

Past and Present Uses of Rocket Grade Hydrogen Peroxide

E. Wernimont, M. Ventura, G. Garboden and P. Mullens
General Kinetics, LLC Aliso Viejo, CA 92656

Abstract

Hydrogen peroxide has been used in many applications for propulsion and power in the past 60 years. The general history of hydrogen peroxide and its evolution as a propellant are discussed from first discovery, its first major use during World War II and the subsequent uses after the war. Reasons for the decline in use and the effects on the propulsion community as it struggles to use this unique chemical today.

History of the Chemical

Discovery[1]

Hydrogen peroxide was discovered by Louis-Jacques Thenard in July, 1818 and was described as an “oxygenated water”. While other chemists had produced H₂O₂ at approximately the same time as Thenard, he was the first to identify it and to define a procedure to manufacture it. Figure 1 depicts the bust of Thenard. He is honored with a street named after him in the Latin Quarter of Paris as seen pictured with one of the authors (figure 2).

The basic genesis of his discovery was started by a task directed by Napoleon to work on the development of batteries. Through the course of this electro-chemical work he became familiar with alkali metal chemistry. While he was experimenting with alkali metals he found that a reaction between barium peroxide and nitric acid formed hydrogen peroxide.

He investigated various techniques and found that several acids and other alkali metal peroxides would also form hydrogen peroxide. He eventually converged on using hydrochloric acid and barium peroxide because these materials lent themselves to the preparation of higher purity hydrogen peroxide.

The basic process was to heat barium nitrate and drive off the nitrogen forming barium oxide. The

barium oxide was then heated and exposed to oxygen gas, forming barium peroxide. This material was then dissolved in hydrochloric acid, which then forms hydrogen peroxide. Sulfuric acid is then added which precipitates out barium sulfate and regenerates hydrochloric acid.

The formation of barium peroxide and precipitation of barium sulfate is repeated to enrich the solution to ~33% H₂O₂. Various other reactions and separation processes are then performed to remove the impurities and the hydrochloric acid.

Thenard then concentrated the 33% H₂O₂ by pulling a vacuum for extended periods of time. Thenard was able to essentially make anhydrous hydrogen peroxide. Thenard characterized the reactivity of peroxide with many materials and was able to distinguish the difference between materials that participated in the reaction (reactants) versus materials that were unchanged by the reaction (catalysts). This was a very early observation of the then unknown mechanism of catalysis, which was later clarified by other scientist.

Thenard attempted to find applications for peroxide and it was initially used for medicinal purposes (external irritant) and as bleach for the restoration of paintings.

Early Manufacture

After Thenard’s discovery, several techniques and processes for the production of hydrogen peroxide were proposed. Some were impossible, while others were impractical. In 1832, a variant of Thenard’s barium peroxide process used flourosilic acid instead of hydrochloric acid, which automatically precipitated barium flourosilicate, thereby simplifying the overall process. This variant process became the first “mass produced” process for hydrogen peroxide. The barium peroxide process was a batch process and required skill in controlling the reactants. Figure 3 depicts an early H₂O₂ manufacturing plant.

Hydrogen peroxide was first manufactured for sale circa 1867 to 1869 at 3% concentration. Manufacture and sale in the United States started circa 1878. It appears that the larger volume industrial production of hydrogen peroxide started in ~ 1880 with a factory in Brooklyn New York (USA) and at Shipley, Yorkshire (England). The English company was Bernard Laporte, the predecessor of now modern day Solvay Interlox. Industrial production has continued from that date until present. LaPorte began making 27.5% in 1923 [2] and later developed the electrolytic process to produce high quality 35% H₂O₂ shortly after WWII. The price of the chemical varied greatly and Schumb provides an interesting history of the price for hydrogen peroxide (see table 1).

Date	Price (\$/lbm)	Concentration	\$/ lbm H ₂ O ₂
1874	5	3	166.67
1876	1	3	33.33
1879	2	0.8	250.00
1878	0.02	3	0.67
1902	0.04	3	1.33
1909	0.09	3	3.00
1924	0.36	27.5	1.31
1927	0.3	27.5	1.09
1940	0.2	27.5	0.73
1945	0.15	27.5	0.55
1950	0.2	27.5	0.73

Table 1 - Early History of H₂O₂ Prices [1]

Production began to increase quickly after 1925 when H₂O₂ found use in the textile industry.

In the US, production started in 1881 and by 1912 there over 100 manufacturers of hydrogen peroxide using the barium peroxide process. A significant event at this time was the purchase of Barium Products, Modesto, CA by a precursor company of FMC.

Another significant event was the beginning of electrolytic H₂O₂ manufacturing by the Roessler and Hasslacher Chemical Company and the Buffalo Electro-Chemical Company (Becco), both in Niagara Falls, NY. Becco was subsequently acquired by FMC (circa late 1950's) and the electrolytic Becco H₂O₂ was the work horse propellant for the U.S. in the 1950's and 1960's. The electrolytic process is dependent on low cost electricity and electrolytic H₂O₂ plants were located near sources of low cost electrical suppliers (i.e. Niagara Falls). Roessler and Hassalacher were later acquired by DuPont.

The strength of the hydrogen peroxide industrial

economy was eventually founded on its use as an industrial chemical, primarily by the paper pulp and textile industries.

Rocket Propellant

The first major exploitation of hydrogen peroxide as a working fluid for propellant application is attributed to Hellmuth Walter. Walter created a company in 1935 to use 80% hydrogen peroxide as a propellant (at that time the highest concentration ever made in practical quantities). He started with submarine turbine drive systems and assisted take-off units (ATO's, also known as JATO's or RATO's).

During the first large scale U.S. propellant utilization of hydrogen peroxide in the 1940's to 1960's three manufacturing process predominated: electrolytic, anthroquinone, and oxidation of propane or propane derivatives (for example isopropyl alcohol). These processes were used in sufficient industrial capacity to produce large quantities of the chemical for both commercial and propellant grade uses. Each process was nominally associated with a supplier, however each chemical manufacturer also produced H₂O₂ with one or more of the established three processes.

The electrolytic process was primarily Becco/FMC, the anthroquinone process was primarily DuPont, and isopropyl-alcohol oxidation process was primarily Shell.

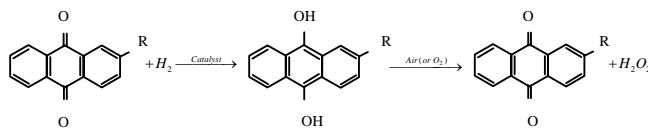
Electrolytic Process[1]

The electrolytic process is an inorganic electrochemical reaction, which involves the use of peroxydisulfuric compounds. One example is the method for which the basic reaction is:

- 1) H₂S₂O₈ + H₂O → H₂SO₅ + H₂SO₄
- 2) H₂SO₅ + H₂O → H₂SO₄ + H₂O₂

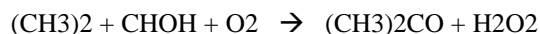
Anthroquinone Process[1]

The anthroquinone process is an organic chemical reaction where an organic compound (anthroquinone) is catalytically reacted with hydrogen. The catalyst is then separated from the reduced anthroquinone molecule, and the compound is oxidized (typically with air) producing hydrogen peroxide and regenerating the anthroquinone molecule. The basic reaction for this process is shown below:



Oxidation of Propane/Propane Derivative[1]

This process is another organic chemical reaction that basically oxidizes propane or a propane derivative, such as isopropyl alcohol, yielding hydrogen peroxide. As an example the isopropyl alcohol reaction is shown below:



All of these processes produce hydrogen peroxide in concentrations of ~30%. For rocket propellant applications, further concentration and purification are required.

Both concentration and some purification can be accomplished by rectified distillation. This is done under a vacuum to lower the operating temperature of the rectification columns to minimize the risk of decomposition of the hydrogen peroxide vapors. Distillation is practically limited to concentrations of approximately 85% to 90%. Safety and liability concerns determine how a hydrogen peroxide supplier will operate their distillation columns.

In order to achieve concentrations above 90 to 92%, different processes are needed to ensure safety and maintain purity. The most common technique for concentration peroxide above to 92% (for example 95% to 98%) has been by fractional crystallization. An example of a fractional crystallization device is shown in figure 4. Fractional crystallization is not currently in use for hydrogen peroxide, however it was used in the 1960's to produce limited bulk quantities of propellant grade material during the peak of hydrogen peroxide usage. An interesting note is the quote from ref. 3 that states: "In 1955, the Becco Chemical Division announced the availability of tonnage quantities of hydrogen peroxide in concentrations up to 99.7% H₂O₂ or virtually anhydrous hydrogen peroxide."

Although Dupont and Shell both supplied 90% hydrogen peroxide for rocket applications FMC's (Becco) electrolytic process came to dominate the market prior to declining demand in the mid 1980's. As hydrogen peroxide fell out of use as a rocket propellant in the 1970's-80's the electrolytic manufacturing method (and others) eventually were replaced by the now dominate method of anthroquinone for purely economic reasons.

When interest in hydrogen peroxide derived propulsion was restarted in the early 1990's there was no source of hydrogen peroxide over 70%. As a consequence of this groups interested in rocket applications at that time either raided the remains of

the old military stockpiles, generated their own small quantities from lower concentrations (i.e. 50%, 70%) or worked with electronic grade 70% (high purity). As the amount of present day investigators increased so did the demand and the chemical manufacturers began to sell concentrated hydrogen peroxide in small quantities. At present there is no chemical manufacturer making >90% H₂O₂. The industry currently provides the following concentrations:

- Solvay Interlox 70% and 85% (85% quantity available dependent upon lot size).
- Degussa 89.5%
- FMC 70%, near term potential for 90%.
- Air Liquid recently made 85% but stopped production in ~ 8/98.

A few small secondary concentration companies have advertised > 90% H₂O₂, however a steady supply of reliable propellant is not yet available.

History of H₂O₂ Power Applications

Germany WWII – Rockets and ATOs [3,4]

The German government developed relatively safe concentrations of 80 to 82% H₂O₂ during the period from 1933 to approximately 1936. Based upon the availability of the new propellant, Walter began his own business of hydrogen peroxide combustion devices in 1935 (Walterwerke), and by 1936 had a 2200 lbf ATO engine and a 400 hp submarine turbine driven by hydrogen peroxide (T-Stoff) and liquid injection of permanganate catalyst (Z-Stoff).

Walter's first product was an ATO for the Heinkel He 176, first flown in 1938. This device used 80% H₂O₂ catalyzed with liquid injection of permanganate salts. In order to increase the performance of the ATO and other rocket engines currently in work, Walter developed a hypergolic liquid fuel made from hydrazine hydrate and methyl alcohol (C-Stoff). This was used in the Walter 105-509 engine, which powered the Messerschmidt Me 163B Komet rocket plane. The German ATO application and the Me 163 would have a significant effect on later U.K. development efforts. Figure 5 shows two of these ATO's and figure 6 shows a photo of the ME163.

The ME163 vehicle had a revolutionary impact on how war was fought, however the limitations of the technology only allowed the Komet to be

deployed near sites to be defended and was fraught with problems typically associated with new rocket propulsion systems. In the greater scheme of the war, it was more of a novelty and did not influence the final outcome.

One of the most important historical applications of hydrogen peroxide by Germany was the V-2 turbo-pump gas generator. This application brought H₂O₂ into the common use in rocket propulsion systems after WWII. The V-2 preeminence as the state of the art in high performance rockets was an important starting point for the majority of rocket propulsion activities that followed afterwards. The V-2 used liquid injection of catalyst (potassium permanganate solution) with 80% H₂O₂. Figure 7 shows the schematic of the V-2 powerplant.

The Walter business also produced one of the most used hydrogen peroxide devices of the war, the V-1 catapult. This device was a simple “cold” device operating on liquid/liquid injection of 80-85% H₂O₂ and water with liquid catalyst. Several hundred of these were manufactured during the war and each saw several thousands of repeat uses.

Germany WWII – Sub & Torpedo [1,5]

Historically one can define the first proposed propulsion and power application of H₂O₂ as a propellant for submarines (proposed by Hellmuth Walter in 1933). This was used to start the development of H₂O₂ powered submarines. A 400 hp turbine driven by hydrogen peroxide with liquid injection of permanganate salt solution catalyst was quickly developed. Figure 8 depicts a simplistic schematic of a submarine H₂O₂ propulsion system.

Another significant application was the Type 18-X 300-ton class submarines, which burned H₂O₂ with kerosene. Fig 9 shows a photo of one of the submarines powered by hydrogen peroxide, which was not available for service until late in 1944.

A natural parallel application to the submarine was the torpedo. Germany also began the development of torpedo propulsion and deployed several devices. Figure 10 shows an H₂O₂ propulsion system schematic for a torpedo. [6]

**Post WWII to Mid 1980’s
United Kingdom [7-15]**

England received significant influence from the Walter ATO’s and the Walter 105-509 rocket engine. Initially the English used 80% propellant taken from Germany, but later developed a more pure and high concentration peroxide (85%) manufactured by LaPorte (now Solvay Interox). The German engines were used as the initial design points to make the U.K. Sprite (a monopropellant

RATO) by de Havilland Engine Co., and later a bi-propellant RATO using kerosene called the Super Sprite. The performance parameters of these motors are shown in Table 2.

ENGINE		SPRITE	SUPER SPRITE
Mode		Mono-Propellant	Bi-Propellant
Peroxide Strength	%	80-85	82-86
Peroxide Mass Flow	lbm/s	33.0	20.0
Fuel		None	Kerosene
Fuel Mass Flow	lbm/s	None	1.0
Length	inches	84.25	117.25
Diameter	inches	20	20.25
Mass, Dry	lbm/s	350	620
Mass, Loaded	lbm/s	925	1,460
Maximum Thrust	lbf	5,000	4,200
Burning Time	s	16	40

RATP Motors Developed by the de Havilland Engine Company

Table 2 - U.K. Sprite and Super Sprite Performance Parameters [14]

In 1952, the UK started the development of the Spectre HTP/kerosene aircraft rocket engine for the Saunter Roe SR53 aircraft [15]. A back-up system to the Spectre was also started based upon some rocket engine component development projects currently in work and another rocket engine was developed designated the Gamma 2.

The Gamma 2 evolved into the Gamma 201, and in 1957, was used by Saunders Roe in the Black Knight launch vehicle. Notably, the engine development fired 2089 tests with 354 tests on complete engine assemblies.

In addition, England would pursue hydrogen peroxide for applications in aircraft rocket assist systems, submarine propulsion, and torpedo’s (see ref. 16 and ref. 6 for the U.K Fancy torpedo). The pinnacle of English use of hydrogen peroxide was the Black Knight and Black Arrow programs.

Black Knight- Black Arrow

Black Knight was one of most successful hydrogen peroxide launch platforms and the engine technology is probably the highest performing hydrogen peroxide engine ever put into production.

The vehicle development started in July 1955 by the Armstrong Siddeley Motors (the rocket engines were later to be acquired by Rolls Royce and even had some temporary ownership by the British government). Black Knight was a one-stage vehicle with a Gross Lift Off Mass (GLOW) of approximately 13,700 lbm [8]. Figure 11 shows the basic configuration of Black Knight.

The Black Knight main engines were four Gamma 201 motors. Each combustion device provided ~4000 lbf of thrust, approximately 16,000 lbf of total vehicle thrust. The motor was a pump fed regeneratively cooled gas generator cycle engine. All of the hydrogen peroxide was pre-decomposed in a silver screen catalyst bed and the hot gases were then after-burned with kerosene at a mixture ratio of 8:1.

A later upgrade to the Gamma 201 was the Gamma 301 (the Stentor engine). This engine was later used on Black Knights and increased the thrust level from 16,000 lbf to 21,600 lbf. The 301 was the similar to the 201, except that the a single set of turbo-machinery provided propellant to four combustion chambers, and an improved nozzle was used for better life and performance. A detailed discussion of these engines are in ref. 12. The basic engine layout of the Gamma 201 is shown in figure 12. Black Knight was launched 22 times from its Woomera facility in Australia from 1958 to 1965.

Larger next generation vehicles named Black Arrow, Blue Streak, and Black Prince were pursued as conceptual designs. Black Prince proved to be an overly ambitious project and unfortunately only Black Arrow was developed as a compromise. The Black Arrow was a three stage designed powered by the Gamma 301. Eight 301s were used on stage I with a total thrust of ~32k lbf. Stage II used 2 Gamma 301s and stage III was a small apogee motor. Only five Black Arrow vehicles were ever built with the fourth flight successfully lofting a British satellite on Oct. 28, 19971 (see figure 13). The fourth and final Black Arrow is on display at the science museum in Kensington. [17]

Black Prince would have been a Thor like vehicle, with three stages. Stage one would use 4 combustors based upon the Stentor engine. The second stage would have used a Gamma 304, and the third stage would have used a four-barrel version of the PR 37. Black Prince would have provided the capability to launch small payloads (1750 lbf) into polar low earth orbit. Note that today this could have been a very attractive vehicle for small commercial and scientific payloads, as well as a few defense missions. Figure 14 shows the vehicle layout for Black Prince.

Numerous rocket engines were developed as a

part of this activity. Derivative engines such as the PR 37 and BS 605 were created as aircraft rocket engines. Table 3 summarizes some of these engines.

Table 3 - Various U.K. H2O2 Rocket Engines [14]

*Post WWII to Mid 1980's
United States - Monopropellant*

The United States initiated a very aggressive space program after WWII in two basic areas: cold war military build-up and civilian space exploration. These efforts produced several H2O2 combustion devices and some deployed systems that were based on H2O2.

Reaction Control Systems [18,19]

A heavily utilized area of H2O2 propulsion was as a Reaction Control System (RCS) monopropellant thruster. H2O2 was basically the first monopropellant and was used on many of the early spacecraft and high altitude X-vehicles. It later would be replaced by hydrazine when the technical issues for that monopropellant were resolved. Table 4 shows some of the diverse uses of H2O2 as a RCS propellant. Some of the more notable RCS systems were the X-1 and the X-15.

RCS Thrusters
X-1
Centaur RCS
Centaur propellant settling
X-15
Mercury
Scout Roll Control
Little Joe II
Burner II
SATAR
122Y
Astronaut Maneuvering Unit
SYNCOM
COMSAT
HS 303A
ATS

Table 4 - Various RCS Thruster Applications

The X-1 RCS used 90% H2O2 thrusters made by Bell Aircraft Co. The thrusters operated across the range of 5 to 75 lbf with specific impulses of 104

ENGINE	OXIDIZER STRENGTH (%)	FUEL	FEED SYSTEM	FLOW RATE		CHAMBER PRESSURE (lbf/in^2)
				OXIDIZER (lbm/s)	FUEL (lbm/s)	
Alpha*	80	C	Pressure	3.03	1.09	270
Beta I	80-85	Kerosene	TP	6.1	3.4	250
Beta II	80-85	Kerosene	TP	8.7	4.9	320
KP 1	80	Kerosene	Pressure	16.62	1.51	260
KP 3*	83-86	Kerosene	Pressure	14.49	1.61	300
Gamma**	83-87	Kerosene	TP	34.96	4.24	465
Gamma 201	80-85	Kerosene	TP	34.8	4.4	450
Gamma 2	80-85	Kerosene	TP	51.9	6.3	450
Spectre	83-87	Kerosene	TP	35.1	3.9	500
LARCH	85	Kerosene	***	26.74	3.47	1,000

* Initial Values Quoted
 ** Original Westcott Engine
 *** were with Pressurized Propellant Delivery Only

(20 lbf, and 118 (42 lbf). Figure 15 shows the X-1 RCS system installation location.

The X-15 used H₂O₂ for attitude control with 4 pairs of 90% H₂O₂ mono-propellant rocket engines (a total of eight engines). Figure 16 shows the relative location of the H₂O₂ subs-systems inside the vehicle.

Gas generators - Turbo-Pumps [20,16]

H₂O₂ has been used in many vehicles as a working fluid to drive turbines. This application is traceable to the first significant application as the V-2 turbo-pump drive gas. It was one of Werner Von Braun's favorite turbo-pump drive gas and has been found in Von Braun's sketches of Mars space planes. Table 5 shows some of the many uses of H₂O₂ as a turbo-pump drive gas.

Description	Device Type
Type 18-X submarine, Germany WWII	300 ton class H ₂ O ₂ -kersosene turbine drive
V-2 turbo-pump gas	Liquid injection of catalyst
V-1 catapult	Liquid injection of catalyst
X-1 turbo-pump gas	Mono-propellant gas generator
Redstone turbo-pump gas	Pellet bed mono-propellant gas
Jupiter turbo-pump gas	Pellet bed mono-propellant gas
Centaur boost pump gas	Mono-propellant gas generator
Viking turbo-pump gas gen.	Mono-propellant gas generator
X-15 turbo-pump gas gen.	Mono-propellant gas generator
Mk 16 torpedo	70% H ₂ O ₂
X-1 mini submarine	Mono-propellant gas generator
GE hybrid	H ₂ O ₂ -PE hybrid
GE plug nozzle	Mono-propellant thrusters
Hyprox system	Mono-propellant gas generator for

Table 5 - Turbo-pump Gas Generator Applications

It is important to note that H₂O₂ is an attractive turbo-pump drive gas because the decomposition

gas temperature is relatively close to the physical limits for uncooled turbine blades and the hot gas temperature can be controlled by varying the amount of water in the peroxide solution. This allows the turbine hot gas temperature to be adjusted to fit the design.

H₂O₂ was the most common source for hot gas to drive turbo-pumps and was used on the Redstone, Jupiter, and Viking launch platforms. Unlike the V-2, the Redstone turbo-pump gas generator (76%) used silicon carbide pellets with impregnated calcium permanganate. These pellets or "stones" produce many of the problems that are endemic with ceramic catalyst by fracturing and producing small particle fines.

Gas Generator - Vacuum Aspiration [21]

A less well known but very useful application of H₂O₂ is to generate large volumes of steam in a very short period of time to aspirate large vacuums.

In the past, H₂O₂ was used to create vacuums with the Thiokol Hyprox system, which was installed in many test facilities and were used with great success.

Figure 17 shows a schematic of the Thiokol Hyprox system and figure 18 shows the relative difference between a conventional steam boiler and a H₂O₂ gas generator.

Rocket Personnel Flying Belts

A very well known application of H₂O₂ was the manned flying belt originally built by Bell. This device provided the capability to loft and fly a human for short periods of time (approximately 30 seconds) by rocket power. The belt was originally conceived as a weapon platform for the U.S. Army but was never used beyond simple field tests. The belt was later replicated and modified and used as a publicity stunt device for the general public.

Other Applications

H₂O₂ has also been used for other aerospace and defense applications that have not attained sustained usage, but are worth noting for their novelty. Table 6 lists some of the more interesting applications of H₂O₂.

Description	Device Type
Man-Heater for Artic Use	Mono-propellant gas generator for thermal energy
Bell Rocket Belt	Mono-propellant thrusters
Lunar Lander Simulator	Mono-propellant thrusters
Decontamination of N2H2 spills	Chemical reaction
Mine sweeping by detonation	Chemical reaction
Rocket on Rotor	Mono-propellant thrusters
Nose Cone Test	Mono-propellant gas generator

Table 6 - Non-Conventional Applications of H2O2

Post WWII to Mid 1980's

United States – Bi-Prop and Hybrid Engines

Little known is that immediately after the war General Electric (Malta Test Operations) experimented with hydrogen peroxide as a mono-propellant (the first major work on aerospike nozzles was with 90% monoprop thrusters at 16k lbf), as an oxidizer for hybrids and as an oxidizer for liquid bi-propellants (JP4, 5-10k lbf class). This work continued until the mid 1950's. The work on hydrogen peroxide hybrids is still the most extensive experimentation in that field. Polyethylene hybrids up to 20k lbf class were fired and over 500 hybrids total were fired in this time frame. Figure 19 shows a typical GE H2O2 - PE hybrid. [22,23]

H2O2 had a relatively small usage as a bi-propellant oxidizer in the late 1950's and was essentially traded out of usage by liquid oxygen and nitrogen tetroxide.

In the mid to late 1950's the U.S. armed forces were becoming involved in the Korean War and a distinct need was found to provide higher thrust performance for U.S. military aircraft. This issue was initially pursued by the U.S. Air Force by developing the AR family of aircraft rocket engines. These engines were developed by Rocketdyne and use 90% H2O2 and aviation kerosene. In general a series of engines were made with the prefix AR: AR-1, AR-2, AR-3, and AR-4. The culmination of this effort was the deployment of the AR2-3, a roughly 6000 lbf pump fed regeneratively cooled reusable rocket engine. The AR-3 and AR-4 were larger higher performing versions of the AR2, which never advanced to qualified production status. It is worth noting that the AR2-3 engine was truly designed for re-usability and had an impressive record for ease of operations, long life, and multiple uses.

Slightly later and generally in parallel, the U.S. Navy began the development of a similar engine

designated the LR-40 (see figure 23), by Reaction Motors Inc. This engine was also to be used for aircraft rocket engines and also used 90% and aviation kerosene. The engine was basically identical in terms of functional requirements to the AR2-3, however it employed more a more advanced closed loop cycle called "topping." The LR-40 can be credited as the first or one of the first staged combustion engine cycles ever developed by the U.S. The LR-40 was never put into production due to a combination of an untimely accident and the elimination of a need for this type of propulsion.

Unfortunately for both the AR2-3 and the LR-40, improvements in aircraft engines performance and air to air missiles capability made aircraft rocket engines obsolete. This type of rocket engine would not be pursued any further and the advancement of the high performance pump fed H2O2 rocket engine cycle would end in the U.S.

An interesting foot note is found in ref. 16 which states that BuAer (the U.S. Navy) consumed seven million pounds of 90% H2O2 from 1956 to 1958 BuAer. This is believed by the authors to have been related to the development of the LR-40 and other H2O2 devices by RMI.

After WWII, the U.S and U.K. also began using H2O2 for torpedoes. The U.S. Navy in particular was a fairly heavy user of H2O2 and probably used H2O2 longer than any other organization in the U.S. H2O2 was used in the MK 16 torpedo (70%) released in 1955 and the X-1 mini-submarine [16].

Post WWII to Mid 1980's

Soviet Union

The authors are aware that significant work was performed by the Soviet Union with hydrogen peroxide rocket propulsion and that hydrogen peroxide is still used by some systems. This information is not readily available to the author's and as such is not covered in this paper. This is not intended as an oversight, but is due to lack of information.

Reduced Usage in 1970's and 1980's

The superior performance of hydrazine displaced H2O2 from spacecraft RCS applications and many gas generator applications. Utilization of hydrazine required the development of an effective catalyst, refinement of the propellant manufacturing processes, and the engineering research to define the proper materials and design features that make hydrazine systems perform reliably. Once these issues were addressed, the high performance of hydrazine allowed an easy trade against H2O2.

From the 1960's to 1980's, performance was much more important than issues such as operations costs, environmental issues, and toxicity.

In a like manner for bi-propellant applications, liquid oxygen provided higher performance and many of the launch platforms, which were also very performance driven, selected propellants based upon mass. The last remaining foothold for H₂O₂ propulsion was non-cryogenic bi-propellant rocket engine systems and in this arena, the successful development of NTO and hydrazine hypergolic reactions provided an acceptable system for military applications. This series of design decision basically rendered H₂O₂ less useful and systems employing it were slowly phased out.

H₂O₂ then was only used in niche applications that could not tolerate these other propellants, such as the extreme confinement of submarines for torpedo propulsion. Eventually H₂O₂ would become an unused propellant in the U.S. by the end of the 1980's. In this environment, many of the propellant suppliers stopped manufacturing the propellant and converted assets to other work or discontinued the production work altogether.

The last significant propulsion application of this type of catalyst in the U.S. was the Scout Roll Control thrusters. The Scout production was stopped in 1982 but the last flight didn't occur until 1994. [24]

Present Usage 1990's

Re-evaluation

Hydrogen peroxide has seen a great deal of renewed interest for production of power and propulsion. There are many reasons why this is true and these reasons are also why it was previously used. The major reasons it has seen increased interest are its minimal environmental impact and simplicity of handling both of which drive toward lower costs. The major advantages hydrogen peroxide enjoys will be discussed in the subsequent sections. (Properties where provided are from ref. 25)

High density

H₂O₂ has a very high density at approximately 87.5 lbm/cu. Ft. for 87% H₂O₂ at room temperature. H₂O₂ has a comparable density to nitric acid and nitrogen tetroxide and is significantly more dense than liquid oxygen. The high density lowers the volume and dry mass of the oxidizer propellant tank, thereby providing higher density specific impulse, a higher mass fraction, or a higher density impulse. This is attractive to systems that

have aerodynamic drag losses or are severely volume constrained.

Storable propellant

Hydrogen peroxide is a liquid at room temperature and can be stored for extended periods of time in properly designed tanks. This feature is attractive for weapon systems, systems that remain in space for extended periods of time, and systems that need less time constraints than are imposed by cryogenics.

Non-toxic

The term "toxic" is generally used to describe chemicals that are carcinogenic, are poisonous in small quantities to humans, or can be easily exposed to humans with lethal effects. H₂O₂ is considered "non-toxic" because it's effects on humans are comparable or much less than other propellants, because the human body naturally decomposes H₂O₂, and because propellant grade H₂O₂ is very difficult to introduce into the human body under reasonable working conditions. The last feature is the most useful for ease of handling.

H₂O₂ cannot easily enter the human body because it has a very low vapor pressure, which significantly reduces the amount of chemical vapor above an exposed liquid surface. An open container of H₂O₂ at room temperature in a reasonably ventilated area does not produce a lethal exposure to H₂O₂. In comparison with the most common storable oxidizer, NTO, the difference is extraordinary. NTO produces fumes at a great rate (the vapor pressure at room temperature of NTO is approximately 12 psia) and the vapors are extremely toxic with exposure and ingestion by inhalation imposing a very real hazard.

The human body is also able to decompose H₂O₂ and in fact human respiration produces H₂O₂ naturally. The human body has its own catalysts to eliminate it from the body (i.e. catalase) and in general most human fluids and tissues are catalytic with H₂O₂. This is a well known by children that use 3% H₂O₂ to make their mouths foam on Halloween.

Non-Reactive with the Atmosphere

It is not well appreciated, but hydrogen peroxide does not chemically react with the elements or compounds of the atmosphere. This is important for applications where H₂O₂ components may be exposed to the atmosphere during operation. An example of this is an RCS thruster on a re-usable space plane.

In this application, the atmosphere can enter into the thruster nozzle during entry when the system is re-pressurized during descent. In general this does not pose a problem for H₂O₂ systems.

However, this condition may create a potential problem if hydrazine is used, because hydrazine chemically reacts with carbon dioxide forming other compounds. These compounds can attack materials inside the thruster. Other conditions can also introduce carbon dioxide into hydrazine systems, such as propellant handling and servicing. The reaction of hydrazine with atmospheric carbon dioxide is a constant concern and a well-known problem with the hydrazine systems on the Space Shuttle.

High Oxidizer to Fuel Ratios

In general, H₂O₂ always optimizes to a relatively high O/F ratio (i.e. ~8 for 85% and kerosene) in comparison to other oxidizers using the same fuel. This is attractive because H₂O₂ has a high density and that leads to a large bulk of the propellant mass having a high density, thereby shrinking the overall system propellant storage (tank) mass. This means that H₂O₂ systems enjoy inherently high mass fractions in comparison to other oxidizers.

Low Vapor Pressure

The very low vapor pressure of H₂O₂ has a feature that has not been well exploited to date. In comparison with other liquid oxidizers, such as NTO and liquid oxygen, H₂O₂ has a vapor pressure that is 1-2 orders of magnitude lower. This permits turbo-machinery to operate with lower inlet pressures, which cascades into lower oxidizer tank mass.

High Specific Heat

H₂O₂ has a very high specific heat and in general can be compared with water. This feature, combined with the high O/F ratios that most H₂O₂ system will have, begs the question that H₂O₂ should be used as a coolant, such as regeneratively cooled nozzle. The cooling capabilities of H₂O₂ can be significantly greater than can be achieved with other propellants, which can simplify the cooling problem and potentially the cooling design. This aspect was used in three high performance pump fed rocket engines: the Rocketdyne AR2-3, the Reaction Motors LR-40, and the Armstrong-Siddeley Gamma 201/301.

Capability to Use Water as a Referee Fluid

H₂O₂ can easily use water as a referee fluid. This is a great benefit for system development,

acceptance, and qualification. Usable referee fluids can sometimes be almost as troublesome as the propellant itself. A good example is when liquid neon is used as a referee fluid for liquid hydrogen. A common referee fluid for NTO/MMH propellants are isopropyl alcohol and Freon. Water is clearly easier to use than these.

This aspect was exploited by Germany in WWII by developing and qualifying systems entirely with water prior to deployment.

Integrated Propulsion and Power Usage

Systems that use H₂O₂ for one application, have the option to use it for others. For example, an upper stage could use H₂O₂ as a main engine oxidizer, for RCS monopropellant thrusters, as a gas generator to drive turbo-pumps, and for liquid injection thrust vector control. More exotic systems could even use H₂O₂ for oxidizer tank, or even fuel tank, pressurization.

Present Usage 1990's Monopropellant Applications

Chemical Laser Vacuum Aspiration Systems

It is the authors' position that the industry leader for utilization of H₂O₂ as a working fluid are chemical laser vacuum aspiration systems. These systems are being developed by the U.S. Army (Tactical High Energy Laser) and the U.S. Air Force (Air Born Laser). All other users of H₂O₂ are in comparison at a lesser stage of development. It is highly probable that the first deployment of H₂O₂ in a major aerospace/defense application will be one of these two chemical laser weapons systems. The H₂O₂ sub-systems of these laser systems are being built by TRW.

Spacecraft Reaction Control [26]

The Lawrence Livermore National Laboratory has been pursuing very small propulsion systems, typically with higher performance hot gas pressurization systems.

The application of these micro-propulsion systems has been underway with H₂O₂ for over 5 years. An illustration of one of these test beds is shown in figure 20.

This spacecraft test bed uses 6 lbf monopropellant thrusters and a small gas generator for the H₂O₂ tank hot gas pressurization. The thruster and gas generator both operate on 85% hydrogen peroxide.

Rocket on Rotor Tip Thrusters

The Rotary Rocket Company has identified H₂O₂ as a potential propellant to be used for tip thrusters for helicopter propulsion for part of the system

operation. While this may not be used on the deployed Roton vehicle, it is used on the current test vehicle for Roton.

Present Usage 1990's Bi-propellant Applications

Orbital Sciences Corporation [27]

The Orbital Sciences Corp. (OSC) is currently performing research and development of a 10,000 lbf bi-propellant rocket engine to be used on the NASA funded Upper Stage Flight Experiment (USFE). This engine is a pressure fed ablative chamber. Qualification testing is expected to begin in the summer of 2000. Figure 21 shows a schematic of this engine.

Rocketdyne

Rocketdyne is responding to the resurgence of H₂O₂ as a propellant by re-starting use of the AR2-3 rocket engine. This engine which was used in experimental aircraft flight tests, is a pump fed regeneratively cooled, man-rated re-usable rocket engine.

Rocketdyne has acquired some engines and engine components from the original production build and is intending to re-furbish and use the engines on the Boeing Future-X vehicle. This engine is intended to be hot fire tested in the fall of 1999.

Beal Aerospace

A private entrepreneurial company, Beal Aerospace, is currently developing an Atlas class launch vehicle using H₂O₂ and kerosene. This platform will have three stages, all of which will be pressure fed, have composite structure, and ablative chambers. Full scale development tests of the third stage engine have been performed. This application would be by far the largest H₂O₂ system ever made. Beal currently intends to deploy this system in approximately 2001 and is targeting commercial payloads.

Naval Air Warfare Center (NAWC)/Purdue U. [28]

The NAWC and more recently Purdue University have been conducting research and development work with H₂O₂ and in particular "hypergolic" fuel formulations. This work has historic precedence to non-toxic hypergolic propellant research that is documented in 1959. Most of this work has been focused on experimenting with various additives for conventional fuels, such as kerosene or alcohol, which are "non-toxic" and permit hypergolic style combustion of H₂O₂ with a liquid fuel.

Hybrid Rocket Research

Purdue University, the U.S. Air Force Academy, and the University at Surrey have been conducting research on H₂O₂ combustion devices (catalyst beds, hybrid rocket engines, and hypergolic fuel formulations) since 1991. This research has resulted in numerous publications and has provided a continuing contribution of scientific knowledge on H₂O₂ combustion to the propulsion community.

Synopsis of Production Decomposition Methods

From the time of hydrogen peroxide's discovery many methods have been developed to decompose it catalytically. A few of these methods have been successful and robust enough to find themselves in production items, which have been fielded. During WWII the Germans employed three main methods of decomposition: Liquid/liquid (hypergolic fuel), liquid/liquid (permanganate catalyst water solution) and pellets (permanganate based). After the war the UK worked almost exclusively with a silver based wire catalyst. In the United States early use was with a permanganate pellet catalyst much like those used in Germany had but eventually went to a silver based wire catalyst. There were several manufacturers of silver based wire catalyst of which the major vendors were: Becco (FMC), Reaction Motors, Rocketdyne, Bell and Walter-Kiddie. Figure 22 illustrates a typical silver based wire catalyst bed from this time period. Presently there is only one vendor of production catalyst beds, General Kinetics and this company produces beds based upon the prior proven technology of silver based wire catalyst. General Kinetics origins and activity actually bridge the gap in production of catalyst devices when there was no aerospace activity (1980's) and its members are in a large part responsible for the resurgence in hydrogen peroxides resurgence.

General Kinetics is a small company formed from two groups of principals, which joined resources under one name in 1997. One segment is GG Industries which was taught the art of catalyst beds in the middle 1970's and was producing devices from that period until the early 1990's for non-classical uses such as oil well pressurization. Oil well pressurization provided remote area steam at 1500 psia for several hours at a time decomposing 90%. The other segment has its origin at Purdue University in 1990 where H₂O₂ hybrid research was begun and continued into 1997, eventually receiving a patent for a consumable catalyst bed for use in hybrids. This segment of principals is also responsible for early OSC H₂O₂ work in 1993 and

early influence at Beal Aerospace during the first year of its inception and design studies for catalyst and combustion chamber design.

Effect of Discontinued Use in 1980's

Procurement Specification[29]

In general two specifications were in wide spread use by the U.S. in the past era (WWII to mid 1980's) of hydrogen peroxide usage. These were a rocket propellant grade specification, MIL-P-16005 (Rev E, 1968 latest revision 1968, canceled 1988), and a torpedo grade propellant, MIL-H-22868. These specifications vary somewhat and in general the torpedo specification had a higher level of stabilizers.

Table 7 shows the present day public domain propellant specifications for the two vendors, which sell fluid concentrations greater than 70%. Note that the column "Type I" refers to the propellant specified in MIL-P-16005, Rev E.

	Type I	Solvay	Degussa
H2O2 Conc. (%)	90.0 to 91.0	84.0 to 85.0	87.5
Aluminum (mg/l)	0.5	0.4	1
Chloride (mg/l)	1.0	0.4	2
Ammonium (mg/l)	3.0	1.5	2
Sulfate (mg/l)	3.0	1.5	5
Nitrate (mg/l)	3.0 < X < 5.0	2.2 < X < 5.2	10
Phosphate (mg/l)	0.2	0.75	0.5
Tin (mg/l)	1.0 < X < 4.0	1.5 < X < 3.0	3 < X < 6
Carbon (mg/l)	200	75	100

Table 7 - Current Public Domain Specifications

It can be seen from table 7 that only the Solvay fluid meets the stabilizer requirements of MIL-P-16005E whereas neither of the fluids produced at present have the concentration required. It is apparent from this that all of the rocket data from the era before 1980's which used fluid, which did meet the specification, may be suspect. This has several unknown effects most of which is the life of catalyst. Previously Becco was making both catalyst and hydrogen peroxide. Hence, they were intimately aware of the influences of fluid on the operations of a given motor. After Becco discontinued manufacturing catalyst they still manufactured the fluid and maintained the knowledge of these effects.

Transportation Vessels

Another item of concern is the laws and or regulations governing the transportation of concentrated hydrogen peroxide. Previously, the peroxide vendors had gathered decades of

experience and put this knowledge in MIL-P-16005, Rev E. These requirements went above and beyond that required by governmental organizations. Section 5 of 16005E states that drums, cargo and tanker cars must be constructed of aluminum where the grades are specified. The specifications for vessel construction were covered under 49CFR parts 171-190 and the venting requirements were covered by the Bureau of Explosives.

Today a situation exists where it has become the responsibility of the fluid producers to determine the most appropriate vessels. The present governing federal regulations are 49CFR parts 100-185, which permits drums, which do *not* conform to MIL-P-16005E. The present CFRs are meant to cover every concentration of hydrogen peroxide below 70% and not intended for rocket concentrations of hydrogen peroxide. As an example the CFRs permit a removable head steel drum with a "compatible" liner. This liner by that definition is permitted to be a polymer hydrocarbon. In such a case a fire may issue if the fluid becomes contaminated or leaks through the liner and contacts the steel drum. Only following the CFRs leads to a higher handling risk than is necessary. It seems that the procuring agency should use the prior wisdom and purchase against the prior specification 16005E at least for the shipping requirements.

Conclusions

The history of hydrogen peroxide as a propellant has two distinct phases. In the first phase, which starts just prior to and during WWII, H2O2 provided itself to be one of the first viable high performance propellants and was an enabling chemical for the advancement to modern rocketry. The features that made it attractive were: monopropellant capability, "non-toxic" usage, high density, and storable. These features were always appreciated but it was subsequently displaced due to performance.

The performance driven environment of the cold war and the space race to the moon, created a design trade space that favored high performance systems. H2O2 was close but never the best in many applications and therefore lost out to hydrazine, liquid oxygen, and NTO for several key propulsion applications. This trade decision and the subsequent development and deployment of the platforms using these propellants defined the end of the first phase of H2O2 usage which occurred in the middle 1980's.

The second phase began in approximately 1990 is driven more by cost, ease of use and environmental factors. In general, the key features that first made H₂O₂ a viable propellant are the driving forces for

using it today: ease of handling and relatively good performance.

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Figure 1 - Thenard: Discoverer of Hydrogen Peroxide

Figure 2 - Rue Thenard in the Latin Quarter of Paris

Figure 3 - Early Batch Process Barium Peroxide H₂O₂ Manufacturing Plant

Figure 4 - H₂O₂ Fractional Crystallization Device

Figure 5 - Walter H₂O₂ ATO's

Figure 6 – ME163

Figure 7 - Schematic of V-2 Powerplant

Figure 8 - Schematic of German WWII H₂O₂ Submarine

Figure 9 – 300 ton Class German Sub

Figure 10 - German Torpedo Propulsion System Schematic

Figure 11 - Basic Configuration of the Black Knight Vehicle

Figure 12 - Gamma 201 Engine Layout

Figure 13 – Black Arrow Launch Oct 28, 1971

Figure 14 - Configuration for Black Prince

Figure 15 - X-1 Aircraft H₂O₂ System Layout

Figure 16 - X-15 Sub-System Installation Cut-Away

Figure 17 - Hyprox Steam Generator Schematic

Figure 18 - Hyprox Steam Generator Size Comparison

Figure 19 - General Electric H₂O₂ Polyethylene Hybrid Rocket Engine

Figure 20 - Lawrence Livermore National Laboratory Micro-Satellite H₂O₂ Hot Gas Pressurization Propulsion System

Figure 21 - Layout of USFE

Figure 22 - A Typical Silver Screen Catalyst Bed

Figure 23 - RMI LR-40 Topping Cycle H₂O₂ Bi-propellant Rocket Engine