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(Quarterly Report)

EMBRITTLEMENT OF METALS BY ORGANIC LIQUIDS

Commanding Officer
Frankford Arsenal
Philadelphia 37, Pennsylvania

Contract No. DA-11-ORD-022-3108

IIT RESEARCH INSTITUTE
Technology Center
Chicago, Illinois 60616

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March 1, 1964 - May 31, 1964

for

Commanding Officer
Frankford Arsenal
Philadelphia 37, Pennsylvania

Attention: Mr. J. M. McCaughey
Pitman-Dunn Laboratories

June 1, 1964

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ABSTRACT

By a test involving a combination of static and dynamic loading, the carboxylic acids are shown to be embrittling to high-strength steel to a degree proportionate to the carbon chain length. It is shown that nonpolar liquids are in general not embrittling but that the magnitude of the dipole moment is not a measure of embrittling propensity. ~~Present~~ evidence indicates that under appropriate conditions, a -Cl group is potentially as embrittling as an -OH or a -O- group.

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EMBRITTLEMENT OF METALS BY ORGANIC LIQUIDS

I. INTRODUCTION

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

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 increasing load, 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.

A special test has been developed to provide a broad scale upon which to measure embrittlement. This involves the use of sheet steel heat-treated to 44 Rc (about 200,000 psi yield strength) which has been deeply notched from both edges. The specimen is stressed by a combination of static and dynamic loads--12,500 psi static plus 4370 psi dynamic. This combination represents a condition below the endurance limit where this steel in this specimen geometry will sustain the combined static and cyclic loading indefinitely when surrounded only by normal air environment.

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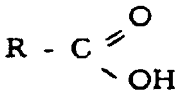
Embrittlement is induced by immersing the notched region in a candidate liquid using various pad or cup arrangements for containment. Under such circumstances failures can be made to occur in as little as 500,000 cycles. Testing is usually stopped for practical reasons if failure has not occurred in six to seven million cycles. If at that time the reservoir still contains liquid, this liquid species is adjudged to be nonembrittling. This caution is necessary because many of the candidates are volatile and in any given test run the sealing system may have been imperfect.

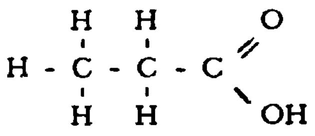
In previous reports under this contract it has been shown that polar organic liquids possessing -OH, -O-, and =O groups have a propensity for embrittlement of both high-strength steel and aluminum. This propensity is most marked in simple long-chain molecule types; of these, the shorter the chain, the greater the embrittling tendency. In the present work, this area of study has been expanded to the carboxylic acid group, to liquids possessing chlorine groups, and to organometallic liquids.

II. EMBRITTLEMENT OF CARBOXYLIC ACIDS

The carboxylic acids are simple long-chain molecules having at one end both an =O and a -OH group. Their general formula is:



and one of its members, propionic acid, has the formula:



or CH_3CH_2COOH

This group is important chiefly because many of the prior published works on surface active agents have made use of members of this family. With chain lengths up to caprylic acid, the pure species is itself a liquid. Above this chain length (i.e., lauric, myristic, palmitic, and stearic acids) for tests at room temperature the solid acids must be dissolved in a solvent which is preferably nonpolar hydrocarbon or nonpolar dioxane. The solubility goes down sharply with increasing molecular weight of the acid.

The trend of embrittlement from formic to lauric acid (50% solution in dioxane) is shown in Figure 1. The decrease of embrittlement with increasing carbon chain length follows the pattern set by alcohols, ethers, glycols, and aldehydes. Palmitic acid (10% in light mineral oil) and stearic acid (6% in dioxane) showed no signs of producing failure after 10,000,000 and 6,000,000 cycles, respectively. Myristic acid, which lies in molecular weight between lauric and palmitic acid, gave erratic results. Since it is a solid at room temperature, a 10% solution in light mineral oil was used--this being the saturation limit. At this concentration, the solution has a gelatinous character. Figure 2 shows that the erratic behavior derives from a very large temperature dependence at about room ambient. Whether the solubility or the viscosity of the solution is the property reflected in the temperature dependence cannot be decided at this point, but the matter demands further study.

It will be noted that at 66°C, a myristic acid solution has as great embrittling influence as water at room temperature. This suggests that the dependence of embrittling propensity on carbon chain length is not an irrevocable condition which, as will be remarked upon later, seems reasonable in the light of the fact that dipole moments are not dependent on carbon chain length.

By way of elaboration, two acids with multiple polar groups were tested. Acetic anhydride, which has the formula $(CH_3CO)_2O$, possesses an -O- group and two =O groups. With an average failure at about 1,300,000 cycles it has approximately the same embrittling potential as the simple four-carbon carboxylic acid (butyric acid).

Oxalic acid (saturated solution in n-heptyl alcohol) with the formula

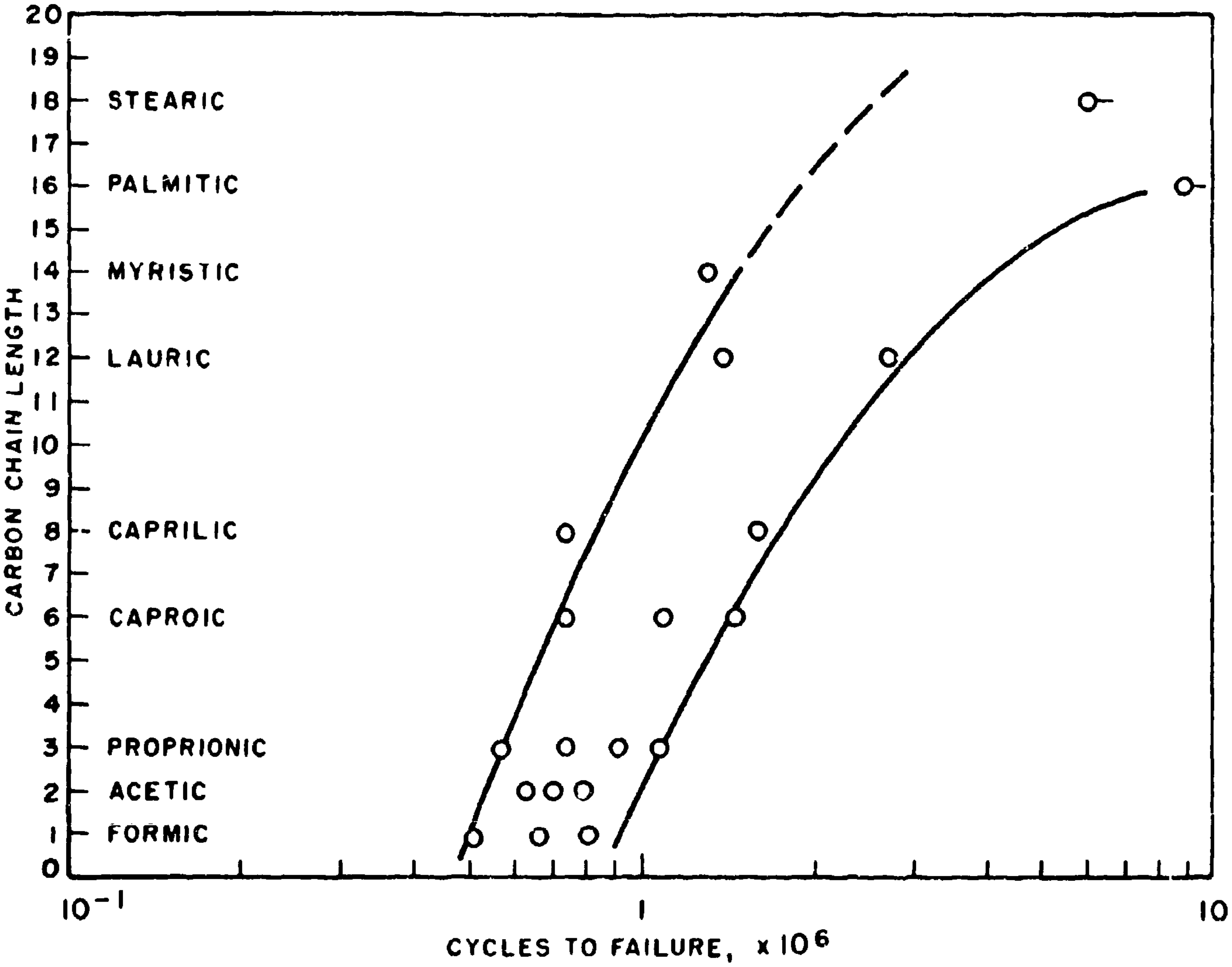


FIG. 1 - FATIGUE LIMIT OF HIGH-STRENGTH STEEL IN CARBOXYLIC ACIDS (V-notched tension-tension specimens, 12,500 psi preload, 4370 psi dynamic load).

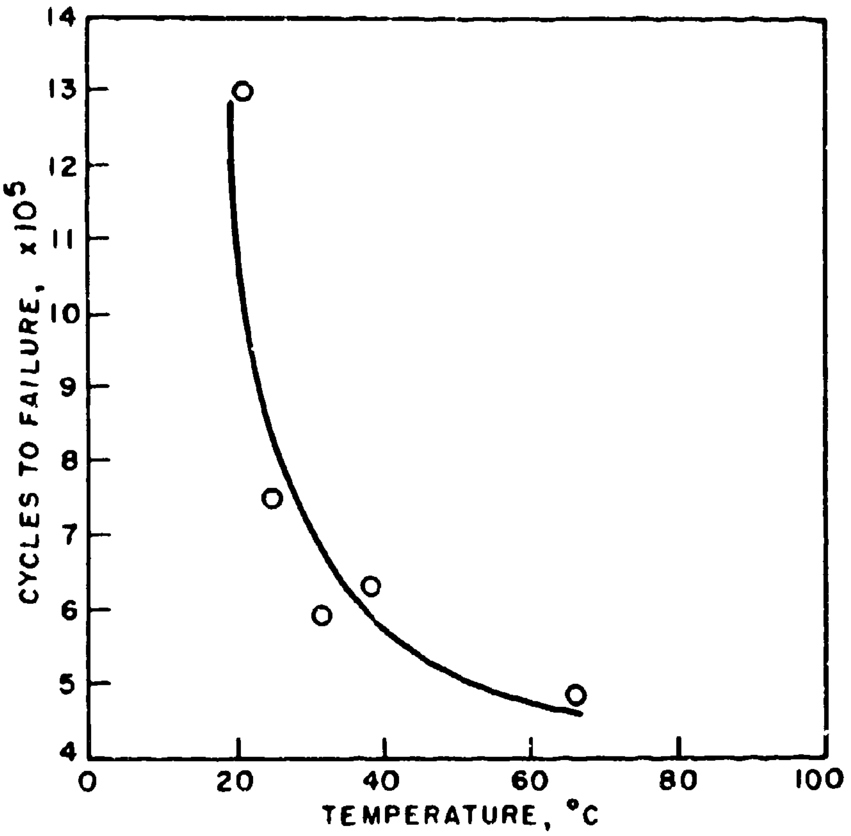
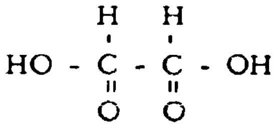


FIG. 2 - TEMPERATURE DEPENDENCE OF FATIGUE LIMIT IN MYRISTIC ACID (10% solution in light mineral oil).



$$\mathrm{HO - \overset{H}{\underset{O}{C}} - \overset{H}{\underset{O}{C}} - OH}$$

has two -OH groups and two =O groups. This two-carbon chain acid is more effective than acetic acid, showing failure at 595, 000 cycles. In this respect it shows a parallel behavior with the glycols as compared to the alcohols of equivalent carbon chain length.

III. EMBRITTLEMENT AND DIPOLE MOMENT

The dipole moment is a measure of the ability of a molecule to interact with external electrostatic fields. This in turn has to do with the symmetry of disposition of electron fields within the molecules themselves. Large dipole moments reflect highly asymmetric distribution of electron charges within the molecule. The existence of a dipole moment or polar character permits the interaction of a polar molecule with the short-range electronic charge field at the surface of a metal. This interaction takes the form of adsorption with bonds of finite strength between the surface atoms of the solid and the adsorbed monolayer. It is likely that the strength of this bond is the dominant factor in the magnitude of embrittlement experienced.

Four nonpolar (zero dipole moment) liquids have been tested for embrittlement, and in each case none was found. These four liquids are:

light mineral oil
dioxane
carbon tetrachloride
tetra-n-butyl tin

We may therefore reasonably conclude that a liquid must be polar to produce accelerated failure.

We must next concern ourselves with the question of the relation between the magnitude of dipole moment and associated embrittlement. On this point it is worthwhile to compare data for the alcohols, glycols, ethers, aldehydes, and carboxylic acids. This is done in Table I. It is to be noted,

TABLE I

COMPARISON OF DIPOLE MOMENTS AND FAILURE MEASUREMENTS

Group	Dipole Moment, esu x 10^{-18}	Failure, cycles
Alcohols	1.7	700,000-4,000,000
Glycols	2.28	800,000
Ethers	1.15-1.30	800,000-1,000,000
Aldehydes	2.72-3.67	900,000-1,500,000
Carboxylic acids	1.5-1.75	600,000-6,000,000+
Water	1.85	400,000-600,000

TABLE II

DIPOLE MOMENTS AND FAILURE MEASUREMENTS OF CERTAIN PHENOLS

Name	Polar Group	Dipole Moment, esu x 10^{-18}	Failure, cycles
Nitrobenzene	$-NO_2$	-3.9	720,000; 550,000
Benzonitrile	-CN	-3.9	781,000; 441,000
Benzaldehyde	-CHO	-2.8	1,245,000; 1,820,000
Carbolic acid*	-OH	-1.7	626,000; 554,000
Chlorobenzene	-Cl	-1.5	741,000; 796,000
Benzoic acid*	-COOH	-1.25	7,000,000 DNF
Benzene	-H	0	7,000,000 DNF
Aniline	$-NH_2$	+1.5	7,700,000 DNF

*10% solution in light mineral oil

DNF - did not fail.

as remarked earlier, that the dipole moment does not depend on carbon chain length. The general conclusion is that although the dipole moment can vary by as much as a factor of 2, this has little influence on severity of embrittlement.

A wider scale of dipole moments is provided by a series of phenol derivatives. These are presently being studied and results are incomplete at the time of writing. Those which are available are summarized in Table II. It is clear again that no simple relation exists between magnitude of dipole moment and severity of embrittlement although a low dipole moment or zero value has no embrittling character.

Another case in point is demonstrated by acetyl chloride, CH_3COCl, which has two polar groups, =O and -Cl. The dipole moment of this molecule is 2.72×10^{-18} esu, which is much larger than for water. Yet no failures were encountered in 7,000,000 cycles. There is a complicating factor here in that this liquid is distinctly corrosive to steel in contrast to all of the other organic liquids tested thus far. It seem reasonable that corrosive action will continuously strip off adsorbed films. There is a general observation in stress-corrosion cracking to the effect that such cracking is unlikely in highly corrosive media.

In attempting to explain the relative ineffectiveness of liquids possessing large dipole moments we must first realize that the dipole moment itself is an integrated measure of charge asymmetry whereas polar adsorption is the interaction of metal surface atoms with only one atom of the molecule. Thus in the case of nitrobenzene with twice the dipole moment of water, the large value derives from the size of the attached group, i.e., $-NO_2$. But of this group only one oxygen or one nitrogen atom can interact with iron. On this basis, nitrobenzene can have no more embrittling action than water if only the one oxygen atom acts in the cracking process.

From this viewpoint, sufficient charge asymmetry is necessary to ensure maximum action by the polar atom, but the maximum magnitude of embrittlement depends on the atomic identity which interacts with the iron lattice. In this respect all of the organic species examined so far should be equally effective under optimum conditions because they all involve the interaction of iron with oxygen.

IV. EMBRITTLEMENT BY POLAR LIQUIDS CONTAINING CHLORINE

Carbon tetrachloride, CCl_4, is nonpolar, i.e., zero dipole moment because the carbon atom is located in the center of a tetrahedron made up by the chlorine atoms. CCl_4 did not produce failure in several attempts with cycling maintained to past 7,000,000.

Propyl chloride (1-chloropropane) has the formula C_3H_7Cl. It is a straight chain analogue of propyl alcohol and therefore offers the opportunity of comparing the strength of interaction against iron of a -Cl group versus an -OH group. The dipole moment of methyl chloride is 1.87×10^{-18} esu, which may be taken as typical also of propyl chloride. In two tests, the steel specimens failed in 496,000 and 476,000 cycles, respectively. On this evidence, propyl chloride is more effective than propyl alcohol.

Another basis for comparison is given by carbolic acid, C_6H_5OH, and chlorobenzene C_6H_5Cl in Table II. Here, the -OH group appears somewhat more effective than the -Cl group. Obviously a third but not dominant factor (such as viscosity,perhaps) is interfering, but a conclusion can be drawn that the -Cl and -OH groups are about equally effective in generating embrittlement.

A number of more complex organic liquids possessing chlorine atoms have yielded results summarized in Table III. These results provide another instance to show that the magnitude of the dipole moment cannot be taken as a probable measure of embrittling propensity.

V. EMBRITTLEMENT BY ORGANOMETALLIC LIQUIDS

A number of organometallic liquids of simple molecular formulae have been tested. A larger number are presently being acquired. Unfortunately, the selection of available species is quite limited, and many are both volatile and toxic. Table IV summarizes some test results.

TABLE III

FATIGUE FAILURE OF STEEL IN THE PRESENCE OF SOME ORGANIC LIQUIDS CONTAINING CHLORINE

Liquid	Dipole Moment, esu x 10^{-18}	Failure, cycles
Chloroform, $CHCl_3$	1.02	830,000 avg
Methylene chloride, CH_2Cl_2	1.54	5,000,000 DNF

DNF - did not fail

TABLE IV

FATIGUE FAILURE OF STEEL IN THE PRESENCE OF SOME ORGANOMETALLIC LIQUIDS

Liquid	Failure, cycles
Di-ethyl mercury, $(C_2H_5)_2$ Hg	554,000
Di-butyl mercury, $(C_4H_9)_2Hg$	704,000; 596,000*
Tetra-n-butyl tin, $(C_4H_9)_4Sn$	7,000,000 DNF
Butyl lithium, C_4H_9Li (15% in hexane)	2,750,000 DNF

*50% in heavy mineral oil.

DNF - did not fail.

The tetra-n-butyl tin molecule is a symmetrical arrangement of butyl carbon chains about the Sn atom and is nonpolar. It is not surprising, therefore, that no embrittlement is encountered. The effectiveness of di-ethyl and di-butyl mercury depends on the angle included by the carbon chains which seems to be unknown. Probably a better measure of the effectiveness of a -Hg group would be gained from an n-butyl mercury, but such does not seem to be available.

VI. PERSONNEL AND LOGBOOKS

The work reported here was done by Mr. H. Nichols, associate metallurgist, in collaboration with the author. Data are recorded in IITRI Logbooks No. 13536 and 14245.

Respectfully submitted,
IIT RESEARCH INSTITUTE

W. Rostoker

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Tech Rev - DJM

WR/pk