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Hydrogen Peroxide-Based Propulsion and Power Systems

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Abstract

Less toxic, storable, hypergolic propellants are desired to replace nitrogen tetroxide (NTO) and hydrazine in certain applications. Hydrogen peroxide is a very attractive replacement oxidizer, but finding acceptable replacement fuels is more challenging. The focus of this investigation is to find fuels that have short hypergolic ignition delays, high specific impulse, and desirable storage properties. The resulting hypergolic fuel/oxidizer combination would be highly desirable for virtually any high energy-density applications such as small but powerful gas generating systems, attitude control motors, or main propulsion. These systems would be implemented on platforms ranging from guided bombs to replacement of environmentally unfriendly existing systems to manned space vehicles.

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Background

Interest in hydrogen peroxide as a propellant began in the 1930's by the US Navy where it saw use in torpedo propulsion. The Germans employed the use of hydrogen peroxide in both monopropellant and bipropellant propulsion applications. It was a favored underwater propellant for U boats. The most significant application was in the design of the type 26 U boats.

Hydrogen peroxide was used as a monopropellant in the reusable catapult gas generators for launching the V-1 "buzz bomb" (the first cruise missile) and in power turbines in the V-2 missile (the first exo-atmospheric ballistic missile). It was used in a hypergolic bipropellant application with a mixture of hydrazine hydrate and methanol in the ME 163 aircraft (the first operational rocket plane). In WWII, hydrogen peroxide saw use in the early fifties by the British in deHavilland Engine Companies Sprite and Super Sprite engines (turbo pump fed and regeneratively cooled with hydrogen peroxide) and in the 225 ft submarine.

The United States found many uses for hydrogen peroxide in propulsion systems until 1970. The Redstone, Mercury, and Scout rocket systems all employed hydrogen peroxide (for guidance and control) as well as the Lunar Landing Simulator (main propulsion), the first telecommunications satellites, SYNCOM and COMSAT (station keeping), and the first exo-atmospheric reusable high speed research aircraft, the X-15 (reaction control thrusters).

The death knell for hydrogen peroxide as a monopropellant was sounded in 1963 with the NASA sponsored development of the Shell 405 catalyst, which caused spontaneous decomposition of hydrazine. The success and high performance of the bipropellant hypergolic nitrogen tetroxide and hydrazine systems similarly eliminated hydrogen peroxide from the bipropellant propulsion arena.

Hydrogen peroxide has recently resurrected itself, not because of some advance in engineering, but because of a concern for environmental health and safety issues (which ultimately translate to added cost and liability). Hydrazine is extremely toxic and carcinogenic. Consequently, the infrastructure associated with manufacture, storage, and use of hydrazine adds additional expense to the already expensive aerospace propulsion field. Interest in hydrogen peroxide has come about as a partial solution to the quest for "green propellants" (environmentally friendly). As a result of this renewed interest, high concentration (99.2%) propellant grade ("clean") hydrogen peroxide is once again available from a domestic manufacturer.

With the advent of the availability from a domestic source of high concentration hydrogen peroxide, Sandia National Laboratories began to investigate hypergolic fuels for use in bipropellant engines through laboratory directed research and development.

Introduction

Hydrogen peroxide serves as an oxidizing agent in the combustion of organic fuels. The driving force behind these reactions is the conversion of oxygen in the -1 oxidation state to oxygen in the -2 (complete valence shell) oxidation state. Fuels that are strong reducing agents should facilitate this conversion and thus be very reactive with hydrogen peroxide. Furthermore, hydrogen peroxide is weakly acidic having a pKa of 11.65.¹ Under basic conditions, peroxide loses a proton and becomes much less stable.² In addition to being good reducing agents, potential fuels should also be basic if possible.

The above conclusions were reinforced by Schumb in his ACS monograph on peroxide.³ Schumb describes several classes of organic compounds that are reportedly hypergolic with hydrogen peroxide. Among those mentioned were inorganic amines, some organic amines, diammines, unsaturated compounds, aldehydes, and compounds containing hydroxy groups. All the fuels mentioned by Schumb have electron rich areas of the molecules that can act as reductants with hydrogen peroxide, and the amino compounds are also basic.

Schumb adds that the effect may be markedly increased by the addition of metal salts. Although details of metal catalysis are not known, the net effect of the metal catalyst is the lowering of the activation energy and the promotion of the reaction between fuel and peroxide.

Based on this information, a number of saturated and unsaturated compounds having hydroxy, carbonyl, and amino functionality were obtained. A hydrazine replacement known as DMAZ (2-Dimethylaminoethylazide) was also obtained. Several hydrocarbon fuels that are non-miscible with peroxide were selected in the hope of finding a soluble organometallic catalyst that would make them hypergolic.

Metallic compounds of Co^{+2} , Co^{+3} , Cu^{+1} , Cu^{+2} , Fe^{+2} , Fe^{+3} , Mn^{+2} , Mn^{+3} , Ag^{+1} , Ru^{+2} , V^{+2} and sodium and calcium hypochlorite were tried as fuel catalysts.

Experimental

Screening of Potential Rocket Fuels

Fuels were screened for hypergolic ignition through "drop testing". The drop test is a simple technique where a small quantity of fuel is placed in a plastic receptacle, such as a watch glass, and hydrogen peroxide is "dropped" onto the fuel remotely via an automatic pipette, a burette, or plastic dropper. In these drop tests; a 0.1 mL portion of candidate fuel was placed into a 5 mL disposable polyethylene beaker. XL Flight Systems 99.3% hydrogen peroxide was used for all tests. Index of refraction gave the concentration at 95%. Approximately 0.4 mL of hydrogen peroxide was added to the fuel using an automatic pipette. A one inch length of silicone rubber tubing was slipped over the tip of the glass pipette and replaced after each test, to prevent contamination and allow re-use of the pipette. Visual observation determined if ignition occurred and the relative rate

and intensity of reaction. If no observable reaction occurred after 30 seconds, the mixture was quenched with water. Figure 1 shows the experimental setup.

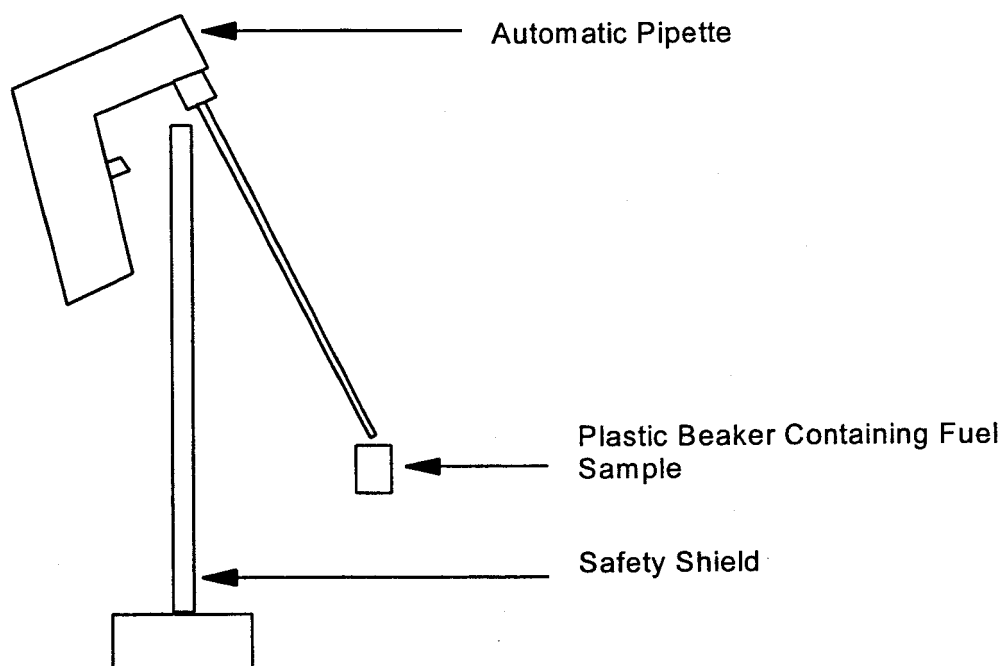


Figure 1: Drop Test Apparatus

Five series of tests were performed.

Test series 1 was aimed at finding fuels that are reactive with hydrogen peroxide. A fuel that is hypergolic with peroxide in the absence of a catalyst is very desirable. Fuels that are very reactive, but not hypergolic, with peroxide may be made hypergolic by adding a small amount of catalyst than less reactive fuels. Less reactive fuels will need correspondingly more catalyst. Of the materials tested, propyl amine, diaminocyclohexane, diaminopropane, ethylenediamine, diaminodipropylamine, ethanolamine and pyrrole showed vigorous reaction with hydrogen peroxide.

Test series 2 and 3 investigated the relative activities and solubilities of various catalysts in ethanol and methanol. The catalysts that showed the greatest reactivity included copper II chloride, iron III chloride, iron III nitrate, iron II chloride, ruthenium III chloride and sodium iodide. Both sodium iodide and ruthenium chloride solutions ignited on contact with concentrated hydrogen peroxide.

Test series 4 explored the hypergolic potential of catalysts mixed with reactive fuels. Propargyl alcohol solutions of sodium iodide, iron III chloride and iron III nitrate all ignited hypergolically. Furfuryl alcohol solutions with sodium iodide, copper II chloride and iron III nitrate also ignited hypergolically, as did diaminopropane solutions with copper II nitrate and with ethanol/sodium iodide.

Test series 5 determined the minimum catalyst concentration necessary to make ethanol and hexane hypergolic. None of the mixtures were hypergolic at the 10% concentration level.

More detail is provided in Tables 1-6.

Table 1: Standard electrode potentials and Gibbs free energies of fuel catalysts.

Reaction	E°, volts	ΔG° , kJ/g	Hypergolic Catalyst ?
$\text{Fe}^{+3} \rightarrow \text{Fe}^{+2}$	+ 0.771	- 1.32	yes
$\text{Cu}^{+2} \rightarrow \text{Cu}^+$	+ 0.153	- 0.23	yes
$\text{Ru}^{+3} \rightarrow \text{Ru}^{+2}$	+ 0.249	- 0.24	yes
$2\text{I}^- \rightarrow \text{I}_2$	+0.536	- 0.20	yes
$\text{Cr}^{+3} \rightarrow \text{Cr}^{+2}$	- 0.407	+ 0.75	no
$\text{Co}^{+2} \rightarrow \text{Co}$	- 0.280	+ 0.46	no

Table 2: Reactivity of fuels containing an easily oxidized moiety with XL Flight Systems 99.3% hydrogen peroxide (Test Series 1).

Fuel	Catalyst	Result
Propyl Amine	None	fast vigorous reaction
Tripropyl Amine	None	no reaction
1,3-Diaminopropane	None	fast vigorous reaction
3,3'-Diaminodipropylamine	None	fast vigorous reaction
1,2-Diaminocyclohexane	None	fast vigorous reaction
Dipentyl Amine	None	no reaction
Tetrahydrofurfuryl Amine	None	no reaction
1,8-Diaminonaphthalene	None	no reaction
Carbohydrazide	None	no reaction
m-Toluidine	None	no reaction
Furfuryl Amine	None	no reaction
Pyrrole	None	delayed vigorous reaction
2-Furaldehyde	None	no reaction
Furfuryl Alcohol	None	no reaction
Ethanolamine	None	delayed vigorous reaction
Ethylenediamine	None	fast vigorous reaction
Triethyl Amine	None	no reaction

Table 3: Reactivity of methanol/catalyst solutions with XL Flight Systems 99.3% hydrogen peroxide (Test Series 2)

Fuel	Catalyst	Result
Methanol	NaI	ignition
Methanol	CuCl	no reaction poor catalyst solubility
Methanol	Cu(NO ₃) ₂	no reaction
Methanol	CuCl ₂	fast vigorous reaction
Methanol	FeCl ₂	fast vigorous reaction moderate catalyst solubility
Methanol	Fe(NO ₃) ₃	fast vigorous reaction
Methanol	FeCl ₃	fast vigorous reaction exothermic mixing of catalyst with fuel resulting in some residue
Methanol	Fe III Ethoxide	slight reaction
Methanol	RuCl ₃	ignition
Methanol	CoCl ₂	delayed reaction
Methanol	Cr(NO ₃) ₃	no reaction
Methanol	MnCl ₂	no reaction
Methanol	Mn II Methoxide	no reaction

Table 4: Reactivity of ethanol/catalyst solutions with XL Flight Systems 99.3% hydrogen peroxide (Test Series 3).

Fuel	Catalyst	Result
Ethanol	NaI	ignition
Ethanol	CuCl	no reaction poor catalyst solubility
Ethanol	Cu(NO ₃) ₂	no reaction moderate catalyst solubility
Ethanol	CuCl ₂	slight reaction
Ethanol	FeCl ₂	fast vigorous reaction
Ethanol	FeCl ₃	delayed vigorous reaction moderate catalyst solubility with residue
Ethanol	Fe(NO ₃) ₃	vigorous reaction
Ethanol	Fe III Ethoxide	no reaction slight catalyst solubility with significant residue
Ethanol	RuCl ₃	ignition
Ethanol	CoCl ₂	no reaction
Ethanol	Cr(NO ₃) ₃	delayed reaction
Ethanol	MnCl ₂	no reaction

Table 5: Reactivity of fuel/catalyst solutions with XL Flight Systems 99.3% hydrogen peroxide (Test Series 4).

Fuel	Catalyst	Result
Propargyl Alcohol	NaI	delayed ignition
Propargyl Alcohol	CuCl	no reaction poor catalyst solubility
Propargyl Alcohol	CuCl ₂	no reaction poor catalyst solubility
Propargyl Alcohol	Cu(NO ₃) ₂	no reaction moderate catalyst solubility
Propargyl Alcohol	FeCl ₂	slight reaction moderate catalyst solubility
Propargyl Alcohol	Fe(NO ₃) ₃	delayed explosion moderate catalyst solubility
Propargyl Alcohol	FeCl ₃	delayed ignition moderate catalyst solubility with residue
Propargyl Alcohol	RuCl ₃	catalyst exothermically reacted with fuel forming tar
Propargyl Alcohol	CoCl ₂	no reaction poor catalyst solubility
Propargyl Alcohol	Cr(NO ₃) ₃	no reaction moderate catalyst solubility
Propargyl Alcohol	MnCl ₂	no reaction slight catalyst solubility
Furfuryl Alcohol	NaI	delayed ignition moderate catalyst solubility
Furfuryl Alcohol	Fe(NO ₃) ₃	ignition catalyst exothermically reacted with fuel forming tar
Furfuryl Alcohol	RuCl ₃	catalyst exothermically reacted with fuel forming tar
Furfuryl Alcohol	FeCl ₃	catalyst exothermically reacted with fuel forming tar
Furfuryl Alcohol	CuCl ₂	delayed ignition catalyst exothermically reacts with fuel to form tar
Diaminopropane	NaI	fast vigorous reaction
Diaminopropane	CuCl ₂	fast vigorous reaction poor catalyst solubility
Diaminopropane	Cu(NO ₃) ₂	ignition moderate catalyst solubility
Diaminopropane/Ethanol	NaI	ignition

Table 6: Minimum catalyst concentration necessary for ignition of various fuels with XL Flight Systems 99.3% hydrogen peroxide (Test Series 5).

Fuel	Catalyst	Result
50.0% Isooctane 37.5% Hexane	12.5% Triethylaluminum	slow reaction with no ignition
25.0% Isooctane 56.3% Hexane	18.7% Triethylaluminum	delayed ignition
75.0% Hexane	25.0% Triethylaluminum	rapid ignition
Ethanol	1% NaI	not tested
Ethanol	5% NaI	not tested
Ethanol	10% NaI	vigorous reaction, but no ignition
Ethanol	1% RuCl ₃	vigorous reaction, but no ignition
Ethanol	5% RuCl ₃	vigorous reaction, but no ignition
Ethanol	20% RuCl ₃	vigorous reaction, but no ignition

It was observed that ruthenium III chloride and iron III chloride dissolved quite exothermically in aqueous and alcoholic solutions. The high solvation enthalpy of these compounds may promote adverse reactions with certain fuels. Rapid, exothermic polymerization of propargyl alcohol was initiated by ruthenium III chloride. Furfuryl alcohol also underwent rapid, exothermic polymerization with copper II chloride, iron III nitrate, iron III chloride and ruthenium III chloride.

Primary amines were the most reactive fuels tested. The lone electron pair in the amino moiety readily participates in oxidation/reduction reactions. Fuel mixtures containing copper II nitrate, copper II chloride, iron III nitrate, iron III chloride, ruthenium III chloride, or sodium iodide showed the highest reactivity with concentrated hydrogen peroxide. It is important to point out that the metal ions in solution do not function as catalysts, but are irreversibly reacted with the peroxide. The data in Table 1 indicates a correlation between standard electrode potential and reactivity with hydrogen peroxide. Fuel mixtures containing chemical species that have negative free energies of reduction are hypergolic with hydrogen peroxide, although a larger data set needs to be tested before this correlation can be confirmed.

Most catalysts gave a vigorous reaction with hydrogen peroxide and those having an organic fraction ignited. Catalyst reactivity was very fast and difficult to rank. Only copper II acetylacetonate failed to react with peroxide. Of the fuels tested, DMAZ, toluidine, diethylenetriamine, ethylenediamine, pyrrole, ethanolamine, and triethyl aluminum/hexane gave noticeable reactions with peroxide. Only pyrrole, ethanolamine, and triethyl aluminum/hexane ignited.

To decrease ignition delay, metal compounds were added to the most reactive fuels. A 1% mass addition of copper II chloride to pyrrole and ethanolamine gave “instant” ignition on contact with hydrogen peroxide. Other mixtures reacted violently with peroxide, but failed to ignite in the drop tests. A 25% solution of triethyl aluminum in hexane was the only non-miscible fuel that was hypergolic with peroxide. No catalysts were found that made the other non-miscible fuels hypergolic.

More work will be done, with emphasis on reactive fuel mixtures and determining the minimum catalyst concentration necessary for rapid ignition. In fact, ignition delay is probably the most important criteria to be considered since most of the candidate fuels considered have similar toxicity and specific impulse.

Computational Modeling of Candidate Fuels

Computer calculations were carried out using the NEWPEP Propellant Evaluation Program to evaluate potential performance and relative ranking of candidate fuels with hydrogen peroxide. NEWPEP was also used to quantify performance when using hydrogen peroxide at a variety of dilutions, as well as 100% purity. A total of 2550 separate fuel/oxidizer system calculations were carried out, for 17 candidate fuels, 5 peroxide concentrations, and 30 fuel/oxidizer ratios. Fuels considered were ammonia, DMAZ, diethylether, ethanol, ethanolamine, furfuryl alcohol, HTPB (hydroxy terminated polybutadiene), hydrazine, isopropyl alcohol, JP5, lithium metal, methanol, octane, propane, propargyl alcohol, RP1 and 25% triethyl aluminum in hexane.

Physical Vapor Deposition to Deposit Catalytic Material

A technique was developed for making reactive, high surface area catalysts to decompose hydrogen peroxide into steam and oxygen for use in propulsion and power systems. Physical vapor deposition (sputtering) was used to deposit a catalytic material (silver) onto high surface area, refractory metal substrates for use in rocket engines. This is in contrast to the traditional preparation technique of electroplating. Sputtering offers a number of advantages over electroplating including the ability to deposit thin films which are uniform in thickness over large areas, have microstructures that are controllable and reproducible, have higher purity levels, and can be made from a wide variety of materials, including insulators.

The decomposition of hydrogen peroxide into water and oxygen is a highly efficient exothermic reaction that can be used for propulsion or power systems. Hydrogen peroxide is desirable as a propellant because it does not possess the health hazards associated with presently used propellants (e.g., hydrazine and nitrogen tetroxide) that are highly toxic, carcinogenic, and ozone depleting.⁴ In addition, the products of the H_2O_2 decomposition are non-toxic and environmentally friendly.

Hydrogen peroxide can be decomposed via thermal decomposition. However, this process is difficult to exploit for power generation because the constant mixing of the hot decomposition products with the relatively cool hydrogen peroxide reactant impedes the reaction.⁵ For this reason, a catalyst is used to promote rapid decomposition. Several

materials have been proposed and utilized as catalysts for decomposition of hydrogen peroxide including silver,^{5,6} silver oxide,⁷ calcium permanganate, manganese oxides,⁸ iron oxide,⁸ and copper oxide. However, these catalysts must be fabricated in such a way that they offer maximum surface area for reaction to occur, have high porosity to allow flow of liquid H_2O_2 , and have thermal and structural stability so they do not disintegrate, delaminate, or melt during the decomposition process. One way to achieve this is to fabricate pellets or to deposit the catalytic material onto screens or reticulated metal substrates that will promote rapid decomposition of H_2O_2 with low impedance to flow. However, the substrates must have high melting points and suitable coefficients of thermal expansion in order to survive the high temperature, high stress environment that occurs during the decomposition process. Refractory metal or ceramic screens are excellent candidates for the substrates in this application. Traditional electroplating is, at best, extremely difficult on these types of substrates.

It was possible to use physical vapor (sputter) deposition to reproducibly coat stainless steel screens for use in a hydrogen peroxide rocket engine. Vapor deposition of catalytic materials for use in H_2O_2 decomposition may offer several advantages over the tradition electroplating preparation technique. In general, vapor deposition is more reproducible than electroplating. The microstructure and surface structure of vapor deposited thin films can be optimized via deposition parameters for a specific application and then consistently reproduced (Figure 2).

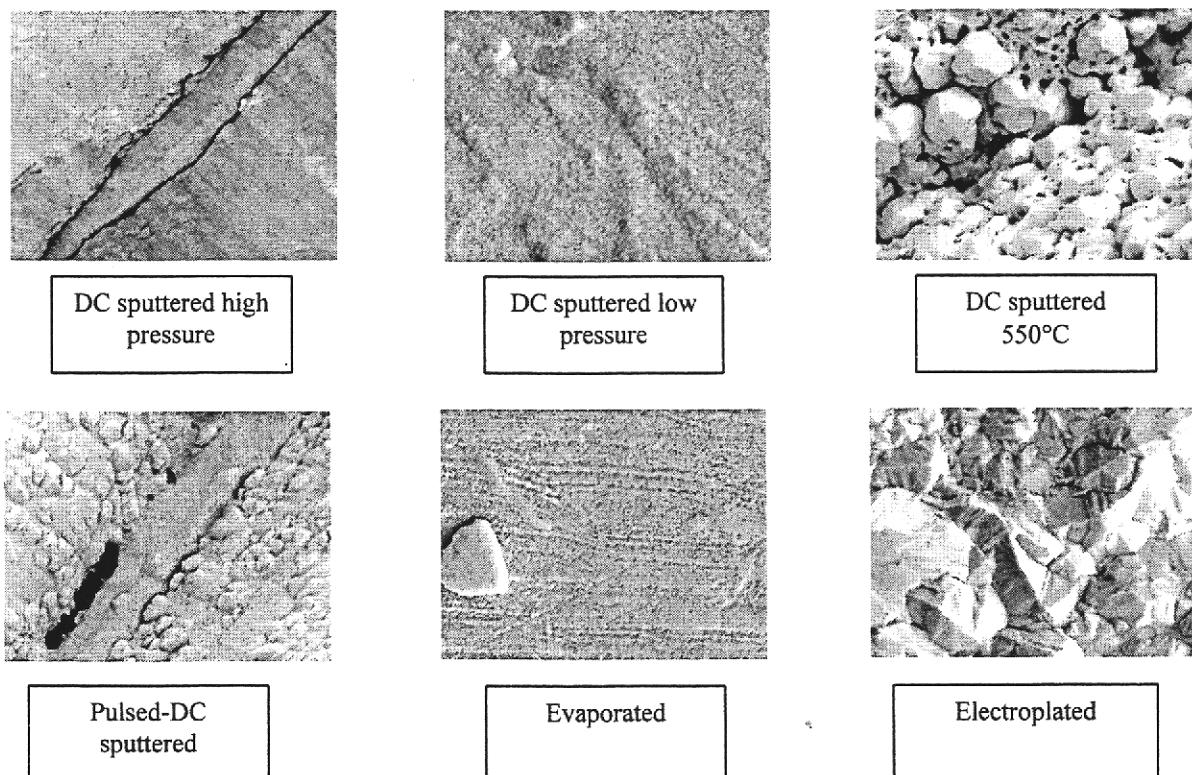


Figure 2: Deposition Parameters for Specific Applications

However, electroplated films that are deposited under nominally identical conditions can exhibit a wide variation in surface structures and catalytic performance. In addition, vapor deposition can be used to deposit a wide variety of thin film materials, including metals, semiconductors, and insulators. Electroplating is limited to the deposition of metallic films. Finally, vapor deposition results in much higher purity levels than electroplating. The purity level can be especially critical in the case where a small amount of an impurity can poison a catalyst.

Results

All catalysts except copper II acetylacetonate reacted quickly and violently with 90% hydrogen peroxide. Manganese, copper, and iron compounds gave the most vigorous reactions followed by silver, cobalt, ruthenium, and vanadium compounds. DMAZ, diethylenetriamine, ethylenediamine, pyrrole, ethanolamine, and triethyl aluminum/hexane reacted with peroxide. The only fuels that ignited were pyrrole, ethanolamine, and triethylaluminum/hexane. A 1% addition of copper II chloride to pyrrole and ethanolamine gave rapidly hypergolic mixtures with 90% peroxide. Upon storage, the pyrrole and copper II chloride mixture polymerized, leaving catalyzed ethanolamine as the only practical hypergolic fuel. Ethanolamine and copper chloride mixtures have a low toxicity, high density, favorable performance, and short ignition delay. The main disadvantages are the high viscosity and high freezing point of the mixture. Addition of alcohol or other amines should eliminate these problems without increasing ignition delay. A 25% solution of triethyl aluminum in hexane was the only hypergolic non-miscible fuel mixture found.

A wide variety of fuels were tested, but only fuels having amino functionality showed any reaction with peroxide. Almost all catalysts greatly accelerated the decomposition of peroxide although no clear trend was observed. Copper salts are very soluble in amines due to complex formation. For this reason, copper II chloride was added to ethylenediamine, ethanolamine, and pyrrole. It was hoped that the addition of catalyst would greatly accelerate the reaction between fuel and peroxide. One thing not tried was mixing metallic catalysts to obtain a synergistic effect. It is reported that pairs of metal catalysts have a greater effect on the decomposition of hydrogen peroxide than either metal alone. This will be investigated in future work.

In physical vapor deposited thin films, microstructure evolves with thickness: the thicker the film, the rougher the surface. In addition, adjusting the substrate temperature, deposition rate, or deposition pressure affects the energy of the adatoms incident on the substrate that ultimately determines the microstructure and surface roughness. A thin film that is deposited with very low energy (e.g., low temperature, low deposition rate, or high deposition pressure) can undergo dendritic growth and exhibit a large surface roughness as a result. Dendritic growth occurs when adatoms arriving at the surface have limited mobility and adhere to the first surface they encounter. On the other hand, a thin metal film deposited with a very high energy also can exhibit a large surface roughness as a result of large crystallite formation. Thin films deposited with moderate energies tend to offer the smoothest surfaces. It is possible to determine and optimize the effects of deposition parameters on surface roughness for this catalytic application.

The thrust curve for the rocket engine containing the Ag coated screens is shown in Figure 2. The engine design goal was for a minimum of 50 lb_F for duration of at least 3 seconds. The figure shows that the thrust reached an average of 65 lb_F for a duration of $\geq$ 3 seconds, exceeding design requirements. The Ag thin films were still well adhered to the stainless steel screens after firing. The adhesion was sufficient to ensure that Ag particulates did not flake off during operation and clog the system. These test results indicate that sputter deposited Ag films may be useful for the catalytic decomposition of H₂O₂-based propulsion systems.

Conclusions

Future work plans for this project had included small rocket engine test firing of all potential fuels to determine the minimum peroxide concentration and minimum catalyst concentration necessary for hypergolic ignition. The effect of mixed catalysts on ignition delay was also to be studied and further attempts will be made at making non-miscible fuels hypergolic with hydrogen peroxide. However, key personnel changes early in FY'03 impeded completion of all objectives of this program. Physical materials (such as fuels, test hardware, etc) were consolidated in Center 2500 along with the data obtained in the FY'02 efforts described throughout this report. Should funding and programmatic support become available in the future this consolidated data base will provide a solid foundation for reinvigorating this challenging technical effort.

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