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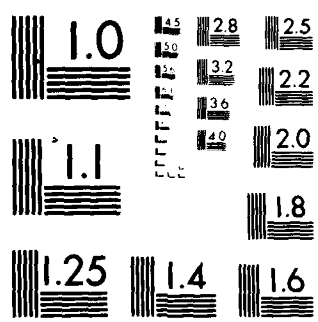

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A survey was conducted to determine the current and anticipated direction of hydraulic fluid research in the Department of Defense (DoD). The principal emphasis currently in each DoD Service is to adapt the Air Force tested, commercially available, halogenated alkanes and halogenated alkyl ethers as nonflammable hydraulic fluids. The use of these materials in Navy systems presents significant problems due to their high density, cost, and potential lack of compatibility with materials in current systems. The

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20. ABSTRACT *(Continued)*

development of new fluids for present systems is seriously hampered by their anticipated overall cost, and with the exception of the Air Force, which is looking toward future systems, the development of new fluids is not expected to be a major direction in other DoD laboratories.

CONTENTS

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CURRENT HYDRAULIC FLUIDS RESEARCH IN THE DEPARTMENT OF DEFENSE

INTRODUCTION

Since 1971, the Advanced Inorganic Materials Section, Code 6137, of the Inorganic and Electrochemistry Branch, of the Chemistry Division at the Naval Research Laboratory, has conducted a research effort directed toward the development of synthetic, non-flammable hydraulic materials. In an effort to determine the future direction for this synthetic program, and to co-ordinate this direction with other Department of Defense (DoD) programs, we reviewed the current and projected direction of hydraulic fluids research in the DoD. The information for this report was obtained from a review of a DoD commissioned report by the National Research Council (NRC) on hydraulic fluids for submarines, from literature searches, and through personal contacts. The report summarizes the attitudes and anticipated directions of these groups as of December, 1980.

CONCLUSIONS AND RECOMMENDATIONS

Our survey and assessment of the current research efforts in hydraulic fluids indicate that the most influential factor considered by the System Commands in their search for new hydraulic fluids is the total cost of the fluid. This cost includes the initial purchase price of the fluid, associated change-over costs, and the maintenance or replacement cost. Currently, no known chemical system can compete with the cost and properties of the water-glycol system for near-term shipboard application.

For aircraft application, and to some degree for submarines, where a non-flammable fluid is required, a different set of problems must be considered in developing a program on hydraulic fluids. Thus, the Commands have placed a significant emphasis on the halocarbon materials to meet the nonflammability requirement, but the high cost and density of these materials may limit their expected usage. If the restrictions of cost and physical properties are allowed to completely dictate the material to be developed and used in the future, then the Navy will have to depend on the outlined formulation programs at NADC and DTNSRDC (Appendix B) to develop nonflammable materials.

Any program to develop nonflammable hydraulic materials must recognize that the properties and cost of such fluids will not be

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comparable to materials currently being used by the Navy. But, the Sea Systems Command will probably resist the use of these fluids in current systems, while the Air Systems Command, which is more willing to redesign systems for future aircraft, may consider the fluid. We believe that any fluid of the type needed by the Air Systems Command would undoubtedly be heavily halogenated and not differ significantly from the industrially developed Air Force materials.

The de-emphasis on hydraulic fluids in the Section was a result of many of the points developed in this report. Earlier discussions with potential Sea Systems Command sponsors regarding ship applications indicated their concern for the potential high cost of the materials, and the system modifications required for their high density. We considered modifying our approach to minimize these problems by reducing the amount of fluorine, and the pentafluorosulfur group content in the materials, but this alternative was unacceptable when considering the overall properties of the resulting materials. Typically, partially halogenated compounds have a significantly reduced thermal stability and fire resistance; in addition, they form large amounts of toxic hydrogen halide gas during decomposition or combustion. A last alternative was to consider mixed halogen materials, but these were commercially available and under study by the Air Force. Therefore, our ability to provide potential hydraulic fluids is limited by the Sea Systems Command's direction.

This restrictive synthetic environment is also presented in the NRC report which gives no encouragement or direction to the synthetic programs. The stated purpose of their recommendations was to completely discourage efforts which do not address all the parameters (pg. 3) for a potential fluid. As a result, the NRC report responds negatively to each area of current synthetic research. Also, the report identifies the lack of direction to these programs due to a poor understanding of the desired "fire safety improvements", and the need to reduce the requirement that the materials developed be responsible for meeting problems of system compatability. In reality, the Sea Systems Command has limited funding for new materials or extensive system modifications and therefore, cannot provide the realistic guidance for new synthetic directions.

At this time, we conclude that limited ONR/NRL 6.1 funds should not be used to support advanced hydraulic fluids research at NRL. The Inorganic and Electrochemistry Branch will retain its synthetic capabilities, but directed to other areas, so that NRL can provide technical assistance to the SYSCOMS/Navy when their program objective is to develop advanced materials with specific properties and the synthesis requires our expertise.

WHAT MAKES A FLUID SUITABLE FOR HYDRAULIC SYSTEMS

A single list of parameters or properties for all hydraulic fluid applications is not realistic. Each parameter from such a list could become sufficiently important in a given situation to eliminate a material under consideration. Therefore, the most important factor is whether the fluid is to be used in an existing or proposed hydraulic system. For example, the types of hydraulic fluids sought by the Navy fall into two classes: (1) improved fluids that can replace current fluids by offering significant improvements in all parameters without requiring an alteration of existing shipboard plumbing, and (2) new fluids for future Navy platforms that will dictate major departures from current hydraulic system designs and components. The System Commands have occasionally sponsored some development work for new fluids, but their primary efforts center on the formulation of fluids from existing materials by the addition of additives, and the testing of available materials for potential application as hydraulic fluids. The parameter that appears to significantly limit the development of improved fluids is the higher cost of these fluids compared to the current materials; although not completely true, this does prevent serious support of programs to develop new materials.

The intent of this report is such that details of the major chemical and physical properties or requirements sought in chosing a hydraulic fluid are not totally necessary. However, a list of important parameters and what we believe to be their order of importance is appropriate. They are:

a. Fire resistance
b. Toxicity
c. Stability toward heat, air, water, and metals of construction (corrosion)
d. Density
e. Lubricity
f. Viscosity
g. Compatability with existing hydraulic plumbing
h. Load-carrying ability
i. Low temperature properties
j. Cost

NAVY DIRECTION IN HYDRAULIC FLUIDS

Programmatically, NAVSEA does not appear to anticipate the need to develop new fluids with superior properties for existing systems at this time. The current philosophy is to use existing fluids (Appendix A) to meet the current requirements and to direct programs toward modifying specific properties rather than developing "super" fluids, (Appendix B). The NAVSEA program managers do not believe a near-term need exists to develop new, high-temperature materials. In addition, they believe any new fluid would cause problems with the operating characteristics of the present plumbing in the hydraulic systems, and would require costly conversions. This extra work to incorporate a new fluid would not be consistent with the extended-life program for ships. Unless major system design changes occur that would result in a significantly higher temperature of the bulk fluid or the fluid film, the long-term development of new high-temperature fluids would not be expected to differ from the current NAVSEA direction. The development of fire-resistant fluids, especially for submarines, is one area in which new materials could be beneficial, but we know of no basic, developmental programs to address this need.

The current fire-resistant fluids cause several problems in shipboard applicatons. Appendix C summarizes NRC's attempt to evaluate materials for hydraulic fluids. The transition from phosphate esters to a water-glycol fluid demonstrates the problem of substituting one material in a system designed for another. The triaryl phosphates are being phased out and many of the systems that used the phosphates are being changed to the water-glycol fluid. The change-over is not straightforward since the operating temperature of the phosphate-designed systems, which are not designed to cool the fluid, is higher than the recommended operating temperature (140°C) of the water-glycol system. The water-gylcol mixture has a tendency to lose water at elevated temperatures which results in a decreased fire-resistance. The use of the water-glycol fluid in the phosphate-designed systems also results in a materials-compatability problem requiring a costly conversion.

Currently, the fluids for Navy aircraft applications are chosen mostly from non-Navy programs. With the exception of a truly nonflammable fluid, the Air Systems Command does not believe the aviation industry is looking for new fluids. Unlike submarines where the potential for hydraulic fires is very real, but actual major hydraulic fires have not occurred; aircraft hydraulic fires are all too common. The Air Command believes that the halocarbon materials formulated by the Air Force have the requisite nonflammability to solve this problem, but the high density of the Air Force fluid could result in an undesirable weight penalty for the aircraft. However, high-pressure hydraulic systems, and dual-fluid systems are currently being evaluated to reduce the amount of high-density material needed.

The initial cost for a fluid was not considered significant by the Air Systems Command since the material is such a small part of the overall cost of an expensive aircraft. However, when the cost over the lifetime of the aircraft is estimated, the impact of the fluid cost on the maintenance budget must be considered. Therefore, a new material may be rejected due to the impact of its cost on the maintenance budget for the aircraft. Consequently, an NADC-developed chlorinated polysiloxane, believed to have a potential application in some current and near-term developed aircraft, is being re-evaluated from a maintenance standpoint due to a projected cost of approximately $60/gallon and a potential problem with hydrolysis.

HYDRAULIC FLUIDS RESEARCH IN THE ARMY AND AIR FORCE

The Army and the Air Force (Appendix B) also have specific requirements for the use of hydraulic fluids, although their systems differ significantly from shipboard requirements. The Army effort is concerned primarily with applications directed to armored vehicles and includes the development of hybrid oils to serve as both hydraulic and transmission oils, fire-resistant fluids, and the improvement of low temperature characteristics of fluids. A complete compatability testing program is currently being conducted to evaluate the Air Force chlorofluorocarbon fluid, and a new start at the Picatinny Arsenal is directed toward developing advanced fluids for weapons recoil systems.

The Air Force, through the Materials Research Laboratories at the Wright-Patterson Air Force Base (WPAFB), appears to be the lead Service laboratory in developing new fluids for high stress applications. As such, the WPAFB group has the research capability for developing new advanced fluids for Navy aircraft and possible future (10 years) shipboard applications.

APPENDIX A

NAVY HYDRAULIC FLUIDS

The fluids used by the Navy can be divided into four classes: (1) water-based, (2) petroleum-based, (3) synthetic hydrocarbon, and (4) phosphate ester.

(1) Water-Based Fluids

The water-based fluids (MIL-H-22072) are composed of water-ethylene glycol mixtures which result in a nonflammable fluid. The Navy use of this class of fluids is approximately 60,000 gallons/year and the cost ranges from $3.60 to $5.60/gallon depending on the size of the container purchased. The presence of a minor impurity in this material is suspected of resulting in the formation of a nitrosamine, a cancer-producing chemical, which has led to a re-evaluation and reformulation of this fluid.

(2) Petroleum-Based Fluids

The petroleum fluids (MIL-L-17662 and 17331) are a variety of oils (basically SAE 5,10,20, and 30) and the Navy usage is approximately 2-4 million gallons/year at a current cost of less than $2.00/gallon. These fluids do not offer significant fire-resistance.

(3) Synthetic Hydrocarbon Fluids

The synthetic hydrocarbon fluid (MIL-H-83282) has become an increasingly important material as the quality of crude oil varies and the dependency on foreign crude supplies continues. The synthetic hydrocarbon is prepared from the hydrogenation of poly(α-olefins) which can be produced from non-petroleum sources and provides a product with fairly reproducible properties. The Navy use of this fluid is approximately

350-400,000 gallons/year in aircraft at a cost of approximately $8.00/gallon, and the Army uses an additional 100-150,000 gallon/year for helicopters. The synthetic hydrocarbon material is a good retrofit material for hydrocarbon-based materials, has reproducible physical properties, and its production is not dependent on oil sources. However, the material does not provide significantly improved fire-resistance.

(4) Phosphate Ester Fluids

The triaryl phoshate fluid (MIL-H-19457) is another nonflammable fluid and its usage is approximately 125,000 gallon/year at a cost $5-$13/gallon. The phosphate fluids lose much of their benefit as a nonflammable fluid because of an extensive materials compatibility problem and a considerable neurotoxicity. The toxicity has been associated with the aryl group, particularly the o-cresyl isomer, but more recent developments have shown that the toxicity can be eliminated by substituting a different organic group. The cost for the improved phosphate fluid is expected to be in the $10-$15/gallon range.

APPENDIX B

DOD RESEARCH TO DEVELOP AND IMPROVE HYDRAULIC FLUIDS

The principal sponsors of hydraulic fluids research within the Navy are the Naval Sea Systems Command (NAVSEA 0524) and the Naval Air Systems Command (NAVAIR 52032). The David Taylor Naval Ships Research and Development (DTNSRDC), Annapolis, MD, and the Naval Air Development Center (NADC), Warminster, PA, perform these Navy sponsored tasks.

The Navy laboratories are taking essentially the same direction as that of the Commands, i.e. over the next 5-10 year period the development of significantly improved fire-resistant fluids is not being sought, but improvements are being directed to the water-based materials or phosphazenes. Currently, the research conducted at DTNSRDC does not involve in-house development of new fluids, although earlier DTNSRDC work led to a promising fluid before projected costs ($30-$35/gallon) prevented further consideration of the material. The current DTNSRDC program, which is mostly test and evaluation, involves industrial proprietary formulations of poly(α-olefins), a reformulated water-glycol mixture to eliminate the nitrosamine problem, and alternative phosphate ester materials. Additional evaluation work regarding the expensive phosphazene and halocarbon materials may also be initiated. Because present systems for conventional fluids are designed to operate with maximum fluid densities of 1.6 grams/milliliter, the ultra-high temperature, fire-resistant halocarbons and halocarbon ethers, which are fluids generally having densities near 2, could present significant problems without major revisions to existing systems. The operating temperature of the bulk fluid in most shipboard systems does not exceed 200^{o}F and is typically 120-130^{o}F. The film temperature of the fluids (230-240^{o}F) does not significantly exceed the bulk operating temperature which also reduces the need to develop special fluids. A similar attitude exists regarding fire-resistant fluids in that breakthroughs in synthetic chemistry to give significantly improved fluids are not anticipated by NAVSEA in the next 5-10 years: therefore, no program is planned to develop new materials.

The NADC group developed (6.2 funded) a chlorinated polysiloxane fluid which is under test for use in lightweight hydraulic systems. The fluid has a maximum operating temperature of approximately 400^{o}F, but its low temperature usage could require some system redesign. In addition, the bulk modulus (which determines the ability of the fluid to transfer a load) is lower than desirable, and the siloxanes appear to be susceptible to hydrolysis; as a result, they can cause severe corrosion problems in the delicate systems.

The current work at NADC is a multiman-year effort concerned with the formulation of fluids by incorporating a variety of additives to improve lubricity, swelling, low-temperature properties, etc. Synthetic work to develop new materials is not being conducted at NADC; the only other program involving hydraulic fluids is an evaluation of the synthetic hydrocarbon materials.

The Air Force has been supporting a sustained in-house and contract research effort in fluids and lubricants for several years and as a result has developed and maintained the personnel and necessary program coordination. This program has been a mix of basic and applied research and has covered all areas from the synthesis of new materials, modification of existing materials, development of additives, and formulation of fluids, to the testing of commercially developed fluids. The current program is a 4 man-year effort and is complemented by an equal effort in engineering and evaluation of materials. The close proximity of these groups allows the rapid transfer of ideas, results, and requirements which enhances their effort by minimizing the administrative and programmatic delays between molecular design, development, and fluid testing.

The Air Force is continuing to develop new high temperature fluids for future application and is now looking at missile requirements in the 600°F region. The research group has studied a range of fluids from heavily fluorinated materials to silicon-based and hydrocarbon materials. The program on fluorinated materials was terminated a few years ago, but, with the renewed emphasis on high temperature materials, is scheduled to resume in FY 83. This technology resulted in three materials being considered as fire-resistant fluids: poly(chlorotrifluoroethylene), $(-CFClCF_2-)_x$, developed by Halocarbon, Inc.; perfluoroalkyl ethers, $(-R_fOR'_fO-)_x$, developed by Montedison (Fomblin fluids); and poly(F-propylene oxide), $(-FC(CF_3)CF_2O-)_x$, duPont's Krytox or Freon E fluid. Since these fluids are commerically available, the emphasis of the WPAFB group has been on testing and evaluating the fluids, and developing compatible additives for the fluids.

In the future the WPAFB research group will continue developing high temperature lubricants and fluids. The requirement for fire-resistant materials is expected to be met by the poly(chlorotrifluoroethylene) fluid with the Freon E as a back-up material. In addition, small volume, high-temperature lubricants will be developed from the fluorinated ethers. The near-term synthetic efforts will center on preparing silicon-centered, long-chain hydrocarbon materials (SiR_4 termed silahydrocarbons), the development of methods to prepare 1,3,5-trisubstituted benzene compounds, and the preparation of synthetic hydrocarbons which lack tertiary hydrogens, i.e. large molecules lacking the RR'R"CH hydrogen, which are associated with reduced thermal stability. Because the latter technology is related to commerical synthetic motor oil developments (Mobil 1, etc.), the WPAFB research group has contracted much of this research to industry. The development of the silahydrocarbons will be an in-house effort (~FY83) and is expected to result in classes of compounds which can be readily altered to change physical properties while maintaining the high thermal stability of model compounds ($\sim 700^{\circ}F$). In addition, these compounds are expected to be hydrolytically stable for extended periods (10 yr. on-line life-time) as opposed to the siloxanes which would be expected to have a significantly lower hydrolytic stability.

The 1,3,5-substituted benzene derivatives will be synthesized by developing specific trimerization techniques for alkynes. The in-house effort will result in pure 1,3,5-substitution rather than mixtures with a variety of substitution patterns. Model compounds show that 1,3,5-substitution has a significantly greater thermal stability compared to mixtures or pure compounds with a different substitution pattern, e.g. 1,2,4-substitution. The derivatives will then be evaluated and their characteristics compared to the similar and more complex triazine ring derivatives which have been proposed as the nucleus for fluids development. A factor that should be evaluated in considering the trisubstituted benzene materials is toxicity. As a general class aromatic compounds are known to be carcenogenic and if the relative amount of benzene in these compounds becomes significant the toxicity may be an important considerations.

APPENDIX C

SUMMARY OF THE NATIONAL RESEARCH COUNCIL REPORT ON "FIRE-RESISTANT HYDRAULIC FLUIDS IN ENCLOSED MARINE ENVIRONMENTS"

The National Materials Advisory Board of the National Research Council issued a report (NMAB-345) in 1979 entitled "Fire-Resistant Hydraulic Fluids In Enclosed Marine Environments". The report, concerned with the submarine environment, covers a variety of topics including failure modes and fire hazards, tests for combustion, corrosion and toxicity, interpretation of test results to fire hazards, and type of fluids. Their evaluations of the materials considered for hydraulic fluids are as follows:

1. Hydrocarbon Fluids

Synthetic hydrocarbon fluids have been developed with improved properties and are the most likely candidates to replace the current petroleum-based fluids. These materials have physical properties sufficiently similar to the current materials that they can be used with little, if any, modification of existing systems, but they do not offer significant improvement in fire-resistance.

2. Halogenated Materials

Three materials were identified in this class of compounds which offer improvements in fire-resistance: chlorotrifluoroethylene-vinylfluoride oligimers, fluorocarbon polyethers, and fluoropolyether triazines. These materials while having improved fire-resistance could present problems in that they have high densities and could require substantial system modifications. In addition, the report expresses concern over the toxic and corrosive properties of the combustion products from these materials (primarily HF or HF generating compounds) and potential explosiveness of some halocarbons when in contact with alloys containing high amounts of aluminum or magnesium.

3. Silicones

The silicone materials were also thought to be a promising class of compounds but requiring additives to improve some properties. The most significant weakness appeared to be that the silicones tended to burn in spray tests.

4. Aryl Phosphate Esters

The neurotoxicity of these phosphate esters was considered to be over-riding. Extensive tests were recommended to demonstrate the lack of toxicity of any new material. In addition, the phosphate esters have a serious problem regarding materials compatibility which would limit their use.

5. Water-Based Fluids

The water-ethylene glycol system is considered to offer improved fire-resistance but cannot be substituted for petroleum-based materials without system modification. Also, the loss of fire-resistance, which occurs when the water evaporates, is considered a significant problem.

The report does not appear to endorse a particular class of compounds or suggest a course which could be pursued toward developing fire-resistant, non-toxic compatible fluids. The recommendation for "Initiating Synthetic Work" is as follows:

> "Guidelines suggested by all of the above recommended research should be considered before new synthetic work is undertaken. The intent is not to stifle new developmental work but is to thwart new synthetic efforts, wasteful of

time and effort, that improve fire safety properties at the expense of introducing other problems such as a toxic threat from hydraulic fluid."

The realities of such a recommendation are that no known systems currently under investigation should be pursued. The report identifies the halocarbon materials as "promising for future application", but those systems identified were also suspect with regard to toxic combustion products and eventually may be cost prohibitive due to required system modifications. Those materials which would require the least system modification, i.e. the synthetic hydrocarbons, do not offer significant fire-resistance for consideration.

The report does little to guide synthetic programs toward the development of new hydraulic fluids. This deficiency cannot be blamed on the committee but more on the problem of the requirements and limitations of the Navy. These points are only briefly touched upon in the report:

> "A thorough hazard analysis could well provide a quantitative basis by which compounds could be assessed and that could guide future fluid synthesis programs and additive selection. A better understanding of the quantitative nature of the fire safety improvement might also provide better motivation for materials and design changes to accommodate fluids that are truly superior from the safety point of view. It is not reasonable to require that the hydraulic fluid carry the complete burden of assuring compatibility."

The Navy, through the Sea Systems Command, continues to require that fluids which are developed assume the complete burden of compatibility. However, the budgetary limitations imposed on the Command severely limit the purchase of expensive materials or the modification/replacement of systems to accept new classes of compounds.