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(Summary Report)

EMBRITTLEMENT OF METALS
BY ORGANIC LIQUIDS

Commanding Officer
Frankford Arsenal
Philadelphia, Pennsylvania 19137

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(Summary Report)

March 1, 1964 to March 31, 1965

Submitted to.

Commanding Officer
Frankford Arsenal
Philadelphia, Pennsylvania 19137
Attention: Mr. J. M. McCaughey

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IIT RESEARCH INSTITUTE

EMBRITTLEMENT OF STEEL BY ORGANIC LIQUIDS

ABSTRACT

The published literature on this subject is reviewed. The essential details of reduced fatigue life of steel in the presence of certain polar liquids discovered by Karpenko are confirmed. Studies on polar liquids and solutions have been expanded to include a wider variety of long-chain organic species and a number of metallo-organic liquids. It is shown that fatigue life increases with increasing carbon chain length. In all cases the plot of fatigue life against carbon chain length extrapolates to the value for water. Further study has shown that in the presence of a strong dehydration agent, the embrittlement effect disappears. It is concluded that water content in solution is the fundamental factor governing the incidence of reduced fatigue life. However, the mechanism of failure in the presence of water is not clear. A number of experiments are described which suggest that current convictions are not tenable.

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EMBRITTLEMENT OF METALS BY ORGANIC LIQUIDS

I. INTRODUCTION

This is a summary report on one portion of a composite program entitled "Fracture of Metals," identified under Contract No DA 11-ORD-022-3108. This report covers the period of March 1, 1964, to March 31, 1965.

This portion of the program on "Fracture of Metals" is directed to explore the existence and nature of embrittlement which might be produced by concurrent exposure of metals to organic liquids and tensile stresses. Organic liquids are defined for present purposes as pure liquid species, miscible liquid species, and solutions of solids in liquids. Embrittlement constitutes the premature incidence of cracking as experienced under continuously increased loading, static loading, or dynamic (cyclic) loading. "Premature" implies a lower maximum load, a shorter time, or fewer cycles than would be expected for the material stressed in air.

The study has made use of two high-strength materials--a quenched and tempered steel and an age-hardened aluminum alloy. A high strength condition was chosen because with environmentally-induced embrittlement, general experience is that such states are most prone to premature cracking and are, therefore, most likely to be influenced by organic liquids. The work with the aluminum alloy is only briefly described in this report. The detailed results are contained in the previous summary report (January 2, 1964) under the same contract.

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II. REVIEW OF PUBLISHED LITERATURE

During the period 1949-1954, G. V. Karpenko and his associates* published the results of a series of investigations on the influence of certain polar organic species in liquid solution form on the fatigue strength of steel. For these experiments, cantilever-loaded or beam-loaded, rotating, smooth bar specimens were mostly used. The liquid medium was drip-fed over the stressed section. Between ten and twenty specimens were used to define the S-N curve. The liquid media included water, aqueous solutions of isoamyl alcohol, mineral oil, heptane, and mineral oil solutions containing isoamyl alcohol, cetyl alcohol, oleic acid, butyric acid, and stearic acid. Water, alcohols, and organic acids are polar species, i.e., having finite dipole moments, while mineral oil and heptane in pure form are nonpolar.

It was shown that the polar or polar-containing liquids reduced the endurance limits of several steels at various heat-treated hardness levels by 5-83%. The results fell into two groupings represented by water- and mineral oil-based solutions. Water and water-based solutions decreased endurance limits by 56-83%, depending on steel hardness, while the mineral oil solutions gave more modest decreases of 5-15%. Purified mineral oils and heptane produced no effect on fatigue life.

A distinction is made between the action of mineral oil solutions, which is characterized as adsorption fatigue, and that of water solutions, which is characterized as corrosion fatigue. In adsorption-reduced fatigue resistance, the transition from the strongly stress-dependent regime of fatigue life to the endurance limit is sharp, as is the case in normal air environment. Corrosion fatigue produces a more gradual transition, and the existence of a true endurance limit is questionable, although the stress dependence in this range is at most very small. An aqueous solution

* These papers appeared in Dokl. Akad. Nauk USSR and Akad. Nauk SSR, as well as in some not readily available monographs. A detailed summary of results and interpretation may be found in references 1 and 2.

of isoamyl alcohol (2%) produces a definite endurance limit, although in all other respects the deterioration of fatigue strength is almost identical to that of pure water. These investigations also draw attention to the observation that many cracks develop in water-induced fatigue failure, whereas relatively few occur in oil-induced failures. This could, however, be merely an association with the more emphatic embrittlement produced by water.

It is shown that both adsorption and corrosion fatigue are less sensitive to surface finish, and that both phenomena show a dependence on frequency of cycling in the direction of increased embrittlement at lower cycling rates.

The explanation given to account for these events is predicated upon earlier and concurrent work on the yield and plastic flow of single crystals immersed in similar polar liquids and liquid solutions. Rebinder and his associates^(1, 3) over a period of years have published the results of experiments to the effect that the yield stresses of Sn, Al, and Pb single crystals are reduced significantly when immersed in mineral oil or octane solutions of oleic acid, palmitic acid, or cetyl alcohol. More particularly, the creep rates of these single crystals are increased substantially in the presence of the so-called surface-active media. These phenomena and their nature are themselves the subject of controversy. Kramer⁽⁴⁾ does not confirm the effect on the critical resolved shear stress of Al, but does confirm other effects, such as reduced work-hardening rate and increased strain in stage I yielding and increased creep rates. Andrade and Roscoe⁽⁵⁾ and Harper and Cottrell⁽⁶⁾ argue that the effects observed are more related to the presence of oxide films than to a true interaction between the metal and a liquid environment. These and other published results are appraised in more detail by Machlin.⁽⁷⁾

The essence of the argument is that surface-active liquids increase the slip activity in surface grains so that failure nuclei are generated in fewer stress cycles. Further, surface-active molecules penetrate deeper to the roots of crack nuclei, exerting a pressure on the walls of the crack tending to separate them. On this latter point, Piggott⁽⁸⁾ states that this separating force is too small to be of significance. He analyzes, however, the possibility that the action of a liquid entering a crack could exert a force through compression of entrapped air or other gases. The results of this analysis show that such forces could be of significant magnitude only in the case of very soft metal having a flow stress less than 0.1 kg/mm^2 .

The corrosion fatigue process is considered to be additive to the adsorption fatigue mechanism by creating surface pits with attendant stress magnification and by producing a corrosion film on the crack walls which imparts a wedging action.

The work of Steigerwald⁽⁹⁾ on static fatigue (fixed load) failure of center-notched, high-strength steel (AISI) in the presence of water and organic liquids is relevant to the present review. At a nominal stress of 75,000 psi (83.5% of the tensile strength as notched), the specimens are capable of sustaining this load indefinitely in air. The following failure times (in minutes) were recorded for various liquid media which totally immersed the crack zone: distilled water (6.5); amyl alcohol (35.8); butyl alcohol (28.0); butyl acetate (18.0); acetone (120); lubricating oils (150); carbon tetrachloride (no failure in 1280); and benzene (2247). In the scheme of testing, the liquid medium was exposed to the air, which will be a point of discussion later.

Very significant are the observations that the range of pH of aqueous solutions between 4.8 and 9.0 produced no variation in failure time. This will also be a subject for subsequent discussion. Steigerwald concluded that no distinction in embrittlement mechanism could be made between corrosion, stress-corrosion, hydrogen-embrittlement, and "stress-sorption" cracking.

In a subsequent reexamination of the subject of static failure in the presence of water and water vapor, ⁽¹⁰⁾ the case was made that hydrogen embrittlement is the responsible mechanism. However, the inability of large anodic potentials to reduce the failure time of steel specimens in distilled water makes this argument quite inconclusive. ⁽¹¹⁾

It is clear that the existence of an embrittlement by polar organic liquids, except in the case of water, has limited experimental verification, and that the arguments on mechanism are largely speculative and based on controversial premises. The present work sets out to reexamine the subject on a broader scope.

III. EXPERIMENTAL METHOD

A. Scope of Investigation

Since Karpenko showed that the greatest losses in fatigue strength were encountered in steels that had been heat-treated to high hardness, this work has confined itself to a single steel at a single hardness level. The steel chosen is a modified AISI 4340 having the composition: 0.40% C, 1.6% Si, 0.75% Mn, 0.85% Cr, 1.85% Ni, 0.40% Mo, 0.08% V (commercial designation: 300M). This steel is air-hardenable and was used in a hardened state tempered to a yield strength of 200,000 psi (44 Rc). A single lot was used throughout in the form of 0.080 in. thick sheet.

The number of potentially important organic-liquid media is legion. However, these may be categorized according to molecular symmetries and appended groups. In a search for basic relationships, systematic selections were made from categories including alcohols, ethers, aldehydes, carboxylic acids, polar-benzo groups, and certain simple metallo-organic species. Less systematically, specific examples of glycols, ketones, amines, and halogenated hydrocarbons were also selected for test.

The major part of this program was involved with fatigue testing. However, preliminary to this, a large number of tensile and static fatigue tests were performed. The surfaces of these specimens were hand-polished, and a saturated swab of the candidate liquid placed thereon. The static fatigue test involved an unnotched bend specimen that was

prestressed to the yield point and held at that stress by a suitable fixture. Static loading was maintained for up to seven days. More than 200 liquid, hydrocarbon solution, or aqueous solution species were screened for premature failure. In no case was it found that the yield stress, ultimate strength, or ductility at rupture were affected by the presence of an organic liquid or aqueous solution. Also, no delayed failures were encountered.

B. System of Fatigue Testing

Edge-notched sheet specimens with a filed 0.001 in. root radius have been tested in tension-tension fatigue. A cyclic stress between zero and some maximum value was superimposed on a constant tensile stress. For an arbitrary static component, the S-N curve in Figure 1 plots the number of cycles to failure against the cyclic stress component. There is a sharp and clearly defined endurance limit. The cracks originate from one or both of the edge-notch roots and propagate in a direction transverse to the axis of stressing until the maximum stress exceeds the ultimate strength of the remaining cross section. About 50% of the total crack surface represents slowly advancing fatigue cracks.

The action of a liquid environment is induced by clamping two liquid-saturated asbestos pads to the faces of the specimen over the whole notched area. A polyethylene (or equivalent clear plastic sheet) envelope prevents volatilization. The specimen geometry and pad arrangement are illustrated in Figure 2. Fatigue testing was done on a Baldwin fatigue machine operating at 1800 cpm. According to previous work, ⁽¹⁾ this slower rate of cycling is more conducive to premature cracking in the presence of a surface-active agent.

While the nominal stresses imposed on the edge-notched sheet specimen are not large, the depth of notch and the notch radius (~ 0.001 in.) are such as to create very large stress magnifications at the root. If one assumes purely elastic behavior, the stress magnification is probably between 20 to 30 times. This means that the stresses at the notch root could exceed 400,000 psi at the endurance limit. Whatever the exact values, we can be assured of a stress regime where embrittlement effects are most clearly resolvable.

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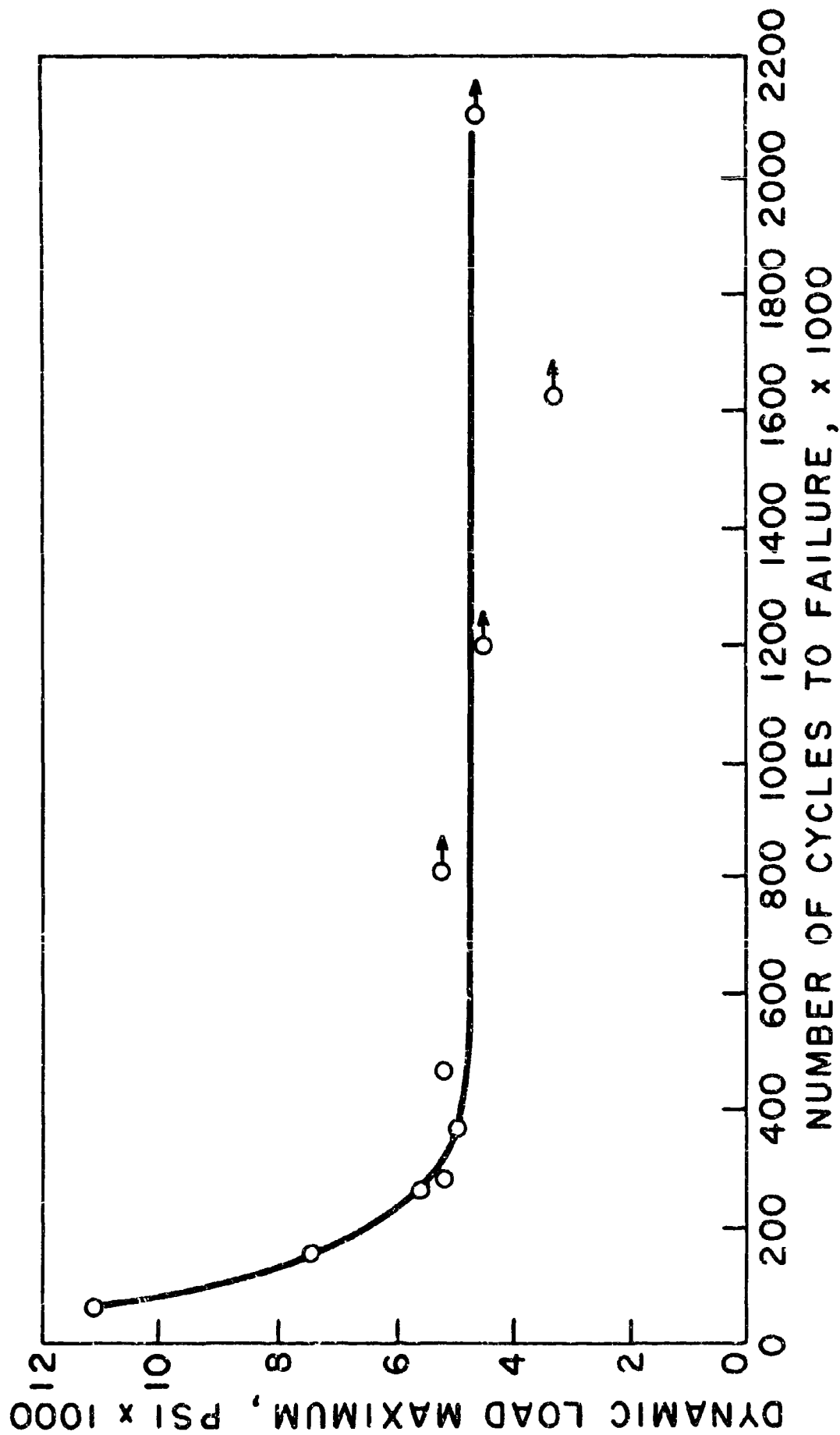
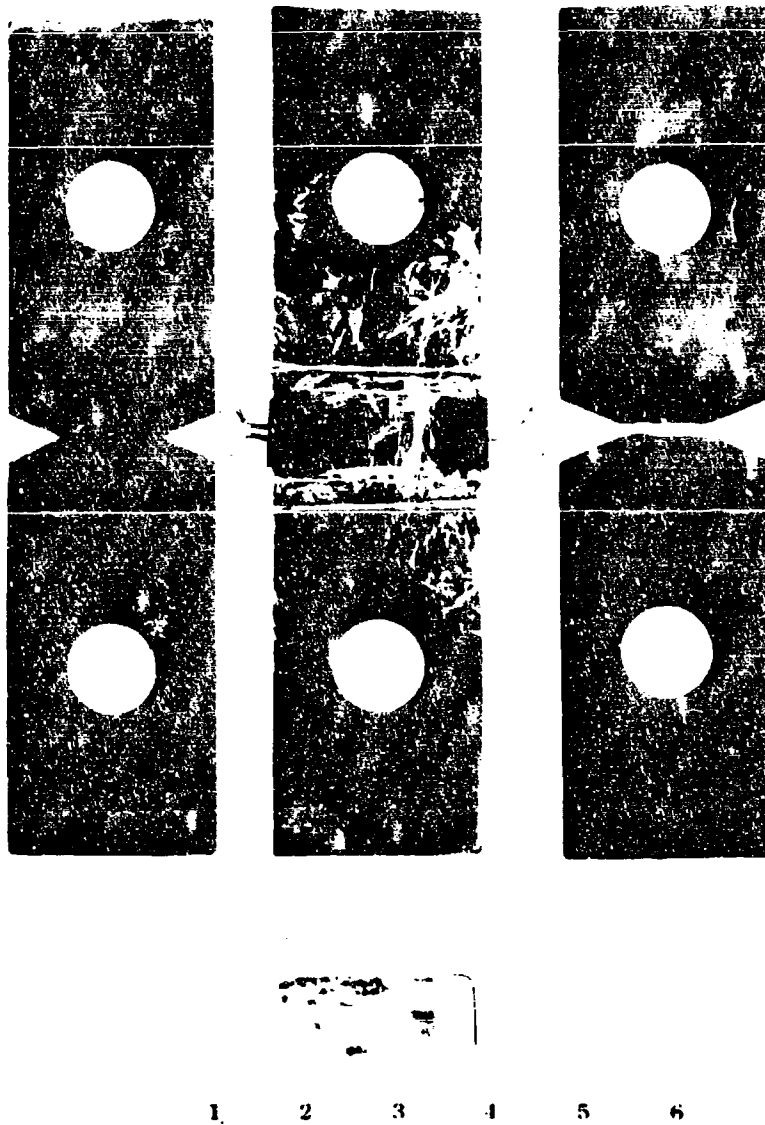


FIG. 1 - FATIGUE FAILURE (S-N) CURVE FOR HEAT-TREATED STEEL (200,000 PSI YIELD STRENGTH) UNDER A STATIC NOMINAL STRESS OF 12,500 PSI AND A VARIABLE DYNAMIC NOMINAL STRESS AT 1800 CPM.



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FIG. 2 - ILLUSTRATION OF EDGE-NOTCHED SHEET SPECIMEN FOR TENSION-TENSION FATIGUE IN THE PRESENCE OF CANDIDATE ORGANIC EMBRITTLING LIQUIDS. Shows arrangement of liquid-saturated pads clipped to the fracture zone and wrapped to prevent volatilization. Character of fracture also shown.

The endurance limit in air for the 12, 500 psi preload occurred at about 4750 psi dynamic increment. In this case, the endurance limit signifies no failure after 21×10^6 cycles. Distilled water was taken as a reference standard for embrittlement. At a dynamic stress increment of 4370 psi, specimens wetted with water failed consistently at 500,000 to 700,000 cycles. The range of $0.7-21 \times 10^6$ cycles therefore provided a broad scale of comparative embrittlement. All tests reported hereafter represent cycles-to-failure at a combination of 12, 500 psi static and 4370 psi dynamic stress. From each new batch of heat-treated specimens, at least one was tested with water as a qualification test.

IV. PRELIMINARY CONFIRMATION OF PREVIOUS WORK

The publications of Karpenko cite a number of polar organic species as capable of measurable embrittlement of steel under cyclic loading. Although the steels and system of testing are not duplicated in the present work, there is no reason why the same general results should not be obtained. A series of preliminary experiments verified the essential details of Karpenko's results. These are summarized in Table I. It is seen that water is most effective, that isoamyl alcohol and oleic acid are nevertheless also very effective, and that stearic acid has no measured effect (Karpenko rates it as mildly effective). It is also seen that relatively low concentrations of polar solutes in a nonpolar solvent are as effective as the pure polar liquid.

V. EMBRITTLEMENT AS A FUNCTION OF MOLECULAR WEIGHT

Using the specimen geometry, wrapped pad system of liquid contact with the stressed zone, and the static-dynamic stress combination described in a previous section, the number of cycles-to-failure may be taken as the scaled index of embrittlement potential. With this approach, a systematic study was made of the influence of molecular weight in simple carbon chain, polar liquids of the alcohol, ether, aldehyde, and carboxylic acid groups. Except for the very long-chain carboxylic acids (e.g., lauric, palmitic, and stearic acid), all of the species tested were liquids in their pure form. At this point there was no need for dilutions. In the case of the solid carboxylic acids, saturated solutions in dioxane or

TABLE I
FATIGUE LIFE IN THE PRESENCE OF
SOME NONPOLAR AND POLAR LIQUIDS AND SOLUTIONS

Liquid or Solution	Cycles to Failure
Distilled water	600,000 - 800,000
Isoamyl alcohol	900,000 - 1,100,000
> 20%* isoamyl alcohol in heavy mineral oil	900,000 - 1,100,000
< 10% isoamyl alcohol in heavy mineral oil	> 7,000,000 DNF
Oleic acid	800,000 - 1,100,000
6% [†] stearic acid in dioxane	> 7,000,000 DNF
Heavy mineral oil	> 7,000,000 DNF
Light mineral oil	> 7,000,000 DNF

* Volume per cent

[†] Weight per cent

DNF - did not fail

heptane were used. Both of these latter solvents are nonpolar and nonembrittling.

Figures 3, 4, 5, and 6 show systematic relationships between carbon chain length and cycles-to-failure. These relationships all have a common character. The embrittlement potential decreases with increasing molecular weight, and the extrapolation to zero carbon chain length coincides with the cycles-to-failure caused by water.

A large number of other polar-liquid types were evaluated in a less comprehensive manner, with the results summarized in Table II. Most of these produced embrittlement. Some were quite as effective as water. Acetyl chloride is an interesting case. It is highly corrosive to steel--much more so than water--yet it produced no measurable embrittlement. This suggests that very active corrosion prevents stable adsorption to the steel surface.

On the assumption that polar groups of metal atoms could have stronger interaction with a metal and produce an effect comparable to liquid metals, a series of simple metallo-organic liquids were tested. Some of these are pyrophoric. It is a tribute to the wrapping system and its capacity to restrict access to air that combustion began only after failure when the wrapped pad was ripped apart. The results of testing metallo-organic liquids are summarized in Table III. In general, their embrittlement potential was variable or nonexistent, but in no case was it more than water.

A number of nonpolar liquids were tested. These included heavy mineral oil, light mineral oil, carbon tetrachloride, benzene, heptane, and dioxane. None of these produced failure. Tests were discontinued after 7,000,000 cycles.

VI. INFLUENCE OF WATER CONTENT

The trends of fatigue life against carbon chain length are temptingly systematic. Since, for example, the dipole moments of all primary alcohols are about the same magnitude, one could conclude that increasing chain length signifies increasing steric obstruction to reaching

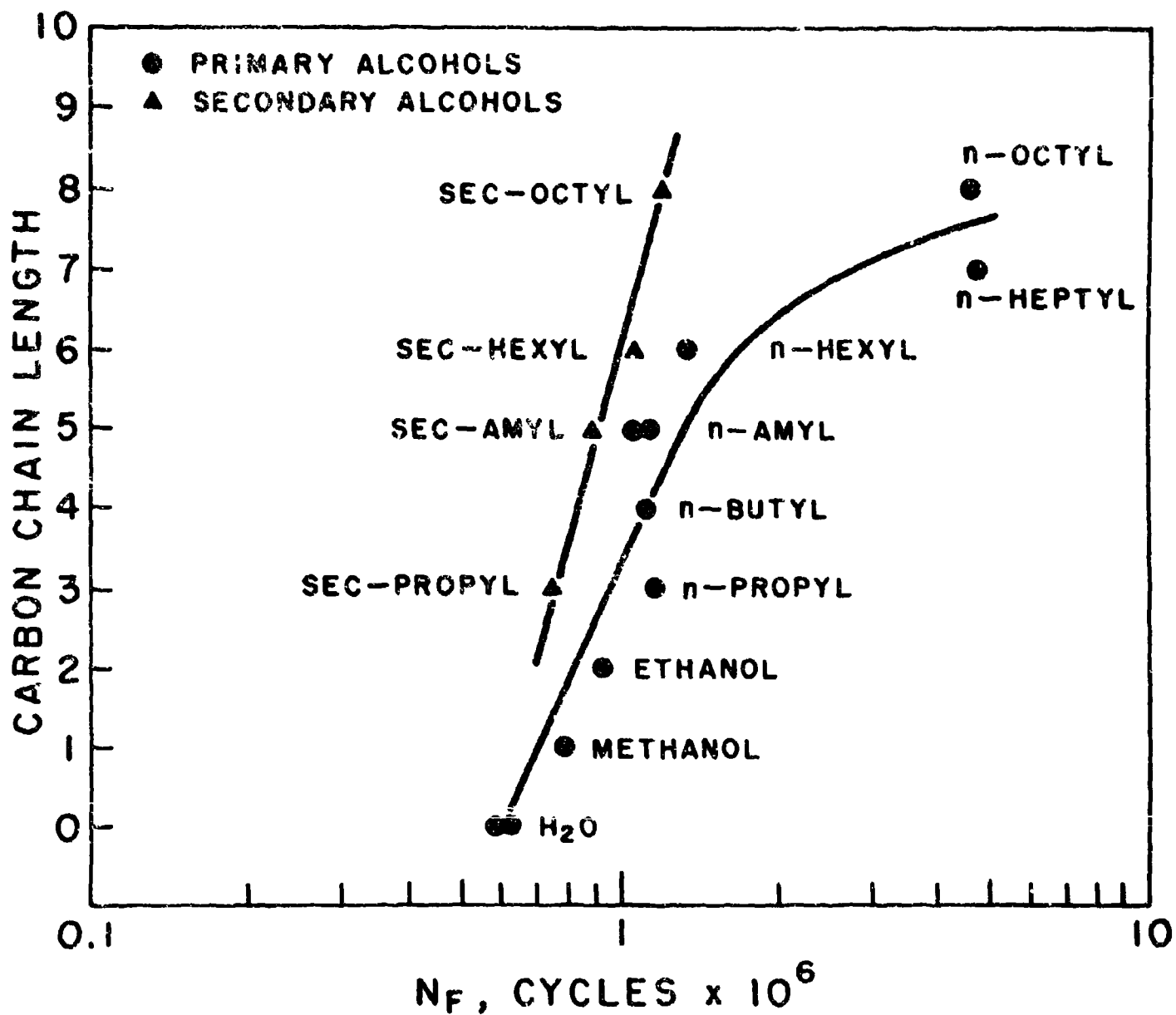


FIG. 3 - FATIGUE LIMIT (N_F) OF HIGH-STRENGTH STEEL IN PRIMARY AND SECONDARY ALCOHOLS. (V-notched tension-tension specimens, 12,500 psi preload, 4370 psi dynamic load.)

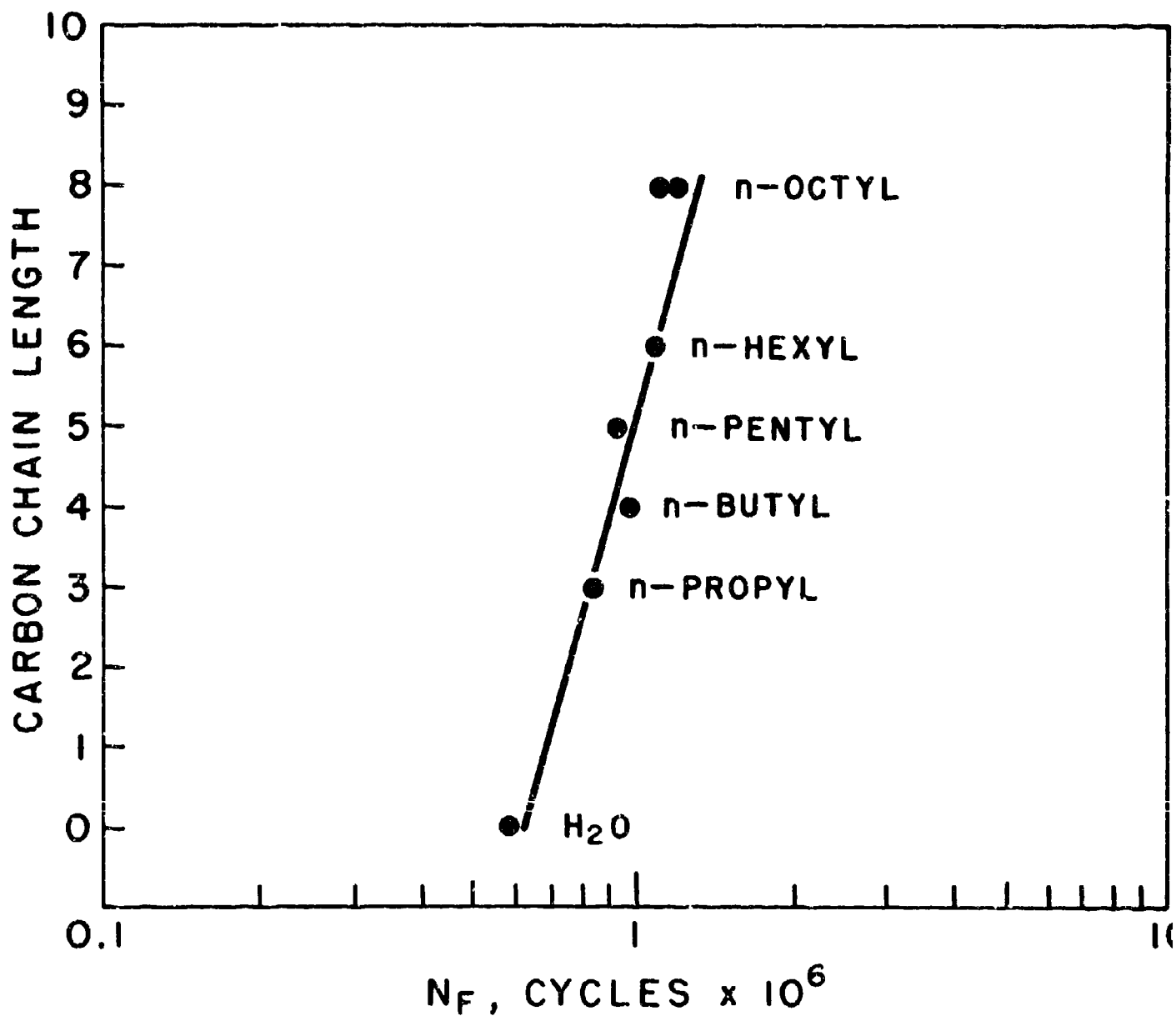


FIG. 4 - FATIGUE LIMIT (N_F) IN SIMPLE ETHERS. (High-strength steel, V-notched tension-tension specimens, 12,500 psi preload, 4370 psi dynamic load.)

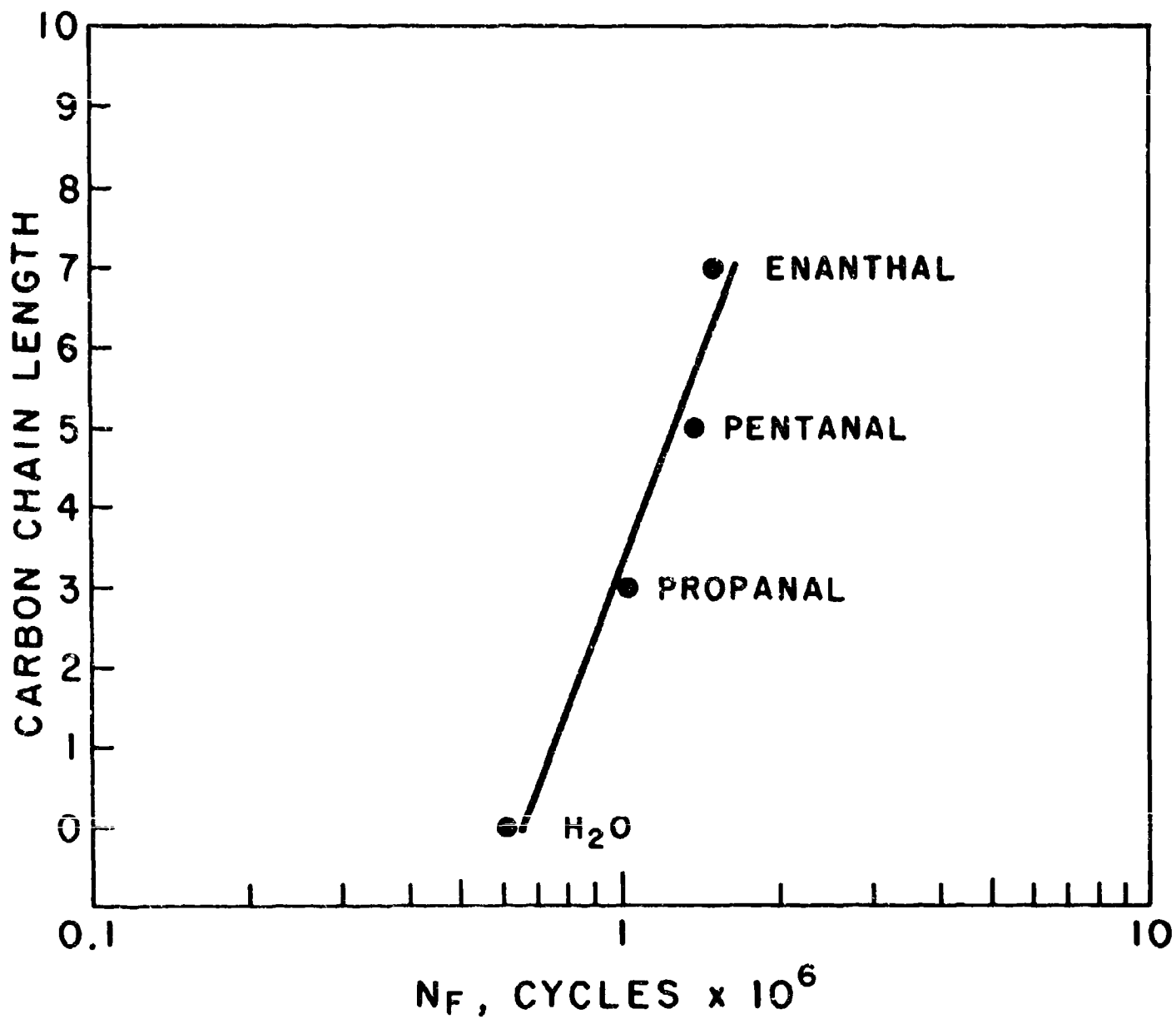


FIG. 5 - FATIGUE LIMIT (N_F) IN ALDEHYDES. (High-strength steel, V-notched tension-tension specimens, 12,500 psi preload, 4370 psi dynamic load.)

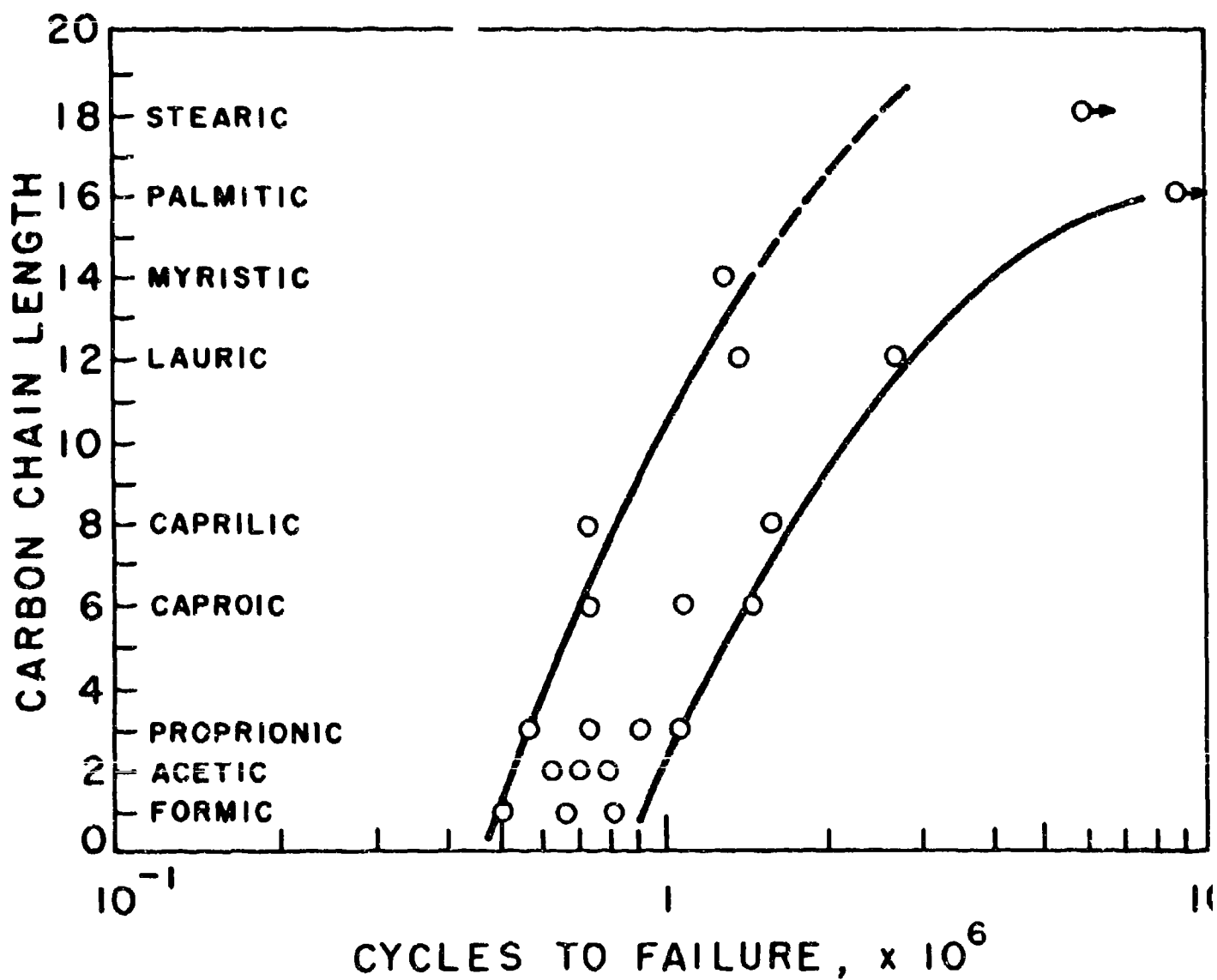


FIG. 6 - FATIGUE LIMIT (N_F) OF HIGH-STRENGTH STEEL IN CARBOXYLIC ACIDS (V-notched tension-tension specimens, 12,500 psi preload, 4370 psi dynamic load).

TABLE II
EMBRITTLEMENT PRODUCED BY VARIOUS POLAR LIQUIDS

Species	Polar Group (number)	Cycles to Failure
Ethylene glycol	-OH (2)	824,000
Diethylene glycol	-OH (2)	756,000
Glycerol	-OH (3)	868,000
Nitrobenzene	-NO ₂ (1)	720,000; 550,000
Benzonitrile	-CN (1)	781,000; 441,000
Benzaldehyde	-CHO (1)	1,245,000; 1,820,000
Chlorobenzene	-Cl (1)	741,000; 796,000
Aniline	-NH ₂ (1)	1,182,000; 1,300,000
Butyl amine	-NH ₂ (1)	625,000; 541,000
Pentyl amine	-NH ₂ (1)	2,733,000 [*]
Hexyl amine	-NH ₂ (1)	2,383,000 [*]
Chloroform	-Cl (3)	834,000
Diethylene chloride	-Cl (2); -O- (1)	1,059,000
Acetyl chloride	-Cl (1); = O (1)	7,000,000 ^{*+}
Methyl chloride	-Cl (1)	496,000; 476,000

^{*} DNF - Did not fail.

⁺ Very corrosive to steel

TABLE III
EMBRITTLEMENT BY METALLO-ORGANIC LIQUIDS AND SOLUTIONS

Species	Cycles to Failure
Diethyl zinc $(C_2H_5)_2 Zn$ in light mineral oil	4,511,000* ; 5,092,000
Ethyl lithium $C_2H_5 Li$ in benzene	1,950,000
Phenyl lithium $C_6H_5 Li$	956,000; 2,269,000*
Triethyl aluminum $(C_2H_5)_3 Al$ in light mineral oil	625,000; 840,000
Triethyl boron $(C_2H_5)_3 B$	746,000; 915,000
Butyl sodium $(C_4H_9) Na$ in heptane	750,000
Diethyl magnesium $(C_2H_5)_2 Mg$ in heptane	1,865,000
Diethyl cadmium $(C_2H_5)_2 Cd$ in heptane	2,844,000*
Dibutyl cadmium $(C_4H_9)_2 Cd$	1,865,000

* DNF - Did not fail.

the root of a crack. The fact that -ON, -O, and = O groups extrapolate to water is encouraging since they all represent interaction between metal and oxygen atoms. On the other hand, the heats of formation of nitrides and chlorides of iron are not as high as the oxides, yet -NH₂ and -Cl polar groups in the form of butyl amine and methyl chloride, respectively, are just as effective as water.

Yet it also happens that the solubility for water decreases with increasing chain length. By the procedure used, it was inescapable that the candidate liquid be exposed to the air for a brief period before encapsulation onto a test specimen and that the container be open for a finite time. In the beginning this caused no concern, because the data seemed quite reproducible. Gradually, however, it became evident that the few occasions when failure was not encountered with a polar liquid coincided with the opening of a fresh bottle.

The possibility of water adsorption or initial contamination was explored in three ways. Choosing ethanol with known propensity for water adsorption, ten tests were run using a cup soldered to the test specimen so that the notched area was submerged in liquid but the liquid surface was exposed to the air. The measured cycles-to-failure are as follows: 1,096,000; 705,000; 2,165,000; 746,000; 1,298,000; 882,000; 615,000; 1,403,000; 405,000; and 1,133,000. The average of these is 946,000, which is very close to the value obtained with a wetted pad wrapped to exclude air and water vapor, but the spread is about a factor of five, whereas a factor of two is normally encountered.

In a second series of experiments, a powerful dehydration agent, anhydrous CaSO₄, was incorporated into the wrapped pad. To increase its effectiveness, the anhydrous CaSO₄ was ground to fine powder immediately before use. Ethyl alcohol, in the presence of a large quantity of the dehydration agent and wrapped as described, did not produce failure in 9,000,000 cycles, whereas under previous conditions of test failure occurred in 600,000-900,000 cycles.

With the indication that effective dehydration precluded failure in the presence of ethyl alcohol, a more comprehensive series of retesting was conducted. The following were retested, using anhydrous CaSO_4 in powdered form in the wrapped pad: methyl alcohol, butyl alcohol, n-propyl ether, acetic acid, isoamyl alcohol, oleic acid, chlorobenzene, 10% phenol in light mineral oil, benzonitrile, dibutyl mercury, triethyl aluminum in light mineral oil, triethyl boron in light mineral oil, and diphenyl magnesium in heptane. In all instances, cycling continued beyond 7,000,000 cycles without failure. The conclusion seems inescapable that water remains the sole agent for embrittlement in all of these experiments.

A third series of experiments involved n-butyl alcohol solutions in water. Using a fresh bottle of alcohol, it was found that no failures occurred after as many as 10,000,000 cycles of stress. Measured amounts of water were deliberately added. The systematic trend of fatigue life against water content is shown in Figure 7. Equimolar solutions are not significantly less embrittling than pure water. At greater alcohol concentrations the curve rises steeply.

In a fourth series of experiments, the comparative efficacy of water emulsions was explored. Water has substantial solubility in butyl alcohol but negligible solubility in heavy mineral oil. Depending on the water content, butyl alcohol-heavy mineral oil-water mixtures form clear solutions or emulsions. In the emulsions, the dispersed phase is primarily water. An old bottle of butyl alcohol contained enough water to induce failure in about 1,100,000 cycles. Binary mixtures of this alcohol and heavy mineral oil formed clear solutions. With water added to the alcohol, the ternary mixtures formed cloudy emulsions. Fatigue lives for various water-alcohol-oil mixtures, both clear and emulsified, are compared in Figure 8. It is evident that the emulsions behave essentially the same as clear solutions; from this it may be deduced that only soluble water contributes to reduced fatigue life.

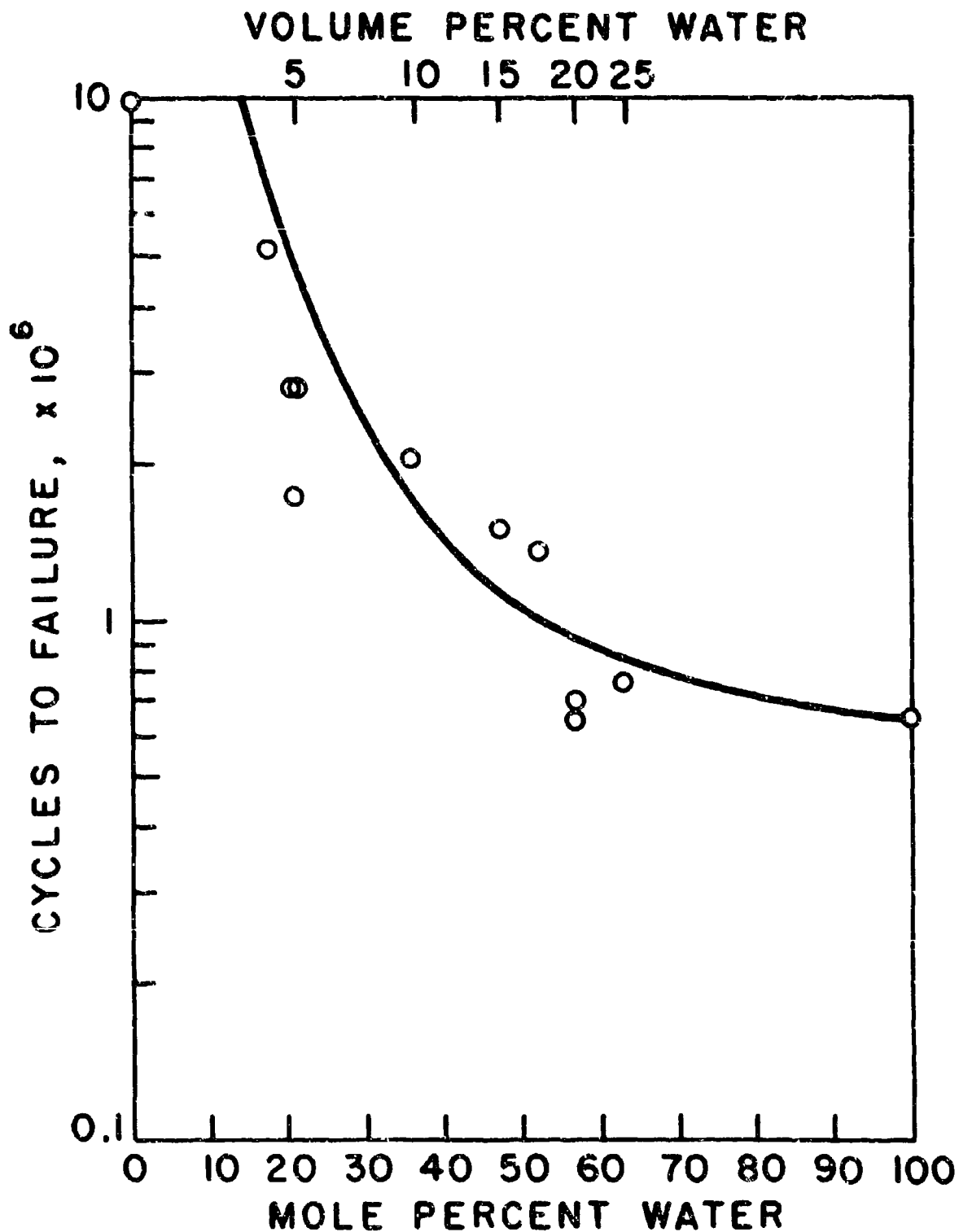


FIG. 7 - FATIGUE LIFE IN THE PRESENCE OF BUTYL ALCOHOL-WATER SOLUTIONS.

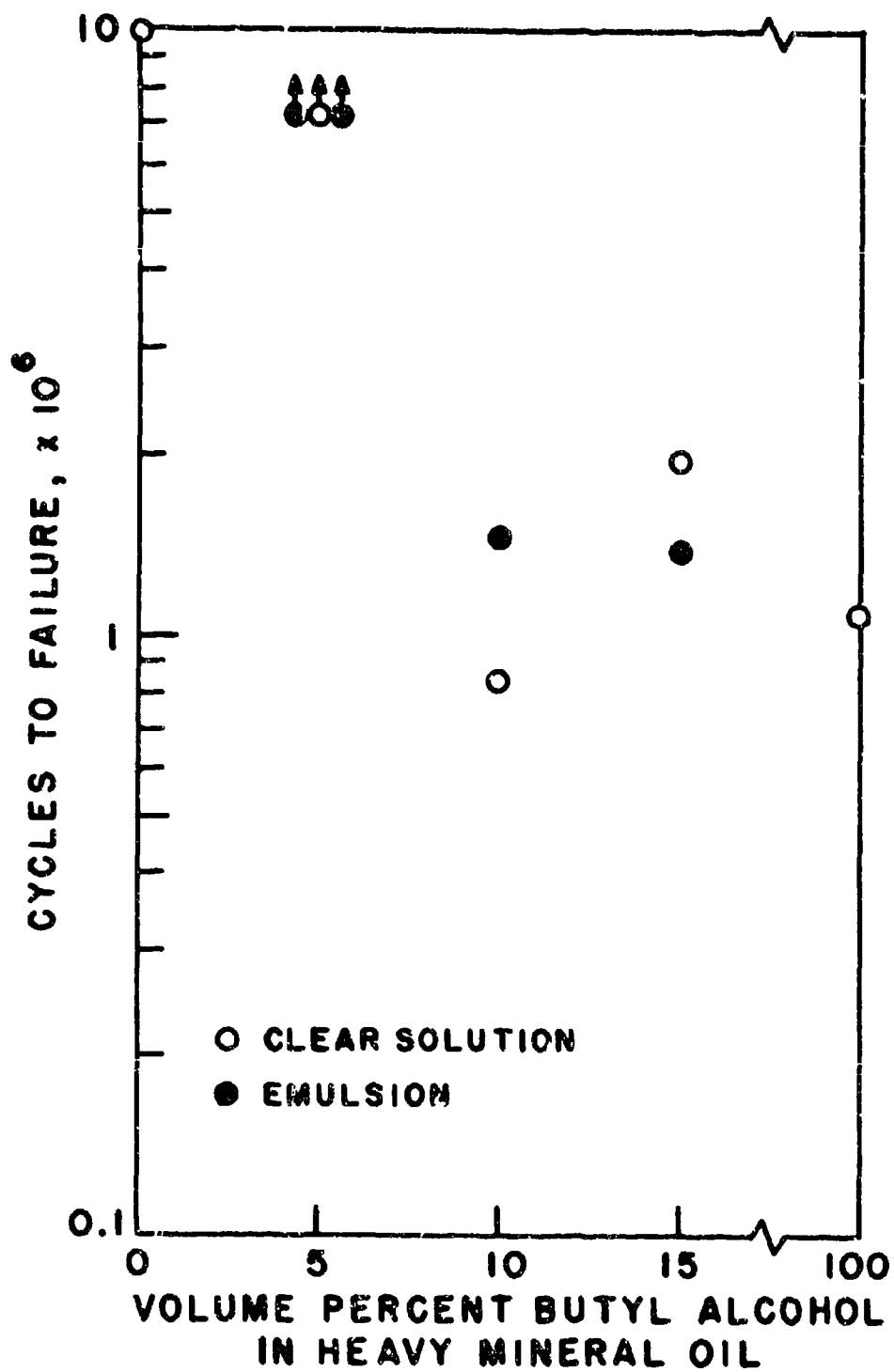


FIG. 8 - FATIGUE LIFE IN THE PRESENCE OF HEAVY MINERAL OIL-BUTYL ALCOHOL-WATER SOLUTIONS AND EMULSIONS

VII. SOME SPECIAL ASPECTS OF WATER EMBRITTLEMENT

Having demonstrated that water adsorption or intrinsic content is the basic source of embrittlement by organic liquids, it would be easy to dismiss the subject as another instance of stress-corrosion cracking, corrosion fatigue, or hydrogen embrittlement--none of which are readily distinguishable under the present circumstances. However, by present concepts of mechanism as applied to high-strength steel, they all have a common character in being the by-product of local electrochemical cell action. This presents something of a dilemma, because electrochemical action requires an electrolyte, and dilute solutions of water in organic liquids are at best very poor conductors. Even the existence of a water emulsion in n-butyl alcohol (heavy mineral oil) solutions does not constrain the mixture to be more active than the ternary water-saturated solution.

Another aspect of electrochemical process control is a sensitivity to ion concentrations. To explore this point, specimens were fatigue tested in the presence of water whose pH had been adjusted by a few drops of either HCl or concentrated NaOH to levels of 1, 4, 7, and 12. In this case, distilled water has a pH of 4, probably because of CO₂ absorption from the air. Specimens were also tested in the presence of water containing 5% NaCl, which is clearly conducive to active corrosion. These results are presented in Figure 9. The trend is of negligible significance and well within the range of variation of one point.

To these results may be added the behavior of large, imposed DC potentials between the specimen and a platinum wire through an electrolyte of distilled water while undergoing cyclic fatigue stressing. These potentials are high enough to promote rapid drift of ions to one or another electrode, depending upon sign. If ion mobility is a significant factor, there should be a significant influence upon fatigue life. The results are as follows:

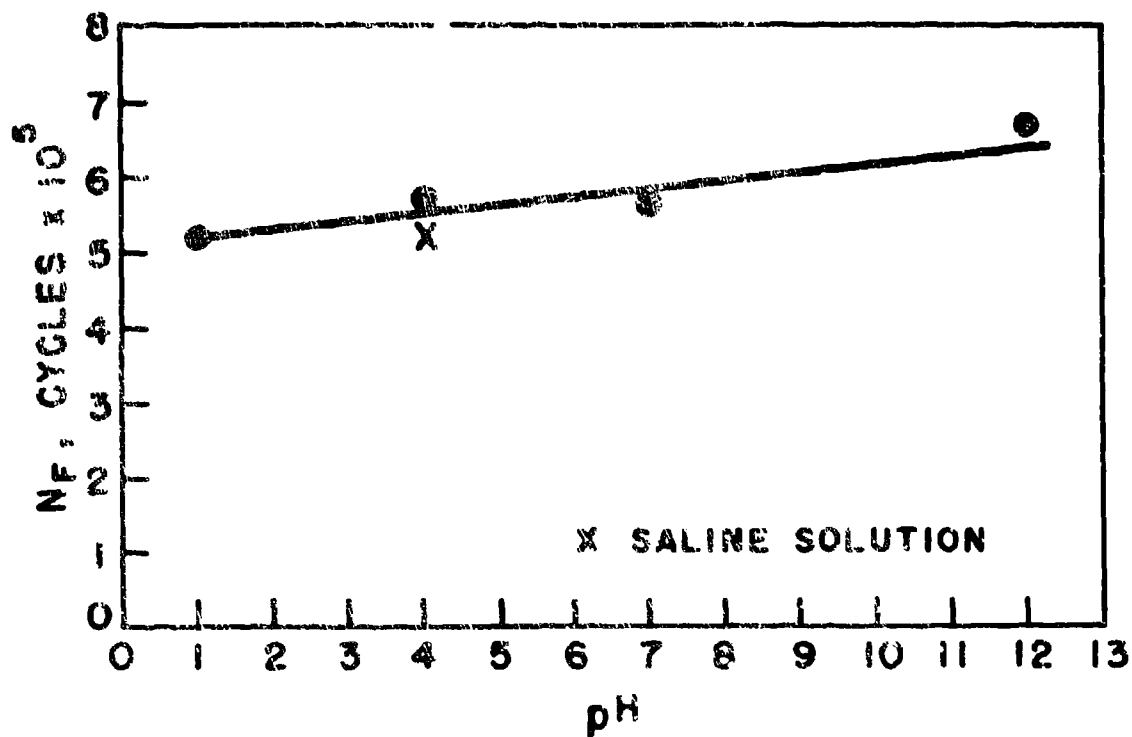


FIG. 9 - INFLUENCE OF THE pH OF WATER ON THE FATIGUE LIMIT OF HIGH-STRENGTH STEEL V-NOTCHED TENSION-TENSION SPECIMEN. (12,500 psi preload, 4370 psi dynamic load.)

<u>Potential</u>	<u>Cycles to Failure</u>
Zero	535,000; 601,000
Specimen negative, 2 v, DC	421,000; 470,000
Specimen positive, 2 v, DC	516,000; 585,000; 912,000

Making the specimen cathodic should have reduced the corrosion activity but enhanced the rate of hydrogen production. The 20% reduction in fatigue strength seems a small effect compared to the potential used. On the other hand, making the specimen anodic should accelerate corrosion but eliminate hydrogen production. This manifestly had no significant effect on fatigue life.

From another viewpoint, a cracking mechanism whose rate is governed by an electrochemical process should be sensitive to the conductivity of the liquid medium. Corrosion currents either causing dissolution of metal or producing hydrogen should be proportionate to the conductivity of the electrolyte; therefore, the ratio of cycles-to-failure in organic liquids containing water to the cycles-to-failure in water should be roughly equal to the ratio of the electrical resistances of these liquids. In the case of butyl alcohol-water solutions (20-50 mol per cent water), the ratio of cycles-to-failure is about 4:1. Using an appropriate conductivity cell with gold foil electrodes and a Wheatstone bridge, the measured comparative resistances of butyl alcohol-water solutions are shown in Figure 10. To take into account the possibility that corrosion of the iron specimen could contribute conductive ions to the solutions, a second series of experiments was run with an iron nail immersed in the solution but isolated from metallic contact with the electrodes. Over a period of about 1 hr, there were continuous drops in conductivity, leveling off to the values shown in Figure 10.

Conservatively, the ratio of comparative resistances of butyl alcohol-water electrolytes causing cracking (20-50 mol per cent water) to water is between 20:1 and 50:1. As mentioned previously, a 5% NaCl solution does not cause failure in less cycles than distilled water. The ratio of butyl alcohol-water solution resistance to saline solution resistance

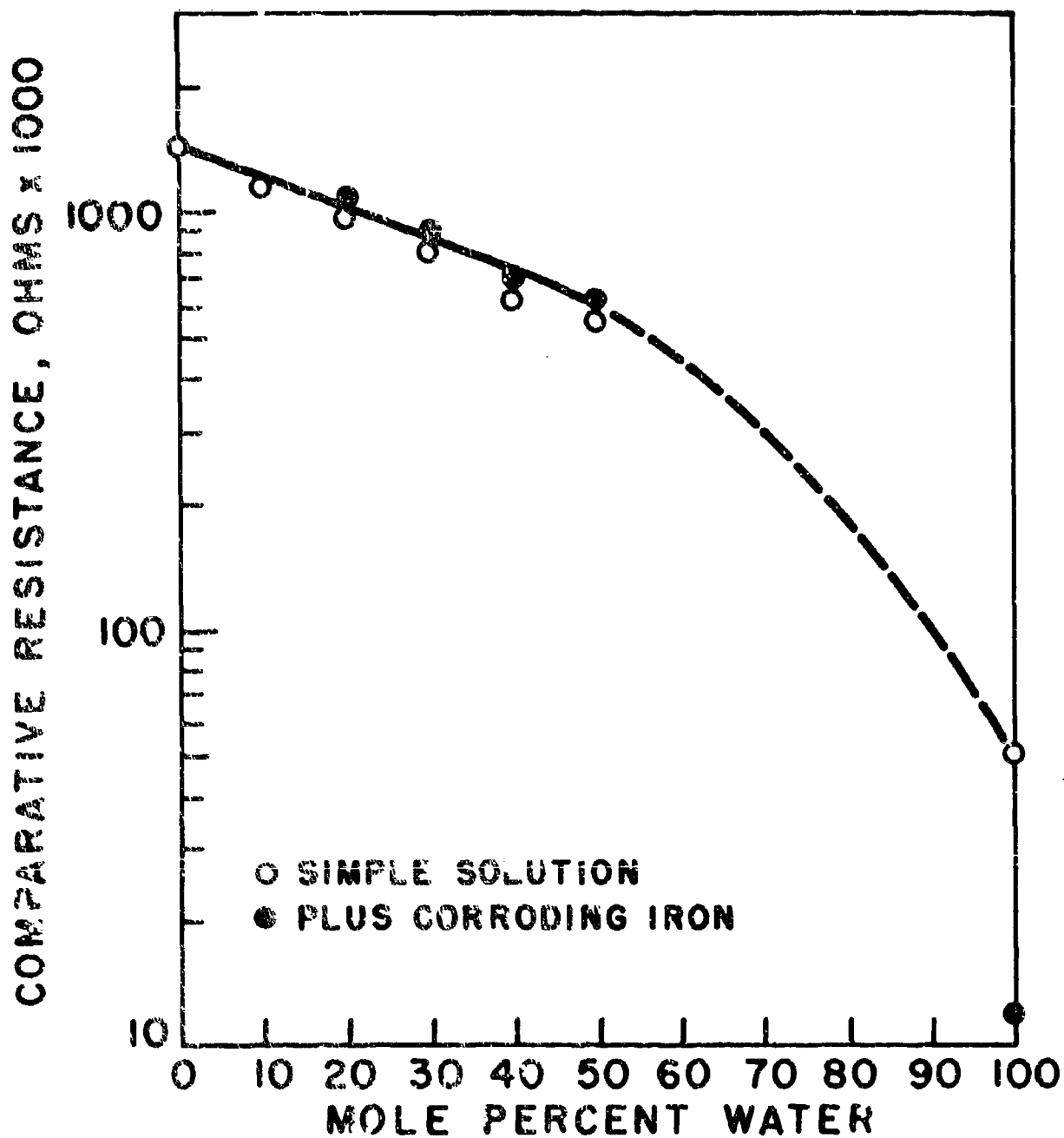


FIG. 10 - COMPARATIVE ELECTRICAL RESISTANCE OF BUTYL ALCOHOL-WATER SOLUTIONS WITH AND WITHOUT IMMERSION OF CORRODING IRON.

becomes about 200,000:1. Clearly, the ratios of electrolyte resistance and cycles to failure are widely disparate.

Since large changes in hydrogen and hydroxyl ion concentration, saline content, ion mobilities, and electrolyte resistance have no appreciable effects on fatigue life, it seems unlikely that electrochemical processes and hydrogen by-product generation are responsible for this form of embrittlement.

Although this study was concerned with embrittlement of steel, a limited number of experiments were performed with identical specimens of the high-strength 2024 aluminum alloy (T4 condition, 47,000 psi yield strength). At 8050 psi static preload and 1210 psi dynamic load, these specimens fail in air at about 4,000,000 cycles. In the presence of distilled water the alloy fails in about 2,650,000 cycles, and in saline solution at about 2,350,000 cycles. Two facts stand out. Distilled water, which is barely aggressive to aluminum, is as potent to embrittlement as the highly corrosive saline solution. Furthermore, the same phenomenon occurs as with steel, although here there is no reason to count on any embrittlement by hydrogen. Methanol, ethanol, n-propyl, n-butyl, and n-amyl alcohols were found to induce measurable reduction in fatigue life in the absence of the dehydration agent.

VIII. SUMMARY AND DISCUSSION

The action of polar organic liquids in reducing the fatigue life of a high-strength steel has been shown to be related to their capacity to adsorb water. The embrittlement encountered is therefore due to the action of the dissolved water. Even small concentrations in solution are capable of substantial reduction in fatigue life. Insoluble water in the form of an emulsion, however, is not active. When proper precautions are taken to remove water from the test system, embrittlement is eliminated.

In considering the origin of the embrittling action of water, there are three reasonable alternatives--stress corrosion, hydrogen, or critical adsorption. It is difficult to make a distinction between these because none are fundamentally well understood. By stress corrosion we mean a highly localized corrosion or dissolution action concentrated at the

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base of a surface imperfection, confined to the root of an advancing crack, and stimulated in rate by the stresses or strains in the crack zone. The process is intrinsically electrochemical in nature, making use of the potential differences between different points in the metal and the ionic conduction character of the liquid medium. If the potentials are sufficiently high, a by-product of electrochemical cell action could be the generation of hydrogen, the adsorption of hydrogen by the ferritic solid, and the consequent embrittlement which is well recognized. The ability of adsorbed atoms or ion complexes on a solid metal surface to reduce fracture strength has been postulated as a mechanism for liquid metal embrittlement and, more recently, as an alternative origin of what is generally termed stress-corrosion cracking.^(12, 13)

The corrosion and hydrogen embrittlement processes are both wedded to the operation of electrochemical oxidation and reduction processes. Several observations indicate that electrochemical processes are not dominant. Polar organic liquids with small amounts of dissolved water are at best very poor electrolytes, yet many of these gave reduced fatigue strengths which were of the same magnitude as distilled water. Water itself produced embrittlement which was insensitive to hydrogen, alkali, and chloride ion concentration. Finally, the implementation of positive cell action of either anodic or cathodic type by the application of potentials introduced no significant changes in the action of water.

By default, therefore, one should give consideration to the action of adsorbed species. Oxygen is certainly strongly interactive with most metals. With diatomic oxygen, as in air, the interaction is so strong that the molecular bonds are broken and a change of state occurs in the form of an oxide which develops as a film, separating the metal substrate from the environment. Continued interaction at low temperatures is therefore self-limiting.

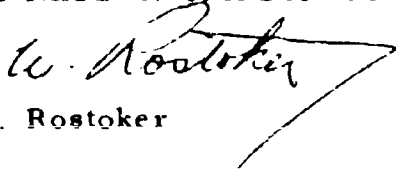
Dimensionally, the water molecule is a large oxygen atom bound rather tightly to its two hydrogen atoms. The geometry of the molecule permits the oxygen atom to nest into the rest positions between

surface iron atoms. From a thermodynamic viewpoint, non-ionized water is only marginally reducible by iron at room temperature so that the process would be slow and physical adsorption could persist for a finite time. This would be sufficient for the conditions of continuously exposed surface, as in an advancing crack. We could reasonably expect, therefore, that adsorption of water molecules could reduce the cohesive strength of the surface atoms of iron. The mobile character of the liquid would permit repeated rupture of atomic bonds as the crack moves into the interior of the solid. Since by this process the oxygen atom is not separated from its host molecule, the inability of other polar liquids with -OH, -O, or =O groups to produce similar effects is related to their inability to reach to the root of a brittle crack, i. e., steric obstruction.

IX. PERSONNEL AND LOGBOOK RECORDS

The work reported is the result of collaboration of the writer with Mr. H. Nichols, Associate Metallurgist. Data are recorded in IITRI Logbook No. 14253.

Respectfully submitted,
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W. Rostoker

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REFERENCES

1. V. I. Likhtman, P. A. Rebinder, and G. V. Karpenko, Effect of Surface-Active Media on the Deformation of Metals, Chemical Publishing Co., Inc., New York, 1960. (English translation; original Russian text published in 1954.)
2. V. I. Likhtman, E. D. Shchukin, and P. A. Rebinder, Fiz.-Khim. Mekhanika Metallov, Akad. Nauk SSSR, Moscow, 1962 (in Russian).
3. P. A. Reginder and V. I. Likhtman, 'Effect of Surface-Active Media on Strains and Rupture in Solids,' Proc. Second International Congress on Surface Activity, Butterworth, London, 1957, pp. 563-580.
4. I. R. Kramer, Trans. AIME, 227, 1003-1010 (1963).
5. E. Andrade and J. Roscoe, Proc. Roy. Soc. (London), 49, 152 (1937).
6. S. Harper and A. Cottrell, Proc. Phys. Soc. (London), B63, 331 (1951).
7. E. S. Machlin, Strengthening Mechanisms in Solids, ASM, Metals Park, Ohio, 1962, pp. 375-404.
8. M. P. Piggott, Acta Met., 12, 803-805 (1964).
9. E. A. Steigerwald, Proc. ASTM, 60, 750-760 (1960).
10. G. L. Hanna, A. R. Troiano, and E. A. Steigerwald, Trans. ASM, 57, 658-671 (1964).
11. W. Rostoker (discussion of Ref. 10), Trans. ASM, 57, 1093-1094 (1964).
12. E. G. Coleman, D. Weinstein, and W. Rostoker, Acta Met., 9, 491-496 (1961).
13. A. R. C. Westwood, E. N. Pugh, and D. L. Goldheim, Phil. Mag., 10, 345 (1964).