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INVESTIGATION OF HYPERGOLIC FUELS WITH HYDROGEN PEROXIDE

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ABSTRACT

A low toxicity, high performance, hypergolic, bipropellant system is desired to replace conventional nitrogen tetroxide (NTO) and hydrazine propulsion systems. Hydrogen peroxide exothermically decomposes to water, and oxygen, making it an ideal oxidizer for more environmentally friendly propulsion systems. Unfortunately, the choice of fuel for such systems is not as clear. Many factors such as ignition delay, performance, toxicity, storability, and cost must be considered. Numerous candidate fuels and fuel/catalyst mixtures were screened using a simple laboratory setup and visual observation. A mixture of ethanolamine and 1% copper (II) chloride was found to rapidly ignite with 90% hydrogen peroxide. Hydrogen peroxide and ethanolamine are much less toxic than NTO and hydrazine. Hydrogen peroxide and ethanolamine have a calculated specific impulse of 245 seconds compared to 284 seconds for NTO and monomethyl hydrazine. A low-freezing blend of furfuryl alcohol (47.5%), ethanolamine (47.5%), and copper (II) chloride (5%) was successfully test fired in a small rocket engine with both 90% and 99% hydrogen peroxide. Hypergolic ignition of this mixture was achieved with 70% hydrogen peroxide.

Our quest for a non-toxic hypergol began by researching the literature. Most current

INTRODUCTION

Many applications such as attitude control thrusters, divert propulsion engines, and small rocket systems require storable, hypergolic, liquid propellants having good performance. Nitrogen tetroxide (NTO) and hydrazine is the traditional propellant combination used for such applications. There are many advantages to this propellant pair such as rapid ignition, good performance, low freezing point, and storability. There are also distinct disadvantages to this propellant combination. NTO has a high vapor pressure and is very corrosive to both rocket hardware and the human body. Hydrazines are reactive, corrosive, and very toxic.¹ Most hydrazine compounds are also carcinogenic.¹

A search is underway for less toxic, hypergolic, liquid propellants that can be used in new propulsion systems and in systems currently using NTO and hydrazine. High concentration hydrogen peroxide is an ideal oxidizer for such applications due to its low toxicity, high density, low vapor pressure, and exothermic decomposition to water and oxygen. The challenge is to find a low toxicity fuel that gives rapid, hypergolic, ignition with hydrogen peroxide, as well as exhibiting good performance, safety, and storability.

publications utilized alcohols as their fuels of choice.²⁻⁴ Alcohols are cheap, storable, have

low freezing points, exhibit good performance, and are non-toxic compared to hydrazines.¹ Unfortunately, hypergolic ignition was only achieved after adding a large amount (>10%) of manganese based catalyst.²⁻⁴ Metallic catalysts are toxic and impair performance, so low concentrations are desired. In addition, an insoluble catalyst may not remain in uniform suspension, converting a hypergolic fuel into one with inconsistent age related performance. We wanted to find a fuel that was hypergolic by itself, or that could be made so with a much smaller addition of metallic catalyst.

BACKGROUND

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 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 11.65.⁵ Under basic conditions, peroxide loses a proton and becomes much less stable.⁶ 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.⁷ Schumb describes several classes of organic compounds that are 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 on the molecule 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 potential 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.

Inorganic and organic 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

A simple laboratory test was developed to screen potential fuels. In these "drop" tests, a 0.1 mL portion of candidate fuel was placed into a 5 mL disposable polyethylene beaker. Approximately 0.4 mL of 90 % hydrogen peroxide was added to the fuel using an automatic pipette. A 1" 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. Figure 1 shows the experimental setup.

RESULTS

Drop test results from 90% hydrogen peroxide and various catalysts, fuels, and fuel/catalyst mixtures are presented in tables 1-3. Reaction rate and ignition potential in a rocket engine between peroxide and candidate materials was

rated on a relative scale from 0 to 3, with 3 being the fastest and most reactive.

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, red phosphorous and triethyl aluminum/hexane ignited. Propargyl amine violently exploded a few seconds after mixing with 90% peroxide.

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, and red phosphorous were the only non-miscible fuels that were hypergolic with peroxide. Although red phosphorous is a solid, it may have an application as an ignition aid in a hybrid rocket engine. No catalysts were found that made the other non-miscible fuels hypergolic.

Furfuryl alcohol was blended with ethanolamine and copper (II) chloride in order to lower the freezing point and viscosity of the ethanolamine. A mixture of 47.5% furfuryl alcohol, 47.5% ethanolamine, and 5% copper (II) chloride showed a much shorter ignition delay with 90% hydrogen peroxide than a mixture comprised solely of ethanolamine and copper (II) chloride. This mixture was even hypergolic with 70% peroxide. The furfuryl alcohol, ethanolamine, copper (II) chloride

blend was successfully test fired in a small, bipropellant rocket engine.

DISCUSSION

A wide variety of fuels were tested, but only the miscible 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 possibility not tried was mixing metallic catalysts to obtain a synergistic effect. It is reported that pairs of metal catalysts can have a greater effect on the decomposition of hydrogen peroxide than either metal alone.⁶ This will be investigated in future work.

The ethanolamine/copper (II) chloride mix ignited very rapidly upon contact with peroxide. The ethylenediamine/copper (II) chloride complex vigorously steamed, but no combustion occurred. The drop tests are not representative of the intense mixing that takes place as a result of injecting propellants into the combustion chamber of a rocket engine. We expect that many of the reactions that were vigorous in the drop test apparatus will be hypergolic in a rocket engine. The pyrrole complex was rapidly hypergolic, but after a week of storage, a thick sludge formed that eventually solidified. This illustrates the need for long term aging and compatibility studies of fuels. DMAZ gave a slight reaction with peroxide, but metal catalysts were not added because the stability of such mixtures was unknown.

Ethanolamine is the best fuel tested due to its

rapid ignition, low toxicity, respectable performance, and high density as seen in Tables 4 and 5. It does however have one major drawback, a freezing point of 10.3 °C. 90% hydrogen peroxide freezes at -11.5 °C. A solution to this problem is the addition of a freezing point depressant such as ethanol (mp -114.1 °C), methanol (mp -97.8 °C), furfuryl alcohol (mp -31 °C), propyl amine (mp -83 °C), or diethylenetriamine (mp -35 °C). In fact a blend of furfuryl alcohol, ethanolamine, and copper (II) chloride proved more hypergolic than mixtures without the alcohol.

Only a brief mention of hypergolic non-miscible fuels was given by Schumb. Hypergolic ignition was achieved by suspending a sizeable percentage of metallic catalyst in the fuel. We wanted to find a soluble catalyst that could be added at low concentrations and still provide hypergolic ignition. There are performance, handling, and cost advantages to using non-miscible fuels such as jet fuel or gasoline. It was theorized that the dicyclopentadienyl complexes of iron, manganese, cobalt, and ruthenium would be soluble in hydrocarbons at a level that would promote hypergolic ignition. Kerosene, trimethyl pentane, and limonene were blended with the aforementioned organometallics. One percent additions of catalyst did not promote ignition in any of the compounds. Again, the drop tests are not representative of the intense mixing that takes place as a result of injecting the propellants into the combustion chamber of a rocket engine. Unfortunately, higher catalyst concentrations exposed solubility limits with many of the fuel/catalyst combinations.

CONCLUSIONS

A simple test was devised to determine if candidate fuels were hypergolic with 90% hydrogen peroxide. Metal catalysts, fuels, and

fuel/catalyst mixtures were tested and their relative reactivities determined by visual observation.

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, red phosphorous, 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 high viscosity and high freezing point of ethanolamine can be reduced through use of miscible freezing point depressants such as furfuryl alcohol. In fact a mixture of furfuryl alcohol, ethanolamine and copper (II) chloride was hypergolic with hydrogen peroxide of only 70% concentration. The furfuryl alcohol blend was successfully test fired in a small bipropellant rocket engine.

Future work includes small rocket engine test firing of all potential fuels and determining the minimum peroxide concentration and minimum catalyst concentration necessary for hypergolic ignition. The effect of mixed catalysts on ignition delay will be studied and further attempts will be made at making non-miscible fuels hypergolic with hydrogen peroxide.

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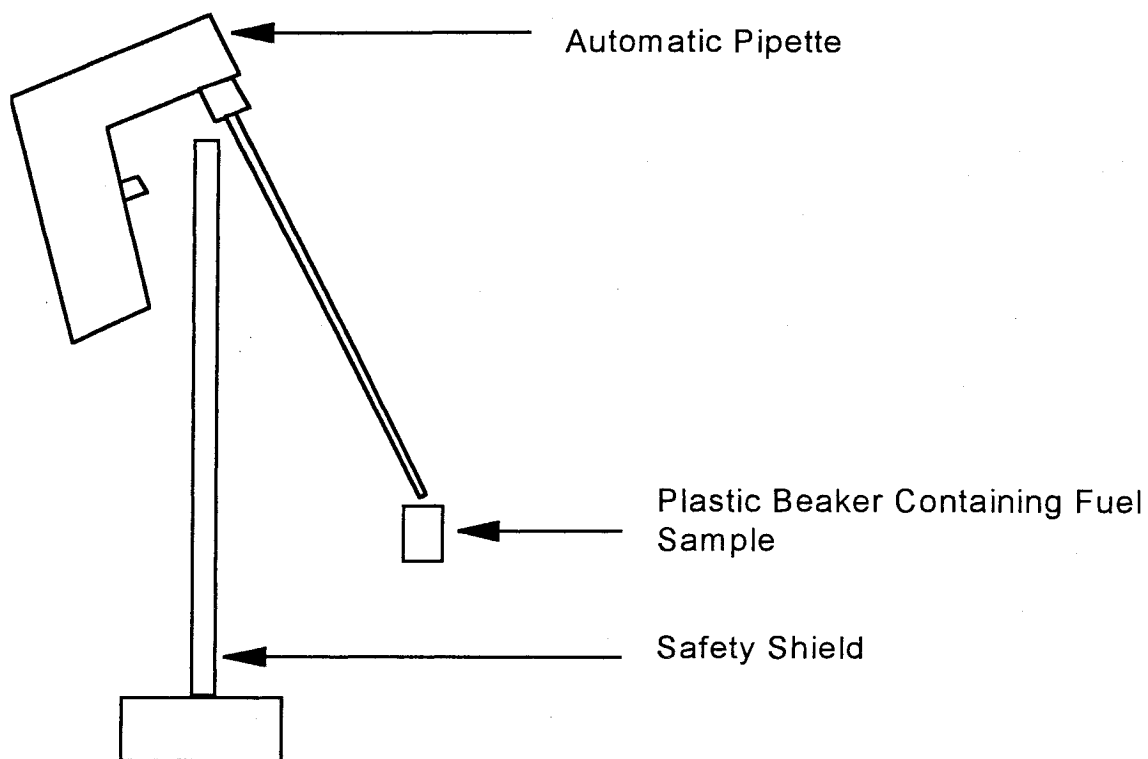


Figure 1: Drop test apparatus.

Table 1. Catalyst drop test results with 90% hydrogen peroxide.

CATALYST	DELAY	COMMENTS
Cobalt (II) Acetyl Acetate	3	Ignition
Cobalt (III) Acetyl Acetate	2	Decomposed then ignited after several seconds
Dicyclopentadienyl Cobalt (II)	3	Ignition
Copper (I) Chloride	3	Violent decomposition
Copper (II) Chloride	3	Violent decomposition
Copper (II) Acetyl Acetate	0	No Reaction
Iron (II) Chloride	3	Violent decomposition
Iron (III) Chloride	3	Violent decomposition
Iron (III) Ethoxide	3	Violent decomposition
Dicyclopentadienyl Iron (II)	2	Decomposed and burned vigorously after several seconds
Manganese (II) Methoxide	3	Ignition
Manganese (II) Acetyl Acetate	3	Ignition
Manganese (III) Acetyl Acetate	3	Ignition
Dicyclopentadienyl Manganese (II)	3	Ignition
Dicyclopentadienyl Ruthenium (II)	3	Ignition
Silver (I) Permanganate	2	Rapid decomposition
Silver (I) Acetyl Acetate	2	Decomposed then ignited after several seconds
Vanadium(II) Acetyl Acetate	3	Ignition
Sodium Hypochlorite	1	Steady decomposition
Calcium Hypochlorite	1	Steady decomposition

Delay:

0 = No Reaction

1 = Slow Reaction

2 = Fast Reaction

3 = Very Fast Reaction

Table 2. Fuel drop test results with 90% hydrogen peroxide.

FUEL	DELAY	IGNITION POTENTIAL	COMMENTS
Methanol	0	0	No Reaction
Ethanol	0	0	No Reaction
Ethylene Glycol	0	0	No Reaction
Furfuryl Alcohol	0	0	No Reaction
α -Terpineol	0	0	No Reaction
Furaldehyde	0	0	No Reaction
Ethylenediamine	2	1	Rapidly decomposed
Dietylenetriamine	2	1	Rapidly decomposed
Triethyl Amine	0	0	No Reaction
Furfuryl Amine	0	0	No Reaction
Propargyl Amine	1	2	Violently Exploded After Mixing
Toluidine	1	1	Decomposed
Pyrrole	2	2	Delayed ignition
Ethanolamine	2	2	Delayed ignition
Phenyl Hydrazine	0	0	No Reaction
2-Dimethylaminoethylazide (DMAZ)	1	1	Slow decomposition
Kerosene	0	0	No Reaction
2,2,4-Trimethyl Pentane	0	0	No Reaction
Limonene	0	0	No Reaction
25% Triethyl Aluminum in Hexane	3	3	Ignition
Red Phosphorous	3	3	Ignition
Decaborane	0	0	No Reaction
1,2,4-Triazole	0	0	No Reaction

Delay:

0 = No Reaction

1 = Slow Reaction

2 = Fast Reaction

3 = Very Fast Reaction

Ignition Potential:

0 = No Potential for Ignition

1 = Slight Ignition Potential

2 = High Ignition Potential

3 = Very High Ignition Potential

Table 3. Fuel mixture drop test results.

MIXTURE	DELAY	IGNITION POTENTIAL	COMMENTS
47.5 % Ethanolamine 47.5 % Furfuryl Alcohol 5.0 % Copper (II) Chloride	3	3	Most rapid ignition of all fuel mixtures tested.
Ethanolamine Copper (II) Chloride	3	3	Instantly ignited with a green flame
Pyrrole Copper (II) Chloride	3	3	Instantly ignited, but solidified during storage
Ethylenediamine Copper (II) Chloride	2	2	Vigorous steam evolution, but no combustion
Ethanol Manganese (II) Acetyl Acetonate	2	2	Vigorous steam evolution, but no combustion
90 % Ethanol 10 % Ruthenium (II) Chloride	2	2	Ignited, but required 10% catalyst
Kerosene Dicyclopentadienyl Iron (II)	1	1	Slight fizzing after many minutes
Kerosene Dicyclopentadienyl Manganese (II)	1	1	Slight fizzing after many minutes
Kerosene Dicyclopentadienyl Cobalt (II)	1	1	Slight fizzing after many minutes
Kerosene Dicyclopentadienyl Ruthenium (II)	1	1	Slight fizzing after many minutes
Trimethyl Pentane Dicyclopentadienyl Iron (II)	1	1	Slight fizzing after many minutes
Trimethyl Pentane Dicyclopentadienyl Manganese (II)	1	1	Slight fizzing after many minutes
Trimethyl Pentane Dicyclopentadienyl Cobalt (II)	1	1	Slight fizzing after many minutes
Trimethyl Pentane Dicyclopentadienyl Ruthenium (II)	1	1	Slight fizzing after many minutes
Limonene Dicyclopentadienyl Iron (II)	1	1	Slight fizzing after many minutes
Limonene Dicyclopentadienyl Manganese (II)	1	1	Slight fizzing after many minutes
Limonene Dicyclopentadienyl Cobalt (II)	1	1	Slight fizzing after many minutes
Limonene Dicyclopentadienyl Ruthenium (II)	1	1	Slight fizzing after many minutes

Except where noted, all mixtures were 99% fuel and 1% catalyst by weight.

Table 4: Propellant performance calculated by NEWPEP.

PROPELLANT		ISP	DENSITY ISP
71.4 %	Nitrogen Tetroxide	287	345
28.6	Monomethyl Hydrazine		
70.3 %	Hydrogen Peroxide (90%)	275	343
29.7	Hydrazine		
89.9 %	Hydrogen Peroxide (90%)	267	334
11.1	JP-4		
83.1 %	Hydrogen Peroxide (90%)	261	321
16.9	Ethanol		
80.1 %	Hydrogen Peroxide (90%)	245	316
19.9	Ethanolamine		

Table 5: Physical properties of ethanolamine.

Molecular Weight, g/mole	61.08
Density, g/mL	1.012
Freezing Point, °C	10.3
Boiling Point, °C	170.8
Flash Point, °C	90.6
Viscosity, cP	19
pKa	9.4