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FLUORINATED HYDRAULIC FLUIDS

A Study of the Direct Partial Fluorination of Synthetic Fluids for Improving Their Fire Resistance Properties

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6 DECEMBER 1976

FINAL REPORT
TASK AREA NO. ZR01309
IR WORK UNIT NO. GC130

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Prepared for
DIRECTOR OF NAVAL LABORATORIES
Department of the Navy
Washington, D.C. 20390

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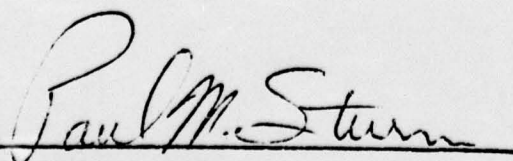
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S U M M A R Y

INTRODUCTION

The currently used petroleum-base military aircraft hydraulic fluid conforming to military specification MIL-H-5606C is an extremely flammable material. This fluid, which was developed in the early phases of World War II, possesses all of the desired properties of a good hydraulic fluid with the one exception of fire resistance. Hydraulic systems in military aircraft under combat or operational conditions are subject to projectile damage or component failures which could result in the release of this fluid under pressures as high as 3,000 psi (21 MPa) in the form of a spray or jet. In the presence of an ignition source, a hazardous condition or fire may result, causing aircraft damage or loss and a threat to crew safety.

The need for the development of a safer, fire-resistant fluid for use in current and future military aircraft is emphasized from statistics obtained from the Naval Safety Center computer file related to the number of hydraulic fluid induced naval aircraft fires. Many accidents were reported due to failure of hydraulic components as a result of improper maintenance procedures, fatigue, etc. which permitted escaping hydraulic fluid to come in contact with hot surfaces such as brakes or engine components. In some instances fatalities occurred as well as total loss of the aircraft. Thus, the need for the development of a safer fire-resistant military aircraft hydraulic fluid is quite evident.

Fire resistant fluids for military aircraft hydraulic systems have been sought for the past 30 years. The most promising fluid to date from an engineering and logistic standpoint has been one based on a synthetic hydrocarbon oligomer which was most recently approved for naval aircraft introduction. This fluid, although exhibiting somewhat improved fire retardancy properties over the currently used petroleum base fluid, is still only less flammable and not truly fire resistant. In order to extend the usefulness of this material and significantly improve its fire resistance properties, a chemical modification based on partial substitution of the hydrogen atoms with fluorine atoms may prove feasible. Therefore, the objective of this independent research program is to provide a basis for the development of a new class of synthetic fluids with superior fire-resistance properties for application to current and future military aircraft hydraulic systems. The successful completion of this program would result in the enhanced survivability of military aircraft under both operational and combat conditions.

SUMMARY OF RESULTS

The direct partial fluorination of synthetic hydrocarbon fluid was limited to about 5 wt. percent fluorine. Attempts to achieve higher concentrations of fluorine exchange without gross decomposition were unsuccessful.

At this concentration level, no improvement in fire retardancy was observed.

Indirect fluorination methods, i.e., fluorination of monomer prior to polymerization are not considered promising.

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The incorporation of fluorine atoms into the alkylated silicone molecule was not achievable.

CONCLUSIONS

The work performed under this program represents a final attempt to provide a basis for the development of superior fire-resistant military aircraft hydraulic fluids suitable as direct replacement fluids in current hydraulic system designs. The results to date have been less than encouraging; therefore, work on this program has been terminated.

The Navy and Army have authorized the use of MIL-H-83282 (synthetic hydrocarbon) fluid in all aircraft hydraulic systems presently using MIL-H-5606. The Air Force has decided to continue using MIL-H-5606. Long range Navy/Air Force/Army plans call for the development of fire-resistant/non-flammable hydraulic fluids for future hydraulic system designs.

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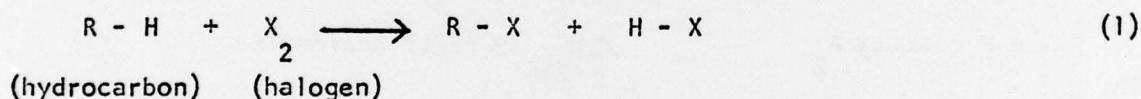
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BACKGROUND

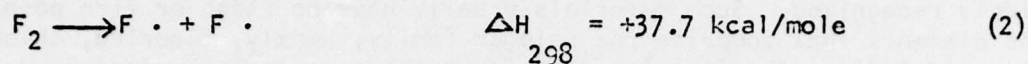
The use of halogenated organic compounds as fire extinguishing agents is widely recognized. Such materials usually have no flash or fire point. Of the elements that comprise the halogen family, namely, fluorine, chlorine, bromine and iodine, the fluorine atom forms the strongest chemical bond in corresponding chemical compounds because of its substantially higher bond energy. Thus our approach to modifying the synthetic hydrocarbon oligomer for improved fire resistance properties will involve the substitution of hydrogen atoms with fluorine atoms. The substitution of all hydrogen atoms with fluorine can be expected to significantly change the properties of the starting material. For example, considering the C₅ to C₁₀ alkane series as model compounds, total fluorination of these materials would increase the density by a factor of about 2.5, increase the vapor pressure thus reducing boiling points and also increase the absolute viscosity. Since we are striving to increase fire resistance properties of the synthetic hydrocarbon oligomer with minimal property changes, the key to the success of this endeavor will be the achievement of fire resistance with minimal fluorine substitution. A review of the literature on fluorine chemistry has indicated that significant fire resistance properties could be achieved in certain hydrocarbon materials with as little as 30% of the hydrogen atoms replaced with halogen.

Elemental fluorine is known to react violently with most organic compounds under ordinary circumstances. The action of fluorine on a carbon compound has been likened to a combustion process where the products are carbon tetrafluoride and hydrogen fluoride. The remaining halogens do not exhibit this type of behavior. The explanation for this behavior can be found by considering the amount of heat given off in the following reaction:

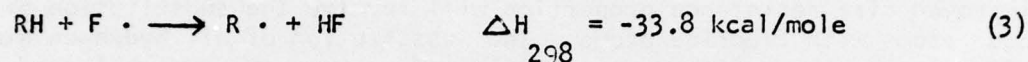


When X represents fluorine, the heat of reaction at room temperature is -103 kilocalories per mole of reactant. Chlorine, bromine and iodine in the same reaction scheme show values of -23, -6 and +14 kilocalories per mole, respectively. The enormous amount of heat evolved with fluorine causes this reaction to reach explosive proportions. In addition, appreciable fragmentation of the hydrocarbon substrate occurs via carbon-carbon bond rupture. The basic problem of direct fluorination involves both kinetics and thermodynamics. The rate of the reaction must be slowed down so that the energy liberated may be absorbed or carried away. The limiting parameter to be considered in attempting to control the reaction of elemental fluorine is the weakest bond in the reactant compound. For hydrocarbons, the example presently under consideration, the average carbon-carbon single bond strength is 84-88 kilocalories per mole. In order to eliminate fragmentation in the reaction, the successful fluorination process must minimize this amount of energy being appropriately localized and available per carbon-carbon bond. Therefore, by reducing the number of collisions of elemental fluorine with the hydrocarbon substrate via dilution techniques and providing a heat sink to remove or absorb the energy liberated, the synthetic hydrocarbon oligomer could be successfully fluorinated.

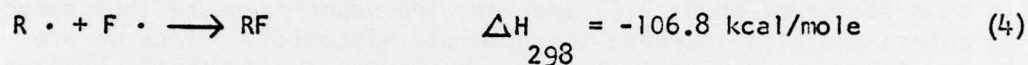
The reaction mechanism can be considered to proceed via two distinct paths. The first involves the dissociation of elemental fluorine into fluorine atoms as the initiation step.



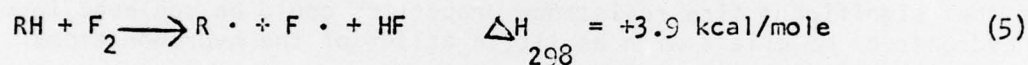
The propagation of free radicals follows as shown:



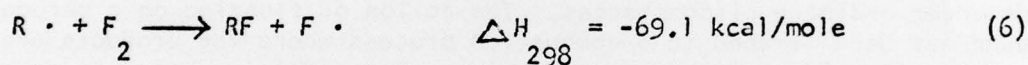
Finally the termination step leads to the desired product



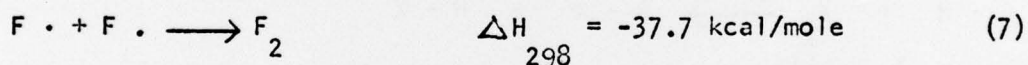
Alternately molecular fluorine can attack the hydrocarbon substrate generating free radicals



followed by propagation of free radicals



with the termination step being the combination of two fluorine atoms as follows:



The net overall reaction in both of these mechanisms results in the following:



EXPERIMENTAL

The direct fluorination technique used in this work is based on the LaMar process and has been previously described in the literature(1).

The synthetic hydrocarbon fluid used in this study is designated Mobil 830A and contained no additives. This material was used as received.

The alkylated silicone used in this study is designated General Electric SF-1147 and contains no additives. This material was used as received. The fluids were tested for physical and chemical property changes as follows:

1. Density was determined using a weld type pycnometer.

2. Viscosity was determined in accordance with ASTM Method D445.
3. Steel on steel wear was determined in accordance with ASTM Method D2266.
4. Wick flammability was determined in accordance with Federal Test Method Standard No. 791B, Method No. 352.
5. Auto ignition temperature was determined in accordance with ASTM Method D2155.
6. The presence of fluorine was determined by decomposing the test fluid with metallic potassium to KF. The KF was then dissolved in H₂O and acidified with dilute HCl. An alcoholic solution of zirconium alizarinate complex was then added drop wise. If fluorine is present the reddish purple complex will decompose to free alizarin which is yellow in color.

RESULTS AND DISCUSSION

SYNTHETIC HYDROCARBON FLUID

This independent research program was initiated in FY-75. As a result of a literature search in the field of fluorine chemistry an approach toward partially fluorinating the synthetic hydrocarbon oligomer was selected utilizing a direct fluorination technique. Experiments aimed at partially fluorinating the synthetic hydrocarbon oligomer were conducted in late FY-75 and early FY-76 with the following results. Initial attempts to partially fluorinate the oligomer directly with a fluorine/nitrogen gas mixture resulted in either no fluorine exchange or only limited exchange (less than 1 wt. percent) depending on reaction time and fluorine/nitrogen gas flow rates. This was somewhat unexpected since materials like polyethylene under similar experimental conditions readily exchanged hydrogen atoms for fluorine atoms. This lack of reactivity suggested the use of a catalytic agent to increase reactivity. Further experiments utilizing sodium fluoride as a catalyst resulted in conversions ranging from approximately 2 to 5 wt. percent fluorine. Efforts to increase the fluorine concentration above 5 wt. percent were unsuccessful. Table I shows property variations of the various fluorinated samples compared to the base fluid (0 percent fluorine). It is evident that the desired increase in fire retardancy capability has not been achieved as measured by two laboratory flammability screening tests. The differences in properties noted suggested that quite possibly the fluorine atoms had concentrated on certain molecular fractions which comprise the synthetic hydrocarbon oligomer. Therefore, an effort was undertaken to vacuum distill each sample and separate molecular components. As presented in Table II, all of the molecular fractions obtained from the fluorinated samples contained some amount of fluorine with no one fraction exhibiting an improvement in fire retardancy.

The difficulty experienced in attaining fluorination levels greater than 5 wt. percent suggested that an alternative approach be considered. The feasibility of fluorinating the starting monomeric components of the synthetic hydrocarbon followed by polymerization to the oligomer was then investigated. Consideration was given to first selectively fluorinating the alpha-olefin monomer. This process would necessitate immobilizing the double bond of the

monomer with a halogen acid group prior to fluorination, followed by dehydrohalogenation to regenerate the double bond for polymerization. The synthesis of the fluorinated synthetic hydrocarbon oligomer from the fluorinated alpha-olefin would require conditions vastly different from those for the non-fluorinated fluid due to the effects of fluorine on the reaction mechanism. These conditions can only be determined by undertaking a study that would be extensive and complex and not within the scope of this study.

ALKYLATED SILICONE FLUID

Another class of fluids namely the alkylated silicones were subjected to the same fluorination procedure as performed on the synthetic hydrocarbon fluid in an attempt to impart enhanced fire-resistance properties to these materials. The fluorination was attempted in several different ways:

1. About 50 ml of this fluid was placed in a pre-fluorinated polyethylene bottle. After 24 hours of fluorine exposure, the I.R. spectrum showed no C-F stretch. Therefore, it was refluorinated for two more days. Even then the C-F stretch was not detected; however, there was a considerable amount of HF in the bottle.

2. In the next attempt a catalyst, solid NaF, was used. About 400 ml of fluid in the presence of NaF was fluorinated for six hours. The product did not show any C-F IR stretch. It was refluorinated for six more hours, but still there was no IR indication of fluorination.

3. A second sample of about 400 ml was fluorinated in the presence of NaF as catalyst for $46\frac{1}{2}$ hours. This fluid too showed no indication of fluorination.

4. In the last study, 400 ml of fluid were fluorinated in the presence of NaF for 113 hours. This sample, too, did not show appreciable evidence for fluorination except for a slight discoloration and for the production of HF fluorination.

In all of these experiments, a considerable amount of HF was present in the bottle after the fluorination reactions. Table III shows the resultant fluid properties after each of those treatments.

R E F E R E N C E S

- 1 - Lagcw, R. J. and Margrave, J. L., Proc. Natl. Acad. Sc., 67, 8A (1970)

TABLE 1. SYNTHETIC HYDROCARBON FLUID PROPERTIES
AS A FUNCTION OF FLUORINE CONTENT

Property	Weight Percent Fluorine				
	0	1.9	2.6	2.9	4.8
Density, g/cc 77 F (298 K)	0.805	0.831	0.830	0.852	0.848
Viscosity, cs or mm ² /s 100 F (311 K)	19.1	23.3	25.9	24.7	37.9
Steel on Steel Wear, 40 kg, 167 F (348 K) 1200 rpm, 1 h (mm)	1.08	0.68	0.77	0.78	0.95
Wick Flammability, Cycles to Ignition	22	17	17	19	23
Auto-Ignition Temp. F (K)	690(639)	640(611)	660(622)	670(628)	610(594)

TABLE II. VACUUM DISTILLATION OF SYNTHETIC HYDROCARBON FLUID

<u>Sample (Wt. % F)</u>	<u>Fraction No.</u>	<u>Qualitative Test For Fluorine</u>	<u>Wick Flammability, Cycles to Ignition</u>
0	1	Negative	3
	2	Negative	4
	3	Negative	20
1.9	1	Positive	16
	2	Positive	16
	3	Positive	15
2.6	1	Positive	18
	2	Positive	16
	3	Positive	17
2.9	1	Positive	10
	2	Positive	10
	3	Positive	19
	4	Positive	10
	5	Positive	19
4.8	1	Positive	10
	2	Positive	12
	3	Positive	9

TABLE III. ALKYLATED SILICONE FLUID PROPERTIES

Property	Sample				
	Original	1	2	3	4
Density, g/cc 77 F (298 K)	0.876	0.897	0.902	0.895	0.904
Viscosity, cs or mm ² /s 100 F (311 K)	35.3	42.3	40.3	42.8	47.1
Steel on Steel Wear, 40 kg, 167 F (348 K), 1200 rpm 1 h (mm)	0.92	1.15	1.03	1.07	1.11
Wick Flammability, Cycles to Ignition	20	17	17	33	17
Auto-Ignition Temp. F (K)	710(650)	645(614)	645(614)	660(622)	650(616)
Flash Point, F (K)	535(552)	435(497)	410(483)	445(502)	445(502)
Fire Point, F (K)	580(577)	540(555)	535(557)	545(558)	550(561)