CORROSION INHIBITING ENGINE OILS
PART II

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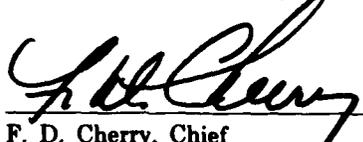
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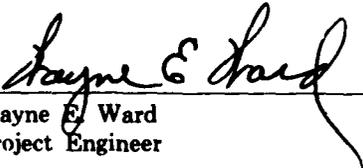
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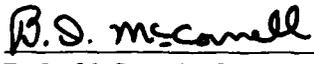
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Corrosion inhibitor analysis	Corrosion inhibiting lubricant

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In anticipation of corrosion problems during long term storage of F-107 gas turbine engines in air-launched cruise missiles, a program was undertaken to develop a corrosion inhibiting engine oil with performance characteristics at least equal to those specified by MIL-L-7808H. Program objectives included development and validation of an accelerated corrosion test procedure, evaluation of representative samples of various chemical classes of potential corrosion inhibiting compounds, and complete characterization of the most promising formulation. An accelerated Corrosion Rate Evaluation Procedure was developed and validated through correlation with the humidity cabinet corrosion test described in the MIL-C-8188C specification. A total of 102 potential corrosion

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inhibitors were evaluated in single additive and two-additive combinations in qualified MIL-L-7808H lubricants. Several very promising formulations were developed and evaluated, leading to the development of a formulation which provides corrosion protection superior to that of MIL-C-8188C and conforms to all MIL-L-7808H requirements specified in the Statement of Work, except that of total acid number.

LMJ 330

FOREWORD

This report describes the technical effort conducted by the Advanced Fuels & Lubricants Group of United Technologies Corporation, Pratt & Whitney Aircraft, Government Products Division under Contract F33615-79-C-5089, Project ILIR, Task 01, Work Unit 25, entitled "Corrosion Inhibiting Engine Oils." The program was administered under the direction of Dr. Wayne E. Ward of the Fluids, Lubricants, and Elastomers Branch of the Materials Laboratory, Air Force Wright Aeronautical Laboratories, Wright-Patterson Air Force Base, Ohio.

The technical effort disclosed herein was performed during the period 2 December 1980 through 1 September 1982 under the direction of Pratt & Whitney Aircraft Program Managers Paul A. Warner and Grayson C. Brown. The report was released by the authors in October 1982.

This is a Final Report concerned with the development and laboratory analysis of corrosion inhibiting engine oil formulations for use in the storage and operation of Williams Research Company's F107 gas turbine engine.

The authors wish to thank Mr. G. A. Beane IV of AFWAL/POSL, Dr. A. J. Gustavsen of King Industries, and Mr. W. C. Gergel of the Lubrizol Corporation for their technical assistance in this program. In addition, the authors wish to express their appreciation for the cooperation of the following companies which supplied candidate corrosion inhibitors for this program:

Alox Corporation
PO Box 517
Niagara Falls, N.Y. 14302

Mooney Chemicals, Inc.
2301 Scranton Road
Cleveland, OH 44113

Bray Oil Company
1925 N. Marianna Ave.
Los Angeles, CA 90032

Nalco Chemical Company
Petroleum Chemicals Division
Sugarland, TX 77478

Edwin Cooper, Inc.
Subsidiary of Ethyl Corp.
1525 S. Broadway
St. Louis, MO 63104

Pfaltz & Bauer, Inc.
375 Fairfield Avenue
Stamford, CT 06902

E. I. DuPont & Co., Inc.
Petroleum Chemicals Division
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Emery Industries, Inc.
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The Lubrizol Corporation
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King Industries, Inc.
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Universal Oil Products Company
UOP Process Division
Des Plaines, IL 60016

Minnesota Mining & Mfg. Co.
3M Center
St. Paul, MN 55101

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Norwalk, CT 06855

TABLE OF CONTENTS

LIST OF ILLUSTRATIONS

LIST OF ILLUSTRATIONS (Continued)

LIST OF TABLES

viii

LIST OF TABLES (Continued)

LIST OF ABBREVIATIONS

AFWAL	Air Force Wright Aeronautical Laboratories
AI	Active ingredient
AISI	American Iron and Steel Institute
ALCM	Air launched cruise missile
AMS	Aerospace Material Specification
ASTM	American Society of Testing and Materials
CCI	Candidate corrosion inhibitors
cm	Centimeters
COS	Corrosion and oxidation stability
CREP	Corrosion Rate Evaluation Procedure
cSt	Centistokes
DOS	Dioctylsebacate
Fed Std.	Federal Standard
FTM	Federal test method
g	Gram
HCCT	Humidity cabinet corrosion test
hr	Hours
in.	Inches
kPa	Kilopascals
MAG	Magnification
max	Maximum
mg	Milligrams
mg KOH/g	Milligrams of potassium hydroxide per gram
min	Minimum
μin.	Microinches
ml	Milliliters
MLBT	Fluids, Lubricants and Elastomers Branch, Materials Laboratory, AFWAL
mm	Millimeters
NBS	National Bureau of Standards
OD	Outside diameter
PAO	Polyalphaolefin
pH	Hydrogen ion concentration
POSL	Lubrication Branch, Aero Propulsion Laboratory, AFWAL
psi	Pounds per square inch
P&WA/GPD	Pratt & Whitney Aircraft, Government Products Division
QPL	Qualified products list
SCCM	Standard cubic centimeters per minute
sec	Seconds
SEM	Scanning electron microscope
SSP	Sequential sampling plan
Sigma (σ)	Standard deviation
ꚋ	Standard taper
TAN	Total acid number
⊕	Trademark
wt %	Percent by weight
WPAFB	Wright-Patterson Air Force Base
$\bar{x}$	Mean

SUMMARY

The Fluids, Lubricants and Elastomers Branch of the Air Force Wright Aeronautical Laboratories established the requirements for a corrosion inhibiting MIL-L-7808H type gas turbine engine oil for use in the storage and operation of gas turbine engines for air launched cruise missiles (ALCM). The new oil formulation is to provide corrosion protection to gears, bearings and other engine components during periods of static storage of the ALCM in uncontrolled environments, with no exercising of the engine to re-establish a protective oil film. In addition, this oil formulation must be capable of performing as a functional lubricating oil and must not impose a sacrifice in the operating performance of Williams Research Company's F-107 gas turbine engine.

This program was directed toward the development and evaluation of candidate corrosion inhibiting oil formulations to provide the necessary corrosion protection and operational characteristics to permit the uncompromised operation of the F-107 gas turbine engine. A detailed description of the first fifteen months of technical effort was provided in an Interim Report dated August 1981 (Reference 1). During the first phase of the program, several approaches were evaluated as accelerated methods for determining the relative corrosion inhibiting properties of candidate corrosion inhibiting gas turbine engine oils. The most promising method, the Corrosion Rate Evaluation Procedure (CREP), was developed to provide an accelerated means of determining the gravimetric corrosion rate of AISI-1010 steel coupons with thin film protection of corrosion inhibiting oil formulations.

The second phase of the program was directed toward development and modification of the CREP in an effort to improve the repeatability of the test, and the subsequent validation of the modified CREP through correlation with the humidity cabinet corrosion test (HCCT) described in the MIL-C-8188C specification. This was accomplished through evaluations of 22 oil formulations with both the CREP and the HCCT. After validation of the CREP as a meaningful screening test, a number of single additive and two-additive formulations were evaluated to determine their corrosion inhibiting capabilities, relative to MIL-C-8188C oil.

The most promising candidate corrosion inhibiting engine oil formulations were subsequently evaluated with physical and chemical property tests to determine their conformance to the MIL-L-7808H specification requirements. The more promising formulations were then evaluated with the corrosion and oxidation stability, oil deposition and elastomer compatibility tests described in the MIL-L-7808H specification. The most promising formulation was selected on the basis of the data generated in these tests and was subsequently evaluated in the bearing deposition test as required by the MIL-L-7808H specification. This final formulation provided corrosion protection superior to MIL-C-8188C and conformed to all MIL-L-7808H requirements specified in the Statement of Work, except that of total acid number.

SECTION I

INTRODUCTION

Gas turbine engine lubricants must provide friction, wear and surface damage control at the surfaces of engine components such as gears and bearings. The lubricant must also remove heat from engine components and protect the engine from corrosion in the operating state and during interim periods between engine operations. In the case of the Air Force air launched cruise missiles, storage intervals of up to 30 months are anticipated. These are static, uncontrolled storage periods, with no exercising of the engine to maintain or re-establish a protective oil film.

Williams Research Company's F-107 gas turbine engine has been designed to power the air launched cruise missile. The F-107 turbine engine has been designed to operate with a MIL-L-7808H type synthetic lubricant. A previously developed, corrosion inhibiting version of MIL-L-7808 type engine oil, specified by MIL-C-8188C, has been found to be limited in both long term corrosion protection and lubrication performance characteristics. The MIL-C-8188C, as currently formulated, does not meet the static foam test requirement specified by MIL-L-7808H, and is not capable of withstanding the thermal and oxidative stresses specified by MIL-L-7808H corrosion/oxidation stability and oil deposition tests.

The objective of this investigation was the development of a corrosion inhibiting oil formulation which provides corrosion protection superior to that of MIL-C-8188C while *maintaining conformance* to the MIL-L-7808H specification requirements. Table 1 lists the target values for physical and chemical properties of the corrosion inhibiting oil formulation, along with the relevant test procedures.

A detailed description of the first fifteen months of technical effort was provided in an Interim Report dated August 1981 (Reference 1). During that phase of the program, several approaches were evaluated as accelerated methods for determining the relative corrosion protection afforded by candidate corrosion inhibiting gas turbine engine oils. The most promising method, the Corrosion Rate Evaluation Procedure (CREP), was subsequently employed in evaluations of 67 candidate corrosion inhibitors at various concentrations in a qualified MIL-L-7808H gas turbine engine oil having the Qualified Products List (QPL) designation 15F-1. Predicated on the results of these evaluations, 26 of the candidate corrosion inhibitors were found to be at least as effective as MIL-C-8188C in the environment of the CREP. Metal salts of alkylated benzene sulfonates were found to be effective corrosion inhibitors, as 14 of the 26 more promising inhibitors were sulfonates. In like manner, alkylated dibasic acids and their derivatives were found to be very tenacious inhibitors in this environment.

Preliminary evaluations were conducted on the 13 most promising inhibitors at a 2.0 percent by weight (wt %) active ingredient (AI) concentration in MIL-L-7808H, QPL 15F-1, to determine their effect on the physical and chemical properties of the matrix oil. All of the sulfonates were found to increase the foaming propensity of the matrix oil. The alkylated organic acids, in spite of their excellent corrosion inhibiting characteristics, increased the total acid number of the oil/inhibitor formulation to 4 to 7 milligrams potassium hydroxide per gram of oil (mg KOH/g).

The second phase of this program was directed toward the development and validation of the CREP and subsequent employment of the modified procedure in the development of several potential candidate corrosion inhibiting MIL-L-7808H lubricating oils.

1

TABLE 1.
TARGET PROPERTIES FOR CORROSION INHIBITING
OIL FORMULATIONS

Physical Property	MIL-L-7808H Requirements	Test Method ASTM	Test Method Fed Std 791
Kinematic viscosity, cSt			
a. 98.9°C (210°F)	3.0 min	D445	
b. −53.9°C (−65°F)		D2532	
@ 35 minutes	17,000 max		
3 hr	17,000 max		
72 hr	17,000 max		
Flash point, °C (°F)	204 (400) min	D92	
Neutralization number (TAN)	0.30 max	D664	
Foaming characteristics (static)			3213
a. Foam volume, ml	100 max		
b. Foam collapse time, sec	60 max		
Evaporation loss @ 204°C (400°F), %	15 max*	D972	
Corrosion and oxidation stability			5307.1
@ 200°C (392°F) for 48 hr			
a. Change in viscosity, %	−5 to 25 max	D445	
b. Change in TAN, mg KOH/g	4.0 max	D664	
c. Metal specimen weight change, mg/cm^2			
Al	±0.2		
Ag	±0.2		
Bz	±0.4		
Fe	±0.2		
M-50	±0.2		
Mg	±0.4		
Ti	±0.2		
Oil deposit rating	1.5 max		5003.1
Bearing deposition			
a. Overall deposit demerit rating	60 max		
b. Change in viscosity, %	25 max	D445	
c. Change in TAN, mg KOH/g	2.5 max	D664	
d. Filter deposits, g	2.0 max		
e. Oil consumption, ml	1440 max		

*This is a Statement of Work (SOW) requirement. The MIL-L-7808H specification requirement is 30% maximum.

In order to accomplish all the objectives, the entire program was divided into six technical tasks, as noted below:

- Literature Search and Custom Synthesis
- Development and Validation of an of Accelerated Corrosion Test Procedure
- Formulation and Evaluation of Candidate Corrosion Inhibiting Engine Oils
- Corrosion and Oxidation Stability Evaluations
- Elastomeric Compatibility Evaluations
- Bearing Deposition Test.

Each of these tasks was proposed as a logical sequence directed toward the development of an improved corrosion inhibiting MIL-L-7808H type engine oil. The technical effort conducted under these tasks is discussed in detail in the body of this report.

SECTION II

LITERATURE AND INDUSTRY SEARCHES

A comprehensive literature search was conducted to evaluate the state-of-the-art in corrosion inhibitors for synthetic lubricants. Several sources of information were used to perform the literature search, including a thorough search of DIALOG® (Lockheed Information Systems), Corrosion Abstracts, and the Defense Documentation Center of the Defense Logistics Agency. The literature search was periodically updated throughout the program. Abstracts of available documents were reviewed to select references relevant to the program. A summary of the reference sources used was provided in the Interim Report (Reference 2).

In addition to the review of technical literature, a major effort was directed toward the acquisition of representative samples of commercially available corrosion inhibitors. Candidate corrosion inhibitors for this application were selected to provide corrosion protection to engine components through a proposed mechanism involving adsorption of molecules with polar groups attached to oleophilic hydrocarbon tails that form a tightly packed, highly oriented, hydrophobic film on the metal surface. The proposed molecular film, in conjunction with oil molecules held on the metal surface by the oleophilic tails of the inhibitor molecules, provides a barrier layer to oxygen and water molecules, thereby inhibiting the corrosion of ferrous engine components (References 3, 4, 5, 6).

Several monovalent and divalent metal salts of sulfonic acids were obtained for this investigation predicated on their proven effectiveness (References 3 through 10). In addition, representative samples of several other classes of polar chemical compounds were obtained, including organic acids, esters, anhydrides, amines, amides, alcohols, phenols, oxygenated hydrocarbons and imidazoline compounds. As the program progressed and specific needs were identified, the industry search was updated periodically to obtain variations of some of the more promising corrosion inhibitors. A total of 102 candidate corrosion inhibitors were obtained during this investigation. These included 11 corrosion inhibitors synthesized by Bray Oil Company of El Monte, California as a subcontract to P&WA/GPD. Bray Oil Co. submitted a Final Report which describes in detail the technical efforts conducted in their investigation (Reference 7). Additional corrosion inhibitors were supplied by the AFWAL/MLBT Program Manager for evaluation in the P&WA developed Corrosion Rate Evaluation Procedure.

All corrosion inhibiting additives are denoted by laboratory identification numbers in this report. Table 2 provides a list of the corrosion inhibitors grouped by chemical classes, along with a general description of the active ingredients comprising each inhibitor. For ease in cross-referring, a complete list of the corrosion inhibitors, in numerical order by laboratory identification number, is provided in Appendix A. The majority of the corrosion inhibitors were supplied in a diluent to accommodate handling and accelerate dissolution in the matrix oil. Appendix A provides the concentration of the active ingredients in the corrosion inhibiting additives as received from suppliers.

TABLE 2.
LIST OF GENERAL DESCRIPTIONS OF THE ACTIVE INGREDIENTS
OF CANDIDATE CORROSION INHIBITORS

Inhibitor Number	Active Ingredient Description
Sulfonates	
PWL 80-1	Mixture of calcium sulfonate and polyglycol
PWL 80-2	Calcium sulfonate from mineral oil
PWL 80-3	Mixture of calcium sulfonate and calcium carbonate
PWL 80-4	Slightly basic calcium sulfonate
PWL 80-5	Morpholine sulfonate plus dialkylbenzene sulfonate
PWL 80-6	Zinc sulfonate from alkylated (C_{30}) benzene
PWL 80-7	Calcium sulfonate from alkylated (C_{30}) benzene
PWL 80-8	Barium sulfonate from alkylated (C_{30}) benzene
PWL 80-9	Magnesium sulfonate from alkylated (C_{30}) benzene
PWL 80-10	Potassium sulfonate from alkylated (C_{45}) benzene
PWL 80-11	Lithium sulfonate from alkylated (C_{45}) benzene
PWL 80-12	Calcium sulfonate from alkylated (C_{45}) benzene
PWL 80-13	Barium sulfonate from alkylated (C_{45}) benzene
PWL 80-14	Calcium sulfonate from alkylated (C_{30}) benzene
PWL 80-15	Barium sulfonate from alkylated (C_{30}) benzene
PWL 80-16	Barium sulfonate from alkylated (C_{20}) benzene
PWL 80-27	Calcium sulfonate
PWL 80-30	Slightly basic calcium sulfonate
PWL 80-31	Sodium sulfonate
PWL 80-37	Barium sulfonate
PWL 80-38	Barium sulfonate
PWL 81-8	Basic calcium sulfonate
PWL 81-25	Calcium dinonylnaphthalene sulfonate
PWL 81-26	Basic barium dinonylnaphthalene sulfonate
PWL 81-27	Neutral barium dinonylnaphthalene sulfonate in mineral oil
PWL 81-28	Neutral barium dinonylnaphthalene sulfonate in DOS
PWL 81-29	Neutral barium dinonylnaphthalene sulfonate in PAO
PWL 81-30	Carbonated basic calcium dinonylnaphthalene sulfonate
PWL 81-31	Zinc dinonylnaphthalene sulfonate
PWL 81-34	Barium dinonylnaphthalene sulfonate and trimer acid
Organic Acids and Anhydrides	
PWL 80-17	Mixture of organic acids
PWL 80-20	Mixture of organic acids
PWL 80-22	Mixture of organic acid and acid phosphate
PWL 80-23	Mixture of alkyl succinic acids and esters
PWL 80-25*	Complex alkenyl succinic acid — hydroxy alkyl ester
PWL 80-26	Alkyl succinic acid plus hydroxylated alkyl phenol
PWL 80-29*	Complex alkenyl succinic acid — hydroxy alkyl ester
PWL 80-32	Alkenyl succinic acid
PWL 80-33	Phosphoric acid
PWL 80-35	High molecular weight alkyl succinic acid
PWL 80-39	Mixture of sulfurized alkyl phenol and alkyl succinic acid
PWL 80-42	Mixture of polycarboxylic acids
PWL 80-49	Fluorinated carboxylic acid
PWL 80-54	Fluorinated carboxylic acid
PWL 80-58	Fluorinated carboxylic acid
PWL 80-66	Mixture of dimer acids
PWL 81-7	Alkyl dibasic acid derivative
PWL 81-13	Alkenyl succinic anhydride/acid/ester
PWL 81-14	Alkenyl succinic anhydride/acid/ester
PWL 81-16	Imide acid

5

TABLE 2.
LIST OF GENERAL DESCRIPTIONS OF THE ACTIVE INGREDIENTS
OF CANDIDATE CORROSION INHIBITORS (Continued)

Inhibitor Number	Active Ingredient Description
Organic Acids and Anhydrides	
PWL 81-17	Complex imide acid
PWL 81-24	Complex ester/acid salt
PWL 81-34	Barium dinonylnaphthalene sulfonate and trimer acid
PWL 81-35	Reaction product of carboxylic acid, polyalkylenepolyamine and alkenyl succinic acid anhydride
PWL 81-10	Complex imide
Amines and Amides	
PWL 80-19	Amine neutralized organic acid
PWL 80-24	Amine, amide, imidazoline product
PWL 80-28	Amine salt of alkyl succinic acid
PWL 80-41	Amine salt of polycarboxylic acid
PWL 80-43	Amine neutralized phosphoramidate plus alkyl phosphate
PWL 80-45	Cyclic amine salt of polycarboxylic acid
PWL 80-46	Secondary amine
PWL 80-47	Secondary amine
PWL 80-48	Primary amine
PWL 80-51	Fluorinated sulfonamide
PWL 80-57	Fluorinated sulfonamide
PWL 80-60	Mixture of amine neutralized dimer acids and amine phosphate esters
PWL 80-63	Amine dimer
PWL 80-65	Amine neutralized dimer acids
PWL 80-67	Mixture of amine neutralized dimer acid and phosphate esters
PWL 81-9	Complex amine/amide
PWL 81-18	Amine salt of alkenyl succinic acid
PWL 81-19	Amine salt of alkenyl succinic acid
PWL 81-20	Amine salt of alkenyl succinic acid
PWL 81-21	Amine salt of alkenyl succinic acid
PWL 81-22	Alkenyl amidic acid salt
PWL 81-23	Alkenyl amidic acid salt
PWL 81-36	Lead naphthenate plus dioctyldiphenylamine
PWL 81-37	Condensation product of primary cationic amine and fatty acid
Esters	
PWL 80-18	Alkylammonium-alkyl acid phosphate
PWL 80-21	Alkylammonium-alkyl acid phosphate
PWL 80-22	Mixture of organic acid and acid phosphate
PWL 80-23	Mixture of alkyl succinic acids and esters
PWL 80-25*	Complex alkenyl succinic acid — hydroxy alkyl ester
PWL 80-29*	Complex alkenyl succinic acid — hydroxy alkyl ester
PWL 80-64	Amine phosphate esters
PWL 81-12	Complex acid ester
PWL 81-15	Complex acid ester
PWL 81-32	Pentaerythritol monooleate
PWL 81-33	Sorbotan monooleate
PWL 81-36	Lead naphthenate plus dioctyldiphenylamine
PWL 81-38	Amine phosphate
PWL 81-42	Triphenylphosphorothionate

TABLE 2.
LIST OF GENERAL DESCRIPTIONS OF THE ACTIVE INGREDIENTS
OF CANDIDATE CORROSION INHIBITORS (Continued)

Inhibitor Number	Active Ingredient Description
Alcohols and Phenols	
PWL 80-52	Fluorinated alcohol
PWL 80-53	Polyalkoxylated fluorinated alcohol
PWL 80-55	Fluorinated alcohol
PWL 80-56	Fluorinated alcohol
PWL 80-59	Polyamino-alcohol
PWL 80-61	Polyamino alcohol
PWL 80-62	Polyamino alcohol
PWL 80-34	Zinc salt of carboxylated alkyl phenol
PWL 80-26	Alkyl succinic acid plus hydroxylated alkyl phenol
PWL 80-36	Hydroxylated alkyl phenol + zinc salt of carboxylated alkyl phenol
PWL 80-39	Mixture of sulfurized alkyl phenol and alkyl succinic acid
PWL 80-40	Mixture of hydroxyethylalkyl phenol, sulfurized alkyl phenol and alkyl succinic anhydride
PWL 81-11	Alkylated phenolic compound
Oxygenated Hydrocarbon-Sulfonate Mixtures	
PWL 81-1	Mixture of oxygenated hydrocarbons and calcium sulfonate
PWL 81-2	Mixture of oxygenated hydrocarbons and barium sulfonate
PWL 81-3	Mixture of oxygenated hydrocarbons and sodium sulfonate
PWL 81-4	Mixture of oxygenated hydrocarbons and sodium sulfonate
PWL 81-5	Mixture of oxygenated hydrocarbons and sodium sulfonate
PWL 81-6	Mixture of oxygenated hydrocarbons and barium sulfonate
Imidazoline Compounds	
PWL 80-44	Imidazoline
PWL 81-40	Substituted imidazoline

* Through an error in cross-referring additives, the supplier inadvertantly shipped two samples, PWL 80-25 and 80-29, which are identical in composition, but were assigned different identification numbers.

SECTION III

DEVELOPMENT AND VALIDATION OF THE CORROSION RATE EVALUATION PROCEDURE

TEST PROCEDURE DEVELOPMENT

The primary objective of this task was the development of an effective, accelerated characterization procedure for determination of the relative corrosion protection capabilities of candidate corrosion inhibiting oil formulations. A major effort was directed toward the improvement and validation of the Corrosion Rate Evaluation Procedure (CREP) developed in the first phase of this program (Reference 11). Several variables of this test procedure were investigated in an effort to further standardize the test and to improve the repeatability of the data generated with this procedure. The test coupon preparation, cleaning procedure, air flowrate, residence time and humidifying solution were investigated during this phase of the program.

Several features of the original test apparatus were modified in an effort to improve the precision of the CREP. Figure 1 shows the modified CREP apparatus at the present state of development. The Graham condenser of the original apparatus was replaced with an Allihn condenser with a 400 millimeter (mm) jacket length. The 24/40 standard taper ($\mathbb{T}$) female joint at the top of the condenser was fitted with a threaded offset adaptor to permit the suspension of the flared borosilicate glass air inlet tube. This combination of air inlet tube and condenser leaves three female joints in the reaction kettle cover for suspension of test coupons. This modification increased the data obtained from each corrosion test from two test coupons in the original test, to three coupons in the modified test.

As shown in Figure 1, the Buna-N stoppers of the original CREP apparatus were replaced with glass stoppers with integral glass loops for test coupon suspension. This modification precludes the possible contamination of the test environment by impurities extracted from the elastomeric stoppers. The test coupon was suspended from the glass loop on a hook formed with 20 gage AMS 5680 corrosion resistant steel wire. The suspension hooks were formed so that the bottom edge of the test coupon was 11 centimeters (cm) (4.3 inches (in.)) above the base of the reaction kettle. In order to prevent splashing of the boiling solution on test coupons during the corrosion test, a Teflon® disc was fabricated to seat loosely against the reaction kettle walls, above the surface of the humidifying solution. The splash suppressing disc was perforated with 0.64 cm (0.25 in.) holes to permit passage of the ascending vapors.

A series of tests was conducted to determine the effect of these modifications on subsequent corrosion rate determinations. These tests were conducted in accordance with the CREP described in Appendix A of the Interim Report (Reference 11), with the exception of the aforementioned modifications to the test apparatus. Test coupons were prepared by vapor blasting with a slurry of 200-grit novaculite. A test coupon support was fabricated to support six coupons during vapor blasting of the faces. The edges of the coupons were vapor blasted before inserting into the support. The test coupon support was developed to improve the repeatability of the surface finish by ensuring the same angle of grit impingement on each sample coupon. After vapor blasting, the coupons were stored in a solution comprised of 50 parts anhydrous methanol and 50 parts toluene until final cleaning was accomplished by immersing the test coupons in boiling toluene, flash drying, then immersing in boiling acetone and flash drying again. The coupons were then stored in a desiccator and allowed to equilibrate to room temperature. After 30 minutes, the test coupons were weighed to ± 0.1 milligram (mg) and

8

immersed for 5 minutes in MIL-C-8188C, as in previous development work. They were then suspended in a dust free environment for 15 minutes to drain excess oil from the coupons. The chamber used for the draining cycle was a scaled-down version of that described in the American Society for Testing and Materials (ASTM) D1748, "Standard Test Method for Rust Protection by Metal Preservatives in the Humidity Cabinet," Appendix Al.13. At the end of this 15-minute coupon draining cycle, excess oil at the base of the test coupon was absorbed by blotting with a laboratory Microwipe⁵. The test specimens were then suspended in the equilibrated atmosphere of the reaction chamber for a residence period of 60 minutes. An air flowrate of 45 standard cubic centimeters per minute (SCCM), and a vapor temperature of 99 ± 1°C were employed in these tests.
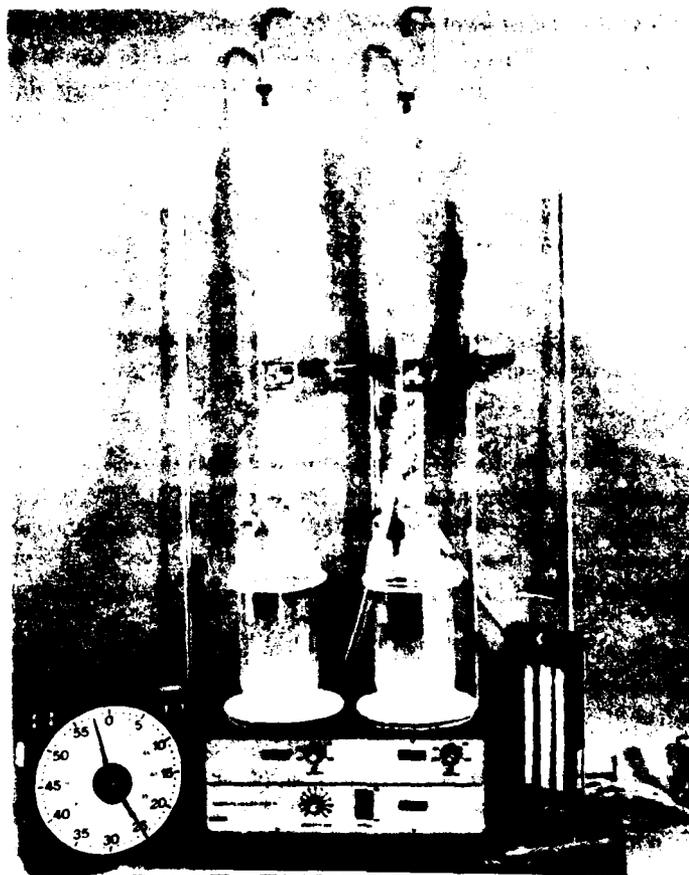
FE 197331

Figure 1. Test Apparatus for the Modified Corrosion Rate Evaluation Procedure

After a 60 minute exposure to the aerated vapors of the boiling acetic acid/sodium acetate buffer solution (pH 4.63), the specimens were removed from the test chamber, rinsed with acetone, and lightly brushed with a soft bristle brush to remove the excess scale from the surface of the metal. Secondary cleaning of the test coupons was accomplished by vigorously wiping the faces and edges of the coupon with Microwipes® saturated with acetone, followed by cleaning with Microwipes® saturated with hot toluene. Final cleaning was accomplished by immersing the sample coupons in boiling toluene, followed by immersing in boiling acetone, and flash drying. The coupons were then cooled to room temperature in a desiccator and reweighed to ± 0.1 mg to determine the metal loss due to corrosive attack.

9

During the preliminary tests with the modified test apparatus of the CREP, there was a wide variation in the boiling rates and the refluxing rates in the reaction kettles. The refluxing rate was approximated by counting the number of drops of condensate falling from the condensor per minute. In preliminary tests, this rate ranged from 27 to 77 drops per minute in four test chambers. In order to reduce this variation, a contact pyrometer was employed in calibrating each hot plate by determining the potentiometer setting which corresponded to a hot plate temperature of $327 \pm 10°C$ ($620 \pm 18°F$). Subsequent tests showed a great reduction in the range of condensation rates.

After calibrating the hot plates, it was found that a period of 30 to 40 minutes was necessary for the reaction chambers to reach thermal equilibrium. This was based on the time taken, from the initial application of heat, to reach a stable refluxing rate. On the basis of this determination, a standard equilibration time of 60 minutes was established for all subsequent tests. The extra 20 to 30 minutes allowed ample time for fine adjustments to air flowrates, and for the oil immersion and oil draining cycles.

In an effort to develop a more standardized cleaning procedure for removing oxides from post-test coupons, 13 potential rust removing solvents were evaluated in conjunction with ultrasonic cavitation. The objective of this investigation was to develop a solvent that would remove the oxides with a minimal attack on the base metal of the test coupon. The cleaning procedure employed in the previous test development effort caused no weight loss to control test coupons, however, the test coupons were left with a discoloration due to oxides that remained on the surface.

The cleaning compounds were evaluated in conjunction with ultrasonic cavitation provided by a Sonicor 600 watt generator operating at an output frequency of 40 kilohertz. The ultrasonic bath was employed in order to accelerate the removal of oxides generated in the corrosion test. The cleaning solutions assessed in this investigation included samples of several classes of compounds, including various inhibited acids, alkali, chelating alkali and hydrocarbon solvents.

The cleaning compounds were initially screened on the basis of their attack on the base metal, AISI-1010 steel. Any solvent which resulted in a significant weight loss in the control test was rejected without further testing. In the control tests, metal coupons were vapor blasted with 200-grit novaculite, precleaned in boiling toluene and boiling acetone, flash dried and preweighed. The coupons were then immersed in a sample of cleaning solution for a 5 minute ultrasonic cleaning cycle. The coupons were subsequently cleaned, cooled and reweighed. Any solution that resulted in a metal weight loss greater than 1.0 mg was rejected.

Table 3 shows the results of screening tests performed with 13 different cleaning solutions. As indicated in the table, all of the inhibited acid solutions were rejected on the basis of their attack on the metal coupons in the controlled test. The chelating alkaline solutions did not attack the metal at room temperature, $25°C$ ($77°F$), but were ineffective in removing oxides at this temperature. When evaluated at $90°C$ ($194°F$), Pennesolve 814 was found to be effective in removing the oxide after 15 minutes. However, after a 15-minute cleaning of a control coupon, a weight loss of 2.8 mg was observed. Preliminary results using trisolvent indicated that it was effective in removing the loosely adhering oxides, but left the metal with a discoloration. The material causing this discoloration was identified through X-ray diffraction analysis as magnetite, (Fe_3O_4).

10

TABLE 3.
RESULTS OF EVALUATIONS OF VARIOUS CLEANING SOLUTIONS IN THE CORROSION RATE EVALUATION PROCEDURE

Name of Cleaning Compound	Class of Cleaning Compound	Concentration in Deionized Water, (%)	Test Temperature (°C (°F))	Weight Loss of Controlled Test* Coupons (mg/minutes)	Results of Cleaning Test*
1. Rohco Corrosol 52959	Inhibited acid	3.0 1.0	25(77) 25(77)	2.8/5 2.7/5	Rejected
2. Oakite 32	Inhibited mineral acid	30 5	25(77) 25(77)	1.2/5 1.2/5	Rejected
3. Oakite 131	Inhibited phosphoric acid	30 5	25(77) 25(77)	3.6/5 2.8/5	Rejected
4. Penetone Formula 990	Inhibited mineral acid	25 5	25(77) 25(77)	2.3/5 2.1/5	Rejected
5. DuPont Sulfamic Acid Plus McGean North-West HIB-98	Inhibited sulfuric acid	10 0.1	25(77)	1.6/5	Rejected
6. Fisher Reagent Grade HCl Plus Rodine No. 50	Inhibited hydrochloric acid	15 1.5	25(77)	4.1/5	Rejected
7. Pennesolve 814	Chelating alkali	11 26 26 20	25(77) 25(77) 90(194) 90(194)	0.0/5 0.1/5 2.8/15 2.6/15	Negative Negative Cleaned Cleaned
8. Pennesolve 209	Chelating alkali	11 30	25(77) 25(77)	0.0/5 0.8/5	Negative Negative
9. Rohco Corrosol 52920	Chelating alkali	20	25(77)	0.6/5	Negative
10. Oakite Rustripper	Chelating alkali	11 38	25(77) 25(77)	0.0/5 0.6/5	Negative Negative
11. Sonicor 201 Rust Remover	Alkali	20 20	25(77) 90(194)	0.1/5 0.7/15	Negative **Partially cleaned
12. Sonicor 102	Alkaline detergent	10	25(77)	0.3/5	Negative
13. Trisolvent	Acetone Toluene Isopropanol	33.3 33.3 33.3	25(77)	0.3/15	**Partially cleaned

* All control tests and cleaning tests were performed with 5.08 × 1.27 × 0.159 cm (2.0 × 0.5 × 0.0625 in.) AISI-1010 metal coupons.

** These solutions resulted in the removal of loosely adhering oxides, however, coupons were left with a dark discoloration. X-ray diffraction analyses were used to identify the material causing the discoloration as magnetite, Fe_3O_4.

Various two-component cleaning systems were evaluated using trisolvent as a preliminary solvent to remove residual oil and loosely adhering oxides, followed by ultrasonic cleaning in a second solvent to remove the remaining magnetite. Various chelating alkaline and inhibited acid solutions were evaluated in this investigation, but none of the solutions were effective in removing the magnetite without attacking the base metal. Normalizing data for metal weight loss due to the cleaning compound would be difficult due to the fact that weight losses would vary with the degree of oxidation of the test coupon. For example, a cleaning solution may cause a 2.0 mg weight loss for a test coupon with minor corrosion, but may cause a 0.5 mg weight loss for a fully oxidized test coupon due to differences in the amount of bare metal surface exposed to the cleaning solution. Further technical effort on the cleaning procedure development was discontinued since the cleaning procedure used in the original CREP had been shown to result in no weight loss of metal coupons in control tests, and none of the test solutions performed more efficiently than the original method.

In preliminary testing with the modified CREP apparatus to generate test coupons for investigation of cleaning solutions, test coupons were suspended with one face toward the wall of the reaction kettle. A more rapid oxidation rate was observed on the faces toward the center of the reaction kettles. A second series of tests was conducted using magnetic stirring to agitate the system in an effort to reduce the difference in corrosion rates on opposite faces. Similar results were obtained in these tests.

To facilitate visual observations of the relative rates and severity of corrosion on the three test coupons in a reaction kettle, the buffer solution was diluted with deionized water. Dilution of the buffer solution reduced the agressiveness of the CREP environment, thereby decreasing the corrosion rates of the test coupons. The results of tests conducted at various concentrations of buffer solution, with and without magnetic stirring, are shown in Table 4. In several of these tests, visual observations were recorded noting unequal corrosion rates on opposite faces. There was no obvious trend for which face was more corroded, however, the inside face was frequently noted as the more oxidized.

TABLE 4.
CORROSION RATES OF AISI-1010 STEEL COUPONS WITH VARIOUS DILUTIONS OF THE HUMIDIFYING SOLUTION IN THE CORROSION RATE EVALUATION PROCEDURE

Test Number	Concentration of Buffer, (% by Volume)	System Agitation*	Mean Corrosion Rate** (mg/hr)
1	25	2	0.0
2	25	2	0.1
3	25	1	0.0
4	25	1	0.1
5	50	2	0.8
6	50	2	0.9
7	50	1	2.3
8	50	1	2.1
9	75	2	4.2
10	75	1	3.9
11	100	2	4.9
12	100	2	5.4
13	100	1	5.4
14	100	1	6.6

* System Agitation Codes
  1 - Magnetic Stirring, no Teflon disc.
  2 - No Magnetic Stirring, perforated Teflon disc to preclude splashing of boiling solution.
** Mean corrosion rate of three test coupons in one test kettle, all three coupons protected by MIL-C-8188C.

Before continuing with development work on the test matrix, it was deemed necessary to verify that the vapor temperature was equal throughout the environment of the reaction kettle. To accomplish this, a chromel-alumel, nonsheathed thermocouple was fabricated for insertion into the test environment through a No. 4 Buna-N stopper. The thermocouple was formed with a wide 90-degree bend to permit movement across an arc from the wall to the center of the reaction kettle, thereby generating a horizontal temperature profile of the vapors within the test chamber. Temperature measurements were recorded at 1 cm intervals across the reaction kettle, starting 2 cm above the boiling solution, and repeated at 2 cm vertical intervals to the top of the reaction kettle.

The temperature profiles were generated at various air flowrates after a one-hour equilibration period, at a hot plate temperature of $327 \pm 10°C$ ($620 \pm 18°F$). At an air flowrate of 45 SCCM, there was a uniform temperature of $100°C$ ($212°F$) throughout the reaction vapors, except at a point directly below the air inlet tube, which was $95°C$ ($203°F$). The temperature 2 cm below the air inlet tube was $100°C$. At an air flowrate of 100 SCCM, the temperature was still quite uniform, ranging from 99 to $100°C$ (210 to $212°F$). On the basis of these data, temperature variation was eliminated as a potential cause for the observed differences in corrosion rates on test specimens.

A series of preliminary corrosion tests was conducted employing 2000-milliliter (ml) reaction kettles in place of the 1000 ml kettles used in previous development work. The larger reaction kettles afforded a greater separation of test coupons and reaction kettle walls, permitting the suspension of test coupons in a plane along a radius of the test kettle, at right angles to the wall of the kettle. The use of 2000 ml kettles resulted in much greater efficiency in the insertion and removal of test coupons from the test environment, precluding contact with condensate on reaction kettle walls. The larger reaction kettle did not prevent the anomalous unequal corrosion rates on opposite faces of test coupons, but was adopted for subsequent testing to prevent contact between metal coupons and kettle walls.

As part of the test matrix designed to improve the repeatability of the CREP, an investigation was conducted to compare the surface finishes provided by three different surface preparation procedures:

1. A hand polished surface prepared with 240-grit aluminum oxide cloth as described in ASTM D1748, item 7.3. These coupons were fabricated and shipped in accordance with paragraphs A1.10.1 through A1.10.3 of ASTM D1748, by Metaspec Company of San Antonio, TX. The surface grinding at Metaspec was accomplished with 280-grit silicon carbide.

2. A sandblasted surface prepared with 30-grit, dry, sharp, silica sand conforming to the sieve requirements specified in ASTM D1748, item 5.2. These coupons were sandblasted with a nozzle pressure of 140 kilopascals kPa (20 psi), with the nozzle held 8 to 10 cm (3 to 4 in.) from the metal surface, at a 45 degree angle to the surface.

3. A vapor blasted surface prepared with a slurry comprised of 30-40 percent by volume 200-grit novaculite in water. These coupons were vapor blasted with a nozzle pressure of 620 kPa (90 psi), with the nozzle held 15 to 20 cm (6 to 8 in.) from the metal surface, at a 45 degree angle to the surface.

Five coupons were prepared with each type of surface finish, and evaluated with a profilometer (Bendix Peak Counter, Type QEH, Model No. 1). The results of the profilometer evaluations were as follows: 240-grit aluminum oxide cloth, 8 to 14 microinches (μ in.); 30-grit silica sand, 120 to 160 μ in.; 200-grit novaculite vapor blasting, 32 to 44 μ in.

13

Each of the three surface finishes was evaluated using a scanning electron microscope (SEM) to determine the extent of grit embedment during coupon surface preparation. All three preparation methods resulted in grit embedment, ranging in severity from a small amount in hand polishing to a relatively large amount in sandblasting. Figure 2 is a SEM photograph of the surface of the AISI-1010 steel as received from the vendor. Also shown in this figure is a silicon X-ray map of the same area as the micrograph, exhibiting the background signals picked up by the X-ray detector. Figure 3 is a micrograph of AISI-1010 steel after vapor blasting with a 200-grit novaculite/water slurry as described above. The corresponding silicon X-ray map reveals numerous silicon rich particles in the field of vision, appearing as clusters of X-ray signals (in white). The surface of the cold rolled steel after sandblasting with 30-grit silica sand is shown by the micrograph in Figure 4. The corresponding silicon X-ray map exhibits the relatively large amount of sand particles embedded in the surface of the metal. As shown in Figure 5, even polishing of the coupons embedded a small amount of silicon carbide grit in the metal. An aluminum X-ray map showed that no aluminum oxide particles were embedded during the hand polishing with aluminum oxide cloth.

During the preliminary cleaning tests summarized in Table 3, a small weight loss (0.3 mg) was observed for metal coupons subjected to 15 minutes of ultrasonic cavitation in a trisolvent medium. This weight loss was thought to be caused by the removal of a small amount of embedded grit during ultrasonic cleaning. To test this hypothesis, a sample coupon was vapor blasted, cleaned and scratched to allow location of a precise area of the metal coupon before and after ultrasonic cleaning. Figure 6 is a micrograph at a magnification (MAG) of 500X showing the surface of the metal before ultrasonic cleaning. The corresponding silicon X-ray map reveals embedded silicon rich particles. After a 15-minute ultrasonic cleaning cycle in trisolvent, the same approximate area was relocated and photographed with the SEM, and is shown in Figure 7. Comparison of the two figures shows that there was, in fact, removal of a small amount of grit (i.e., bracketed particles) during the ultrasonic cleaning.
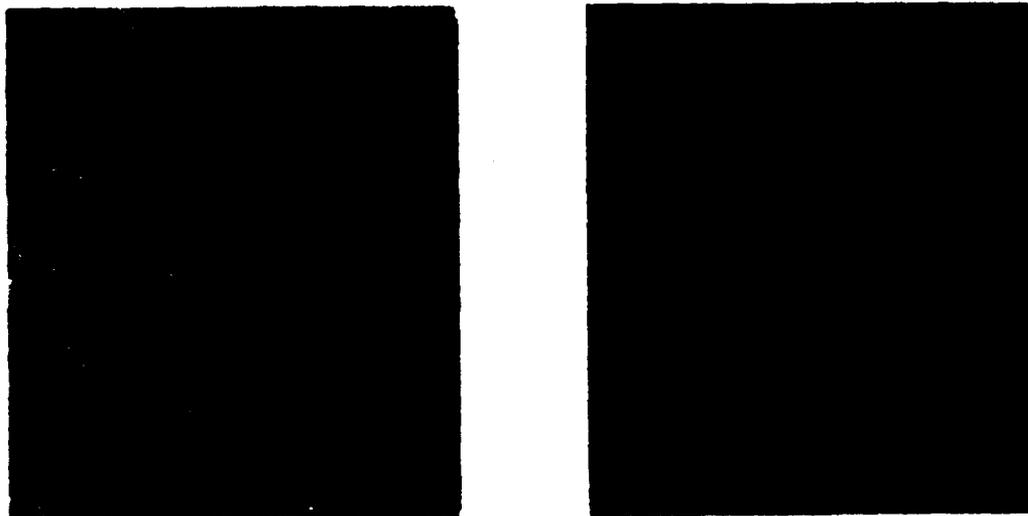
Mag: 100X

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Figure 2. SEM Photograph of the Surface of Steel as Received from Vendor (Left), and the Corresponding Silicon X-Ray Map (Right)

14

A series of ten corrosion tests was conducted to evaluate the effect of surface finish on the magnitude and repeatability of corrosion rates of 5.08 × 1.27 × 0.16 cm (2.0 × 0.5 × 0.062 inch) AISI-1010 steel coupons in the environment of the CREP. These tests were conducted in accordance with the previously defined test procedure and included evaluations of the three aforementioned surface finishes. The results of these tests are shown in Table 5. The sandblasted test coupons exhibited a corrosion rate approximately twice that of the vapor blasted coupons. Hand polished coupons exhibited the lowest corrosion rates. The vapor blasted surface finish demonstrated the most acceptable combination of magnitude and repeatability of corrosion rates. Consequently, vapor blasting with the novaculite/water slurry was selected for subsequent testing. Special care was practiced in subsequent tests to maintain the same nozzle pressure, nozzle to coupon distance, angle, and blasting time interval in an effort to control the amount of grit embedment during test coupon preparation.
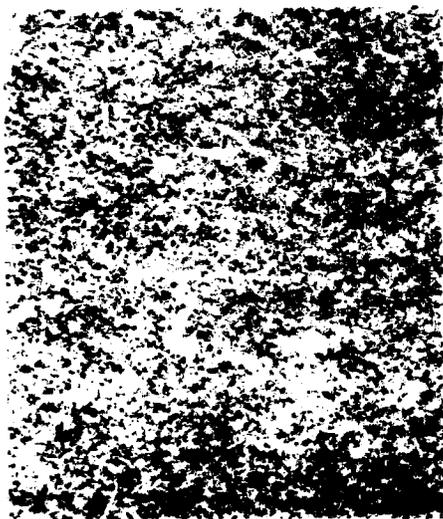
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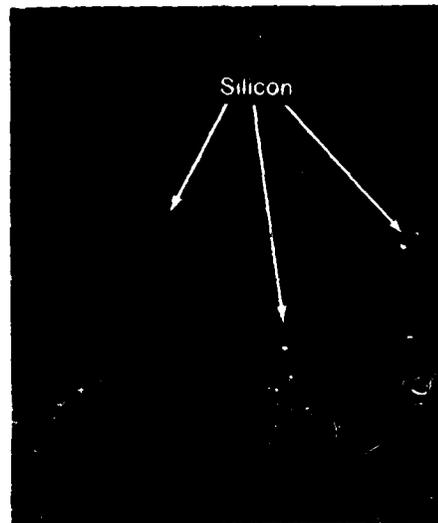
FD 216741

Figure 3. *SEM Photograph of the Surface of Steel After Vapor Blasting with a 200-Grit Novaculite/Water Slurry (Left), and the Corresponding Silicon X-Ray Map (Right) Revealing Embedded Grit*

TABLE 5.
CORROSION RATES OF AISI-1010 STEEL COUPONS WITH VARIOUS
SURFACE FINISHES IN THE CORROSION RATE EVALUATION PROCEDURE*

Test Number	Surface Finish**	Corrosion Rates, mg/hr		
		Coupon No. 1	Coupon No. 2	Coupon No. 3
1	HP	3.7	2.4	3.5
2	HP	2.7	3.7	4.2
3	VB	—	6.0	5.7
4	VB	6.0	5.3	5.8
5	VB	6.1	6.3	5.5
6	VB	6.4	7.2	6.5
7	SB	10.9	10.6	9.4
8	SB	—	12.4	11.4
9	SB	14.3	13.2	11.4
10	SB	15.2	14.0	13.5

* All coupons protected by MIL-C-8188C
** Surface finish abbreviations designate hand polished (HP), vapor-blasted (VB), and sandblasted (SB) finishes.

In an investigation to determine the effect of air flowrate on the magnitude and repeatability of corrosion rates in the modified CREP, a series of tests was conducted using the 2000-ml reaction kettle, a hot plate temperature of $327 \pm 10°C$ ($620 \pm 18°F$), and test coupons vapor blasted with 200-grit novaculite. Corrosion tests were conducted with air flowrates of 45, 100, 200, 300, 400, 500, 600 and 800 SCCM. All other parameters were held constant from test to test except the air flowrate and the concomitant change in vapor temperature. A series of tests was conducted with test coupons protected by MIL-C-8188C and another series using test coupons protected by a neat base stock for Mobil MIL-L-7808H, QPL 15F-1.

Mag: 100X
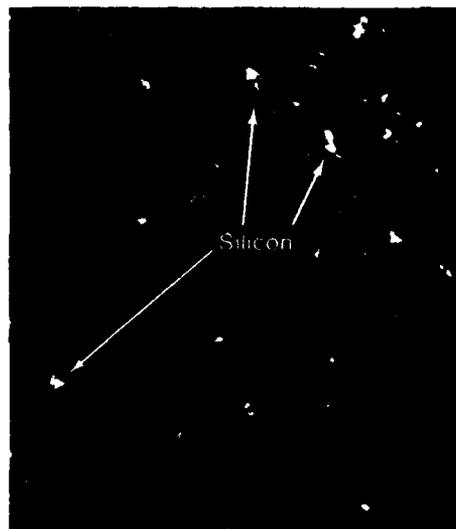
FD 216742

Figure 4. SEM Photograph of the Surface of Steel After Sandblasting with 30-Grit Silica Sand (Left), and the Corresponding Silicon X-Ray Map (Right) Revealing Embedded Sand Particles

16
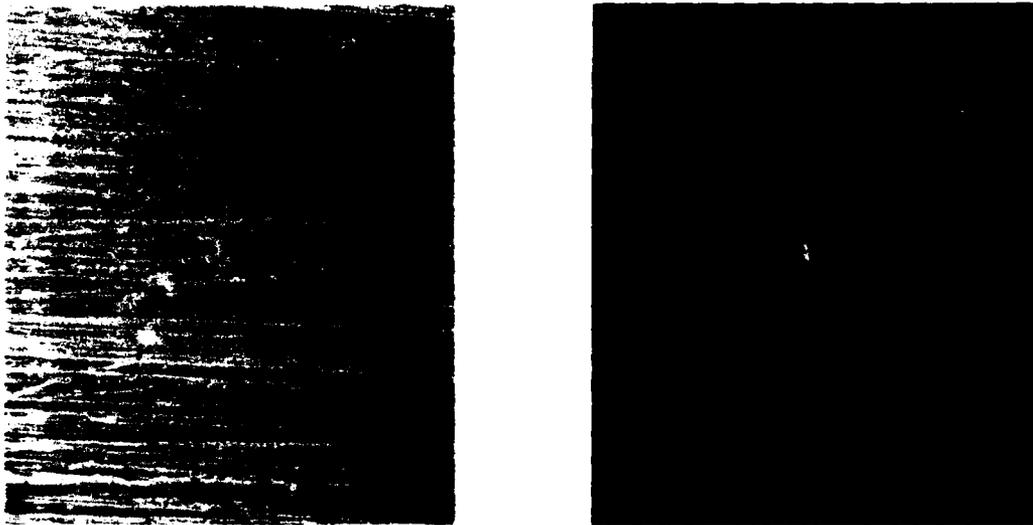
Mag: 100X

Figure 5. SEM Photograph of the Surface of Steel After Polishing with 280-Grit Silicon Carbide and 240-Grit Aluminum Oxide Cloth (Left), and the Corresponding Silicon X-Ray Map (Right) Showing Minor Grit Embedment

The objective of the aforementioned investigation was to produce curves showing corrosion rate as a function of air flowrate for both the Mobil 15F-1 base stock and the MIL-C-8188C oils. These data would provide a means for selection of an air flowrate which resulted in the best combination of magnitude and repeatability of corrosion rates. Figure 8 shows a plot of the data points generated in these tests and the general shape of the curves for the two oils. Both curves exhibit a positive slope for air flowrates of 45 through 300 SCCM but taper off to a negigible slope for flowrates of 300 through 800 SCCM. Predicated on the curves generated in this investigation, an air flowrate of 500 SCCM was selected for subsequent testing with the CREP. Using an air flowrate of 500 SCCM, a slight variation between replicate tests would result in a minimum variation in the corrosion rate determinations, whereas at lower air flowrates, a small variation in air flowrates could contribute to increased data scatter. An air flowrate of 500 SCCM results in a significant separation between corrosion rates of coupons protected by MIL-L-7808H and MIL-C-8188C, and a large enough corrosion rate for coupons protected by MIL-C-8188C to easily distinguish the more effective corrosion inhibiting formulations in a one hour test.

Test coupons protected by MIL-L-7808H generated a heavy layer of oxide during the first 20 minutes at higher air flowrates. In order to evaluate the effect of this initial oxide layer on the subsequent corrosion rate of test coupons, a series of tests was run with various residence times in the test environment. The buffer solution was diluted to 50 percent by volume in deionized water in order to reduce the initial corrosion rate of test coupons protected by MIL-L-7808H, thereby providing data points before the coupon surface was fully coated with oxide. Two sets of tests were run, under identical test conditions, to evaluate the effect of residence time on the corrosion rates of coupons protected by qualified MIL-L-7808H and MIL-C-8188C oils.

17

Mag: 500X

FD 216744

Figure 6. SEM Photograph of the Surface of Steel Vapor Blasted with 200-Grit Novaculite (Left), and the Coresponding Silicon X-Ray Map (Right) Before Ultrasonic Cleaning

Mag: 500X

FD 216745

Figure 7. SEM Photograph of the Steel Surface in Approximately the Same Area as Figure 6 (Left), and the Corresponding Silicon X-Ray Map (Right) After Ultrasonic Cleaning

18
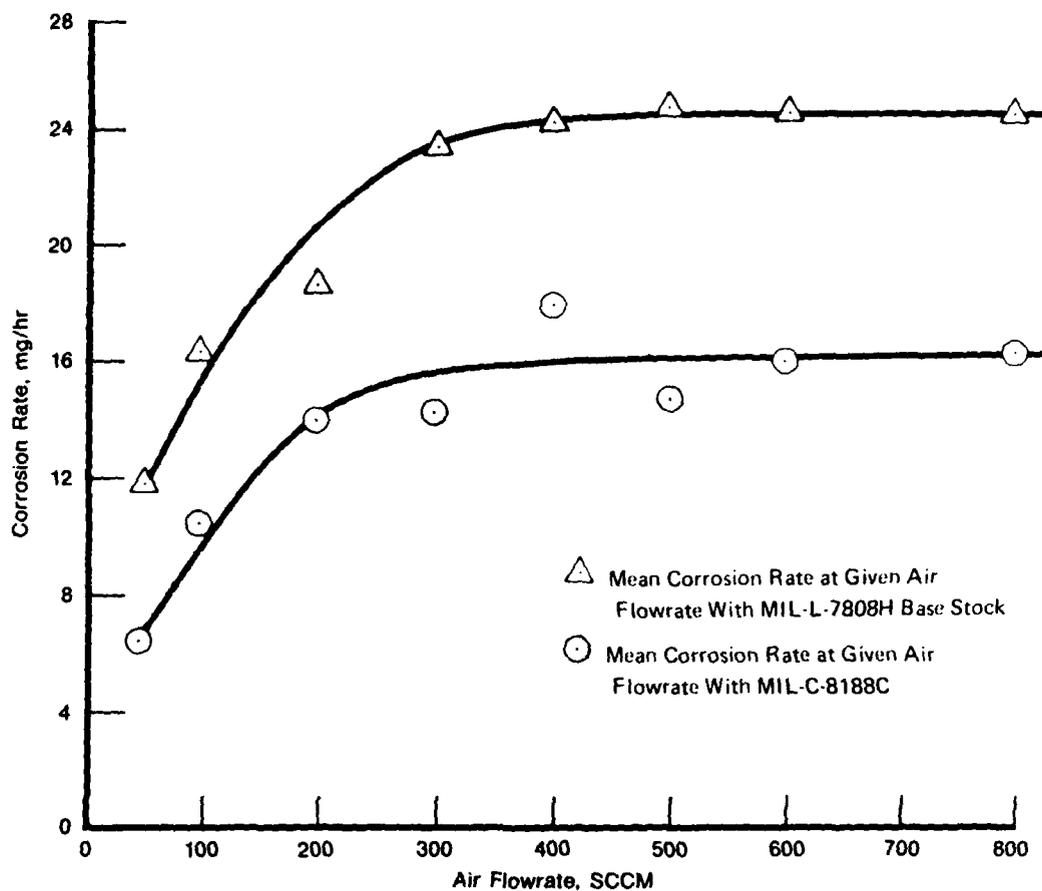
Figure 8. Corrosion Rate of AISI-1010 Steel Coupons as a Function of Air Flowrate in the Corrosion Rate Evaluation Procedure

In the first set of tests, coupons were vapor blasted, cleaned, preweighed and coated with MIL-C-8188C. After the oil draining cycle, all test coupons were inserted in the test environment at the same time, and were removed at 60-minute intervals: 60, 120 and 180 minutes. Data generated in these tests showed no indication of corrosion rate inhibition by oxides produced early in the test. The test coupons exhibited increased corrosion rates with increased residence time. The increase in corrosion rate with time may be a result of the increase in metal surface area exposure as corrosion inhibitor is leached from the surface.

Under the same test conditions, test coupons protected by a qualified MIL-L-7808H lubricating oil exhibited a decrease in corrosion rate with increased residence time. Two tests were conducted to determine data points at 60, 120 and 180 minutes, and another two tests to determine data points at 30, 90 and 150 minutes. Figure 9 shows the data generated in these tests. As shown, the corrosion rate of test coupons protected by MIL-L-7808H was much more rapid than test coupons protected by MIL-C-8188C in the initial period of the tests. However, as residence time in the environment increased, the corrosion rate of test coupons protected by MIL-L-7808H decreased. There was, in fact, a greater corrosion rate for test coupons protected by MIL-C-8188C after three hours residence time. One explanation for this phenomenon is that the heavy oxide layer produced in the initial phase of the test forms a partial barrier between

the metal surface and the corrosive environment, thereby inhibiting further corrosion. This information is important in that it limits the residence time of tests used to evaluate poor corrosion inhibiting formulations. It was, however, of little concern in determining the relative corrosion rates for the screening of candidate corrosion inhibiting oils for this program. Indeed, those formulations of interest in this program were formulations performing more effectively than MIL-C-8188C. A 60 minute residence time was selected for subsequent investigations with the CREP.
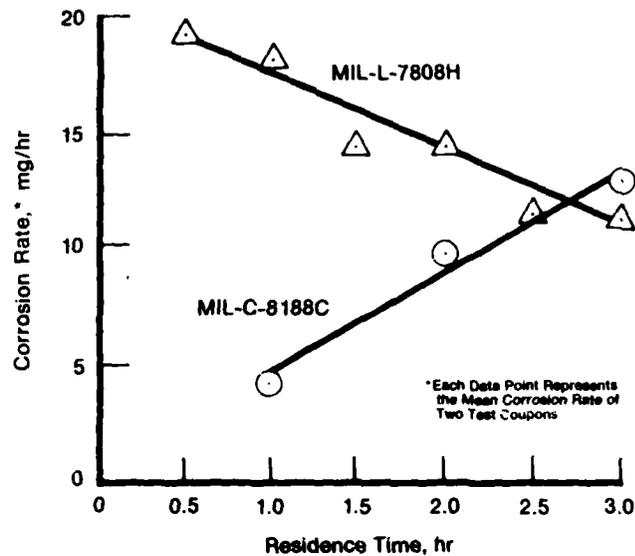
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Figure 9. *Corrosion Rate of AISI-1010 Steel Coupons as a Function of Residence Time, Using a Modified Corrosion Rate Evaluation Procedure*

Several different humidifying solutions were evaluated during the development of the CREP. In addition to liquids investigated during the first phase of the program (Reference 12), deionized water and synthetic seawater were evaluated with the modified CREP. The composition of the synthetic seawater, as shown in Table 6, was in accordance with MIL-E-5009D. The purpose of these tests was to evaluate the severity of deionized water and seawater relative to the acetate buffer solution, and the feasibility of employing either of these liquids in an accelerated corrosion test.

TABLE 6.
THE COMPOSITION OF SYNTHETIC SEA WATER PER MIL-E-5009D

Name of Salt	Chemical Formula	Weight per Liter of Solution,* (g)
Sodium chloride	NaCl	23.0
Magnesium chloride hexahydrate	$MgCl_2 \cdot 6\ H_2O$	11.0
Sodium sulfate decahydrate	$Na_2SO_4 \cdot 10\ H_2O$	8.0
Calcium chloride hexahydrate	$CaCl_2 \cdot 6\ H_2O$	2.2
Potassium bromide	KBr	0.9
Potassium chloride	KCl	0.2

* Deionized water added to salts to make 1 liter of solution.

20

In corrosion tests conducted using the modified CREP with 100 ml of acetate buffer solution, test coupons protected by qualified MIL-L-7808H and MIL-C-8188C oils exhibited corrosion rates of approximately 25 and 15 mg/hr, respectively. In comparative tests using a 100-ml aliquot of deionized water in place of the acetate buffer solution, there was no detectable weight loss to AISI-1010 test coupons protected by MIL-L-7808H after a one hour residence time. Using synthetic seawater and a two hour residence time, test coupons protected by MIL-L-7808H exhibited a mean corrosion rate of 2.1 mg/hr. Test coupons protected by MIL-C-8188C exhibited no measurable weight loss in the two hour test. In order to employ synthetic seawater as the humidifying solution in tests to distinguish between MIL-C-8188C and more promising corrosion inhibiting formulations, the residence time of the test would have to be extended beyond that of a normal 8 hour working shift. This would negate one original objective of this investigation; i.e. the development of an accelerated corrosion test procedure. Consequently, the technical effort was directed back to the modified CREP using the Fisher Certified® acetic acid/sodium acetate buffer solution.

During subsequent corrosion tests conducted by a second operator, a problem was discovered with the use of the contact pyrometer for calibrating hot plate temperatures. The reproducibility of temperature readings of the contact pyrometer was found to be poor, as it was dependent upon the applied pressure and the angle at which the probe was held on the surface. In order to circumvent this problem, two chromel-alumel thermocouples were installed in each hot plate. The thermocouples were installed by drilling two holes through the aluminum plate beneath the heating coil, 2.5 cm (1 in.) and 5 cm (2 in.) from the center, at an angle of 180 degrees. The thermocouples were inserted through the aluminum plate, in contact with the asbestos disc beneath the heating coil. The two thermocouples were then wired in parallel at the readout connector to obtain an average heating coil temperature. The voltage input to the individual heating plates was subsequently controlled by variable voltage transformers.

Preliminary tests were conducted with the modified units employing a heating coil temperature of 327 ± 10°C (620 ± 18°F). Results of these tests did not repeat previous results. Subsequent tests conducted with a heating coil temperature of 380 ± 10°C (716 ± 18°C) produced more repeatable data. The temperature of the vapor in these tests was 98 ± 1°C (208 ± 2°F). The condensation rate was approximately 60 ± 10 drops per minute.

After establishing the various parameters of the CREP, a series of tests was conducted to establish the magnitude and repeatability of the corrosion rate determinations for AISI-1010 test coupons protected by MIL-L-7808H and MIL-C-8188C oils. The procedure and test parameters used for these tests are described in detail in Appendix B. Figure 10 shows the corrosion rates of 54 test coupons protected by MIL-C-8188C and 33 test coupons protected by MIL-L-7808H. The mean of 54 corrosion rate determinations for MIL-C-8188C was 13.3 mg/hr and the standard deviation was 1.6 mg/hr. The mean and standard deviation of 33 test coupons protected by uninhibited MIL-L-7808H were 22.0 and 1.5 mg/hr, respectively. The 99.9 percent (%) confidence interval for MIL-L-7808H corrosion rates was from 17.8 to 26.1 mg/hr.
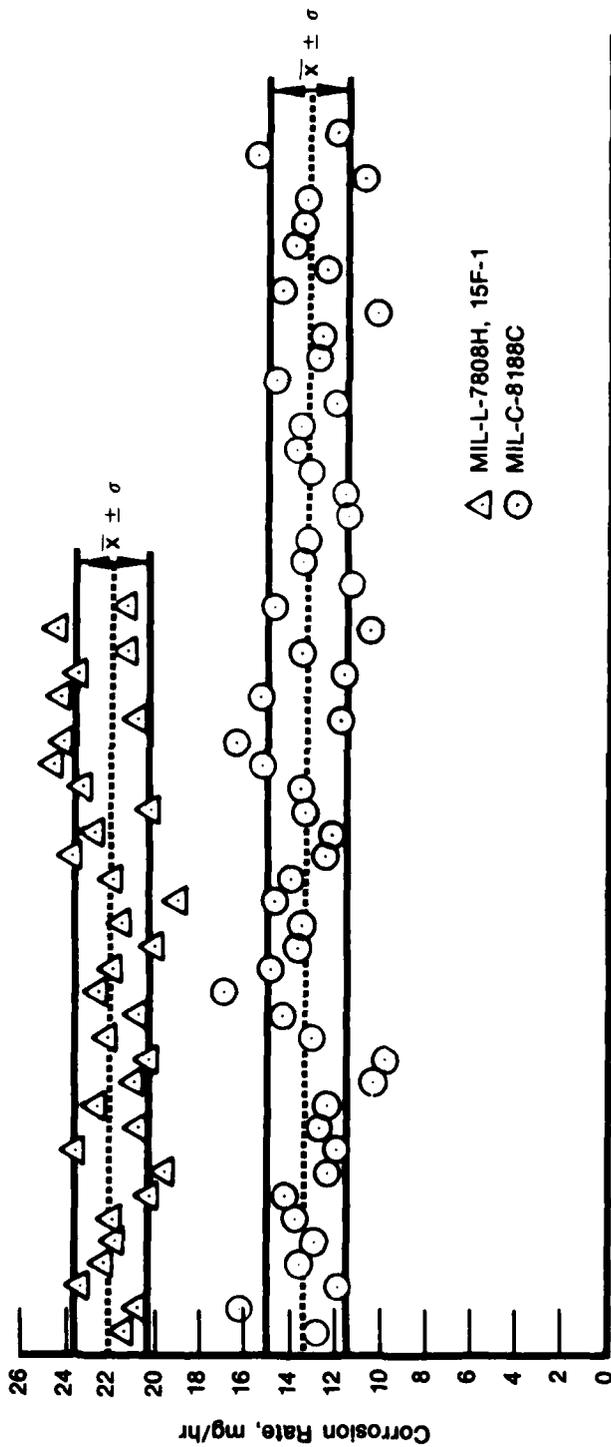
Figure 10. Corrosion Rate Data for AISI-1010 Metal Coupons in the Corrosion Rate Evaluation Procedure

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22

On the basis of these data, the 99.9% confidence interval for corrosion rates of test coupons protected by MIL-L-7808H was established as a control to verify that no significant differences occurred between subsequent tests. All corrosion tests performed subsequent to these included two test coupons protected by a candidate oil formulation and one test coupon protected by MIL-L-7808H. If the corrosion rate of the control coupon protected by MIL-L-7808H was outside the 99.9% confidence interval, then the data were considered invalid and the test was repeated.

TEST PROCEDURE VALIDATION

As acknowledged in the Statement of Work for this program, (Reference 13) the humidity cabinet corrosion test (HCCT) described in MIL-C-8188C is currently considered to be most representative of simulating the environment for which the corrosion inhibiting oil developed in this program must provide protection. Although the HCCT is adequate in terms of the data required, it was considered too time consuming for this investigation due to the large number of candidate corrosion inhibitors to be evaluated. However, in order to validate the P&WA/GPD developed CREP, it was deemed necessary to establish a relationship between the CREP and the HCCT.

To accomplish this task, a total of 22 oil formulations were evaluated with both the modified CREP and the HCCT described in the MIL-C-8188C specification. Ten of these oil samples were supplied as unknowns by the AFWAL/MLBT Program Manager for validation of the CREP as a meaningful accelerated corrosion test procedure. One additional sample was supplied by the Air Force as a candidate formulation. Eleven oil samples were formulated at P&WA/GPD for correlation of the test data from the CREP and the HCCT. The 11 formulations blended at P&WA/GPD included formulations of five of the more promising candidate corrosion inhibitors from the first phase of the program, two different lots of MIL-C-8188C, and samples of neat base stock and fully formulated MIL-L-7808H, QPL 15F-1.

Each of the 22 formulations was evaluated at Phoenix Chemical Laboratories using a modified version of the HCCT described in MIL-C-8188C. The only modifications to the test procedure were in the number of test coupons per sample formulation and the residence time in the humidity cabinet. Three test coupons were used for each test formulation instead of the five specified in MIL-C-8188C. The residence time was extended from 144 to 480 hours with the objective of distinguishing between the corrosion protection efficiencies of the test formulations. The test coupons were suspended in the humidity cabinet on a Friday and the first inspection was conducted on Monday, after 72 hours exposure. Subsequent inspections were conducted at 24-hour intervals except on weekends. Inspections were omitted at 192, 216, 360, and 384 hours due to their occurrence on weekends. Test coupon failures were predicated on the criteria specified in paragraph 4.6.11.3 of MIL-C-8188C, and were removed from the humidity cabinet at the time of failure.

Each of the 22 oil samples was also evaluated with the CREP defined in Appendix B. Each corrosion test contained three steel coupons. One coupon in each test was protected by MIL-L-7808H and served as a control to verify that no change occurred in the test procedure. The remaining two coupons in each test were protected by a thin film of the test formulation. Four corrosion tests were conducted with each formulation, which generated eight corrosion rate determinations. The highest and lowest corrosion rates were deleted and the mean and standard deviation were calculated for the remaining six.

The data generated in the CREP and HCCT evaluations of the 22 oil formulations are presented in Table 7. As shown by these data, there is a general agreement between the relative efficiency ratings as determined by these two test methods. The most promising formulations selected with the CREP functioned at least as well as MIL-C-8188C in the HCCT. Predicated on

23

these data, the CREP was accepted as a valid procedure for screening candidate corrosion inhibiting oils on the basis of the relative corrosion protection afforded by each formulation.

TABLE 7.
CORROSION RATE DATA FOR FORMULATIONS WITH THE CORROSION
RATE EVALUATION PROCEDURE (CREP) AND THE HUMIDITY
CABINET CORROSION TEST (HCCT)

Corrosion Inhibitor and Wt % Active Ingredient[a]	CREP[b] Mean Corrosion Rate ± One Sigma, (mg/hr)	HCCT[c] Hours to Failure in 480-hr Test		
1. 2.0% PWL 80-20 in MIL-L-7808H, 15F-1	0.2 ± 0.2	Pass	Pass	Pass
2. 2.0% PWL 80-32 in "Neat" MIL-L-7808H, 15F-1	0.4 ± 0.4	Pass	Pass	Pass
3. 2.0% PWL 80-32 in MIL-L-7808H, 15F-1	0.4 ± 0.5	Pass	Pass	Pass
4. 2.0% PWL 80-29 in MIL-L-7808H, 15F-1	1.8 ± 1.1	Pass	Pass	480
5. 2.0% PWL 80-29 in "Neat" MIL-L-7808H, 15F-1	2.4 ± 0.3	Pass	Pass	Pass
6. 2.5% PWL 81-35 in MIL-L-7808H, 15F-1	3.1 ± 1.5	Pass	Pass	Pass
7. 2.0% PWL 80-25 in MIL-L-7808H, 15F-1	3.1 ± 1.2	408[d]	408[d]	408[d]
8. 5.0% PWL 80-18 in MIL-L-7808H, 15F-1	9.1 ± 1.9	Pass	Pass	Pass
9. MIL-C-8188C, Lot 58	13.4 ± 2.7	408[d]	408[d]	408[d]
10. 4.5% PWL 81-36 in MIL-L-7808H, 15F-1	14.0 ± 0.8	72	72	72
11. 5.0% PWL 81-37 in MIL-L-7808H, 15F-1	14.8 ± 1.5	Pass	Pass	Pass
12. 5.0% PWL 81-38 in MIL-L-7808H, 15F-1	15.2 ± 0.8	Pass	Pass	264
13. 2.0% PWL 80-4 in MIL-L-7808H, 15F-1	15.4 ± 0.8	408[d]	408[d]	408[d]

24

TABLE 7.
CORROSION RATE DATA FOR FORMULATIONS WITH THE CORROSION
RATE EVALUATION PROCEDURE (CREP) AND THE HUMIDITY
CABINET CORROSION TEST (HCCT) (Continued)

Corrosion Inhibitor and Wt % Active Ingredient[a]	CREP[b] Mean Corrosion Rate ± One Sigma, (mg/hr)	HCCT[c] Hours to Failure in 480-hr Test		
14. MIL-C-8188C, Lot 57	15.5 ± 1.2	Pass	Pass	480
15. 5.0% PWL 81-39 in MIL-L-7808H, 15F-1	15.9 ± 0.8	72	72	72
16. 5.0% PWL 81-40 in MIL-L-7808H, 15F-1	17.3 ± 2.0	72	72	72
17. 2.5% PWL 81-40 in MIL-L-7808H, 15F-1	18.9 ± 2.4	72	72	72
18. 2.5% PWL 81-37 in MIL-L-7808H, 15F-1	20.4 ± 1.2	Pass	Pass	Pass
19. MIL-L-7808H, 15F-1	20.9 ± 1.1	72	72	72
20. 5.0% PWL 81-41 in MIL-L-7808H, 15F-1	21.4 ± 1.9	72	72	72
21. MIL-L-7808H, 1N-1	22.7 ± 0.7	72	72	72
22. "Neat" MIL-L-7808H, 15F-1	24.8 ± 2.0	72	72	72

a. All concentrations represent the percentage by weight of the active ingredient in the "As Received" additive which was formulated in MIL-L-7808H.
b. These tests were conducted in accordance with the Corrosion Rate Evaluation Procedure (CREP) defined in Appendix B.
c. Humidity Cabinet Corrosion Tests were conducted in accordance with MIL-C-8188C, except that three test coupons were used instead of five, and the residence time was extended to 480 hours.
d. Failure occurred during a weekend. Coupons failed between 336 and 408 hours.

SECTION IV

FORMULATION AND EVALUATION OF CANDIDATE CORROSION INHIBITING ENGINE OILS

Three different qualified MIL-L-7808H gas turbine engine lubricants were acquired to formulate the candidate corrosion inhibiting oils in this program. Three different qualified lubricants were selected because of variations in composition that exist in qualified lubricants from different manufacturers. These variations in composition may lead to misleading conclusions due to the possible interaction with the organic corrosion inhibiting compounds. For example, a given corrosion inhibitor may be compatible with all components in one qualified lubricant, but may be incompatible with one or more components of another lubricant conforming to the same specification requirements.

The major portion of this investigation was conducted using candidate corrosion inhibiting oils formulated with a MIL-L-7808H lubricant having the Qualified Products List (QPL) designation 15F-1. The selection of QPL 15F-1 was predicated on its relatively low volatility and evaporation rate, and the importance of minimizing oil volume losses during operation of ALCM engines. The most promising corrosion inhibitors were subsequently evaluated in qualified MIL-L-7808H lubricants having QPL designations 11E-1 and 15E-1 to verify their compatibility and corrosion inhibiting properties.

During the first phase of the program, a test matrix was developed to provide a means for the sequential elimination of the less desirable corrosion inhibitors on the basis of their solubility and corrosion inhibiting characteristics. A total of 67 candidate corrosion inhibitors were screened in this test matrix during the first phase of the program. Of the 67 inhibitors evaluated during the investigation, 21 were found to be immiscible at a 2.0 percent by weight (wt %) active ingredient concentration in MIL-L-7808H.* The 46 inhibitors which were found to be miscible at this concentration were subsequently evaluated in the Corrosion Rate Evaluation Procedure (CREP) described in Appendix A of the Interim Report (Reference 11). These 46 inhibitors were evaluated at 0.5 and 2.0 wt % active ingredient concentrations. None of the inhibitors were found to be more effective than MIL-C-8188C at 0.5 wt %; however, at 2.0 wt %, 13 inhibitors were found to be more effective than MIL-C-8188C and 13 were found to be at least as effective as MIL-C-8188C.

After development and validation of the modified CREP during the second phase of the program, a total of 61 candidate corrosion inhibitors were evaluated in a test matrix similar to that employed in the first phase of the program. The 61 inhibitors included 25 of the more promising from the first phase of the program, 33 inhibitors acquired during the second phase of the program, and 3 inhibitors rejected during the first phase of the program. The latter 3 inhibitors were included in order to verify that candidate inhibitors rejected with the original CREP were, in fact, less effective then MIL-C-8188C when evaluated with the modified CREP.

The 61 candidate corrosion inhibitors were initially screened on the basis of their miscibility in MIL-L-7808H, QPL 15F-1 lubricant. The inhibitors were blended at 2.0 wt % using a magnetic stirring hot plate to effect dissolution. Most of the inhibitors dissolved readily at room temperature, 25°C (77°F). Those that were difficult to formulate at room temperature were heated to a maximum temperature of 68°C (155°F), in conjunction with magnetic stirring. The maximum temperature of 68°C (155°F) was selected to preclude thermal degradation of oil/inhibitor formulations during the blending procedure.

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* All subsequent references to inhibitor concentrations will indicate the percentage of corrosion inhibiting active ingredient.

26

A 100 milliliter (ml) aliquot of each oil/inhibitor formulation was subsequently subjected to a 30 minute centrifugation at a relative centrifugal force of 560. Centrifugation provided an accelerated means of determining the extent of dissolution of the inhibitors by concentrating sludges, precipitates or colloidal suspensions. Predicated on the importance of eliminating the potential for sludge formation during long term storage of the oil formulations, any candidate formulations exhibiting measurable amounts of sediment in the miscibility tests were rejected. Four of the corrosion inhibitors were found to be immiscible at 2.0 wt %. These four inhibitors, PWL 81-8, 81-11, 81-17 and 81-34, were subsequently evaluated at 0.5 wt %. All four were found to be immiscible at 0.5 wt % and were therefore rejected from investigations of single additive formulations.

The next phase of the screening test matrix involved evaluating the relative corrosion inhibiting characteristics of the 57 inhibitors found to be soluble at 2.0 wt %. The corrosion tests used to assess these oil/inhibitor formulations were performed according to the CREP defined in Appendix B and the sequential sampling plan (SSP) defined in Appendix C. These tests defined the corrosion protection provided by a thin film of each formulation, relative to the protection provided by MIL-C-8188C.

An SSP was developed to expedite the elimination of the less effective corrosion inhibitors with 95% confidence. The SSP was based on the results of 54 corrosion rate determinations on AISI-1010 steel test coupons protected by MIL-C-8188C. The mean of the 54 corrosion rates was 13.3 mg/hr and the standard deviation was 1.6 mg/hr. Based on these data, a truncated SSP was constructed which allowed for an early termination of testing and provided a means for determining the relative corrosion protection of an oil/inhibitor formulation in a maximum of three tests. Using the SSP in conjunction with the CREP, a maximum of three tests was required to determine whether a formulation was less effective or at least as effective as MIL-C-8188C.

The SSP provided an excellent means of accelerating the elimination of less effective corrosion inhibitors with a very reasonable level of confidence. The acceptable quality level of the plan was 13.3 mg/hr and had an alpha risk of 0.05 associated with it. The rejectable quality level of the plan was 14.9 mg/hr and had a beta risk of 0.23 associated with it. A larger beta risk level was accepted because subsequent tests were to be performed on the more promising corrosion inhibitors to verify their effectiveness. A more detailed explanation of the usage and associated risk levels of the SSP is provided in Appendix C.

The corrosion rate data generated in the screening of the candidate corrosion inhibitors is listed in Table 8. As previously mentioned, each test conducted with the CREP contained two steel test coupons protected by the test formulation and one coupon protected by MIL-L-7808H which served as a control coupon to verify that no change occurred in the test procedure. Table 8 shows the number of data points, the mean corrosion rate, and the total acid number (TAN) of each formulation. Of the 57 candidate corrosion inhibitors evaluated in this phase of the screening test matrix, 23 were found to be at least as effective as MIL-C-8188C in the environment of the CREP. All three of the corrosion inhibitors rejected in the first phase of the program (PWL 80-24, 80-36, and 80-40) were also rejected with the modified CREP.

27

TABLE 8.
CORROSION RATE DATA FOR CANDIDATE CORROSION INHIBITORS
AT A 2.0 Wt % ACTIVE INGREDIENT CONCENTRATION IN MOBIL
MIL-L-7808H, QPL 15F-1

	Corrosion Inhibitor	Number of Data Points	Mean Corrosion Rate (mg/hr)	Total Acid Number (mgKOH/g)
1.	MIL-L-7808H, 15F-1	410	20.5	0.10
2.	MIL-C-8188C	80	13.3	0.11
3.	PWL 80-20	6	0.2	5.71
4.	PWL 80-32	6	0.4	7.50
5.	PWL 80-29	6	1.8	4.79
6.	PWL 80-25	6	3.1	4.97
7.	PWL 80-22	4	3.1	4.36
8.	PWL 81-7	2	3 2	4.78
9.	PWL 81-18	2	3.3	2.34
10.	PWL 80-23	2	4.8	4.84
11.	PWL 81-21	4	5.6	3.36
12.	PWL 81-13	4	6.4	3.53
13.	PWL 80-14	2	7.6	1.34
14.	PWL 80-64	2	7.8	2.40
15.	PWL 80-7	2	8.2	0.97
16.	PWL 81-20	2	8.7	2.06
17.	PWL 81-15	2	10.0	4.70
18.	PWL 80-8	2	10.8	0.31
19.	PWL 80-12	2	11.3	1.00
20.	PWL 80-10	2	11.4	0.12
21.	PWL 80-42	2	11.4	3.32
22.	PWL 81-19	2	11.5	2.86
23.	PWL 80-11	4	12.3	0.26
24.	PWL 81-35	6	12.9	2.13
25.	PWL 80-2	6	13.2	0.50
26.	PWL 80-30	6	14.5	0.00
27.	PWL 81-5	6	14.6	0.50
28.	PWL 80-4	6	15.2	1.06
29.	PWL 80-28	6	15.5	1.53
30.	PWL 80-37	4	16.0	0.33
31.	PWL 81-14	2	16.4	2.28
32.	PWL 81-29	6	16.5	0.33
33.	PWL 80-31	4	16.5	0.09
34.	PWL 80-33	2	16.6	5.00
35.	PWL 81-25	2	17.2	0.56
36.	PWL 80-39	4	17.4	1.24
37.	PWL 81-28	4	17.7	0.31
38.	PWL 81-40*	2	17.8	—
39.	PWL 81-22	2	18.5	1.34
40.	PWL 81-9	2	18.7	0.13
41.	PWL 81-27	2	18.7	0.25
42.	PWL 81-31	2	18.8	2.08
43.	PWL 81-33	2	18.8	–
44.	PWL 81-32	2	18.9	—
45.	PWL 80-1	4	19.0	1.93
46.	PWL 80-34	2	19.2	–
47.	PWL 81-3	2	19.3	0.32
48.	PWL 80-38	2	19.4	0.21
49.	PWL 81-24	2	19.6	1.09
50.	PWL 81-10	2	19.8	0.53
51.	PWL 80-40	2	20.0	1.24
52.	PWL 81-16	2	20.1	4.70
53.	PWL 80-24	2	20.2	—
54.	PWL 80-36	2	20.2	—
55.	PWL 81-23	2	20.4	1.82

TABLE 8.
CORROSION RATE DATA FOR CANDIDATE CORROSION INHIBITORS
AT A 2.0 Wt % ACTIVE INGREDIENT CONCENTRATION IN MOBIL
MIL-L-7808H, QPL 15F-1 (Continued)

Corrosion Inhibitor	Number of Data Points	Mean Corrosion Rate (mg/hr)	Total Acid Number (mgKOH/g)
56. PWL 81-2	2	20.6	0.45
57. PWL 81-6	2	21.2	0.25
58. PWL 81-4	2	21.4	0.22
59. PWL 81-12	2	23.0	0.17
60. PWL 81-1	2	23.2	0.21

*This formulation was supplied by AFWAL/MLBT as MLO 81-249. The results are included here but were not considered an integral part of the miscibility/corrosion rate screening test matrix.

During the first phase of the program all corrosion inhibitors were evaluated at both 2.0 and 0.5 wt % to preclude the rejection of a corrosion inhibitor that may have been more effective at a lower concentration. Of the 46 inhibitors evaluated at 0.5 and 2.0 wt %, none were more effective at 0.5 wt % than at 2.0 wt % (Reference 14). Consequently, this series of tests was omitted during the second phase of the program. Figure 11 summarizes the results of screening the 61 candidate corrosion inhibitors on the basis of miscibility and corrosion protection. The 34 inhibitors found to be less effective than MIL-C-8188C and the 4 inhibitors found to be insoluble at 2.0 wt % were rejected from the investigation of single additive formulations.

Table 9 shows the 23 most promising candidate single additive formulations along with the mean corrosion rate, TAN and flash point of each formulation. The procedure employed for determining the TAN was a modified version of ASTM D664. A weighed aliquot of the formulation was blended in 125 ml of titration solvent. then titrated with a potassium hydroxide/isopropanol solution of predetermined normality. The solutions were titrated to an endpoint of pH 11.0 as specified in the MIL-L-7808H specification. The Beckman SS-1 pH meter and electrodes used for these analyses were calibrated prior to each series of TAN determinations using Fisher Certified buffer solutions. The normality of the potassium hydroxide/isopropanol was determined by titrating a series of weighed samples of potassium acid phthalate certified by the National Bureau of Standards (NBS). The flash points shown in Table 9 are Cleveland Open Cup flash points, determined with the procedure described in ASTM D92.
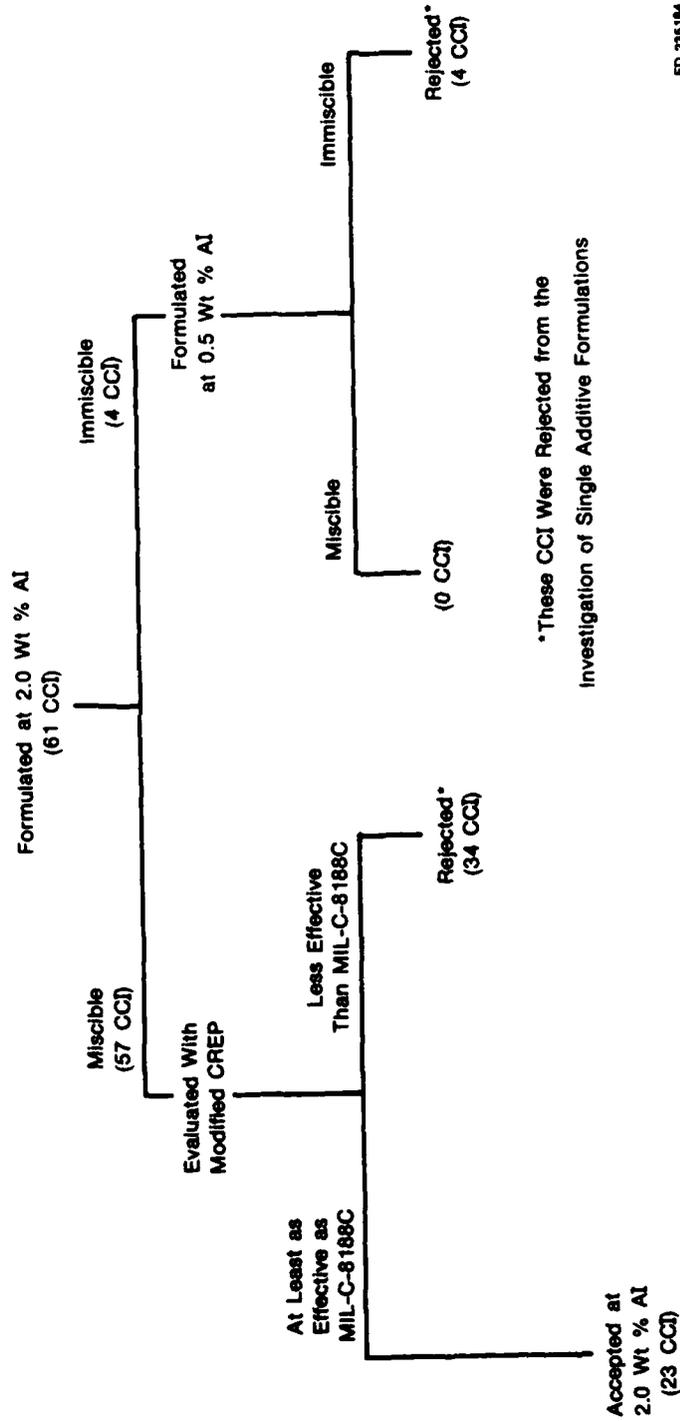
Figure 11. Miscibility/Corrosion Rate Test Results After Screening 61 Candidate Corrosion Inhibitors with the Corrosion Rate Evaluation Procedure

TABLE 9.
DATA FOR THE MOST PROMISING CORROSION INHIBITOR FORMULATIONS AT A 2.0 Wt % ACTIVE INGREDIENT CONCENTRATION IN MOBIL MIL-L-7808H, QPL 15F-1, LOT 72

Corrosion Inhibitor	Mean Corrosion Rate, (mg/hr)	Total Acid Number, (mgKOH/g)	Flash Point (°C(°F))
1. MIL-L-7808H, 15F-1	20.5	0.10	214(417)
2. PWL 80-20	0.2	5.71	200(392)
3. PWL 80-32	0.4	7.50	212(414)
4. PWL 80-29	1.8	4.79	214(417)
5. PWL 80-25	3.1	4.97	208(406)
6. PWL 80-22	3.1	4.36	156(313)
7. PWL 81-7	3.2	4.78	212(414)
8. PWL 81-18	3.3	2.34	208(406)
9. PWL 80-23	4.8	4.84	152(306)
10. PWL 81-21	5.6	3.36	208(406)
11. PWL 81-13	6.4	3.53	214(417)
12. PWL 80-14	7.6	1.34	—
13. PWL 80-64	7.8	2.40	188(370)
14. PWL 80-7	8.2	0.97	—
15. PWL 81-20	8.7	2.06	216(421)
16. PWL 81-15	10.0	4.70	208(406)
17. PWL 80-8	10.8	0.31	—
18. PWL 80-12	11.3	1.00	214(417)
19. PWL 80-10	11.4	0.12	216(421)
20. PWL 80-42	11.4	3.32	170(338)
21. PWL 81-19	11.5	2.86	200(392)
22. PWL 80-11	12.3	0.26	—
23. PWL 81-35	12.9	2.13	218(424)
24. PWL 80-2	13.2	0.50	—

As shown by the data in Table 9, the most promising single additive formulations had TAN over an order of magnitude greater than the MIL-L-7808H specification requirement of 0.3 mg KOH/g. In addition, several formulations had flash points less than the 204°C (400°F) minimum specified by MIL-L-7808H. Foaming tests conducted during the first phase of the program on formulations of 2.0 wt % PWL 80-2, 80-7, 80-14, 80-20, and 80-22 indicated excessive foaming propensities for these formulations (Reference 15).

Technical correspondence with corrosion inhibitor manufacturers and specialists indicated that synergism had been observed in various applications of sulfonate/organic acid and sulfonate/ester combinations. Since sulfonates at 2.0 wt % exhibited excessive foaming and organic acid type inhibitors at 2.0 wt % exhibited excessive TAN, a series of preliminary tests was conducted on two-additive formulations to achieve a lower TAN and foaming propensity, while maintaining superior corrosion protection. Three different sulfonates were selected for this preliminary investigation: a dinonylnaphthalene sulfonate (PWL 81-27), a mineral oil sulfonate (PWL 80-30), and an alkylbenzene sulfonate (PWL 80-10). These sulfonates were evaluated in combinations with several of the more promising organic acids, esters, and amine salts of organic acids. The mean corrosion rates from one test in the CREP are presented in Table 10, in addition to the TAN of each formulation.

TABLE 10.
CORROSION RATE DATA FOR CANDIDATE TWO-ADDITIVE FORMULATIONS
IN MOBIL MIL-L-7808H, QPL 15F-1, LOT 72

Corrosion Inhibitor and Wt % Active Ingredients (AI)	Mean Corrosion Rate, (mg/hr)	Total Acid Number, (mgKOH/g)
1. 1.5% AI PWL 81-27 + 0.5% AI PWL 80-20	0.5	1.87
2. 0.75% AI PWL 81-27 + 0.25% AI PWL 80-20	1.7	0.91
3. 0.75% AI PWL 81-27 + 0.1% AI PWL 80-20	9.2	0.59
4. 1.5% AI PWL 81-27 + 0.5% AI PWL 80-32	3.0	2.00
5. 0.75% AI PWL 81-27 + 0.25% AI PWL 80-32	6.0	1.16
6. 0.75% AI PWL 81-27 + 0.1% AI PWL 80-32	8.2	0.69
7. 1.5% AI PWL 81-27 + 0.5% AI PWL 80-25	5.1	1.80
8. 0.75% AI PWL 81-27 + 0.25% AI PWL 80-25	8.0	0.79
9. 0.75% AI PWL 81-27 + 0.1% AI PWL 80-25	17.8	0.55
10. 1.5% AI PWL 81-27 + 0.5% AI PWL 81-18	8.1	0.99
11. 0.75% AI PWL 81-27 + 0.25% AI PWL 81-18	11.3	0.64
12. 1.5% AI PWL 81-27 + 0.5% AI PWL 81-21	6.9	1.09
13. 0.75% AI PWL 81-27 + 0.25% AI PWL 81-21	12.8	0.70
14. 1.5% AI PWL 80-30 + 0.5% AI PWL 80-20	10.8	1.48
15. 1.5% AI PWL 80-30 + 0.5% AI PWL 80-32	10.8	1.74
16. 1.5% AI PWL 80-30 + 0.5% AI PWL 80-25	15.1	1.04
17. 1.5% AI PWL 80-30 + 0.5% AI PWL 81-18	11.7	1.06
18. 1.5% AI PWL 80-30 + 0.5% AI PWL 81-21	9.3	1.43
19. 1.5% AI PWL 80-10 + 0.5% AI PWL 80-20	6.6	1.47
20. 1.5% AI PWL 80-10 + 0.5% AI PWL 80-25	8.9	1.41
21. 1.0% AI PWL 81-32 + 1.0% AI PWL 80-8	13.2	0.36
22. 1.0% AI PWL 81-32 + 1.0% AI PWL 80-2	13.2	0.89
23. 1.0% AI PWL 81-32 + 1.0% AI PWL 80-30	13.9	—
24. 1.0% AI PWL 81-32 + 1.0% AI PWL 81-27	17.1	0.47
25. 1.0% AI PWL 81-38 + 1.0% AI PWL 81-42*	22.9	—

*Supplied by Air Force as MLO 81-250

The preliminary test results in Table 10 indicated a possible synergism between the barium dinonylnaphthalene sulfonate (PWL 81-27) and a mixture of organic acids (PWL 80-20). A series of tests was run to substantiate these data. Figure 12 illustrates the synergism of these two additives in the environment of the CREP. The mean corrosion rate of the combination of 0.5 wt % PWL 81-27 + 0.5 wt % PWL 80-20 was significantly lower than either the 1.0 wt % PWL 81-27 or 1.0 wt % PWL 80-20. Each formulation was evaluated in four corrosion tests. The highest and lowest corrosion rate for each formulation was deleted and the mean and standard deviation were calculated for the remaining six. Figure 12 shows the mean ± one standard deviation for each formulation.

The preliminary results shown in Table 10 were promising in that several very effective inhibitor combinations were found with a significant reduction of the TAN. However, the TAN were still in excess of the 0.30 mg KOH/g maximum specified by MIL-L-7808H. One of the major concerns with high acid numbers arises from the fact that some acids will cause corrosive wear of various engine components during high temperature engine operations. Therefore, a series of preliminary corrosion and oxidation stability (COS) tests was conducted to evaluate the effect of representative samples of the more promising high acid number formulations on typical engine component metals and on the thermal and oxidative stability of the matrix oil.
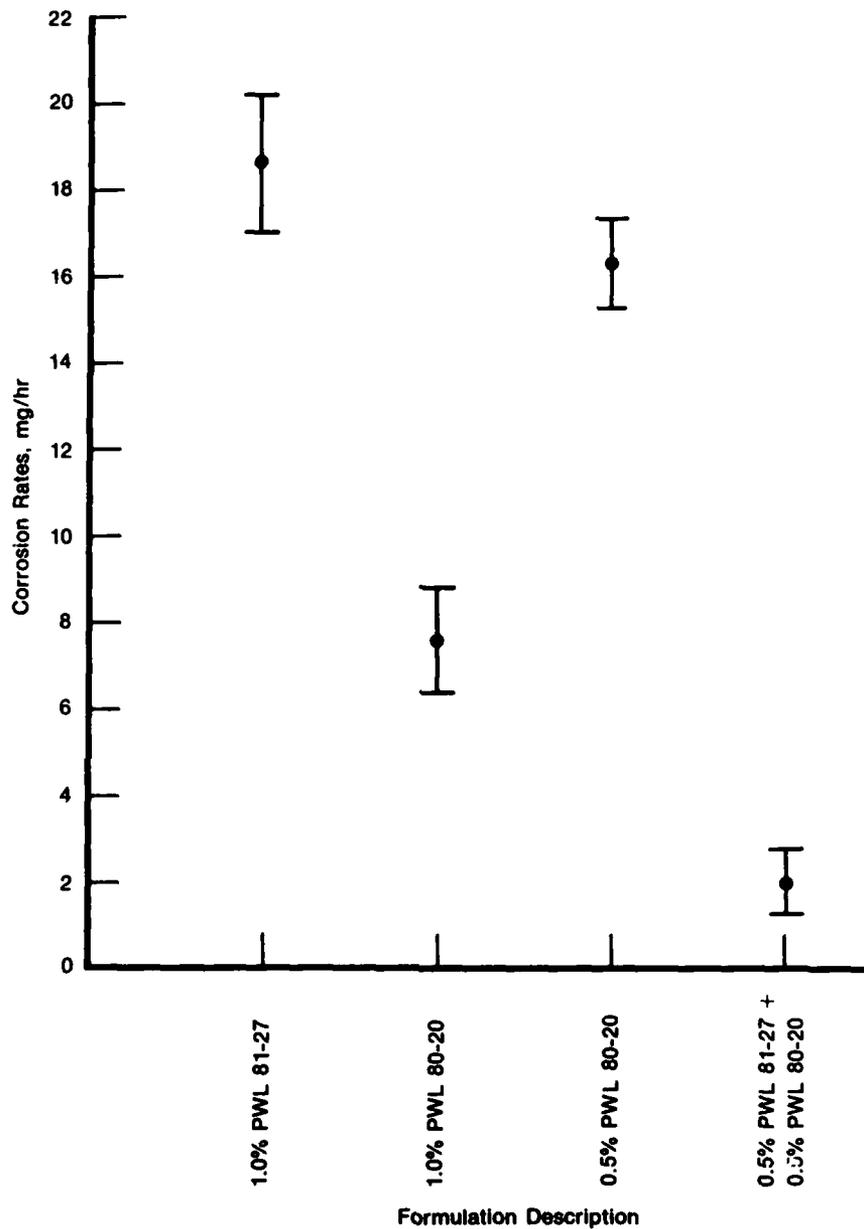
Figure 12. Corrosion Rate Data Exhibiting Synergism in One of the Most Promising Two-Additive Combinations

The COS tests were conducted in accordance with MIL-L-7808H, employing Federal Test Method (FTM) 5307.1 The alternate test procedure specified in FTM 5307.1 was used with an air flowrate of 10 ± 1 liter/hour, an oil temperature of 200°C (392°F), and a residence time of 48 hours. Table 11 shows the data generated during evaluations of the MIL-L-7808H matrix oil and the five representative candidate formulations. As shown by these data, the excessive TAN resulting from 2.0 wt % of an alkenyl succinic acid (PWL 80-32) or 2.0 wt % of an alkenyl

33

succinic acid-hydroxy alkyl ester (PWL 80-29) caused no more corrosive wear to metal specimens than the matrix oil. The formulation containing 2.0 wt % of a potassium salt of an alkylbenzene sulfonate exhibited a very significant increase in TAN and viscosity during the 48-hour test. The formulation containing 2.0 wt % of an amine salt of alkenyl succinic acid generated an excessive amount of sludge, but exhibited no excessive corrosive attack on metal specimens. The two-additive combination containing 0.75 wt % of barium dinonylnaphthalene sulfonate and 0.25 wt % of organic acids exhibited data similar to that of the matrix oil except that it produced a small amount of sludge during the thermal stressing.

At this point in the program, a complete review of the data with the AFWAL/MLBT Program Manager resulted in the establishment of a secondary target value for the TAN of candidate corrosion inhibiting oil formulations. A maximum TAN of 2.0 mg KOH/g was established, and a maximum of 4.3 mg KOH/g for the TAN after a 48-hour COS test at 200°C (392°F). The post-COS maximum was based on the MIL-L-7808H requirements for initial TAN, and the change in TAN during a 48-hour COS test, which are 0.30 and 4.0 mg KOH/g, respectively. In addition, these technical discussions resulted in the development of a test matrix for a more in-depth investigation of potential synergistic combinations of the more promising corrosion inhibitors. The data presented in Table 10 indicated a potential synergism between some sulfonate inhibitors with organic acids and their derivatives. Previous data, however, had demonstrated that some sulfonates increased the propensity for foaming of MIL-L-7808H oils (Reference 15). Therefore, the first phase of the test matrix involved screening the more promising sulfonates on the basis of their foaming characteristics at 0.75 wt % in MIL-L-7808H.

Eleven sulfonate inhibitors were evaluated in the static foam test procedure defined in FTM-3213 to determine their effect on the foaming propensity of the matrix oil, MIL-L-7808H, QPL 15F-1. These sulfonates included mineral oil sulfonates, monovalent and divalent alkylbenzene sulfonates, and dinonylnaphthalene sulfonates. Technical conversations with inhibitor manufacturers with regard to the sludge generation in the 48-hour COS test resulted in the acquisition of two additional sulfonates believed to have greater high temperature stability. These included a basic barium dinonylnaphthalene sulfonate (PWL 81-26) and a carbonated calcium dinonylnaphthalene sulfonate (PWL 81-30). These sulfonates were also evaluated in the static foam test. The results of these foaming tests are presented in Table 12. Five of the sulfonates were rejected on the basis of their excessive foaming characteristics. Subsequent review of the data in Table 10 resulted in the rejection of PWL 80-30 since there was no apparent synergism with the more promising corrosion inhibitors comprised of organic acids or organic acid derivatives. The remaining five sulfonates, PWL 80-11, 80-12, 81-25, 81-26 and 81-27, were selected for more in-depth analyses of corrosion inhibition in two-additive combinations.

TABLE 11.
CORROSION AND OXIDATION STABILITY TEST DATA FOR REPRESENTATIVE CORROSION INHIBITORS IN MOBIL MIL-L-7808H, QPL 15F-1 AFTER 48 HOURS AT 200°C

Formulation Description Wt. % Active Ingredient (Al)	Change In Viscosity, % 37.8°C (100°F)	98.9°C (210°F)	Total Acid Number, mg KOH/g Before	After	Change	Sludge, % by Volume	Metal Specimen Weight Change, mg/cm² Al ±0.20	Ag ±0.20	Bz ±0.40	Fe ±0.20	M-50 ±0.20	Mg ±0.40	Ti ±0.20
MIL-L-7808H Specification Requirements	−5 to 25	Report	0.30 Max	Report	4.0 Max	Report							
1. MIL-L-7808H, QPL 15F-1	10.1	6.7	0.11	2.52	2.41	0.0	+0.01	−0.05	+0.01	+0.02	+0.02	+0.01	0.00
2. 2.0% Al PWL 80-32	6.4	5.5	8.71	6.14	−2.57	0.0	+0.01	−0.04	−0.01	+0.02	+0.01	0.00	+0.01
3. 2.0% Al PWL 80-29	9.1	6.5	5.69	5.18	−0.51	0.0	0.00	−0.03	−0.02	+0.01	0.00	0.00	0.00
4. 2.0% Al PWL 80-10	29.1	23.6	0.10	3.82	+3.72	0.8	+0.02	−0.15	−0.04	+0.01	+0.02	+0.01	+0.01
5. 2.0% Al PWL 81-21	12.4	9.4	3.36	3.08	−0.28	2.4	+0.01	0.00	−0.08	0.00	+0.01	+0.02	+0.01
6. 0.75% Al PWL 81-27 + 0.25% Al PWL 80-20	11.1	8.5	0.91	2.89	+1.98	0.6	+0.02	−0.06	−0.06	+0.02	+0.01	+0.02	+0.01

TABLE 12.
STATIC FOAM TEST DATA FOR CANDIDATE
SULFONATE-TYPE CORROSION INHIBITORS
AT A 0.75 Wt % ACTIVE INGREDIENT
CONCENTRATION IN MOBIL MIL-L-7808H,
QPL 15F-1, LOT 72

	Corrosion Inhibitor	Maximum Foam Volume (ml)	Collapse Time, (sec)
1.	PWL 81-25	10	3
2.	PWL 81-26	10	3
3.	PWL 81-27*	20	7
4.	PWL 80-11	15	4
5.	PWL 80-12	30	13
6.	PWL 80-30	25	4
7.	PWL 80-14	90	20
8.	PWL 80-6	115	38
9.	PWL 80-8	115	22
10.	PWL 80-10	200	48
11.	PWL 81-30	305	31

* Evaluated at 1.0 Wt % active ingredient.

The next phase of the test matrix involved blending each of the five sulfonate inhibitors in two-additive combinations with six of the most promising acidic corrosion inhibitors. On the basis of test data in Table 10, a 0.75 wt % sulfonate plus 0.25 wt % organic acid or organic acid derivative was selected for this investigation. A total of 30 candidate formulations were blended and tested in the CREP defined in Appendix B. One corrosion test was conducted on each formulation. All formulations resulting in mean corrosion rates less than 10.2 mg/hr after one test were evaluated in three additional tests to verify their effectiveness. A corrosion rate of 10.2 mg/hr is the lower bound of the 95% confidence interval for corrosion rates of test coupons protected by MIL-C-8188C. Consequently, a corrosion rate less than 10.2 mg/hr is lower than 95% of the corrosion rates generated with MIL-C-8188C. The results of these tests are shown in Table 13. All five sulfonates were found to be very effective when evaluated in combination with the alkenyl succinic acid (PWL 80-32) and the mixture of organic acids (PWL 80-20).

TABLE 13.
CORROSION RATE DATA FOR CANDIDATE
TWO-ADDITIVE FORMULATIONS IN MOBIL
MIL-L-7808H, QPL 15F-1, LOT 72

Formulation Number*	Number of Data Points	Mean Corrosion Rate, (mg/hr)
1. PWL 82-18	8	5.3
2. PWL 82-12	8	6.7
3. PWL 82-6	8	6.7
4. PWL 82-13	8	7.4
5. PWL 82-19	8	8.3
6. PWL 82-23	8	8.7
7. PWL 82-22	8	8.8
8. PWL 82-20	8	8.8
9. PWL 82-7	8	9.2
10. PWL 82-21	8	9.6
11. PWL 82-25	8	9.6
12. PWL 82-44	2	10.4
13. PWL 82-41	2	10.4
14. PWL 82-42	2	10.6
15. PWL 82-34	8	10.8
16. PWL 82-37	8	11.0
17. PWL 82-30	2	11.3
18. PWL 82-40	2	11.8
19. PWL 82-33	2	11.8
20. PWL 82-39	2	12.2
21. PWL 82-26	6	12.2
22. PWL 82-38	2	12.4
23. PWL 82-29	2	12.6
24. PWL 82-43	2	13.3
25. PWL 82-36	2	14.7
26. PWL 82-35	2	15.0
27. PWL 82-27	2	15.1
28. PWL 82-32	2	15.6
29. PWL 82-28	2	15.6
30. PWL 82-31	2	16.0

* These formulations are various two-additive combinations of the five more
promising sulfonate type inhibitors with six of the most effective high acid
number inhibitors. See Appendix D for formulation descriptions.

Because the large number of tests necessary to conduct a test matrix of two-additive combinations, only the most promising combinations were evaluated in further investigations. Based on preliminary tests indicating synergism involving a dinonylnaphthalene sulfonate and organic acid combination, the three dinonylnaphthalene sulfonates (PWL 82-25, PWL 82-26, PWL 82-27), were subsequently evaluated in two-additive combinations with four of the most promising corrosion inhibitors. These formulations contained 0.5 wt % sulfonate plus 0.5 wt % of an organic acid or organic acid derivative. All twelve formulations exhibited corrosion inhibition superior to that of MIL-C-8188C. The results of these tests are shown in Table 14. These twelve formulations and the 10 most promising formulations listed in Table 13 were retained for screening in physical and chemical property tests.

TABLE 14.
CORROSION RATE DATA FOR TWO-ADDITIVE FORMULATIONS WITH EQUAL CONCENTRATIONS OF THE MOST PROMISING CORROSION INHIBITORS IN MOBIL MIL-L-7808H, QPL 15F-1

Formulation Number*	Number of Data Points	Mean Corrosion Rate, (mg/hr)
1. PWL 82-8	8	1.4
2. PWL 82-14	8	1.7
3. PWL 82-2	8	2.1
4. PWL 82-15	8	2.3
5. PWL 82-9	8	2.6
6. PWL 82-3	8	3.4
7. PWL 82-11	8	6.3
8. PWL 82-5	8	6.6
9. PWL 82-4	8	6.8
10. PWL 82-16	8	6.9
11. PWL 82-17	8	7.5
12. PWL 82-10	8	7.6

* These formulations are various two-additive combinations of naphthalene sulfonates with four of the more promising organic acid/ester type inhibitors. See Appendix D for formulation descriptions.

In order to verify the compatibility and effectiveness of the more promising two-additive combinations in various qualified MIL-L-7808H lubricants, three of the most promising two-additive combinations were evaluated in MIL-L-7808H lubricants having QPL designations 11E-1 and 15E-1. Two corrosion tests were conducted on each formulation. As shown in Table 15, all three two-additive combinations provided excellent protection in the various qualified lubricants. The uninhibited qualified lubricants exhibited approximately equal corrosion rates in these tests. Figure 13 illustrates the protection provided by these two-additive combinations relative to MIL-C-8188C and uninhibited MIL-L-7808H (QPL 15F-1) in the environment of the CREP.

TABLE 15.
CORROSION RATE DATA FOR THREE OF THE MOST PROMISING TWO-ADDITIVE FORMULATIONS IN THREE DIFFERENT MIL-L-7808H QUALIFIED LUBRICANTS

Corrosion Inhibitors, Wt % Active Ingredient	MIL-L-7808H, QPL Designation	Mean Corrosion Rate,* (mg/hr)
No corrosion	15F-1	20.5
inhibitors	15E-1	21.7
	11E-1	20.6
0.5% PWL 81-26 +	15F-1	1.4
0.5% PWL 80-20	15E-1	2.0
	11E-1	0.9
0.5% PWL 81-26 +	15F-1	2.6
0.5% PWL 80-32	15E-1	2.0
	11E-1	1.6
0.5% PWL 81-26 +	15F-1	6.3
0.5% PWL 80-25	15E-1	7.8
	11E-1	4.7

*Mean corrosion rates represent the mean of four test coupons for each formulation.

Vapor   PWL 82-1   PWL 82-8   PWL 82-9   PWL 82-10   PWL 82-24
Blasted   (MIL-L-7808H)   (MIL-C-8188C)
Coupon

FE247390

Figure 13. AISI-1010 Test Coupons After One Hour Residence Time in Environment of the Corrosion Rate Evaluation Procedure

To further substantiate the effectiveness of candidate corrosion inhibiting engine oils developed with the CREP, eight representative samples were selected for evaluation in the HCCT. The eight representative samples were selected from the 22 most promising two-additive formulations. In addition, samples of MIL-L-7808H and MIL-C-8188C were evaluated in this investigation. The HCCT were conducted at Phoenix Chemical Laboratories using the procedure defined in MIL-C-8188C with the exception of using three test coupons instead of five, and a 480-hour residence time instead of the 144-hour residence time specified in MIL-C-8188C. Table 16 shows the data generated in HCCT and CREP analyses of these formulations. As shown by these data, all of the representative samples provided excellent protection in the environments of both the CREP and the HCCT.

39

TABLE 16.
CORROSION TEST DATA FOR REPRESENTATIVE SAMPLES
OF THE MORE PROMISING CORROSION INHIBITING
OIL FORMULATIONS

Formulation Number[a]	CREP[b] Mean Corrosion Rate ± One Sigma (mg/hr)	HCCT[c] Hours to Failure In 480-hr test		
1. PWL 82-8	1.3 ± 0.5	Pass	Pass	Pass
2. PWL 82-18	5.2 ± 2.5	Pass	Pass	Pass
3. PWL 82-5	6.4 ± 1.4	312	Pass	Pass
4. PWL 82-12	7.0 ± 1.5	Pass	Pass	Pass
5. PWL 82-16	6.9 ± 1.7	Pass	Pass	Pass
6. PWL 82-13	7.2 ± 2.0	Pass	Pass	312
7. PWL 82-22	8.8 ± 0.9	Pass	Pass	Pass
8. PWL 82-20	9.0 ± 1.1	Pass	Pass	Pass
9. PWL 82-24 (MIL-C-8188C)	13.3 ± 1.6	480	Pass	Pass
10. PWL 82-1 (MIL-L-7808H)	20.5 ± 1.9	72	72	72

a. See Appendix D for formulation descriptions
b. These tests were conducted in accordance with the Corrosion Rate Evaluation Procedure (CREP) defined in Appendix B.
c. Humidity Cabinet Corrosion Tests (HCCT) were conducted in accordance with MIL-C-8188C, except that three test coupons were used instead of five and the residence time was extended to 480 hours.

The next phase of the investigation involved evaluating the physical and chemical properties of the more promising formulations to verify their conformance with the target values listed in Table 1 of this report. Table 17 lists the Cleveland Open Cup flash points, TAN, and foaming propensities of the candidate formulations. The test procedures employed in these evaluations were presented in Table 1. All 22 candidate formulations conformed to the MIL-L-7808H specification requirements for flash point and foaming propensities. The MIL-C-8188C, however, overfoamed with greater than 350 ml of foam during the first three minutes of the test. The TAN ranged from 0.78 to 1.94 mg KOH/g for the more promising formulations, all less than the secondary target value of 2.0 mg KOH/g maximum.

Kinematic viscosities were determined at 98.9°C (210°F) for all 22 formulations, and at 37.8°C (100°F) and −53.9°C (−65°F) for representative samples. These data are shown in Table 18. Kinematic viscosities at 37.8 and 98.9°C (100 and 210°F) were determined at P&WA/GPD in a constant temperature viscometer bath according to the procedure described in ASTM D445. All viscometers were previously calibrated with stable Newtonian calibration fluids with viscosities traceable to the NBS. All formulations conformed to the specification requirements for kinematic viscosity at 98.9°C (210°F), which stipulates a minimum of 3.0 centistokes (cSt). The viscosities at −53.9°C (−65°F) were determined at WPAFB using the procedure defined in ASTM D2532. All samples tested conformed to the MIL-L-7808H requirement for kinematic viscosity after 35 minutes, 3 hours and 72 hours at −53.9°C (−65°F).

TABLE 17.
PROPERTIES OF THE MOST PROMISING CORROSION INHIBITING OIL FORMULATIONS BLENDED WITH MOBIL MIL-L-7808H, QPL 15F-1, LOT 104

Formulation Number*	Mean Corrosion Rate ± One Sigma, (mg/hr**)	Flash Point (°C(°F))	Foaming Propensity Foam Volume/Collapse Time, (ml/sec)	Total Acid Number, (mgKOH/g)
MIL-L-7808H Specification Requirements	—	204(400) Minimum	100/60 Maximum	0.3 Maximum
1. PWL 82-1 (MIL-L-7808H)	20.5±1.9	222(432)	5/2	0.09
2. PWL 82-8	1.3±0.5	210(410)	15/7	1.43
3. PWL 82-14	1.6±0.4	212(414)	15/4	1.57
4. PWL 82-2	2.0±0.7	216(421)	15/4	1.53
5. PWL 82-15	2.4±0.7	218(424)	15/5	1.94
6. PWL 82-9	2.6±0.8	214(417)	15/5	1.81
7. PWL 82-3	3.3±1.8	214(417)	10/6	1.91
8. PWL 82-18	5.2±2.5	222(432)	15/4	1.00
9. PWL 82-5	6.4±1.4	214(417)	10/5	1.39
10. PWL 82-11	6.2±2.1	220(428)	10/6	1.26
11. PWL 82-4	6.7±1.6	218(424)	10/6	1.43
12. PWL 82-12	7.0±1.5	218(424)	15/5	0.78
13. PWL 82-16	6.9±1.7	216(421)	15/6	1.45
14. PWL 82-6	7.0±2.2	220(428)	35/5	0.92
15. PWL 82-13	7.2±2.0	222(432)	15/5	0.92
16. PWL 82-17	7.5±1.7	218(424)	15/5	1.44
17. PWL 82-10	7.7±1.6	218(424)	10/3	1.30
18. PWL 82-23	8.6±1.0	216(421)	25/16	1.13
19. PWL 82-7	9.0±0.6	216(421)	15/5	1.08
20. PWL 82-22	8.8±0.9	222(432)	15/12	0.88
21. PWL 82-19	8.3±1.7	222(432)	30/7	1.12
22. PWL 82-20	9.0±1.1	212(414)	45/10	0.90
23. PWL 82-21	9.8±0.5	216(421)	10/3	1.09
24. PWL 82-24 (MIL-C-8188C)	13.3±1.6	244(471)	Overfoam/39	0.11

* See Appendix D for formulation descriptions.
** Four tests were conducted on each formulation generating eight corrosion rates. The high and low corrosion rates were deleted and the mean and standard deviations were calculated for the remaining six.

TABLE 18.
KINEMATIC VISCOSITIES OF THE MORE PROMISING CORROSION INHIBITING OIL FORMULATIONS

Formulation Number*	37.8°C (100°F)	98.9°C (210°F)	−53.9°C (−65°F)		
			35 minutes	3 hr	72 hr
MIL-L-7808H Specification Requirements	Report	3.0 min	17,000 max	17,000 max	17,000 max
1. PWL 82-1	14.04	3.44	13,910	13,784	13,712
2. PWL 82-8	14.47	3.50	14,868	14,650	14,581
3. PWL 82-14	14.52	3.53	15,000	15,100	15,100
4. PWL 82-2	14.52	3.51	—	—	—
5. PWL 82-15	14.62	3.54	15,799	15,558	15,312
6. PWL 82-9	14.57	3.55	—	—	—
7. PWL 82-3	—	3.53	—	—	—
8. PWL 82-18	14.65	3.53	14,936	15,300	15,663
9. PWL 82-5	14.61	3.52	15,586	15,318	15,242
10. PWL 82-11	14.53	3.51	15,100	15,100	15,100
11. PWL 82-4	—	3.52	—	—	—
12. PWL 82-12	14.53	3.51	14,711	14,876	15,263
13. PWL 82-16	14.67	3.54	15,707	15,456	15,214
14. PWL 82-6	14.55	3.54	—	—	—
15. PWL 82-13	14.55	3.54	15,000	15,000	15,000
16. PWL 82-17	—	3.53	—	—	—
17. PWL 82-10	14.54	3.53	15,200	15,300	15,100
18. PWL 82-23	14.62	3.56	14,493	14,762	15,175
19. PWL 82-7	—	3.53	—	—	—
20. PWL 82-22	—	3.54	—	—	—
21. PWL 82-19	—	3.54	—	—	—
22. PWL 82-20	14.69	3.57	14,349	14,602	15,004
23. PWL 82-21	14.69	3.56	14,800	14,800	14,800
24. PWL 82-24	13.56	3.44	12,692	12,410	12,732

*See Appendix D for formulation descriptions.

SECTION V

EVALUATION OF THE CORROSION AND OXIDATION STABILITY AND OIL DEPOSITION RATINGS OF THE MOST PROMISING FORMULATIONS.

After completion of the physical and chemical property evaluations of the 22 most promising candidate corrosion inhibiting oil formulations, representative samples were screened in corrosion and oxidation stability (COS) tests. The most stable formulations were subsequently evaluated in the oil deposition test specified by MIL-L-7808H to evaluate their sludge and deposit forming tendencies.

Since the 22 most promising formulations were actually various combinations of nine different corrosion inhibitors, representative formulations were selected for screening in the COS tests at 200°C (392°F) for 48 hours. These tests were conducted in accordance with MIL-L-7808H requirements, employing the alternate test procedure defined in FTM-5307.1. An air flowrate of 10 ± 1 liters per hour was used in these tests. Preliminary COS tests were conducted on the qualified matrix lubricant without corrosion inhibitors (PWL 82-0 and PWL 82-1), and five representative formulations, each containing one of the five more promising sulfonates. The preliminary results indicated a tendency for sludge formation in formulations containing neutral barium dinonylnaphthalene sulfonate (PWL 81-27), calcium dinonylnaphthalene sulfonate (PWL 81-25) and calcium alkylbenzene sulfonate (PWL 80-12). No sludge was observed in post-test oil evaluations of formulations containing basic barium dinonylnaphthalene sulfonate (PWL 81-26) or lithium alkylbenzene sulfonate (PWL 80-11).

Subsequent tests were conducted on other promising formulations which verified the sludge forming tendencies exhibited in preliminary tests. The results of these evaluations are presented in Table 19. Six different two-additive formulations containing basic barium dinonylnaphthalene sulfonate (PWL 82-8, 82-9, 82-10, 82-11, 82-12 and 82-13) were evaluated in this investigation. None of these formulations exhibited sludge in post-test oil centrifugations. In contrast, all three formulations containing neutral barium dinonylnaphthalene sulfonate (PWL 82-2, 82-5 and 82-6) generated a small amount of sludge during the 48-hour COS tests. The three formulations containing calcium dinonylnaphthalene sulfonate (PWL 82-15, 82-16 and 82-18) also exhibited a small amount of sludge formation in addition to more significant increases in TAN and viscosity during the COS test. No sludge was observed in post-test evaluations of formulations containing lithium alkylbenzene sulfonate (PWL 82-20 and 82-21); however, a low concentration of sludge was exhibited by the formulation containing calcium alkylbenzene sulfonate (PWL 82-23). An excessive amount of sludge was generated in the COS evaluation of MIL-C-8188C.

Kinematic viscosities of all formulations were determined at 37.8°C(100°F) and 98.9°C (210°F) before and after the COS tests. As shown in Table 19, all of the formulations conformed to viscosity change requirements specified by MIL-L-7808H. Formulations containing the basic barium dinonylnaphthalene sulfonate exhibited a trend toward slightly lower viscosity changes than the MIL-L-7808H used as the matrix oil (PWL 82-1).

43

TABLE 19.

CORROSION AND OXIDATION STABILITY TEST DATA FOR THE MORE PROMISING CORROSION INHIBITING OIL FORMULATIONS AFTER 48 HOURS AT 200°C

Formulation Number*	Change In Viscosity, % 37.8°C (100°F)	Change In Viscosity, % 98.9°C (210°F)	Total Acid Number, mg KOH/g Before	Total Acid Number, mg KOH/g After	Total Acid Number, mg KOH/g Change	Sludge, % by Volume	Metal Specimen Weight Change, mg/cm²** Al	Ag	Bz	Fe	M-50	Mg	Ti
MIL-L-7808H Specification Requirements	-5 to 25	Report	0.30 Max	Report	4.0 Max	Report	±0.20	±0.20	±0.40	±0.20	±0.20	±0.40	±0.20
1. PWL 82-0 (MIL-L-7808H)	+10.1	+6.7	0.11	2.52	+2.41	0.0	+0.01	-0.05	+0.01	+0.02	+0.02	+0.01	0.00
2. PWL 82-1 (MIL-L-7808H)	+9.6	+6.7	0.09	2.59	+2.50	0.0	0.00	-0.03	0.00	+0.02	+0.01	0.00	0.00
3. PWL 82-8	+9.4	+6.9	1.43	2.63	+1.20	0.0	+0.01	-0.04	-0.05	-0.01	+0.01	-0.10	+0.01
4. PWL 82-9	+8.2	+5.6	1.81	2.46	+0.65	0.0	0.00	-0.04	-0.05	+0.01	+0.01	0.00	0.00
5. PWL 82-12	+8.7	+6.3	0.78	2.13	+1.35	0.0	+0.01	-0.05	-0.03	0.00	0.00	-0.08	0.00
6. PWL 82-13	+8.2	+5.9	0.92	2.29	+1.37	0.0	0.00	-0.04	-0.04	+0.01	+0.01	0.00	0.00
7. PWL 82-11	+8.0	+6.0	1.26	2.56	+1.30	0.0	0.00	-0.04	-0.06	+0.01	0.00	-0.01	0.00
8. PWL 82-10	+8.9	+5.7	1.30	2.70	+1.40	0.0	0.00	-0.05	-0.05	0.00	0.00	0.00	0.00
9. PWL 82-15	+10.9	+7.9	1.94	3.25	+1.31	0.5	+0.01	-0.03	-0.06	+0.02	+0.01	+0.01	+0.01
10. PWL 82-16	+10.3	+7.6	1.45	3.10	+1.65	0.4	+0.01	-0.04	-0.08	+0.02	+0.01	0.00	+0.01
11. PWL 82-18	+13.2	+9.9	1.00	3.19	+2.19	0.4	+0.01	-0.06	-0.07	0.00	+0.01	+0.01	0.00
12. PWL 82-2	+10.3	+8.3	1.53	2.69	+1.16	0.7	+0.02	-0.03	-0.04	+0.03	+0.01	+0.02	+0.01
13. PWL 82-5	+9.2	+6.8	1.39	2.84	+1.45	0.6	+0.02	-0.02	-0.06	+0.02	+0.01	+0.02	+0.01
14. PWL 82-6	+11.1	+8.5	0.91	2.89	+1.98	0.6	+0.02	-0.06	-0.06	+0.02	+0.01	+0.02	+0.01
15. PWL 82-20	+9.8	+7.6	0.90	2.65	+1.75	0.0	+0.01	-0.06	-0.03	+0.01	0.00	+0.01	+0.01
16. PWL 82-21	+10.2	+7.3	1.09	2.45	+1.36	0.0	+0.01	-0.10	-0.04	0.00	0.00	0.00	0.00
17. PWL 82-23	+11.5	+9.0	1.13	2.59	+1.46	0.8	+0.01	-0.07	-0.05	+0.01	0.00	0.00	+0.01
18. PWL 82-24 (MIL-C-8188C)	+4.2	+1.7	0.11	3.44	+3.33	4.2	+0.16	+0.14	+0.24	+0.17	+0.18	+0.03	+0.20

* See Appendix D for formulation descriptions.
** Metal weight changes indicated are before cathodic cleaning. Cathodic cleaning was necessary only with MIL-C-8188C samples.

Metal test coupons were polished with 240 and 400-grit silicon carbide paper, cleaned, dried and weighed to ±0.01 mg before each test. At the conclusion of the test, the test metals were removed from the oil, cleaned by swabbing with cotton saturated with hexane, immersed in boiling toluene, flash dried, immersed in boiling acetone, flash dried, and stored in a desiccator. After equilibrating to room temperature, the test coupons were reweighed to ±0.01 mg. There was no significant increase in corrosive wear of test coupons caused by the more promising additive combinations. Metal weight changes for the corrosion inhibiting formulations were approximately equal to those for the matrix oil. Cotton swabbing with hexane was sufficient for removing deposits from all formulations except MIL-C-8188C. The carbonaceous deposits on these coupons were removed by the cathodic cleaning procedure defined in FTM-5307.1. The metal weight increases shown in Table 19 were before cathodic cleaning of the test specimens. Cathodic cleaning removed all deposits so that test coupons exhibited little or no change from initial weights.

Since there is no specification requirement limiting the amount of sludge formation during COS tests, all formulations conformed to the MIL-L-7808H requirements for corrosion and oxidation stability. However, the formulations exhibiting no sludge formation were considered more promising and were retained for further evaluation in oil deposition and elastomer compatibility evaluations.

Oil deposition tests were performed at Alcor Inc. of San Antonio, Texas in accordance with the test procedure defined in FTM-5003.1. This test involved circulating a sample of lubricant through an aerated test chamber containing a heated aluminum coking tube. From the chamber the oil was circulated through a cooler, a 100-mesh stainless steel screen, a circulating pump and back into the chamber. After a 12-hour test at an input oil temperature of 149°C(300°F) and a coking tube temperature of 310°C(590°F), the deposit rating was determined by adding the number of grams of sludge collected on the filter screen to ten times the number of grams of coke collected on the aluminum coker tube. The kinematic viscosities of pretest and post-test oil samples were determined at 37.8°C (100°F), in addition to changes in TAN which occurred during the 12-hour test.

Oil deposition tests were conducted on all formulations which exhibited no sludge formation in the COS test. In addition, four formulations which had generated sludge in the COS tests were evaluated to determine their sludge and deposit forming tendencies under the dynamic conditions of the oil deposition test. The data from these tests, along with test data for MIL-L-7808H and MIL-C-8188C, are presented in Table 20. As shown by these data, all of the more promising formulations conformed to MIL-L-7808H specification requirements except PWL 82-18 and PWL 82-20. Based on the repeatability* of this test procedure, the failure of PWL 82-20 was considered to be questionable. Furthermore, PWL 82-21 has a composition very similar to that of PWL 82-20 and exhibited a deposit rating of only 1.13.

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* Two or more runs on the same oil in the same apparatus and by the same operator should not differ by more than 0.75 deposit rating (Reference 16).

TABLE 20.
OIL DEPOSITION DATA FOR REPRESENTATIVE SAMPLES OF
THE MOST PROMISING CORROSION INHIBITING OIL FORMULATIONS

Formulation Number*	Deposit Rating	Viscosity Change, %	TAN Change, mg KOH/g	Cooler Sludge	Oil Consumption, ml
MIL-L-7808H Specification Requirements	1.5 Max	Report	Report	Report	Report
1. PWL 82-1 (MIL-L-7808H)	0.50	100.7	10.83	Clean	50
2. PWL 82-13	0.17	22.8	6.20	Clean	75
3. PWL 82-11	0.26	16.6	5.75	Clean	100
4. PWL 82-8	0.50	24.4	5.03	Light	75
5. PWL 82-12	0.53	31.0	6.45	Clean	75
6. PWL 82-2	0.65	29.7	6.29	Light	50
7. PWL 82-10	0.77	36.6	9.41	Clean	100
8. PWL 82-9	0.80	13.0	3.99	Clean	75
9. PWL 82-22	0.95	30.1	8.97	Light	50
10. PWL 82-15	1.10	25.2	6.84	Light	50
11. PWL 82-21	1.13	30.6	8.25	Light	50
12. PWL 82-20	1.62	38.0	7.46	Light	75
13. PWL 82-18	2.90	23.1	7.99	Moderate	100
14. PWL 82-24 (MIL-C-8188C)	7.70	17.7	12.63	Heavy	75

*See Appendix D for formulation descriptions

SECTION VI

ELASTOMER COMPATIBILITY OF THE MORE PROMISING CANDIDATE
CORROSION INHIBITING ENGINE OILS

Concurrent with oil deposition evaluations, five of the most promising candidate formulations were subjected to the elastomer compatibility tests designated in the MIL-L-7808H specification. Selection of the five formulations (PWL 82-10, 82-11, 82-13, 82-18 and 82-20) was predicated on the relative corrosion protection, TAN, and COS data. In cases where two formulations containing the same corrosion inhibitors at different concentrations were considered, the formulation with the lower TAN was selected for elastomer compatibility tests. For example, PWL 82-9 and 82-13 contained different concentrations of basic barium dinonylnaphthalene sulfonate and alkenyl succinic acid. The TAN of PWL 82-9 and 82-13 were 1.81 and 0.92 mg KOH/g, respectively. The PWL 82-9 exhibited much better corrosion protection in the CREP, however, predicated on the present concern with high TAN, the PWL-82-13 was selected for further evaluations.

Formulations PWL 82-8 and 82-12 were not subjected to elastomer compatibility tests due to a precipitate formation during storage of these formulations. During evaluations of these additive combinations in a MIL-L-7808H having a QPL designation 11E-1, a small amount of precipitate was observed after 4 to 5 days storage. Subsequent examination of formulations containing these same additive combinations in a MIL-L-7808H with a QPL designation 15F-1 after approximately three months storage also revealed a small amount of sludge. The precipitate was isolated and evaluated by infrared spectrometry and electron microscopy to determine its composition. The precipitate was determined to be a salt formed from the reaction of metal ions present in the additive containing basic barium dinonylnaphthalene sulfonate (PWL 81-26) and organic acids present in the PWL 80-20.

It is interesting to note that no sludge was formed during high temperature COS tests of this additive combination, yet there was sludge formation during room temperature 25°C (77°F) storage for approximately three months. Conversely, combinations of neutral barium dinonylnaphthalene sulfonate (PWL 81-27) and the mixture of organic acids (PWL 80-20) exhibited sludge formation in the COS tests but no sludge during the three months storage at room temperature.

Elastomer compatibility tests were conducted at Alcor Inc. The H elastomer compatibility tests were performed with the test procedure described in FTM 3604.1, which involved determining the changes in volume of standard rubber specimens after a 168-hour immersion in the test formulations at 70°C (158°F). The FS and QVI elastomers were subjected to a 72-hour immersion in the test formulations at 150°C (302°F), and the FA elastomers were subjected to a 72-hour immersion at 175°C (350°F). Changes in tensile strength, elongation, hardness and volume were determined in accordance with FTM-3432. Table 21 lists the data generated in these tests to determine the compatibility of the four elastomer stocks with PWL 82-10, 82-11, 82-13, 82-18 and 82-20 relative to the MIL-L-7808H (PWL 82-1) used as the matrix oil. As shown by these data, all five of the corrosion inhibiting engine oil formulations conformed to elastomer compatibility requirements specified by MIL-L-7808H.

47

TABLE 21.

ELASTOMER COMPATIBILITY TEST DATA FOR MIL-L-7808H (QPL 15F-1) AND THE
MOST PROMISING CORROSION INHIBITING FORMULATIONS

Elastomer Types and Physical Properties	MIL-L-7808H Requirement	PWL 82-1*	PWL 82-10	PWL 82-11	PWL 82-13	PWL 82-18	PWL 82-20
H Elastomer Compatibility, 168 hr at 70°C							
Volume, % Change	12 min - 35 max	+24.4	+26.5	+25.8	+24.7	+26.2	+24.6
FA Elastomer Compatibility, 72 hr at 175°C							
Volume, % Change	2 min - 25 max	+12.4	+11.4	+12.0	+12.0	+11.7	+12.3
Tensile Strength, % Change	50 max	−18.4	−10.4	−21.6	−14.8	−14.0	−18.0
Elongation, % Change	50 max	0	+7.1	+8.6	+17.1	+4.2	+7.1
Hardness, Shore Durometer, No. Change	20 max	−5	0	−10	−10	−10	−10
FS Elastomer Compatibility, 72 hr at 150°C							
Volume, % Change	2 min - 25 max	+11.4	+10.7	+9.3	+11.6	+11.4	+11.1
Tensile Strength, % Change	50 max	−35.0	−31.7	−30.4	−43.3	−29.9	−28.1
Elongation, % Change	50 max	−12.7	−13.6	−10.9	−22.7	−6.4	−8.0
Hardness, Shore Durometer, No. Change	20 max	−5	0	−5	−5	−5	−10
QVI Elastomer Compatibility, 72 hr at 150°C							
Volume, % Change	2 min - 30 max	+15.8	+18.0	+16.0	+17.3	+18.0	+17.3
Tensile Strength, % Change	50 max	−25.5	−17.0	−16.3	−4.2	−40.4	−29.1
Elongation, % Change	50 max	−36.9	−9.2	+3.1	−13.8	−29.2	−16.9
Hardness, Shore Durometer, No. Change	20 max	−5	−10	−10	−5	−15	−10

*MIL-L-7808H, QPL 15F-1 used as matrix oil in blending formulations.

SECTION VII

BEARING DEPOSITION TEST

At this point in the program, a complete review of the data generated for potential corrosion inhibiting formulations led to the selection of one candidate fluid for evaluation in the bearing deposition test.

Technical conversations with the corrosion inhibitor suppliers during final evaluations of the most promising corrosion inhibitors revealed that two of the most promising corrosion inhibitors were in fact identical in composition. During the corrosion inhibitor acquisitions in September through November 1979, the supplier shipped P&WA/GPD two candidate additives, PWL 80-25 and 80-29, under different vendor identification numbers. During review of laboratory records in July of 1982, the supplier found that these two additives were synthesized by identical procedures and were, in fact, the same product. Subsequent review of P&WA/GPD data revealed that formulations containing these additives exhibited amply reproducible protection in the Corrosion Rate Evaluation Procedure (CREP). Data for single additive formulations of PWL 80-25 and 80-29 are shown in Tables 8 and 9. In addition, because of their excellent corrosion inhibiting properties, these additives were carried through investigations of two-additive formulations. Consequently, the following formulations are nearly identical in composition: PWL 82-4 and 82-5, 82-10 and 82-11, 82-16 and 82-17, 82-25 and 82-26, 82-29 and 82-30, 82-33 and 82-34, 82-37 and 82-38, and finally, 82-41 and 82-42. Referring to Tables 13 and 14 provides evidence for substantiation of the reproducibility of data generated with the CREP.

Formulation number PWL 82-13 was selected for evaluation in the bearing deposition test in accordance with the MIL-L-7808H specification. The selection of PWL 82-13 encompassed data from the accelerated corrosion tests in conjunction with physical property tests, corrosion and oxidation stability, oil deposition and elastomer compatibility evaluations of potential formulations.

The bearing deposition test was conducted by Alcor, Inc., of San Antonio, Texas, in accordance with the test procedure defined in Appendix 1A of the MIL-L-27502 specification. The test parameters were those described in the procedure with the exception of the following:

- Test-oil sump temperature: 177°C(350°F)
- Test bearing temperature: 260°C(500°F)

A summary of the demerit ratings for the various test components is provided in Table 22. As shown, the overall deposit demerit rating was 34.6. The changes in viscosity and total acid number (TAN) during the 48-hour test are listed in Table 23 and plotted in Figure 14. As shown in Figure 14, there was a sharp drop in TAN during the first four hours of the test, then a gradual increase throughout the remainder of the test. A comparison of the bearing deposition characteristics with the MIL-L-7808H specification requirements is provided in Table 24. As shown, the PWL 82-13 meets all the requirements specified by MIL-L-7808H for the bearing deposition test.

TABLE 22.
DEMERIT RATING SUMMARY FOR BEARING DEPOSITION TEST OF PWL 82-13

Item	Demerits	Factor	Rating
End Cover	1.8	1	1.8
Spacer and Nut	7.0	2	14.0
Heater-Mount Front	21.5	3	64.5
Heater-Mount Rear	25.2	3	75.6
Seal Plate	10.0	1	10.0
Test Bearing	8.4	5	42.0

Overall Rating = 207.9/6 = 34.6

TABLE 23.
PERFORMANCE OF PWL 82-13 IN THE BEARING DEPOSITION TEST

Elapsed Time (hrs)	Viscosity at 37.8°C(100°F) (cSt)	Viscosity Increase (%)	Total Acid Number (TAN) (mg KOH/g)
0.0	14.7	—	0.79
4.0	14.8	0.68	0.50
8.0	15.0	2.04	0.56
12.0	15.0	2.04	0.56
16.0	15.0	2.04	0.68
20.0	15.1	2.72	0.72
24.0	15.1	2.72	0.78
28.0	15.2	3.40	0.78
32.0	15.2	3.40	0.78
36.0	15.3	4.08	0.84
40.0	15.3	4.08	0.84
44.0	15.3	4.08	0.84
48.0	15.3	4.08	0.90

TABLE 24.
BEARING DEPOSITION CHARACTERISTICS OF PWL 82-13

Property	MIL-L-7808H Specification Requirements	PWL 82-13
Deposit Demerit Rating	60 max	34.6
Filter Deposits, g	2.0 max	0.49
Oil Consumption, ml	1440 max	400
Viscosity Change at 37.8°C, %	25 max	4.1
Total Acid Number Change, mg KOH/g	2.5 max	+0.11
Metal Weight Change, mg/cm^2		
Al	±0.2	0.000
Ag	±0.2	−0.040
Bz	±0.2	−0.099
Fe	±0.2	+0.079
M-50	±0.2	−0.099
WSP	±0.2	0.000
Ti	±0.2	+0.040
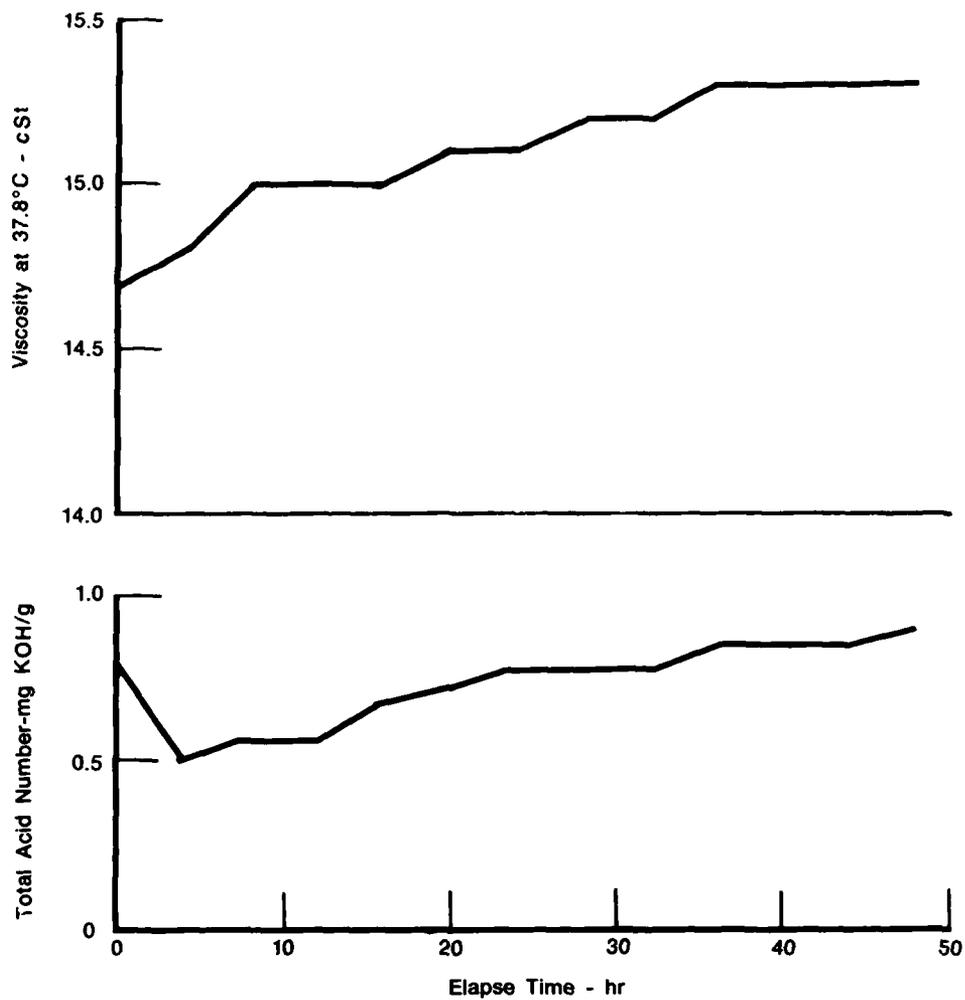
Figure 14. Plot of Viscosity and Total Acid Number Changes During Bearing
Deposition Test of PWL 82-13

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SECTION VIII

CONCLUSIONS

The Corrosion Rate Evaluation Procedure (CREP) developed in this program has demonstrated excellent potential as a screening test for use in selection of lubricant formulations to provide corrosion protection to gas turbine engine components. The CREP has exhibited a general correlation with the humidity cabinet corrosion test (HCCT) described in MIL-C-8188C and ASTM D1748. The more promising corrosion inhibiting oil formulations developed with the CREP exhibited excellent protection in the HCCT.

Some sulfonate inhibitors were shown to impart corrosion protection to steel coupons when evaluated at 2.0 wt % in qualified lubricants. In general, the alkylbenzene sulfonates exhibited a greater reduction in the corrosion rates of steel coupons in the CREP than mineral oil or naphthalene sulfonates. However, it was also demonstrated that a majority of the alkylbenzene sulfonate inhibitors increase the foaming propensity of the matrix lubricant.

In like manner, the alkylated dibasic acids and derivatives were found to be very effective corrosion inhibitors, forming very tenacious films which provided excellent protection in both the CREP and the HCCT. A concomitant increase in the total acid number (TAN) was observed in formulations containing the organic acid inhibitors. However, preliminary physical and chemical property and corrosion and oxidation stability tests indicated that the organic acid inhibitors may have no detrimental effect on the functional properties of the lubricating oil.

Several two-additive combinations were developed which impart corrosion inhibiting potential to qualifed MIL-L-7808H lubricants and are innocuous to the functional properties of the lubricating oil. The most promising formulation, PWL 82-13, has demonstrated corrosion protection superior to MIL-C-8188C oil, and conforms to all requisite properties for a MIL-L-7808H gas turbine engine oil except the total acid number. Table 25 provides a comparison of the properties of PWL 82-13 and a qualified MIL-C-8188C oil with the target properties established at the onset of the program.

Corrosion data generated in this program indicated a synergistic action between dinonylnaphthalene sulfonates and organic acids present in PWL 80-20 and 80-32. The combination of 0.5 wt % basic barium dinonylnaphthalene sulfonate (PWL 81-26) plus 0.5 wt % alkenyl succinic acid (PWL 80-32) which constitutes formulation number PWL 82-9 exhibited excellent corrosion protection, with no detrimental effect on the functional properties of the matrix lubricant. This formulation was not retained for elastomer compatibility and bearing deposition tests solely on the basis of its relatively high total acid number. However, predicated on the excellent corrosion protection and the physical property, COS, and oil deposition data, this formulation warrants futher consideration as a potential corrosion inhibiting gas turbine engine oil.

52

TABLE 25.
PROPERTIES OF PWL 82-13 AND MIL-C-8188C

Property	MIL-L-7808H Requirements	PWL 82-24 MIL-C-8188C, Lot 57	PWL 82-13
Kinematic viscosity, cSt			
a. 98.9°C (210°F)	3.0 min	3.44	3.54
b. −53.9°C (−65°F)			
@ 35 minutes	17,000 max	12,692	15,000
3 hr	17,000 max	12,410	15,000
72 hr	17,000 max	12,732	15,000
Flash point, °C (°F)	204 (400) min	244	222
Neutralization number (TAN)	0.30 max	0.11	0.92
Foaming characteristics (static)			
a. Foam volume, ml	100 max	Overfoam	15
b. Foam collapse time, sec	60 max	39	5
Evaporation loss @ 204°C (400°F), %	15 max*	—	10.4
Corrosion and oxidation stability @ 200°C (392°F) for 48 hr			
a. Change in viscosity, %	−5 to 25 max	+4.2	+8.2
b. Change in TAN, mg KOH/g	4.0 max	+3.33	+1.37
c. Sludge, Volume %	Report	+4.2	0.0
Oil deposit rating	1.5 max	7.70	0.17
Bearing deposition			
a. Overall deposit demerit rating	60 max	—	34.6
b. Change in viscosity, %	25 max	—	4.1
c. Change in TAN, mg KOH/g	2.5 max	—	0.11
d. Filter deposits, g	2.0 max	—	0.49
e. Oil consumption, ml	1440 max	—	400

* This is a Statement of Work (SOW) requirement. The MIL-L-7808H specification requirement is 30% maximum.

SECTION IX

RECOMMENDATIONS FOR FUTURE INVESTIGATIONS

The Corrosion Rate Evaluation Procedure (CREP) developed during this program should be employed in a round-robin investigation to determine the reproducibility of the data generated by different laboratories. This may lead to the development of variations in the procedure which effectuate improvements in both the repeatability and reproducibility of the test data. The pretest coupon surface preparation, post-test removal of oxides, and the method of controlling the refluxing rate of the solution are areas that should be addressed in future investigations of the CREP.

Selected samples of the most promising corrosion inhibiting engine oil formulations have been sent to the Naval Air Propulsion Center for evaluation in the Navy Ball Bearing Corrosion Test (Reference 4). These included aliquots of formulations assessed in the CREP and the humidity cabinet corrosion test (HCCT). The Ball Bearing Corrosion Test addresses a different corrosion mechanism than either the CREP or the HCCT, therefore these evaluations will provide valuable data with regard to the CREP and the corrosion inhibiting formulations developed in this program.

Based on the sludge formation observed for formulations PWL 82-8 and 82-12, long term storage stability tests should be conducted with other promising formulations. Furthermore, the excellent corrosion protection exhibited by the combination of dinonylnapthalene sulfonates and the mixture of organic acids in PWL 80-20 merits further investigative efforts to develop a combination which maintains the observed synergism yet remains stable under long term storage conditions.

Investigations should be conducted to determine the significance of high acid values brought about by the more promising corrosion inhibitors. The primary concerns regarding high acid values include control of the esterification process in the synthesis of ester based lubricants, control of the corrosion of engine component metals, and the large data base with regard to total acid number (TAN) as an indicator of the extent of lubricant oxidation. The preliminary data generated in this program in corrosion and oxidation stability (COS), oil deposition and bearing deposition tests shows no evidence of increased corrosivity or oxidative instability of formulations with high acid numbers resulting from the more promising corrosion inhibitors. As previously mentioned, PWL 82-13 was accepted over 82-9 solely on the basis of total acid number. Indeed, since exceptional corrosion protection is requisite for the intended application of the final formulation, the PWL 82-9 merits consideration for future bench and engine tests.

54

APPENDIX A.
A GENERAL DESCRIPTION OF THE ACTIVE INGREDIENTS OF
CANDIDATE CORROSION INHIBITORS

Inhibitor Number	Active Ingredient Description	Active Ingredient (Wt %)
PWL 80-1	Mixture of calcium sulfonate and polyglycol	31
PWL 80-2	Calcium sulfonate from mineral oil	40
PWL 80-3	Mixture of calcium sulfonate and calcium carbonate	30
PWL 80-4	Slightly basic calcium sulfonate from mineral oil	40
PWL 80-5	Morpholine sulfonate plus dialkyl benzene sulfonate	100
PWL 80-6*	Zinc sulfonate from alkylated (C_{30}) benzene	45
PWL 80-7*	Calcium sulfonate from alkylated (C_{30}) benzene	44
PWL 80-8*	Barium sulfonate from alkylated (C_{30}) benzene	46
PWL 80-9*	Magnesium sulfonate from alkylated (C_{30}) benzene	43
PWL 80-10*	Potassium sulfonate from alkylated (C_{45}) benzene	29
PWL 80-11*	Lithium sulfonate from alkylated (C_{45}) benzene	28
PWL 80-12*	Calcium sulfonate from alkylated (C_{45}) benzene	31
PWL 80-13*	Barium sulfonate from alkylated (C_{45}) benzene	31
PWL 80-14*	Calcium sulfonate from alkylated (C_{30}) benzene	44
PWL 80-15*	Barium sulfonate from alkylated (C_{30}) benzene	47
PWI 80-16*	Barium sulfonate from alkylated (C_{20}) benzene	30
PWL 80-17	Mixture of organic acids	75
PWL 80-18	Alkyl ammonium — alkyl acid phosphate	100
PWL 80-19	Amine neutralized organic acid	78
PWL 80-20	Mixture of organic acids	75
PWL 80-21	Alkyl ammonium — alkyl phosphate	80
PWL 80-22	Mixture of organic acid and organic acid phosphate	50
PWL 80-23	Mixture of alkyl succinic acids and esters	63
PWL 80-24	Amine, amide/imidazoline product from fatty acids	75
PWL 80-25**	Complex alkenyl succinic acid - hydroxy alkyl ester	63
PWL 80-26	Alkyl succinic acid plus hydroxylated alkyl phenol	89
PWL 80-27	Calcium sulfonate	40
PWL 80-28	Amine salt of an alkyl succinic acid	61
PWL 80-29**	Complex alkenyl succinic acid - hydroxy alkyl ester	63
PWL 80-30	Slightly basic calcium sulfonate	43
PWL 80-31	Sodium sulfonate	60
PWL 80-32	Alkenyl succinic acid	61
PWL 80-33	Phosphoric acid _ .	100
PWL 80-34	Zinc salt of a carboxylated alkyl phenol	54
PWL 80-35	High molecular weight alkyl succ ic acid	100
PWL 80-36	Hydroxylated alkyl phenol plus a zinc salt of a carboxylated alkyl phenol	60
PWL 80-37	Barium sulfonate	56
PWL 80-38	Barium sulfonate	51
PWL 80-39	Mixture of sulfurized alkyl phenol and alkyl succinic acid	82
PWL 80-40	Mixture of hydroxy ethyl alkyl phenol, sulfurized alkyl phenol, and alkyl succinic anhydri-le	82
PWL 80-41	Polycarboxylic acid salt of a fatty acid/polyamine reaction product	50
PWL 80-42	Mixture of polycarboxylic acids	50
PWL 80-43	Amine neutralized phosphoramidate/alkyl phosphate	80
PWL 80-44	Imidazoline	100
PWL 80-45	Cyclic amine salt of a polycarboxylic acid	63
PWL 80-46	Secondary amine	100
PWL 80-47	Secondary amine	100
PWL 80-48	Primary amine	100
PWL 80-49	Fluorinated carboxylic acid	100
PWL 80-50	Fluorinated quaternary ammonium salt	100
PWL 80-51	Fluorinated sulfonamide	100
PWL 80-52	Fluorinated alcohol	100
PWL 80-53	Polyalkoxylated fluorinated alcohol	100
PWL 80-54	Fluorinated carboxylic acid	100

55

APPENDIX A.
A GENERAL DESCRIPTION OF THE ACTIVE INGREDIENTS OF
CANDIDATE CORROSION INHIBITORS (Continued)

Inhibitor Number	Active Ingredient Description	Active Ingredient (Wt %)
PWL 80-55	Fluorinated alcohol	100
PWL 80-56	Fluorinated alcohol	100
PWL 80-57	Fluorinated sulfonamide	100
PWL 80-58	Fluorinated carboxylic acid	100
PWL 80-59	Polyamino-alcohol	20
PWL 80-60	Mixture of amine neutralized dimer acids and amine phosphate esters	50
PWL 80-61	Polyamino-alcohol	50
PWL 80-62	Polyamino-alcohol	50
PWL 80-63	Amine dimer	20
PWL 80-64	Amine phosphate ester	50
PWL 80-65	Amine neutralized dimer acid	60
PWL 80-66	Dimer acid	50
PWL 80-67	Mixture of amine neutralized dimer acid and phosphate esters	40
PWL 81-1	Mixture of oxygenated hydrocarbons and calcium sulfonate	100
PWL 81-2	Mixture of oxygenated hydrocarbons and barium sulfonate	100
PWL 81-3	Mixture of oxygenated hydrocarbons and sodium sulfonate	100
PWL 81-4	Mixture of oxygenated hydrocarbons and sodium sulfonate	100
PWL 81-5	Mixture of oxygenated hydrocarbons and sodium sulfonate	100
PWL 81-6	Mixture of oxygenated hydrocarbons and barium sulfonate	100
PWL 81-7	Alkyl dibasic acid derivative	70
PWL 81-8	Basic calcium sulfonate	29
PWL 81-9	Complex amine/amide	100
PWL 81-10	Complex imide	100
PWL 81-11	Alkylated phenolic compound	100
PWL 81-12	Complex acid ester	100
PWL 81-13	Alkenyl succinic anhydride/acid/ester	75
PWL 81-14	Alkenyl succinic anhydride/acid/ester	100
PWL 81-15	Complex acid ester	85
PWL 81-16	Imide acid	100
PWL 81-17	Complex imide acid	70
PWL 81-18	Amine salt of alkenyl succinic acid	83
PWL 81-19	Amine salt of alkenyl succinic acid	79
PWL 81-20	Amine salt of alkenyl succinic acid	63
PWL 81-21	Amine salt of alkenyl succinic acid	63
PWL 81-22	Alkenyl amidic acid salt	100
PWL 81-23	Alkenyl amidic acid salt	80
PWL 81-24	Complex ester/acid salt	80
PWL 81-25	Calcium dinonylnaphthalene sulfonate	50
PWL 81-26*	Basic barium dinonylnaphthalene sulfonate	52
PWL 81-27	Neutral barium dinonylnaphthalene sulfonate in mineral oil	50
PWL 81-28	Neutral barium dinonylnaphthalene sulfonate in DOS	50
PWL 81-29	Neutral barium dinonylnaphthalene sulfonate in PAO	50
PWL 81-30*	Carbonated basic calcium dinonylnaphthalene sulfonate	40
PWL 81-31	Zinc dinonylnaphthalene sulfonate	40
PWL 81-32	Pentaerythritol monooleate	100
PWL 81-33	Sorbotan monooleate	100
PWL 81-34	Mixture of barium dinonylnaphthalene sulfonate and trimer acid	50
PWL 81-35	Reaction product of carboxylic acid polyalkylene polyamine alkenyl succinic acid anhydride	48

APPENDIX A.
A GENERAL DESCRIPTION OF THE ACTIVE INGREDIENTS OF
CANDIDATE CORROSION INHIBITORS (Continued)

Inhibitor Number	Active Ingredient Description	Active Ingredient (Wt %)
PWL 81-36	Lead naphthenate + dioctyldiphenyl amine	90
PWL 81-37	Condensation product of primary cationic amine and fatty acid	100
PWL 81-38	Amine phosphate	100
PWL 81-39	Benzotriazole derivative	100
PWL 81-40	Substituted imidazoline	100
PWL 81-41	Mixture of high boiling substituted pyridines	100
PWL 81-42	Triphenylphosphorothionate	100

* The average length of the alkyl chains is indicated parenthetically.
** Through an error in cross-referring additives, the supplier inadvertently shipped two samples, PWL 80-25 and 80-29, which are identical in composition, but were assigned different identification numbers.

CORROSION RATE EVALUATION PROCEDURE FOR THE GRAVIMETRIC DETERMINATION OF THE RELATIVE CORROSION PROTECTION PROVIDED BY CORROSION INHIBITING ENGINE OILS

SCOPE

The following Corrosion Rate Evaluation Procedure (CREP) is used to determine the relative corrosion protection afforded by corrosion inhibiting MIL-L-7808H-type turbine engine lubricants.

SUMMARY OF METHOD

A vapor blasted, precleaned, preweighed metal coupon, conforming to the AISI-1010 specification requirements, is coated with the test oil formulation and suspended in a dust free environment for a 15-minute oil draining cycle. The test coupons are then suspended in the equilibrated $98 \pm 1°C$ vapor phase of the boiling acetic acid/sodium acetate buffer solution for a 60-minute residence time. At the end of this exposure cycle the metal coupons are cleaned, dried, and reweighed to ± 0.1 milligrams (mg) to determine the metal loss due to corrosive attack.

SIGNIFICANCE

The test procedure described herein has been used to determine the relative corrosion protection provided by various candidate corrosion inhibiting engine oils under the prescribed test conditions. Discrimination between oil formulations exhibiting very similar corrosion prevention properties may not be possible due to the present limitations in repeatability of test data. However, the procedure has been found to be a valuable screening device for the selection of lubricant formulations which show promise for use as corrosion inhibiting engine oils. No correlation has yet been established between test results and actual field service corrosion, although a general agreement has been established between relative corrosion protection ratings based on this procedure and those obtained using the humidity cabinet corrosion test described in MIL-C-8188C and ASTM D1748.

APPARATUS, MATERIALS, AND REAGENTS*

The following are used in this procedure:

- Reaction kettle[1], PYREX®, 2000 milliliters (ml) capacity, complete with cover having a finely ground flange for a tight seal. Each cover has one standard taper (ꕦ) 34/45 female joint in the center, and three ꕦ 24/40 female joints spaced 120 degrees apart with their centers 5.1 centimeters (cm) (2.0 inches (in.)) from the center of the cover.

- Bushing type reducing adapter,[2] male ꕦ 34/45 outer joint, female ꕦ 24/40 inner joint.

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* Numerical superscripts in this procedure refer to acceptable sources for apparatus materials and reagents listed at the end of this procedure.

- Allihn condenser,[3] water cooled, 40.0 cm (15.7 in.) jacket length, with a $\mathbb{S}$ 24/40 male joint to match the female joint of the 34/45 to 24/40 bushing type reducing adapter.

- Ace-Thred Offset Adapter,[4] with a No. 7 Ace-Thred, a threaded nylon bushing, and a Buna-N O-ring.

- Air injection tube,[5] borosilicate glass, 85.0 cm (33 in.) in length, 0.6 cm (0.24 in.) outside diameter (OD) with one end flared from 0.6 cm to 1.2 cm (0.24 to 0.47 in.) OD over a distance of 3 cm (0.12 in) at one end of the tube.

- Glass stopper with glass loop.[6] Hollow pennyhead stopper with glass loop fabricated from 0.3 cm (0.12 in.) OD glass rod; the distance from the base of the stopper to the base of the glass loop is 0.9 cm (0.35 in.).

- Perforated Teflon[®] splash suppressor, fabricated from 0.32 cm (0.125 in.) Teflon[®] sheet stock. Splash suppressor disk is 12.7 cm (5.0 in.) in diameter and perforated with 0.64 cm (0.25 in.) diameter holes in seven equally spaced rows, with the center row passing through the diameter.

- Metal test coupons,[7] AISI-1010 low carbon steel, 5.08 × 1.27 × 0.16 cm (2.00 × 0.50 × 0.063 in.). One 0.24 cm (0.094 in.) diameter hole is drilled 0.32 cm (0.125 in.) from one end of each coupon. All surfaces and edges are polished to a 10 to 20 microinch finish. The test coupons are then coated with a nonvolatile, water insoluble rust preventative and packaged in a moisture-proof package as specified in ASTM D1748, Appendix A1.10.2 – A1.10.3.

- Suspension wire, AMS 5680, stainless steel, 20 gage, cut and formed to the required geometrical configuration.

- Boiling beads, KIMAX®, (Kimble 13500), 0.3 cm (0.12 in.) diameter.

- Hot plate,[8] electric, Thermolyne Model SP-13115. Hot plates were modified by installing two chromel-alumel thermocouples in each hot plate. The thermocouples were fastened by drilling two holes through the aluminum plate beneath the ceramic cover and mounting with screw mounts so that the thermocouple junctions were in contact with the asbestos disc between the aluminum plate and heater coil. The thermocouples were positioned 180 degrees apart, 2.5 cm (1.0 in.) and 5.1 cm (2.0 in.) from the center of the metal plate. These thermocouples were then wired in parallel at the readout connector to obtain an average temperature.

- Air flowmeters,[9] Matheson mass flowmeters or rotometers have been found to be satisfactory.

- Metering valve for air flow control, Whitey Model 22RS4 or equivalent.

- Compressed dry air, Size A cylinder, complete with two stage regulator.

- Laboratory timer; Model 171 Universal Timer has been found to be satisfactory.[10]

- Analytical balance, readability 0.1 mg.

- Desiccator.[11]

- Microwipes[9].[12]

- Soft bristle brush, IBM Typewriter brush has been found to be satisfactory.

- Novaculite grit,[13] 200-grit powder used as abrasive for vapor-blasting AISI-1010 test coupons.

- Buffer Solution,[14] pH 4.63, acetic acid/sodium acetate, 0.1 molar total acetate.

- Toluene,[15] reagent grade, for cleaning test specimens.

- Acetone,[16] reagent grade, for cleaning test specimens.

- Methanol,[17] absolute, reagent grade.

- Dow Corning High Vacuum Grease,[18] or an equivalent inert silicone grease.

- Coupon draining chamber to provide dust free environment for oil draining cycle. A scaled-down version of the box described in ASTM D1748, Appendix A1.13 has been found to be satisfactory.

- Test coupon support for vapor-blasting test coupons.

TEST SPECIMEN PREPARATION

Corrosion test coupons are fabricated from open-hearth, killed, low carbon, No. 4 soft temper strip steel conforming to the specification requirements of AISI-1010. The coupon dimensions are 5.08 × 1.27 × 0.16 cm (2.0 × 0.5 × 0.06 in.), with one hole 0.24 cm (0.09 in.) in diameter drilled 0.32 cm (0.12 in.) from one end of the test coupon and centered across the width. Each coupon is identified using die-cut 0.32 cm (0.12 in.) numbers positioned immediately below the suspension hole. All surfaces and edges of the test coupons are polished to a 10 to 20 microinch finish so that faces are entirely free of pits, scratches or other imperfections. All surface grinding is in the direction parallel to the length of the coupon. The test coupons are then coated with a nonvolatile, water insoluble rust preventative and packaged in a moisture-proof package for shipment or storage.

After removing test coupons from protective packaging, all edges of the test coupons are vapor-blasted for 60 seconds using a 30 to 40 percent-by-volume 200-grit novaculite/water slurry as the abrasive medium. The vapor-blast nozzle is operated at a nozzle pressure of 620 kilopascals (kPa) (90 psi) and is held 20 to 25 cm (8 to 10 in.) from the coupon during surface preparation. After vapor-blasting the edges of six test coupons at a time, these coupons are then placed in the test coupon support shown in Figure B-1. The test coupons are secured at a 45-degree angle in the support and are vapor-blasted by moving the nozzle back and forth across the set of six coupon faces at an angle of 90 degrees to the support (45 degrees to the coupon) for 3 minutes. It is important to maintain the 90-degree angle, the nozzle pressure, and nozzle to coupon distance during surface preparation. After vapor-blasting both faces of the test coupons, the coupons are rinsed with water, air dried, and stored in a solution comprised of 50 parts toluene and 50 parts absolute methanol until final cleaning is accomplished by immersing each coupon in boiling toluene, flash drying, and immersing in boiling acetone and flash drying again. The test coupons are stored in a desiccator for 30 minutes to equilibrate to ambient temperature, then weighed to ± 0.1 mg prior to testing. Specimen cleanliness is maintained by handling with forceps.
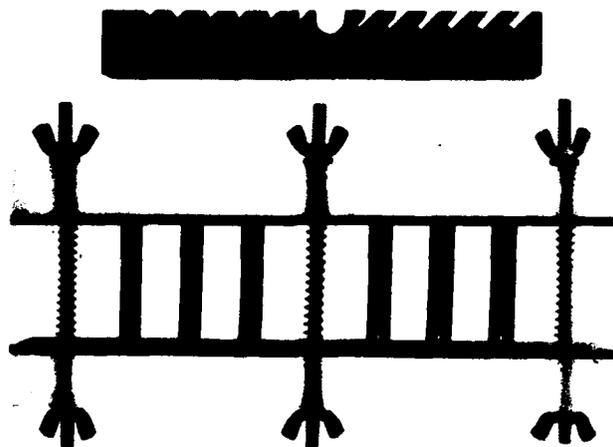
Figure B-1. Test Coupon Support Used for Vapor Blasting

REACTION KETTLE PREPARATION

Cleaning of the reaction kettle prior to test cycles is accomplished by first wiping both flanges of the assembly with Microwipes to remove residual silicone grease. The kettle, cover, stoppers and Teflon® splash suppressor are cleaned by washing with hot water and Alconox® detergent, followed by rinsing with deionized water. The assembly is then rinsed with acetone and dried by blowing with dry compressed air. The condensers are flushed with acetone and air dried prior to each test cycle.
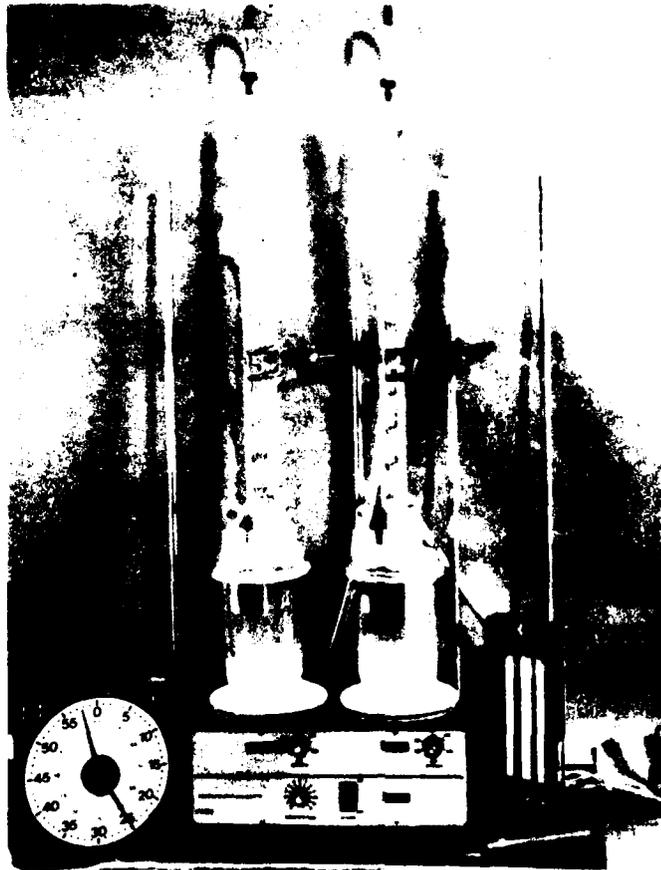
TEST APPARATUS

The dual apparatus shown in Figure B-2 is the system employed at P&WA/GPD to evaluate the rust preventative properties of the various candidate corrosion inhibiting engine oils.

After carefully cleaning and drying the entire apparatus, the perforated Teflon splash suppressor is placed in the 2000-ml reaction kettle such that it is loosely seated against the reaction kettle walls and rests approximately 4 cm (1.6 in.) above the base of the kettle. At this time approximately ten boiling beads are added to the reaction kettle to preclude bumping and splashing of the boiling solution.

Each reaction kettle cover has one ẞ 34/45 female joint in the center, and three ẞ 24/40 female joints spaced 120 degrees apart with their centers 5.1 cm (2.0 in.) from the center of the cover. The ground glass flange of the reaction kettle is coated with a thin film of inert silicone grease to prevent condensate leakage and the cover is centered on the reaction kettle. The center female joint is fitted with a ẞ 34/45 to 24/40 reducing type bushing adapter. The 24/40 male joint of the Allihn condenser is inserted into this bushing adapter and the male joint of the threaded offset adapter is inserted into the female joint at the top of the condenser. A flared borosilicate glass air inlet tube is inserted through the center of the Allihn condenser and offset adapter and sealed with an O-ring in the threaded bushing of the adapter. The air inlet tube is

positioned such that the flared end is 5.1 cm (2.0 in.) above the base of the kettle. The remaining three female joints of the cover are used for the glass stoppers with glass loops for test coupon suspension. The test coupons are suspended from the glass loop by wire hooks shaped from AMS 5680 20-gage stainless steel wire. The suspension hooks are formed such that the bottom edge of the test coupon is 11 cm (4.3 in.) from the base of the kettle.


FE 197331

Figure B-2. Test Apparatus for the Corrosion Rate Evaluation Procedure

TEST PROCEDURE

After the aforementioned test apparatus has been assembled, the reaction kettle and cover are removed, leaving the condenser and air flow assembly with the support stand. The hot plates are preheated and allowed to equilibrate to 380 ± 10°C (716 ± 18°F). A 100-ml aliquot of buffer solution is added to each reaction kettle and the apparatus is re-assembled on the equilibrated hot plate. A regulated flow of clean, dry air is provided from a compressed air cylinder, controlled by a micrometer valve, and measured with a calibrated flow meter. An air flowrate of 500 standard cubic centimeters per minute (SCCM) to each reaction kettle is established before the buffer solution starts to boil. This system is allowed to equilibrate for 60 minutes before the test specimens are introduced.

62

The test coupons, previously vapor-blasted, cleaned, and weighed to ±0.1 mg, are immersed in the test oil or corrosion inhibiting oil formulation for 5 minutes. At the end of the immersion cycle, the coupons are removed and suspended in a vertical position in a dust free environment such as that provided by the oil draining chamber shown in Figure B-3. During this 15-minute oil draining cycle, the required 380 ± 10°C (716 ± 18°F) hot plate temperature and the 500 SCCM air flowrate are checked to verify temperature and air flow equilibrium. At the end of the 15-minute draining cycle, the excess oil at the bottom edge of the test coupons is removed by blotting with a Microwipe. The three test coupons are suspended by wire hooks from the glass stoppers and inserted into the test environment for a residence period of 60 minutes. Figure B-4 shows a close-up view of a reaction kettle with test coupons, air inlet tube, and Teflon splash suppressor.
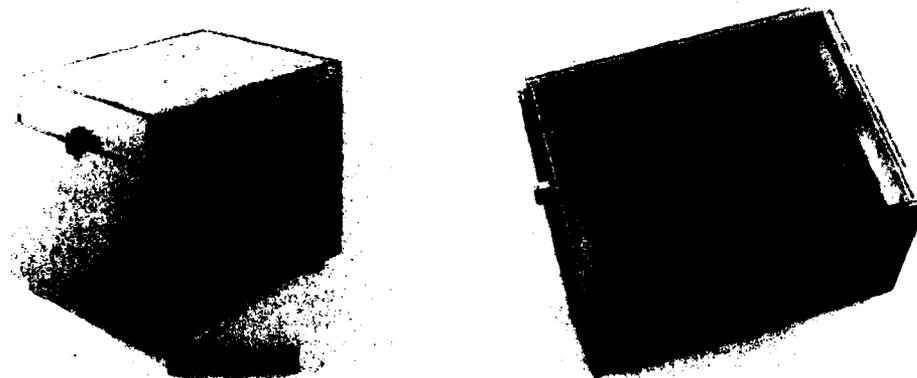

FD 216739

Figure B-3.   Coupon Draining Chamber To Provide Dust Free Environment for Test Coupons During the Oil Draining Cycle

The test coupons are removed from the reaction kettle at the end of the 60-minute residence period. The adhering oxides and oil are removed from the coupons by wetting with acetone and lightly brushing with a soft bristle brush. Secondary cleaning is accomplished by vigorously wiping all surfaces and edges with Microwipes saturated with acetone. This is followed by wiping all surfaces and edges with Microwipes saturated with hot toluene until no further oxides can be removed. Final cleaning of the test coupons is accomplished by immersing each test coupon in boiling toluene, followed by immersion in boiling acetone. The coupons are then flash dried and placed in a desiccator to equilibrate to ambient temperature.

After 30 minutes, the test coupons are weighed to ± 0.1 mg, and the weight differential from pretest weight determinations is calculated.
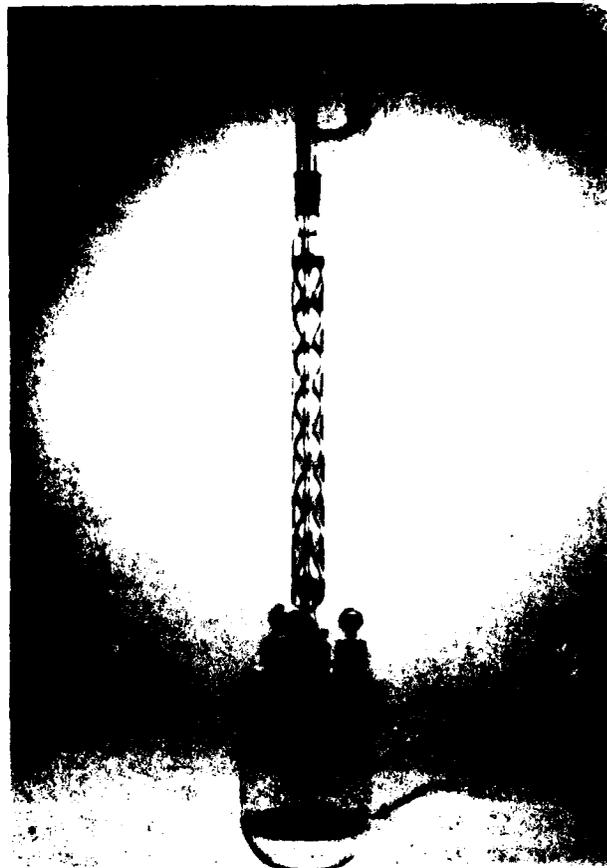
1. Test Specimen
2. Air Inlet Tube
3. Teflon Splash Suppressor

FD 220900

Figure B-4. Reaction Kettle With Test Coupons

64

ACCEPTABLE SOURCES FOR APPARATUS, MATERIALS, AND REAGENTS

1. VWR Scientific Inc., P.O. Box 13007, Station K, Atlanta, GA, catalog No. 36390-064.

2. VWR Scientific Inc., catalog No. 62904-114.

3. Ace Glass Company, P.O. Box 688, Vineland, NJ, catalog No. 5945-15.

4. Ace Glass Company, catalog No. 5101-54.

5. Houston Glass Fabricating, 305 Lenox Street, Houston, TX, drawing No. 014118.

6. Houston Glass Fabricating, drawing No. 014104.

7. Metaspec Company, P.O. Box 6715, San Antonio, TX 78209, part No. G-304-0.

8. VWR Scientific Inc., catalog No. 33922-950.

9. Scientific Gas Products, Inc., 2330 Hamilton Blvd, South Plainfield, NJ, catalog No. FT2DOZ.

10. Fisher Scientific Company, P.O. Box 829, Norcross, GA, catalog No. 06-656.

11. Fisher Scientific Company, catalog No. 8-632.

12. Scott Paper Company, Philadelphia, PA, Scottbrand 05310.

13. Malvern Minerals Company, Inc., P.O. Box 1246, Hot Springs National Park, AR.

14. Fisher Scientific, catalog No. So-B-100.

15. J.T. Baker Co., 222 Red School Lane, Phillipsburg, NJ 08865, Catalog No. 3-9460.

16. J.T. Baker Co., catalog No. 3-9006.

17. J.T. Baker Co., catalog No. 3-9070.

18. Dow Corning Corporation, Midland, MI 48640.

APPENDIX C

SEQUENTIAL SAMPLING PLAN

INTRODUCTION

The sequential sampling plan described herein was developed in conjunction with the Corrosion Rate Evaluation Procedure to aid in the determination of whether a test formulation was more effective or less effective than MIL-C-8188C as a corrosion inhibiting oil. Because of the large number of formulations being tested, it was necessary to make the determination in as few tests as possible. Therefore the sequential sampling plan was truncated at a maximum of three tests.

DISCUSSION

Table C-1 presents a sequential sampling plan with an acceptable risk level (alpha) of 0.05 and a rejectable risk level (beta) of 0.23. The acceptance and rejection regions are based on the mean of the observations. This sequential sampling plan was predicated on the results of 54 corrosion test specimens evaluated with the Corrosion Rate Evaluation Procedure with a thin film protection of MIL-C-8188C. These data points are shown in Figure 10 of this report. The mean and standard deviation ($\bar{x}$ and σ) of the corrosion rates for AISI-1010 metal coupons protected by MIL-C-8188C were 13.3 and 1.6 milligrams per hour (mg/hr) respectively.

TABLE C-1.   SEQUENTIAL SAMPLING PLAN

Number of Test Coupons	Accept if Mean Corrosion Rate <, (mg/hr)	Reject if Mean Corrosion Rate >, (mg/hr)
2	12.7	16.3
4	13.5	15.2
6	14.4	14.4

NOTE: The acceptable quality level is 13.3 mg/hr, and the rejectable quality level is 14.9 mg/hr.

Table C-1 also shows the two quality levels used in this analysis. The acceptable quality level is 13.3 mg/hr (mean of 54 corrosion rates) and has a risk level of 0.05 (alpha) associated with it. This implies that 5 percent of the time a sample formulation will be rejected that actually has a mean corrosion rate less than 13.3 mg/hr. The second quality level is the rejectable quality level which is 14.9 mg/hr (mean + standard deviation) and has a risk level (beta) of 0.23 associated with it. This implies that 23 percent of the time a sample formulation will be accepted that actually has a mean corrosion rate greater than 14.9 mg/hr.

In order to ensure that no change in the test procedure occurred during the course of the testing, a control coupon (protected by MIL-L-7808H, QPL 15F-1) was included in each test. Using the mean and standard deviation of 33 corrosion rate determinations for MIL-L-7808H, the upper and lower 99.9 percent tails of the normal distribution were calculated. The lower 99.9 percent tail is 17.8 mg/hr and the upper 99.9 percent tail is 26.1 mg/hr. If the corrosion rate of the control coupon was outside the ±99.9 tails of the normal distribution, then the test was considered invalid and was repeated.

66

Two examples of the decision process for evaluating the experimental data are provided below.

1. The first test is completed with corrosion rates of 21.1 mg/hr for the coupon protected with MIL-L-7808H and 10.8 and 9.2 mg/hr ($\bar{x}$ = 10.0 mg/hr) for the two coupons protected by the sample formulation. Since the control coupon is within the 99.9 percent confidence interval, the test is considered valid. The mean corrosion rate with the sample formulation is less than the acceptance value (12.7 mg/hr) for two test coupons from the sequential sampling plan in Table C-1. Therefore, we cannot reject *the hypothesis that the mean corrosion rate* with the sample formulation is less than the mean corrosion rate with MIL-C-8188C. A decision is made — no further testing is required.

2. The first test is completed with corrosion rates of 12.2 and 14.4 mg/hr ($\bar{x}$ = 13.3 mg/hr) for the test formulation and 22.3 mg/hr for the control coupon. Since the control coupon is within the 99.9 percent confidence interval, the test is considered valid. The mean corrosion rate for the sample formulation is between the acceptance and rejection regions, so no decision can be made without further testing. A second test is conducted and corrosion rates of 14.8 and 15.8 mg/hr are obtained for the sample formulation, and 19.6 for the control coupon. The mean corrosion rate of the four test coupons is 14.3 mg/hr. Again, no decision can be made since the mean corrosion rate falls between the acceptance and rejection regions of the sequential sampling plan in Table C-1.

   A third and final test is run and the sample formulation exhibits corrosion rates of 13.9 and 16.2 mg/hr. The mean corrosion rate of the six test coupons is 14.6 mg/hr, which is greater than the rejection value for six test coupons (14.4 mg/hr); therefore, it is *concluded that the mean corrosion rate with the sample formulation is greater than the* mean corrosion rate with MIL-C-8188C. As implied by the alpha risk level, this determination is made with a 95 percent confidence level.

67

APPENDIX D
CANDIDATE CORROSION INHIBITING OIL FORMULATIONS EVAL-
UATED WITH THE CORROSION RATE EVALUATION PROCEDURE

Formulation Number	Corrosion Inhibitors and Wt % of Active Ingredient in MIL-L-7808H, QPL 15F-1 Lot 104
PWL 82-0	MIL-L-7808H, QPL 15F-1, Lot 72
PWL 82-1	MIL-L-7808H, QPL 15F-1, Lot 104
PWL 82-2	0.5% PWL 81-27 + 0.5% PWL 80-20
PWL 82-3	0.5% PWL 81-27 + 0.5% PWL 80-32
PWL 82-4	0.5% PWL 81-27 + 0.5% PWL 80-29
PWL 82-5	0.5% PWL 81-27 + 0.5% PWL 80-25
PWL 82-6	0.75% PWL 81-27 + 0.25% PWL 80-20
PWL 82-7	0.75% PWL 81-27 + 0.25% PWL 80-32
PWL 82-8	0.5% PWL 81-26 + 0.5% PWL 80-20
PWL 82-9	0.5% PWL 81-26 + 0.5% PWL 80-32
PWL 82-10	0.5% PWL 81-26 + 0.5% PWL 80-29
PWL 82-11	0.5% PWL 81-26 + 0.5% PWL 80-25
PWL 82-12	0.75% PWL 81-26 + 0.25% PWL 80-20
PWL 82-13	0.75% PWL 81-26 + 0.25% PWL 80-32
PWL 82-14	0.5% PWL 81-25 + 0.5% PWL 80-20
PWL 82-15	0.5% PWL 81-25 + 0.5% PWL 80-32
PWL 82-16	0.5% PWL 81-25 + 0.5% PWL 80-29
PWL 82-17	0.5% PWL 81-25 + 0.5% PWL 80-25
PWL 82-18	0.75% PWL 81-25 + 0.25% PWL 80-20
PWL 82-19	0.75% PWL 81-25 + 0.25% PWL 80-32
PWL 82-20	0.75% PWL 80-11 + 0.25% PWL 80-20
PWL 82-21	0.75% PWL 80-11 + 0.25% PWL 80-32
PWL 82-22	0.75% PWL 80-12 + 0.25% PWL 80-20
PWL 82-23	0.75% PWL 80-12 + 0.25% PWL 80-32
PWL 82-24	MIL-C-8188C, Lot 57
PWL 82-25	0.75% PWL 81-27 + 0.25% PWL 80-25
PWL 82-26	0.75% PWL 81-27 + 0.25% PWL 80-29
PWL 82-27	0.75% PWL 81-27 + 0.25% PWL 81-18
PWL 82-28	0.75% PWL 81-27 + 0.25% PWL 81-7
PWL 82-29	0.75% PWL 81-26 + 0.25% PWL 80-25
PWL 82-30	0.75% PWL 81-26 + 0.25% PWL 80-29
PWL 82-31	0.75% PWL 81-26 + 0.25% PWL 81-18
PWL 82-32	0.75% PWL 81-26 + 0.25% PWL 81-7
PWL 82-33	0.75% PWL 81-25 + 0.25% PWL 80-25
PWL 82-34	0.75% PWL 81-25 + 0.25% PWL 80-29
PWL 82-35	0.75% PWL 81-25 + 0.25% PWL 81-18
PWL 82-36	0.75% PWL 81-25 + 0.25% PWL 81-7
PWL 82-37	0.75% PWL 80-11 + 0.25% PWL 80-25
PWL 82-38	0.75% PWL 80-11 + 0.25% PWL 80-29
PWL 82-39	0.75% PWL 80-11 + 0.25% PWL 81-18
PWL 82-40	0.75% PWL 80-11 + 0.25% PWL 81-7
PWL 82-41	0.75% PWL 80-12 + 0.25% PWL 80-25
PWL 82-42	0.75% PWL 80-12 + 0.25% PWL 80-29
PWL 82-43	0.75% PWL 80-12 + 0.25% PWL 80-18
PWL 82-44	0.75% PWL 80-12 + 0.25% PWL 80-7

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12. Reference 1, p 7.

13. WPAFB Contract F33615-79-C-5089, P00002, Statement of Work, 16 April 1980.

14. Reference 1, pp 39-47.

15. Reference 1, p 54.

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