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**FIRE-RESISTANT HYDRAULIC FLUIDS
IN ENCLOSED MARINE ENVIRONMENTS**

Report of

THE COMMITTEE ON FIRE-RESISTANT HYDRAULIC FLUIDS

**NATIONAL MATERIALS ADVISORY BOARD
Commission on Sociotechnical Systems
National Research Council**

**Publication NMAB-345
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This report has been reviewed by a group other than the authors according to procedures approved by a Report Review Committee consisting of members of the National Academy of Sciences, the National Academy of Engineering, and the Institute of Medicine.

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ABSTRACT

This report is the result of a review of the status of research directed toward the reduction of fire hazards associated with hydraulic systems. Particular attention was given to the problems associated with the search for less flammable hydraulic fluids. The nature and significance of tests to evaluate the flammability of candidate fluids and such practical considerations as toxicity and corrosivity, which affect the selection and use of hydraulic fluids, were emphasized. A statistical fire-hazard evaluation study of each hydraulic system and its environment is a key factor in determining the desired properties of candidate fluids and must be used as a guide to the search for new, improved fluids.

PREFACE

To date, improved fire-resistant hydraulic fluids compatible with submarine systems designs, operating conditions, and environmental and human factors have not been found. As a result, the Department of Defense requested that the National Research Council appoint a committee to identify means of finding and testing suitable hydraulic fluids for submarines.

Previous efforts with candidate fluids to replace the petroleum-based hydrocarbon fluids presently in use in submarines have been unsuccessful for a variety of reasons:

- Their physical properties do not meet the requirements of the hydraulic system.
- They do not remain inert to materials of construction of the hydraulic system.
- They are not inert to items outside the hydraulic systems (important in case of leaks or spills).
- They do not protect the system from damage when seawater contamination occurs.
- They are toxic.
- And of less importance, they are expected to be too costly.

The ultimate goals of the sponsor were to find:

- A single fire-resistant fluid suitable to replace the three petroleum-based hydrocarbon fluids now in use in submarine internal main and vital, and external hydraulic systems. However, the Navy would consider two or even three replacement fluids if fire resistance were improved and if requisite physical properties were equal or superior to those of presently used fluids.
- A fluid that is or could be made available in the quantity required (approximately 200,000 gallons per year).
- Laboratory tests that can simulate submarine conditions to determine the required fire resistance of submarine hydraulic fluids.

With these goals, the NMAB ad hoc committee was established to:

- Review problems posed by hydraulic fluids in an essentially closed environment.
- Propose means for finding new fluids and estimating the likelihood of their success.
- Provide bases for the development of tests to determine submarine hydraulic fluid fire resistance.

No known catastrophic fire attributable to hydraulic fluid has occurred on a submarine--a credit to those who design, build, and operate submarines. Obviously then, this places a great responsibility on the committee to assure that its recommendations do not result in research directions that would lead to an increased fire hazard potential or introduce or aggravate other hazards.

In order to review the hazards posed by hydraulic fluids in a specific environment, it is necessary to know the characteristics of that environment and the probability that a particular failure mode will occur. Similarly, the means of fluid development can only be identified for a specific system after the critical parameters of greatest significance have been identified and the magnitude of the desired properties estimated. It is further evident that the development of laboratory tests to determine fire resistance requires a thorough knowledge of the subject environment.

Since specific data were not available for submarine systems, it became evident that this study could not address all of the goals listed previously as they pertain to submarines. In view of several reports dealing with hydraulic fluid flammability (ASTM, 1959, 1966; U.S. Bureau of Mines, 1975; Ames Research Center, 1976), it was decided that this study should emphasize several problems that had received less attention in previous work and were still of relevance to some aspects of the submarine environment. Operation in seawater emphasizes the problem of corrosion if saltwater contamination occurs, and the fact that the hydraulic system exists in a closed, inhabited environment makes the problem of toxicity of the hydraulic fluids and their reaction products an important hazard consideration. Since the screening of potential hydraulic fluids is usually accomplished through the use of laboratory tests, the interpretation of laboratory tests was the focal point.

To obtain information needed to arrive at the conclusions and recommendations presented in this report, the committee held a workshop. The workshop was chaired by Dr. Edward A. Fletcher because of the illness of the undersigned. We are indebted to him for his able assistance and extensive contributions to the writing and editing of this report.

Leaders of workshop sessions and contributors to various topics of the report were as follows:

Chemistry--Drs. Paul Tarrant and Martel Zeldin
Combustion--Drs. Melvin Gerstein and Edward A.
Fletcher
Corrosion--Mr. Joseph F. Rynewicz
Toxicity--Dr. Paul L. Wright

We also gratefully acknowledge the assistance of Drs. Charles F. Reinhardt and Seymour L. Friess for their contributions to the toxicity discussion, and to the following for their tutorial presentations at the workshop: Keith B. Baucom, William Cassanos, Barrett L. Cupples, Roger Hatton, James E. Jones, Reinhold Kratzer, Walter E. Lewis, and Carl E. Snyder; and to Drs. Robert E. Singler and Paul Becher for technical assistance. To all who attended the workshop we extend our appreciation. The committee also wishes to express its gratitude to Dr. Stanley Barkin for his coordination of a variety of activities, including his assistance in collecting relevant reports. It is a pleasure to acknowledge the help of Mrs. Stephanie Paul who organized my efforts and typed the original drafts of this manuscript.

Melvin Gerstein, Chairman

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CHAPTER I

INTRODUCTION

Hydraulic systems are an essential part of complex vehicles such as aircraft and ships. These systems include a network of lines that carry at elevated pressure a fluid whose flammability affects safety throughout the vehicle. Construction is facilitated by routing hydraulic lines, steam pipes, electrical wiring, and various other lines through common channels. Thus, failure of one of the components may involve others; good planning dictates that great effort be made to minimize failures that could be disastrous. Any measures that reduce the potential of hydraulic fluid to start or to aggravate fires will contribute substantially to the safety of a vehicle.

It is tempting to try to reduce the fire hazard by searching for an ideal fluid that will not burn; is compatible with all materials; possesses the properties of lubricity, density, and compressibility necessary for efficient operation; and is, of course, plentiful and cheap. Such a fluid may someday be found, but until it is compromise will be necessary. The difficult problem is to decide which compromises must be made.

A great deal of research has already been done to find hydraulic fluids of improved fire safety compared with petroleum-based fluids. Some alternative fluids are already in use, but the search continues. It is evident that no fluid is completely satisfactory. Fluids showing advantages in one property often have major deficiencies in other properties.

There has been a tendency to place the complete responsibility for compatibility with all other systems and components on the candidate fluid. In any serious effort to improve fire safety, some system alterations may have to be made to accommodate the characteristics of substitute fluids.

With regard to fire safety, the guidelines for fluid selection have to be formulated on the basis of laboratory tests whose relationships to the real fire hazards are

well established. Each system and its environment must be analyzed to establish goals for finding new fluids and relaxing requirements for properties that are not of major importance.

Chapter II of this report contains a summary of the major conclusions of the committee and recommendations for future work. While this section is written so that it can be read independently of the remainder of the report, its contents rest on the discussion contained in the rest of the report.

Chapters III-VI and the Appendix contain the main body of the considerations from which the conclusions and recommendations were drawn. The report is intended neither as a handbook nor as a complete survey of the state of the art, although a bibliography is included that could serve as an introduction to the state of the art. Chapters III and IV are introductory in nature and are included to facilitate subsequent discussion and assist in defining some terms and points of view. Chapter III deals with typical failure modes in hydraulic systems and Chapter IV with a description of some of the tests used to evaluate the combustibility, corrosivity, and toxicity of candidate fluids. Chapter V, on fluids, reviews the present status of available fluids, points out promising areas of research, and highlights some of the problems of finding improved hydraulic fluids. Chapter VI deals with the interpretation of combustion tests in relationship to fire hazard.

The use and interpretation of laboratory tests is important in evaluating candidate fluids and in establishing criteria for judging the nature and degree of a new fluid's improvement in fire safety. This measure is, indeed, crucial since only by an evaluation of the gains in safety can a decision be made as to the cost and inconvenience merited by that gain. That decision cannot be made in this report, but the report does discuss the technology involved in establishing the background for such decisions.

CHAPTER II

CONCLUSIONS AND RECOMMENDATIONS

The committee has reviewed the status of knowledge with respect to hydraulic-fluid fire hazards. The fire hazard problem is a complex one that depends on interaction between fluids, hydraulic systems, and the surroundings. Lacking an adequate description of a given system and its surroundings, we cannot estimate the likelihood of success. We have examined a variety of fire safety tests and have made recommendations for future research that we believe would significantly improve fire safety.

The committee has drawn the following conclusions and recommendations.

CONCLUSIONS

Knowledge and Understanding

1. The search for safe hydraulic fluids must be based on two conditions.

One is a precise knowledge of the conditions under which they are to be used. By this we mean conditions that a hydraulic fluid might encounter inside or outside the system as a result of a mishap or malfunction as well as normal operating conditions within the hydraulic system.

The other is an understanding of the relationship between fluid properties and fire hazards. Conventional fire hazard indices are often not good predictors of fire hazard. Competent analysis is needed to correlate test results with fire hazard.

Test Methods

2. Present test methods to establish hydraulic-fluid fire hazard are inadequate. They do not adequately simulate actual conditions; neither do they permit reliable extrapolation to actual conditions, nor do they provide bridges by means of which such extrapolations can be made.

3. Methodology for the quantitative assessment of toxic hazard to human health and the environment from exposure to hydraulic fluids is ambiguous.

4. Present test methods for corrosion resistance are generally satisfactory but do not simulate the combination of dynamic and static conditions typical of hydraulic systems.

Hydrocarbon Fluids

5. An ideal hydraulic fluid is not known to exist. Many fluids with improved fire resistance are not compatible with existing hydraulic system components and design characteristics. The prime retrofitting candidate fluids to replace the petroleum-based hydraulic fluids now in use are synthetic hydrocarbons that have physical properties similar to these petroleum-based fluids. However, they offer little in the way of improved fire safety.

Nonhydrocarbon Fluids

6. Halogenated Materials. Halogenated materials appear to have a very high fire resistance, but their products of combustion are toxic and corrosive. Certain halogenated materials are very resistant to biodegradation and may accumulate in biological organisms, thus they are unacceptable for any system that could discharge into the environment.

Three classes--chlorotrifluoroethylene-vinylidene fluoride oligomers, fluorocarbon polyethers, and fluoropolyether triazines--show promise, but because of high densities, for example, may require system modifications.

7. Silicones. Silicone fluids as a class show promise. They have good material compatibility but poor lubricity and high compressibility, and, unlike halocarbons, they burn in a spray test.

8. Aryl Phosphate Esters. Certain substituted aryl phosphate esters cause delayed neurotoxicity. The most active neurotoxic, commercially available phosphates are those produced from cresols from natural sources. Extensive testing has demonstrated that synthetic hydraulic fluid manufactured from tertiary butylated phenol is not neurotoxic. A clear demonstration of the lack of toxicity of the fluid and its degradation and combustion products would be required to renew interest in phosphate esters.

9. **Water-Based Fluids.** Water-based fluids offer improved fire resistance in their formulated states, but many leave flammable residues when the water evaporates. Generally they cannot be substituted for petroleum-based fluids without system modification.

RECOMMENDATIONS

Fire Hazard Analysis

1. A thorough fire hazard analysis should be made of the system in question. Such an analysis should include consideration of possible failure modes, the properties of all flammable materials as well as those of hydraulic fluids, and the potential of the environment to furnish interactions that can lead to ignition.

Modified Conditions of Use of Fluids

2. Serious attempts should be made to find ways in which the conditions under which hydraulic fluids are used can be modified to improve safety, such as changes in the ambient conditions and system characteristics.

Improved Fire Testing

3. Research to develop improved fire test methods for hydraulic fluids should be undertaken.

4. A research program should be initiated to develop laboratory tests that correlate with the fire hazard in the system considered. Emphasis should be placed on how the surroundings may act either as a promoter or inhibitor of ignition and combustion processes.

Toxicity Evaluation

5. The recommended approach to toxicity evaluation--a tier approach--is one in which preliminary, i.e., simple and acute, toxicity evaluation is conducted early in the development of a fluid, and further toxicity evaluation (chronic and special) proceeds as interest in the fluid develops.

The toxicity of hydraulic fluids presently in use should be tested according to the procedures recommended for new fluids and thus serve as a basis for comparison.

Corrosion Testing

6. The test for corrosion resistance should be changed to an "on-off" procedure to simulate static conditions. The test specimens should be not only steel, but also galvanic couples of the materials that simulate actual material combinations in the hydraulic systems.

Guidelines for Initiating Synthetic Work

7. 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 development 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 the hydraulic fluid.

CHAPTER III

FAILURE MODES AND FIRE HAZARD

In evaluating the risks associated with the use of hydraulic fluids we must keep in mind that the hazard is a consequence of the way the fluid interacts with its surroundings. It depends not only on the properties of the fluid but on the nature of accidents as well as routine use, and on the environment in which the fluid may be placed. The falling beam that slices through a hydraulic line is also likely to cut the nearby electric cable, which will produce an arc far from where it is anticipated that there would ever be one. An overheated pump bearing may simultaneously produce a very hot surface and a fluid leak. The number of hazardous situations is limited only by one's imagination. In citing some failure modes and hazards in this section, we point out what seem to be the generic natures of the most likely predictable hazards.

Some of the failure modes that can occur are the following:

1. A stream or spray is ejected from a break or leak in the hydraulic system. It encounters sooner or later (the time involved changes the nature of the hazard) an ignition source such as a spark, flame, or hot surface. In this example, the difficulty of correlating fluid properties with the seriousness of a hazard is well illustrated. If the leak is not too large, the fluid ignites quickly, and the flame is observed, the hazard might be quickly eliminated. If the leak does not ignite quickly and produces a fog that accumulates and is subsequently ignited, the result is likely to be a disastrous explosion. Because hydraulic systems operate at high pressure, leaks must be anticipated that can lead to hazards associated with ignition of the fluid sprays and fogs formed.

2. An air bubble is suddenly compressed in the hydraulic system. It is the belief of the committee that the nature of this hazard is generally not well understood. It is widely held that chemical reaction takes place only at a fluid-air interface; this is probably not true. The pressure is quite likely to be above the critical pressure

of the fluid. Moreover, after compression, the air is quite likely to be at a temperature above the critical temperature of the fluid. The air space, after the compression, more closely resembles a hot, inhomogeneous, one-phase region that contains a fuel-air mixture having a wide range of compositions. The likelihood that such a mixture will explode is very dependent on how effectively it is cooled by its surroundings.

3. A hydraulic fluid spills or drips onto a hot surface, wets it or forms a pool, and is eventually ignited. Perhaps it undergoes a pyrolytic chemical change or is separated by distillation into two or more components, one of which is easily ignited by the surface or a nearby spark or flame.

4. Porous or wicklike material such as polyurethane foam insulation or steam pipe lagging slowly becomes impregnated with hydraulic fluid whose composition may change over long periods of time ultimately to produce a hazardous situation. There are really two distinct hazards here. One stems from the fact that some fluids that cannot be easily ignited when they are exposed to a flame can be easily ignited by a flame when they are held on a wick. The other stems from the fact that when combustible mixtures, especially in large volumes, are insulated against heat loss, they can self-heat and ignite spontaneously.

5. Hydraulic lines often parallel electrical power lines. Leaking fluid may interact with electrical insulation (perhaps in the presence of water) to provide conducting paths that become fire hazards.

The fluid properties that affect the nature and degree of fire hazard differ for different failure modes. If one failure mode is more probable than others, and would produce a serious fire hazard, improvements in the fluid property to reduce the fire risk associated with that failure mode may substantially increase safety even if the properties associated with other failure modes increase the fire risk associated with those modes.

CHAPTER IV

TESTS

A large number of diverse types of tests can be used to characterize the properties of candidate hydraulic fluids. A complete description, even a complete listing, of all the available tests is beyond the scope of this report. This chapter briefly describes some of the major types of tests used to evaluate combustibility, corrosivity, and toxicity. It should be understood that each class of tests may have many variations that are not discussed here but may be found in the literature.

COMBUSTION TESTS

There is a vast technical literature on combustion tests. These tests are intended to provide a small-scale, reproducible, and convenient method for predicting the behavior of combustibles in practical, full-scale situations. They attempt to predict when a given situation will lead to an unwanted fire or explosion and also guide the selection of fluids, design of systems, and establishment of operating procedures to eliminate or at least minimize fire risk. Unfortunately this objective is often not reached. It is often replaced by a listing of test results, ranking of materials, and other numerical data that may provide little or no insight into the actual fire hazard. If conclusions are drawn from "handbook" test data without regard to the significance of the results and resolution of apparent contradictions, substitutions may be made that increase the fire risk rather than reduce it, or conversely, useful materials may be unnecessarily excluded. Because of the complexity of real fire hazard situations, those tests that most closely resemble the actual problem are often the most useful. It is not always feasible to design such tests, however, and a variety of "standard" tests have evolved, some of which are briefly described below. A more detailed discussion of the relevance, advantages, disadvantages, and interpretation of some of these tests will be discussed in the interpretation of test results. (See Chapter VI.)

Flash point

The flash point (ASTM D-92) is one of the most widely used measurements to assess the fire risk of fluids. The temperature of a sample of liquid is varied and the vapor above the liquid is tested with a small flame to determine whether the vapor-air mixture is flammable (flashes). If the liquid continues to burn after ignition of the vapor-air mixture, the measurement is called a fire point. This test is intended to measure whether a liquid spill at ambient temperature will provide a vapor-air mixture that can be ignited by a flame, spark, or other ignition source. Because the liquid/vapor volume ratio in the test does not usually conform to the conditions existing in the system being evaluated, the complexities of mixtures of fluids cannot be adequately considered.

Thermal ignition

The most widely known thermal ignition test is the ASTM Autogenous Ignition Temperature Measurement (ASTM D-2155). In this test, a measured volume of liquid fuel is dropped into a heated flask containing air at 1 atm pressure; the temperature at which ignition occurs is recorded. This test is intended to measure the lowest temperature at which a liquid impinging on a hot surface will ignite.

Due to the complexity of the thermal ignition process, a large number of other tests have been devised to simulate other geometries such as exposed hot pipes, ventilated surfaces, surface materials variations, and scale. Although the ignition of spills on hot surfaces is a widely acknowledged fire hazard, the testing, understanding, and interpretation of thermal ignition data are some of the most difficult problems in fire hazard evaluation.

Compression ignition

Air in contact with hydraulic fluid can be rapidly heated by compression. A number of tests have been devised to estimate the susceptibility of hydraulic fluids to compression ignition (e.g., Military Specification MIL-H-19457). These include compression in a modified motored diesel fuel cetane number rating engine (CFR engine) and a variety of tests involving rapid compression in pipes. In typical pipe compression tests, air at pressures comparable to those found in hydraulic systems is suddenly admitted through a valve into a small-diameter pipe whose inner surface has previously been wetted with the test fluid.

The laboratory tests generally do not simulate the heat transfer characteristics of actual hardware.

Spray ignition

In a sense, spray ignition tests fill a gap between the tests of vapor-air mixtures and those of liquid pools, solid jets of liquid, and liquid drop impingement. In these tests, a spray or mist is exposed to a flame, a spark, a hot surface, or another ignition source to determine whether it will ignite, continue to burn, propagate flame, etc. (e.g., ASTM D-3119). There is no accepted "standard" test for spray ignition in spite of its obvious importance in high-pressure hydraulic systems. This class of tests is also very difficult to interpret. Results obtained from different tests often seem contradictory because of the wide range of variables that can influence the results.

Other tests

Hydraulic fluids can be subjected to the wick test--also called the windshield wiper or pipe cleaner test (e.g., Wright Air Development Center, 1952). A wick, wet with the fluid being tested, is attached to a windshield wiper and is repeatedly passed through a flame. The number of passes leading to ignition is recorded. This test is obviously affected by volatility, but it permits observation of the ignition of residues formed by evaporation (water mixtures, for example) or decomposition.

In an effort to simulate situations not satisfactorily represented by the types of tests described and to overcome their shortcomings, many other tests have been devised (e.g., spark ignition). Some of these have relatively broad application, while others apply to unique situations.

CORROSION TESTS

Corrosion tests, like combustion tests, attempt to simulate in the laboratory the corrosion problems that might occur in practice. These tests attempt to simulate the environment of the real system in some cases and, in others, to provide an artificial environment to obtain in a relatively short time an understanding of the types of problems that may occur over extended periods of time in a real system. The prediction of long-term effects may be particularly significant in the case of hydraulic fluids and hydraulic systems since exposure of the fluid to the components of the system could extend over a very long period of time.

Corrosion testing procedures

A hydraulic fluid system consists of components that are manufactured from aluminum, low-alloy steel, stainless steel, copper, nickel, brass, bronze, and titanium alloys. For this reason the hydraulic fluid must not be a good electrolyte; in other words, it must be of very low conductivity to inhibit corrosion, particularly galvanic corrosion. The fluid must also be able to inhibit corrosion when seawater accidentally intrudes. Corrosion by a hydraulic fluid can be lessened by inhibitors.

Some halocarbon-type fluids used as hydraulic fluids would introduce the possibility of hydrolytic formation of corrosive acids such as hydrochloric acid, since water intrusion into the hydraulic system can be assumed with certainty. Although the amount of acid produced by hydrolysis may be minute, surface corrosion can occur.

Past corrosion problems have been stress-corrosion cracking of aluminum valves and corrosion of steel valve, bearing, and pump components that resulted in wear or fracture and malfunction of the components. These problems have been resolved through the selection of an aluminum alloy resistant to stress-corrosion cracking and the addition of corrosion inhibitors. Any new hydraulic fluid must have corrosion inhibition properties at least as good as these.

The present corrosion test requirement for submarine hydraulic fluids is ASTM D-665. This test method is not considered adequate since it exposes a steel specimen to a continuously stirred hydraulic fluid-seawater mixture for a period of 48 hours. This does not simulate the static conditions that frequently prevail in submarine hydraulic systems.

ASTM D-3603 is a test method quite similar to ASTM D-665 in that it exposes a vertical (and horizontal) test specimen to a continuously stirred mixture of hydraulic fluid and distilled water for 6 hours. By also using a horizontal test specimen an attempt is made to get information under static conditions.

It is recommended that the corrosion test requirement be changed to an "on-off" modification of ASTM D-3603 where the test specimens are exposed to the hydraulic fluid-seawater mixture under static and dynamic conditions. The recommended static period is 16 hours as opposed to 8 hours of continuous stirring. The test specimens evaluated by

this method should be not only steel but also galvanic couples of the materials that simulate actual material combinations in the hydraulic systems. ASTM G-1 methods should be used for preparation, cleaning, and evaluation of the test specimens.

Candidate hydraulic fluids in the halocarbon family must be tested for the possible formation of mineral acid. This is accomplished by determining the acidity of the hydraulic fluid by pH measurements after introduction of small quantities of water over a long period of time such as 30 days.

Overall performance testing of a candidate hydraulic fluid should include a test period of 4 weeks in the simulated hydraulic system at David Taylor Naval Ship Research and Development Center (DTNSRDC) as the final qualification test of the hydraulic fluid. This test should consist of 8 hours of operation and 16 hours of nonoperation each day, 5 days a week. At the end of the test period, the system components such as valve seats and pump bearings should be examined for evidence of corrosion. The testing period in the simulated hydraulic system should be no less than 24 hours when the hydraulic fluid is contaminated with seawater.

Water-emulsifying-type and the corrosion-inhibited water-base fluids are promising hydraulic fluids from a corrosion protection standpoint. Both of these fluids in past testing programs have demonstrated their corrosion protection capabilities.

TOXICITY TESTS

In an inhabited area, hydraulic fluid toxicity becomes a significant concern. Not only is the toxicity of the fluid itself important but also of its products of hydrolysis, thermal degradation, and combustion. It is possible, for example, for a relatively nontoxic fluid to produce toxic reaction products.

A comprehensive discussion of a toxicity test program is presented in the Appendix. This program constitutes a tier approach to toxicity evaluation in that early in the development of hydraulic fluids, only simple or acute toxicity testing would be performed. Results from these tests would delineate the need for further toxicity evaluation (chronic or special tests). A brief summary of this program is presented in this section of the report.

Inhalation toxicity

Acute Toxicity. Groups of test animals are exposed to measured atmospheric concentrations (as aerosols or vapors) of the test material. The animals are observed for physical, behavioral, or body weight changes following exposure. The approximate lethal concentration (ALC) and concentration causing death in 50 percent of the exposed animals (LC50) are determined.

Subacute Toxicity. Animals are exposed to fractions of the ALC or LC50 and are compared with a control group not exposed to the test material. Histopathologic examination of half the animals from both groups is performed at the end of the test period. The remaining animals are tested after a recovery-observation period, usually 14 days.

Dermal and ocular effects

Animals are exposed to various concentrations of the test material to establish skin irritation by observations of erythema, edema, and necrosis, and eye irritation by observing injury to the cornea, iris, and conjunctiva. Acute toxicity is established by skin tests where skin contact with the irritant leads to mortality. The approximate lethal dose-skin (ALD-Skin) is defined as the lowest dose that produces death by application to the skin. Subacute toxicity is established on the basis of histopathologic tests at levels below the fatal level.

Combustion products

The combustion products of a hydraulic fluid may be toxic. The toxicology of some highly toxic gases produced by combustion is given in Table 1.

CO may be produced from any carbon-containing compound. NO and NO₂ may be produced from nitrogen-containing compounds, while NH₃ and HCN may result from nitrogen in the presence of hydrogen and carbon. Halogen-containing compounds can produce HX, X₂, and COX₂ (where X represents the halogen).

The equilibrium concentrations of the major combustion products of some typical fluorine-containing compounds are given in Table 2. The fluorine compounds were selected since this family of compounds often shows improved behavior over hydrocarbon-based fluids in laboratory combustion tests,

and since many of the compounds, per se, are not highly toxic. The combustion products contain species listed as highly toxic in Table 1. COF_2 , which does not appear in Table 1, hydrolyzes to form HF on contact with water.

Because the combustion products strongly depend on the conditions of thermal degradation, the toxicity tests should attempt to duplicate the type and concentration of pyrolysis or combustion products that might occur during the use of the hydraulic fluid.

Table 1. Toxicology of Some Highly Toxic Gases Produced by Combustion [Concentration (ppm), 760 mm, 25°C]

Gas	LTV*	Dangerous 0.5 to 1 h	Fatal 0.5 to 1 h	Effects
CO	50	1,500-2,000 (1 h)	4,000	Combines with hemoglobin in blood to form carbohemoglobin thereby preventing O ₂ transport. CO is a chemical asphyxiant.
NO NO ₂	n.a. 5	100-150	400-800	Forms nitrous and nitric acids in presence of O ₂ and H ₂ O in respiratory tract. Nitrates form methemoglobin while the nitrates lead to edema of the lungs. The latter are more dangerous.
HCl	5	1,000-2,000 (dangerous for brief exposure)	4,350	Neutralizes tissue alkali in upper respiratory tract. Causes death due to edema or spasm of larynx and upper respiratory tract.
Cl ₂	1	50 (short exposure)	1,000 (brief exposure)	Hydrolyzes to nascent O ₂ and HCl in respiratory tract.
COCl ₂	0.1	12.5	25 (0.5 h)	Hydrolyzes to HCl and CO at bronchioles and alveoli of the lungs. Pulmonary edema and asphyxiation.
HF	3	50-250 (brief exposure)	—	Ulceration of mucous membranes, chemical pneumonia.
COF ₂	n.a.	—	—	Hydrolyzes to HF and CO. Similar to COCl ₂ .
H ₂ S	10	400-700	800-1,000 (high concentrations instantly fatal)	Irritant; combines with alkalis in skin to form Na ₂ S; pulmonary edema at high concentrations. Asphyxiant; paralysis of respiratory center.
HCN	10	400-700	100-200	Protoplasmic poison. Combines with enzymes associated with cellular oxidation. Death occurs through asphyxiation.
NH ₃	50	2,500-6,500 (0.5 h)	5,000-10,000 (rapidly fatal)	Pulmonary edema.

*Lower threshold value; time-weighted average concentrations for a 7- or 8-hour period.

Note: Data from Table VI in J. P. Wagner, "Survey of Toxic Species Evolved in the Pyrolysis and Combustion of Polymers," *Fire Research Abstracts and Reviews* 14 1-23 1972 based on:

"Effects of Chronic Exposure to Low Levels of Carbon Monoxide on Human Health," National Academy of Sciences Publication 1735, Washington, D.C. 1969, Standard Book No. 309-01735-1.

L. T. Fairhall, *Industrial Toxicology*, 2nd ed., Williams and Wilkins, Co., 1957.

M. B. Jacobs, *Analytical Chemistry of Industrial Poisons, Hazards and Solvents*, Vol. 1, Interscience, 1944; (also 1967).

F. A. Patty, *Industrial Hygiene and Toxicology*, Vol. 1, *General Principles of Industrial Hygiene and Toxicology*, Wiley, 1958; Vol. 2, *Toxicology*, Wiley, 1967.

E. R. Plunkett, *Handbook of Industrial Toxicology*, Chemical Publishing Company, Inc., New York, 1966.

N. I. Sax, *Dangerous Properties of Industrial Materials*, 3rd ed. Rheinhold, New York, 1968.

Source: National Academy of Sciences (1977d).

Table 2. Equilibrium Products of Combustion of Various Fluids (Stoichiometric Composition)

Fluid*	°K	Products of Combustion								
		CF ₄	CO	COF ₂	CO ₂	F	N ₂	HF	Cl	Cl ₂
A.	1898	0.081	0.008	0.172	0.081	0.016	0.64	-	-	-
B.	1888	0.064	0.007	0.161	0.091	0.014	0.61	0.054	-	-
C.	1800	0.119	0.004	0.193	0.080	0.007	0.60	-	-	-
	700	0.143	-	0.117	0.107	-	0.61	-	-	-
D.	1800	0.100	0.004	0.185	0.087	0.007	0.57	0.050	-	-
	700	0.180	-	0.031	0.167	-	0.57	0.050	-	-
E.	1800	0.009	0.029	0.064	0.119	0.001	0.62	0.11	0.033	0.010

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- *A. Calculated on the basis of (CF₂)_n in dry air.
- B. Calculated on the basis of (CF₂)_n in air saturated with water.
- C. Perfluorodi-n-pentyl ether in dry air.
- D. Perfluorodi-n-pentyl ether in air saturated with water.
- E. (C₄F₅ClH₂)_n (chlorotrifluoroethylene-vinylidene fluoride).

Source: Fletcher, 1979.

CHAPTER V

FLUIDS

A large number of fluids have been considered for many applications where improved fire resistance is desired. Some of these fluids were specifically selected as potential hydraulic fluids while others were selected for other purposes and then examined to determine if they could serve as hydraulic fluids. It is beyond the scope of this report to describe all of the substances that have been or could be considered to have potential as hydraulic fluids.

The substitution of one fluid for another in a hydraulic system may not be a simple matter. The new fluid may not be compatible with seals, gaskets, and other elastomers, or the new fluid may require design changes in the system to correct for changed properties. It is of some practical value to examine potential hydraulic fluids in three categories:

- Fluids of improved fire resistance that are completely compatible with the existing hydraulic system;
- Fluids of improved fire resistance that would require minimum modification of the existing hydraulic system; and
- Fluids of greatly improved fire resistance that could only be used with major modification or redesign of the hydraulic system.

An assessment of the improvement in fire safety achieved by substituting one fluid for another cannot be made until a study has been conducted to determine the importance of each combustion-related fluid property on the fire risk in a specific system and its environment. For example, an improvement in autogenous ignition temperature (AIT) of 200°F (such as from 500 to 700°F) may be of minimal significance if there are no surfaces with a temperature above 400°F or if there are many surfaces with temperatures in excess of 800°F. On the other hand, if there are many surfaces with a temperature of 550°F, and none greater than 600°F, the change in the fluid may bring about a considerable improvement in fire safety. A similar

argument could be made for other properties. To judge the relative merits of various candidate fluids and to guide the development of new fluids, it is necessary to evaluate the properties that can reduce fire risk to the greatest extent, and the magnitude of property change required. The lack of such evaluations of specific systems has been one of the major weaknesses in the search for improved fire-resistant hydraulic fluids. The tendency has been to search for or synthesize fluids and compare them on the basis of test data whose significance has not been established.

In addition to the improvement in fire safety, the replacement fluid must usually be completely compatible with the existing system. Although it is necessary to consider cost of a changeover and the complexity of making changes, in any serious effort to improve safety it is unreasonable to place the entire burden of compatibility on the fluid. Incompatibility of a new hydraulic fluid with electrical insulation may be an adequate reason for rejection in a situation involving complex wiring systems in close proximity to hydraulic lines; but incompatibility with wall paint or floor tiles may be an inadequate reason to reject a fluid that meets all other requirements and provides greatly improved fire safety.

HYDRAULIC FLUID SPECIFICATIONS AND IMPORTANT CHARACTERISTICS

To show the properties required of hydraulic fluids, the current specifications and some important physical and chemical properties or requirements of the three petroleum-based hydraulic fluids presently used in submarines are listed in Table 3. Most of these properties are concerned with practical considerations; flash point is the only combustion test. Corrosion tests are included, but toxicity tests are not specified because the hydrocarbon materials, long used, were not expected to be toxic; for example, MS 2190-TEP has been used in submarine environments for at least 25 years with no known harmful effects.

COMBUSTION TEST COMPARISONS

The only hydraulic fluids likely to replace petroleum-based hydraulic fluids, with minimum or no system changes, are other hydrocarbons. Unfortunately, it is not clear that the changes in flash point and ignition characteristics warrant a substitution. Selected combustion properties of MIL-H-83282, a synthetic hydrocarbon fluid, and MS-2190 TEP are compared in Table 4.

TABLE 3. Chemical and Physical Properties or Requirements of Petroleum-Based Hydraulic Oils

Characteristics	Military Symbol		
	2075T-H ¹	2110T-H ¹	2190-TEP ²
Specific gravity 60/60°F (15.6°/15.6°C)	0.86	0.87	0.88
Pour point, degrees F (max.) (°C)	-20 (-28.9)	-10 (-23.3)	20 (-6.67)
Flash point, degrees F (min.) (°C)	315 (157)	325 (163)	400 (204)
Viscosity, centistokes,			
at 210°F (99°C)	4.3-5.3	5.3-6.7	8.2 (min.)
at 100°F (38°C)	—	—	82-110
at 40°F (4.44°C)	—	—	870 (max.)
at 0°F (-17.8°C)	1200 (max.)	2400 (max.)	—
Viscosity Slope, ASTM	0.775	0.771	0.680
Neutralization number (max.), mg KOH/g	0.20	0.20	0.30
Neutrality, qualitative (Methyl Orange)	neutral	neutral	neutral
Corrosion, at 212°F, copper strip appearance rating ³	1 (max.)	1 (max.)	1 (max.)
Rust preventive characteristics in the presence of seawater, 48 hours ⁴	pass	pass	pass
Water, percent (max.)	0.05	0.05	0.05
Emulsion, after 30 min settling time,			
oil layer (max.), ml	40	40	40
water layer and lacy cuff (max.), ml	40	40	40
lacy cuff (max.), ml ⁵	3	3	3
Foaming characteristics: after 10-min collapse time,			
Sequence I, ml (max.)	300	300	300
Sequence II, ml (max.)	25	25	25
Sequence III, ml (max.) ⁶	300	300	300
Oxidation test, time required in hours to reach neutralization value of 2.0 mg KOH/g (min.)	1000	1000	1000
Total sludge, mg (max.)	100	100	100
Total Fe, mg (max.)	100	100	100
Total Cu, mg (max.) ⁷	100	100	100
Cleanliness, mg/100 ml (max.) ⁸	4.0	4.0	4.0
Bearing compatibility ⁹	—	—	pass ¹⁰
Work factor (min.) ⁹	—	—	0.9
Load-carrying ability, lb/in. ¹¹ (min.)	—	—	2200
Wear test, scar diameter, mm (max.) ¹²	—	—	0.33

¹ Covered by MIL-17672.

² Covered by MIL-L-17331.

³ ASTM D-130.

⁴ Modified ASTM D-665, Procedure B.

⁵ Modified ASTM D-1401.

⁶ ASTM D-892.

⁷ Modified D-943.

⁸ SAE ARP-785.

⁹ FED-STD-791, modified Method No. 3452.

¹⁰ Evidence of significant corrosion or deposit will be disqualifying. A new bearing is required for each test.

¹¹ ASTM D-1947.

¹² FED-STD-791, modified Method No. 6503.

Combustion Property	Hydrocarbon Fluid	
	83282	2190-TEP
Flash point, °F	425	415
Fire point, °F	490	475
AIT (ASTM D-2155), °F	650	745

Only a detailed study of a specific system could establish whether a higher flash point, fire point, and AIT result in significant improvement in fire safety.

There are a number of nonhydrocarbon-based fluids that appear to have some potential to decrease fire risk if system changes are made, particularly the replacement of elastomeric materials in seals, gaskets, etc. In this category, too, the degree of improvement in safety cannot be established until a systems study has been made. Fluids providing improvements in flash point, fire point, SIT, and several other properties are compared in Table 5.

Nonhydrocarbon-Based Fluid	Combustion Property				
	SIT ^a (°F)	Pipe Cleaner (Cycles)	Flash Point (°F)	Fire Point (°F)	CFR(Com- pression Ratio)
MIL-H-19457 triaryl phosphate ester	1045	100+	515	690	>42:1
Skydrol II-B 500B	950	—	360	420	—
Silicone	770	100+	540	615	<35:1
Fluorocarbon	1190	—	—	—	—
Water-glycol fluid ^b	486	—	280 ^c	285 ^c	>50:1

^aSpontaneous ignition temperature. ^bApproximately 50 percent water.
^cAfter water is driven off.

Ignition temperatures for a variety of hydraulic fluids are given in Table 6. The 0.46-m sphere experiment is a departure from the ASTM procedure and illustrates clearly that the ASTM procedure does not give the "minimum" ignition temperature. Some reversals also occur. For example, Skydrol 500C has a higher ignition temperature than Skydrol 500A in the 0.46-m sphere and lower in the ASTM test.

The phosphate esters create many compatibility problems, some of major significance. The compression ignition characteristic, while better than that of hydrocarbons, may still be less than desired.

The silicones also look promising, the major concerns dealing with problems of lubricity, which may be overcome by additives, and their reduced bulk modulus, which may require design changes. In addition, unlike halocarbons, silicones burn in a spray test.

Water emulsions and solutions offer the possibility of improved fire resistance over that of the base fluid, but the organic base is often quite flammable and a serious hazard can exist under some failure modes. Lubricity may also be a problem.

Halocarbons are of continuing interest and offer major improvement in fire-test evaluations. These compounds are not unreactive, however, and major concern exists with respect to the corrosivity and toxicity of the hydrolysis, pyrolysis, and oxidation products of compounds containing halogens. Some compounds of this class react explosively with alloys high in aluminum and magnesium under high shearing conditions (ASTM D-3115).

TOXICITY

Each fluid possesses its own characteristic toxicologic properties. A ruptured line or loose fitting could aerosolize hydraulic fluid into the environment and result in direct exposure via inhalation and skin and eye contact. Furthermore, the aerosol could impinge on a hot surface or ignition source resulting in potential high-level exposure to pyrolysis or combustion products; adsorb to charcoal air filters with subsequent prolonged desorption posing a long-term, low-level exposure hazard; or pass through the hopcalite catalyst used in submarines, resulting in long-term, low-level exposure to subsequent reaction products. Oral exposure of personnel involved in an accidental fluid discharge is less likely.

Table 6. Data on Flammability of Hydraulic Fluids and Lubricating Oil

Fluid	Fluid type	Minimum SIT, °C		Flash point,** °C
		0.46-m sphere	ASTM methods*	
DTD 585	Mineral oil	220 (liquid)	225	93
XRM 206 A	Synthetic hydrocarbon	247	340	204
Oronite M2	Silicate ester	270	404	210
Skydrol 500A	Phosphate ester	285	593	200
Skydrol 500C	Phosphate ester	310	482	200
MCS 4630	Organo phosphate	293	388	210
Silkodyne H	Chlorinated silicone	375	480	300
Hydraunycoil	Diester	270	400	210
Reolube Hyd 21	Phosphonate-based fluid	256	-	-
Aerosafe 2300	Phosphate ester	276	405	185
Hijet III	Phosphate ester	286	528	171
OX-38 (lubricating oil)	Diester	271	-	216

* Two ASTM methods were available; where both tests were made, the test giving the minimum value was chosen.

** Extracted from firm's technical brochure.

Source: MacDonald and Cansdale, 1974.

Hydrocarbon-based hydraulic fluids

There is little in the way of acute toxicity to man to be expected from ingestion of small quantities of the hydrocarbons. If the mixtures contain significant proportions of components in the C₅-C₈ range, the possibility arises that bio-oxidation to mono- and diketones will produce analogs of a compound, such as 2,5-hexanedione, that is severely neurotoxic to mammals.

A second health hazard, chronic exposure to aromatic compounds present in hydrocarbon mixtures--especially benzene, toluene, and polynuclear aromatic hydrocarbons--can induce leukemogenic or carcinogenic processes.

Aryl and aralkyl phosphate esters

Members of this important class of fire-resistant hydraulic fluids can pose multiple threats to human health, based on three types of intrinsic toxicity. First, depending on the structure of ortho- or para-constituents in the aryl nuclei, the very real threat of irreversible, delayed neurotoxicity is present following chronic exposures. Such toxic potency is exemplified by the well-documented neurotoxic actions of tri-*o*-tolyl phosphate as a model compound of the series used in ester mixtures. However, synthetic phosphate esters produced from tertiary butylphenol do not induce delayed neurotoxicity (National Academy of Sciences, 1977c).

A second facet of intrinsic toxicity from phosphate esters lies in the possibility of direct action of these compounds on organ targets other than nerve, leading to loss of function.

The third threat is posed by the newly expressed concern that agents that can phosphorylate macromolecules and thereby induce delayed peripheral neuropathy may also, on prolonged exposure, be capable of inducing processes leading to carcinogenesis, mutagenesis, or teratogenesis in the human.

As with all industrial chemicals, appropriate tests must be conducted to identify acceptable materials with low potential toxicity.

Ethylene glycol-water mixtures

Much is known about the intrinsic toxicity of ethylene glycol in man and in animal models, on both acute and

chronic bases. The metabolism of such products as glyoxylic and oxalic acids has been well worked out. The contribution to hazard from this particular component of the hydraulic fluid mixture is not adjudged to be highly significant. But the contribution to biohazard stemming from interactions between some corrosion inhibitors and antioxidants added to the mixture cannot be ignored.

SUMMARY

A summary of the qualitative estimate of characteristics of potential fire-resistant hydraulic fluids is given in Table 7.

Three major new candidates appear promising for future applications provided that system design and material compatibility are tailored to their use. These compound classes are chlorotrifluoroethylene-vinylidene fluoride oligomers, fluorocarbon polyethers, and fluoropolyether triazines. All are likely to be very expensive, and the latter class has essentially the same characteristics as the polyethers. Furthermore, the toxicological properties and environmental acceptability of these fluids are unknown. These compounds all contain appreciable amounts of halogen atoms and have an inherently high density (1.7 to 1.9) with which the system design would have to be compatible. In the event that fluid density is too high for the system, the committee recommends, as an alternative to system design changes, that efforts be made to develop blends of these compounds with other materials to lower the density without compromising other properties too drastically; for example, a blend of chlorotrifluoroethylene-vinylidene fluoride copolymers with hydrocarbons, esters, or silicones, etc. The presence of halogen atoms poses a toxicity problem with products of combustion.

Potentially useful fluids may exist for more fire-resistant hydraulic fluids. Those requiring the least changes in materials (for example, lower vapor pressure or higher flash point hydrocarbons derived from α -olefins) also provide the least improvement in fire safety. 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 improved hydraulic fluid carry the complete burden of assuring compatibility.

Table 7. Qualitative Estimate of Characteristics of Potential Fire-Resistant Hydraulic Fluids

Characteristic	Fluid Class								
	Cyclic Phosphazenes ^a	Chlorotrifluoroethylene/Vinylidene Fluoride Oligomers (C11 ₂ CF ₂) _x (C1C2P ₃) _y	Synthetic Hydrocarbons (MIL H-38282)	Tri-Aryl Phosphate Esters	Silicones	Water/Glycol Type Fluids	Fluoropolyether Triazines	Fluorocarbon Polyethers (E Fluids)	Polyolesters
Flash Point	+	+	-	+	+	+	+	+	-
AIT	+	+	-	+	+	+/-	+	+	-
Density	+	-	+	+	+	+	-	-	+ ^b
Compatibility	+	+ ^b	+	-	+	-	?	+ ^b	?
Bulk Modulus	+	?	+	+	-	+	?	-	?
Oxidative Stability	+	+	+	+	+	+	+	+	?
Lubricity	?	+	+	+	-	+/-	?	+	+
Viscosity-Temp. Properties	+	+	+	+/-	+	+	+	+	+
Corrosion Inhibition	?	+	+/-	+/-	+/-	+/-	+	+	-
Toxicity ^c	?	+	+	+/-	+	+ ^d	+	+	+
Hydrolytic Stability	+	+	+	+	+	+	+	+	-
Cost	high	high	low	low	high	low	very high	very high	low
Life-time	?	+	+	+	+	- ^e	+	+	+

KEY: + indicates satisfactory; - indicates unsatisfactory performance; ? indicates unknown behavior; +/- indicates that performance depends on conditions and/or formulation.
 a. Not discussed in enough detail at the workshop to support further conclusions and recommendations.
 b. Assumes suitable elastomeric seals.
 c. Refers to primary material, not by-products of reaction.
 d. By avoidance of combination of amino and nitrite additives.
 e. Due to inability to separate components after seawater intrusion.

CHAPTER VI

INTERPRETATION OF TEST RESULTS WITH RESPECT TO FIRE HAZARDS

Ideally, tests should explicitly predict when a given situation will lead to an unwanted fire and when it will not. Unfortunately, such tests do not exist. There is much concern with the development and standardization of tests and the rankings of materials according to how they perform in them. These rankings often endow substances with advantages or penalties they should not have. As long as test results are interpreted wisely and mature decisions are made about how particular tests relate to particular hazard situations, they have value. Improperly interpreted, they can be misleading. What we usually want to know is the answer to the question: If so and so happens in such and such a place, will there be an ignition and explosion or fire? Ideally, we would like yes or no answers to questions that involve complex interactions between many components of complicated systems; however, we do not wish to engender a hazard we are trying to avoid by conducting imperfect tests. Since we cannot precisely scale fire hazards, the objective of good testing is to do manageable things on a small scale that can provide us with an intellectual bridge, in which we have confidence, for making reasonable predictions about what will happen in potentially hazardous situations.

Standardized tests necessarily control and fix as many variables as possible. Thus, these tests can serve only to guide the decision process. It is wrong to use tests or test results as a device for avoiding the difficult task of a thorough system analysis. Nevertheless, properly interpreted, and with their results related to the characteristics of a potentially hazardous situation, such tests can be useful. Specification of fluid properties based on laboratory tests may be simply our best judgment as to what we can hope to accomplish with the knowledge and technology available to us. The following section relates the interpretation of test results to the hazardous situations previously mentioned. Since the development of a perfectly noncombustible hydraulic fluid is unlikely, we have sometimes made observations in this section about how increased safety might be achieved with less-than-perfect fluids.

STREAM OR SPRAY FROM A HYDRAULIC SYSTEM

A stream or spray of a combustible fluid from a hydraulic system may produce many kinds of hazards. For example:

- The spray itself may be ignited by sparks or open flames with which it comes in contact. It then becomes a torch.
- It may not be ignited immediately. If it is a very coarse spray, it may collect in a pool on the floor or deck where it may eventually be ignited by an external source. In some circumstances, it might spontaneously ignite.
- A fine spray might fill a chamber with a fog of combustible droplets and subsequently be ignited by a spark or flame, or it might be carried through a ventilating system far from its origin to an ignition source.
- It may impinge upon a hot surface or settle into a hot chamber where, after some time and after having undergone a change in composition, it ignites.

It is evident that a break in a hydraulic line can produce many different kinds of situations and that no single test result or small set of tests is an adequate measure of the hazard.

If the spray is fine, all sprays that fall within a combustible composition range may be ignited by a flame or an energetic spark. The fact that a fluid has a flash point well above the temperature of the spray will not prevent it from burning and propagating flame from a distant ignition source.

Flash point is not a direct measure of the magnitude of this hazard. If the spray happens to impinge against a hot surface in a well-ventilated area, the fluid with the low flash point (and, hence, high volatility) may simply evaporate, be diluted by air, and blow away, while the fluid with the high flash point (and, hence, low volatility) may retain contact with the hot surface long enough to undergo an eventual ignition. Thus, the use of flash point as a hazard predictor in some situations involving sprays and clouds of droplets might produce a misleading result.

Flash and fire point tests represent a generic family that measure the temperature above which the vapor pressure of a fluid is great enough to allow formation of a combustible gas mixture above the surface of the liquid. In their several arrangements they are probably the most thoroughly standardized and widely used and understood of the combustion tests. They provide a quick, intuitively perceivable measure of the temperature above which a clean pool of liquid (perhaps from a coarse spray) might be expected to ignite in the presence of a flame (and usually a rough measure of the speed with which a flame may be expected to propagate across a pool). However, a high flash point does not guarantee safety even in pools; for example, pools of liquids that contain wicks of sand or dirt can be ignited and will burn at temperatures below their flash points.

It would appear that the best test for assessing the possibility of a spray being ignited by a spark or open flame would be one of the several spray ignition tests that are now undergoing development. However, these tests illustrate an important shortcoming of fire hazard testing programs and procedures in general. Their main objective should not be a ranking of various substances in the tests but an interpretation of the observations made during them; nor should the primary goal be reproducibility but rather interpretation for the purpose of predicting what may happen in a situation that is not carefully controlled. For example, a fluid that "passes" with flashes and streaks and a little flame spread in a test that has been carefully standardized to be reproducible may presage a disastrous propagation through a large cloud of real mist that has characteristics a little different from those of the test spray. It is evident that more severe tests than those now in use should be developed. Perhaps they should embody the use of such devices as large-scale ignition sources, oxygen enrichment, and fluid preheating. The observations recorded should include any evidence of propagation away from the ignition source, since large variations are made in spray patterns and characteristics. There is also a need for analytical models that will be useful in the understanding of the propagation of flames through sprays and mists.

Inasmuch as the consequences of ignition of fluid from such a failure mode are likely to be very serious, we believe that the use of preventive measures such as additional spray shielding of hydraulic lines in fire hazard areas and the elimination of ignition sources from regions in which protective spray shielding is impractical should be explored.

Another approach to the reduction of spray and mist flammability is to increase the N_2/O_2 ratio of the environment (Carhart and Gann, 1974). If the pressure in an enclosed space is increased to above atmospheric by the addition of N_2 , the physiological effects are negligible, but the flammability of hydrocarbons is dramatically decreased. For example, at a total pressure of 2 atm, in an atmosphere containing 10 percent O_2 , hydrocarbons would be very difficult to ignite, but the oxygen pressure would still be the 0.2 atm required for respiration.

AIR COMPRESSED IN THE HYDRAULIC SYSTEM

When a gas is compressed adiabatically, its temperature goes up. When the gas is air and it is compressed by a combustible liquid, mixtures that can ignite spontaneously can be produced. If they do ignite, the hydraulic system may rupture. Such situations have been addressed by compression ignition tests exemplified by the pipe compression test or by compression in a CFR engine. Neither test, in the opinion of this committee, is adequate.

In the pipe compression test, air at a pressure comparable to the pressure in a hydraulic system is suddenly admitted through a valve into a small-diameter pipe (of the order of a few centimeters) whose inner surface has been previously wetted with the test fluid. We believe the test to be inadequate for the following reasons:

1. The method of air introduction into the test section does not always simulate either the temperature or pressure that would result from the many likely ways in which air might inadvertently be compressed in a hydraulic system. The test was originally devised to simulate an occurrence that led to an explosion and fire in an aircraft carrier hydraulic system. It does simulate that particular situation and a fluid that fails it is not desirable.

It is not a good general test for compression ignition. In this test the air is first expanded into and subsequently recompressed in the test chamber. It is quite likely that the air will not reach as high a temperature as it does if a pocket of air is compressed by the flow of hydraulic fluid.

2. In many operational hydraulic systems there is apt to be a large excess of hydraulic fluid; i.e., there is an unlimited reservoir of fluid at a pressure probably above its critical pressure, in contact with air heated to a

temperature probably also above the critical temperature of the fluid. There is thus no clearly defined surface of discontinuity between vapor and liquid phases. There is instead a hot, highly compressed, one-phase region that contains a mixture of hydraulic fluid and air continuously varying in composition from that of pure fluid to pure air.

It is unlikely that the pipe test, in which hydraulic fluid comes only from a wetted surface, can simulate the condition most likely to cause an ignition as described above.

3. The pipe test is conducted in pipes of a few centimeters in diameter; however, hydraulic systems often contain chambers of the order of meters in diameter. The test does not take into consideration the fact that the size of the device may play an important role in determining the likelihood of a compression ignition, and that systems that have small surface-to-volume ratios, i.e., large systems, are more likely to ignite when subjected to a given pressure stress than are small ones.

The effect of the size of the device can be inferred from the following exercise. In this exercise, we do not mean to imply that the results are quantitatively correct. Our purpose is to demonstrate that an important problem of scale exists.

The rate of temperature rise, dT/dt , in a substance that can undergo an exothermic chemical reaction can be reasonably well approximated by

$$\frac{dT}{dt} = - \frac{\Delta\mu_0 k_\infty C_{OR}^{(\nu-1)} e^{-E/RT}}{c_v} - \frac{kA (T - T_0)}{c_v C_{OR} V} \quad (1)$$

where $\Delta\mu_0$ is the isothermal internal energy change associated with the reaction, k_∞ is a constant characteristic of a given reaction, C_{OR} is the initial concentration of reactants, ν is the order of the reaction, c_v is the constant volume heat capacity, E is the activation energy, R is the universal gas constant, k is the appropriate coefficient for heat transfer to the walls, A is the surface area of the containment vessel, V is its volume, and T_0 is its wall temperature. The first term on the right side represents the rate of temperature rise due to chemical reaction; the second term represents the rate of temperature drop due to

heat loss to the wall. This equation is a starting point for the development of Semenov's thermal explosion theory. It is also a convenient starting point for evaluating the effect of the size of a device on the likelihood of its having a thermal explosion.

After a sudden compression, the fluid phase will be much hotter than the walls. We postulate that if, after such a compression, conditions are such that $dT/dt < 0$, i.e., that the mixture will start to cool, it is unlikely to explode. Conversely, if $dT/dt > 0$, the mixture is likely to explode. The limiting condition is therefore the condition for which $dT/dt = 0$ and the condition that leads to an explosion is the condition that

$$-\Delta\mu_0 k_\infty c_{OR} e^{-E/RT} \geq \frac{kA(T - T_0)}{V} \quad (2)$$

The effect of scaling can be simplified. We note that $A/V = a/r$, where r is a typical dimension of the reaction vessel and a is a constant that depends on its shape. For example, a is 3 for a sphere. If a fluid (here assumed to be an ideal gas with constant heat capacities equal to those of air at ordinary temperature, $\gamma = 1.4$) is subjected to a sudden compression from 1 atm, immediately after the compression the following conditions prevail:

$$P = P_R \quad (3)$$

where P_R = compression ratio (starting at 1 atm),

$$T = T_0 P^{\gamma-1/\gamma} = T_0 P^{0.286} \quad (4)$$

and

$$c_{OR} = \frac{n_{OR}}{V} = \frac{P}{RT} = \frac{P}{RT_0 P^{0.286}} = Z P^{0.714} \quad (5)$$

where Z is a constant.

We also assume that $k = k_1 \text{ atm}^{0.5}$, i.e., that the heat transfer coefficient is proportional to the square root of the pressure. Expression 2 can then be rewritten, assuming the ambient temperature T_0 to be 300°K. The

chamber dimensions that will produce thermal explosions are given by the expression

$$r > \frac{C (p^{0.286} - 1) e^{E/300Rp^{0.286}}}{p^{0.214}} \quad (6)$$

where C is a constant that depends on the particular kind of fluid with which we happen to be concerned.

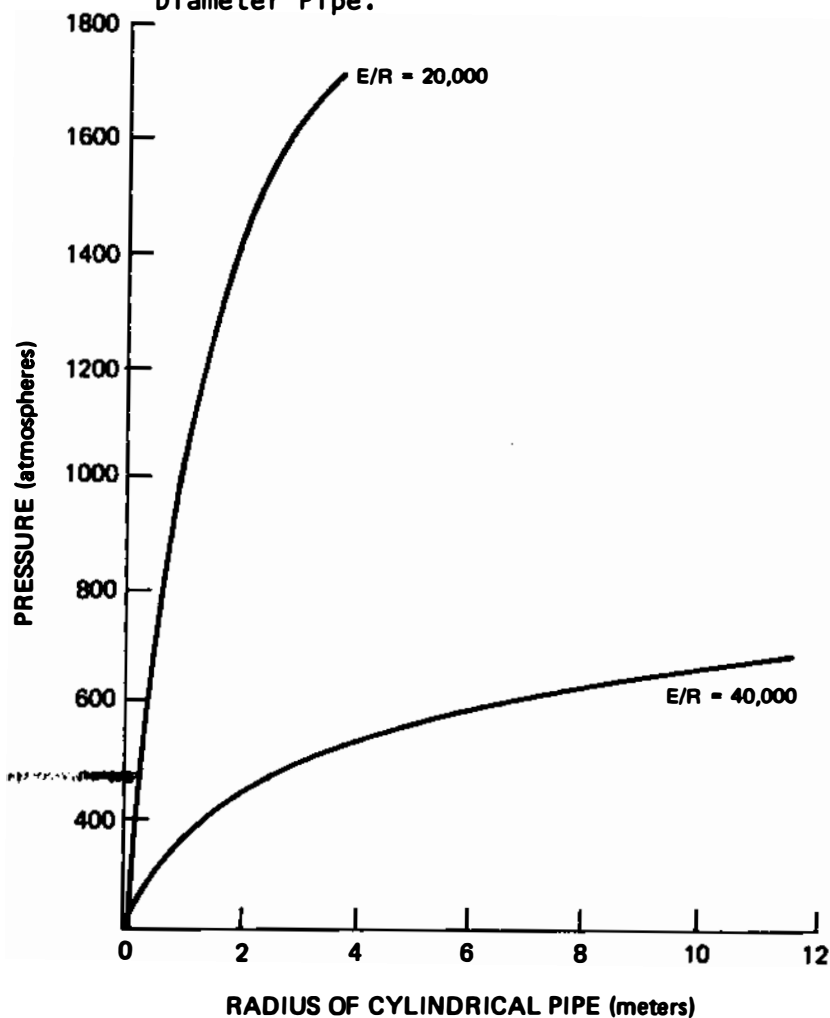
It is now pertinent to ask the following question: If, in a compression ignition test in which a combustible mixture is kept compressed in a chamber whose walls are at ambient temperature (300°K), one observes an ignition at a given pressure, what pressure will lead to an ignition when the size of the chamber is different from that of the test chamber? The answer is that if the chamber is larger, the ignition pressure will probably be substantially lower.

Insofar as hydraulic systems are concerned, a more pertinent question is: To what pressure should one compress in a small test chamber in order to discover whether a large fluid-air space that has been suddenly compressed to hydraulic system pressure (200 atm) is dangerously near to a state leading to an ignition?

An approach to an answer is to be found in Figure 1 for two values of E/R. In Figure 1, the abscissa is the radius of a cylindrical pipe in which the possibility of a compression ignition exists. On the ordinate is plotted the pressure to which one would have to suddenly compress a test mixture in a test pipe having a 1.0-cm diameter in order to achieve a condition comparable to the spontaneous ignition condition in a larger pipe when air in the larger pipe is suddenly compressed to 200 atm. For example, if the activation energy that characterizes the ignition reaction is 40 kcal (E/R = 20,000), a mixture that ignites in a cylinder having a radius of 1 m in the hydraulic system would not have ignited in a 1-cm diameter pipe unless it had been compressed to about 1100 atm. If the activation energy is 80 kcal, a test compression to 400 atm in a 1-cm pipe would "simulate" compression to 200 atm in a 1-m radius component of a hydraulic system.

In the foregoing presentation, the problem has been ultrasimplified and the extrapolations go far beyond those

Figure 1. Radius of a Cylinder in which Contents Explodes on Suddenly Compressing to 200 atm versus Pressure in a 1-cm Diameter Pipe.



acceptable for quantitative calculations. Nevertheless, they illustrate the point that the pipe test is far from adequate.

A similar criticism could be made of the CFR engine tests. But in addition, in the cetane engine test, because the compression is followed by an expansion, the test is an even less realistic simulator of the hazard that is likely to exist in practice.

Finally, the point should be made that, because of inertial effects, a pressure much higher than the system static pressure can be experienced in an air bubble in a hydraulic system.

It is evident that better compression ignition tests than are now available should be developed. They should be characterized by the following features:

- They should permit compression to pressures substantially greater than the maximum pressures that might be encountered in the hydraulic system.
- It should be possible to vary the size of the test chamber or its surface-to-volume ratio for the purpose of evaluating scaling parameters.
- They should maintain fluid compression for a reasonable period of time.
- The interpretation should take account of the possibility that pressures much higher than the system static pressure can occur.

Education of persons who operate and repair hydraulic systems as to the seriousness of the hazard seems likely to help prevent compression ignition accidents. In addition, purging of systems with N₂ or some other inert gas to eliminate trapped air should be examined.

FLUID SPILLS OR DRIPS ONTO A HOT SURFACE OR INTO A CHAMBER

The spraying or streaming of fluid from a rupture in a pressurized hydraulic system is bound to attract attention. Slower leaks, drips, and spills may produce less obtrusive hazards in several ways. They may provide pools or fluid-soaked thermal insulation, rags, or dirt. Or they may drip into hot chambers or cavities where they can be heated to a temperature at which they will autoignite.

Under such conditions, a fluid that cannot ordinarily even be burned, such as a dilute organic fluid-water solution, may lose water, leaving a combustible material that may then ignite. These hazards may be substantially reduced by frequent inspections and good housekeeping.

Results of a flash or fire point test are helpful in determining the likelihood that a clean pool of liquid may be ignited by a spark or flame. Since it is strongly dependent on vapor pressure, flash point also may be used as a (sometimes unreliable) measure of the rate at which such a flame will spread across a pool of liquid. The flame spread also depends on vapor pressure. Flame spread can also be misleading if its magnitude is taken as an unqualified measure of a fire hazard. A relatively volatile fluid with a low flash point may evaporate and be blown away from an environment in which a fluid with a high flash point would spontaneously ignite. There are no tests to assess unambiguously and reliably the hazard in all situations of this kind.

The windshield wiper test is a kind of accelerated aging test that can call attention to the existence of a hazard that would probably be missed in a fire or flash point test or in a spray ignition test and possibly even in a compression ignition test. The hazard is the kind that can arise when aging or heating can cause a slow separation of components of a hydraulic fluid, a slow thermal decomposition, or a change in structure. A water-based polyol fluid, for example, might be unignitable in a properly done flash point test. Nevertheless, it could become hazardous in the lagging on a steam pipe or after it had lost water by evaporation. The pipe cleaner test would have a better chance of revealing the hazard than the other tests. Present practice of counting the number of cycles to an ignition, however, and reporting that as some sort of measure of safety is, in the opinion of the committee, pointless. The windshield wiper test tells the observer that a particular fluid can, under conditions simulated by the test, become hazardous, but it imposes much too limited a range of variability to be considered a guarantee of safety.

Spontaneous (SIT) and autogenous ignition temperature (AIT) tests also simulate aging to some extent. They are relatively widely used. SIT values are often cited as measures of relative hazard, but they should be used only with great caution. These tests are, like many of the other tests reported here, unrealistic for quantitative evaluation of a hazard because they differ from real situations in not

presenting the fluid being tested with catalytic surfaces, dirt, and other things that may greatly affect the processes leading to pyrolysis and ignition. In addition, this test, like the compression ignition test, is subject to misinterpretation because of scaling effects. Nevertheless, it can give information that can help make decisions.

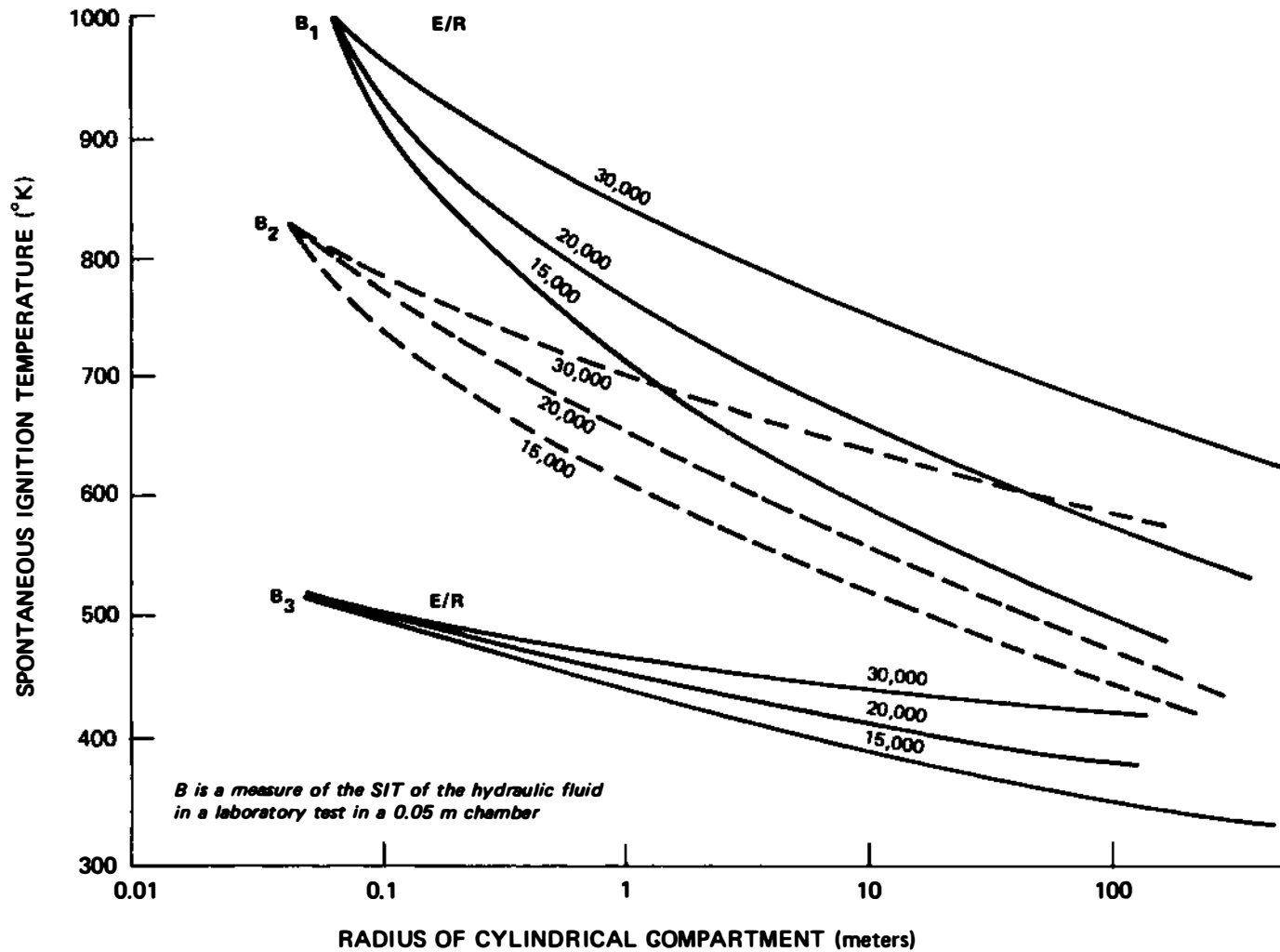
The effect of scaling on the results is not so important with these tests as it is with the compression ignition test because the SITs of the fluids under consideration are much higher than ambient temperatures. It is thus not likely that a fluid would find its way into a large hot environment. Nevertheless, a misinterpretation of an SIT might lead one to overlook a potential hazard that depends on the size of a space in which a spill occurs.

Application of thermal explosion theory and the use of considerations similar to those that led to expression 6 in the section on compression ignition suggest that the condition for spontaneous ignition in a space whose walls are at a temperature T_0 is given by

$$r \geq BT_0 \left(Re^{E/RT_0/E} \right)^{\frac{1}{2}} \quad (7)$$

where B is a constant that depends on the hydraulic fluid. Thus, T_0 is a spontaneous ignition temperature. B and E might presumably be evaluated in a series of scaled tests. Figure 2 shows how spontaneous ignition temperatures would be expected to depend on a particular dimension of the test chamber for three different values of E . Suppose, for example, that laboratory tests are done in a chamber having a dimension of 5 cm (0.05 m). If E/R is 20,000, then if the SIT measured in the laboratory is 800°K, the SIT in a 1-m compartment would be 630°K and in a 10-m compartment it would be 550°K. If the SIT were 500°K, it would be 430°K in a 1-m compartment and 390°K in a 10-m compartment. Spontaneous ignition is thus not likely to present much of a hazard with most hydraulic fluids. Nevertheless, if there are large spaces in which spills may be subjected to high temperatures or to large surfaces that are at temperatures much higher than ambient or to catalytic surfaces, the increased hazards of spontaneous ignition associated with their size should not be overlooked, and tests should perhaps include the effects of size on SITs.

Figure 2. Dependence of the Spontaneous Ignition Temperature on the Radius of the Test Chamber.



INTERACTIONS RESULTING FROM PROXIMITY OF HYDRAULIC LINES TO STEAM PIPES AND ELECTRIC POWER LINES

A situation may arise in which materials (such as those used for lagging steam pipes) accumulate, over long periods of time, hydraulic fluids and hydraulic fluid residues and decomposition products from leaks. Fluids may drip onto power lines and react with insulating materials. It is apparently not uncommon to have lagged steam pipes and hydraulic lines and power lines running through common channels. The committee feels that such problems are best discussed with specific systems in mind. Lacking a specific system, we can only guess about what kinds of situations may be expected to arise and what the sources of fire hazard will be. It seems evident that in such a situation, prevention of the hazard is as much a matter of good house-keeping as it is a matter of hydraulic fluid properties. Virtually anything can become a fire hazard if one is careless (or foolish) enough with it.

SUMMARY

The lack of correlation between fire hazard and the numerical value of a measured property in any single standardized test is not surprising. In ignition, flame spreading, and other combustion phenomena of interest because of their hazardous nature, the way the surroundings interact with the combustible substance is what produces the result. The surroundings may act either as a promoter or inhibitor (or both) of ignition and combustion processes. Some phenomena of importance in ignition and combustion have a strong dependence on the effective volume of the system, others on the effective surface area. The size and shape of a system are therefore important variables. But such effects are hardly ever addressed in standard tests that purport to evaluate fire hazards. The modification of standard tests to provide a better bridge between the laboratory and practical systems is thus a major problem for future work.

APPENDIX

TOXICITY TEST PROGRAM

The use of hydraulic fluids in high-pressure systems encapsulated in closed environments generates a variety of possibilities for human exposure to these materials. The fluids can be emitted from containment in the form of finely divided aerosols, fluid sprays, and drips or slow leaks, making possible human intake by inhalation of aerosols or vapors, by skin contact, or by accidental ingestion. Therefore, it is clear that acute or chronic exposures in confined spaces to these materials may pose hazards to human health, which directly depend on the nature of the chemicals involved, the dynamics of intake, the intrinsic toxicities of the components, and the mechanisms by which they may be metabolized or excreted. It is important that the magnitudes of these chemical hazards, both to human health and to other life in the environment, be assessed on some scale of values in order to make it possible to reach rational decisions as to whether the benefits of deployment of these hydraulic fluids are commensurate with the biological hazards attendant on their use. The remainder of this section deals explicitly with the factors that enter into the human hazard assessment for use of various chemical classes of hydraulic fluids.

NATIONAL REQUIREMENTS FOR HAZARD ASSESSMENT

The exposure of humans and other biota in the environment to chemicals used for specific operational purposes is being increasingly regulated under federal legislation that extends to all sectors of national endeavor. Particular reference can be made to the powers inherent in two laws that can apply to military operations as well as to occupational activities in the civilian sector: the Occupational Safety and Health Act of 1970, administered by the Occupational Safety and Health Administration of the Department of Labor; and the Toxic Substances Control Act of 1976, administered by the Environmental Protection Agency. Under these regulatory acts, strict limitations can be placed on the extent of hazard permissible for humans exposed to operational chemicals, even in their deployment in closed environments as part of military platforms or weapons systems. The restrictions that can be imposed under these authorities, to avoid "unreasonable risk"

to human health or the environment, can range from strict control of the specific uses permissible for a given chemical down through control of the levels of exposure resulting from a given use in terms of exposure times and permissible ambient concentrations. These restrictions can also be rules that specify absolute bans on use, promulgate restriction on volumes of chemicals deployed, or specify requirements to develop a broader information base for research and development on which a quantitative hazard assessment can be developed. Each of these powers ultimately requires a decision-making process for each potential use of each important chemical by an administrator attempting to balance operational benefits versus biological and other hazards. Therefore, the development of clear, unambiguous methodology for hazard assessment that will be generally accepted by the nation is a matter of high priority.

THE CONCEPT OF HAZARD ASSESSMENT

It would be most gratifying to report that a clear analytical statement exists, and is broadly supported, relative to quantitative assessment of potential hazard to human health and the environment from exposure to an operational chemical such as a hydraulic fluid. Such a statement and the steps required for its implementation do not exist in a fully explicit form, although the philosophy underlying the generation of a useful mathematical expression for a hazard function from factors contributing to hazard has been probed in recent publications (National Academy of Sciences, 1975a,b).

Therefore, at present, an ad hoc rationale for biological hazard assessment relating to potential exposure to a given chemical is being deployed in an experimental fashion, most notably in recent times by the Toxic Substances Control Act Interagency Testing Committee. This rationale assumes that the hazard function H can be generated by a linear combination of factors F of the form

$$\text{Hazard (health, environment)} = H = aF_1 + bF_2 + cF_3 + dF_4 + \dots$$

where the factors F_1, F_2, \dots relate to specific contributors to the total hazard function and can be quantified on some numerical scale, and the coefficients, a, b, \dots can be used as normalizing factors to bring the separate numerical scales onto a common basis, or to weight the contributions of the various F factors to the total hazard assessment for

a given chemical in a given mode of use. For present purposes, the H function for hazard assessment of hydraulic fluids deployed in confined spaces, with the added possibility of leakage to the aquatic or terrestrial environment, would be cast in the linear array

$$H_{h,e} = aF_{\text{intrinsic toxicity}} + bF_{\text{exposure}} + cF_{\text{decomposition products}} + dF_{\text{environmental effects}}$$

where:

$F_{\text{intrinsic toxicity}}$ is a relative measure or index of the intrinsic toxicity of a given chemical, say on a scale of 1 to 10, as assessed by a major biological effect in a test animal or on a target organ seen in acute or chronic exposures;

F_{exposure} is an intensity index factor encompassing the modes of exposure, the numbers of people potentially exposed, the concentrations encountered, the time factors involved, and the probability that exposure will result in chemical entry and retention in the body;

$F_{\text{decomposition products}}$ is an index factor reflecting the intrinsic toxicity (summation) of decomposition products that might be generated from deployment of a given fluid under environmental conditions (temperature, pressure, etc.) that could cause decomposition or by metabolism in a target organism; and

$F_{\text{environmental effects}}$ is an intensity factor reflecting the probability (again on a numerical scale) that some important organism(s) in the environment might be adversely affected by leakage of the fluid to the external environment.

Assuming the legitimacy of linear combination of F factors to form a hazard function H for a given chemical in a given use and exposure pattern, the coefficients a,b,c,d would for simplicity be given uniform weights of 1, and used simply as normalizing coefficients to make the numerical scales of the four F factors equivalent.

An important consideration in the evaluation of the intrinsic factor relates to the emphasis placed on the toxicity weighting of acute toxicity signs versus chronic toxicity manifestations leading to irreversible effects in animal models or man. As a tentative working guide in this respect, it is recommended that acute effects be surveyed first. When such effects are largely negative, and information on chronic deleterious effects is absent, the toxicity index is governed by the acute findings. When positive effects in man or animal models are available on both the acute and chronic exposure bases, the latter will be given higher weight in generating the intrinsic toxicity index for the given exposure modality.

Some hydraulic fluids may possess unique toxic effects. For example, some phosphate esters have been shown to induce delayed neurotoxicity in man and test animals (Johannsen et al., 1977). Such specific toxic effects should be recognized and dealt with independently from the general toxicity.

The following general format provides a minimal toxicological evaluation of hydraulic fluids. This program constitutes a tier approach to toxicity evaluation. Early in the development of hydraulic fluids, only simple or acute toxicity testing would be performed. Results from these tests would delineate need for further toxicity evaluation (chronic or special tests).

At the conclusion of all toxicity testing, the data would be used in conjunction with proper hazard evaluation to determine the optimum hydraulic fluid for use in the given environment. For reference, an example classification system for acute inhalation and dermal toxicity is presented below. More detailed descriptions of these procedures have been published (National Academy of Sciences, 1977a).

INHALATION TOXICITY

Acute toxicity

Groups of test animals (6-10 per group, generally rats) are exposed to a given atmospheric concentration of the test material (as an aerosol or vapor) for a single 4-hour exposure. Atmospheric concentrations of the test materials and particle size analysis of any aerosol should be determined. Mortality, body weight, and outward observations that denote toxicity are recorded during exposure and for a postexposure recovery period (generally about 14 days).

Gross autopsies are conducted on all animals dying or sacrificed during the test or observation period. Histopathologic examination of the test animals would be optional. The approximate lethal concentration (ALC) is defined as the lowest concentration that produces death in the exposed group. The LC50 is defined as the concentration expected to cause death in 50 percent of the exposed animals.

Subacute toxicity

Test groups of 10 to 20 rats are exposed to fractions of the ALC or LC50 (e.g., 0.03 and 0.3) for 4 to 6 hours a day, 5 days a week over a 2- to 4-week period. Atmospheric concentrations of the test materials and particle size analysis of aerosols should be measured. Simultaneously, a control group of animals is subjected to the same procedures minus compound administration. Upon termination of the test sequence, half of the animals from both groups should be sacrificed for histopathologic examination of all major organs and tissues. The remaining rats are retained for a recovery-observation period (generally 14 days). At the conclusion of this period, the remaining rats are sacrificed for comparative histopathologic examination.

DERMAL AND OCULAR TOXICITY

Skin and eye irritation

The interest is to determine whether a material will injure the skin or eye after direct application. Guinea pigs or rabbits are the animals of choice, depending on the specific test. With skin irritation, observations for erythema, edema, and necrosis are recorded as a function of the amount of material applied. In the case of eye irritation, injury to the cornea, iris, and conjunctiva are evaluated (Code of Federal Regulations).

Acute toxicity

Test animals, generally rabbits, are exposed by direct application of the test compound to the skin for a 24-hour period and held postexposure (generally 14 days) during which signs of toxicity and mortality are recorded. Histopathologic examination would be optional. The ALD-skin is defined as the lowest dose that will produce death in one or more of the test groups. The LD50 is defined as the dose expected to cause death in 50 percent of the treated animals.

Subacute toxicity

Test animals, generally, rabbits, are exposed to fractions of the ALD or LD50 for 4 to 6 hours a day, 5 days a week over a 2- to 4-week period. Following each exposure the material is washed from the skin and the animals are returned to their cages. General observations may be supplemented by clinical biochemistry and/or histopathologic evaluation of tissues. Treatment groups are compared with concurrent control groups.

PYROLYSIS AND COMBUSTION TOXICITY STUDIES

No specific protocol has been adopted by a government agency for this type of test. Because the products of thermal degradation strongly depend on test conditions, the investigator should attempt to duplicate the type of pyrolysis or combustion that might occur in product use or disposal. In some applications, combustion devices are used to rid recirculated air of some noxious substances. It is most pertinent to inquire what would be the effect of such devices on new kinds of hydraulic fluids.

Different applications may require different test designs (Wright and Adams, 1976; National Academy of Sciences, 1977b). Thus, toxicity should be evaluated in both flaming and nonflaming combustion modes near the auto-ignition temperature of the test material. Chamber oxygen concentrations and temperatures should be monitored during each exposure. The procedure suggested herein follows guidelines recently issued by the National Academy of Sciences (1977b).

The apparatus may be comprised of an exposure chamber and a pyrolysis or combustion device, such as a tube furnace, heated cup, or torch. Groups of test animals, typically 6 to 10 rats per group, are exposed briefly (30 min) to the pyrolysis or combustion atmospheres. The run begins when a weighed amount of fluid is placed in the preheated cup or furnace. The resultant gases may be either diverted into (dynamic operation) or accumulated in (static operation) the exposure chamber. A major index is animal mortality occurring during the exposure and 14-day post-exposure period. The mortality observed should be compared with the concentration of expected degradation products, such as CO, CO₂, and others. An example is the use of chlorinated hydrocarbons where HCl would also be an expected combustion product. Following the exposure, blood carboxyhemoglobin (CO-Hb) levels should be measured in dead rats to determine whether the mortality is due to elevated CO

concentrations or to the presence of some other agents. If no rats died during the test, two may be sacrificed for the CO-Hb determination so the severity of the CO exposure may be estimated more quantitatively. Dose response data may be obtained by varying the amount of test material combusted.

In addition to mortality, it is becoming increasingly evident that some measure of animal incapacitation is necessary in the total evaluation of pyrolysis or combustion toxicity. This could be particularly important in a closed environment where there is little room for error in daily operations. There is no single accepted test for incapacitation, although several techniques (rotorod, exercise wheel, shuttle box, hind-leg flexure, and others) are currently being evaluated. At this time, selection of an appropriate incapacitation test is best left up to the particular investigator.

Because pass-fail criteria are not established for this type of testing, the results can only be evaluated subjectively. Slight variations (up to threefold) in performance should not be considered significant. Differences of 100-fold in performance (material A versus others), or production of toxicologically significant amounts of unexpected toxicants would suggest a potential hazard in use.

Other indices such as histopathology or detailed blood chemistry may be included in the test protocol. Data obtained in the preliminary evaluation of acute toxicity may warrant these more in-depth studies.

SPECIAL TOXICITY EVALUATIONS

When unique toxic effects are observed, specific testing programs may be initiated. In the case of delayed neurotoxicity, the protocol developed by Johannsen et al. (1977) would be appropriate for comparing the neurotoxicity of the candidate fluid with the neurotoxicity of known neurotoxins such as tri-o-cresyl phosphate.

More subtle toxic effects such as carcinogenicity are normally expressed over longer periods of time and would not be observed in the tests described earlier. Animal carcinogenicity studies are so expensive and time-consuming that it would not be possible to thoroughly test all suspected carcinogens. Therefore, short-term tests are being developed to screen materials for their carcinogenic potential. These tests evaluate materials for their mutagenic potential, which is correlated with carcinogenic potential.

One of these tests, the Ames Test (salmonella/microsome), has demonstrated a reasonable correlation between mutagenic potential and known animal carcinogens. The test is brief, inexpensive, and promising as a preliminary screening test to determine the need for long-term animal carcinogen testing.

Animal carcinogen studies require large groups of test animals (60 to 120 rats/sex/level) which are exposed to atmospheres containing the test material. Frequently a second test species is desirable. Two to three groups are exposed to different concentrations of the test material for 6 hours a day, 5 days a week for 18 to 24 months. Simultaneously, a group of control animals is subjected to the same procedures minus compound administration. Toxic signs and animal body weights are recorded on a regular basis. General hematology, clinical chemistry and urinalysis are performed at appropriate intervals (e.g., 3, 12, and 24 months) throughout the test. Likewise, gross pathology and histopathologic examination of the test animals are also performed at appropriate intervals. The assessment of carcinogenic potential is possible only after detailed examination of the chemical, pathologic, and clinical data.

In addition to neurotoxicologic, mutagenic, and carcinogenic testing, other special toxicity tests might be necessary. For example, if women of childbearing age may be exposed, it would be advisable to conduct teratogenic toxicity tests. These and other types of toxicity tests have been dealt with in more depth elsewhere (National Academy of Sciences, 1977a).

Where continuous, round-the-clock exposure is involved, it might be necessary to design a specific test protocol to assess the toxicity associated with continuous 24-hour exposure to these compounds over a period of 60 to 90 days.

ENVIRONMENTAL FATE

Hydraulic fluids are intended to be used in enclosed fluid systems, thus limiting their distribution into the environment. However, accidental discharge or discharge during maintenance operations cannot always be prevented. Consideration of probable environmental effects of candidate fluids must be included in the early stages of evaluation. These factors are the degradability of the material (photochemical, chemical, and biochemical), the toxicity of the material and its stable metabolites, and its bioconcentration potential.

The determination of expected environmental levels can be calculated on the basis of the expected production, use, and disposal patterns and the chemistry and degradation of a material. Both minimum and maximum expected levels should be calculated.

Acute toxicity tests should be run on a representative invertebrate and one or two fish species. Water fleas, bluegill sunfish, rainbow trout, and fathead minnows are the species of preference. By determining the LC50 of a material, data are obtained for comparison with other materials and for anticipation of problems caused by spills.

The bioconcentration potential of a candidate hydraulic fluid can be assessed by determining its water/octanol partition coefficient. For example, chlorinated hydrocarbons that are easily stored in body fat have high partition coefficients. Ultimately, actual in vivo accumulation studies with representatives of the species at risk may be necessary.

Should a material readily degrade, the aforementioned abbreviated hazard evaluation should be carried out on its stable metabolites.

The following are suggested as an approach to evaluate the toxicity of hydraulic fluids to aquatic organisms in the environment. This abbreviated format provides a beginning hazard evaluation of materials and also generates a baseline on which the need for further toxicity testing could be planned. More detailed descriptions of the procedures listed below are provided in the references.

Chemistry

Calculations can be made to determine the oxidation, reduction, hydrolysis, and photo-oxidation potential of a material. Synergistic reactions need also to be assessed. Does the fluid volatilize, solubilize in water, or selectively partition into organic solvents?

Bioconcentration potential

The octanol-water partition coefficient is a physical measurement that may be used to estimate the bioconcentration potential of a hydraulic fluid. By shaking the material in a separatory funnel containing distilled water and n-octanol, the lipophilicity of the compound can be determined. The concentration of the material is measured in each phase and the partition coefficient is calculated as the ratio of the concentration in the octanol phase to that in the water phase (Kimmerle et al., 1975).

Biodegradation

Primary biodegradation is defined as the disappearance of the original material due to bacterial action as evidenced by a specific analytical technique. Two procedures that have been widely used in primary biodegradation measurements are the semicontinuous activated sludge (SCAS) test, which simulates a secondary sewage treatment process, and the river die-away test, which simulates the natural environment of a river.

In the SCAS test activated sludge and its liquor from a domestic sewage treatment plant are spiked with the test material (generally in ethanol) and synthetic or raw sewage. The mixture is aerated for 23 to 176 hours and allowed to settle, and a liter of effluent is drained and analyzed for the test material. The result is expressed as percent degradation. The cycle is reinitiated by the addition of water, sewage, and test material (Saeger and Tucker, 1976).

The river die-away test consists of exposing a low level of test material to organisms in natural river-water samples. Periodically, water is analyzed for concentrations of the test material. Sterile water controls are included to verify that changes in concentration are due to degradation and not physical or chemical phenomena. The duration of the test is generally 6 weeks. The result is expressed as half-life of the test material (Saeger and Tucker, 1976).

Acute toxicity to invertebrates

Groups of test organisms (5-10 per group, generally first instar daphnids) are exposed in a static system for 48 hours in at least four concentration levels. Mortality and behavior observations are made at 24-hour intervals (U.S. Environmental Protection Agency, 1975). The LC50 is calculated by probit, logit, or moving average method, or by that of Litchfield and Wilcoxon, 1949.

Acute toxicity to fish

Groups of test organisms (5-10 per group, generally fingerling fathead minnows, bluegill sunfish, or rainbow trout) are exposed in a static system for 96 hours to at least five concentration levels. Mortality and behavior observations are made at 24-hour intervals, (U.S. Environmental Protection Agency, 1975). The LC50 is calculated by the same methods as described in invertebrate acute toxicity above.

Additional testing

A decision may be made to do further testing at this point. An invertebrate chronic study or in vivo bioconcentration studies may be desired, should further information be required.

SUMMARY

In summary, a tier approach to toxicity evaluation is proposed. Preliminary toxicity evaluation should be conducted early in the development of a fluid. Based on these results further toxicity evaluation (chronic and special) might be proposed. Use of the resulting data in conjunction with the physical properties of the hydraulic fluid and a proper hazard evaluation should provide an adequate basis for the selection of an optimum hydraulic fluid.

REFERENCES

- Ames Research Center, Conference on Hydraulic Fluids: A Compilation of Presentations and Papers. Joint Technical Coordinating Group/Aircraft Survivability, NASA TM-73, 142, Moffett Field, CA, February 24 and 25, 1976.
- ASTM, Symposium on Hydraulic Fluids, Third Pacific Area National Meeting, American Society for Testing Materials, ASTM Special Technical Publication No. 267, San Francisco, CA, October 13, 1959.
- ASTM, Fire Resistance of Hydraulic Fluids, Committee D-2 on Petroleum Products and Lubricants, American Society for Testing Materials, and Committee A-6 on Aerospace Fluid Power Technology, Society of Automotive Engineers, ASTM Special Technical Publication No. 406, New Orleans, LA, January 26 and 27, 1966.
- ASTM D-92, "Standard Test Method for Flash and Fire Points by Cleveland Open Cup."
- ASTM D-665, "Standard Test Method for Rust Preventing Characteristics of Steam Turbine Oils in Presence of Water."
- ASTM D-2155, "Standard Test Method for Autoignition Temperature of Liquid Petroleum Products."
- ASTM D-3115, "Standard Method of Test for Explosive Reactivity of Lubricants with Aerospace Alloys Under High Shear."
- ASTM D-3119, "Standard Method for Mist Spray Flammability of Hydraulic Fluids."

- ASTM D-3603, "Standard Test Method for Rust-Preventing Characteristics of Steam Turbine Oil in Presence of Water" (Horizontal Disk Method).
- ASTM G-1, "Standard Recommended Practice for Preparing, Cleaning, and Evaluating Corrosion Test Specimens."
- Carhart, H. and R. Gann, "Fire Suppression in Submarines," Report of NRL Progress, pp. 4-13, May 1974.
- Code of Federal Regulations, Fed. Hazardous Substance Act, Chapter 2, Title 16, as cited in National Academy of Sciences, 1975b reference, pp. 119-124.
- Fletcher, E.A., University of Minnesota, private communication, 1979.
- Johannsen, F.R., P.L. Wright, D.E. Gordon, G.J. Levinskas, R.W. Radue, and P.R. Graham, "Evaluation of Delayed Neurotoxicity and Dose-response Relationships of Phosphate Esters in the Adult Hen." Toxicol. Appl. Pharmacol. 41: 291-304, 1977.
- Kimmerle, R.A., R.D. Swisher, and R.M. Camotto, Surfaced Structure and Aquatic Toxicity, Chapter 2 of Structure-Activity Correlations in Studies of Toxicity and Bioconcentration with Aquatic Organisms, Proceedings of a Symposium, Burlington, Ontario, Canada, pp. 25-55, March 11-13, 1975.
- Military Specification, MIL-H-19457 (SHIPS), "Hydraulic Fluid, Fire Resistant."
- National Academy of Sciences, Washington, D.C., "Principles for Evaluating Chemicals in the Environment," A Report of the Committee for the Working Conference on Principles of Protocols for Evaluating Chemicals in the Environment, 1975a.
- National Academy of Sciences, Washington, D.C., "Decision Making for Regulating Chemicals in the Environment," A Report of the Committee on Principles of Decision Making for Regulating Chemicals in the Environment, 1975b.

- National Academy of Sciences, Washington, D.C.,
"Principles and Procedures for Evaluating
Toxicity of Household Substances," NRC Publica-
tion 1138, 1977a.
- National Academy of Sciences, Washington, D.C.,
"Fire Toxicology: Methods for Evaluation of
Toxicity of Pyrolysis and Combustion Products,"
Committee on Fire Toxicology, Report No. 2, 1977b.
- National Academy of Sciences, Washington, D.C.,
Committee on Toxicology, "Toxicity of Synthetic
Hydraulic Fluids," December 1977c.
- National Academy of Sciences, Washington, D.C.,
Committee on Fire Safety Aspects of Polymeric
Materials, Vol. 6, "Aircraft: Civil & Military,"
p. 185, 1977d.
- Saeger, V.W. and E.S. Tucker, "Biodegradation of
Phthalic Acid Esters in River Water and Activated
Sludge," Applied and Environmental Microbiology,
Volume III-I; 29-34, 1976.
- U.S. Bureau of Mines, "Summary of Ignition Properties
of Jet Fuels and Other Aircraft Combustible
Fluids," Pittsburgh Mining and Safety Research
Center, Technical Report AFAPL-TR-75-70,
September 1975.
- U.S. Environmental Protection Agency, "Methods
for Acute Toxicity Tests with Fish, Macroinver-
tebrates, and Amphibians," National Environmental
Research Center, Office of Research and Develop-
ment, Corvallis, Oregon 72330, EPA - 330, EPA -
660/3-75-009, April 1975.
- Wright Air Development Center, "Development of
High-Temperature Aircraft Hydraulic Fluids,"
WADC Technical Report 6685, Supplement 1,
October 1952.
- Wright, P.L. and C.H. Adams, "Toxicity of Combustion
Products from Burning Polymers: Development and
Evaluation of Methods," Environmental Health
Perspectives, 17:75, 1976.

BIBLIOGRAPHY

- Brown, C.L., "Fluid Structural Factors Versus Fire Resistance," R and D Report 95 648C, Sub-project S-R001 07 01, U.S. Navy, Marine Engineering Laboratory, Annapolis, MD, November 9, 1962.
- Brown, C.L., "A Water-Glycol-Type Interim Fire-Resistant Submarine Hydraulic Fluid," Report 2598 (MAT LAB 206) DTNSRDC, Annapolis, MD, October 1968.
- Carhart, H.W. and J.K. Thompson, "Removal of Contaminants from Submarine Atmospheres," ACS Meeting, 1974.
- "Fire Resistance of Hydraulic Fluids." Symposium presented at a meeting of ASTM Committee D-2 and Society of Automotive Engineers Committee A-6, January 26-27, 1966, New Orleans, LA. Published by ASTM, Philadelphia, PA 19103.
- Gunderson, R.C. (ed.), "Synthetic Lubricants." New York: Reinhold Publishing Co., 1962.
- Hammond, J.L. and A.A. Conte, Jr., "Silicone-Base Fire-Resistant Hydraulic Fluid for Potential Use in Armored Surface Vehicle Hydraulic Systems," Final Report MIPR No. 401-74, Naval Air Development Center, Warminster, PA, May 21, 1975.
- Hatton, R. (ed.), "Introduction to Hydraulic Fluids." New York: Reinhold Publishing Co., 1962.
- Lipowitz, J. and M.J. Ziemelis, "Flammability of Poly(dimethylsiloxanes). II. Flammability and Fire Hazard Properties." J. Fire and Flammability 7 504-529, October 1976.

- Litchfield, J.T., Jr. and F. Wilcoxon, "A Simplified Method of Evaluating Dose-Effect Experiments," *Journal of Pharmaceutics and Experimental Therapeutics*, Volume 96: 99-113, 1949.
- MacDonald, J.A. and J.T. Cansdale, "Spontaneous Ignition of Aircraft Hydraulic Fluids," RAE Technical Report 74066, 1974.
- "Symposium on Hydraulic Fluids." Presented at the Third Pacific Area National Meeting of the ASTM, October 13, 1959, San Francisco, CA, ASTM Special Technical Publication No. 267.

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