

AD-A261 041



2

Report No. NAWCADWAR-92112-60



MACROMOLECULES FOR INHIBITION OF CORROSION AND WEAR

Alfeo A. Conte, Jr. and Vinod S. Agarwala
Air Vehicle and Crew Systems technology Department (Code 6062)
NAVAL AIR WARFARE CENTER
AIRCRAFT DIVISION WARMINSTER
P.O. Box 5152
Warminster, PA 18974-0591

14 DECEMBER 1992

PROGRESS REPORT
Aircraft Materials Block (AW2A)
Project Number RS34A52

DTIC
ELECTE
MAR 02 1993
S E D

Approved for Public Release; Distribution is Unlimited.

Prepared for
CHIEF OF NAVAL RESEARCH (ONT-225)
800 North Quincy Street
Arlington, VA 22217

08 6 1 027

93-04245



NOTICES

REPORT NUMBERING SYSTEM — The numbering of technical project reports issued by the Naval Air Development Center is arranged for specific identification purposes. Each number consists of the Center acronym, the calendar year in which the number was assigned, the sequence number of the report within the specific calendar year, and the official 2-digit correspondence code of the Command Officer or the Functional Department responsible for the report. For example: Report No. NADC-88020-60 indicates the twentieth Center report for the year 1988 and prepared by the Air Vehicle and Crew Systems Technology Department. The numerical codes are as follows:

CODE	OFFICE OR DEPARTMENT
00	Commander, Naval Air Development Center
01	Technical Director, Naval Air Development Center
05	Computer Department
10	AntiSubmarine Warfare Systems Department
20	Tactical Air Systems Department
30	Warfare Systems Analysis Department
40	Communication Navigation Technology Department
50	Mission Avionics Technology Department
60	Air Vehicle & Crew Systems Technology Department
70	Systems & Software Technology Department
80	Engineering Support Group
90	Test & Evaluation Group

PRODUCT ENDORSEMENT — The discussion or instructions concerning commercial products herein do not constitute an endorsement by the Government nor do they convey or imply the license or right to use such products.

Reviewed By: *Arthur Fletcher* Date: 11-9-92
Branch Head

Reviewed By: *James J. P. [Signature]* Date: 11/13/92
Division Head

Approved By: *J. O. Schuman, acting* Date: 11/17/92
Director/Deputy Director

REPORT DOCUMENTATION PAGEForm Approved
OMB No. 0704-0188

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.

1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE 14 December 1992	3. REPORT TYPE AND DATES COVERED Progress	
4. TITLE AND SUBTITLE MACROMOLECULES FOR INHIBITION OF CORROSION AND WEAR			5. FUNDING NUMBERS	
6. AUTHOR(S) Alfeo A. Conte, Jr. and Vinod S. Agarwala				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Air Vehicle and Crew Systems Technology Department (Code 6062) NAVAL AIR WARFARE CENTER-AIRCRAFT DIVISION WARMINSTER P.O. Box 5152 Warminster, PA 18974-0591			8. PERFORMING ORGANIZATION REPORT NUMBER NAWCADWAR-92112-60	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) CHIEF OF NAVAL RESEARCH (ONT-225) 800 North Quincy Street Arlington, VA 22217			10. SPONSORING/MONITORING AGENCY REPORT NUMBER	
11. SUPPLEMENTARY NOTES				
12a. DISTRIBUTION / AVAILABILITY STATEMENT Approved for Public Release; Distribution is Unlimited			12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) The phthalocyanines and Schiff base compounds are uniquely qualified inhibitors for corrosion. They are high electron density molecules for interaction with the metal surface, and possess large spatially arranged structures to serve as environmental barriers. Additionally, these compounds do stack-up as layered structures which provides shear planes, thus serving as lubricants. A number of these compounds have been synthesized and studied. Both electrochemical impedance spectroscopic and potentiostatic polarization techniques were used to determine their corrosion inhibition efficiencies. Wear studies were made using grease lubricated stainless steel miniature bearings. The results have shown that Schiff base compounds can be good additives for greases as they enhance wear life of bearings and inhibit corrosion by at least an order of magnitude. Although phthalocyanines, both monomers and polymers, provided a significant corrosion inhibition efficiencies (> 90%), they were not effective lubricants compared to the Schiff bases.				
14. SUBJECT TERMS Schiff Base, Phthalocyanine, Additives, Fluorinated Grease			15. NUMBER OF PAGES	
			16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT UNCLASSIFIED	18. SECURITY CLASSIFICATION OF THIS PAGE UNCLASSIFIED	19. SECURITY CLASSIFICATION OF ABSTRACT UNCLASSIFIED	20. LIMITATION OF ABSTRACT UL	

TABLE OF CONTENTS

Page

INTRODUCTION.....	1
BACKGROUND.....	1
EXPERIMENTAL.....	2
POTENTIODYNAMIC POLARIZATION STUDIES.....	2
AC-IMPEDANCE MEASUREMENTS.....	4
INSTRUMENT BEARING TESTS.....	4
RESULTS AND DISCUSSION.....	5
CORROSION INHIBITION OF PHTHALOCYANINES.....	5
CORROSION AND WEAR INHIBITION OF MACROCYCLIC COMPOUNDS.....	8
CONCLUSION.....	16
ACKNOWLEDGMENT.....	16
REFERENCES.....	17

NOT RECORDED

ii

Accession For	
NTIS	CRA&I ☒
DTIC	TAB ☐
Unannounced ☐	
Justification	
By	
Distribution /	
Availability Codes	
Dist	Avail and/or Special
A-1	

LIST OF TABLES

Table		Page
1	ABBREVIATIONS USED FOR VARIOUS PHTHALOCYANINE COMPOUNDS ..	7
2	RESULTS OF ELECTROCHEMICAL POLARIZATION MEASUREMENTS ON MILD STEEL TREATED WITH PHTHALOCYANINES IN 1% NaCl (pH 2)..	7
3	RESULTS OF ELECTROCHEMICAL POLARIZATION MEASUREMENTS ON MILD STEEL TREATED WITH POLYPHTHALOCYANINES IN 1% NaCl (pH 2).....	8
4	RESULTS OF THE AC IMPEDANCE MEASUREMENTS ON MILD STEEL TREATED WITH MONOMER AND POLYMER PHTHALOCYANINES IN 1% NaCl SOLUTION (pH 2).....	9
5	THE EFFECT OF TIN CERAMIC COATED 440C STEEL BEARINGS ON THE WEAR LIFE OF PFPE LUBRICANT.....	12
6	THE MELTING POINT AND THERMAL STABILITY OF SELECTED SCHIFF BASE COMPOUNDS.....	12
7	R-4 INSTRUMENT BEARING TEST RESULTS (PERFLUOROLPOLYALKYLETHER GREASE).....	13

LIST OF FIGURES

Figure		Page
1	Chemical structures of (A) porphyrins and (B) phthalocyanines.....	2
2	Synthesis of various Schiff base compounds.....	3
3	Synthesis of various copper chelated Schiff base compounds.....	3
4	The effects of phthalocyanines on the polarization of mild steel in 1% NaCl solution of pH 2.....	6
5	Nyquist plots for mild steel in 1% NaCl solution (pH 2) with: (a) uncoated, (b) three coatings of Co(II)TCPC and (c) single coating of Fe(III)TCPC polymer.....	6
6	Polarization curves for chelated and non-chelated Schiff bases [10^{-3} M] dissolved in 10 mL of DMF and dispersed in 1% NaCl (aqueous).....	9
7	The chemical structure of various perfluoroalkylpolyether (PFPE) fluids.....	10
8	PFPE degradation in the presence of FeF_3 Lewis Acid.....	11
9	The degradation mechanism for PFPE fluids operating in a steel bearing.....	11
10	DSC thermogram of 4,4'-benzidine-salicylaldehyde in nitrogen.....	14
11	DSC thermogram of 4,4'-benzidine-salicylaldehyde in air.....	14

INTRODUCTION

Currently there are no known chemical compounds which function as both antiwear and corrosion inhibiting agents. Our earlier study (1) established that there is a synergistic relationship between corrosion and wear. Enhancement of passivity or a build-up of corrosion resistant film on rubbing surfaces reduces wear significantly.

Molybdenum disulfide and graphite are by far the best and most widely used lubricating agents for elevated temperatures and loads that are available today. However, they possess no intrinsic properties which enable them to also function as corrosion inhibiting agents. In fact, in certain cases they are known to cause corrosion.

For example, in the hydrolysis of molybdenum disulfide, acidic components can be produced which readily attack metal and cause corrosion. Graphite is electrochemically very noble compared to most bearing materials used today. It is, therefore, well known for its ability to form galvanic cells with them whenever there is presence of moisture or any anionic media; causing corrosion of bearing metals. In the area of corrosion inhibition, chromates, sulfonates, nitrites and molybdates, among others, have been well documented to inhibit corrosion under a variety of conditions. However, they are not used as antiwear additives because they rapidly oxidize organic materials.

BACKGROUND

Generally most corrosion inhibitors are not custom made items. Classically, the development of the largest class of corrosion inhibiting substances was based on their molecular size which allows them to adsorb on the metal surface and suppress metal dissolution and reduction reactions. Now, it is accepted that the effectiveness of inhibitors is better predicted by the nature of chemical bonds than by the mere sizes of the molecule and their adsorption characteristics. Since porphyrins were discovered as a potential source for corrosion inhibitors (2-5), a considerable amount of interest has been generated in a family of such macrocyclic compounds (6,7). In addition to porphyrins, phthalocyanines also open up an excitingly new field in corrosion inhibition. Structurally, both of these parent compounds are similar with some subtle differences. The macrocyclics of these types are extremely stable, highly planar and possess high electron density in the pi-orbital system of the molecule for strong interactions with the conduction band of the surface metal atoms (8-13). Their generalized structures are as shown in Figure 1.

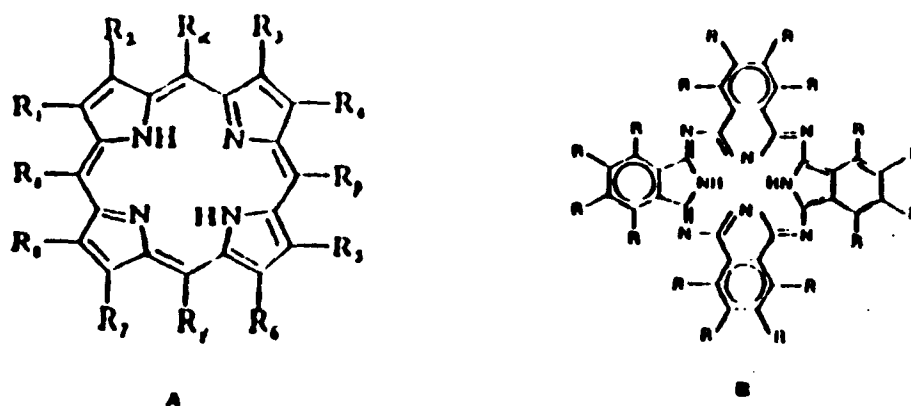


Figure 1 - Chemical structures of (A) porphyrins and (B) phthalocyanines.

Research on the lubricating properties of macrocyclic compounds and their corrosion inhibiting ability has uncovered another class of compounds (14) which possess the unique duality of antiwear and corrosion protection, simultaneously. These compounds are identified as Schiff bases which are the product of the chemical reaction between an aldehyde and an amine. In addition to their planar structure and quadridentate metal bonding characteristics similar to those of porphyrins and phthalocyanines, the Schiff base compounds exhibit appropriate thermal stabilities. Figures 2 and 3 show the reactions leading to some representative Schiff base chemical structures.

EXPERIMENTAL

POTENTIODYNAMIC POLARIZATION STUDIES

The effectiveness of phthalocyanines as acid corrosion inhibitors for steel was studied by conventional electrochemical dc and ac techniques. The details of these tests have been reported elsewhere in the literature(15-16). A rotating disk electrode at 1800 RPM (30 Hz) was been used for the polarization measurements.

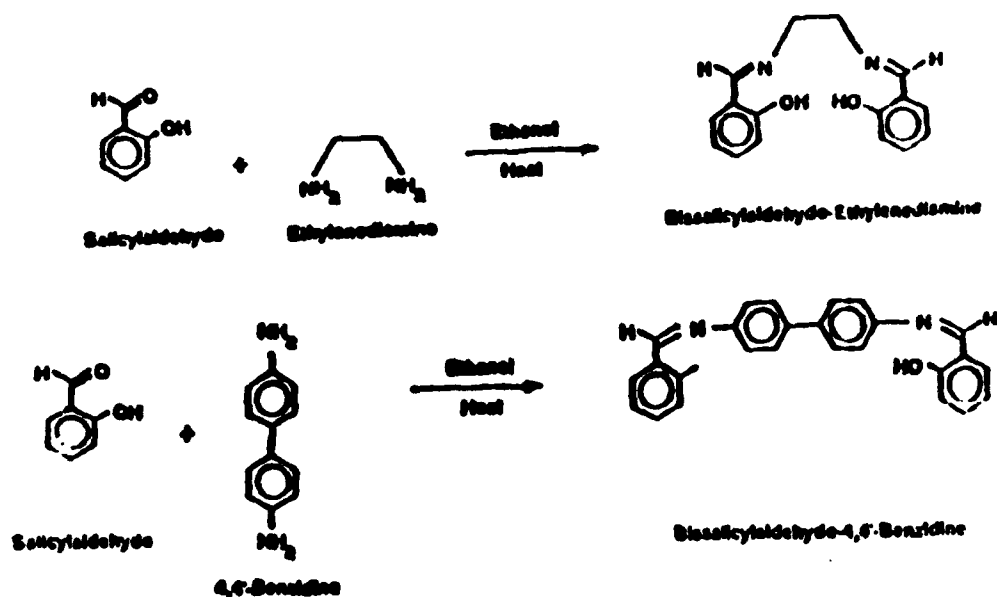


Figure 2 - Synthesis of various Schiff base Compounds.

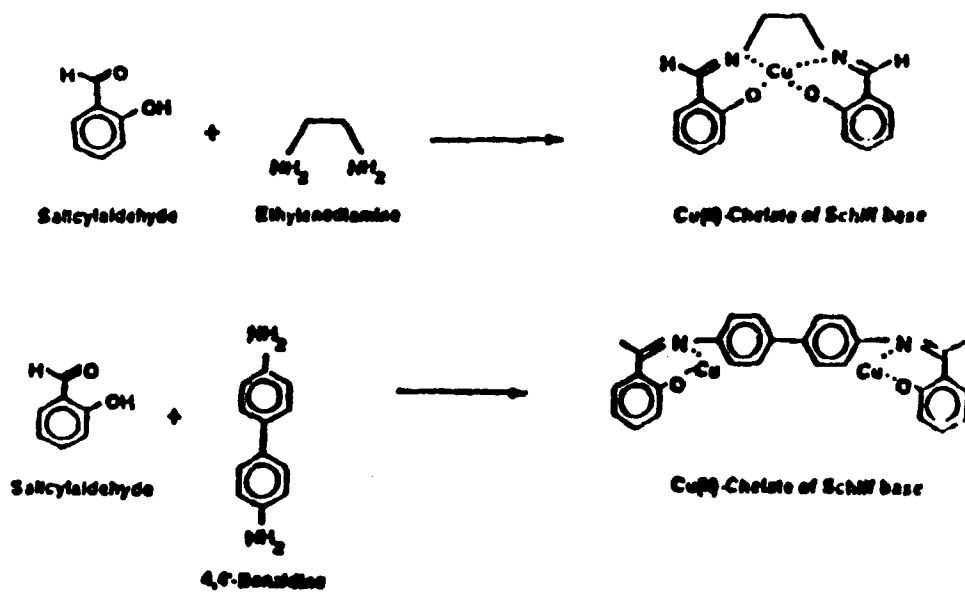


Figure 3 - Synthesis of various copper chelated Schiff base compounds.

To study polyphthalocyanine coatings for corrosion inhibition, the electrochemical testing was performed with a rotating cylinder electrode instead of using a rotating disk arrangement (17). This change was deemed necessary because it was not possible to heat treat the phthalocyanine coated metal disk at 450 C due to the inability of the Teflon mount to withstand such temperatures. The problem was overcome by using a removable cylinder electrode. Additionally, since the rotating cylinder electrode renders mass transfer rates much faster at reasonably slow rotational speeds, all the experiments with polyphthalocyanine coatings were performed with a rotating cylinder electrode at a rotational speed of 255 RPM.

AC-IMPEDANCE MEASUREMENTS

The ac-impedance studies on polymeric phthalocyanine coatings were studied at the free corrosion potential by holding the potential at this value, using a PAR Model 173 potentiostat. The impedance measurements over a wide frequency range (1 kHz to 10 MHz or less) were made with the help of a Solartron Model 1250 Transfer Function Analyzer. The amplitude of the ac signal used was 8 mV. Evaluation of the corrosion behavior of a polymer-coated metal, such as that used in this case, was made possible by the wideband ac impedance measurements, which provided information on both the resistive and the capacitive behavior of the interface.

INSTRUMENT BEARING TESTS

Instrument bearing tests were performed in accordance with ASTM Method D-3337, Standard Method for Evaluation of Greases in Small Bearings(18), under the test conditions given below.

TEST CONDITIONS USED FOR INSTRUMENT BEARING TESTS

Bearing Size: R-4 (6.35 mm bore dia.) stainless steel
Load: 2.2N radial, 22N axial
Speed: 12,000 rpm
Temperature: 204°C
Grease Wt.: 75mg

RESULTS AND DISCUSSION

CORROSION INHIBITION OF PHTHALOCYANINES

The study of phthalocyanines was directed to explore their ability to act as acid corrosion inhibitors for steel. It was believed that phthalocyanines would be more effective as corrosion inhibitors than porphyrins because of the almost rigid planarity of the phthalocyanine molecule. In addition to the chemisorption pathways, a higher degree of planarity is expected to increase the interaction between the pi-electron system of the phthalocyanine with the conduction band of the metal. Furthermore, the more planar the molecule, the higher degree of coverage and hence a higher inhibition efficiency. The planarity and electron density in the pi-system of molecules affect their surface adsorption properties and are specifically useful for the formation of stable films.

The study of polyphthalocyanines was considered more useful than their monomers in the respect that polyphthalocyanines could form a new revolutionary class of inhibitors because of their high electronic conductivity. An important feature here is that polyphthalocyanines while inhibiting corrosion are capable of retaining an important property expected from the metal, i.e. its electrical conductivity. This suggests some tremendously useful practical applications of electrically conducting coatings to protect sensitive electrical components from extraneous electromagnetic interferences.

Water soluble TSPC (see Table 1 for nomenclature) derivatives with metal centers were found to exhibit poor corrosion inhibition, as shown in Table 2. Water insoluble TAPC derivatives served as better corrosion inhibitors than their water soluble counterparts when the metal surface was coated with an adsorbed layer of the compound. The polarization plots (E vs. $\log i$) showed no significant differences in the presence or absence of phthalocyanines. A summarized view of the electrochemical parameters is reported in Table 2, indicating the influence of these monomers. Compared to Co(II)-TAPC, Fe(III)-TAPC showed higher degree of corrosion inhibition, however, the inhibitor efficiency was still far too low to be of any significance. Thus, the investigation centered on the formation of stable polymeric phthalocyanine coatings on the metal surface.

The results of the potentiodynamic polarization measurements for the mild steel in 1% NaCl solution (pH 2) with and without polymeric coatings were as shown in Figure 4. The number of distinct features noted from this figure are: (i) the corrosion potential shifted to more positive values with the polymer, Fe(III)-TCPC showed the most positive shift; (ii) both the anodic and cathodic polarization curves shifted to

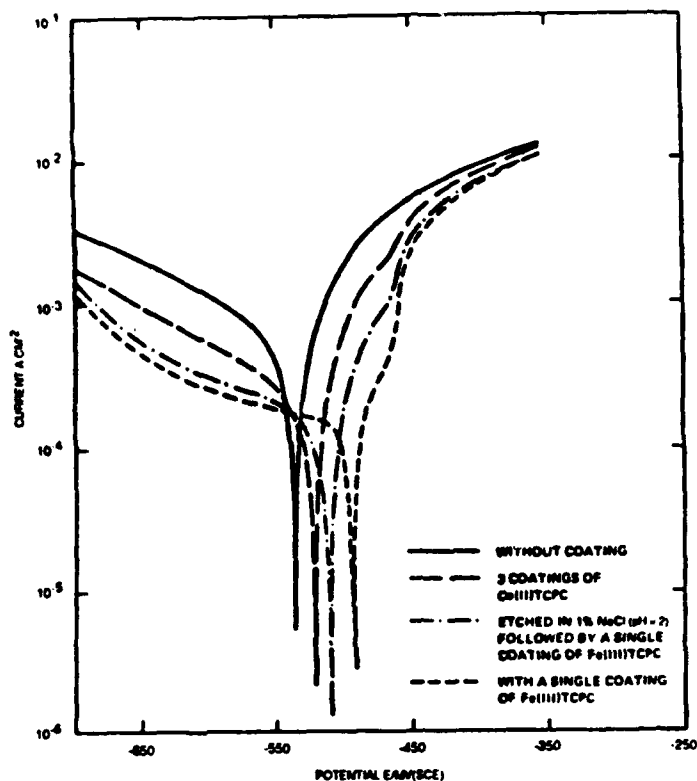


Figure 4 - The effects of phthalocyanines on the polarization behavior of mild steel in 1% NaCl solution of pH 2.

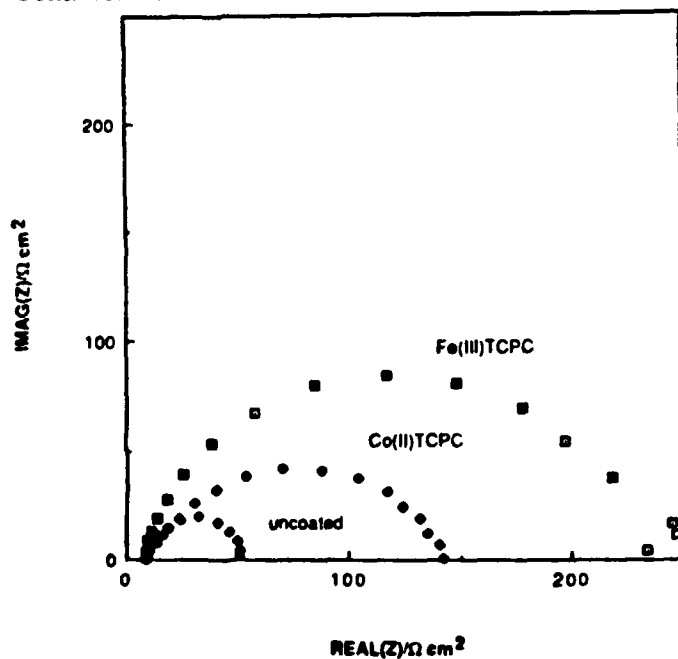


Figure 5 - Nyquist plots for mild steel in 1% NaCl solution (pH 2) with: (a) uncoated, (b) three coatings of Co(II)TCPC and (c) single coating of Fe(III) TCPC polymer.

Table 1

ABBREVIATIONS USED FOR VARIOUS PHTHALOCYANINE COMPOUNDS

<u>Designation</u>	<u>Nomenclature</u>
TSPC	tetrasulfo-phthalocyanine
TAPC	tetraamino-phthalocyanine
TCPC	tetracarboxy-phthalocyanine
TCAUPC	tetrakis-(N-carboxy-12-aminoundecanoic acid) phthalocyanine
TCACPC	tetrakis-(N-carboxy-6-aminocaproic acid) phthalocyanine

Table 2

RESULTS OF ELECTROCHEMICAL POLARIZATION MEASUREMENTS ON MILD STEEL TREATED WITH PHTHALOCYANINES IN 1% NaCl (pH 2).

<u>Inhibitor System</u>	<u>Ecorr mV(SCE)</u>	<u>mV/Decade</u>		<u>Icorr mA/cm²</u>	<u>% Inhibition Efficiency</u>
		<u>Ba</u>	<u>Bc</u>		
None	-500	45	-370	1.05	--
*VO-TSPC	-488	43	-350	1.0	5
*Co(II)-TSPC	-498	38	-300	0.95	10
*Fe(III)-TSPC	-490	39	-475	0.93	7
Co(II)-TAPC	-505	45	-325	0.95	10
Co(II)-TAPC (on etched steel)	-493	43	-370	0.82	22
Fe(III)-TAPC	-505	45	-340	0.65	37
Fe(III)-TAPC (on etched steel)	-500	44	-372	0.88	16

* 1 mM concentration in test solution (water soluble).

lower current densities; and (iii) the anodic reaction rates (polarization curves) were reduced by almost two orders of magnitude with the coatings. The results of these studies are summarized in Table 3.

Table 3

RESULTS OF ELECTROCHEMICAL POLARIZATION MEASUREMENTS ON MILD STEEL TREATED WITH POLYPHTHALOCYANINES IN 1% NaCl (pH 2).

Inhibitor System	E _{corr} mV(SCE)	mV/Decade		I _{corr} mA/cm ²	% Inhibition Efficiency
		B _a	B _c		
None	-538	247	-193	0.48	--
Co(II)-TCPC (3 coats)	-525	260	-205	0.20	55
Fe(III)-TCPC	-495	225	--	0.08	83
Fe(III)-TCPC (on etched steel)	-512	228	--	0.16	66

AC-impedance studies were also performed on the above polymeric coatings. The results of these experiments were shown as Nyquist plots [$\text{Re}|Z|$ vs. $\text{Imag.}|Z|$] of the interfacial impedance as a function of frequency, as in Figure 5. The curves, slightly suppressed semicircles, show the characteristics of steel in chloride solutions with and without the presence of polyphthalocyanines. The polarization resistance (R_p) values, calculated from these impedance spectra, were determined from the intercepts (lengths of the diameters) of the suppressed semicircles along the [$\text{Re}(Z)$] axis. As shown in Table 3, the R_p values increased 3 and 6 folds when three coatings of polymeric Co(II)-TCPC and a single coat of Fe(III)-TCPC were applied on the steel surface, respectively; the corresponding calculated inhibitor efficiencies were approximately 68% and 83%, respectively. Pre-treatment of the metal surface, such as etching, did not improve the bonding of the polymer Fe(III)-TCPC.

CORROSION AND WEAR INHIBITION OF MACROCYCLIC COMPOUNDS

Electrochemical polarization curves were generated for various Schiff base compounds, as shown in Figure 6. It can be observed that <0.001 molar unchelated Schiff base in 1% sodium chloride solution will protect a 1010 steel by decreasing anodic and cathodic currents by at least three orders of magnitude. This is interpreted as lowering the corrosion rates by the same order of magnitude. In contrast, the copper chelated Schiff bases were found to be ineffective in lowering corrosion currents. This suggested that the key to providing corrosion

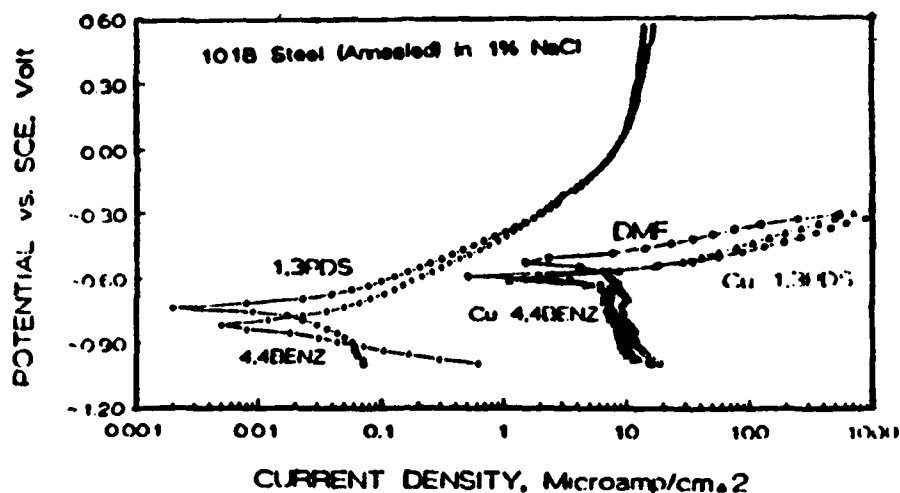


Figure 6 - Polarization curves for chelated and non-chelated Schiff bases [10^{-3} M] dissolved in 10 ml of DMF and dispersed in 1% NaCl (aqueous).

Table 4

RESULTS OF THE AC IMPEDANCE MEASUREMENTS ON MILD STEEL TREATED WITH MONOMER AND POLYMER PHTHALOCYANINES IN 1% NaCl SOLUTION (pH 2),

Inhibitor System	Rp in Ohm.cm ²	Wmax, rad./s	Cp in uF/cm ²	% Inhibition Efficiency
None	42	63	378	--
Poly Co(II)-TCPC (3 coats)	137	10	750	68
Poly Fe(III)-TCPC	240	13	318	83
Poly Fe(III)-TCPC (on etched steel)	159	16	400	74
Poly Fe(III)-TCPC ** (low void fraction)	174	2	3640	77
*Fe(III)-TCAUPC	323	16	196	88
*Co(II)-TCAUPC	243	4	1038	83
*Fe(III)-TCACPC	255	25	157	84
*Co(II)-TCACPC	114	40	222	65

- * Phthalocyanine containing long chain hydrocarbon groups: [TCAUPC] - tetrakis (N-carboxy-12-aminoundecanoic acid); [TCACPC] - tetrakis(N-carboxy-6-aminocaproic acid).
- ** Containing p-hydroxy pyridine groups in the voids.

protection involved the nitrogen centers on the Schiff base compounds. These sites reacted with the metal surface to provide corrosion protection.

The next phase of this study centered on investigating the effect of macrocyclic additives on the enhancement of lubricating properties of a high temperature grease. A perfluoropolyalkylether (PFPE) grease was chosen as the base line for comparison purposes since it is representative of the state-of-the-art for high temperature greases and any increase in wear life realized would extend functionality. The chemical structure of various PFPE fluids is shown in Figure 7. Structure (II) is representative of the type of fluid used in the current investigation.

The advantageous properties of PFPE fluids include: chemical resistance to hot hydrofluoric acid, liquid oxygen and strong bases as well as low vapor pressure and possessing a wide temperature range (-35°-300°C). Their "Achilles Heel" is caused by catalytic attack with Lewis Acids. As shown in Figure 8, in the presence of a typical Lewis Acid such as FeF_3 , the thermal stability of the fluid is reduced by about 30°C. On a kinetic scale, this can be interpreted as representing an eight fold decrease in stability.

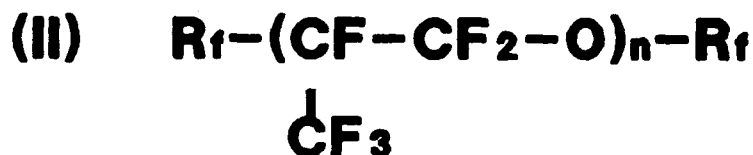


Figure 7: The chemical structure of various perfluoroalkyl-poluether (PFPE) fluids.

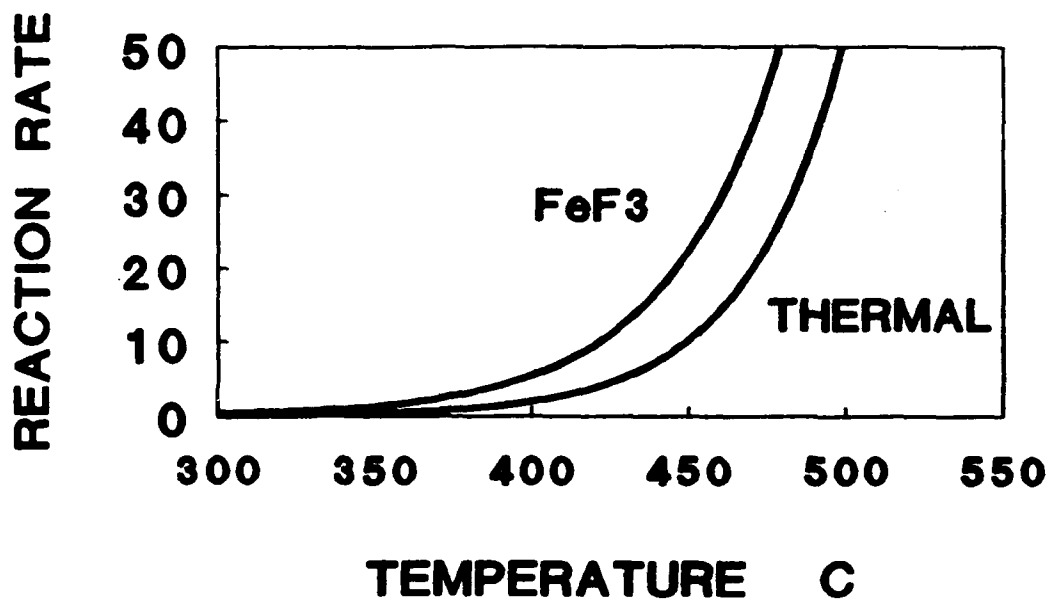
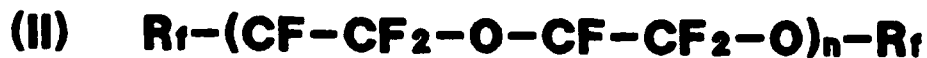


Figure 8: PFPE degradation in the presence of FeF_3 Lewis acid.



*** = SITE OF REACTIVITY**

Figure 9: The degradation mechanism of PFPE fluids operating in a steel bearing.

The implication of this phenomena for reducing lubricant life for bearings is shown in Figure 9. As the steel bearing wears, elemental Fe is produced which can react with the PFPE by extracting fluorine atoms and forming FeF_3 . The FeF_3 is then capable of catalyzing the degradation of PFPE by splitting its molecular structure at the sites indicated in Figure 9.

One approach that demonstrates the effect of altering this reaction scheme is to prevent exposure of the PFPE lubricant to Fe wear debris by coating the bearings with a ceramic such as TiN. As shown in Table 5, the wear life of TiN ceramic coated bearing is increased by a factor of 8.8, compared to the non-coated bearing.

Table 5

CERAMIC SURFACE EFFECT ON WEAR LIFE

BEARING MATERIAL	COATING	WEAR LIFE (hrs)	IMPROVEMENT FACTOR
440C	None	3.8	---
440C	TiN	33.3	8.8

TEST CONDITIONS:

* SPEED: 1750rpm	* LUBRICANT: PFPE OIL
* LOAD: 200N	* QUANTITY: 10uL
* TEMP: AMBIENT	

Table 6

THE MELTING POINT AND THERMAL STABILITY
OF SELECTED SCHIFF BASE COMPOUNDS

SCHIFF BASE	MP ($^{\circ}\text{C}$)	%WT. LOSS AT 350 $^{\circ}\text{C}$	
		AIR	NITROGEN
Ethylenediamine Salicylaldehyde	123	70	58
1,3-Phenylenediamine Salicylaldehyde	105	37	24
4,4'-Benzidine Salicylaldehyde	264	3	0

A less expensive approach toward achieving the same results involved the use of Schiff base compound as an additive to the PFPE grease. Table 6 shows the melting point and stability properties of selected Schiff base compounds. The 4,4' benzidine-salicylaldehyde Schiff base was observed to possess one of the highest melting points and in addition was the most stable in air and nitrogen at temperatures as high as 350°C. Figure 10 and 11 show the DSC thermograms obtained on for the 4,4' benzidine-salicylaldehyde Schiff base in nitrogen and air, respectively.

Table 7 shows the results of Instrument Bearing tests conducted on various grease formulations containing macrocyclic compounds of phthalocyanine and Schiff base types incorporated into the grease at a concentration of 5 w/o. The most striking improvement in wear life was observed with a Schiff base of 4,4' Benzidine and Salicylaldehyde, which exhibited an improvement ratio of 16.4 in comparison to the uninhibited grease. Phthalocyanine and other Schiff bases exhibited only slight improvement ratios ranging from 1.2 to 1.8. The copper chelate of 4,4' Benzidine and Salicylaldehyde showed no improvement.

Table 7

R-4 INSTRUMENT BEARING TEST RESULTS
(PERFLUOROLPOLYALKYLETHYER GREASE)

Additive (5w/o)	Avg. Wear Life, hrs	Improvement Ratio
1. None	65	--
2. Phthalocyanine	78	1.2
3. Schiff base of 4,4' Benzidine & Salicylaldehyde	1067	16.4
4. Cu chelate of #3	41	0.6
5. Schiff base of 1,3 Phenelynediamine & Salicylaldehyde	104	1.6
6. Cu chelate of #5	110	1.8

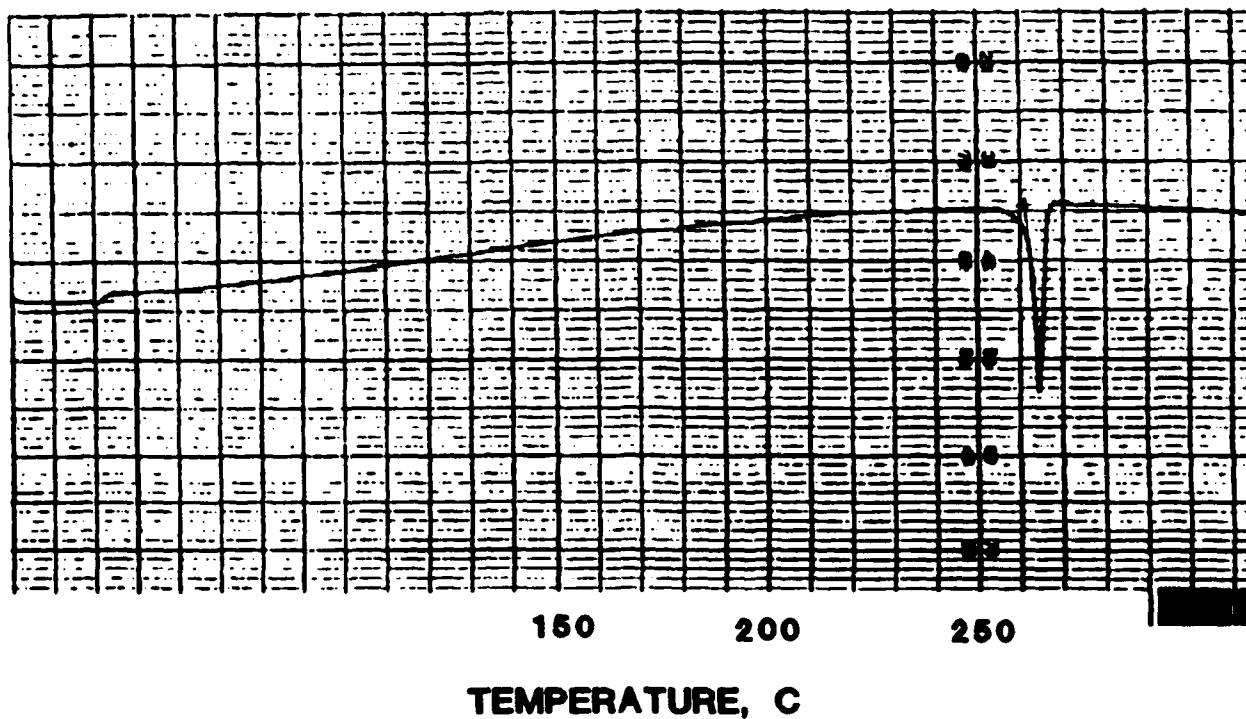


Figure 10: DSC thermogram of 4,4'-benzidine-salicylaldehyde in nitrogen.

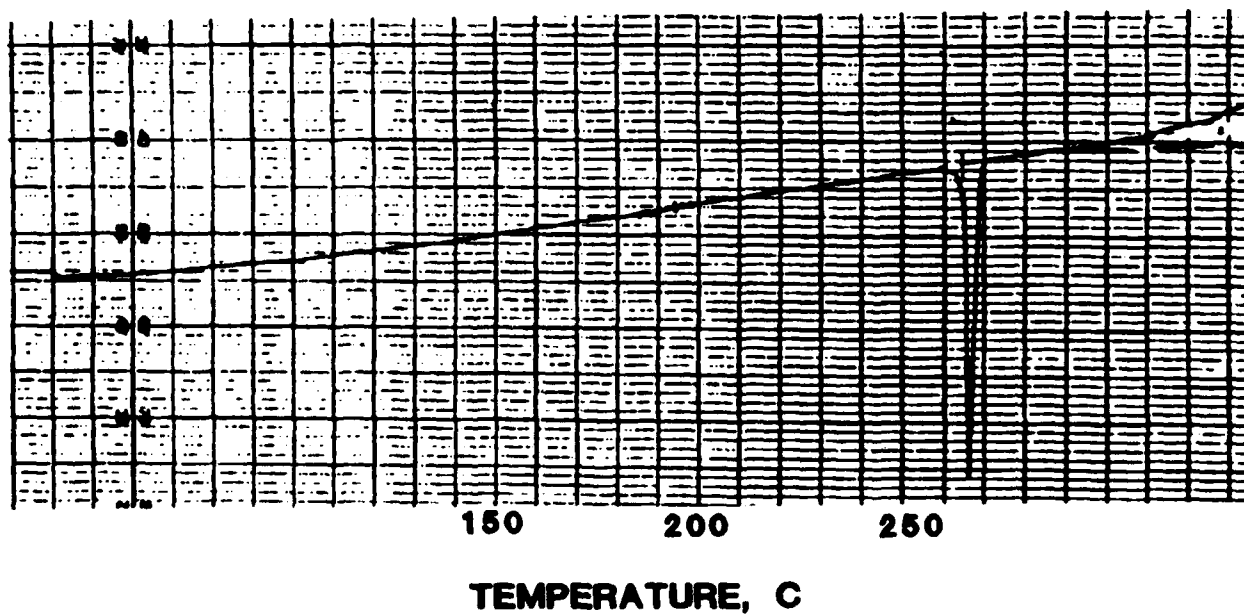


Figure 11: DSC thermogram of 4,4'-benzidine-salicylaldehyde in air.

From previous studies (19) it was determined that the key to achieving extended lubricant life with PFPE high temperature lubricants is to prevent their degradation as a result of Lewis-Acid catalysis. Although PFPE lubricants are considered to be one of the most stable lubricating media, their one weakness is their reactivity with metals, such as Fe, which are generated during the wear process. Fe reacts with C-F to form $\text{FeF}_2/\text{FeF}_3$ (Lewis-Acids) which further catalyzes degradation. The action of Schiff base additives is essentially to minimize or eliminate this degradation process by "chelating" with Fe (either on the surface or as wear debris) at their nitrogen centers. Also reactivity at the bearing surface was found to play a key role in achieving extend life. This same reactivity is responsible for their corrosion protection capability. This duality (antiwear and corrosion inhibition) is unique to Schiff base additives. That reactivity at the nitrogen centers plays a key role is demonstrated by the fact that synthesized "chelated" Schiff Bases exhibited only limited to no improvement in wear life ratios and no improvement in corrosion protection.

CONCLUSION

In general, macromolecules have shown good corrosion inhibition properties and, seemingly due to their high configurational electron density and bonding characteristics, i.e. reactivity of the nitrogen centers with the metal surface. It was also concluded that a similar mechanism applies to develop wear resistance, compounds which were chelated had shared nitrogen atom activity, and thus, showed poorer resistance to wear and corrosion. However, for a compound to exhibit duality (both wear and corrosion inhibition) in a formulation such as grease, it was necessary for the medium (grease) to provide activation energy for bonding with the metal surface. It was determined that fluorides in the grease were a combining factor. This was shown for Schiff bases when formulated in fluoride containing lubricants. In particular, Schiff base of 4,4' benzidine and salicylaldehyde in PFPE (perfluoropolyalkylether) showed a 16 fold improvement in bearing life of the R-4 bearing, whereas non-fluorinated lubricants showed no significant improvement. Here, the tribochemical actions in the presence of fluoride were able to create bonding with the Schiff base compound to form a passive film of the metal.

Application of Schiff base inhibitors to lubricant formulations will increase the "Mean Time Before Failure" (MTBF) of bearings, splines, gears and rotors by several orders of magnitude over current state-of-the-art materials. In addition, temperature excursions of 50C can be tolerated without undue concern for reduction in life expectancy. Bearing assembly failures due solely to corrosion will be greatly diminished or completely eliminated. As a result of these aforementioned benefits, reduced maintenance man-hours will be realized especially for instrument bearings which are often located in difficult to access areas and require costly maintenance procedures.

ACKNOWLEDGMENT

The authors thank Lee Hammond and Martin Ruzansky for their contributions in carrying out bearing and wear tests. Financial assistance from the Navy's Materials Block Program is greatly appreciated.

REFERENCES

1. B. Panda, "Corrosion-Wear Process Under Rolling-Sliding Motion," IIT Research Institute Report No. M06140-6, Naval Air Development Center Contract No. N62269-85-C-0265, February 1987.
2. J. Assour, J. Chem. Phys., Vol. 43, 2477 (1965).
3. F. R. Longo, J.J. De Luccia and V.S. Agarwala, Proc. 6th European Symposium on Corrosion Inhibitors, Univ. of Ferrara, Ferrara, Italy, pp.155-166, September 1985.
4. V.S. Agarwala, Proc. International Congress on Metallic Corrosion, Toronto, Canada, Vol.1, p. 380, June 3-7, (1984).
5. V.S. Agarwala and F.R. Longo, "Porphyrins: A New Class of Corrosion Inhibitors" in Surfaces, Inhibition and Prevention, eds., E. McCafferty and R.J. Brodd, The Electrochemical Society Publication, Vol.86-7, pp.56-68, 1986.
6. K. Rajan, Natl. Intelligence. Serv., AD Department of Commerce, Washington, DC (1970).
7. K. Rajan, Final Technical Report, IITRI-C6202-6, Contract No. N00019-70-C-0180, Washington, DC (1970).
8. E.B. Fleischer and J.H. Wang, J. Am. Chem. Soc., Vol.82, 3498 (1960).
9. B.F. Burnham and J.J. Zukerman, J. Am. Chem. Soc., Vol.92, 1547(1970).
10. K. Letts and R.A. McKay, Inorg. Chem., Vol.14, 2993 (1975).
11. W.G. Rau and F.R. Longo, Inorg. Chem., Vol.16, 1372 (1976).
12. M. Zerner and M. Gouterman, Theor. Chim. Acta., Vol.4, 44 (1966).
13. A. Snow and N. Jarvis, J. Am. Chem. Soc., Vol.106, 4706 (1984).
14. K.S. Rajan, P. Sen, E. Vesely, S. Varma, A.A. Conte, Jr. and V.S. Agarwala, "Macrocyclic Compounds for Corrosion-Wear," Corrosion 90, Paper No. 444, April 1990.

15. Standard Reference Method for Making Potentiostatic and Potentiodynamic Anodic Polarization Measurements, G 5-82, Annual Book of ASTM Standards, Vol 03.02, 1984.
16. W.J. Lorenz and F. Mansfeld, Corrosion Science, Vol.21, 647 (1981).
17. S. Hettiarachchi, Y.W. Chan and R.B. Wilson, Jr., "Corrosion Inhibitors for Metals In a Naval Environment", SRI International Project 1178, Naval Air Development Center Contract No N62269-85-C-0290, February 1988.
18. Annual Book of ASTM Standards, Vol 05.02, 1988.
19. D.J. Carre, "Perfluoropolyalkylether Oil Degradation: Inference of FeF₃ Formation on Steel Surfaces Under Boundary Conditions," ASLE Trans., Vol. 29, 2, pp.121-125, 1986.

DISTRIBUTION LIST (Continued)
Report No. NAWCADWAR-92112-60

	No. of Copies
Commanding Officer Naval Aviation Depot Norfolk, VA 23511	1
Commanding Officer Naval Aviation Depot North Island San Diego, CA 92135	1
Commanding Officer Naval Aviation Depot Pensacola, FL 32508	1
Commanding Officer Naval Aviation Depot Marine Corp. Air Station Cherry Point, NC 28533	1
Commander Naval Air Force U.S. Atlantic Fleet Code 5281 Norfolk, VA 23511	1
Commander Naval Air Force U.S. Pacific Fleet Code 7412 San Diego, CA 92135	1

DISTRIBUTION LIST (Continued)
Report No. NAWCADWAR-92112-60

	No. of Copies
Dr. Theodore R. Beck Electrochemical Technology Corp. 1601 Dexter Avenue N. Seattle, WA 98109	1
Dr. John Gudas Code 2810 David Taylor Research Center Annapolis, MD 21402	1
Mr. I. Kaplan Code 0115 David Taylor Research Center Annapolis, MD 21402-5067	1
Mr. J.J. Kelly Defense Advanced Research Projects Agency 1400 Wilson Blvd. Arlington, VA 22209	1
Dr. M. W. Kendig Rockwell International Science Center 1049 Camino Dos Rios P.O. Box 1085 Thousand Oaks, CA 91360	1
Mr. M. Kinna Office of Naval Technology 800 North Quincy Street Arlington, VA 22217	1
Mr. M. Lepera (DRXFB-GC) Belvoir Research, Development & Engineering Center Fort Belvoir, VA 22060-5606	1
Dr. Norbert D. Greene U-136 University of Connecticut Storrs, CT 06268	1
Commanding Officer Naval Aviation Depot Alameda, CA 94501	1
Commanding Officer Naval Aviation Depot Jacksonville, FL 32212	1

DISTRIBUTION LIST (Continued)
Report No. NAWCADWAR-92112-60

	No. of Copies
Dr. J. Kruger Dept. of Materials Science & Engineering Johns Hopkins University Baltimore, MD 21218	1
Mr. Milton Levy SLCMT-MN U.S. Army Materials Technology Laboratory Watertown, MA 02172-0001	1
Mr. B. Lifka ALCOA Technical Center ALCOA Center, PA 15069	1
Dr. Digby D. Macdonald SRI International 333 Ravenswood Avenue Menlo Park, CA 94025	1
Dr. Glenn Stoner Dept. of Materials Science & Engineering University of Virginia Charlottesville, VA 22901	1
Dr. R. Sutula R-33 Naval Surface Warfare Center Silver Springs, MD 20910	1
Dr. Barry C. Syrett Electric Power Research Institute 3412 Highview Avenue P.O. Box 10412 Palo Alto, CA 94303	1
Dr. A. Thompson Dept. of Metallurgical Engineering & Materials Science Carnegie Mellon University Pittsburg, PA 15213	1
Commander Naval Sea Systems Command Washington, DC 20362	1
Dr. Lionel J. Ballin Lockheed Missile & Space Co. Inc. 3251 Hanover Street Palo Alto, CA 94304-1187	1

DISTRIBUTION LIST (Continued)
Report No. NAWCADWAR-92112-60

	No. of Copies
Dr. A.R. Trolano Dept. Of Metallurgy & Materials Science Case Western Reserve University Cleveland, OH 44106	1
Dr. Ellis Verink Dept of Materials Science & Engineering University of Florida Gainsville, FL 32611	1
Dr. A.K. Vasudevan Code 1216 Office of Naval Research 800 Quincy Street Arlington, VA 22217-5000	1
Dr. J. Wells SLCMT-MCZ Materials Technology Laboratory Watertown, MA 02172-0001	1
Dr. Bryan E. Wilde Fontana Corrosion Center The Ohio State University Columbus, OH 43210	1
Naval Air Warfare Center Warminster, PA 18974-0591 (25 for Code 6062) (2 for Code 0471) (1 for Code 01B)	28
Dr. Florian Mansfeld Dept. of Materials Science University of Southern California Los Angeles, CA 90009-0241	1
Mr. C.E. Snyder AFWAL/MLBT Wright Patterson AFB Ohio 45433	1
Mr. R. Kinsey MEMMC, Air Force Logistics Center Warner-Robins AFB Warner, GA 31908	1

DISTRIBUTION LIST (Continued)
Report No. NAWCADWAR-92112-60

	No. of Copies
Dr. C.E. Mueller	1
Code R30	
Naval Surface Weapons Center	
White Oak	
Silver Springs, MD 20910	
 Dr. James S. Murday	 1
Code 6100	
Naval Research Laboratory	
Washington, DC 20375	
 Dr. Ken Shaffer	 1
Martin Marietta Laboratory	
1450 South Rolling Road	
Baltimore, MD 21227	
 Dr. Howard W. Pickering	 1
Penn State University	
209 Steible Building	
University Park, PA 16802	
 Dr. E.N. Pugh	 1
Room B254 Bldg. 223	
National Institute for Standards and Technology	
Washington, DC 20234	
 Dr. K.S. Rajan	 1
Chemistry Department	
I.T.T. Research Institute	
10 West 35th Street	
Chicago, IL 60616	
 Dr. B. Rath	 1
Code 6000	
Naval Research Laboratory	
Washington, DC 20375	
 Dr. Robert Reeber	 1
U.S. Army Research Office	
P.O. Box 12211	
Research Triangle Park, NC 27709	
 Dr. L. E. Slotter	 1
Air 5304	
Naval Air Systems Command	
Washington, DC 20361	

DISTRIBUTION LIST
Report No. NAWCADWAR-92112-60

	No. of Copies
Center for Naval Analyses 4401 Fort Avenue P.O. Box 16268 Alexandria, VA 22302-0268	1
Mr. Joseph Collins Code 5304 Naval Air Systems Command Department of the Navy Washington, DC 20361	1
Mr. Anthony Corvelli Code 36621 Naval Underwater Systems Center Newport, RI 02841	1
Defense Technical Information Center ATTN: DTIC-DDA-1 Cameron Station, Bldg. 5 Alexandria, VA 22314	2
Dr. R. De Marco Code 1113 Office of Naval Research 800 N. Quincy Street Arlington, VA 22217	1
Dr. R. Derr Code 38 Naval Weapons Center China Lake, CA 93555	1
Mr. A.J. D'Orazio, Mr N. Rebuck Code PE-72 Naval Air Propulsion Center Trenton, NJ 08628	2
Dr. Richard W. Drisco Code 152 Naval Civil Engineering Laboratory Port Hueneme, CA 93043	1
Mr. Dario A. Emeric (STRBE-VC) Belvoir Research, Development & Engineering Center Fort Belvoir, VA 22060-5606	1