion and power, the propulsion industry in general is still not intimately familiar with the chemical and as such often makes decisions with inadequate information.

The authors of this paper have had extensive experience with handling and testing hydrogen peroxide based systems and have been involved with a majority of the hydrogen peroxide propulsion and power efforts conducted over the past decade. Our goal in writing this paper is to provide potential users with facts and background references that can provide them with information for basing sound propellant selection and design decisions for future aerospace systems.

II. Historical Perspective

Hydrogen peroxide has had a long and complex history. Initially it was widely used as the first generally used monopropellant. In many applications it was replaced with higher performing chemistries such as the conventional storable hypergolic chemicals, hydrazine and its variants; monomethyl hydrazine (MMH), unsymmetric dimethyl hydrazine (UDMH) and the various blends of nitric oxide and nitrogen tetroxide. Various arguments against hydrogen peroxide and for conventional storable chemicals were developed during this transition period and the remnants of that transition exist today generally as limited summary references in texts and reference books.

Several of the potential factors affecting the image held by hydrogen peroxide can be attributed to the treatment in the academic texts by Sutton^{5,6,7} and the popular rocket propellant history book *Ignition*⁸ by Clark, as well as anecdotal recollections of heritage accidents and mishaps from before approximately 1970. The combination of anecdotal histories and the treatment of hydrogen peroxide by Clark and Sutton may have created a natural bias to simply dismiss hydrogen peroxide as a non-viable design solution without conducting a trade based upon fundamental merits. An example of this kind of dismissal of hydrogen peroxide⁹ and the recent negative assessment of the Blue Origin New Shepard launch system¹⁰ illustrate the still existing rejection of hydrogen peroxide in propulsion and power applications without consideration of all available facts and information.

Sutton’s, *Rocket Propulsion Elements*, now in its 7th edition, is probably the most popular rocket propulsion reference for students and young engineers. Particularly in the early editions of the book, the discussion of hydrogen peroxide as an oxidizer focused on its instability in storage, with such phrases as “Even under favorable conditions H₂O₂ will often decompose at a slow rate...” and “In spite of its hazards...” which gives the reader the impression that the fluid is less stable and more difficult to handle than other oxidizers such as liquid oxygen, inhibited red fuming nitric acid (IRFNA) or nitrogen tetroxide (NTO) variants. Recently, Mr. Sutton has changed

the tones of the passages involving hydrogen peroxide, but many readers still have older editions of the book that negatively characterize hydrogen peroxide in comparison to others rocket propellants discussed in the text. Moreover, many of the current decision maker's in the propulsion community have been exposed to prior editions of Sutton's text and have not had direct experience with hydrogen peroxide and must rely on what they are taught and what they acquire from corporate histories which tend to propagate anecdotal data. A comparison of Sutton's text and the dates of these editions are shown in Table 1. Note that the 2nd edition was published in 1956 and the 6th edition was published in 1992.

Edition and Copyright Date	H2O2 Summary
2 nd (1956)	"In spite of its fire and explosive hazard, hydrogen peroxide has become a desirable oxidizer, primarily because of its high specific weight.
6 th (1992)	"...but it is no longer used today, primarily because of its storage stability problems."

Table 1 – Comparison of Sutton's 2nd and 6th Editions

Clark's book, *Ignition*, provides an interesting comparison of the perceived natures of hydrogen peroxide in comparison to its most similar chemical hydrazine. As Clark's title indicates, this book is an informal discussion and is meant to be enjoyed as a story and not necessarily a compendium of engineering facts. Table 2 shows the language used by Clark in his description of comparable features of hydrogen peroxide and various forms of hydrazine.

Propellant Feature	Hydrogen Peroxide	Hydrazine
Chapter Title	Peroxide – Always a Bridesmaid	The Hunting of the Hypergol
Stability	Clark devotes almost a full page to the mechanism of catalytic decomposition however this is a feature that is discussed in the same degree of detail with hydrazine. "And it's unstable."	"It was somewhat sensitive to catalytic decomposition, but if you used the right materials to make your tanks of, and were reasonably careful about cleanliness, that was no real problem."
Freezing Point	"... the freezing point of 100 percent H2O2 was only half a degree below that of water." He discusses various attempts to lower the freezing point, none of which were adopted.	"But that freezing point -1.5 C – was just too high for anything that was going to be used in a tactical missile." The rest of the chapter is devoted to the process of lowering the freezing point of hydrazine with the creation of UDMH and MMH.
Combustion Hazard	Demonstrated a H2O2/kerosene explosion by floating kerosene on top of H2O2 and igniting the fuel. This is compared to an acid/UDMH spill and H2O2 is considered worse.	No mishaps discussed expect cryptic mentions of catalytic decomposition and thermal stability.
Future of the Propellant	"Peroxide just didn't make it."	"So now the designer has a family of high performing fuels at his disposal – reliable, easy to handle, and available."

Table 2 - Comparison of Clark's Assessment of Hydrogen Peroxide and the Hydrazine Family

Clark's assessment of hydrogen peroxide is decidedly negative: the stability of the chemical is implied as highly questionable, the high freezing point is considered a fundamental problem and that the non-hypergolic reactivity of the propellant is shown as a negative in comparison to hypergolics. Later in Clark's chapter on hydrazines, his treatment of the hydrazine family is decidedly less aversive even though hydrazine fundamentally shares many of the same chemical issues (neat hydrazine has a similar freezing point and has catalytic reactivity concerns). It is

notable that Clark illustrates a specific event that shows the danger of hydrogen peroxide but does not document any hypergolic mishaps or accidents for the hydrazines.

The early implementation of hydrogen peroxide was a period of time when specific industrial practices for handling and operating rockets, rocket propellants and monopropellants was immature. This period of time (1930's to 1960's) is marked by a large number of incidents with many different propellants and in fact, accidents and mishaps were a common experience. After this period of time, propellants have mostly been constant and there has been an accumulation of experience and general practices which has progressively lowered the rate of incidents as well as generally trained the industry to be familiar with the standard set of chemicals¹³. The standard set of most commonly used liquid rocket propellants are:

Liquid Oxygen (LO2)
Liquid hydrogen (LH2)
Kerosene (RP-1 and other variants)
Monomethyl hydrazine (MMH)
Nitrogen Tetroxide and variants (MON-X)
Hydrazine (N2H4)
Unsymmetrical dimethyl hydrazine (UDMH)

Table 3 - Standard Liquid Rocket Propellants

Hydrogen peroxide can be fairly seen as a trail blazer propellant for rocket propulsion in general and more specifically for monopropellants. The concepts, general designs, and practices for monopropellant propulsion were first created with hydrogen peroxide and some of these applications were later replaced by other chemicals, most notably hydrazine. In its role as a trail blazing technology it has suffered the history of failures necessary to educate the propulsion community in general while parallel to the initial hydrogen peroxide experience, the research and development of hydrazine effectively used these lessons learned to ensure hydrazine would not have to suffer the same history of events, and as one would expect, the usage of hydrazine has been quite successful.

Recent incidents with hydrogen peroxide are due to lack of industrial experience. As the industry transitioned from the general propulsion research and development of the 1940's through the 1960's the practices of handling and using the propellants in Table 3 have become the norm and standard of business. The experience of prior usage with other chemicals, including hydrogen peroxide, has been mostly forgotten and the general practices for handling unknown chemicals is less common, so personnel revert to what they understand and know, which may be inappropriate for a different chemical. The current incidents with hydrogen peroxide can be traced to lack of information and lack of education on the proper handling of rocket propellant grade hydrogen peroxide.

Historically, many of the accidents and failures associated with hydrogen peroxide systems have been from gross neglect with regard to material compatibility and operational uses of hydrogen peroxide. If hydrogen peroxide is placed in incompatible containers without venting (or without sufficient venting), decomposition products will build up until the container ruptures. Of course, similar results would happen with other propellants if mishandled incorrectly. For example: an unvented LO2 vessel would eventually burst if boil-off gases are not vented from the vessel. Similarly hydrazines must be stored in compatible containers to prevent self pressurization due to catalytic decomposition, nitrogen tetroxide can cause stress corrosion cracking in containers, and inhibited red fuming nitric acid (IRFNA) must be stored in a suitable tank. Like other propellants, hydrogen peroxide needs to handle with appropriate regard to material compatibility. The U.S. Navy investigated¹⁴ many of the hydrogen peroxide incidents in the 1940's to 50's in an investigation into the suitability of the fluid for use as a torpedo propellant. This document provides an excellent reference describing many of the early mishaps concerning the fluid in the U.S., U.K. and Germany.

The document provides many strong conclusions concerning the use of hydrogen peroxide:

“By itself, hydrogen peroxide is a safe material to handle. The record of 30 years experience with this material has shown no case wherein permanent injury to personnel resulted from detonation, explosion, fire, or accidental spillage of high concentration hydrogen peroxide alone”.

“The accidents described in this report have as a common denominator, contamination of the peroxide, and in most cases by organic liquids”.

“Without exception, the explosions that have been reported have occurred in test cells or research vehicles. This only points up the fact that it is the detail design of the system, not the peroxide concentration, which ultimately determines system safety”.

Within the recent past few years, two incidents of notable significance provided a substantial negative impact on the perception of hydrogen peroxide. A fluid transfer system made with some incompatible materials was used to deliver hydrogen peroxide from a holding tank to a run tank in testing at NASA Stennis Space Center. This system failed (burst) due to over-pressurization. Obviously, this unfortunate incident could have been avoided by the use of a pump made of the appropriate materials. This failure was due to a specific design practice of cladding or lining an incompatible material with a compatible material and the liner failed allowing propellant to migrate behind the liner and react with the incompatible material. The inherent risk with any liner application is that failure of the liner can cause this kind of over pressurization mishap. It is not a recommended practice to line incompatible materials for propellant grade hydrogen peroxide applications.

In another incident at Stennis Space Center a thrust chamber was destroyed in testing of a hypergolic fuel with hydrogen peroxide. This failure was attributed to the use of an “oxidizer lead rather than a fuel lead” for this new propellant combination, which was presumably an operational fix to a design-related problem of local overheating. The majority of the fielded and flown hydrogen peroxide rocket engines have used catalytic reaction of hydrogen peroxide instead of liquid injection^{15,16,17,18}. Deployed systems that have used liquid injected hydrogen peroxide have also used either separate injection of a liquid catalyst or a fuel mixture that includes a catalyst or is hypergolic. Hydrogen peroxide has a very low vapor pressure which is one of the features that makes it an attractive propellant for handling. However this low vapor pressure makes it more difficult to produce large amounts of vaporized hydrogen peroxide in a combustion chamber during a start transient and as such it should be more difficult to ignite liquid-liquid bi-propellant hydrogen peroxide combustors in comparison to other liquid oxidizers that have higher vapor pressures¹⁹.

In addition, historically, with the hypergolic propellant combination such as NTO/MMH, propulsion system designers chose to lead with the oxidizer. This was because the oxidizer was NOT a monopropellant and the fuel was usually energetic. In other words the rocket engine designer chooses to lead with the endothermic propellant component in order to avoid a build up of a monopropellant component in the chamber. Unfortunately the concept is misconstrued by many to “lead with the oxidizer” since this is usually not an energetic component. Clearly this is not so with hydrogen peroxide in a bipropellant system. This was confirmed in testing at Sandia National Laboratories, Purdue²⁰ and at China Lake²¹. While hard starts of this nature have long been accepted as a consequence of a development program, the failure in this case has somehow been misconstrued as a problem particular to hydrogen peroxide. Since several other groups have successfully demonstrated operation of various hypergolic fuels with hydrogen peroxide, it is obviously not warranted to attribute this particular problem to hydrogen peroxide.

A recent example of this bias and how it may influence design decisions will serve to as an example. During a relatively recent professional training seminar on lessons learned in liquid rocket propulsion in 1993²⁵, an example of a Centaur stage failure was attributed to a leaking hydrogen peroxide fitting or hydrogen peroxide line. Leakage from the line prevented the RL-10 from operating properly and the stage failed. It is significant that the failure of the Centaur stage was attributed to hydrogen peroxide and not due to a leaking fitting or line. The professional training class conclusion on this topic was that the lesson learned was *do not use hydrogen peroxide*. The anecdotal event alluded to in this training class was probably the Atlas-Centaur launch AC-8 launched in April 1966. During this launch, a leak in the hydrogen peroxide attitude control system prevented the Centaur from properly settling propellants after a coast and prevented one engine from igniting. The Centaur used two RL-10 engines and the resulting single engine thrust unbalanced the stage and sent it into a tumble²⁶. Compare that anecdotal hydrogen peroxide reference, to the recent failure of the SpaceX Falcon 1 which was also attributed to a fluid leak, in this case a leaking fluid fitting nut for kerosene²⁷. Correctly so, the investigation assigns the leakage failure to the fitting nut (in this case caused by environmental or galvanic corrosion of the nut) and corrective actions are taken to change the fitting nut material and the system returns to flight. The irrational decision to attribute the failure to kerosene is not made. The lesson learned by SpaceX was not to reject kerosene, but to try to identify the cause of the failure and take corrective action.

III. H₂O₂ Stability and Storability

This has been one of the primary arguments against the use of hydrogen peroxide and it is best summarized as a belief that the chemical cannot be stored in any reasonable manner. This is refuted by the large commercial utilization of the chemical²⁸, past historical applications^{1,2,3,14,15,16,17,18}, modern applications^{29,30} and recent improvements in chemical purities³¹ that are probably improving the chemicals stability and storability.

The stability of a liquid propellant is generally considered by characteristics such as: tolerance to heat, length of storage and other parameters that define how well the chemical can be stored and handled. Stable chemicals are highly tolerant to variations in environmental conditions and can be routinely handled and transferred with some reasonable precautions. Unstable chemicals are highly intolerant to factors that may be difficult or impossible to control. Liquid ozone is an example of a chemical that is considered generally unstable. Hydrocarbon fuels such as ethanol and kerosene are generally considered stable. Monopropellants and solid propellants occupy a special place in the discussion of stability because they can react by themselves and as such pose a more particular hazard. The definition of stability becomes more specific and pertinent in regards to chemicals that can react wholly by themselves. In practice there are some common but not necessarily consistent means to define and test for the stability of these chemicals. Solid propellants has specific criteria and test requirements for defining and classifying solid chemistries which essentially defines stability for solid propellants. Hydrazine and hydrogen peroxide have developed similar but different criteria for characterizing stability. A detailed discussion of hydrazine stability is provided by Schmidt. The overall features of hydrogen peroxide stability are discussed in several sources^{32,33,34,35}.

Prior test data and historical application of hydrogen peroxide has shown that the chemical is stable enough for use as a propellant and power fluid. Hydrogen peroxide tolerates a reasonable range of temperatures and has demonstrated long term storage without hazards. It is suggestive that the stability of hydrogen peroxide may have improved recently due to improvements in commercial hydrogen peroxide manufacturing purity standards to support the higher cleanliness levels required by the electronics industry³¹.

An example of the long term safe production of hydrogen peroxide is seen with FMC. FMC has had a safe and effective history of the manufacturing and storage of high concentration hydrogen peroxide. Both 90% and greater than 98% hydrogen peroxide have been produced by FMC for more than 30 years. There has been no incident in the manufacturing and the storage of the product at any FMC site during this period. FMC has conducted significant material compatibility testing. Equipment passivation and cleaning³² are routinely conducted to ensure no hydrogen peroxide contamination occurs. In order to maintain safe operation, FMC follows its own strict general hydrogen peroxide safety rules.

Following recent incidents involving hydrogen peroxide produced by others, FMC stepped up its surveillance and safety training for all new customers. FMC provides customer safety training and on-site facility inspection before selling hydrogen peroxide to all new customers. As a result of this practice, there have been no incidents reported in the storage and transportation of 90% and 98% hydrogen peroxide by any of FMC's customers. Hydrogen peroxide has been stored and used in numerous propulsion and power systems since WWII. It has seen extensive use in submarine and torpedo propulsion systems, telecommunications satellites, and primary and secondary propulsion systems in rocket and manned aircraft.

In addition, a common misconception is that H₂O₂ cannot be stored for extended periods of time in a sealed container. Propellant grade H₂O₂ has been stored in sealed spacecraft for several years^{36,31,35} (an example is the COMSAT spacecraft) and has been safely stored in vented containers for greater than 17 years³¹.

Another feature of interest is the improvement in storability of hydrogen peroxide as the concentration increases the stability improves, which is somewhat counter intuitive.

Oxygen Loss - 100 Deg. C in Pyrex, 24 hrs, Stabilized Hydrogen Peroxide

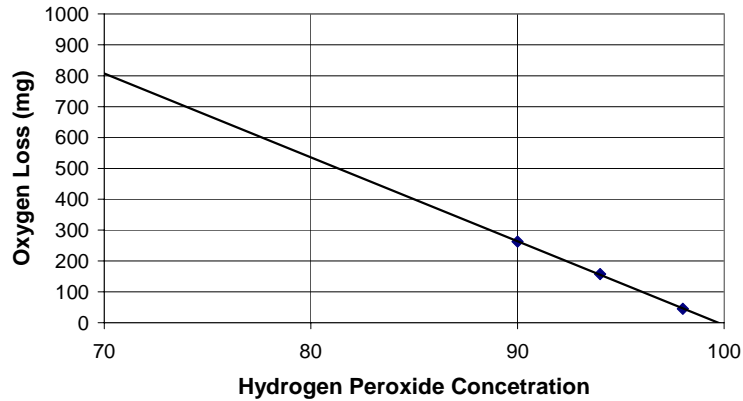


Figure 1 - Effect of Water on the Stability of Hydrogen Peroxide³¹

Much of the historical, literature, and even recent long term storability data and experience have been with 70% to 90% hydrogen peroxide while it is apparent that storability will improve with higher concentrations of hydrogen peroxide and notably with anhydrous hydrogen peroxide. In addition, recent improvements in the raw chemical feed stock of hydrogen peroxide may permit propellant with lower levels of impurities and higher overall purity and stability. The proposed trend³¹ for the current potential stability of hydrogen peroxide is shown in Figure 2. It is possible that modern more pure or perhaps more particularly, refined and purified hydrogen peroxide such as anhydrous ultra high pure hydrogen peroxide produced by fractional crystallization may have fundamentally superior storability.

Change in Decomposition of Hydrogen Peroxide

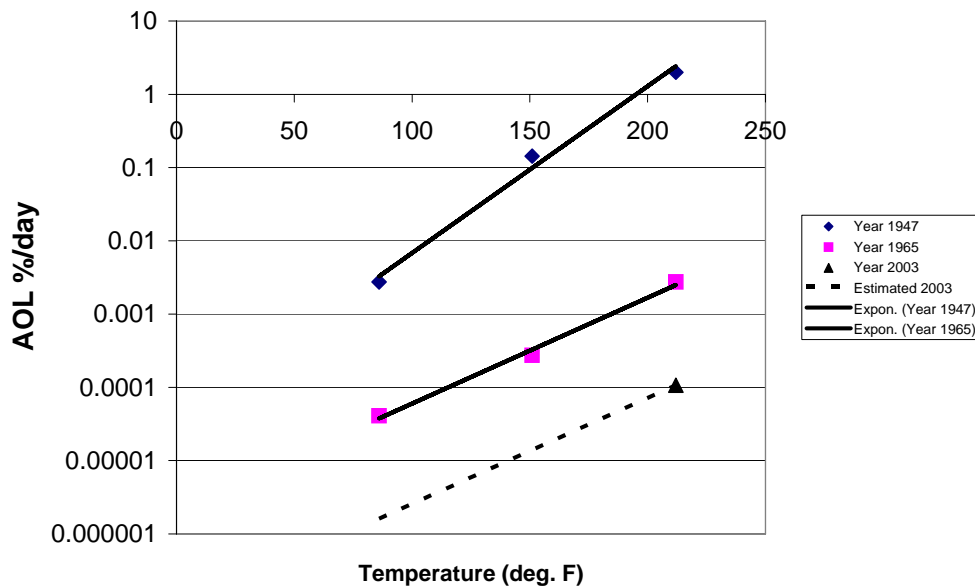


Figure 2 – Improvements in Hydrogen Peroxide Stability with Time

Recent testing indicated that 98% RGHP stored in a passivated & heat treated Pyrex flask has 99.9% stability @ 100 deg. C for 24 hours or about 0.1% decomposition rate per year at ambient temperature^{43,37}. NASA MSFC recently developed several new high strength aluminum alloys⁴³ that are compatible with 90% RGHP. The yield strengths for some of these Al-Mg based alloys are more than 3 times stronger than the conventional 5354-H112 aluminum alloy, while maintaining excellent H2O2 compatibility similar to 5254 alloy (class I category). These newly developed Al-Mg alloys were intended to be used for the RGHP oxidizer tank of the X-43B hypersonic vehicle.

Recent Long Term Storage Test Demonstration

To provide an unequivocal example that hydrogen peroxide does not decompose rapidly or dangerously in an unpredictable manner, a test was conducted over the past 10 months to demonstrate that hydrogen peroxide can be safely handled and stored in commercially available materials without significant or unpredictable hazards.

90% hydrogen peroxide was procured from FMC using MIL-P-160005F and this hydrogen peroxide was placed into three chemical crucibles made from: aluminum, tantalum, and zirconium. Tables 4, 5, and 6 show the chemical composition of these crucibles respectively. Note that the supplier did not know the aluminum sample alloy so it was determined by optical emission testing to be aluminum alloy AA3003. Aluminum alloy AA3003 is a class 2 material and is generally not recommended for long term usage. Note that aluminum alloy 3003 has a significant amount of manganese (approximately 1%), a well known and powerful catalyst with hydrogen peroxide. Class 2 materials are typically considered acceptable for 4 hours at 160 degrees F or 1 week at 70 degrees F³⁸. These crucibles were commercially procured from the Alfa Aesar chemical supply company. The crucibles were cleaned and passivated using a commercial ASTM passivation specification and a commercial passivation company. Hydrogen peroxide was placed into the crucibles and the crucibles were sealed inside cleaned glass Kimax 250 ml No. 14000 beaker to prevent environmental contamination from contacting the test beaker or the hydrogen peroxide. A photograph of the glass beaker and one of the metal test crucibles is shown in Figure 3.

The beaker test arrangement was designed to handle any range of decomposition reaction. The beakers are isolated from the outside with a low pressure water trap that is fully capable of venting the expected very low rate of gas evolution. The water trap was sealed with a balloon which can expand significantly before creating significant back pressure. The glass beaker was closed out with a stopper that can blow off in the event that a low level of pressure was produced inside the beaker. The beaker assembly was placed on a hydrogen peroxide stainless steel secondary containment system to trap any ejected liquids.

Element	%
Silicon	0.1
Manganese	1.0
Iron	0.6
Copper	0.07
Zinc	0.01
OE	0.05
OT	0.15
Aluminum	Balance

Table 4 – Aluminum Test Sample Chemical Composition

Element	ppm
Aluminum	< 1
Carbon	< 50
Copper	< 5
Chromium	< 1
Iron	< 10
Hydrogen	< 10
Molybdenum	< 5
Nitrogen	< 50
Nickel	< 10
Oxygen	< 100
Silicon	< 10
Sodium	< 1
Titanium	< 10
Tungsten	< 30
Tantalum	Balance (+99.95%)

Table 5 – Tantalum Test Sample Chemical Composition

Element	ppm
Aluminum	28
Boron	< 0.2
Carbon	60
Cadmium	< 0.2
Cobalt	< 10
Chromium	50
Copper	< 10
Iron	475
Hydrogen	10
Hafnium	45
Magnesium	< 10
Manganese	< 25
Molybdenum	< 10
Nitrogen	11
Nickel	< 35
Oxygen	800
Tin	< 25
Silicon	< 10
Uranium	< 1
Tungsten	< 25
Zirconium	Balance

Table 6 – Zirconium Test Sample Chemical Composition



Figure 3 - Example of Test Beaker Set-up

The glass beaker was closed out with a #13 rubber stopper that was isolated from the test beaker with a Teflon cover. A glass air lock made by Barkingside, was installed in the beaker. The gas trap was filled with deionized water. The outlet of gas trap was covered with a balloon to provide an indication of any reaction. Figure 4 shows these components.



Figure 4 – Stoppers, Teflon Shield, and Water Trap Test Set-Up

The beakers will filled with 90% H₂O₂ with the initial and final masses are shown in Table 7:

Beaker Material	Initial Mass of H ₂ O ₂ Loaded (g)	Final Mass of H ₂ O ₂ (g)
Zirconium	29.67	28.37
Aluminum	30.07	17.73
Tantalum	30.07	18.70

Table 7 - Beaker H₂O₂ Masses

The test was started on 8/21/2006 and was terminated on 6/8/2007, which is in excess of 9 months. The temperature during the period of gas evolution observation is shown in Figure 5. Nominally the day to day variation is approximately 5 degrees F. The intent of the test was three-fold:

- 1) Demonstrate that hydrogen peroxide is not “inherently unstable” by visual examination of the test apparatus for gross or rapid decomposition.

- 2) Demonstrate that currently manufactured hydrogen peroxide can be safely transferred and stored in a several materials, preferably materials that are not excessively exotic.
- 3) Characterize the materials and determine if there is a qualitative different between materials and if this test set-up was suitable as a simple screening test of materials.

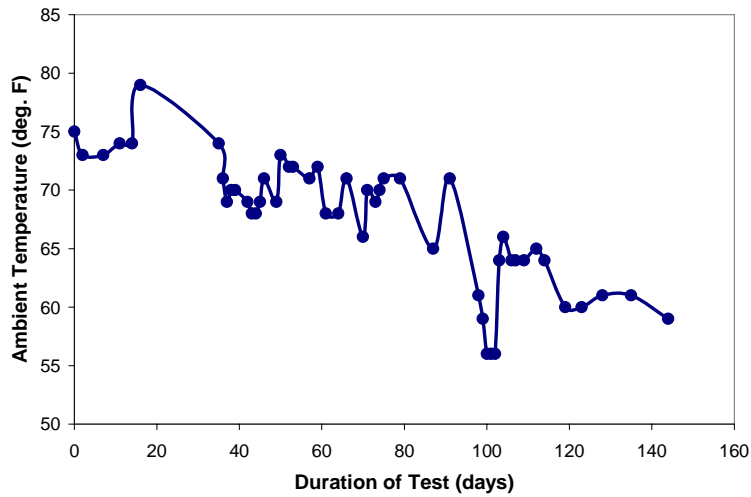


Figure 5– Test Temperature

Examples of the test systems with uninflated balloons and balloon inflation are shown in Figure 6 and Figure 7.



Figure 6 – Uninflated Balloons

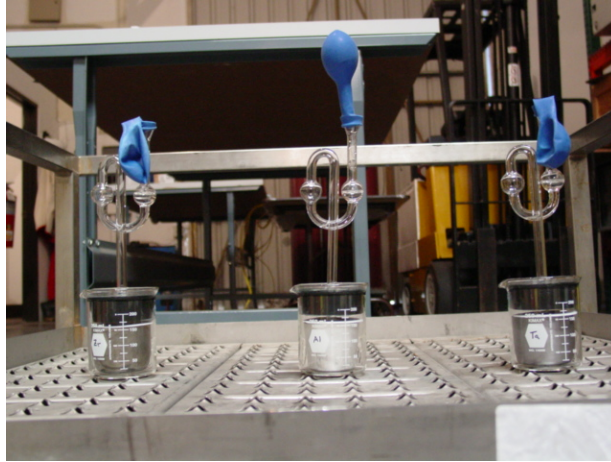


Figure 7 – Test Set-Up with Balloon Inflation

The test measured the ambient temperature and made visual examinations of the test containers and balloons on an approximately daily basis for a period greater than 4 months. If the balloons inflated enough to put the balloon skin under tension, the balloon was deflated. This event was recorded and periodically pictures were taken of the apparatus. The rate of balloon inflation is shown in Figure 9. The balloons were removed on 1/12/2007, however the test apparatus was left intact and no excessive or dangerous reaction was observed. The test lasted greater than 9 months.

Before and after pictures of the test crucibles and propellant are shown in Figure 8. One sees that the propellant is not exhibiting any visual indications of decomposition such as active streams of bubbles or even evidence of bubbles of any surfaces. Some slight discoloration is evident on the upper vapor side of the aluminum and tantalum crucibles indicating some evaporation or gasification of hydrogen peroxide in the vapor zone of the crucible. The zirconium test article rubber stopper shows evidence of attack by hydrogen peroxide (blistering). It was noted that the Teflon shield was slightly off center on this test article and that permitted a small vapor path from the hydrogen peroxide to the rubber stopper. This may have allowed vaporized hydrogen peroxide to react with the rubber and create a diffusion gradient allowing more hydrogen peroxide to vaporize. This would indicate a conservative decomposition rate for zirconium. In addition the aluminum rubber stopper shows evidence of liquid on the stopper surface but no significant degradation of the stopper. This is likely vaporized water that was entrained upward when hydrogen peroxide reacted with the aluminum crucible.

The tantalum mass loss is just slightly less than the aluminum loss which is not expected when comparing a Class 2 material (Aluminum 3003) with a Class 1 material (tantalum). The tantalum crucible had a rough surface from the crucible forming process. This is undesirable as it increases surface area and may imbed forming tool materials into the surface. This test demonstrated that this tantalum crucible is more like a Class 2 material.

Material	BEFORE	AFTER
Aluminum 3003		
Tantalum		
Zirconium		

Figure 8 - Before and After Photos of Test Crucibles with RGHP

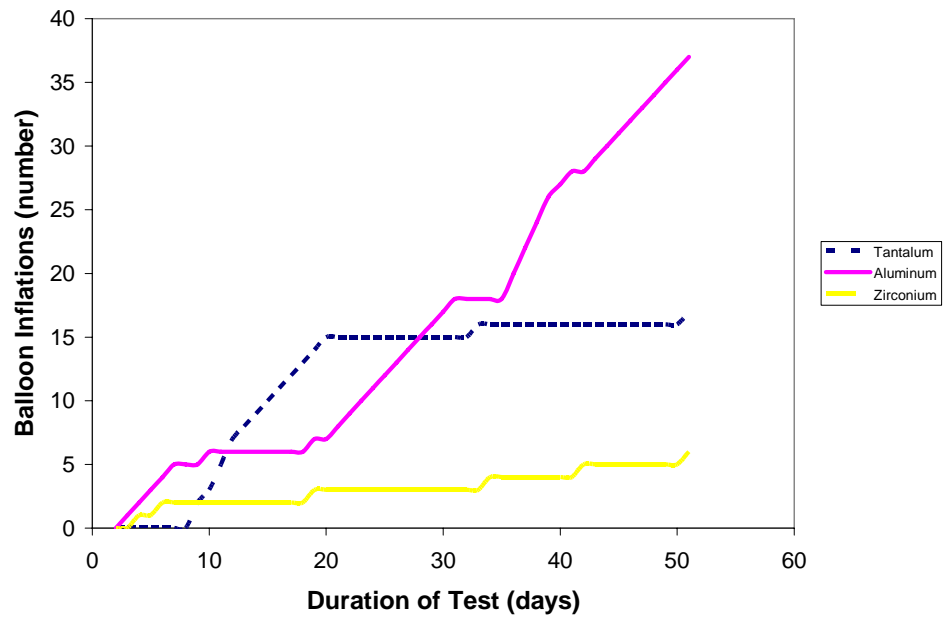


Figure 9 - Rate of Gas Evolution

This test has shown that hydrogen peroxide does not decompose dangerously or unpredictably after having been transferred into containment systems and can be safely stored in various materials for extended durations of time without excessive rapid decomposition. The limited sample indicates a notable difference in decomposition between the samples. Overall, zirconium appears to be superior; and tantalum exhibited an initial higher rate of decomposition which seems to have become moderated as it aged. After the “aging” period for tantalum, the gas evolution rate of tantalum appears to be lower than zirconium.

The expected storability of hydrogen peroxide could be improved by considering the effect of hydrogen peroxide concentration. It is currently believed that hydrogen peroxide stability is a function of the concentration. Tests at higher concentrations and perhaps even anhydrous hydrogen peroxide may yield very high stability. In addition, the limited modern propellant compatibility data, when compared to historical data, suggests that recent improvements in chemical manufacturing is producing a more pure (less contamination) propellant which is improving the propellant stability. The next logical step in the maturation of hydrogen peroxide is to consider highly purified hydrogen peroxide through fractional crystallization purification, as is done with Ultra-High Pure (UHP) hydrazine. This will yield a very pure and likely even more stable chemical. An excellent prospect for future research would be to investigate and compare the stability of anhydrous UHP hydrogen peroxide.

IV. H₂O₂ Detonability

Hydrogen peroxide detonations and other mono-propellant combustion phenomenon can be separated into three groups: gas phase, liquid phase, and gas-liquid two-phase. The gas phase of hydrogen peroxide has well documented ignition and detonation conditions and like other monopropellants the gas phase is susceptible to ignition and resulting deflagration and possibly detonations. In general, for safe operations, methods and procedures must be utilized to avoid the formation of certain vapor phase conditions and this is an accepted and common condition for all monopropellants.

Of greater concern is whether a detonation is possible in the liquid phase, as this sets up the possibility of a liquid explosive or the possibility of an aberrant combustion event, such as a hard start, that could initiate a detonation in the liquid mass that would propagate through a system causing extensive damage. Testing is done to ascertain if a detonation can be initiated in the liquid phase, what sort of environment is necessary to initiate a detonation, and whether the detonation can propagate through a system.

Finally, two-phase mixtures can also undergo detonations differently than single phase liquids and in fact the presence of small bubbles in liquid explosives is of concern because the propagation of a detonation wave can refract around existing bubbles in the liquid and create reinforced pressures that help to propagate a detonation wave. Under some conditions some liquids can propagate detonations better if they contain small amounts of gas bubbles. This is of interest with monopropellants as the normal slow decomposition of a monopropellant produces small amounts of dissolved gases or small bubbles in the propellant. Theoretically one could postulate that a monopropellant could be susceptible to detonations due to the aggravating effect of gas bubbles.

Gas phase hydrogen peroxide, like other monopropellants, can ignite, burn, explode, and detonate. Various efforts have been made to determine the conditions that allow any of the gas phase reactions to occur.

Little no information has been found that addresses two-phase mixtures with hydrogen peroxide and in a sense there is almost always a small amount of dissolved oxygen in hydrogen peroxide so the remaining case of liquids will offer some information for both of these conditions. With regard to liquid phase detonations of hydrogen peroxide, there is some confusion as to whether or not and under what conditions liquid phase hydrogen peroxide does or does not detonate and whether all hydrogen peroxide reactions are detonations or some other explosive reaction.

Much of the confusion regarding this issue revolves around the fact that someone unfamiliar with hydrogen peroxide may classify explosive events (actually pressure induced mechanical failures) or runaway unintended decomposition of hydrogen peroxide as detonations. A mechanical failure or explosion can occur if the pressure exceeds the design margins of a container or plumbing system. A detonation in an energetic material is a reaction front that travels faster than the sound speed in that material. Since the shock pressures are much higher in detonations than simple pressure failure explosions, they can cause substantially more damage. Failure analysis of components or analytical modeling can reveal if the failure was attributed to a simple over-pressure caused by rapid decomposition or a true detonation event. Considering the duration it takes to complete the conversion of hydrogen peroxide to gaseous products, most of the explosive events would be classified as deflagrating reactions and not a true detonation. Given sufficient confinement and a strong shock impulse hydrogen peroxide is detonable. Examples of cited detonation tests for hydrogen peroxide are provided as follows.

Detonation sensitivity and detonation velocities of liquid phase hydrogen peroxide have been investigated in numerous sources. Formal testing for detonation of energetic materials is a well-established practice. Table 8 shows a specific test that created and measured to detonation velocities. Very strong 150 g pentolite charges in 2.5 inch seamless tubing initiated detonations were measured. Table 9 summarizes various other tests for liquid phase detonations. Table 10 provides examples of standard “Card-Gap” impacts tests on various concentrations and temperatures of hydrogen peroxide. The test data indicates that initiated detonations in 99% hydrogen peroxide decreased considerably with distance from the booster⁴⁰ and that detonation speeds decreased with decreasing tube diameter⁴⁰. At diameters less than 1.0 inch, the detonation terminated inside the tube⁴⁰.

In addition to classic liquid phase detonations, another phenomenon termed adiabatic compression reaction is encountered when a two-phase mixture of the propellant moves rapidly through lines or components created localized compression of the gas phase leading to compression heating and thermal ignition or detonation of the gas phase. This can cause local failures of systems and is sometimes considered a “detonation” failure. Historical dynamic pressure load tests have not indicated the ability to initiate this reaction under severe loading. Table 11 summarizes adiabatic compression test data.

Concentration (%)	Temperature (deg. C)	Velocity (m/sec.)
90	30 to 50	5340 to 5510
83	40	5230
86	40	5340
78	70	2180 to 3580

Table 8 - Detonation Velocities of Liquid Hydrogen Peroxide³⁹

H2O2 Concentration	Propellant Temperature (deg. F)	Test Description	Test Result	Reference
90% & 99.5%	160	15 grams #15 Hercomite #2 dynamite in center of 250 lbm of propellant, 604,000,000 ft-lbs/second and 184,000 atmospheres in 17 microseconds	Minor damage to drum	35
98%	Unknown	Detonation initiated in 1.5 inch schedule 80 SS pipe with 1,860,000,000 ft-lbs/second and 576,000 atmospheres in 12.5 microseconds	Detonation initiated in pipe. Pipe was connected to 250 lbm drum. Detonation did not propagate into drum.	35
99%	Unknown	Detonation initiated in 1 inch 0.18 inch wall SS tube.	1 inch tube was connected to 0.5 inch 0.035 inch wall SS tube. Detonation did not propagate into 0.5 inch tube.	35
99%		1 inch ID, 3/16 inch wall, SS, 20 gram tetryl booster	Detonation speeds starting at 7060 m/sec. decreasing to 4715 m/sec. with average of 5590 m/sec. across 1 meter	40
99%		1 inch ID, 3/16 inch wall, SS, 10 gram tetryl booster	No explosion	40
90%		1 inch ID, 3/16 inch wall, SS, 20 gram tetryl booster	No explosion	40
98%	20 deg. C	35 gallon drum with 25 gallons H2O2 plus 2 #20 PPETN, #6 blasting cap inside sch 80 pipe inside drum	No detonation in drum	35
99.5%	160 deg. F	15 g dynamite in center of drum. 15 g dynamite is maximum charge with water that will not rupture drum	Drum bulged.	39
90.5	29 deg. C	304 SS 45.47 mm ID tube	6144 m/sec.	41

Table 9 – Various Detonation Tests with Hydrogen Peroxide

Card Gap Test - Number of Cards Required to Obtain Negative Results

H2O2 Concentration	Ambient Temperature	160 +/- 4 deg. F
90%	0	16
95.5%	7	25
99.5%	9	23
Cavea B-110	12	27

Table 10 - Card Gap Tests with Hydrogen Peroxide³⁵

H2O2 Concentration	Propellant Temperature (deg. F)	Test Description	Test Result	Reference
90% & 98%	70 – 72	Adiabatic compression 231,000 pounds/second	No effect	35
90%	70 – 90	Adiabatic compression 3,000,000 pounds/second	No adverse effect	35
“All concentrations”	Ambient and 160 deg F	230,000 psi/sec adiabatic compression tests	Negative response	39

Table 11 – Hydrogen Peroxide Adiabatic Compression Reaction Tests

Recent testing of hydrogen peroxide in heated tubes⁴² has led to tube failures that have been characterized as detonations. While no analysis has been conducted, we feel it is much more likely that the events were explosions resulting from runaway decomposition of the heated fluid/vapor mixture being evolved in the tube.

Since the decomposition rates are greatly enhanced with temperature, the use of hydrogen peroxide as a coolant has to be approached very carefully. With most fuels, hydrogen peroxide tends to optimize at a high oxidizer to fuel (O/F) ratio. This permits a large amount of the total propellant flow rate to be used as coolant with a corresponding lower propellant temperature rise with regenerative cooling. The Rocketdyne AR2-3 and the Reaction Motors LR-40 operated very successfully using regenerative cooling of the main combustion chamber with 90% hydrogen peroxide¹⁸. If the hydrogen peroxide begins to decompose, the additional energy released will raise the temperature and accelerate the process leading to a runaway condition. The gas pressure can build in a local region until hardware failure results.

Recent demonstrations and analyses of very high material compatibility⁴³ as well as the recent improvements in catalyst bed longevity illustrate the possibility that modern hydrogen peroxide chemistry is more pure than historical propellants and detonation sensitivity may have changed. It would be advantageous to re-test hydrogen peroxide preferably using techniques that are modern and comparable to other shock sensitive materials.

In summary, hydrogen peroxide appears to be insensitive to mechanical impacts and can propagate a liquid phase detonation at concentrations above 90-92% with significant confinement and a strong initiating charge. At concentrations below 90-92% it appears that a detonation is much harder to initiate. Liquid phase hydrogen peroxide detonations are harder to propagate as the line size is reduced. Detonations were unable to propagate through transitions to smaller diameter lines and were unable to propagate into large masses of liquid⁴⁰. Hydrogen peroxide does not seem to suffer from adiabatic compression reactions. Existing test data does not indicate that under typical operating conditions that this reaction occurs. Recent testing in heated tubes may indicate that at elevated temperatures it is possible to create this reaction.

V. H2O2 Catalyst Longevity

With proper operation and fluid use, catalyst beds can operate successfully for time periods well in excess of 1000 seconds. Current test data has not effectively determined the upper bounds for modern catalyst beds operating with modern propellants. The operational lifetime is strongly dependent on the application and the pedigree of the fluid used, but reasonable life can easily be demonstrated with current technology designs and propellant.

A list of currently developed catalyst beds with the demonstrated expected lifetimes is shown in Table 12. The actual lifetimes are probably well in excess of the reported values, however these are the values that have been demonstrated by testing. The degradation of the catalyst is by several mechanisms and these can be generally grouped into three categories:

1) Accumulation of non-volatile materials in the propellant. Chemicals compounds in the propellant that do not become gases will remain behind in the catalyst bed as accumulated deposits. These include stabilizers and general propellant contamination. In general the cleaner the propellant and the lower the stabilizer level, the longer the catalyst will last.

2) De-activation of catalyst by stabilizers. The propellant stabilizers are designed to stop the catalytic action of materials in the propellant and they are quite effective at poisoning catalyst beds. Over long periods of time, these stabilizers will slowly deactivate a catalyst bed.

3) Pressure/thermal stress loads in the catalyst will mechanically damage the catalyst bed internal components creating particles and general degradation that can cause propellant channeling or clogging.

Recent testing of 98% catalyst beds appears to indicate that end of life is possibly quite remote at least for 98% H₂O₂⁴⁴. Testing demonstrated life times in excess of 5000 seconds. Post test examination of the catalyst does not indicate any apparent failure or impending failure and the catalyst bed appears the same as at beginning of life. Rocketdyne has corroborating data with life testing a different 98% catalyst bed configuration^{45,44}.

Another notable example is recent testing done on a 7/8 inch diameter catalyst bed, General Kinetics P/N GK-PD001-201-004. This design was originally qualified and tested for 240 seconds of accumulated life. The development tests were conducted before 1996 using the only available propellant grade hydrogen peroxide at that time which was 85-87% hydrogen peroxide procured from Air Liquide using an Air Liquide specification. Note that this propellant is no longer available. This design had demonstrated end of life by test at approximately 240 seconds. Recently one of the development units for this part number that had accumulated approximately 240 seconds of life (P/N GK-PD001-201-004) was returned to service and tested using 90% H₂O₂ procured in 2006 from FMC using propellant specification MIL-P-16005F. This part has accumulated an *additional* 3000 seconds of life and is not exhibiting any indications that it is approaching end of life, even though this part had already reached “end of life” under a previous test program. Moreover the part has been subjected to deliberate excessive abuse; such as higher than design flow rates, off-nominal (high and low) pressure operation, and operation with hydrogen peroxide concentrations of 30% and 50% concentration (which fully floods the catalyst bed and produces two phase flow throughout the entire catalyst bed).

Note that a part which exhibited end of life behavior at 240 seconds has now operated for an addition of over ten times the previous specification life at off nominal specification conditions and appears to be fully operable and is still being used for research and development work.

It is believed that some of the propellant produced today is superior to that which was produced in the 1996 time period and is likely to be superior to that produced before the 1980's³¹. If that is true, it is possible that unprecedented life times greater than shown in Table 12 and those found in the literature are possible.

Manufacturer	Part Number/Model	H2O2 Concentration (%)	Life time (seconds)
General Kinetics	GK-PD022-201-001	98	> 5000 ⁴⁴
General Kinetics	GK-PD001-201-004	30-90	> 3200
General Kinetics	GK-PD032-201-001	90	> 1000
General Kinetics	GK-PD020-201-001	98	> 1800
General Kinetics	GK-PD023-201-003	90	> 1000
General Kinetics	GK-PD033-201-002	90	> 1000
General Kinetics	GK-PD014-201-001	70-90	> 2500
General Kinetics	GK-ED002-202-001	70	> 6000
General Kinetics	GK-ED001-201-001	70	> 1000
General Kinetics	GK-PD027-201-001	70	> 1000
General Kinetics	GK-PD010-201-001	90	> 1000
General Kinetics	GK-ED008-201-001	85	> 12,500
General Kinetics	GK-ED008-201-002	70	> 58,000
Rocketdyne	NASA-Stennis Test Article	98	10,285 ⁴⁵
Rocketdyne	NASA NRA 8-21	98	5000 ⁴⁴
Aerojet	ISTAR RBCC development	90	900 ⁴⁶

Table 12 - Life Times of Recently Tested Catalyst beds

VI. H2O2 in Space Based and Launch Vehicle Applications

Hydrogen peroxide has been replaced by other chemicals for most space based applications, such as hydrazine and its variants and the blends of nitrogen tetroxide and nitric oxide. Monopropellant hydrazine has a noticeably higher specific impulse than hydrogen peroxide and for long duration spacecraft, the added specific impulse becomes important for maintaining long satellite life. Note that hydrazine has a significantly lower density than hydrogen peroxide but for applications such as spacecraft often the density impulse is less important than the specific impulse. However in the early space program, all monopropellant propulsion systems were hydrogen peroxide. Hydrogen peroxide was used in Syncom, COMSAT, and early Bird spacecraft, the Centaur upperstage, the Mercury Spacecraft, the X-15 rocket plane, the X-1 rocket plane, the D558 X-plane, the NF-104A Aerospace Trainer Plane, the Lunar Landing Simulator, and other U.S. aerospace vehicles. Syncom II demonstrated 6 years of operation from 1963 to 1969 of on-orbit active service and the last known Syncom II longitude was measured in 1995.

As a liquid oxidizer, hydrogen peroxide competed most directly with nitrogen tetroxide and to a lesser extent with liquid oxygen. The selection of nitrogen tetroxide and hydrazines as a standard for storable propellants has made these chemicals heavily invested in the industrial knowledge and supplier base. The selection of nitrogen tetroxide and liquid oxygen as a main oxidizer over hydrogen peroxide occurred in the early 1950's with the development of the Atlas and Titan Intercontinental Ballistic Missiles (ICBM's) and the Thor Intermediate Range Ballistic Missile (IRBM). These systems were heavily interested in performance due to the large size of nuclear warheads at that time. In terms of propellant selection, almost all criteria expect launch system flight performance were sacrificed. These systems used toxic chemicals and even cryogenic chemicals which are not ideally suited for a launch on demand system. Many of the launch systems of today are evolved versions of these early ICBM's: Atlas, Titan and Delta (derived from Thor IRBM). Had the extreme performance requirements of the cold war not been a driving design requirement and an emphasis on cost and operations been more significant, as they are today with the desire for low cost non-weaponized launch systems, the choice of propellants would probably have been different. This idea may be becoming more apparent when observing the private investment in launch systems seems to be trending towards other design solutions that are possibly more driven by cost and operations than performance. Examples of variously privately funded launch systems and their propellant choices are shown in Table 13.

Launch System	Main Propellants
Beal Aerospace BA-1	Hydrogen peroxide – Kerosene
Virgin Galactic, Space Ship Two	Nitrous Oxide – Rubber
SpaceX, Falcon	Liquid Oxygen – Kerosene
Blue Origin, New Shepard	Hydrogen peroxide – Kerosene
Armadillo Aerospace	Liquid oxygen – hydrocarbon fuels
Pioneer Rocketplane	Liquid oxygen – hydrocarbon fuels

Table 13 – Examples of Privately Funded Launch Systems

Numerous other entities are also pursuing the use of various other propulsion schemes for the various Xprizes and other privately funded space businesses. Note that these privately funded systems conspicuously avoid the conventional hypergolic propellants (hydrazines and mixed oxides of nitrogen) and liquid hydrogen, while hydrogen peroxide is well represented.

Hydrogen peroxide had been used extensively in launch systems as a power system fluid particularly for driving turbo-pumps and for a period of time as the propellant for reaction control fluids. The claim that hydrogen peroxide has not been used on launch systems is historically incorrect. England brought the use of hydrogen peroxide as a main propellant to a high level of maturity with the Black Arrow launch system. This technology would have advanced further except that England chose to discontinue its launch vehicle efforts for other reasons. The Black Arrow launch system stopped operating for reasons other than the fact that it used hydrogen peroxide. Had England chosen to continue with its launch vehicle work, hydrogen peroxide would probably be one of the standard propulsion industry propellants today.



Figure 10 – Black Arrow Launch, October 28, 1971

VII. H₂O₂ Toxicity

Hydrogen peroxide is a widely used commercial chemical and is being used more frequently commercially as an alternative to other more toxic chemistries. A detailed discussion of the toxicity and how hydrogen peroxide interacts with humans and the environment shows that hydrogen peroxide is a common and naturally occurring chemical that is very non-toxic⁴⁷.

Hydrogen peroxide does not cause burns per se when it contacts human skin. Hydrogen peroxide is a chemical commonly found in the environment and is manufactured inside the human body as part of normal body metabolism and chemical reactions. Hydrogen peroxide has properties similar to water and can be absorbed into skin like water. The hydrogen peroxide that penetrates into skin quickly reacts with various body chemicals including blood, glutathione, and other compounds and decomposes into water and oxygen. The decomposed hydrogen peroxide forms gas bubbles in the skin surface capillaries creating micro-embolisms which locally block blood flow in the skin causing a lack of blood flow and a change in the skin color from its natural flesh tone to white. Once the oxygen bubbles are absorbed into the body, blood flow returns to the skin and the color returns to normal. Extreme exposure may cause distended gas bubbles in skin and created a feature like a chemical burn. It is important to note that hydrogen peroxide does not produce classic chemical burns that destroy skin or flesh such as seen with nitric acid.

A recent review of hydrogen peroxide with hydrazine⁴⁸ indicates that the toxicity and handling characteristics of hydrogen peroxide are comparable or superior to those of hydrazine. Typically the most dangerous transport mechanism for toxic propellants is inhalation – since hydrogen peroxide has a low vapor pressure it is much less likely to cause tissue damage. A common misunderstanding of hydrogen peroxide is based on the NIOSH limit of 1 ppm. This low level is compared to other chemicals with 1 ppm levels and it is assumed that hydrogen peroxide has a comparable toxicity. The 1 ppm level is based on a conservative assessment of an irritation limit of 10 ppm. Humans are regularly exposed to greater than 1 ppm in some common foods and human breath can exceed 1 ppm from the natural hydrogen peroxide produced inside humans⁴⁷. Hydrogen peroxide has been routinely handled in very large quantities for over 100 years in the commercial industrial community with little evidence of toxicity on industrial workers or surrounding communities.

VIII. Conclusions

Hydrogen peroxide has been historically treated as a fundamentally flawed propellant due to implied properties that render it inherently ill-suited for any reasonable application. This argument is made based upon inadequate information due to a general lack of understanding and familiarity within the professional community regarding the facts pertaining to the propellants and its characteristics. Several key parameters that are commonly invoked in anecdotal data including: Stability and storage; propellant detonations; catalyst bed longevity, space applications, and chemical toxicity. Each of these topics was addressed and referenced data was provided with a summary and notation of specific data. The available data shows that these issues have been successfully managed in the past and are currently being successfully managed today. The general dismissal of hydrogen peroxide as an inherently unsuitable propellant is unreasonable based upon the facts and data available. Recent changes in the propellant manufacturing process suggest that the propellant properties may have improved and that the possibility exists for further improvements if desired. Future work in characterizing the propellant and investigating more stable forms of the propellant are recommended.

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